

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**CHARACTERIZATION AND TREATMENT
ALTERNATIVES OF SOME BROMINATED,
NITROSO, FLUORO AND PHENOLIC
MICROPOLLUTANTS IN HOSPITAL
WASTEWATER**

by
Gökçe GÜNEY

June, 2020
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WASTEWATER**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree Doctor of
Philosophy in Environmental Engineering, Environmental Engineering
Program**

**by
Gökçe GÜNEY**

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**CHARACTERIZATION AND TREATMENT ALTERNATIVES OF SOME BROMINATED, NITROSO, FLUORO AND PHENOLIC MICROPOLLUTANTS IN HOSPITAL WASTEWATER**” completed by **GÖKÇE GÜNEY** under supervision of **PROF. DR. DELYA SPONZA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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I am dedicating this Ph.D. thesis to my beloved mother Saime PEHLİVANER. I know you are watching us from somewhere above the sky...

Gökçe GÜNEY

CHARACTERIZATION AND TREATMENT ALTERNATIVES OF SOME BROMINATED, NITROSO, FLUORO AND PHENOLIC MICROPOLLUTANTS IN HOSPITAL WASTEWATER

ABSTRACT

The biological, photocatalytic, ultrasound and membrane treatment of some brominated, fluoro, aromatic, phenolic and nitroso micropollutants were investigated from a raw hospital wastewater. The maximum removal efficiencies of all studied micropollutants (higher than 18 per cent) and macropollutants (higher than 64 per cent) were obtained at 55 days SRT in anaerobic UASB/aerobic CSTR sequential biological reactor system at a pH of 7.50 under mesophilic conditions. The maximum removals of all studied micropollutants were found with 0.50 gram per liter nanoparticle concentration (both for titanium (IV) oxide and cerium (IV) oxide), for 45 min irradiation time, at 210 W UV light power, at 60 celsius degree in the photocatalytic experiments. The maximum removals were found at pH 4.00 for PFOA, PFOS and NDMA (higher than 93 per cent); at pH 7.00 for α -HBCDD, PBEB, PBT, TBBPA, TCS and CIP (higher than 96 per cent); at pH 8.50 for AHTN, GFZ and IBU (higher than 96 per cent). The maximum removals of all studied micropollutants were found with 0.40 gram per liter nanoparticle concentration (both for titanium (IV) oxide and cerium (IV) oxide), for 60 min sonication time, at a sonicator power of 120 W, at a pH of 4.00 and at 40 celsius degree for a sonicator frequency of 132 kHz in the ultrasound experiments. The maximum removals of all studied micropollutants (higher than 95 per cent) and conventional pollutants (higher than 95 per cent) were achieved with RO membrane at a transmembrane pressure of 4.75 bar, at a permeate flux of 104.17 liter per square meter per hour, at a cross-flow velocity of 0.10 meter per hour, for 60 min, at a pH of 8.00 and at 25 celsius degree. The cost to treat one cubic meter of raw hospital wastewater was calculated for each treatment option and the cheapest one was calculated as 0.67 Euro with RO.

Keywords: Anaerobic/aerobic treatment, aromatic, brominated, cost analysis, fluoro, membrane, micropollutant, nitroso, phenolic, photocatalytic, reuse, ultrasound

HASTANE ATIKSUYUNDA BULUNAN BAZI BROMLU, FLORLU, NİTRO VE FENOL GRUBU İÇEREN MİKROKİRLİTİCİLERİN KAREKTERİZASYONU VE ARITMA ALTERNATİFLERİ

ÖZ

Bazı bromlu, florlu, aromatik, fenol ve nitro grubu içeren mikrokirleticilerin ham hastane atıksuyundan biyolojik, fotokatalitik, ultrason ve membran yöntemleri ile arıtımı incelenmiştir. Maksimum giderim verimleri çalışılan tüm mikrokirleticiler (yüzde 18’den fazla) ve makrokirleticiler (yüzde 64’ten fazla) için 55 günlük çamur yaşında pH 7,5’da ve mezofilik koşullar altında anaerobik UASB/aerobik CSTR ardışık biyolojik reaktör sisteminde elde edilmiştir. Fotokatalitik deneylerde çalışılan tüm mikrokirleticilerin maksimum giderimleri 0,50 gram bölü litre nanopartikül konsantrasyonu ile (hem titanyum dioksit hem de seryum dioksit için), 45 dk ışınım süresi için, 210 W UV ışığı gücünde, 60 santigrat derece için bulunmuştur. Maksimum giderimler PFOA, PFOS ve NDMA için (yüzde 93’ten fazla) pH 4’te; α -HBCDD, PBEB, PBT, TBBPA, TCS ve CIP için (yüzde 96’dan fazla) pH 7’de; AHTN, GFZ ve IBU için (yüzde 96’dan fazla) pH 8,5’ta bulunmuştur. Ultrason deneylerde çalışılan tüm mikrokirleticilerin maksimum giderimleri 0,40 gram bölü litre nanopartikül konsantrasyonu ile (hem titanyum dioksit hem de seryum dioksit için), 60 dk sonikasyon süresi için, 120 W sonikatör gücünde, pH 4’te ve 40 santigrat derecede 132 kHz sonikatör frekansı için bulunmuştur. Maksimum giderimler çalışılan tüm mikrokirleticiler (yüzde 95’ten fazla) ve konvansiyonel kirleticiler (yüzde 95’ten fazla) için RO membran ile 4,75 bar transmembran basıncında, 104,17 litre bölü metrekare bölü saat permeat akısında, 0,10 metre bölü saat çapraz akış hızında, 60 dk için, pH 8’de ve 25 santigrat derecede elde edilmiştir. Bir metreküp hastane atıksuyunu arıtmak için gereken maliyet tüm arıtma seçenekleri için hesaplanmıştır ve en ucuz olanı 0,67 Avro olarak RO ile hesaplanmıştır.

Anahtar kelimeler: Anaerobik/aerobik arıtma, aromatik, bromlu, maliyet analizi, florlu, membran, mikrokirletici, nitro, fenollü, fotokatalitik, yeniden kullanım, ultrason

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

A great deal of persistent, bioaccumulative or toxic compounds such as pharmaceuticals, personal care products, disinfectants, radionuclides and solvents are found in different concentration ranges in raw hospital wastewaters (Chonova et al., 2016). These compounds are determined in a quite low concentration range such as ng L^{-1} or $\mu\text{g L}^{-1}$ in hospital, domestic, municipal or industrial wastewaters and they are called as micropollutants (Ouarda et al., 2018).

Micropollutants are detected in hydrosphere (surface waters, groundwaters, drinking waters), geosphere and biosphere owing to the developing measurement techniques. Hospitals are one of the main sources of micropollutant emissions because of large quantities of consumption such as; medical activities performed inside, laboratory researches and drugs eliminated from the human body via excretion with urine and feces. Usually, hospital wastewaters are not treated before sending to wastewater treatment plants (WWTPs) (Frédéric & Yves, 2014). The micropollutants in the hospital wastewaters are directly discharged into the sewage system in Turkey without treatment since the conventional WWTPs can only treat macropollutants such as biological oxygen demand, chemical oxygen demand, suspended solids, heavy metals, total nitrogen and total phosphorus. Some micropollutants are not biologically removed and even decrease the biological treatment efficiency during conventional biological treatment step of the WWTPs. In addition to this, micropollutants can be sorbed onto sewage sludge because of their some physicochemical properties like hydrophobicity, low solubility and high sorption potential in the sludges of WWTPs (Petrie, McAdam, Lester, & Cartmell, 2014). If micropollutants in hospital wastewaters are not treated and discharged into the surface waters, they cause ecotoxic effects in the aquatic ecosystem and accumulates in time because of low treatment efficiencies. Also, the sludge cake obtained from the sludge dewatering process of the WWTPs containing the

micropollutants can be applied onto soils as fertilizer. Entrapped micropollutants in fertilizers leaks into the groundwaters with the help of rain waters. In this way, a hydrologic cycle occurs for the untreated micropollutants and human take the micropollutants into his body repeatedly (Figure 1.1). Therefore, treating the hospital wastewaters having a wide range of micropollutants is a very important issue in wastewater treatment.

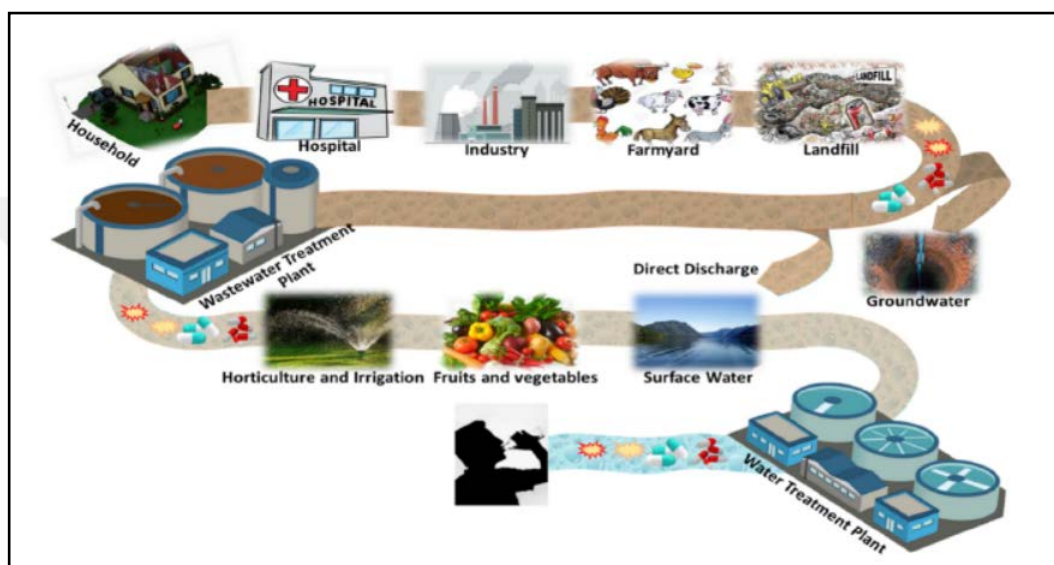


Figure 1.1 Potential sources and pathways of micropollutants (Khanzada et al., 2019)

In Turkey, there are not any limitations for the discharge of raw hospital wastewater into sewage channels. Moreover, there are no WWTPs to treat both macro and micropollutants simultaneously in wastewater for hospitals in Turkey. The Ministry of Environment and Urbanization should take some precautions and impose some restraints about treating or pre-treating raw hospital wastewaters in Turkey.

Ratola, Cincinelli, Alves, & Katsoyiannis (2012) suggested that the pH-dependent $\log K_{ow}$ values should be used to understand the removal mechanisms of micropollutants in biological treatment processes (Ratola et al., 2012). Micropollutants with a $\log K_{ow}$ of less than 2.5, exhibit minimal sorption potential onto solids (sludge/soil/sediment) and the major removal mechanism is biodegradation if micropollutants are susceptible. For micropollutants with $\log K_{ow}$ values higher than 4.0, which are resistant to biodegradation, removal via adsorption

on solids will be the major removal pathway due to their high adsorption potential (Ratola et al., 2012). If micropollutant concentration is low, biological degradation occurs in the presence of a primary substrate. This mechanism is called as co-metabolic removal for the micropollutant having low influent concentration (Kumwimba & Meng, 2019). The solids retention time (SRT) becomes an important operating parameter if the micropollutant will be degraded in co-metabolic removal as a co-substrate. The bacteria population and bacterial growth rate are related with SRT for the co-metabolic degradation of micropollutant (Langford, Scrimshaw, & Lester, 2007). In the co-metabolic degradation of micropollutant, the bacteria population consume the micropollutant concentration as an energy and carbon source (Langford et al., 2007).

Further improvement to biological wastewater treatment can also be obtained by adopting novel treatment technologies that may prove more efficient and less time consuming. The special oxidation techniques known collectively as advanced oxidation processes (AOPs) include technologies such as photocatalysis and ultrasound (acoustic cavitation) treatment (Zupanc et al., 2013). In an AOP, powerful oxidizing species e.g. hydroxyl radicals ($\text{OH}^\bullet$) are formed. Compared to other oxidants like O_3 , H_2O_2 and KMnO_4 , hydroxyl radicals ($\text{OH}^\bullet$) are among the strongest oxidizing species commonly used for water and wastewater treatment. They readily and non-selectively attack micropollutants present in effluent waters and accelerate the rate of oxidation, preferably resulting in their complete mineralisation to CO_2 and H_2O (Zupanc et al., 2013).

Implementing advanced treatment technologies such as membrane processes is essential to remove micropollutants before entering the aquatic environment. The rejection mechanisms of micropollutants by UF or RO membranes include electrostatic repulsion, size exclusion and hydrophobic adsorption between solute and membrane. The removal of micropollutants is occurred depending on their physicochemical properties (hydrophobicity, charge, polarity and molecular size), membrane characteristics (porosity, surface charge and material) and feed solution chemistry (ionic composition and pH) (Jin, Shan, Wang, Wei, & Tang, 2012).

Generally, low micropollutant removals were obtained with UF which was attributed to the bigger pore size of the UF membrane failing to act as a physical barrier for retaining the micropollutants (Pramanik, Pramanik, Sarker, & Suja, 2017). RO is more suitable for removing micropollutants from wastewater because RO has many advantages such as high rejection, simple operation and small footprint. Although RO has many advantages, it is quite sensitive to fouling by microorganisms, salt precipitates, particulate matter and dissolved matter (Cartinella et al., 2006).

1.2 Novelty of the Study

Due to low micropollutant removals were observed both for conventional and advanced treatment processes in recent literature studies, the novelty of the study is to treat some brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) micropollutants present in raw hospital wastewater discharging from a university hospital located in Izmir using four different treatment processes under laboratory conditions for the first time in Turkey. These micropollutants were treated in an anaerobic/aerobic sequential biological reactor system, in an ultrasound process using a sonicator, in a photocatalytic reactor and in membrane treatment process using UF and RO. The removal mechanisms were determined both for micropollutants and their metabolites in the biological treatment process. Fish acute toxicity was evaluated for the biological reactors. Reusability of nanoparticles used in the photocatalytic and ultrasound experiments were investigated after each treatment step. The experimental data obtained from the biological, photocatalytic and ultrasound treatments of the micropollutants were applied to various kinetic models in order to determine the optimum micropollutant removal kinetics. The adsorbed micropollutant amounts onto membrane surfaces were calculated in the membrane systems. A cost analysis was carried out for all treatment options to treat all studied micropollutants from 1 m³ raw hospital wastewater at the optimum experimental conditions.

1.3 Aim of the Study

The aim of this study was to evaluate:

The effect of increasing solids retention time (SRT) (5, 30, 45 and 55 days) on the macropollutants (COD and sCOD) and brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) micropollutants yields were investigated in the biological reactors. The effect of increasing SRT (5, 30, 45 and 55 days) on TVFA accumulation, bicarbonate (HCO_3^-) alkalinity and methane (CH_4) gas levels were researched in the anaerobic reactor, while, TOC, TS, TDS, TSS removals and fish acute toxicity were investigated both in the anaerobic and aerobic reactors. The metabolites released during the anaerobic and aerobic treatment of each micropollutant and the removal efficiencies of them were evaluated at different SRTs. Removal efficiencies, removed masses and removal mechanisms of both macropollutants (COD and sCOD) and all studied micropollutants were calculated at different SRTs in the biological reactors. Fish acute toxicity was evaluated after each SRT operation for the anaerobic and aerobic biological reactors. The experimental data obtained from the biological treatment of the macropollutant and micropollutants were applied to various kinetic models such as, Monod, zero, half, first and second-order to determine the optimum macropollutant and micropollutant removal kinetics. A cost analysis was carried out for the biological treatment of all studied micropollutants from 1 m³ raw hospital wastewater at the optimum experimental conditions.

The effects of using different nanoparticles (silicon dioxide, zinc oxide, graphene, titanium (IV) oxide and cerium (IV) oxide), nanoparticle concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹), irradiation times (15, 30, 45, 60 and 90 min), light powers (120, 210 and 300 W), temperatures (25, 35, 45 and 60 °C), pHs (4.00, 7.00 and 8.50), adsorption and photolysis on the photocatalytic removals of all studied micropollutants were investigated during photocatalytic processes. Reusability of nano-TiO₂ and nano-CeO₂ used in the photocatalytic experiments were determined at

the optimum experimental conditions. The experimental data obtained from the photocatalytic treatment of the micropollutants were applied to various adsorption isotherms such as, Langmuir and Freundlich to determine the optimum micropollutant removal kinetics. A cost analysis was carried out for the photocatalytic treatment of all studied micropollutants from 1 m³ raw hospital wastewater at the optimum experimental conditions.

The effects of sonicator powers (20, 70 and 120 W), sonication times (15, 30, 45, 60 and 90 min), pHs (4.00, 7.00 and 8.50), temperatures (25, 40, 50, 65 and 80 °C), nano-TiO₂ and nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) at a constant sonicator frequency of 132 kHz on the ultrasound removals of all studied micropollutants were investigated during ultrasound processes. Reusability of nano-TiO₂ and nano-CeO₂ used in the ultrasound experiments were studied at the optimum experimental conditions. The experimental data obtained from the ultrasonic treatment of the micropollutants were applied to various kinetic models such as, zero, half, first and second-order to determine the optimum micropollutant removal kinetics. A cost analysis was carried out for the ultrasound treatment of all studied micropollutants from 1 m³ raw hospital wastewater at the optimum experimental conditions.

The effects of operational parameters such as transmembrane pressure (TMP), permeate flux (J_v) and cross-flow velocity (CFV) were researched on the removals of conventional pollutants (TSS, TDS, TOC, COD and sCOD) and all studied micropollutants in UF and RO membranes. The removal mechanisms of both conventional pollutants (TSS, TDS, TOC, COD and sCOD) and all studied micropollutants were investigated in UF and RO. The adsorbed micropollutant amounts onto UF and RO membrane surfaces were calculated in this study. A cost analysis was carried out for the membrane treatment of all studied micropollutants from 1 m³ raw hospital wastewater at the optimum experimental conditions. Also, the irrigation water quality of RO permeate was researched according to some Turkish regulations and the benefit from the irrigation water was calculated if the RO permeate was used as irrigation water in the hospital area.

CHAPTER TWO

PROPERTIES OF MICROPOLLUTANTS

2.1 Properties of Micropollutants Found in Raw Hospital Wastewater

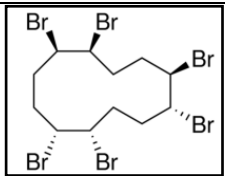
Twelve micropollutants were measured in the raw hospital wastewater regarding brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) groups. Most of them were accepted as quite persistent, accumulative and toxic in the environment and resistant to biodegradation.

2.1.1 Brominated Micropollutants

2.1.1.1 α -Hexabromocyclododecane (α -HBCDD)

α -Hexabromocyclododecane (α -HBCDD) is the third most widely used brominated flame retardant following tetrabromobisphenol A (TBBPA) and decabromodiphenyl ether (BDE 209). α -HBCDD is commonly added to polystyrene foams, upholstery textiles, and electronic devices as it exhibits excellent properties for flame protection purposes in these commercial products (Zhao et al., 2017). The molecular structure of α -HBCDD was shown in Table 2.1.

Table 2.1 α -Hexabromocyclododecane (α -HBCDD)

Micropollutant	Classification*	Structure**
α -HBCDD	Brominated flame retardant	

*: taken from Zhao et al. (2017)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

α -HBCDD can be discharged during the industrial process or washed from waste products, then released into municipal wastewater treatment plants or was washed from waste products and infiltrated various ecosystems. α -HBCDD was reported in water, soil, sediment, plants, animals, humans, and even indoor dust (Peng, Wei,

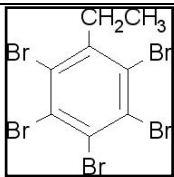
Huang, & Jia, 2018). Due to its highly hydrophobic nature ($\log K_{OW} = 7.74$), α -HBCDD released to aquatic environments tends to partition to and be accumulated in soil, sediment or sludge (Zhong et al., 2018).

α -HBCDD is persistent, bioaccumulative and known to undergo long-range transport. α -HBCDD is an enzyme inducer, endocrine disruptor, and developmental neurotoxicant. Specifically, α -HBCDD exposure leads to changes in thyroid hormone systems, neurodevelopmental effects in children or mice, alters rat hepatic gene expression profiles for cholesterol biosynthesis and lipid metabolism in a sex specific manner and induces genetic recombination (Hakk, Szabo, Huwe, Diliberto, & Birnbaum, 2012).

2.1.1.2 Pentabromoethylbenzene (PBEB)

Pentabromoethylbenzene (PBEB) is an additive flame retardant suitable for use in thermoset resins in circuit boards, adhesives, textiles, wire and cable coating, polyurethane and thermoplastic resins (De Wit, Herzke, & Vorkamp, 2010). The molecular structure of PBEB was shown in Table 2.2.

Table 2.2 Pentabromoethylbenzene (PBEB)

Micropollutant	Classification*	Structure**
PBEB	Brominated flame retardant	

*: taken from De Wit et al. (2010)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

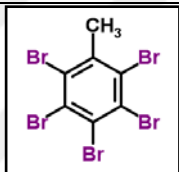
PBEB has been found in the environmental matrices such as sediment, sludge or air, and in biological samples such as fish, birds, cetaceans or even humans. PBEB is quite hydrophobic because of its low water solubility ($2.90 \times 10^{-7} \text{ g L}^{-1}$) with high octanol/water partition coefficient ($\log K_{OW} = 7.48$) and also lipophilic, persistent and toxic to wildlife and humans (Barón et al., 2015).

PBEB causes thyroid disruption, neurobiological development and fetal toxicity/teratogenicity in mammals (Alonso et al., 2014).

2.1.1.3 Pentabromotoluene (PBT)

Pentabromotoluene (PBT) is used as an additive flame retardant in unsaturated polyester resins, mainly for electrical equipment, and in polyethylene, polypropylene, polystyrene and textile (Ezechiáš, Covino, & Cajthaml, 2014). The molecular structure of PBT was shown in Table 2.3.

Table 2.3 Pentabromotoluene (PBT)

Micropollutant	Classification*	Structure**
PBT	Brominated flame retardant	

*: taken from Ezechiáš et al. (2014)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

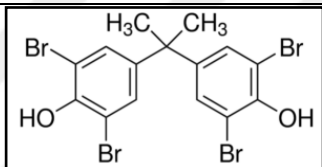
PBT is released from materials and reach surface water from industrial and wastewater treatment plants discharges and from atmospheric depositions (Cristale, Katsoyiannis, Sweetman, Jones, & Lacorte, 2013). Because of its low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$) and high hydrophobicity ($\log K_{OW} = 6.99$), PBT preferentially partition onto sludge during wastewater treatment (Gevao, Muzaini, & Helaleh, 2008).

Because of its persistence and probable toxicity and carcinogenic/mutagenic human health effects, PBT as well as its potential risks to human health has received more concerns (Fang, Huang, Yu, & Wang, 2008). PBT exposure is linked to hormone disruption and thyroid problems on humans (Wang, Wang, Giesy, & Lu, 2013).

2.1.1.4 Tetrabromobisphenol A (TBBPA)

Tetrabromobisphenol A (TBBPA) is the most extensively consumed brominated flame retardant in global scale (Zhao et al., 2017). TBBPA is used during the production of plastic polymers and electronic circuit boards, as well as being incorporated into consumer electronics, office and communication equipment, automotive, aviation and entertainment equipment (McAvoy, Pittinger, & Willis, 2016). The molecular structure of TBBPA was shown in Table 2.4.

Table 2.4 Tetrabromobisphenol A (TBBPA)

Micropollutant	Classification*	Structure**
TBBPA	Brominated flame retardant	

*: taken from Zhao et al. (2017)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

It is released into the environment during the production, use and disposal of TBBPA containing products. TBBPA is very persistent and has been found in air, water, soil, sediment and even in human tissues and plasma (Li, Xiong, Wong, & An, 2016a). TBBPA tends to accumulate on soil, sediment or sludge due to its highly hydrophobic nature ($\log K_{OW} = 5.90$).

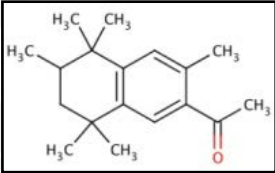
TBBPA can interfere with endocrine system, affect metabolism and cause serious health consequences (Yang, Liao, Ku, & Chang, 2018a). It was also reported that TBBPA is related to toxicological effects in aquatic ecosystem and mammals. TBBPA has disruptive effects on thyroid and estrogen regulative functions, it has damages on liver and kidney, besides, it increases risks of uterine cancer in mammals (Lefevre, Cooper, Stapleton, Claudia, & Gunsch, 2016).

2.1.2 Aromatic Micropollutant

2.1.2.1 Musk Tonalide (AHTN)

Musk tonalide (AHTN) is a synthetic musk and uses as lowcost fragrances in soaps, shampoos, lotions, perfumes, air fresheners, detergents, fabric softeners and other house-hold cleaning products, results to relatively high concentrations in the environment, in biota, as well as in wastewater treatment plants (Artola-Garicano, Hermens, & Vaes, 2003). The molecular structure of AHTN was shown in Table 2.5.

Table 2.5 Musk tonalide (AHTN)

Micropollutant	Application*	Type*	Structure**
AHTN	Synthetic musk	Personal care product	

*: taken from Martin, Moeder, Daniel, Krauss, & Schlosser (2007)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

AHTN is discharged after use into the sewer system and subsequently to wastewater treatment plants. It is expected to be released into the environment in two compartments; in aqueous sewage effluent and in biosolids. It could enter the aquatic environment through discharges of treated sewage into surface waters such as streams, rivers, lakes and it could enter the terrestrial environment through the application of nutrient-rich biosolids to agriculture lands for soil amendment (Yang & Metcalfe, 2006). AHTN tends to accumulate on soil, sediment or sludge due to its highly hydrophobic nature ($\log K_{OW} = 5.70$).

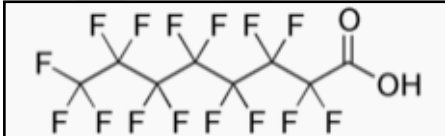
AHTN exhibits endocrine disrupting activities and acts as estrogen receptor modulators when tested with in vitro reporter gene assays, indicating potential for either estrogenic or antiestrogenic activity, depending on the cell line and the estrogen receptor subtype used in the test system. AHTN also exhibits antagonist activities for estrogen, progesterone and androgen receptors, having greater potency for the progesterone receptor (Lefebvre, Kimpe, Metcalfe, Trudeau, & Blais, 2017).

2.1.3 Fluoro Micropollutants

2.1.3.1 Perfluorooctanic Acid (PFOA)

Perfluorooctanic acid (PFOA) is an emerging persistent micropollutant that consists of a fully fluorinated hydrophobic alkyl chain attached to a hydrophilic end group (Arvaniti & Stasinakis, 2015). PFOA has been widely used in several industrial and household applications due to the properties of thermal stability and oxidative resistance. It is extensively used in surfactants, fire-fighting foams and food packing paper. Additionally, the applications of PFOA in textile, carpet and leather treatment are also available (Ahrens, 2011). PFOA can also found in adhesives, cleaners, coatings, shampoos, electroplating, fire-fighting foams, herbicides, insecticides, polishes, wetting agents and stain repellants for furniture (Schultz et al., 2006). The molecular structure of PFOA was shown in Table 2.6.

Table 2.6 Perfluorooctanic acid (PFOA)

Micropollutant	Application*	Type*	Structure**
PFOA	Tenside	Additive in pharmaceuticals	

*: taken from Trojanowicz, Bojanowska-Czajka, Bartosiewicz, & Kulisa (2018)

***: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

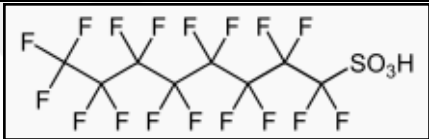
It is commonly accepted that PFOA enters the environment either by direct sources through production use and disposal of consumer products that contain PFOA (Prevedouros, Cousins, Buck, & Korzeniowski, 2006). As a result, PFOA can be found in surface water, sediments, humans and biota (Wang et al., 2013). The physicochemical properties of PFOA (low water solubility = $0.481 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.81$) and the high degree of fluorination besides the strength of the carbon-fluorine (C-F bond) leads to the hydrophobic behavior of PFOA (Ross et al., 2018).

Regarding its toxicity on humans, medical research has associated PFOA with adverse effects on growth, thyroid malfunction, carcinogenesis, phenomena of early menopause in women and fertility disorders (Rahman, Peldszus, & Anderson, 2014).

2.1.3.2 Perfluorooctanesulfonic Acid (PFOS)

Perfluorooctanesulfonic acid (PFOS) is an emerging micropollutant due to its bioaccumulative character, toxicity and recalcitrance (Sun et al., 2013). PFOS has been used in adhesives, cleaners, coatings, shampoos, electroplating, fire-fighting foams, herbicides, insecticides, polishes, wetting agents, stain repellants for furniture, carpets and textile (Schultz et al., 2006). The molecular structure of PFOS was shown in Table 2.7.

Table 2.7 Perfluorooctanesulfonic acid (PFOS)

Micropollutant	Application*	Type*	Structure**
PFOS	Tenside	Hormone active substances (effect on the hormone balance)	

*: taken from Das et al. (2016)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

PFOS is moderately persistent in water ($\log K_{OW} = 4.49$) and can be present in the environmental compartments such as air, surface waters, groundwater, biota, sediment and nonoccupationally-exposed humans (Schultz et al., 2006).

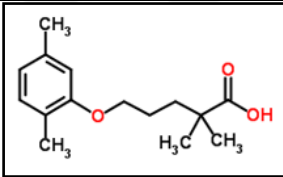
Reports of PFOS showed that it has a potential to accumulate in human blood and tissues and there is an increasing concern about its possible adverse effects on human health. PFOS can also affect the neuroendocrine system, which has lead to its classification as an endocrine disruptor (Sun et al., 2013).

2.1.4 Phenolic Micropollutants

2.1.4.1 Gemfibrozil (GFZ)

Gemfibrozil (GFZ) belongs to the fibrates group of drugs that is used to lower lipid levels. GFZ is useful to increase high-density lipoprotein (HDL, “good cholesterol”) and it is also useful to decrease the levels of triglycerides, very low-density lipoprotein (VLDL, “bad cholesterol”) and low-density lipoprotein (LDL, “bad cholesterol”). GFZ has plenty of additional effects on regulating oxidative stress, reducing inflammation, increasing myelination, promoting signal transduction, etc. which have led to many past and ongoing clinical trials in other disease pathologies (Kim, Kleinman, Lee, & Pahan, 2017). The molecular structure of GFZ was shown in Table 2.8.

Table 2.8 Gemfibrozil (GFZ)

Micropollutant	Application*	Type*	Structure**
GFZ	Lipid-lowering drug	Pharmaceutical	

*: taken from Das et al. (2016)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

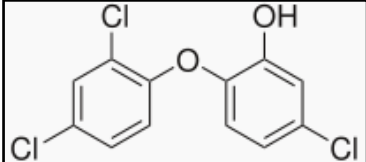
GFZ is moderately persistent in water ($\log K_{OW} = 4.77$), which occurs in treated wastewater, surface water and drinking water. Furthermore, the environmental behavior, transformation products and ecological risks posed by GFZ are of great concern, due to its potential ecotoxicity. It has the potential to be taken up from water and concentrated in goldfish blood, which might subsequently have a negative impact on fish physiology and reproduction (Ma et al., 2016). It should be noted that GFZ can be classified as harmful to aquatic organisms (Araujo et al., 2011).

2.1.4.2 Triclosan (TCS)

Triclosan (TCS) is a broad-spectrum bacteriostatic synthetic chemical commonly used in many personal care and household products (Veetil, Nadaraja, Bhasi, Khan,

& Bhaskaran, 2012). TCS has been connected into a lot of personal care, industrial and household products due to its activity as a broad-spectrum antimicrobial agent (Lee, 2015). The molecular structure of TCS was shown in Table 2.9.

Table 2.9 Triclosan (TCS)

Micropollutant	Application*	Type*	Structure**
TCS	Disinfectant	Personal care product	

*: taken from Das et al. (2016)

**:: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

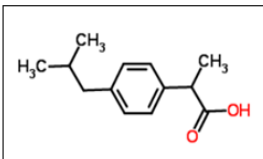
The increased concern about TCS is due to the fact that TCS has been recently found in surface waters, wastewater, soil, sediment and even in human blood, breast milk and urine (Lee, 2015). Due to its hydrophobic nature ($\log K_{OW} = 4.76$), TCS released to aquatic environments tends to partition to and be accumulated in soil, sediment or sludge.

TCS is a micropollutant of concern because it affects a wide variety of organisms. TCS can decrease aggression and alter swimming behavior in fathead minnows and decrease strength in mice. Because TCS is a biologically active compound that specifically targets bacteria, it can also affect microorganisms in environmental and engineered systems. For example, in activated sludge biomass, TCS can decrease oxygen uptake and inhibit nitrification. In addition, sublethal exposure to TCS can increase cross-resistance to other antimicrobials and potentially increase the number of antimicrobial resistance genes in a given environment (McNamara, LaPara, & Novak, 2014).

2.1.4.3 Ibuprofen (IBU)

Ibuprofen (IBU) is a most commonly used non-steroidal anti-inflammatory drug (NSAID) all over the world (Almeida et al., 2013). IBU used against pain, fever and inflammation and can be used without prescription (Langenhoff et al., 2013). The molecular structure of IBU was shown in Table 2.10.

Table 2.10 Ibuprofen (IBU)

Micropollutant	Application*	Type*	Structure**
IBU	Analgesic-antiinflammatory	Pharmaceutical	

*: taken from Das et al. (2016)

**: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

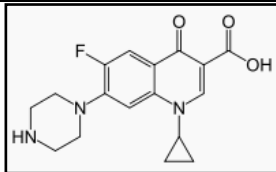
Several authors have found IBU in different environmental compartments such as sediments, surface water, groundwater and even in drinking water (Ferrando-Climent et al., 2012). Although having a low solubility in water ($4.105 \times 10^{-4} \text{ g L}^{-1}$) IBU has a moderate octanol/water partition coefficient ($\log K_{OW} = 3.79$) allows IBU to be removed via biodegradation (Li et al., 2016b).

IBU was shown to affect the growth and reproduction of aquatic species and having genotoxic effects for fish (Almeida et al., 2013).

2.1.4.4 Ciprofloxacin (CIP)

Ciprofloxacin (CIP) is a broad spectrum fluoroquinolone antibiotic widely used in both human and veterinary medicine. It is commonly utilized for the treatment of diseases such as pharyngitis, sinusitis, and earaches, as well as airway diseases, such as pneumonia and bronchitis (Yi et al., 2017). The most widely prescribed fluoroquinolone antibiotic is CIP (Nguyen et al., 2019). The molecular structure of CIP was shown in Table 2.11.

Table 2.11 Ciprofloxacin (CIP)

Micropollutant	Application*	Type*	Structure**
CIP	Antibiotic	Pharmaceutical	

*: taken from Das et al. (2016)

**: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

Hospitals, clinics, health care centers, pharmaceutical-drug industries and wastewater treatment plants are considered the major sources of antibiotic spread in the environment. The existence of CIP in surface water, rivers, groundwater, drinking water, tap water, soil, sediments, wastewater and sewage sludge has been previously reported (Al-Maadheed, Goktepe, Latiff, & Shomar, 2019). Since CIP has high solubility in water ($1.148 \times 10^4 \text{ g L}^{-1}$) with low $\log K_{OW} = 0.28$, it can be effectively treated in wastewater owing to a hydrophilic compound with low adsorption to the solids.

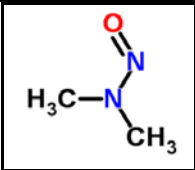
Due to the toxicity of CIP towards the nervous system, heart and the blood stream and inducing expression of resistant genes in microorganisms, it is necessary to develop novel treatment technologies for degradation of CIP (Sani, Fezabady, Yazdani, & Taghavi, 2019).

2.1.5 Nitroso Micropollutant

2.1.5.1 N-Nitrosodimethylamine (NDMA)

N-Nitrosodimethylamine (NDMA) belongs to a family of extremely potent carcinogens and mutagens known as N-nitrosoamines. NDMA is a very soluble micropollutant in water. NDMA was also used as an intermediate in the production of rocket fuel in past years. It was also an important additive to lubricants, a solvent in fiber and plastic industry, and food processing. Recently, NDMA was found to be an emerging disinfection byproduct from chloramination or chlorination in the presence of ammonia (Wang, Li, & He, 2014). The molecular structure of NDMA was shown in Table 2.12.

Table 2.12 N-Nitrosodimethylamine (NDMA)

Micropollutant	Application*	Type*	Structure**
NDMA	Disinfectant	Personal care product	

*: taken from Fournier, Hawari, Streger, McClay, & Hatzinger (2006)

**: taken from United States Environmental Protection Agency [EPI Suite database] (2018)

NDMA is used as a fire retardant and in the organic chemical industry as an antioxidant, catalyst, softener of copolymers and additive for lubricants. NDMA is discharged into the environment as a result of use of certain pesticides. NDMA is presented in various commercial and technical pesticides used in hospitals agriculture and homes (World Health Organization [WHO], 2002). Having lower octanol-water partition coefficient ($\log K_{OW} = -0.57$) makes NDMA easily biodegradable owing to its hydrophilic nature.

Toxicology studies showed that NDMA could induce human organs to produce tumors. The chronic toxicity of NDMA may lead to liver cancer, lung cancer and also damage the nervous system (Bian et al., 2019).

CHAPTER THREE

LITERATURE REVIEW FOR MICROPOLLUTANTS

3.1 Studied Micropollutants

Twelve micropollutants belonging to brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) groups were investigated in the content of this study.

3.1.1 Brominated Micropollutants

3.1.1.1 α -Hexabromocyclododecane (α -HBCDD)

There are limited data for the treatability of α -HBCDD in the literature. Davis, Gonsior, Markham, & Marty (2004) studied aerobic treatability of α -HBCDD and reported that it was not significant and did not follow further degradation to CO₂ and H₂O because of its physicochemical properties like low solubility (2.089×10^{-5} g L⁻¹) and high hydrophobicity (log K_{OW} = 7.74) (Davis et al., 2004). Peng et al. (2018) reported that α -HBCDD can be biodegraded by the anaerobic bacteria at the end of 300 days for 500 μ g L⁻¹ initial concentration at pH 7.00 at 30 °C together with the carbon source (glucose) for a degradation rate of 92.4% in a synthetic wastewater (Peng et al., 2018).

3.1.1.2 Pentabromoethylbenzene (PBEB)

No study was found investigating the treatability of PBEB with conventional or advanced treatment processes in literature.

3.1.1.3 Pentabromotoluene (PBT)

There is not any study investigating the treatability of PBT with conventional or advanced treatment processes in literature.

3.1.1.4 Tetrabromobisphenol A (TBBPA)

There are limited studies for the treatability of TBBPA in the literature. TBBPA removed less than 10% during 120 days in an anaerobic digester sludge experiment at a pH of 7.10 at 35 °C for 0.445 $\mu\text{g } \mu\text{L}^{-1}$ initial TBBPA concentration (McAvoy et al., 2016). TBBPA biodegraded 17.5% during six months of an aerobic soil treatment study for 0.097 $\mu\text{g } \mu\text{L}^{-1}$ initial concentration at a pH of 7.00 and at 21±4 °C (McAvoy et al., 2016). Cao et al. (2015) removed 65.8% TBBPA after 60 min irradiation time at 230 W UV light power at room temperature (20 °C) at a neutral pH (7.00) for an initial TBBPA concentration of 10 mg L^{-1} (Cao et al., 2015).

3.1.2 Aromatic Micropollutant

3.1.2.1 Musk Tonalide (AHTN)

The removal efficiency of approximately 50% for AHTN calculated in the Peterborough WWTP at a HRT of 22 h and at a SRT of 10 days for 137 ng L^{-1} initial AHTN concentration (Yang & Metcalfe, 2006).

3.1.3 Fluoro Micropollutants

3.1.3.1 Perfluorooctanic Acid (PFOA)

Moriwaki et al. (2005) achieved 85% of PFOA removal for the initial concentration of 10 mg L^{-1} at 20 °C at 200 kHz for 1 h ultrasound treatment with a pH range of 3.5 to 4.8 (Moriwaki et al., 2005).

3.1.3.2 Perfluorooctanesulfonic Acid (PFOS)

Conventional and advanced treatability studies of PFOS is limited in the literature. Yu, Hu, Tanaka, & Fujii (2009) obtained maximum 34.0% of PFOS removal efficiency in dry season (September) for an influent concentration of 25.3 ± 4.2 ng L^{-1}

¹ at a SRT of 15 days and a HRT of 8 h in a real scale sewage treatment plant (Yu et al., 2009). Moriwaki et al., (2005) achieved 60% of PFOS removal for the initial concentration of 10 mg L⁻¹ at 20 °C at 200 kHz for 1 h ultrasound treatment with a pH range of 3.5 to 4.8 (Moriwaki et al., 2005).

3.1.4 Phenolic Micropollutants

3.1.4.1 Gemfibrozil (GFZ)

No study was found investigating the treatability of GFZ with biological treatment processes in literature. However, some authors studied the treatment of GFZ with advanced treatment technologies. Ma et al. (2016) investigated photolytic removal of GFZ (initial concentration of 10 mg L⁻¹) through 90 min irradiation time with 500 W UV light power at a pH of 5.00 and achieved 82.0% of GFZ removal (Ma et al., 2016). The highest photocatalytic removal efficiency was above 70% for GFZ at a pH of 5.00 with 1.50 g L⁻¹ nano-TiO₂ concentration throughout 30 min under 100 W UV light power at 20±2 °C for the initial GFZ concentration of 2 mg L⁻¹ (Alvarez-Corena, Bergendahl, & Hart, 2016). There are some available data on GFZ removal by membrane treatment processes. Urtiaga, Pérez, Ibáñez, & Ortiz (2013) reported 71.0% rejection for GFZ at initial concentration of 18.5 µg L⁻¹ in UF having an average pore size of 0.2 µm and at an average flowrate of 2.5 m³ h⁻¹ at pH 7.30 for a secondary effluent of a WWTP (Urtiaga et al., 2013). Snyder et al. (2007) determined higher than 85% of rejection for GFZ having initial concentration of 234 ng L⁻¹ in RO at 12 gallons feet⁻² day⁻¹ flux for a saline groundwater at 25 °C and at pH 7.00-8.00 (Snyder et al., 2007). Radjenović, Petrović, Ventura, & Barceló (2008) obtained GFZ removal in a range of 50-70% with RO at a TMP of 7.3-8.7 kg cm⁻² for an initial GFZ concentration of 10.3 ng L⁻¹ in a full-scale drinking wastewater treatment plant effluent at 17 °C and at a pH range of 5.6-6.1 (Radjenović et al., 2008). GFZ rejected 95% by RO operating at 25 bar pressure through electrostatic repulsion from the negatively charged membrane surface at neutral pH (7.00) for the initial concentrations of 2 µg L⁻¹ in synthetic wastewater (D'Haese et al., 2013). Urtiaga et al. (2013) found 98.8% rejection for GFZ at initial concentration of 18.5

$\mu\text{g L}^{-1}$ in RO at a constant flowrate of $2.4 \text{ m}^3 \text{ h}^{-1}$ and at 11 bar pressure gradient at pH 6.40 for a secondary effluent of a WWTP (Urtiaga et al., 2013).

3.1.4.2 Triclosan (TCS)

One study estimated that 79% and 15% of TCS was removed by biodegradation and adsorption onto sludge, respectively, and then the remaining 6% of TCS was discharged into the receiving water (Singer, Mueller, Tixier, & Pillonel, 2002). Veetil et al. (2012) reported that 87% and 96% of TCS was co-metabolized in 10 days and 5 days under anaerobic and aerobic conditions, respectively at 10 mg L^{-1} TCS level (Veetil et al., 2012). Neves (2014) studied the photocatalytic treatability of TCS and reported that under 5 h irradiation time 0.01 g L^{-1} of TCS removed by 78% at a pH value of 7.00 with 0.50 g L^{-1} nano- TiO_2 with UV irradiation (Neves, 2014). A study about ultrasound treatability of TCS obtained 88% of TCS removal at 35°C under 170 W sonicator power after 15 min sonication time at 850 kHz frequency and at a pH of 2.50 for an initial TCS concentration of 5 mg L^{-1} (Ren et al., 2014). Another study from the literature related to the membrane treatment process determined higher than 85% of rejections for TCS having initial concentration of 166 ng L^{-1} in RO at 12 gallons $\text{feet}^{-2} \text{ day}^{-1}$ flux for a saline groundwater at 25°C and at pH 7.00-8.00 (Snyder et al., 2007). Xie, Nghiem, Price, & Elimelech (2012) determined 96% of TCS removal with RO at pH = 8.50 for $500 \mu\text{g L}^{-1}$ initial TCS concentration at an operating pressure of 10 bar and at $25 \pm 1^\circ\text{C}$ with synthetic wastewater (Xie et al., 2012).

3.1.4.3 Ibuprofen (IBU)

Biological and advanced treatment processes have been investigated to remove IBU from different wastewater matrices. Verlicchi et al. (2013) studied IBU removal from a municipal wastewater in a horizontal subsurface flow bed. The biodegradation removal efficiency of IBU was 28% in the horizontal subsurface flow bed during 1 day of HRT at a constant flowrate of $8 \text{ m}^3 \text{ day}^{-1}$ and at an average temperature of 10°C (Verlicchi et al. 2013). IBU biodegradation was also performed

by Almeida et al. (2013) in activated sludge samples, where a maximum removal efficiency of 50% was observed for IBU biodegradation after 323 h for 250 $\mu\text{g L}^{-1}$ initial IBU concentration by activated sludge (Almeida et al. 2013). Zupanc et al. (2013) investigated IBU removal from a synthetic wastewater by biological treatment process. The experiments were performed in suspended activated sludge reactor containing anoxic, aerated and settlement compartments. IBU removal efficiency measured as $86\pm 10\%$ with an IBU influent of 1.00 $\mu\text{g L}^{-1}$ at a HRT of 48 h (Zupanc et al. 2013). Miranda-García et al. (2011) studied the photocatalytic degradation of 100 $\mu\text{g L}^{-1}$ IBU under 30 W m^{-2} UV light intensity in a synthetic wastewater having a pH range of 7.53 to 8.01. Almost 90% of IBU was degraded within 120 min of irradiation time with 0.335 g L^{-1} nano-TiO₂ concentration (Miranda-García et al., 2011). The photocatalytic degradation of IBU (initial concentration of 213 mg L^{-1}) in pharmaceutical industry wastewater was evaluated using 2.50 g L^{-1} nano-TiO₂ concentration at 25 °C at a pH of 5.30 under 10 W UV LED lamps. IBU was below the detection limit after 240 min of photocatalysis time (Jallouli et al., 2018). Méndez-Arriaga et al. (2008) investigated the ultrasonic degradation of IBU and obtained a high degradation rate ($6.1 \mu\text{mol L}^{-1} \text{min}^{-1}$) for an initial concentration of 21 mg L^{-1} at 80 W sonicator power at 300 kHz for 30 min sonication time at 25 °C and at a pH of 3.00 (Méndez-Arriaga et al, 2008). Snyder et al. (2007) observed only 7% of rejection in UF (35 gallons $\text{feet}^{-2} \text{day}^{-1}$ flux) but measured higher than 85% of rejections in RO (12 gallons $\text{feet}^{-2} \text{day}^{-1}$ flux) for IBU (initial concentrations of 39 and 302 ng L^{-1} for UF and RO, respectively) for a secondary effluent from a municipal WWTP and a saline groundwater, respectively at pH 7.00 (Snyder et al., 2007). Urtiaga et al. (2013) reported 1.2% and 96.9% rejections for IBU for an initial concentration of 2.5 $\mu\text{g L}^{-1}$ in UF and RO, respectively at an average flowrate of 2.5 $\text{m}^3 \text{h}^{-1}$ for a secondary effluent of a WWTP (Urtiaga et al., 2013). IBU rejected 95% by RO operating at 25 bar pressure at neutral pH (7.00) for the initial concentration of 2 $\mu\text{g L}^{-1}$ in synthetic wastewater (D’Haese et al., 2013).

3.1.4.4 Ciprofloxacin (CIP)

Biological treatment processes were used for the treatment CIP from both hospital and municipal wastewaters. Chatila et al. (2016) found 92% CIP removals in a horizontal-flow anaerobic reactor at an HRT of 24 h, at influent CIP concentrations of 2.0–5.0 $\mu\text{g L}^{-1}$ (Chatila et al., 2016). The CIP yields were found to be 64% in the anaerobic stage of an anaerobic/anoxic/aerobic sequential reactor system treating 99 ng L^{-1} CIP at an HRT of 2 h treating raw sewage (Jia, Wan, Xiao, & Hu, 2012). Petrie et al. (2014) reported 46% CIP removal in an aerobic reactor after 24 h HRT at a CIP loading of 165 $\mu\text{g day}^{-1}$ (Petrie et al., 2014). Hamjinda, Chiemchaisri, Watanabe, Honda, & Chiemchaisri (2018) obtained 79% CIP removal efficiency for 3.44 $\mu\text{g L}^{-1}$ concentration in a conventional activated sludge system treating hospital wastewater (Hamjinda et al., 2018). The biological treatability studies of CIP performed by Jia et al. (2012), Petrie et al. (2014) and Hamjinda et al. (2018) exhibited low removals (Jia et al., 2012, Petrie et al., 2014 and Hamjinda et al., 2018). The treatability studies of CIP performed with ultrasound and photocatalytic processes are limited in recent literature and low CIP yields were obtained. De Bel, Dewulf, De Witte, Van Langenhove, & Janssen (2009) observed 57% removal efficiency with ultrasound treatment at a frequency of 520 kHz and a power of 92 W with an initial CIP concentration of 15 mg L^{-1} after 120 min sonication time (De Bel et al., 2009). Xiao, He, Diaz-Rivera, Pee, & Weavers (2014) determined 4.4 $\mu\text{m min}^{-1}$ CIP sono-degradation rate at 100 μm initial CIP concentration in a sonicator reactor having a frequency of 620 kHz and 400 W power (Xiao et al., 2014). Vasconcelos, Kümmerer, Henriques, & Martins (2009) found 67% photocatalytic degradation of CIP using nano-TiO₂ in a hospital wastewater effluent (Vasconcelos et al., 2009). Li, Guo, Su, & Xu (2012) investigated the photodegradation of CIP by nano-TiO₂ under simulated solar light irradiation. Complete elimination of CIP was achieved in a reaction system composed of 0.5 g L^{-1} of TiO₂ and 82.5 mg L^{-1} of H₂O₂ at pH 6 after 90 min irradiation (Li et al., 2012).

3.1.5 Nitroso Micropollutant

3.1.5.1 N-Nitrosodimethylamine (NDMA)

Conventional and advanced treatability studies of NDMA is limited in the literature. Sharp, Wood, & Alvarez-Cohen (2005) used aerobic bacteria to deal with 200 $\mu\text{g L}^{-1}$ initial NDMA concentration in 15 kinds of sewage and the removal rate is more than 50% within the 30 days (Sharp et al., 2005). Zhou et al. (2009) monitored NDMA in groundwater over 7 years and found that about 90% of NDMA was degraded by microorganisms for an initial NDMA concentration of 10 ng L^{-1} (Zhou et al., 2009). Steinle-Darling, Zedda, Plumlee, Ridgway, & Reinhard (2007) studied the removal of NDMA by RO at 15.5 bar TMP with 10 cm sec^{-1} CFV at 25 ± 0.5 °C for an initial concentration of 200 $\mu\text{g L}^{-1}$ and obtained 56% removal efficiency for NDMA in deionized water (Steinle-Darling et al., 2007).

CHAPTER FOUR

MECHANISMS FOR TREATMENT PROCESSES

4.1 Biological Treatment

The wastewater treatment should not address only the removal of conventional pollutants, such as nitrogen or organic matter, but also the presence of organic micropollutants, an issue of increasing concern in the society. There is a consensus in considering the effluents from conventional wastewater treatment plants as the main entrance of these substances into the aquatic environment since common treatment processes are not able to effectively remove many of them (Arias et al., 2018). High micropollutant removal efficiencies can be achieved by the application of biological configurations upgraded with using sequential biological reactors. Thus, an alternative approach would be develop to enhance the removal of macro and micropollutants with biological processes.

Micropollutants are biologically eliminated to varying degrees, resulting in mineralization or incomplete elimination (formation of transformation products or metabolites). The metabolites are connected to the operating conditions and can be sometimes comparable or even more persistent and toxic than their parent compounds (Kumwimba & Meng, 2019). The removal of micropollutants in WWTPs is commonly evaluated as a mass balance between concentrations in influent and effluent wastewater (Martín, Camacho-Muñoz, Santos, Aparicio, & Alonso, 2012). The two mayor removal pathways in WWTPs for micropollutants are sorption to the sludge and biodegradation of the micropollutant in the aeration tank. The removal efficiency of each micropollutant is dependent on its physicochemical properties, as well as on the operation efficiency of the plants (Artola-Garicano et al., 2003). Micropollutants could not absolutely treated during wastewater treatments and, as a result, they are discharged into the receiving waters and could be end up onto soils when the sludge cake obtained from the sludge dewatering process is applied as fertilizer (Clarke et al., 2008).

4.1.1 Anaerobic Treatment

Anaerobic treatment uses less energy, has a lower sludge yield and lower nutrient requirements, is cheaper to implement, uses less space, and offers improved biogas recovery in comparison with aerobic treatment (Aydin et al., 2015). However, in the modern high-rate anaerobic reactors, the start-up and the control of the processes are relatively complex because of the low specific growth rate of their microorganisms, their sensitivity to variations in environmental conditions and the variations of incoming wastewater flow and its composition. Furthermore, the sludge granulation inside the reactor complicated the system (Mullai, Arulselvi, Ngo, & Sabarathinam, 2011).

The anaerobic treatment is mostly preferred the technology of upflow anaerobic sludge blanket (UASB) reactor. The influent wastewater is introduced at the bottom of the UASB reactor and moves forward in an upflow way through the sludge blanket. The critical design elements of the UASB reactor are gas-solids separator, influent distribution system and effluent withdrawal design. High COD loadings can be used in UASB reactors. It is a great advantage that granulated sludge can be developed densely in the UASB reactors. It takes a long period of time (several months) for the development of dense granulated sludge, however, the seed can be provided from another plant to fasten the start-up of the UASB reactor. The wastewater characteristics, pH, upflow velocity and nutrient addition have important effects on the sludge development (Metcalf & Eddy, 2004).

4.1.2 Aerobic Treatment

The aerobic treatment is commonly used in wastewater treatment plants. Microorganisms are added to the pretreated wastewater and in this way, nutrients are removed, moreover, the carbonaceous biological matter and nitrogenous matter are oxidized. The polluted municipal or industrial wastewater mix in an aerated reactor with an aerobic bacterial culture. The aeration tank retention time is arranged to make sure of effluent wastewater is effectively treated before sending a

sedimentation tank. The settled activated sludge is recycled back to the aeration tank in order to provide a stable and fixed concentration of aerobic microorganisms (Grandclément et al., 2017).

Influent wastewater and recycled return activated sludge are introduced typically into the continuous-flow stirred-tank reactor (CSTR) which was the most commonly used aerobic treatment process. The oxygen demand, organic load and substrate concentration are uniform and the F/M ratio is low throughout the CSTR owing to the fully mixing conditions in the CSTR. The most important operating condition in CSTR is to provide a well mixing between the influent wastewater and the aerobic microorganisms. The shape and dimension of CSTR depends mainly on the size, type and mixing pattern of the aeration equipment (Metcalf & Eddy, 2004).

4.2 Photocatalytic Treatment

Further improvement to biological wastewater treatment can also be obtained by adopting novel treatment technologies that may prove more efficient and less time consuming. Nowadays, attention has turned to special oxidation techniques known collectively as advanced oxidation processes (AOPs). These include technologies based on ozonation, sonolysis, photolysis and photocatalysis (Sturini et al., 2012). In an AOP, powerful oxidizing species e.g. hydroxyl radicals ($\text{OH}^\bullet$) are formed. Compared to other oxidants like O_3 , $\text{H}_2\text{O}_2^\bullet$ and KMnO_4 , $\text{OH}^\bullet$ radicals are among the strongest oxidizing species commonly used for water and wastewater treatment. They readily and non-selectively attack organic compounds present in wastewaters and accelerate the rate of contaminants oxidation, preferably resulting in their complete mineralisation (Zupanc et al., 2013). However, the photocatalytic ability of a photocatalyst largely depends on its crystal structure, crystallite size, surface area, thickness and porosity (Hu et al., 2017). The photocatalytic processes have been reported to be effective for the degradation of many organic pollutants, such as carboxylic acids, chloroanilines, mono-chlorocarboxylicacids, chlorophenols, dyes, fungicides, herbicides, ketones, phenolics and pharmaceuticals (Li et al., 2012).

Explanation of a semiconductor by photons having an energy level that exceeds its bandgap energy excites electrons (e^-) from the valence band to the conduction band and produces holes (h^+) in the valence band (Equation 4.1) (Figure 4.1).

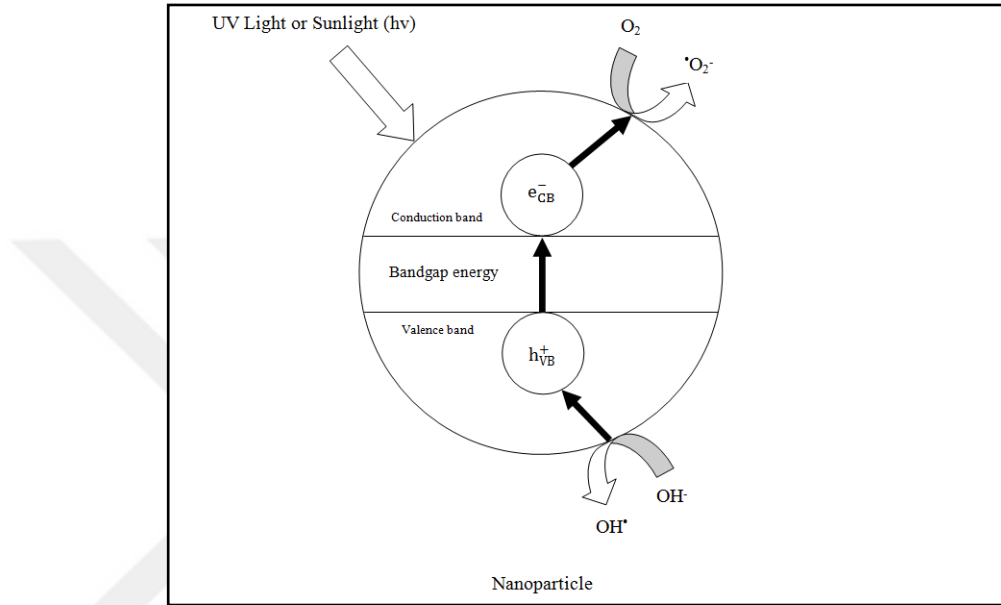
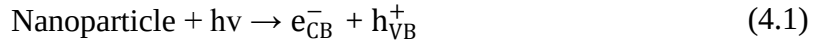


Figure 4.1 Schematic mechanism of photocatalysis (Paul, Dodd, & Strathmann, 2010)

The photogenerated valence band holes react with either water (H_2O) or hydroxyl ions (OH^-) adsorbed on the catalyst surface to generate strong oxidant hydroxyl radicals ($OH^\bullet$) (Equation 4.2) (Figure 4.1).



The photogenerated electrons in the conduction band may react with oxygen to form superoxide ions ($\bullet O_2^-$) (Equation 4.3) (Figure 4.1).



The superoxide ions can then react with water to produce hydrogen peroxide and hydroxyl ions. Cleavage of hydrogen peroxide by the conduction band electrons

yields further hydroxyl radicals and hydroxyl ions. The hydroxyl ions can then react with the valence band holes to form additional hydroxyl radicals. Degradation of micropollutants can be achieved by their reaction with hydroxyl radicals ($\text{OH}^\bullet$) or direct attack from the valence band holes (Equation 4.4).



4.3 Ultrasound Treatment

Advanced oxidation processes (AOPs) have the potential to substantially reduce contaminants from water and wastewater. Ultrasonic degradation is an emerging AOP with advantages over other AOPs due to its ease of use, lack of chemical addition and unique degradation mechanisms. The ultrasonic process is also not restricted by toxicity or low biodegradability of contaminants. The chemical effect of ultrasound is caused by the phenomenon of cavitation. Acoustic cavitation is the formation, growth and implosive collapse of small bubbles in a liquid blasted with sound. The collapse of these bubbles leads to surprisingly high local temperatures and pressures (Figure 4.2).

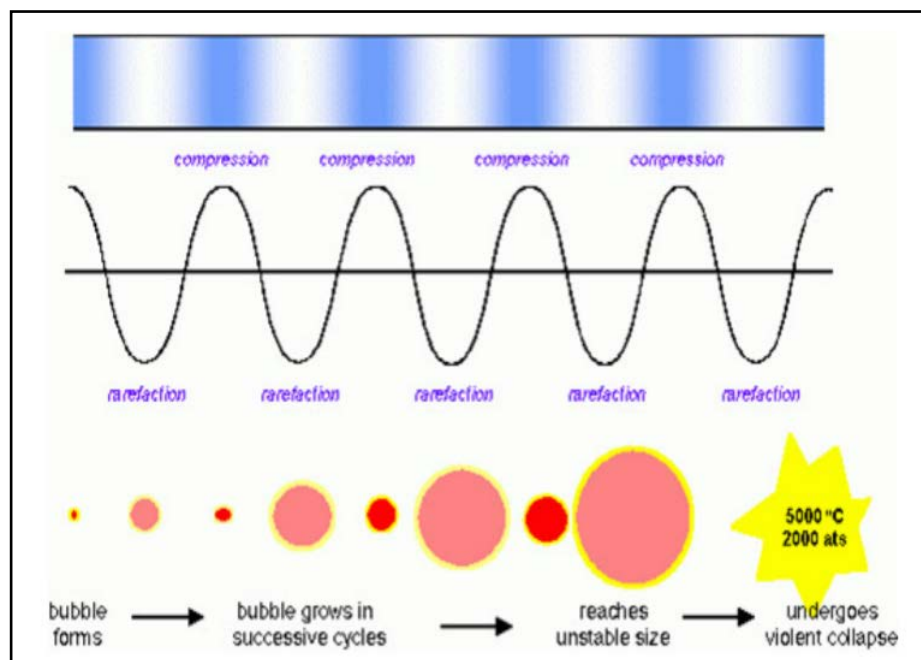


Figure 4.2 Generation of an acoustic bubble (Oztekin, 2011)

These localized hot spots were estimated to have temperatures of roughly 5200 K, pressures of about 500 atm and lifetimes of a few microseconds (Figure 4.3). Temperatures in the interfacial region between the solution and the collapsing bubbles can still reach 1900 K (De Bel, Janssen, De Smet, Langenhove, & Dewulf, 2011).

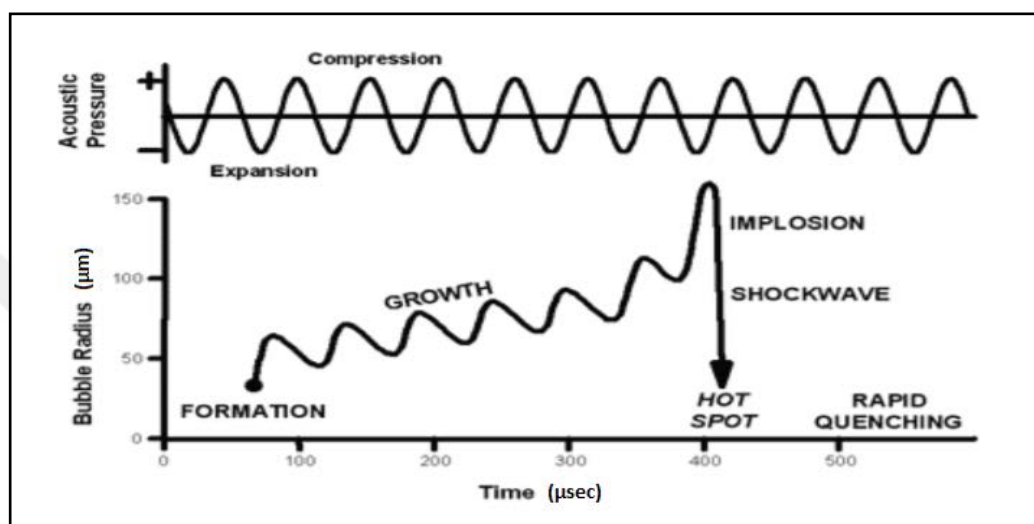


Figure 4.3 Transient acoustic cavitation (Oztekin, 2011)

Considering these cavitation bubbles as microreactors, three different reaction zones have been postulated: (i) the gaseous interiors of collapsing cavities resulting in the dissociation of volatile compounds including water through thermolysis; (ii) the interfacial liquid surrounding cavitation bubbles where high temperature (ca. 1000–2000 K) and high concentrations of hydroxyl radicals ($\text{OH}^\bullet$) exist; and (iii) bulk solution (at ambient temperature) where small amounts of $\text{OH}^\bullet$ radicals diffusing from bubble interfaces may contribute to contaminant destruction reactions (Figure 4.4) (Xiao et al., 2014). Two reaction mechanisms have mainly been proposed to explain ultrasonic degradation of organic compounds in aqueous solutions. The first mechanism is pyrolysis in the cavitation bubbles. The second mechanism is the generation of $\text{OH}^\bullet$ radicals in the cavitation bubbles due to thermolysis of water. These radicals can subsequently oxidize the organic compounds in the interfacial region (De Bel et al., 2011).

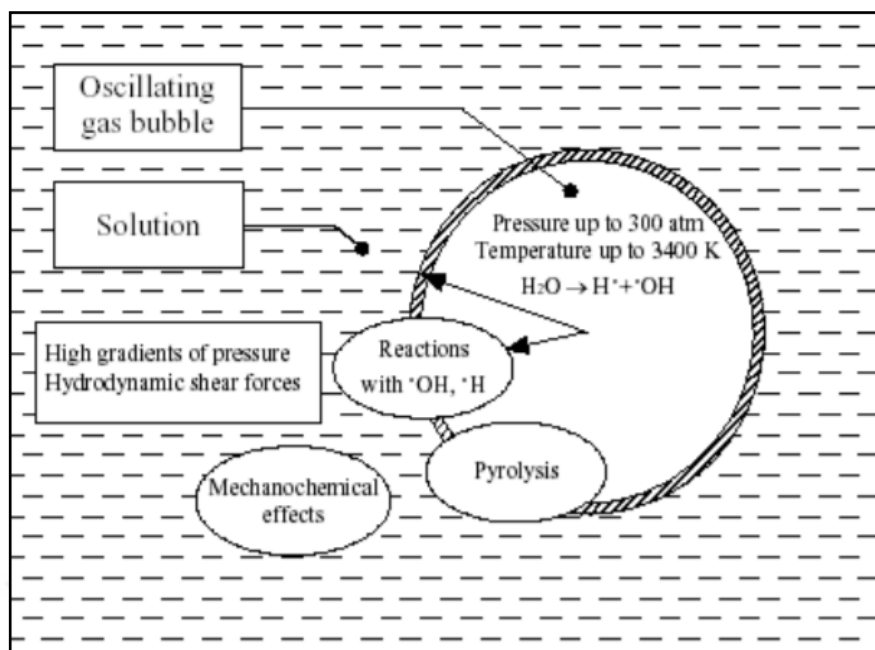


Figure 4.4 Compression of a cavitations bubble in aqueous solutions (Oztekin, 2011)

The degradation pathway of a micropollutant depends on its physicochemical properties, surface activity and $OH^{\bullet}$ radical reactivity. Micropollutants with low solubility and/or high volatility are expected to go through fast ultrasonic degradation since they have a tendency to accumulate inside or around the gas–liquid interface. Therefore, ultrasound treatment may be a proper method for the removal of hydrophobic micropollutants (Mowla, Mehrvar, & Dhib, 2014).

The disadvantages of ultrasonic process are the required large amount of energy to remove organic pollutants and the long treatment time due to the low reaction rates. In order to accomplish these disadvantages, semiconductive materials are used as catalysts to increase the process efficiency. The catalyst application can increase the ultrasonic efficiency because more reactive radicals occurs by supporting more active sites for nucleation process and microbubbles formation. TiO_2 is the most studied sonocatalyst owing to its many advantages, including physical and chemical stability and low cost (Hassani, Khataee, Karaca, Karaca, & Gholami, 2017).

4.4 Membrane Treatment

In membrane processes, the micropollutants have different type of physicochemical characteristics such as; size, charge, solubility, diffusivity and hydrophobicity (Khanzada et al., 2019).

The UF membranes were not effective for removing micropollutants owing to their high molecular weight cut-off (MWCO) values than the molecular weight of the micropollutants (Narbaitz et al., 2013). Koyuncu (2018) explained that the UF membranes having a MWCO value between 1 and 500 kDa could be removed the molecules having particle sizes between 1 and 30 nm (Koyuncu, 2018). The molecular weight of most micropollutants are approximately (≈ 1 kDa) (Kim et al., 2018). Therefore, the removal efficiencies of UF could be higher for uncharged macropollutants having higher particle sizes than the micropollutants having lower particle sizes. Pollutants separation by the charge repulsion mechanism in UF arises when the electrostatic repulsive forces between the charged membrane surface and the ions of electrolyte pollutants prevent the ion from contacting the membrane (Narbaitz et al., 2013). The hydrophobic adsorption mechanism in UF takes place if the pollutant has high hydrophobicity and therefore, the pollutant is adsorbed on the membrane surface (Khanzada et al., 2019).

The fundamental removal mechanisms of micropollutants in RO are size exclusion, electrostatic interaction and hydrophobic adsorption (Figure 4.5) (Khanzada et al., 2019).

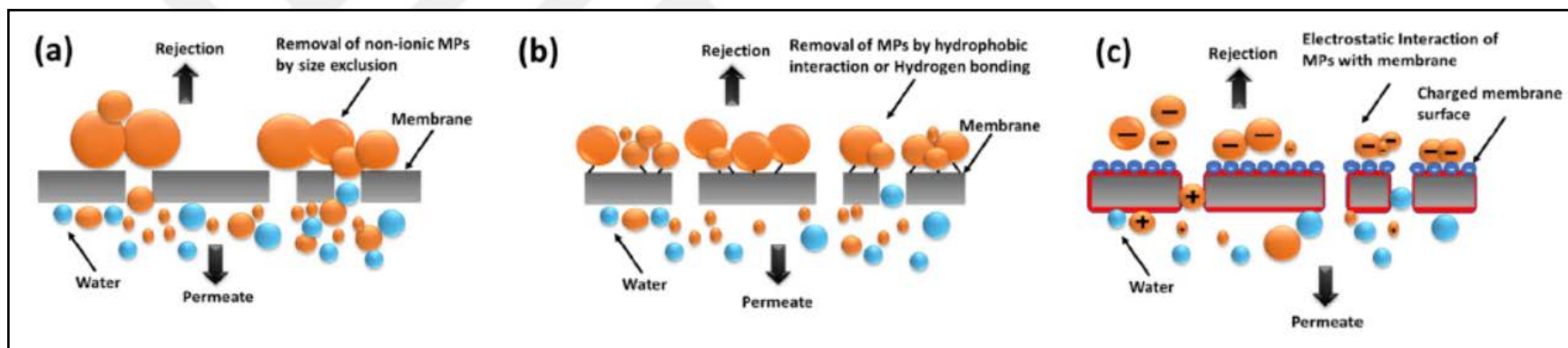


Figure 4.5 Mechanism of micropollutants (MPs) removal from membrane: (a) size exclusion, (b) hydrophobic adsorption and (c) electrostatic interaction (Khanzada et al., 2019)

The separation process for RO is most often explained via the solution-diffusion model, which states that both water and solute passing through the membrane must first dissolve into the membrane matrix, then diffuse through it to reach the permeate side. Many compounds, such as those carrying charge, will be repelled by the membrane surface and be immediately rejected. Uncharged solutes can approach the membrane surface, where they presumably follow the process outlined in the solution-diffusion model. The extent of compound rejection is therefore controlled by the relative rates of dissolution into and diffusion within the membrane matrix between water and solute. Additionally, surface adsorption and internal absorption have been shown to play a role in the initial rejection of some compounds, where the rejection decreases over time until all sorption sites are filled. Many factors may influence these processes, amongst them charge, size, hydrophobicity, hydrogen bonding capacity and dipole moment (Steinle-Darling et al., 2007).

Unlike RO, the removal of organic micropollutants by UF (particularly by size exclusion) is often considered negligible owing to the large molecular weight cut off (MWCO) value of UF membranes (1–100 kDa), which is generally larger than the molecular weight of most MPs (<1 kDa) (Kim et al., 2018). Since UF membranes are not effective in retaining micropollutants based on size exclusion, adsorption is thus considered the mainstream mechanism contributing to the removal of micropollutants by UF membranes. This can be attributed to the fact that the adsorption of micropollutants in membrane filtration is not only restricted to the membrane surface but can also occur in the membrane's porous structure and is often directly related to pore radius (Khanzada et al., 2019). Generally, membranes with larger pore sizes (UF membranes) allow micropollutants to access the membrane's internal porous structure (more adsorption sites), whereas the access of these pollutants to the internal sites may be limited in dense membranes (RO). Hence, the more porous the membrane, the more micropollutants the membrane may allow to adsorb within the membrane pores in addition to its surface as a function of their physicochemical characteristics (Khanzada et al., 2019).

CHAPTER FIVE

MATERIALS AND METHODS

5.1 Source and Characterization of Raw Hospital Wastewater

The raw hospital wastewater was supplied from sewer connection line belonging to Dokuz Eylul University Hospital (Izmir, Turkey). It is discharged directly through the sewer system without any treatment and it is transferred directly to the related wastewater treatment plant. The aliquot samples of the raw hospital wastewater were taken from the sewer channel during 6 h sampling period in November, 2015. The raw hospital wastewater was filtered from a coarse filtration with having 0.075 mm pore sized metallic strainers by gravity to remove the big particles before the analysis. Characterization of the raw hospital wastewater is given in Table 5.1.

Table 5.1 Characterization of the raw hospital wastewater (n=3, mean $\pm$ SD)

Parameter	Level, concentration ^a	Parameter	Level, concentration ^b
pH	8.25 $\pm$ 0.50	α -Hexabromocyclododecane (α -HBCDD)	0.0115 $\pm$ 0.001
Temperature(°C)	18.0 $\pm$ 2.00	Pentabromoethylbenzene (PBEB)	0.00328 $\pm$ 0.001
Total Nitrogen (TN)	0.50 $\pm$ 0.05	Pentabromotoluene (PBT)	0.00231 $\pm$ 0.001
Total Phosphorus (TP)	1.00 $\pm$ 0.05	Tetrabromobisphenol A (TBBPA)	0.0170 $\pm$ 0.001
Total Solids (TS)	380.00 $\pm$ 0.50	Musk tonalide (AHTN)	0.206 $\pm$ 0.020
Total Dissolved Solids (TDS)	250.00 $\pm$ 0.50	Perfluorooctanic acid (PFOA)	0.1770 $\pm$ 0.001
Total Suspended Solids (TSS)	130.00 $\pm$ 0.50	Gemfibrozil (GFZ)	53.30 $\pm$ 0.05
Total Organic Carbon (TOC)	325.0 $\pm$ 1.00	Triclosan (TCS)	361.00 $\pm$ 0.05
Biological Oxygen Demand (BOD ₅)	630.00 $\pm$ 10.00	Perfluorooctanesulfonic acid (PFOS)	0.0180 $\pm$ 0.001
Chemical Oxygen Demand (COD)	950.00 $\pm$ 10.00	Ibuprofen (IBU)	42.50 $\pm$ 0.05
Soluble Chemical Oxygen Demand (sCOD)	850.00 $\pm$ 10.00	Ciprofloxacin (CIP)	522.00 $\pm$ 0.05
		N-Nitrosodimethylamine (NDMA)	0.165 $\pm$ 0.020

^a: All concentrations (except pH and temperature) in mg L⁻¹^b: All concentrations in μ g L⁻¹

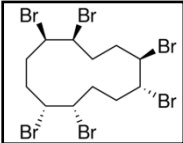
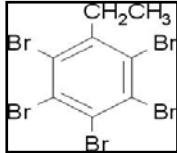
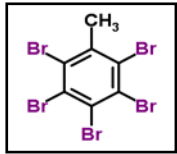
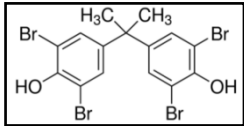
5.2 Physicochemical Properties of the Studied Micropollutants

The physicochemical properties of micropollutants are important in the prediction of their environmental fate and in the development of analytical detection methods. Based on the calculated octanol/water partition coefficients (log K_{OW}) and water solubilities for the micropollutants, it can be said that having higher log K_{OW} values (>4.00) and lower water solubilities classified as hydrophobic micropollutants. The hydrophobic micropollutants have been found to sorb onto sewage sludge and soil/sediment thus, can be resist to biological treatment. Having lower log K_{OW} values (<2.00) and higher water solubilities classified as hydrophilic micropollutants. The hydrophilic micropollutants can be easily biodegraded with biological treatment methods. Point of zero charge (pzc) values are important to understand the behaviors

of the micropollutants under different operating pH conditions. Physicochemical properties of the studied micropollutants for this study are given in Table 5.2.

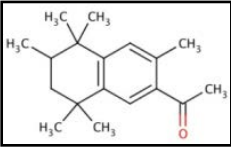
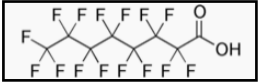
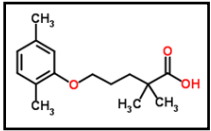
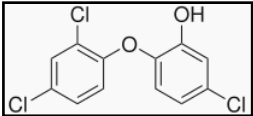


Table 5.2 Physicochemical properties of the studied micropollutants (United States Environmental Protection Agency [EPI Suite database], 2018)

IUPAC name	CAS No	Abbreviation	Chemical formula	Molecular weight (g mol ⁻¹)	Henry's Law constant, k_H at 25 °C (atm m ³ mol ⁻¹)	Solubility in water, at 25 °C (g L ⁻¹)	Point of zero charge, pzc (unitless)	Octanol/water partition coefficient, log K_{OW} (unitless)	Soil organic carbon/water partition coefficient, log K_{OC} (unitless)	Molecular structure
α-Hexabromocyclododecane ((1R,2R,5S,6R,9R,10S)-1,2,5,6,9,10-hexabromocyclododecane)	134237-50-6	α -HBCDD	C ₁₂ H ₁₈ Br ₆	641.70	1.72×10^{-6}	2.09×10^{-5}	7.5, 8.5	7.74	6.717	
2,3,4,5,6-Pentabromoethylbenzene (1,2,3,4,5-pentabromo-6-ethylbenzene)	85-22-3	PBEB	C ₈ H ₅ Br ₅	500.65	7.92×10^{-5}	2.90×10^{-7}	7.5, 8.5	7.48	6.491	
Pentabromotoluene (1,2,3,4,5-pentabromo-6-methylbenzene)	87-83-2	PBT	C ₇ H ₃ Br ₅	486.62	5.97×10^{-5}	9.35×10^{-7}	7.5, 8.5	6.99	6.066	
3,3',5,5'-Tetrabromobisphenol A (2,6-dibromo-4-[2-(3,5-dibromo-4-hydroxyphenyl)propan-2-yl]phenol)	79-94-7	TBBPA	C ₁₅ H ₁₂ Br ₄ O ₂	543.88	1.47×10^{-5a}	7.65×10^{-6}	7.5, 8.5	5.90	N.A.	

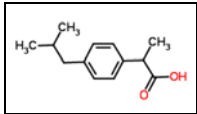
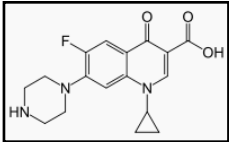
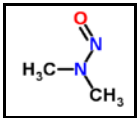
N.A.: Not available, ^a: Kuramochi et al., 2008, ^b: Wang et al., 2017a, ^c: De Bel et al., 2009, ^d: Alvarez-Corena et al., 2016

Table 5.2 continues

IUPAC name	CAS No	Abbreviation	Chemical formula	Molecular weight (g mol ⁻¹)	Henry's Law constant, k_H at 25 °C (atm m ³ mol ⁻¹)	Solubility in water, at 25 °C (g L ⁻¹)	Point of zero charge, pzc (unitless)	Octanol/water partition coefficient, log K_{ow} (unitless)	Soil organic carbon/water partition coefficient, log K_{OC} (unitless)	Molecular structure
Musk Tonalide 6-Acetyl-1,1,2,4,4,7-hexamethyl-tetralin	21145-77-7	AHTN	C ₁₈ H ₂₆ O	258.41	1.40×10^{-4}	1.25×10^{-3}	N.A.	5.70	N.A.	
Perfluorooctanic acid (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanoic acid)	335-67-1	PFOA	C ₈ HF ₁₅ O ₂	414.07	9.08×10^{-2}	4.81×10^{-4}	2.8 ^b	4.81	2.816	
Gemfibrozil (5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid)	25812-30-0	GFZ	C ₁₅ H ₂₂ O ₃	250.34	1.19×10^{-8}	4.964×10^{-3}	4.75	4.77	2.850	
Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol)	3380-34-5	TCS	C ₁₂ H ₇ Cl ₃ O ₂	289.55	4.99×10^{-9}	4.621×10^{-3}	7.9	4.76	3.925	

N.A.: Not available, ^a: Kuramochi et al., 2008, ^b: Wang et al., 2017a, ^c: De Bel et al., 2009, ^d: Alvarez-Corena et al., 2016

Table 5.2 continues

IUPAC name	CAS No	Abbreviation	Chemical formula	Molecular weight (g mol ⁻¹)	Henry's Law constant, k_H at 25 °C (atm m ³ mol ⁻¹)	Solubility in water, at 25 °C (g L ⁻¹)	Point of zero charge, pzc (unitless)	Octanol/water partition coefficient, log K_{ow} (unitless)	Soil organic carbon/water partition coefficient, log K_{OC} (unitless)	Molecular structure
Perfluorooctanesulfonic acid (1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro-1-octanesulfonic acid)	1763-23-1	PFOS	C ₈ HF ₁₇ O ₃ S	500.13	1.10×10 ⁻²	0.104×10 ⁻³	< 1.0	4.49	3.409	
Ibuprofen (2-(4-Iso butylphenyl) propanoic acid)	15687-27-1	IBU	C ₁₃ H ₁₈ O ₂	206.29	1.52×10 ⁻⁷	4.105×10 ⁻⁴	4.91	3.79	2.352	
Ciprofloxacin 1-Cyclopropyl-6-fluoro-4-oxo-7-(1-piperazinyl)-1,4-dihydro-3-quinolinecarboxylic acid	85721-33-1	CIP	C ₁₇ H ₁₈ FN ₃ O ₃	331.35	5.09×10 ⁻¹⁹	1.148×10 ⁻⁴	3.6 ^c , 5.6, 6.2, 8.8	0.28	-0.004	
N-Nitroso dimethylamine (N,N-dimethylnitrous amide)	62-75-9	NDMA	C ₂ H ₆ N ₂ O	74.08	2.06×10 ⁻⁶	4.104×10 ⁻⁵	3.52 ^d	-0.57	0.566	

N.A.: Not available, ^a: Kuramochi et al., 2008, ^b: Wang et al., 2017a, ^c: De Bel et al., 2009, ^d: Alvarez-Corena et al., 2016

5.3 Biomass and Synthetic Media

Methanogenic granular sludge from a full-scale upward-flow anaerobic sludge blanket reactor (UASB) treating yeast industry wastewater of PAKMAYA in Izmir, Turkey, was used as the inoculum of our anaerobic reactor. At the beginning of the study, anaerobic sludge was fed with vanderbilt mineral medium together carbon source (950.00 mg L⁻¹ glucose). Vanderbilt mineral medium consisted of the following inorganic composition (in mg L⁻¹): Na₂SeO₃, 0.5; Na₂WO₄.2H₂O, 0.5; NiCl₂.6H₂O, 0.5; H₃BO₃, 0.5; Na₂MoO₄.2H₂O, 0.5; NH₄VO₃, 0.5; ZnCl₂, 0.5; CuCl₂, 0.5; MnCl₂.4H₂O, 0.5; AlCl₃.6H₂O, 0.5; L-cysteine, 10; (NaPO₃)₆, 10; KI, 10; CoCl₂.6H₂O, 10; FeCl₃.4H₂O, 40; CaCl₂.2H₂O, 50; (NH₄)₂HPO₄, 80; Na₂S.9H₂O, 300; KCl, 400; MgSO₄.7H₂O, 400 and NH₄Cl, 400 (Speece, 1996). The anaerobic conditions were maintained by adding 667 mg L⁻¹ of sodium thioglycollate (0.067 %) that is proposed between 0.01-0.2% (w/w) for maintaining anaerobic conditions. Aerobic biomass used in this study was taken from the aeration tank of the wastewater treatment plant of Izmir AOSB Wastewater Treatment Plant (Izmir, Turkey). At the beginning of the study, aerobic sludge was fed with 450.00 mg L⁻¹ glucose. The alkalinity and neutral pH were adjusted by the addition of NaHCO₃ and 1 N NaOH or 1 N HCl for the desired levels, respectively in anaerobic and aerobic reactors.

5.4 Reactor Configurations of the Treatment Processes

5.4.1 Continuous Operated Anaerobic UASB, Aerobic CSTR and Anaerobic/Aerobic Sequential Biological Reactor Systems

Laboratory scale quartz glass anaerobic reactor is an upflow anaerobic sludge blanket reactor (UASB) without sludge return and has a total volume of 2.5 liters. The effluent of the anaerobic UASB reactor was used as the influent of aerobic CSTR reactor. The anaerobic biological reactor was equipped with influent and effluent valves, sampling valves and gas outlet valves. The influent feed was pumped upward using peristaltic pump.

Laboratory scale quartz glass aerobic reactor consist of a continuous flow stirred tank reactor (CSTR) without sludge return and has a total volume of 2.0 liters. In this reactor, the raw hospital wastewater was aerated from the bottom with diffuser by an air pump, RESUN AIR-8000 (China) (240 V, 8.0 W, 9.0 L min⁻¹ air flow, ≥ 0.014 Mpa air pressure). The dissolved oxygen concentration did not decrease below 2.0 mg L⁻¹, for the bacterial growth and the mixing liquor. Turbulence produced from the air pump in suspended liquid provided homogenous mixed liquor in the aerobic reactor. The sedimentation of the microorganisms was provided with the stability of the mixed liquor by the hesitation of the air pump before the sampling.

Laboratory scale anaerobic/aerobic sequential reactor system consists of a quartz glass upflow anaerobic sludge blanket reactor (UASB) without sludge return following a quartz glass aerobic continuous flow stirred tank reactor (CSTR) without sludge return. The sedimentation of the microorganisms was provided with the stability of the mixed liquor by the hesitation of the air pump before the sampling. The required temperature conditions for the both reactors were provided with an infrared heater at mesophilic conditions. A schematic of the lab-scale biological reactors used in this study is presented in Figure 5.1. All the biological reactors were operated in continuously fed conditions. The feed was preserved in a refrigerator at 4°C in order to keep the substrate undecomposed particularly in summer.

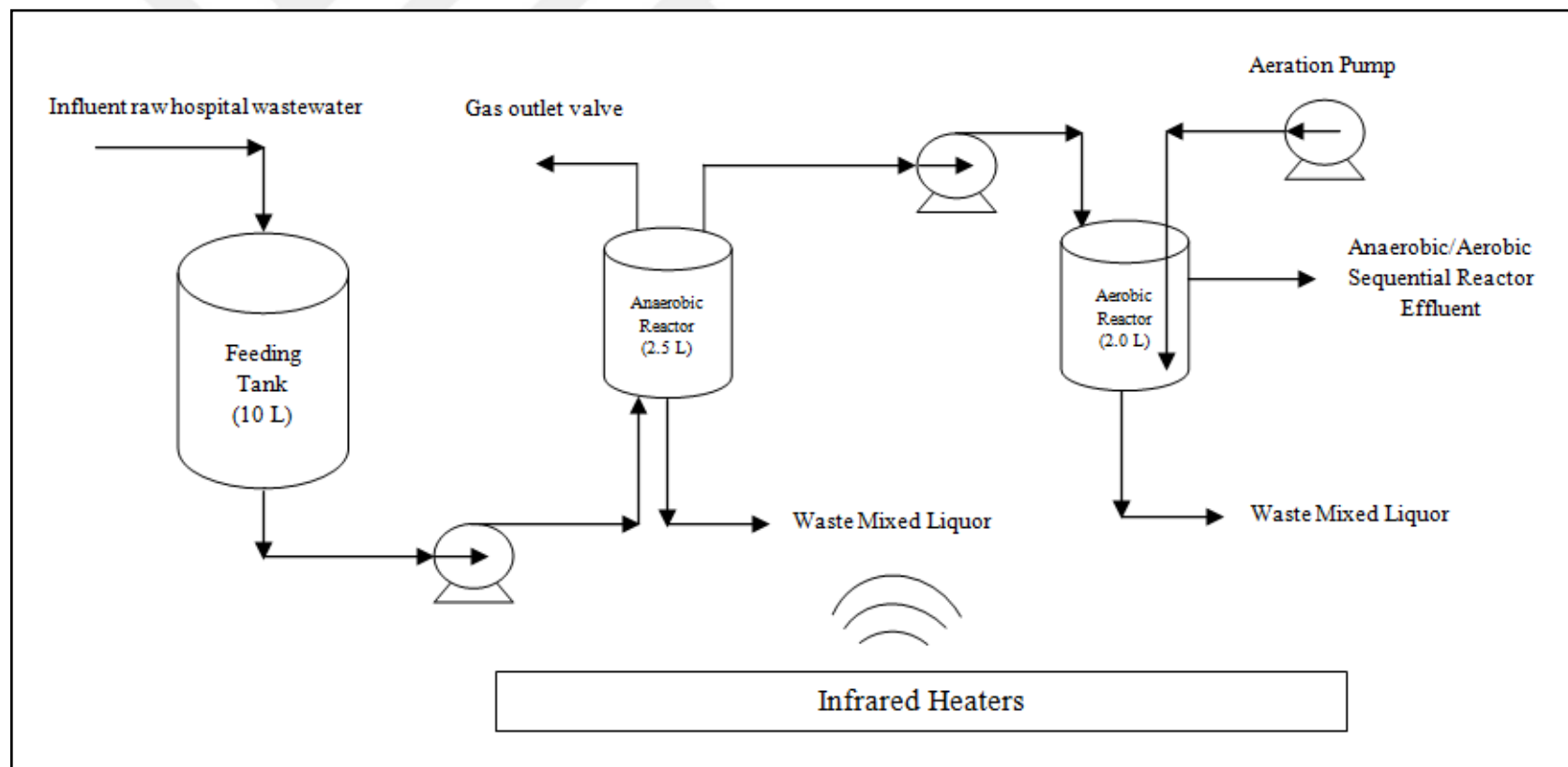


Figure 5.1 Laboratory scale anaerobic/aerobic sequential biological reactor system

5.4.2 Photocatalytic Treatment Process

5.4.2.1 Photocatalytic Treatment Process with UV Light

The photocatalytic experiments under Ultraviolet (UV) light were carried out in a covered stainless steel system including quartz glass reactors with a volume of 1 L and the UV light lamps having 254 nm wavelength. In this study, ten UV light lamps were used. Each of the lamps have a size of 895.0 mm× 26.0 mm and a power of 30.0 Watt (G13 Model, OSRAM). The light power required was provided by increasing or decreasing the UV lamp numbers. The distance between the UV lamps and quartz glass reactors was 15 cm. The temperature was changed using a heated magnetic stirrer in the covered stainless steel system. The raw hospital wastewater was first filtered through 0.075 mm coarse filters to remove physical impurities. After then, the studied nanoparticles was added to the filtered hospital wastewater and mixed through the photocatalytic experiments with a magnetic fish on a magnetic stirrer. The temperature of the nanoparticle added hospital wastewater was monitored regularly with a mercury thermometer (Figure 5.2). All the experiments were in batch mode and samples were analyzed immediately after the photocatalytic treatment process. All the experiments were performed in triplicate.

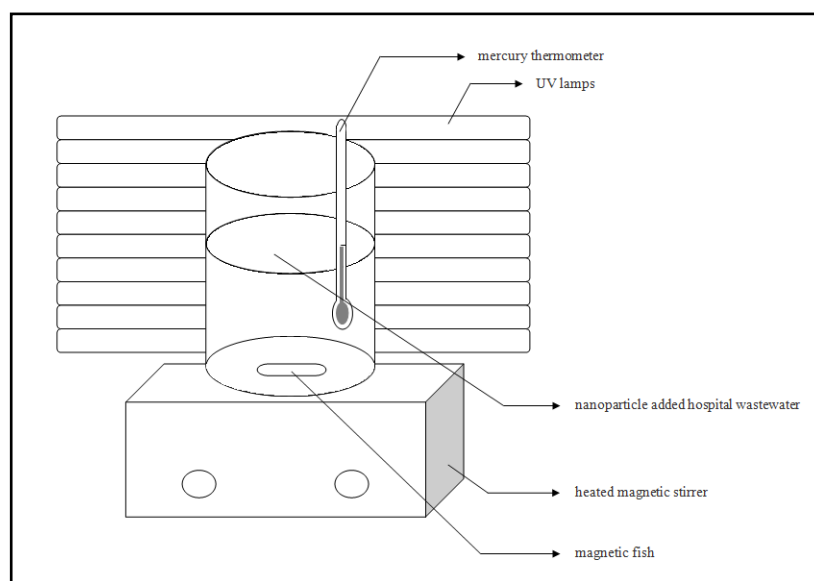


Figure 5.2 The photocatalytic reactor system using UV lamps

5.4.2.2 Photocatalytic Treatment Process with Sunlight

The photocatalytic experiments with sunlight were conducted with sunny and cloudless outdoor conditions in July-August at an atmospheric temperature of 35 ± 2.00 °C and a raw hospital wastewater temperature of 25 ± 2.00 °C. The sunlight power was measured using a luxmeter (PCE Instruments) and it was measured around 80.0 Watt. A volume of 1 L quartz glass reactors were used in the sunlight experiments. The raw hospital wastewater was first filtered through 0.075 mm coarse filters to remove physical impurities. After then, the studied nanoparticles was added to the filtered hospital wastewater and mixed through the photocatalytic experiments with a magnetic fish on a magnetic stirrer. The temperature of the nanoparticle added hospital wastewater was monitored regularly with a mercury thermometer (Figure 5.3). All the experiments were in batch mode and samples were analyzed immediately after the photocatalytic treatment process. All the experiments were performed in triplicate.

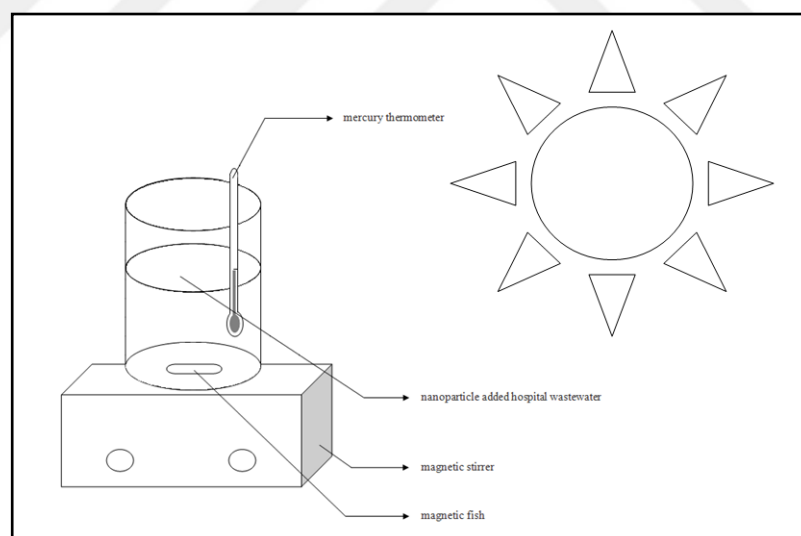


Figure 5.3 The photocatalytic reactor system using sunlight

5.4.3 Ultrasound Treatment Process

A VWR USC600 DF sonicator was used for the ultrasound treatment of the raw hospital wastewater samples. The sonicator has a volume of 5.40 L, a frequency of

132 kHz, a power of 120 W (Figure 5.4). It can be set up at a power range of 1-120 W and a temperature range of 1-90 °C in manual operation. The quartz glass reactors were filled to volumes of 250 mL with the raw hospital wastewater and were placed in the sonicator. They were then closed with teflon coated stoppers throughout the sonication process of the samples. The temperature in the sonicator was monitored continuously with a mercury thermometer to control the heating conditions of the sonicator and was adjusted to the desired level with the automatic heater of the sonicator. The stainless steel sonicator was equipped with a teflon holder to prevent temperature losses. The sonicator reactor was sealed with a water jacket to maintain a constant temperature and to minimize the temperature losses. The cooling water was circulated through the jacket of the reactor throughout the experiments in order to remove the heat generated during the sonication process. This procedure maintains the temperature of the reaction medium almost constant. The schematic configuration of the sonicator used in this study was shown in Figure 5.5 (Oztekin, 2011). All the experiments were in batch mode and samples were analyzed immediately after the sonication process. All the experiments were performed in triplicate.



Figure 5.4 VWR USC600 DF sonicator (Personal archive, 2016)

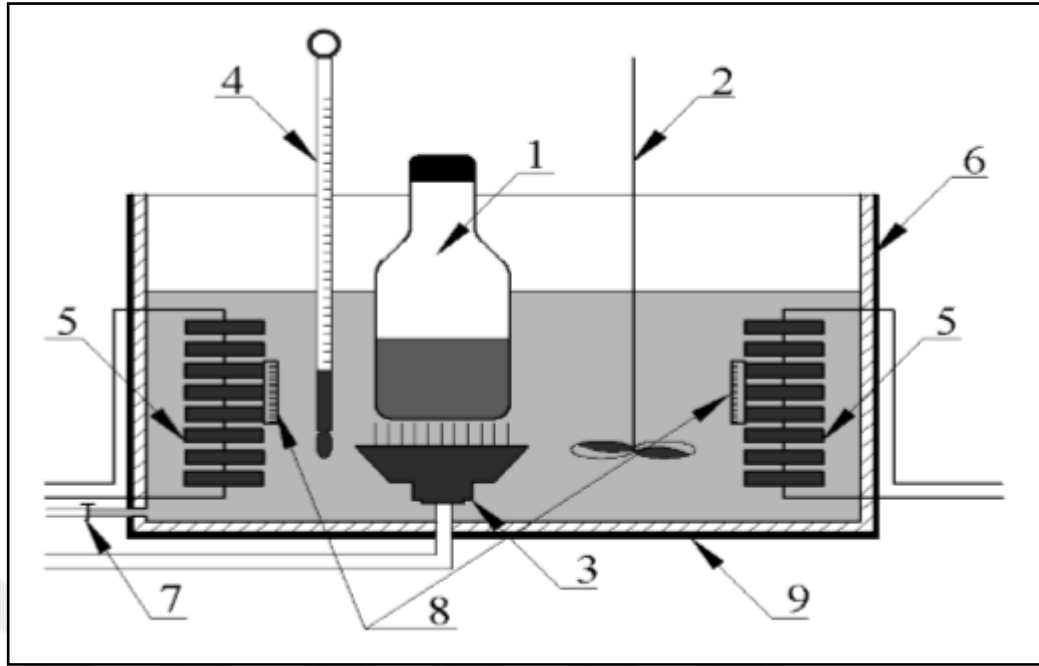


Figure 5.5 The structural diagram of the sonicator used in this study: (1) glass reactor, (2) stirrer, (3) energy conversion device, (4) thermometer, (5) heater, (6) stainless steel bath, (7) water exit valve, (8) thermostat, (9) teflon cover (Oztekin, 2011)

5.4.4 Membrane Treatment Process

UF membrane was purchased from AO Smith (Turkey) and LAL-WP model UF membrane was used in the experiments (Figure 5.6.a). RO membrane was purchased from DowDuPont (USA) and FilmTec XLE-2521 model RO membrane used in the experiments (Figure 5.6.b). The schematic configurations of the UF and RO used in this study were shown in Figure 5.7. UF was made of polyethersulfone and RO was made of polyamide thin-film composite (TFC) material. Molecular weight cut-off (MWCO) values were 10000 and 100 g mol⁻¹ for UF and RO, respectively. Furthermore, the pores of UF and RO with diameters varying between 0.01-0.1 µm and 0.22-0.44 nm, respectively while the membranes had negatively charged surfaces in the pH range of 4.50-8.50 (provided by the manufacturer). UF and RO were operated in cross-flow modes with a total membrane area of 0.640 m² and 0.960 m², respectively. In order to prevent clogging of the membranes, coarse filters were placed before the UF and RO membranes. The sedimentation, granular activated carbon and block carbon filters having a pore size of 5 µm were placed before the UF

and a pre-filter having a pore size of 1 μm was placed before the RO membrane treatment system. A feeding tank was placed before the membranes and made of high density polyethylene with a capacity of 50 L. The transmembrane pressure (TMP), rejection rate (R), permeate flux (J_v), flowrate (Q), cross-flow velocity (CFV) and permeability (L_p) parameters of UF and RO membranes were evaluated and monitored during the experiments. All the experiments were in batch mode and samples were analyzed immediately after the membrane treatment process. All the experiments were performed in triplicate.



Figure 5.6 Reactor configurations of (a) UF membrane and (b) RO membrane (Personal archive, 2016)

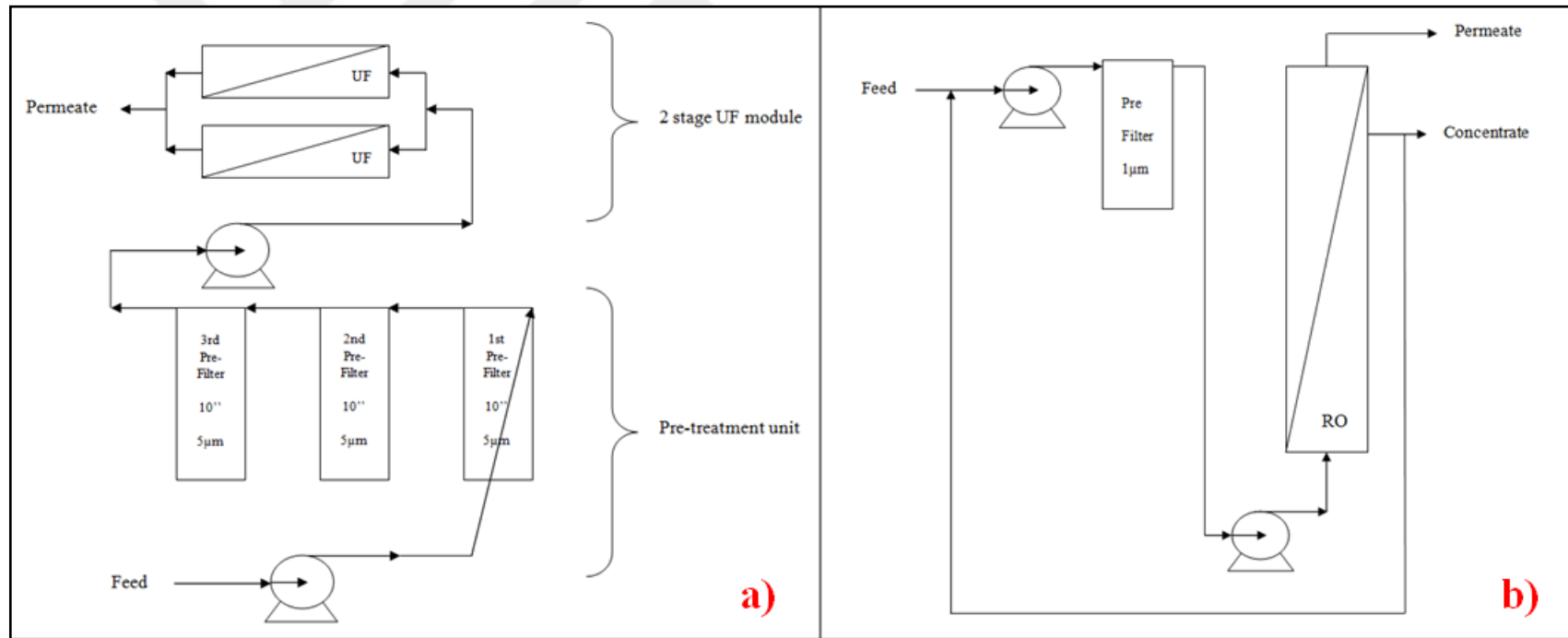


Figure 5.7 Schematic reactor configurations of (a) UF membrane and (b) RO membrane

5.4.4.1 Preparation and Cleaning Procedure of Membranes

Before the first usage, UF and RO were washed with ultrapure water and then soaked in ultrapure water for least 12 h in order to remove conservation products. After this procedure, UF and RO were compacted with ultrapure water for 8 h under pressure of 5 bar in order to obtain stable membranes and minimize membrane compaction during the experiments. After compaction, UF and RO were cleaned chemically before the first usage and after each experiments with the raw hospital wastewater. Chemical solutions were prepared as acidic (nitric acid, HNO_3) and alkaline (sodium hydroxyde, NaOH) solutions. Acidic cleaning was used for removal of inorganic particles (scaling) while alkaline cleaning was used for removal of organic materials (fouling). UF and RO were kept in the 0.1 N HNO_3 solution having a pH of 4.00 for 1 h. After acidic cleaning, UF and RO were washed by ultrapure water to remove the cleaning chemical on the surface of the membranes and soaked in the ultrapure water for 1 h. Thereafter, they were washed under alkaline conditions with 0.1 N NaOH solution having a pH of 10.00 for 1 h. After washing with ultrapure water, UF and RO were soaked in the ultrapure water for 1 h. The cleaned UF and RO were always kept in an aqueous solution of 0.25% sodium bisulfite (NaHSO_3) at 4 °C when they were not used in the experiments for preventing biofouling phenomenon occurred by the growth of bacteria cells on membrane surfaces (Tunc, Yilmaz, Yetis, & Culfaz-Emecan, 2014).

5.4.5 Reusability of Nanoparticles Used in Photocatalytic and Ultrasound Treatment Processes

After the first utilization of nanoparticles in the photocatalytic and ultrasound experiments, the nanoparticles were separated by filtering the nanoparticle through 0.45 μm pore sized membranes. Then, the nanoparticles were regenerated using ethanol with 0.10 mol L^{-1} HCl (Chowdhury & Balasubramanian, 2014). The nanoparticles were dried under vacuum and they were recovered for the second treatment process to treat the micropollutants again. For each new treatment step the same procedure was applied to the nanoparticles. Six sequential treatment steps were

investigated in order to detect the effect of reusability of the nanoparticles from the raw hospital wastewater after each treatment.

5.5 Operational Conditions in the Reactors Used in This Study

5.5.1 Operational Conditions for Continuous Operated Anaerobic UASB, Aerobic CSTR and Anaerobic/Aerobic Sequential Biological Reactor Systems

The effect of increasing SRT (5, 30, 45 and 55 days) and HRT (5, 30, 45 and 55 days) on COD, sCOD, micropollutants yields in anaerobic UASB, aerobic CSTR and anaerobic/aerobic sequential biological reactors were determined. The OLRs were 0.180, 0.032, 0.021 and 0.017 g COD L⁻¹ d⁻¹ for anaerobic UASB reactor, 0.088, 0.012, 0.007 and 0.005 g COD L⁻¹ d⁻¹ for aerobic CSTR while they were 0.268, 0.044, 0.028 and 0.022 g COD L⁻¹ d⁻¹ for anaerobic/aerobic sequential biological reactor system (Table 5.3).

Table 5.3 The operational conditions for the biological reactor systems

The operational conditions	Anaerobic UASB Reactor					Aerobic CSTR Reactor			Anaerobic/ Aerobic Sequential Biological Reactor System			
HRT (day)	5	30	45	55	5	30	45	55	5	30	45	55
SRT (day)	5	30	45	55	5	30	45	55	5	30	45	55
OLR (g COD/L×d)	0.180	0.032	0.021	0.017	0.088	0.012	0.007	0.005	0.268	0.044	0.028	0.022
MLSS (mg L⁻¹)	18000±0.5	23900±0.5	25650±0.5	34500±0.5	3950±0.5	4000±0.5	4450±0.5	4980±0.5	21950±0.5	27900±0.5	30100±0.5	39480±0.5
MLVSS (mg L⁻¹)	14400±0.5	19120±0.5	20520±0.5	27600±0.5	3160±0.5	3200±0.5	3560±0.5	3980±0.5	17560±0.5	22320±0.5	24080±0.5	31580±0.5
Temp. (°C)	37 ± 2.00					37 ± 2.00			37 ± 2.00			
pH	8.50 ± 0.50					7.50 ± 0.50			7.50 ± 0.50			
DO (mg L⁻¹)	0.00					2.00			-			
ORP (mV)	-610					+145			-			

Methane gas (CH_4) productions, TVFA accumulation and the ratio of TVFA to bicarbonate alkalinity were monitored in the anaerobic UASB reactor of the anaerobic/aerobic sequential biological reactor system. pH changes, dissolved oxygen (DO) variations and redox potentials (ORPs) were monitored in the anaerobic UASB and aerobic CSTR reactors. MLSS values varied between 18000-345000 mg L^{-1} for anaerobic UASB reactor, 3950-4980 mg L^{-1} for aerobic CSTR and 21950-39480 mg L^{-1} for anaerobic/aerobic sequential biological reactor system. As well as, MLVSS values varied between 14400-27600 mg L^{-1} for anaerobic UASB reactor, 3160-3980 mg L^{-1} for aerobic CSTR and 17560-31580 mg L^{-1} for anaerobic/aerobic sequential biological reactor system.

The steady state conditions were defined with constant daily methane gas (CH_4) production, effluent COD and sCOD concentrations, effluent total volatile fatty acid (TVFA) concentrations and operating pH values within 5% variation for the consecutive days in the each reactor. The samples were collected and analyzed for at least 5 consecutive days. The steady state value of a given parameter was taken as the average of these consecutive measurements for that parameter when the deviations between the observed values were less than 5% in all cases. Each experiment had a duration of two to three times according to the corresponding loading condition. The liquid samples were taken from the supernatants of the anaerobic UASB and aerobic CSTR reactors while the sludge samples were taken at the bottom of the anaerobic UASB and aerobic CSTR reactors. Furthermore, the gas samples were taken from the polyurethane foam (PUF) disks placed in the headspace of the each biological reactor.

5.5.2 Operational Conditions for Photocatalytic Treatment Processes

The effect of increasing nano- SiO_2 , nano- ZnO , graphene, nano- TiO_2 and nano- CeO_2 concentrations (0.25, 0.50 and 1.50 g L^{-1}), nano- TiO_2 and nano- CeO_2 concentrations (0.25, 0.50, 1.00 and 1.50 g L^{-1}), irradiation times (15, 30, 45, 60 and 90 min), light powers (80 (sunlight), 120, 210 and 300 W), temperatures (25, 35, 45 and 60 $^{\circ}\text{C}$) and pHs (4.00, 7.00 and 8.50) on the micropollutants removals were

investigated in the raw hospital wastewater. The operational conditions for the photocatalytic treatments were summarized in Table 5.4.

Table 5.4 The operational conditions for the photocatalytic treatment process

The operational conditions	Photocatalytic treatment process
Nanoparticle types	nano-SiO ₂ , nano-ZnO, graphene, nano-TiO ₂ and nano-CeO ₂ (0.25, 0.50 and 1.50 g L ⁻¹)
Nano-TiO ₂ and nano-CeO ₂ concentrations (g L ⁻¹)	0.25, 0.50, 1.00, 1.50
Irradiation time (min)	15, 30, 45, 60, 90
Light power (Watt)	80, 120, 210, 300
Temperature (°C)	25, 35, 45, 60
pH	4.00, 7.00, 8.50

5.5.2.1 Adsorption and Photolysis in Photocatalytic Treatment Process

The control and the hospital wastewater experiments were carried out under dark experimental conditions for the adsorption capacity of the nanoparticles. The raw hospital wastewater was first filtered through 0.075 mm coarse filters to remove physical impurities. After then, the nanoparticle was added to the filtered hospital wastewater in a quartz glass reactor and it was stirred slowly at 0.20 rpm at 25 ± 2.00 °C.

The control and the hospital wastewaters experiments for photolysis was carried out both under UV light and sunlight without nanoparticles to determine the photolysis capacity of the micropollutants. The raw hospital wastewater was filtered through 0.075 mm coarse filters and then irradiated both under UV and sunlight in photocatalytic reactors without nanoparticles at 25 ± 2.00 °C. All the experiments were performed in triplicate.

5.5.3 Operational Conditions for Ultrasound Treatment Process

The effect of sonicator powers (20, 70 and 120 W), sonication times (15, 30, 45, 60 and 90 min), pHs (4.00, 6.00 and 8.00) and temperatures (25, 40, 50, 65 and 80 °C) on the micropollutants yields were investigated at a constant sonicator frequency of 132 kHz for all the conducted experiments. Furthermore, in order to detect the

simultaneous effects of ultrasound and nanoparticle addition, TiO_2 and CeO_2 nanoparticles (0.00, 0.20, 0.40, 0.60 and 0.80 g L^{-1}) were added to the sonicator. The operational conditions for the ultrasound treatment were summarized in Table 5.5.

Table 5.5 The operational conditions for the ultrasound treatment process

The operational conditions	Ultrasound treatment process
Sonicator power (Watt)	20, 70, 120
Sonication time (min)	15, 30, 45, 60, 90
pH	4.00, 6.00, 8.00
Temperature ($^{\circ}\text{C}$)	25, 40, 50, 65, 80
Nano- TiO_2 and nano- CeO_2 concentration (g L^{-1})	0.00, 0.20, 0.40, 0.60, 0.80
Sonicator frequency (kHz)	132

5.5.4 Operational Conditions for Membrane Treatment Process

Polyethersulfone based UF (MWCO = 10 000 g mol^{-1}) with a pore size range of 0.01-0.1 μm operated in cross-flow mode with a total membrane area of 0.640 m^2 . TMP of UF kept constant at 2.75 bar at a pH of 8.00 ± 0.50 and at a temperature of 25 ± 2.00 $^{\circ}\text{C}$ and micropollutant removal efficiencies were investigated (Table 5.6). Polyamide thin-film composite based RO (MWCO = 100 g mol^{-1}) with a pore size range of 0.22-0.44 nm operated in cross-flow mode with a total membrane area of 0.960 m^2 . The effect of operational parameters [transmembrane pressure (TMP), permeate flux (J_v) and cross-flow velocity (CFV)] on the removals of conventional pollutants (TOC, TSS, TDS, COD and sCOD) and all studied micropollutants were investigated in UF and RO at a pH of 8.00 ± 0.50 and at a temperature of 25 ± 2.00 $^{\circ}\text{C}$ (Table 5.6). When the permeate fluxes reached to steady state conditions after 5 min for UF and RO, the permeates were collected after 60 min of membrane operation time.

Table 5.6 The operational conditions for the membrane treatment process

The operational conditions	UF membrane system	RO membrane system
Operating pressure (bar)	5	5, 7, 9
TMP (bar)	2.75	2.75, 3.75, 4.75
J_v (L m ⁻² h ⁻¹)	78.13, 104.17, 156.25	52.08, 69.44, 104.17
CFV (m h ⁻¹)	0.08, 0.11, 0.16	0.05, 0.07, 0.10
pH	8.00 ± 0.50	8.00 ± 0.50
Temperature (°C)	25 ± 2.00	25 ± 2.00
Operation time (h)	1, 1.5, 2	1, 1.5, 2

5.5.4.1 Calculation of Operational Parameters (Transmembrane Pressure, Permeate Flux, Flowrate and Cross-Flow Velocity) in UF and RO

5.5.4.1.1 *Transmembrane Pressure (TMP)*. The transmembrane pressure (TMP) difference across the membranes were calculated by taking the arithmetic average of the pressures measured on the feed side-inlet and the retentate side-outlet, where the permeate side was open to the atmosphere (Equation 5.1) (Tunc et al., 2014).

$$\text{TMP (bar)} = (P_1 + P_2)/(2-P_3) \quad (5.1)$$

where P1, P2 and P3 are pressure at the inlet (bar), outlet (bar) and permeate side of the membrane (bar), respectively.

TMP of the UF was calculated by taking the arithmetic average of the operating pressure measured at the inlet (5 bar) and the outlet (0.5 bar), where the permeate side was open to the atmosphere (0 bar) (Equation 5.2).

$$\text{TMP}_{\text{UF}} = (5 + 0.5)/(2-0) = 2.75 \text{ bar} \quad (5.2)$$

RO was operated at three different operating pressures (5, 7 and 9 bars) corresponding to three different TMPs as 2.75, 3.75 and 4.75 bar calculated in Equations 5.3 to 5.5, respectively.

$$\text{TMP}_{\text{RO at 5 bar}} = (5 + 0.5)/(2-0) = 2.75 \text{ bar} \quad (5.3)$$

$$\text{TMP}_{\text{RO at 7 bar}} = (7 + 0.5)/(2-0) = 3.75 \text{ bar} \quad (5.4)$$

$$\text{TMP}_{\text{RO at 9 bar}} = (9 + 0.5)/(2-0) = 4.75 \text{ bar} \quad (5.5)$$

5.5.4.1.2 *Permeate Flux (J_v)*. Permeate flux (J_v) of the UF and RO membranes was derived from the Equation 5.6 (Bunani et al., 2015).

$$J_v \text{ (L m}^{-2} \text{ h}^{-1}) = [V/(S \times t)] \quad (5.6)$$

where V, S and t are volume of the permeate (m^3), membrane area (m^2) and time (h), respectively.

At a constant TMP of 2.75 bar and for a constant raw hospital wastewater volume of 100 L, the UF membrane showed permeate fluxes (J_v) up to 78.13 and 156.25 $\text{L m}^{-2} \text{ h}^{-1}$ according to its membrane surface area of 0.64 m^2 during 1.0, 1.5 and 2.0 h membrane operation times at 25 °C and at a pH of 8.00 (Equation 5.7, 5.8 and 5.9).

$$J_{v, \text{UF at TMP}=2.75} = [100/(0.64 \times 1.0)] = 156.25 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.7)$$

$$J_{v, \text{UF at TMP}=2.75} = [100/(0.64 \times 1.5)] = 104.17 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.8)$$

$$J_{v, \text{UF at TMP}=2.75} = [100/(0.64 \times 2.0)] = 78.13 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.9)$$

For RO, at a constant TMP of 2.75 bar and for a constant raw hospital wastewater volume of 100 L, the UF membrane showed permeate fluxes (J_v) up to 52.08 and 104.17 $\text{L m}^{-2} \text{ h}^{-1}$ according to its membrane surface area of 0.96 m^2 during 1.0, 1.5 and 2.0 h membrane operation times at 25 °C and at a pH of 8.00 (Equation 5.10, 5.11 and 5.12).

$$J_{v, \text{RO at TMP}=2.75} = [100/(0.96 \times 1.0)] = 104.17 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.10)$$

$$J_{v, \text{RO at TMP}=2.75} = [100/(0.96 \times 1.5)] = 69.44 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.11)$$

$$J_{v, \text{RO at TMP}=2.75} = [100/(0.96 \times 2.0)] = 52.08 \text{ L m}^{-2} \text{ h}^{-1} \quad (5.12)$$

5.5.4.1.3 *Flowrate (Q)*. Flowrate (Q) of the UF and RO membranes was derived from the Equation 5.13.

$$Q \text{ (m}^3 \text{ h}^{-1}\text{)} = V/t \quad (5.13)$$

where V and t are volume of the permeate (m³) and time (h), respectively.

Flowrates of the UF for 100 L (0.10 m³) constant raw hospital wastewater volume at 2.75 bar of TMP were derived from the Equation 14, 15 and 16 for 1.0, 1.5 and 2.0 h operation times, respectively at 25 °C and at a pH of 8.00.

$$Q_{UF,TMP=2.75} = (0.10)/(1.0) = 0.10 \text{ m}^3 \text{ h}^{-1} \quad (5.14)$$

$$Q_{UF,TMP=2.75} = (0.10)/(1.5) = 0.07 \text{ m}^3 \text{ h}^{-1} \quad (5.15)$$

$$Q_{UF,TMP=3.75} = (0.10)/(2.0) = 0.05 \text{ m}^3 \text{ h}^{-1} \quad (5.16)$$

Flowrates of the RO for 100 L (0.10 m³) constant raw hospital wastewater volume at 2.75 bar of TMP were derived from the Equation 17, 18 and 19 for 1.0, 1.5 and 2.0 h operation times, respectively at 25 °C and at a pH of 8.00.

$$Q_{RO,TMP=2.75} = (0.10)/(1.0) = 0.10 \text{ m}^3 \text{ h}^{-1} \quad (5.17)$$

$$Q_{RO,TMP=2.75} = (0.10)/(1.5) = 0.07 \text{ m}^3 \text{ h}^{-1} \quad (5.18)$$

$$Q_{RO,TMP=3.75} = (0.10)/(2.0) = 0.05 \text{ m}^3 \text{ h}^{-1} \quad (5.19)$$

5.5.4.1.4 *Cross-Flow Velocity (CFV)*. Cross-flow velocity (CFV) of the UF and RO membranes was derived from the Equation 5.20.

$$CFV \text{ (m h}^{-1}\text{)} = Q/S \quad (5.20)$$

where Q and S are flowrate (m³ h⁻¹) and membrane area (m²), respectively.

The flowrates were divided by the membrane areas and give CFVs for 1.0 h, 1.5 h and 2.0 h operation times in UF at 2.75 bar TMP at 25 °C and at a pH of 8.00 (Equation 5.21, 5.22 and 5.23).

$$CFV_{UF,TMP=2.75} = 0.10/0.64 = 0.16 \text{ m s}^{-1} \quad (5.21)$$

$$CFV_{UF,TMP=2.75} = 0.07/0.64 = 0.11 \text{ m s}^{-1} \quad (5.22)$$

$$CFV_{UF,TMP=2.75} = 0.05/0.64 = 0.08 \text{ m s}^{-1} \quad (5.23)$$

The flowrates were divided by the membrane areas and give CFVs for 1.0 h, 1.5 h and 2.0 h operation times in Equations 5.24, 5.25 and 5.26 for RO at 2.75 bar TMP at 25 °C and at a pH of 8.00.

$$CFV_{RO,TMP=2.75} = 0.10/0.96 = 0.10 \text{ m s}^{-1} \quad (5.24)$$

$$CFV_{RO,TMP=2.75} = 0.07/0.96 = 0.07 \text{ m s}^{-1} \quad (5.25)$$

$$CFV_{RO,TMP=2.75} = 0.05/0.96 = 0.05 \text{ m s}^{-1} \quad (5.26)$$

5.5.4.1.5 Removal Efficiency (R%). Removal efficiency (R%) of the UF and RO membranes was derived from the Equation 5.27 (Bunani et al., 2015).

$$R (\%) = [1 - (C_p/C_0)] \times 100 \quad (5.27)$$

where C_p and C_0 are concentration in the permeate (mg L^{-1} or $\mu\text{g L}^{-1}$) and concentration in the feed (mg L^{-1} or $\mu\text{g L}^{-1}$), respectively.

5.5.4.2 Adsorption Masses and Adsorption Efficiencies for Micropollutants in UF and RO

5.5.4.2.1 Adsorption Masses and Adsorption Efficiencies for Micropollutants in UF. The total amount of micropollutant (M_{feed}) per unit membrane area ($\mu\text{g m}^{-2}$) in the influent of UF can be determined using Equation 5.28.

$$M_{\text{feed}} (\mu\text{g m}^{-2}) = \frac{(C_f \times V_f)}{A} \quad (5.28)$$

where C_f is the feed concentration ($\mu\text{g L}^{-1}$), V_f is the feed volume (L) and A is the effective membrane area (m^2) of UF (Yoon, Westerhoff, Snyder, & Wert, 2006).

Adsorbed mass of a micropollutant (M_{ads}) onto the membrane surface and into the membrane pores was calculated using Equation 5.29 considering the feed and permeate in UF system (Yoon et al., 2006).

$$M_{\text{ads}} (\mu\text{g m}^{-2}) = \frac{[(C_f \times V_f) - (C_p \times V_p)]}{A} \quad (5.29)$$

where C_f is the feed concentration ($\mu\text{g L}^{-1}$), V_f is the feed volume (L), C_p is the permeate concentration ($\mu\text{g L}^{-1}$), V_p is the permeate volume (L) and A is the effective membrane area (m^2) of UF. Consequently, M_{ads} is the amount of micropollutant adsorbed per unit membrane area ($\mu\text{g m}^{-2}$) (Yoon et al., 2006).

Micropollutant removal efficiencies via adsorption onto membrane surface and into membrane pores in UF were calculated according to the Equation 5.30 as mentioned by Yoon et al. (2006).

$$\text{Adsorption (\%)} = \frac{M_{\text{ads}}}{M_{\text{feed}}} \times 100 \quad (5.30)$$

5.5.4.2.2 Adsorption Masses and Adsorption Efficiencies for Micropollutants in RO. The total amount of micropollutant (M_{feed}) per unit membrane area ($\mu\text{g m}^{-2}$) in the influent of RO can be determined using Equation 5.31.

$$M_{\text{feed}} (\mu\text{g m}^{-2}) = \frac{(C_f \times V_f)}{A} \quad (5.31)$$

where C_f is the feed concentration ($\mu\text{g L}^{-1}$), V_f is the feed volume (L) and A is the effective membrane area (m^2) of RO (Yoon et al., 2006).

Adsorbed mass of a micropollutant (M_{ads}) onto the membrane surface and into the membrane pores was calculated using Equation 5.32 considering the feed, permeate and retentate in RO system.

$$M_{ads} (\mu\text{g m}^{-2}) = \frac{(C_f \times V_f) - [(C_p \times V_p) + (C_r \times V_r)]}{A} \quad (5.32)$$

where C_f is the feed concentration ($\mu\text{g L}^{-1}$), V_f is the feed volume (L), C_p is the permeate concentration ($\mu\text{g L}^{-1}$), V_p is the permeate volume (L), C_r is the retentate concentration ($\mu\text{g L}^{-1}$), V_r is the retentate volume (L) and A is the effective membrane area (m^2) of RO. Consequently, M_{ads} is the amount of micropollutant adsorbed per unit membrane area ($\mu\text{g m}^{-2}$) (Yoon et al., 2006).

Micropollutant removal efficiencies via adsorption onto membrane surface and into membrane pores in RO were calculated according to the Equation 5.33 as mentioned by Yoon et al. (2006).

$$\text{Adsorption (\%)} = \frac{M_{ads}}{M_{feed}} \times 100 \quad (5.33)$$

5.6 Analytical Methods

5.6.1 pH, Temperature (T), Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP) and Electrical Conductivity (EC) Measurements

The pH, temperature (T) and dissolved oxygen (DO) were measured using pH meter (WTW pH 330i), an electronic digital heater and an oxygen meter (WTW Oxi330/SET), respectively. The oxidation reduction potential (ORP) was measured using SenTix ORP digital electrode (WTW pH 330i) with an Ag/AgCl₂ reference electrode which is saturated with KCl solution and Pt electrode. The electrical conductivity was determined with a WTW Cond 315i using Tetracon 325 electrode.

5.6.2 Total Nitrogen (TN) and Total Phosphorus (TP) Measurements

The total nitrogen (TN) and total phosphorus (TP) were analyzed by using analytical kits (Spectroquant N 1.14537.0001 and Spectroquant PO₄-P 1.14543.0001, Merck Chemical Company, Germany) and a NOVA-60 spectrophotometer (Merck).

5.6.3 Total Organic Carbon (TOC), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Total Solids (TS), Mixed Liquor Volatile Suspended Solids (MLVSS) and Mixed Liquor Suspended Solids (MLSS) Measurements

TOC was determined according to Standard Methods for Examination of Water and Wastewater with a Rosemount Dohrmann DC-190 high-temperature total organic carbon (TOC) analyzer (APHA-AWWA-WEF 2005) (SM-5310). Biomass in aerobic and anaerobic biological reactor system was measured as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). Assays of MLSS, MLVSS, TS, TDS and TSS were performed according to Standard Methods for Examination of Water and Wastewater in the aerobic and anaerobic biological reactor systems and raw hospital wastewater composition (APHA-AWWA-WEF 2005) (SM-2540-A-G).

5.6.4 Methane (CH₄) Gas Measurements

Methane (CH₄) gas productions were measured by using a liquid containing 3% NaOH to scrub out the CO₂ from the total biogas (Razo-Flores, Luijten, Donlon, Lettinga, & Field, 1997).

5.6.5 Bicarbonate (HCO₃⁻) Alkalinity and Total Volatile Fatty Acid (TVFA) Measurements

An alkalimetric method is used to determine bicarbonate (HCO₃⁻) and total volatile fatty acid (TVFA) concentrations in the anaerobic reactor by a two-stage sequential titration. The TVFA concentrations were measured by using Anderson &

Yang (1992). Samples were titrated by 0.1 N H₂SO₄ then the bicarbonate (HCO₃⁻) and TVFA concentration were determined with a computer program. Firstly, the pH of the sample was detected with a pH probe. Then, the sample was titrated with standard H₂SO₄ solution through two stages. Titration was made until the pH of the sample decreased to 5.10 (first stage). Then, titration was held to a pH value of 3.50 (second stage). Finally, the bicarbonate (HCO₃⁻) and TVFA concentrations were determined with the help of a computer program solving the Equation 5.34 and 5.35.

$$A_1 = \frac{[HCO_3^-] \times ([H]_2 - [H]_1)}{[H]_1 + K_C} + \frac{[VA] \times ([H]_2 - [H]_1)}{[H]_2 + K_{VA}} \quad (5.34)$$

$$A_2 = \frac{[HCO_3^-] \times ([H]_3 - [H]_1)}{[H]_3 + K_C} + \frac{[VA] \times ([H]_3 - [H]_1)}{[H]_3 + K_{VA}} \quad (5.35)$$

where A₁ and A₂ are the molar equivalent of the standard acid consumed to the first and second end points; [HCO₃⁻] the bicarbonate concentration; [VA] the volatile fatty acid ion concentration; [H]_{1,2,3} the hydrogen ion concentrations of the original sample and at the first and the second end points; K_C is the conditional dissociation constant of carbonic acid; K_{VA} is the combined dissociation constant of the volatile fatty acids (C₂–C₆), this pair of constants was assumed, being 6.6×10⁻⁷ for bicarbonate and 2.4×10⁻⁵ for volatile acids (Kuscu, 2007).

5.6.6 Biological Oxygen Demand (BOD₅) Measurements

A manometric respirometric test was carried out for BOD₅ measurements with the OxiTop IS 12 system (WTW Merck Company, Germany). The range of expected BOD₅ values was then deduced and hence led to the volumes of sample and nitrification inhibitor (10 mg L⁻¹ solution of N-allylthiourea) which have to be added to the bottles of the OxiTop apparatus. The bottles were sealed with a rubber sleeve containing a CO₂ absorber immediately after the bottles were filled with the sample and the nitrification inhibitor N-allylthiourea was added. The measuring heads were screwed onto the bottles and the samples were stabilized in the incubation cabinet (20.0 ± 0.2 °C) for two hours before measurements began. Microsoft Excel 2010 was

used in the evaluation of BOD₅ values after the experiments completed at the end of five days (Roppola, Kuokkanen, Rämö, Prokkola, & Heiska, 2007).

5.6.7 Chemical Oxygen Demand (COD) and Soluble Chemical Oxygen Demand (sCOD) Measurements

The chemical oxygen demand (COD) was measured with Close Reflux Method following the Standard Methods 5220-D (APHA-AWWA-WEF, 2005) using an Aqua mate thermo electron corporation UV visible spectrophotometer. Firstly, the samples were centrifuged for 10 min at 9000 rpm. Secondly, 2.50 mL volume wastewater samples were treated with 1.50 mL 10216 mg L⁻¹ K₂Cr₂O₇ with 33.30 g L⁻¹ HgSO₄ and 3.50 mL H₂SO₄ which contains 0.55% (w/w) Ag₂SO₄. Thirdly, the closed sample tubes were stored in a 148 °C heater (thermo reactor, CR 4200 WTW, 2008) for 2 h. Finally, after cooling, the samples were determined at 610 nm with an Aqua mate thermo electron corporation UV visible spectrophotometer.

The soluble chemical oxygen demand (sCOD) samples were first filtered through 0.45 µm membrane filters and then filtered samples were determined with Close Reflux Method following the Standard Methods 5220-D (APHA-AWWA-WEF, 2005) according to the aforementioned procedure.

5.6.8 Chloride (Cl⁻), Bicarbonate (HCO₃⁻), Sulfate (SO₄²⁻), Ammonium (NH₄⁺) and Fluorine (F) Measurements

The chloride (Cl⁻), bicarbonate (HCO₃⁻), sulfate (SO₄²⁻), ammonium (NH₄⁺) and fluorine (F) were measured according to Standard Methods using 4500-B, 2320-B, 4500-E, 4500-B-C and 4110-B, respectively (APHA-AWWA-WEF, 2005).

5.6.9 Heavy Metal Measurements

Zinc (Zn), vanadium (V), sodium (Na), selenium (Se), nickel (Ni), molybdenum (Mo), manganese (Mn), magnesium (Mg), lithium (Li), lead (Pb), iron (Fe), copper

(Cu), cobalt (Co), chromium (Cr), calcium (Ca), cadmium (Cd), boron (B), beryllium (Be), arsenic (As) and aluminium (Al) were determined with the method of TS EN ISO 17294-2 following the Turkish Standard (Turkish Standard, 2005).

5.6.10 Fecal Coliform Measurement

The fecal coliform was determined with membrane filtration method following the Standard Methods 9222-D (APHA-AWWA-WEF, 2005).

5.6.11 Fish Acute Toxicity Test

Experiments were carried out using 10 *Lepistes reticulatus* fish in test aquarium with 15 liters of total volume at a pH of 7.00 ± 0.20 and at a temperature of 20 ± 1 °C, providing approximately 4 mg L^{-1} of dissolved oxygen with an air pump. Required wastewater dilutions were practiced according to the method's instructions. Results were expressed after 24 and 48 h. The immobile animals which were not able to move were determined as death of fish. The minimum dilution which any of the fish is dead is given as the toxicity dilution factor (Su Kirliligi Kontrolu Yonetmeligi [SKKY], 2009).

5.6.12 Removal Mechanisms of COD, sCOD and Micropollutants

In order to detect the main removal mechanisms of COD, sCOD and micropollutants; biodegradation, sorption, adsorption and volatilization tests were performed. The biodegraded, adsorbed, sorbed and volatilized COD, sCOD and micropollutants masses were calculated. Furthermore, the biodegraded, adsorbed, sorbed and volatilized COD, sCOD and micropollutants percentages were detected in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations.

5.6.12.1 Total COD, sCOD and Micropollutant Removals in Biological Treatment Process

The total COD, sCOD and micropollutant removal efficiencies in the effluents of the anaerobic and aerobic biological reactors were determined according to Equation 5.36.

$$\text{Total removal efficiency (\%)} = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100 \quad (5.36)$$

Where C_{inf} represents the influent COD (mg L^{-1}), sCOD (mg L^{-1}) and micropollutant ($\mu\text{g L}^{-1}$ or ng L^{-1}) concentrations of the biological reactor and C_{eff} represents the effluent COD (mg L^{-1}), sCOD (mg L^{-1}) and micropollutant ($\mu\text{g L}^{-1}$ or ng L^{-1}) concentrations of the biological reactor.

5.6.12.2 COD, sCOD and Micropollutant Removal Mechanisms in Biological Treatment Process

C_{RE} , C_{ES} , C_{EB} , and C_{PD} represent the COD (mg L^{-1}), sCOD (mg L^{-1}) and micropollutant ($\mu\text{g L}^{-1}$ or ng L^{-1}) concentrations measured in the biological reactor effluent, in the eluate prepared from biological sludge, in the eluate prepared from killed-death biomass and in the eluate prepared from PUF disk, respectively. V_R (L) represent the volume of the biological reactor where V_s (mL) represent the sample volumes for adsorption, sorption and volatilization tests. m_1 (g) and m_2 (g) represent the dry weight of the sludge used in the analysis and the dry weight of the sludge in the biological reactors, respectively. M_{BIO} shows the COD (mg), sCOD (mg) and micropollutant (μg or ng) amount in the effluent of the biological reactor (Equation 5.37).

$$M_{BIO} = C_{RE} \times V_R \quad (5.37)$$

M_{ADS} shows the COD (mg), sCOD (mg) and micropollutant (μg or ng) amount adsorbed onto the sludge of the biological reactor (Equation 5.38).

$$M_{ADS} = [C_{ES} \times V_S / m_1] \times m_2 \times 10^{-3} \text{ (L mL}^{-1}\text{)} \quad (5.38)$$

To determine the adsorption of the COD, sCOD and micropollutants onto the anaerobic and aerobic biological sludges, eluates were prepared from the biological sludge samples taken from the aerobic and anaerobic reactors. Granular sodium sulfate was burnt at 450 °C for 2 hours firstly, and then it was desiccated for 1 hour. Burnt sodium sulfate was added to the activated sludge sample to the dewatering process. Methanol was added to the dewatered biological sludge samples and the eluate was stirred for 24 hours on magnetic stirrers. The eluate was filtered firstly from the 0.45 µm cellulose acetate membrane filter (Sartorius Stedim Biotech) and then was filtered through 0.45 µm PVDF membrane filter (Pall Corporation). The eluates were extracted according to the appropriate solid-phase extraction (SPE) method and then, they were measured in UV visible spectrophotometer, HPLC, GC-MS or LC-MS/MS. The blank samples contained only wastewater. The micropollutant concentrations in the eluates were measured periodically and compared with the blank samples as control.

M_{SORP} shows the COD (mg), sCOD (mg) and micropollutant (µg or ng) accumulation inside granular sludge of the biological reactor (Equation 5.39).

$$M_{SORP} = [C_{EB} \times V_S / m_1] \times m_2 \times 10^{-3} \text{ (L mL}^{-1}\text{)} \quad (5.39)$$

Harvested biomass samples were washed and re-suspended in distilled water for sorption experiments. The anaerobic and aerobic sludges were inactivated in an autoclave at 121 °C for 15 minutes under a pressure of 1.5 atm. The autoclaved sludge were inoculated on the glass plates containing suitable media and incubated to determine whether they were alive. It was found that all the sludge samples were death. Control and 2 L reactors containing 1 L of raw wastewater were seeded with autoclaved death anaerobic and aerobic biomasses. The anaerobic death biomass had approximately 14.40, 19.12, 20.52 and 27.60 g VSS L⁻¹ at 5, 30, 45 and 55 days of SRTs, respectively while the aerobic death biomass had approximately 3.16, 3.20, 3.56 and 3.98 g VSS L⁻¹ at 5, 30, 45 and 55 days of SRTs, respectively. They were

incubated for two days at an ambient temperature. The anaerobic and aerobic reactors were sealed with teflon lined caps and shaken at 21 °C for 3 days. The control bottles contained no wastewater. The wastewater samples containing micropollutant taken from the test reactors aforementioned and they were measured periodically and compared with a control. After three days, the glass bottles containing the samples and the death biomass were centrifuged sufficiently to remove the death bacteria. The supernatant, the upper phase of the glass bottles, was harvested and the micropollutants in the supernatant were analyzed. The glass bottles containing control without biomass were compared to glass bottles containing death biomass to determine the amount of micropollutants sorbed. This test was performed following the procedure given by Sponza & Gok (2010). The samples prepared from the effluents of the anaerobic and aerobic reactors were extracted according to the appropriate solid-phase extraction (SPE) method and then, they were measured in UV visible spectrophotometer, HPLC, GC-MS or LC-MS/MS.

M_{VOL} shows the COD (mg), sCOD (mg) or micropollutant (μ or ng) amount in the headspace of the biological reactor (Equation 5.40).

$$M_{VOL} = C_{PD} \times V_S \times 10^{-3} \text{ (L mL}^{-1}\text{)} \quad (5.40)$$

The polyurethane foam (PUF) disks were used both for anaerobic and aerobic reactors for the determination of volatility of COD, sCOD and micropollutants. PUF disks were placed to the headspace of the each reactor and the reactors were placed in a closed glass system. At the end of the each SRT operations, PUFs samples were soaked with 1:1 acetone:hexane for 24 hours. Then the PUFs samples were sonicated for 60 min after they were soaked in 1:1 acetone:hexane overnight. Using a rotary evaporator, the 1:1 acetone:hexane mixture was dried. The dried extract volume was increased to 5 mL by adding hexane. Furthermore, it was dried completely under a stream of high purity N_2 . This process was repeated two times. Finally the dried extract volume was adjusted to 1 mL with hexane. Then, they were measured in UV visible spectrophotometer, HPLC, GC-MS or LC-MS/MS.

The percentage removal via biodegradation, adsorption, sorption and volatilization were calculated according to the Equation 5.41, 5.42, 5.43 and 5.44, respectively.

$$\text{Biodegradation (\%)} = (M_{\text{BIO}} \times 100) / (M_{\text{BIO}} + M_{\text{ADS}} + M_{\text{SORP}} + M_{\text{VOL}}) \quad (5.41)$$

$$\text{Adsorption (\%)} = (M_{\text{ADS}} \times 100) / (M_{\text{BIO}} + M_{\text{ADS}} + M_{\text{SORP}} + M_{\text{VOL}}) \quad (5.42)$$

$$\text{Sorption (\%)} = (M_{\text{SORP}} \times 100) / (M_{\text{BIO}} + M_{\text{ADS}} + M_{\text{SORP}} + M_{\text{VOL}}) \quad (5.43)$$

$$\text{Volatilization (\%)} = (M_{\text{VOL}} \times 100) / (M_{\text{BIO}} + M_{\text{ADS}} + M_{\text{SORP}} + M_{\text{VOL}}) \quad (5.44)$$

Where M_{BIO} represents the biodegradation amount of COD (mg), sCOD (mg) and micropollutant (μg or ng) in the biological reactor. M_{ADS} represents the adsorption amount of COD (mg), sCOD (mg) and micropollutant (μg or ng) in the biological reactor. M_{SORP} represents the sorption amount of COD (mg), sCOD (mg) and micropollutant (μg or ng) in the biological reactor. M_{VOL} represents the volatilization amount of COD (mg), sCOD (mg) and micropollutant (μg or ng) in the biological reactor.

5.6.13 Measurements of Phenolic Micropollutants (IBU, CIP, TCS and GFZ) and Their Metabolites (1-OH IBU, 2-OH IBU, CBX IBU, SCP, OCP, FCP, MTCS and 2,H-5,MBA) in HPLC

Phenolic micropollutants namely ibuprofen (IBU), ciprofloxacin (CIP), triclosan (TCS) and gemfibrozil (GFZ) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and they were measured in HPLC. Metabolites of IBU namely 1-hydroxyibuprofen (1-OH IBU), 2-hydroxyibuprofen (2-OH IBU) and ibuprofen carboxylic acid (CBX IBU); metabolites of CIP namely Sulfociprofloxacin (SCP), Oxociprofloxacin (OCP) and Formylciprofloxacin (FCP); metabolite of TCS namely Methyl triclosan (MTCS); metabolite of GFZ namely 2-Hydroxy-5-Methylbenzaldehyde (2,H-5,MBA) were also extracted from raw hospital wastewater by SPE method and then measured in HPLC.

5.6.13.1 Extraction of Phenolic Micropollutants (IBU, CIP, TCS and GFZ) and Their Metabolites (1-OH IBU, 2-OH IBU, CBX IBU, SCP, OCP, FCP, MTCS and 2,H-5,MBA) From Raw Hospital Wastewater by SPE Method

A solid-phase extraction (SPE) method was used to extract the phenolic micropollutants and their metabolites from the raw hospital wastewater. The extraction experiments were carried out using Oasis HLB cartridges (200 mg). 0.45 μm pore-sized membrane filter papers were used to clarify the raw hospital wastewater having a volume of 100 mL. The filtered raw hospital wastewater was acidified with sulfuric acid ($\text{pH} = 3.00$) before loading on cartridges. The adsorbed samples on the cartridges were eluted with 5 mL MeOH (methanol) containing 5% $(\text{C}_2\text{H}_5)_3\text{N}$ (triethylamine). A nitrogen evaporator was used to evaporate the eluants collected from the cartridges. Pure acetonitrile was added to the dried extract obtained at the end of the evaporation process and the final volume of the sample was finalised to 1 mL (Diwan et al., 2010). The extracted samples were then measured in HPLC.

5.6.13.2 Measurement of IBU and Its Metabolites (1-OH IBU, 2-OH IBU and CBX IBU) in Raw Hospital Wastewater Using HPLC

Analytical standard of Ibuprofen (IBU)(CAS No: 15687-27-1) and its metabolites namely 1-hydroxyibuprofen (1-OH IBU) (CAS No: 53949-53-4), 2-hydroxyibuprofen (2-OH IBU) (CAS No: 51146-55-5) and ibuprofen carboxylic acid (CBX IBU) (CAS No: 15935-54-3) were purchased from Fluka (Germany). Solutions of IBU, 1-OH IBU, 2-OH IBU and CBX IBU were diluted by using methanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of IBU, 1-OH IBU, 2-OH IBU and CBX IBU were drawn for 0.01-0.10-1.00-10.00-50.00-100.00 $\mu\text{g L}^{-1}$ and the regression coefficients of the calibration curves were above 0.999 for IBU and its metabolites (1-OH IBU, 2-OH IBU and CBX IBU). Accuracy of the concentrations were tested in HPLC and the analysis were performed on an Agilent 1100 Series HPLC equipped with a diode-array-detector (DAD).The mobile phase consisted of

methanol and 0.05 M Na_2HPO_4 in distilled water at pH 6.50 (60:40 v:v). A Thermo C18 column (5 μm , 250 mm $\times$ 4.6 mm, Thermo Scientific) was used and the injection volume was 20 μL . The flowrate was 0.6 mL min^{-1} and the column oven temperature was 30°C. The signal wavelength was determined as 210 nm (Hassan et al., 2008). The retention times for IBU, 1-OH IBU, 2-OH IBU and CBX IBU were calculated as 5.778, 4.750, 4.312 and 2.029 min, respectively. The average extraction and method recovery rates for IBU and its metabolites (1-OH IBU, 2-OH IBU and CBX IBU) monitored by the HPLC as were shown in Table 5.7.

Table 5.7 The average extraction and method recovery rates for IBU and its metabolites (1-OH IBU, 2-OH IBU and CBX IBU)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration ($\mu\text{g L}^{-1}$)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration ($\mu\text{g L}^{-1}$)	Method recovery (%)		
IBU	5.778	0.01	0.229	0.216	94.32	0.00946	94.60	96.18	96.27
		10.00	230.86	221.99	96.16	9.616	96.16		
		100.00	2394.50	2348.05	98.06	98.06	98.06		
1-OH IBU	4.750	0.01	0.233	0.247	106.00	0.0112	112.00	100.78	110.03
		10.00	210.00	204.36	97.31	11.89	118.90		
		100.00	2436.36	2412.72	99.03	99.20	99.20		
2-OH IBU	4.312	0.01	0.281	0.293	104.27	0.0108	108.00	98.36	104.31
		10.00	222.11	202.69	91.26	10.65	106.50		
		100.00	2461.54	2450.19	99.54	98.44	98.44		
CBX IBU	2.029	0.01	0.256	0.266	103.91	0.0104	104.00	99.94	100.71
		10.00	231.00	224.40	97.14	10.01	100.10		
		100.00	2480.80	2450.00	98.76	98.02	98.02		

The average extraction recovery rates for IBU, 1-OH IBU, 2-OH IBU and CBX IBU were obtained as 96.18%, 100.78%, 98.36% and 99.94%, respectively where the average method recovery rates were calculated as 96.27%, 110.03%, 104.31% and 100.71%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for IBU and its metabolites (1-OH IBU, 2-OH IBU and CBX IBU) were suitable to use.

5.6.13.3 Measurement of CIP and Its Metabolites (SCP, OCP and FCP) in Raw Hospital Wastewater Using HPLC

Analytical standard of Ciprofloxacin (CIP) (CAS No: 85721-33-1) was purchased from Fluka (Germany) and its metabolites namely Sulfociprofloxacin (SCP) (CAS No: 105093-21-8), Oxociprofloxacin (OCP) (CAS No: 103237-52-1) and Formylciprofloxacin (FCP) (CAS No: 93594-39-9) were purchased from Novachemistry (United Kingdom). Solutions of CIP, SCP, OCP and FCP were diluted by using 10% solution of H₂SO₄ in water. They were stirred for 4 hours on magnetic stirrers to provide a homogenous distribution. Calibration curves of CIP, SCP, OCP and FCP were drawn for 0.10-1.00-10.00-100.00-500.00-1000.00 µg L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for CIP, SCP, OCP and FCP. Accuracy of the concentrations were tested in HPLC and the analysis were performed on an Agilent 1100 Series HPLC equipped with a diode-array-detector (DAD). The mobile phase consisted of 0.02 M KH₂PO₄ in distilled water and pure acetonitrile (95:5v:v). A Thermo C18 column (5 µm, 250 mm × 4.6 mm, Thermo Scientific) was used and the injection volume was 20 µL. The flowrate was 1.5 mL min⁻¹ and the column oven temperature was 20°C. The signal wavelength was determined as 280 nm (Guney & Sponza, 2016). The retention times for CIP, SCP, OCP and FCP were calculated as 11.597, 8.905, 12.103 and 17.012 min, respectively. The average extraction and method recovery rates for CIP and its metabolites (SCP, OCP and FCP) monitored by the HPLC as were shown in Table 5.8.

Table 5.8 The average extraction and method recovery rates for CIP and its metabolites (SCP, OCP and FCP)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration ($\mu\text{g L}^{-1}$)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration ($\mu\text{g L}^{-1}$)	Method recovery (%)		
CIP	11.597	0.10	0.126	0.120	95.24	0.0949	94.90	95.57	95.69
		100.00	126.00	121.16	96.16	96.16	96.16		
		1000.00	1260.00	1200.99	95.32	960.02	96.00		
SCP	8.905	0.10	0.128	0.127	99.22	0.0919	91.90	99.66	94.60
		100.00	124.16	123.91	99.80	96.00	96.00		
		1000.00	1260.80	1260.12	99.95	959.00	95.90		
OCP	12.103	0.10	0.129	0.128	99.22	0.105	105.00	99.67	99.16
		100.00	123.78	123.61	99.86	96.50	96.50		
		1000.00	1258.90	1258.15	99.94	959.80	95.98		
FCP	17.012	0.10	0.123	0.118	95.93	0.108	108.00	98.65	100.44
		100.00	123.26	123.15	99.91	96.55	96.55		
		1000.00	1260.30	1261.81	100.12	967.60	96.76		

The average extraction recovery rates for CIP, SCP, OCP and FCP were obtained as 95.57%, 99.66%, 99.67% and 98.65%, respectively where the average method recovery rates were calculated as 95.69%, 94.60%, 99.16% and 100.44%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for CIP and its metabolites (SCP, OCP and FCP) were suitable to use.

5.6.13.4 Measurement of TCS and Its Metabolite (MTCS) in Raw Hospital Wastewater Using HPLC

Analytical standard of Triclosan (TCS) (CAS No: 3380-34-5) was purchased from Fluka (Germany) and its metabolite namely Methyl triclosan (MTCS) (CAS No: 4640-01-1) were purchased from LGC Standards (Germany). Solutions of TCS and MTCS were diluted by using methanol and they were stirred for 4 hours on magnetic stirrers to provide a homogenous distribution. Calibration curves of TCS and MTCS were drawn for 0.10-1.00-10.00-100.00-500.00-1000.00 $\mu\text{g L}^{-1}$ and the regression coefficients of the calibration curves were above 0.999 for TCS and MTCS. Accuracy of the concentrations were tested in HPLC and the analysis were performed on an Agilent 1100 Series HPLC equipped with a diode-array-detector (DAD). The mobile phase consisted of pure acetonitrile and HPLC grade water (90:10 v:v). A Thermo C18 column (5 μm , 250 mm $\times$ 4.6 mm, Thermo Scientific) was used and the injection volume was 20 μL . The flowrate was 1.0 mL min^{-1} and the column oven temperature was 40°C. The signal wavelength was determined as 210 nm (Maarroof & Uysal, 2014). The retention times for TCS and MTCS were calculated as 3.606 and 3.696 min, respectively. The average extraction and method recovery rates for TCS and its metabolite (MTCS) monitored by the HPLC as were shown in Table 5.9.

Table 5.9 The average extraction and method recovery rates for TCS and its metabolite (MTCS)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration ($\mu\text{g L}^{-1}$)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration ($\mu\text{g L}^{-1}$)	Method recovery (%)		
TCS	3.606	0.10	2.987	3.081	103.15	0.1173	117.30	105.39	109.10
		100.00	2916.30	3163.43	108.47	106.92	106.92		
		1000.00	29935.00	31301.40	104.56	1030.80	103.08		
MTCS	3.696	0.10	2.127	2.097	98.59	0.109	109.00	99.84	106.85
		100.00	2063.50	2053.70	99.53	101.00	101.00		
		1000.00	28127.00	28517.90	101.40	1105.60	110.56		

The average extraction recovery rates for TCS and MTCS were obtained as 105.39% and 99.84%, respectively where the average method recovery rates were calculated as 109.10% and 106.85%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for TCS and its metabolite (MTCS) were suitable to use.

5.6.13.5 Measurement of GFZ and Its Metabolite (2,H-5,MBA) in Raw Hospital Wastewater Using HPLC

Analytical standard of Gemfibrozil (GFZ) (CAS No: 25812-30-0) was purchased from Fluka (Germany) and its metabolite namely 2-Hydroxy-5-Methylbenzaldehyde (2,H-5,MBA) (CAS No: 613-84-3) was purchased from Sigma Aldrich (Germany). Solutions of GFZ and 2,H-5,MBA were diluted by using methanol and they were stirred for 4 hours on magnetic stirrers to provide a homogenous distribution. Calibration curves of GFZ and 2,H-5,MBA were drawn for 0.01-0.10-1.00-10.00-50.00-100.00 $\mu\text{g L}^{-1}$ and the regression coefficients of the calibration curves were above 0.999 both for GFZ and 2,H-5,MBA. Accuracy of the concentrations were tested in HPLC and the analysis were performed on an Agilent 1100 Series HPLC equipped with a diode-array-detector (DAD). The mobile phase consisted of pure acetonitrile, pure methanol and 0.05 M $\text{NH}_4\text{H}_2\text{PO}_4$ at a pH of 7.00 (60:30:10 v:v:v). A Thermo C18 column (5 μm , 250 mm $\times$ 4.6 mm, Thermo Scientific) was used and the injection volume was 20 μL . The flowrate was 0.8 mL min^{-1} and the column oven temperature was 20°C. The signal wavelength was determined as 276 nm (Elsherif, Abas, Abdelwahab, & El-Weshahy, 2013). The retention times for GFZ and 2,H-5,MBA were calculated as 4.351 and 3.129 min, respectively. The average extraction and method recovery rates for GFZ and its metabolite (2,H-5,MBA) monitored by the HPLC as were shown in Table 5.10.

Table 5.10 The average extraction and method recovery rates for GFZ and its metabolite (2,H-5,MBA)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration ($\mu\text{g L}^{-1}$)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration ($\mu\text{g L}^{-1}$)	Method recovery (%)		
GFZ	4.351	0.01	0.0161	0.0150	93.17	0.009851	98.51	95.01	98.10
		10.00	6.53	6.26	95.86	9.90	99.00		
		100.00	76.63	73.56	95.99	96.80	96.80		
2,H-5,MBA	3.129	0.01	0.0150	0.0146	97.33	0.0107	107.00	96.50	100.18
		10.00	5.75	5.72	99.48	9.67	96.70		
		100.00	63.50	58.86	92.69	96.84	96.84		

The average extraction recovery rates for GFZ and 2,H-5,MBA were obtained as 95.01% and 96.50%, respectively where the average method recovery rates were calculated as 98.10% and 100.18%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for GFZ and its metabolite (2,H-5,MBA) were suitable to use.

5.6.14 Measurement of Aromatic Micropollutant (AHTN) and Its Metabolite (3-ETTN) in GC-MS

Aromatic micropollutant namely 6-Acetyl-1,1,2,4,4,7-hexamethyl-tetralin (AHTN) and its metabolite namely 3-Ethyl-5,6,7,8-Tetrahydro-5,5,8,8-Tetramethyl-2-Naphthaldehyde (3-ETTN) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and were measured in GC-MS.

5.6.14.1 Extraction of Aromatic Micropollutant (AHTN) and Its Metabolite (3-ETTN) From Raw Hospital Wastewater by SPE Method

A solid-phase extraction (SPE) method was used to extract the aromatic micropollutant and its metabolite from the raw hospital wastewater. The extraction experiments were carried out using Oasis HLB cartridges (200 mg). 0.45 µm pore-sized membrane filter papers were used to clarify the raw hospital wastewater having a volume of 100 mL. Firstly, a solution of 30% MeOH (methanol) in DCM (dichloromethane) and secondly, MeOH (methanol) having volumes of 6 mL were loaded on the cartridge. After passing the sample through the conditioned cartridge, the cartridge was dried under vacuum for 1 hour. The adsorbed samples on the cartridges were eluted with 6 mL of mixture of DCM (dichloromethane) – hexane (4:1 v:v). A nitrogen evaporator was used to evaporate the eluants collected from the cartridges. Pure hexane was added to the dried extract obtained at the end of the evaporation process and the final volume of the sample was finalised to 1 mL (Chokwe, Okonkwo, Sibali, & Ncube, 2015). The extracted samples were then measured in GC-MS.

5.6.14.2 Measurement of AHTN and Its Metabolite (3-ETTN) in Raw Hospital Wastewater Using GC-MS

Analytical standard of 6-Acetyl-1,1,2,4,4,7-hexamethyl-tetralin (AHTN) (CAS No: 21145-77-7) was purchased from Fluka (Germany) and its metabolite namely 3-Ethyl-5,6,7,8-Tetrahydro-5,5,8,8-Tetramethyl-2-Naphthaldehyde (3-ETTN) (CAS No: 58243-85-9) was purchased from Sigma Aldrich (Germany). Solutions of AHTN and 3-ETTN were diluted by using methanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of AHTN and 3-ETTN were drawn for 0.1-1.00-10.00-100.00-500.00-1000.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for AHTN and its metabolite (3-ETTN). Analysis were performed in a gas chromatograph coupled to a quadrupole mass spectrometer, in electron ionization (EI) mode, using a GC-MS (Agilent 7890A) combined with a mass selective detector (Agilent 5975C inert MSD) equipped with a flame ionization detector and an HP-5MS capillary column with a length of 30.0 m × 0.25 mm (I.D.) × 0.25 µm (film thickness) (Agilent Technologies Inc.). Helium (purity 99.999%) was employed as carrier gas with a constant flow of 1.0 ml min⁻¹. The standards were injected (2 µL) into the GC system in splitless mode, with a splitless time of 1.5 min. The injector, quadrupole, transfer line and ion source were set at 275, 150, 300 and 230 °C respectively. The oven program was set at 35 °C for 0 min then 5 °C min⁻¹ to 200 °C for 0 min then to 20 °C min⁻¹ to 285 °C for 5 min. Acquisition was performed by Selected Ion Monitoring (SIM) and the monitored ions were 243 and 258 m/z for AHTN. The retention time was determined as 30.891 min (Simonich, Begley, Debaere, & Eckhoff, 2000). The monitored ions were found as 260 and 245 m/z and the retention time was found as 30.832 min for 3-ETTN (Valdersnes, Kallenborn, & Sydnes, 2006). The average extraction and method recovery rates for AHTN and its metabolite (3-ETTN) monitored by the GC-MS as were shown in Table 5.11.

Table 5.11 The average extraction and method recovery rates for AHTN and its metabolite (3-ETTN)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration (ng L ⁻¹)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration (ng L ⁻¹)	Method recovery (%)		
AHTN	30.891	0.10	3202	3101	96.85	0.0977	97.70	100.62	101.00
		100.00	2999214	3245336	108.21	105.54	105.54		
		1000.00	35259480	34129080	96.79	997.64	99.76		
3-ETTN	30.832	0.10	2911	2850	97.90	0.0984	98.40	96.59	99.54
		100.00	2926506	2773795	94.78	100.35	100.35		
		1000.00	34160270	33167218	97.09	998.55	99.86		

The average extraction recovery rates for AHTN and 3-ETTN were obtained as 100.62% and 96.59%, respectively where the average method recovery rates were calculated as 101.00% and 99.54%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for AHTN and its metabolite (3-ETTN) were suitable to use.

5.6.15 Measurement of Nitroso Micropollutant (NDMA) and Its Metabolite (DMA) in HPLC

Nitroso micropollutant namely N-Nitrosodimethylamine (NDMA) and its metabolite namely Dimethylamine (DMA) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and were measured in HPLC.

5.6.15.1 Extraction of Nitroso Micropollutant (NDMA) and Its Metabolite (DMA) From Raw Hospital Wastewater by SPE Method

A solid-phase extraction (SPE) method was used to extract the nitroso micropollutant and its metabolite from the raw hospital wastewater. The extraction experiments were carried out using Oasis HLB cartridges (200 mg). 0.45 µm pore-sized membrane filter papers were used to clarify the raw hospital wastewater having a volume of 100 mL. The filtered raw hospital wastewater was acidified with sulfuric acid (pH = 3.00) before loading on cartridges. The adsorbed samples on the cartridges were eluted with 5 mL MeOH (methanol) containing 5% (C₂H₅)₃N (triethylamine). A nitrogen evaporator was used to evaporate the eluants collected from the cartridges. Pure acetonitrile was added to the dried extract obtained at the end of the evaporation process and the final volume of the sample was finalised to 1 mL (Diwan et al., 2010). The extracted samples were then measured in HPLC.

5.6.15.2 Measurement of NDMA and Its Metabolite (DMA) in Raw Hospital Wastewater Using HPLC

Analytical standard of N-Nitrosodimethylamine (NDMA) (CAS No: 62-75-9) was purchased from Supelco (Germany) and its metabolite namely Dimethylamine (DMA) (CAS No: 124-40-3) was purchased from Sigma-Aldrich (Germany). Solutions of NDMA and DMA were diluted by using methanol and they were stirred for 4 hours on magnetic stirrers to provide a homogenous distribution. Calibration curves of NDMA and DMA were drawn for 0.01-0.10-1.00-10.00-100.00-1000.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for NDMA and its metabolite (DMA). Accuracy of the concentrations were tested in HPLC and the analysis were performed on an Agilent 1100 Series HPLC equipped with a diode-array-detector (DAD). The mobile phase consisted of pure ethanol and 0.01 M ammonium acetate at a pH of 4.00 (5:95 v:v). A Thermo C18 column (5 µm, 250 mm × 4.6 mm, Thermo Scientific) was used and the injection volume was 20 µL. The flowrate was 1.0 ml min⁻¹ and the column oven temperature was not controlled. The signal wavelength was determined as 254 nm (McDay, 2010). The retention times for NDMA and DMA were calculated as 3.582 and 4.094 min, respectively. The average extraction and method recovery rates for NDMA and its metabolite (DMA) monitored by the HPLC as were shown in Table 5.12.

Table 5.12 The average extraction and method recovery rates for NDMA and its metabolite (DMA)

Compound	Retention time, RT (min)	Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Actual concentration (ng L ⁻¹)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined concentration (ng L ⁻¹)	Method recovery (%)		
NDMA	3.582	0.01	0.0540	0.0528	97.78	0.009764	97.64	97.43	97.93
		10.00	47.48	45.85	96.57	9.85	98.50		
		1000.00	5396.80	5285.80	97.94	976.40	97.64		
DMA	4.094	0.01	0.0577	0.0573	99.31	0.0101	101.00	99.45	99.29
		10.00	45.50	45.13	99.19	9.89	98.90		
		1000.00	5310.00	5302.56	99.86	979.75	97.98		

The average extraction recovery rates for NDMA and DMA were obtained as 97.43% and 99.45%, respectively where the average method recovery rates were calculated as 97.93% and 99.29%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for NDMA and its metabolite (DMA) were suitable to use.

5.6.16 Measurement of Fluoro Micropollutants (PFOA and PFOS) and Their Metabolites (PFHpA and FTA) in LC-MS/MS

Fluoro micropollutants namely Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and were measured in LC-MS/MS. Metabolite of PFOA namely Perfluoroheptanoic Acid (PFHpA) and metabolite of PFOS namely 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decanol (FTA) were also extracted from raw hospital wastewater by SPE method and then measured in LC-MS/MS.

5.6.16.1 Extraction of Fluoro Micropollutants (PFOA and PFOS) and Their Metabolites (PFHpA and FTA) From Raw Hospital Wastewater by SPE Method

A solid-phase extraction (SPE) method was used to extract the fluoro micropollutants and their metabolites from the raw hospital wastewater. The extraction experiments were carried out using Oasis HLB cartridges (200 mg). 0.45 µm pore-sized membrane filter papers were used to clarify the raw hospital wastewater having a volume of 100 mL. Firstly, a solution of 30% MeOH (methanol) in DCM (dichloromethane) and secondly, MeOH (methanol) having volumes of 6 mL were loaded on the cartridge. After passing the sample through the conditioned cartridge, the cartridge was dried under vacuum for 1 hour. The adsorbed samples on the cartridges were eluted with 6 mL of mixture of DCM (dichloromethane) – hexane (4:1 v:v). A nitrogen evaporator was used to evaporate the eluants collected from the cartridges. Pure hexane was added to the dried extract obtained at the end of the

evaporation process and the final volume of the sample was finalised to 1 mL (Chokwe et al., 2015). The extracted samples were then measured in LC-MS/MS.

5.6.16.2 Measurement of PFOA and Its Metabolite (PFHpA) in Raw Hospital Wastewater Using LC-MS/MS

Analytical standard of Perfluorooctanoic acid (PFOA) (CAS No: 335-67-1) and its metabolite namely Perfluoroheptanoic Acid (PFHpA) (CAS No: 375-85-9) were purchased from Sigma Aldrich (Germany). Solutions of PFOA and PFHpA were diluted by using methanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of PFOA and PFHpA were drawn for 0.10-1.00-10.00-100.00-500.00-1000.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for PFOA and its metabolite (PFHpA). Analytes were determined using an LC-MS/MS system comprising a Waters 2690 HPLC coupled to a Waters Micromass Quattro tandem mass spectrometer (Waters, Milford, MA). The separation was performed on an Ascentic C18 reversed phase column (25 × 4 mm, 5 µm, Supelco, St. Louis, MO). The mobile phase consisted of 2mM ammonium acetate water solution (A) and methanol (B) at a flowrate of 0.4 mL min⁻¹. The gradient program lasted 17 min and programmed as follows: 50% B was increased linearly to 90% in 3 min, and hold 90% till 14 min, and then reduced to 50% at 14.1 min, and held for additional 3 min. The electrospray ionization in a negative mode was used with the following parameters: capillary voltage 20 V, cone voltage 11 V. Desolvation temperatures was at 300 °C, and the source block at 100 °C. Nitrogen (Airgas, >99.999% purity) was used as the nebulizer and drying gas at the flowrates of 34 and 198 L hour⁻¹, respectively. The quantitative analysis was performed using selected reaction ion monitoring for PFOA and PFHpA. The transitions were found as 413 and 369 m/z for PFOA and were found as 363 and 319 m/z for PFHpA, respectively (Zhang et al., 2016). The average extraction and method recovery rates for PFOA and its metabolite (PFHpA) monitored by the LC-MS/MS as were shown in Table 5.13.

Table 5.13 The average extraction and method recovery rates for PFOA and its metabolite (PFHpA)

Compound	Retention time, RT (min)	m/z transitions		Recovery Study			Average Method Recovery (%)	LOD (ng L ⁻¹)
		Ion 1	Ion 2	Actual concentration (ng L ⁻¹)	Determined concentration (ng L ⁻¹)	Method Recovery (%)		
PFOA	12.6	413	369	0.10 100.00 1000.00	0.0952 91.60 972.00	95.20 91.60 97.20	94.67	0.010
PFHpA	11.1	363	319	0.10 100.00 1000.00	0.0964 106.80 961.30	96.40 106.80 96.13	99.78	0.010

The average method recovery rates for PFOA and PFHpA were obtained as 94.67% and 99.78%, respectively where the limit of detection (LOD) values were found as 0.010 ng L⁻¹. It is expected that the average method recovery rate must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for PFOA and its metabolite (PFHpA) were suitable to use.

5.6.16.3 Measurement of PFOS and Its Metabolite (FTA) in Raw Hospital Wastewater Using LC-MS/MS

Analytical standard of Perfluorooctanesulfonic acid (PFOS) (CAS No: 1763-23-1) was purchased from Fluka (Germany) and its metabolite namely 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decanol (FTA) (CAS No: 307-37-9) was purchased from Sigma Aldrich (Germany). Solutions of PFOS and FTA were diluted by using methanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curve of PFOS and FTA were drawn for 0.01-0.10-1.00-10.00-50.00-100.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for PFOS and its metabolite (FTA). As in the previous measurement method, PFOS and FTA samples were measured by following the procedure given for PFOA in section 5.6.16.2. The quantitative analysis was performed using selected reaction ion monitoring for PFOS and FTA. The transitions were found as 499 and 80 m/z for PFOS and were found as 69 and 119 m/z for FTA, respectively (Zhang et al., 2016). The average extraction and method recovery rates for PFOS and its metabolite (FTA) monitored by the LC-MS/MS as were shown in Table 5.14.

Table 5.14 The average extraction and method recovery rates for PFOS and its metabolite (FTA)

Compound	Retention time, RT (min)	m/z transitions		Recovery Study			Average Method Recovery (%)	LOD (ng L ⁻¹)
		Ion 1	Ion 2	Actual concentration (ng L ⁻¹)	Determined concentration (ng L ⁻¹)	Method Recovery (%)		
PFOS	15.5	499	80	0.01	0.00926	92.60	95.62	0.010
				10.00	9.36	93.60		
				100.00	100.67	100.67		
FTA	13.8	69	119	0.01	0.00942	94.20	102.20	0.010
				10.00	10.56	105.60		
				100.00	106.80	106.80		

The average method recovery rates for PFOS and FTA were obtained as 95.62% and 102.20%, respectively where the limit of detection (LOD) values were found as 0.010 ng L⁻¹. It is expected that the average method recovery rate must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for PFOS and its metabolite (FTA) were suitable to use.

5.6.17 Measurement of Brominated Micropollutants (PBT, PBEB, α -HBCDD and TBBPA) and Their Metabolites (4-MBB, BMB, 2-BCD and BPA) in GC-MS and LC-MS/MS

Brominated micropollutants namely Pentabromotoluene (PBT) and its metabolite namely 4-Methylbromobenzene (4-MBB), 2,3,4,5,6-Pentabromoethylbenzene (PBEB) and its metabolite namely (Bromomethyl)benzene (BMB) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and were measured in GC-MS. Brominated micropollutants namely α -Hexabromocyclododecane (α -HBCDD) and its metabolite namely 2-Bromocyclododecan-1-ol (2-BCD), 3,3',5,5'-Tetrabromobisphenol A (TBBPA) and its metabolite namely 2,2-Bis(4-hydroxyphenyl)propane (BPA) were extracted from raw hospital wastewater by solid-phase extraction (SPE) method and were measured in LC-MS/MS.

5.6.17.1 Extraction of Brominated Micropollutants (PBT, PBEB, α -HBCDD and TBBPA) and Their Metabolites (4-MBB, BMB, 2-BCD and BPA) From Raw Hospital Wastewater by SPE Method

A solid-phase extraction (SPE) method was used to extract the brominated micropollutants and their metabolites from the raw hospital wastewater. The extraction experiments were carried out using Oasis HLB cartridges (200 mg). 0.45 μ m pore-sized membrane filter papers were used to clarify the raw hospital wastewater having a volume of 100 mL. Firstly, a solution of 30% MeOH (methanol) in DCM (dichloromethane) and secondly, MeOH (methanol) having volumes of 6 mL were loaded on the cartridge. After passing the sample through the conditioned

cartridge, the cartridge was dried under vacuum for 1 hour. The adsorbed samples on the cartridges were eluted with 6 mL of mixture of DCM (dichloromethane) – hexane (4:1 v:v). A nitrogen evaporator was used to evaporate the eluants collected from the cartridges. Pure hexane was added to the dried extract obtained at the end of the evaporation process and the final volume of the sample was finalised to 1 mL (Chokwe et al., 2015). The extracted samples of PBT, 4-MBB, PBEB and BMB were measured in GC-MS, while α -HBCDD, 2-BCD, TBBPA and BPA were measured in LC-MS/MS.

5.6.17.2 Measurement of PBT and Its Metabolite (4-MBB) in Raw Hospital Wastewater Using GC-MS

Analytical standard of Pentabromotoluene (PBT) (CAS No: 87-83-2) was purchased from TCI (Japan) and its metabolite namely 4-Methylbromobenzene (4-MBB) (CAS No: 106-38-7) was purchased from Sigma Aldrich (Germany). Solutions of PBT and 4-MBB were diluted by using hexane and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of PBT and 4-MBB were drawn for 0.01-0.10-1.00-10.00-50.00-100.00 $\mu\text{g L}^{-1}$ and the regression coefficients of the calibration curves were above 0.999 for PBT and its metabolite (4-MBB). Analysis were performed in a gas chromatograph coupled to a quadrupole mass spectrometer, in electron ionization (EI) mode, using a GC-MS (Agilent 7890A) combined with a mass selective detector (Agilent 5975C inert MSD) equipped with a flame ionization detector and an HP-5MS capillary column with a length of 30.0 m $\times$ 0.25 mm (I.D.) $\times$ 0.25 μm (film thickness) (Agilent Technologies Inc.). Helium (purity 99.999%) was employed as carrier gas with a constant flow of 1.7 ml min^{-1} . The standards were injected (2 μL) into the GC system in splitless mode, with a splitless time of 1.5 min. The injector, quadrupole, transfer line and ion source were set at 270, 150, 300 and 230 $^{\circ}\text{C}$ respectively. The oven program was taken from Cristale, Quintana, Chaler, Ventura, & Lacorte (2012) and developed as following: The oven program was set at 60 $^{\circ}\text{C}$ for 0 min then 20 $^{\circ}\text{C min}^{-1}$ to 220 $^{\circ}\text{C}$ for 0 min then to 16 $^{\circ}\text{C min}^{-1}$ to 315 $^{\circ}\text{C}$ for 5 min. Acquisition was performed by Selected Ion Monitoring (SIM) and the monitored ions were 485.7,

487.7 and 406.7 m/z for PBT. The retention time was determined as 10.550 min for PBT. The monitored ions were found as 90.9, 169.9 and 171.9 m/z and the retention time was found as 8.455 min for 4-MBB, respectively (Cristale et al., 2012). The average extraction and method recovery rates for PBT and its metabolite (4-MBB) monitored by the GC-MS as were shown in Table 5.15.



Table 5.15 The average extraction and method recovery rates for PBT and its metabolite (4-MBB)

Compound	Retention time, RT (min)	m/z transitions			Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Ion 1	Ion 2	Ion 3	Actual conc. ($\mu\text{g L}^{-1}$)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined conc. ($\mu\text{g L}^{-1}$)	Method recovery (%)		
PBT	10.550	485.7	487.7	406.7	0.01	87	84	96.55	0.0093	93.00	98.12	101.16
					10.00	84792	82646	97.47	9.62	96.20		
					100.00	818197	820873	100.33	114.27	114.27		
4-MBB	8.455	90.9	169.9	171.9	0.01	84	83	98.81	0.0097	97.00	99.83	106.42
					10.00	83672	83752	100.10	11.46	114.60		
					100.00	823440	828160	100.57	107.65	107.65		

The average extraction recovery rates for PBT and 4-MBB were obtained as 98.12% and 99.83%, respectively where the average method recovery rates were calculated as 101.16% and 106.42%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for PBT and its metabolite (4-MBB) were suitable to use.

5.6.17.3 Measurement of PBEB and Its Metabolite (BMB) in Raw Hospital Wastewater Using GC-MS

Analytical standard of 2,3,4,5,6-Pentabromoethylbenzene (PBEb) (CAS No: 85-22-3) was purchased from Dr Ehrenstorfer (Germany) and its metabolite namely (Bromomethyl)benzene (BMB) (CAS No: 100-39-0) was purchased from Sigma Aldrich (Germany). Solutions of PBEb and BMB were diluted by using hexane and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of PBEb and BMB were drawn for 0.01-0.10-1.00-10.00-50.00-100.00 $\mu\text{g L}^{-1}$ and the regression coefficients of the calibration curves were above 0.999 for PBEb and its metabolite (BMB). As in the aforementioned measurement method, PBEb and BMB samples were determined by following the procedure given for PBT in section 5.6.17.2. Acquisition was performed by Selected Ion Monitoring (SIM) and the monitored ions were 499.7, 484.7 and 486.7 m/z for PBEb. The retention time was determined as 10.786 min for PBEb. The monitored ions were found as 91.0, 65.0 and 63.0 m/z and the retention time was found as 9.026 min for BMB, respectively (Cristale et al., 2012). The average extraction and method recovery rates for PBEb and its metabolite (BMB) monitored by the GC-MS as were shown in Table 5.16.

Table 5.16 The average extraction and method recovery rates for PBEB and its metabolite (BMB)

Compound	Retention time, RT (min)	m/z transitions			Recovery Study						Average Extraction Recovery (%)	Average Method Recovery (%)
		Ion 1	Ion 2	Ion 3	Actual conc. (µg L ⁻¹)	Peak area of the standard	Peak area of the sample	Extraction recovery (%)	Determined conc. (µg L ⁻¹)	Method recovery (%)		
PBEB	10.786	499.7	484.7	486.7	0.01	79	77	97.47	0.0096	96.00	98.40	99.62
					10.00	82915	80219	96.75	9.71	97.10		
					100.00	848294	856539	100.97	105.76	105.76		
BMB	9.026	91.0	65.0	63.0	0.01	75	74	98.67	0.0097	97.00	99.17	94.41
					10.00	82651	80256	97.10	9.41	94.10		
					100.00	853020	867744	101.73	92.12	92.12		

The average extraction recovery rates for PBEB and BMB were obtained as 98.40% and 99.17%, respectively where the average method recovery rates were calculated as 99.62% and 94.41%, respectively. It is expected that the average extraction and method recovery rates must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for PBEB and its metabolite (2,5-BMB) were suitable to use.

5.6.17.4 Measurement of α -HBCDD and Its Metabolite (2-BCD) in Raw Hospital Wastewater Using LC-MS/MS

Analytical standard of α -Hexabromocyclododecane (α -HBCDD) (CAS No: 134237-50-6) was purchased from Sigma Aldrich (Germany) and its metabolite namely 2-Bromocyclododecan-1-ol (2-BCD) (CAS No: 83602-77-1) was purchased from DayangChem (China). Solutions of α -HBCDD and 2-BCD were diluted by using methanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of α -HBCDD and 2-BCD were drawn for 0.10-1.00-10.00-100.00-500.00-1000.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for α -HBCDD and its metabolite (2-BCD). α -HBCDD and 2-BCD were analysed using liquid chromatography with tandem mass-spectrometry (Agilent LC 1290/QQQ 6490), fitted with a Luna C18 column (Phenomenex Luna, 3 μ m C18 100 Å, 150 $\times$ 2 mm²) using electron spray ionisation in negative mode. Instrument parameters were as follows; Vcharging was 0 and 500 V, capillary was 0 and 3500 V, sheath gas flow was 11 and 11 L min⁻¹, sheath gas heater was 350 and 350 °C, nebulizer was 30 and 30 psi, gas flow was 14 and 14 L min⁻¹, gas temperature was 250 and 250 °C for (+) and (-) values, respectively. Ion funnel parameters were as follows; positive and negative low pressure RF values were 60 and positive and negative high pressure RF values were 150, respectively. Injection volume was 10 μ L, mobile phases A and B Methanol (MeOH)/Water (H₂O) each with 10 mM Ammonium acetate at a flowrate of 0.2 mL min⁻¹. The solvent gradient was as follows: initial 70:30 MeOH:H₂O for 4 min, 90:10 MeOH:H₂O for 7 min, 95:5 MeOH:H₂O for 3 min and 70:30 MeOH:H₂O for a final 4 min. The samples were provided in 70:30 MeOH:H₂O. The quantitative analysis

were performed using selected reaction ion monitoring for α -HBCDD and 2-BCD. The transitions were found as 640.7, 78.7 and 80.7m/z for α -HBCDD and were found as 640.7 and 296.7 for 2-BCD, respectively (Sühling, Barber, Wolschke, Kötke, & Ebinghaus, 2015). The average extraction and method recovery rates for α -HBCDD and its metabolite (2-BCD) monitored by the LC-MS/MS as were shown in Table 5.17.



Table 5.17 The average extraction and method recovery rates for α -HBCDD and its metabolite (2-BCD)

Compound	Retention time, RT (min)	m/z transitions			Recovery Study			Average Method Recovery (%)	LOD (ng L ⁻¹)
		Ion 1	Ion 2	Ion 3	Actual conc. (ng L ⁻¹)	Determined conc. (ng L ⁻¹)	Method Recovery (%)		
α -HBCDD	9.70	640.7	78.7	80.7	0.10	0.094	94.00	96.40	0.010
					100.00	98.40	98.40		
					1000.00	968.00	96.80		
2-BCD	11.02	640.7	296.7	N.A.	0.10	0.092	92.00	97.03	0.010
					100.00	96.80	96.80		
					1000.00	1022.80	102.28		

N.A. : Not available

The average method recovery rates for α -HBCDD and 2-BCD were obtained as 96.40% and 97.03%, respectively where the limit of detection (LOD) values were found as 0.010 ng L⁻¹. It is expected that the average method recovery rate must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for α -HBCDD and its metabolite (2-BCD) were suitable to use.

5.6.17.5 Measurement of TBBPA and Its Metabolite (BPA) in Raw Hospital Wastewater Using LC-MS/MS

Analytical standard of 3,3',5,5'-Tetrabromobisphenol A (TBBPA) (CAS No: 79-94-7) and its metabolite namely 2,2-Bis(4-hydroxyphenyl)propane (BPA) (CAS No: 80-05-7) were purchased from Sigma Aldrich (Germany). Solutions of TBBPA and BPA were diluted by using ethanol and was stirred for 4 hours on magnetic stirrers and was ensured a homogenous distribution. Calibration curves of TBBPA and BPA were drawn for 0.10-1.00-10.00-100.00-500.00-1000.00 ng L⁻¹ and the regression coefficients of the calibration curves were above 0.999 for TBBPA and its metabolite (BPA). TBBPA and BPA were analysed by following the procedure given for α -HBCDD in the aforementioned section 5.6.17.4. The quantitative analysis were performed using selected reaction ion monitoring for TBBPA and BPA. The transitions were found as 542.9, 79.1 and 290.8 m/z for TBBPA and were found as 213.0, 119.0 and 228.0 m/z for BPA, respectively (Sühling et al., 2015). The average extraction and method recovery rates for TBBPA and its metabolite (PBA) monitored by the LC-MS/MS as were shown in Table 5.18.

Table 5.18 The average extraction and method recovery rates for TBBPA and its metabolite (BPA)

Compound	Retention time, RT (min)	m/z transitions			Recovery Study			Average Method Recovery (%)	LOD (ng L ⁻¹)
		Ion 1	Ion 2	Ion 3	Actual conc. (ng L ⁻¹)	Determined conc. (ng L ⁻¹)	Method Recovery (%)		
TBBPA	7.10	542.9	79.1	290.8	0.10 100.00 1000.00	0.091 106.60 1020.80	91.00 106.60 102.08	99.89	0.010
BPA	6.19	213.0	119.0	228.0	0.10 100.00 1000.00	0.094 114.20 1026.40	94.00 114.20 102.64	103.61	0.010

The average method recovery rates for TBBPA and BPA were obtained as 99.89% and 103.61%, respectively where the limit of detection (LOD) values were found as 0.010 ng L⁻¹. It is expected that the average method recovery rate must be in a range of 80 – 120%. Therefore it can be concluded that the aforementioned measurement methods for TBBPA and its metabolite (BPA) were suitable to use.

5.7 Calculation of Solids Retention Time (SRT) and Hydraulic Residence Time (HRT)

Solids retention time (SRT) is the total quantity of active biomass in thereactor divided by the total quantity of active biomass withdrawn daily. Since nosludge wasting was applied for granule formation in the anaerobic UASB reactor, SRT in this reactor was determined using Equation 5.45 and 5.46 (Metcalf & Eddy, 2004).

$$SRT = \frac{V_r \times X_r}{Q_e \times X_e + Q_w \times X_w} \quad (5.45)$$

Q_w and X_w were defined as flowrate and microorganism concentrations, respectively in wasted sludge stream. The term $Q_w \times X_w$ only makes sense if there is a waste sludge stream. Since there is no a sludge wastage in the anaerobic UASB reactor, SRT can be expressed as follows:

$$SRT = \frac{V_r \times X_r}{Q_e \times X_e} \quad (5.46)$$

Stepwise increases in organic loading cause increases in both flow rates (Q_e) and microorganism concentrations in the effluent (X_e) of the anaerobic UASB reactor. Therefore, SRT in the anaerobic UASB reactor was calculated on the basis of Equation 5.46 and varied depending to shock organic loading applied.

The sludge wasting in a conventional CSTR reactor occurred from the settling tank and the solids in the effluent (X_e) were taken into consideration. Therefore, SRT in this reactor was calculated by using Equation 5.47 with rearranged Equation 5.48.

$$SRT = \frac{V_r \times X_r}{Q_w \times X_w + Q_e \times X_e} \quad (5.47)$$

V_r and X_r are effective volume of reactor and microorganism concentration in the aerobic CSTR reactor. Q_e and X_e were defined as flowrate and microorganism concentration measured in the aerobic CSTR reactor. Q_w and X_w are the flowrate and microorganism concentration wasted from the reactor. If the concentration of microorganism in the effluent of the settling tank is low, X_e is negligible (Metcalf & Eddy, 2004). The aerobic CSTR used in this study is an aerobic CSTR reactor without sludge return. In this study, the activated sludge was withdrawn from the inside of the aeration stage, the microorganism concentration in the reactor (X_r) was equal to the wasted microorganism concentration (X_w). Therefore, Equation 5.48 was used to calculate the SRT in the aerobic CSTR reactor.

$$SRT = \frac{V_r}{Q_r} \quad (5.48)$$

V_r and Q_r were defined as reactor volume (L) and influent flowrate (L day⁻¹), respectively.

In our study, because of the biological reactors were without sludge returns, SRTs were equal to the hydraulic residence times (HRTs).

5.8 Kinetic Studies

5.8.1 Zero-Order Pollutant Removal Model

The rate of change in micropollutant, COD and sCOD concentrations in the system with assuming zero-order removal model for pollutant removal can be expressed in Equation 5.49 (Benefield, 1980).

$$-\frac{dS}{dt} = \frac{Q}{V} \times S_i - \frac{Q}{V} \times S_e - k_0 \quad (5.49)$$

Under steady-state conditions, the rate of change in pollutant concentration ($-dS/dt$) is negligible and the Equation 5.49 can be reduced to Equation 5.50 as follows:

$$S_i - S_e = k_0 \times t \quad (5.50)$$

Where, S_i and S_e are influent and effluent micropollutant, COD and sCOD concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively. t is solids retention time (SRT) through pollutant removal (day). k_0 is zero-order kinetic constant (day^{-1}) and can be obtained from the slope of the line plotting the $(S_i - S_e)$ versus time (t) using Equation 5.50. The slope of the line gives the k_0 value (day^{-1}) (Kuscu, 2007).

5.8.2 Half-Order Pollutant Removal Model

The rate of change in micropollutant, COD and sCOD concentrations in the system with assuming the half-order removal model for pollutant removal could be expressed as follows (Equation 5.51) (Benefield, 1980).

$$-\frac{dS}{dt} = k \times \sqrt{S} \quad (5.51)$$

The integrated half-order rate law is given in Equation 5.52.

$$\sqrt{S_e} = \sqrt{S_i} - \frac{1}{2} k_{1/2} \times t \quad (5.52)$$

Where, S_i and S_e are influent and effluent micropollutant, COD and sCOD concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively. t is solids retention time (SRT) through pollutant removal (day). $k_{1/2}$ is the half-order kinetic constant (day^{-1}) and can be obtained by plotting the $1/\sqrt{S_i - S_e}$ versus time (t) using Equation 5.52. The slope of the line gives the $k_{1/2}$ value (day^{-1}) (Gok, 2012).

5.8.3 First-Order Pollutant Removal Model

The rate of change in micropollutant, COD and sCOD concentrations in the system with assuming the first-order removal model for pollutant removal could be expressed as follows (Equation 5.53) (Benefield, 1980).

$$-\frac{dS}{dt} = \frac{Q}{V} \times S_i - \frac{Q}{V} \times S_e - k_1 \times S_e \quad (5.53)$$

Under steady-state conditions, the rate of change in pollutant concentration ($-dS/dt$) is negligible and the equation given above can be reduced to the Equation 5.54.

$$\frac{S_i - S_e}{t} = k_1 \times S_e \quad (5.54)$$

The integrated first-order rate law is given in Equation 5.55 and can be rearranged as Equation 5.56.

$$\ln S_e = \ln S_i - k_1 \times t \quad (5.55)$$

$$S_e = S_i \times e^{-k_1 \times t} \quad (5.56)$$

Where, S_i and S_e are influent and effluent micropollutant, COD and sCOD concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively. t is solids retention time (SRT) through pollutant removal (day). k_1 is the first-order kinetic constant (day^{-1}). k_1 can be obtained by plotting the $\ln (S_i - S_e)$ versus time (t) using Equation 5.56. The slope of the line gives the k_1 value (day^{-1}) (Gok, 2012).

5.8.4 Second-Order Pollutant Removal Model

The rate of change in micropollutant, COD and sCOD concentrations in the system with assuming second-order removal model for pollutant removal can be expressed in Equation 5.57 (Benefield, 1980).

$$-\frac{dS}{dt} = \frac{Q}{V} \times S_i - \frac{Q}{V} \times S_e - k_2 \times S_e^2 \quad (5.57)$$

Under steady-state conditions, the rate of change in pollutant concentration ($-dS/dt$) is negligible and the equation given above can be reduced to the Equation 5.58.

$$\frac{S_i - S_e}{t} = k_2 \times S_e^2 \quad (5.58)$$

The integrated second-order rate law is given in Equation 5.59.

$$\frac{1}{S_e} = \frac{1}{S_i} + k_2 \times t \quad (5.59)$$

Where, S_i and S_e are influent and effluent micropollutant, COD and sCOD concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively. t is solids retention time (SRT) through pollutant removal (day). k_2 is the second order kinetic constant ($\text{L } \mu\text{g}^{-1} \text{ day}^{-1}$) and can be obtained by plotting the $1/(S_i - S_e)$ versus time (t) using Equation 5.59. The slope of the line gives the k_2 value ($\text{L } \mu\text{g}^{-1} \text{ day}^{-1}$) (Gok, 2012).

5.8.5 Monod Kinetic Model

The Monod kinetic model was used to describe the biodegradation of micropollutants, COD and sCOD. Equation 5.60 and 5.61 represent growth and pollutant removals, respectively. For an anaerobic UASB reactor with no biomass recycle and an aerobic CSTR with no biomass recycle, microbial and substrate mass balance can be expressed using Equation 5.60 and 5.61.

Microorganism mass balance. A mass balance for the microorganisms in the entire system for anaerobic UASB and aerobic CSTR can be as follows:

$$(\text{Accumulation})^a = (\text{Inflow})^b - (\text{Outflow})^c + (\text{Net growth})^d \quad (5.60)$$

Where; a is the rate of accumulation of microorganism within the system boundary, b is the rate of flow of microorganism into the system boundary, c is the rate of flow of microorganism out of the system boundary and d is the net growth of microorganism within the system boundary.

Mathematically, Equation 5.60 can be written as Equation 5.61.

$$\frac{dX}{dt} = \left(\frac{Q}{V} \times X_i\right) - \left(\frac{Q}{V} \times X_e\right) + (\mu \times X) - (k_d \times X) \quad (5.61)$$

Where; V is reactor volume (L); Q is the flow rate (L day⁻¹); X_i and X_e are the influent and effluent biomass concentration (g L⁻¹), respectively; X is concentration of biomass in the reactor (g L⁻¹); μ is specific growth rate (day⁻¹) and k_d is endogenous decay coefficient (day⁻¹).

If it is assumed that the concentration of biomass in the influent can be neglected (X_i = 0) at steady-state (dX/dt = 0) conditions therefore, Equation 5.61 can be written as Equation 5.62.

$$\mu - k_d = \frac{Q}{V} \times \frac{X_e}{X_r} \quad (5.62)$$

Since no sludge wasting was applied in the anaerobic reactors, solids retention time (SRT) was calculated from the Equation 5.63 based on both MLVSS concentration into reactor and MLVSS concentration in the effluent of reactor.

$$SRT = \frac{V}{Q} \times \frac{X_r}{X_e} \quad (5.63)$$

Equation 5.63 can be rearranged in Equation 5.64 as follows:

$$\mu - k_d = \frac{1}{SRT} \quad (5.64)$$

where $(\mu - k_d)$ is the net specific growth rate (day^{-1}). Equation 5.64 indicates that the net microbial growth decreases as the sludge retention time (SRT) increases.

The relationship between the specific growth rate and the limiting pollutant concentration can be expressed by the Monod equation (Equation 5.65) (Monod, 1949).

$$\mu = \frac{\mu_{\max} \times S}{K_s + S} \quad (5.65)$$

Where; K_s is the half-saturation concentration ($\mu\text{g L}^{-1}$ or mg L^{-1}). It determines how rapidly μ approaches $\mu_{\max}$ and is defined as the pollutant concentration at which μ is equal to half of $\mu_{\max}$. The smaller K_s is the lower the pollutant concentration at which μ approaches $\mu_{\max}$. S is pollutant concentration ($\mu\text{g L}^{-1}$ or mg L^{-1}).

Mathematically, Equation 5.65 can be written as Equation 5.66 after then Equation 5.67, using the Equation 5.64.

$$\frac{\mu_{\max} \times S_e}{K_s + S_e} = \frac{1}{\text{SRT}} + k_d \quad (5.66)$$

$$\frac{\text{SRT}}{1 + (\text{SRT} \times k_d)} = \left(\frac{K_s}{\mu_{\max}} \times \frac{1}{S_e} \right) + \frac{1}{\mu_{\max}} \quad (5.67)$$

The value of maximum specific growth rate ($\mu_{\max}$) (day^{-1}) and half saturation concentration (K_s) ($\mu\text{g L}^{-1}$ or mg L^{-1}) can be obtained by plotting $\text{SRT}/(1 + \text{SRT} \times k_d)$ versus $1/S_e$ in Equation 5.67. The slope of the line gives the K_s value while the intercept point of the line gives the $\mu_{\max}$ (Kuscu, 2007).

Substrate Mass Balance. A substrate mass balance for the reactor can be described as Equation 5.68:

$$\text{Subs. change rate} = (\text{Subs. input rate}) - (\text{Subs. utilization rate}) - (\text{Subs. output rate}) \quad (5.68)$$

This equation can be rearranged to estimate the effluent pollutant concentration at the steady state condition as follows (Equation 5.69):

$$S = \frac{K_s \left(k_d + \frac{1}{SRT} \right)}{\mu_{max} - k_d - \frac{1}{SRT}} \quad (5.69)$$

Where; S is pollutant concentration ($\mu\text{g L}^{-1}$ or mg L^{-1}). The rate of change in pollutant concentration in the system could be expressed with Equation 5.70:

$$-\frac{dS}{dt} = \left(\frac{Q}{V} \times S_i \right) - \left(\frac{Q}{V} \times S_e \right) - \frac{\mu \times X}{Y} \quad (5.70)$$

Where; dS/dt is defined as the rate of pollutant removal ($\mu\text{g L}^{-1} \text{ day}^{-1}$ or $\text{mg L}^{-1} \text{ day}^{-1}$). S_i and S_e are influent and effluent pollutant concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively. Y is defined the growth yield coefficient (g VSS/g). k_d is the endogenous decay coefficient (day^{-1}). Under steady-state conditions, the rate of change in pollutant concentration dS/dt is negligible and by a similar technique to that used for the pollutant concentration, the above equation with substituting Equation 5.70 can be reduced to Equation 5.71;

$$\frac{(S_i - S_e)}{SRT} = \frac{X}{Y} \left(\frac{1}{SRT} + k_d \right) \quad (5.71)$$

The above equation can then be rearranged to estimate the effluent biomass concentration under steady-state condition as follows (Equation 5.72):

$$X = \frac{SRT \times Y \times (S_i - S_e)}{SRT \times (1 + k_d \times SRT)} \quad (5.72)$$

The kinetic parameters Y, k_d can be obtained by rearranging Equation 5.72 as shown below (Equation 5.73):

$$\frac{(S_i - S_e)}{SRT \times X} = \left(\frac{1}{Y} \times \frac{1}{SRT} \right) + \left(\frac{1}{Y} \times k_d \right) \quad (5.73)$$

The values of Y and k_d can be obtained by plotting $(S_i - S_e / \text{SRT} \times X)$ versus $(1/\text{SRT})$ in Equation 5.73, which is obtained by rearranging Equation 5.72. The value of Y can then be calculated from the slope of line while k_d can be obtained from the intercept of line (Gok, 2012).

5.9 Adsorption Isotherms

In this study, adsorbate (micropollutants, COD and sCOD) and adsorbent (anaerobic sludge, aerobic sludge and nanoparticles) are the two phases where adsorption process takes place. The adsorbates are attached the surface or the interface of the adsorbents. If the adsorbate (micropollutants, COD and sCOD) and adsorbent (anaerobic sludge, aerobic sludge and nanoparticles) are contacted enough time, an equilibrium will be formed between the amount of adsorbates adsorbed and the amount of adsorbates in the effluent. The equilibrium relationship could be described with different isotherms. These isotherms can then be used to predict the performance of the adsorption contact processes under a range of operating conditions. In this study, Langmuir and Freundlich isotherms were used for the adsorption of micropollutants, COD and sCOD to the anaerobic sludge, aerobic sludge and nanoparticles.

5.9.1 Langmuir Isotherm

The Langmuir adsorption isotherm is often expressed as equation Equation 5.74;

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \quad (5.74)$$

The Langmuir constants, K_L and q_m were calculated by the linearization of Equation 5.74 and this gives the Equation 5.75.

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{1}{q_m} \times C_e \quad (5.75)$$

where C_e is the effluent adsorbate concentrations ($\mu\text{g L}^{-1}$ or mg L^{-1}), q_e is the capacity of the adsorbent ($\mu\text{g g}^{-1}$ or mg g^{-1}), q_m is the maximum capacity of the adsorbent ($\mu\text{g g}^{-1}$ or mg g^{-1}), K_L is the Langmuir isotherm constant (function of enthalpy of adsorption and temperature, $\text{L } \mu\text{g}^{-1}$ or L mg^{-1}), respectively. The capacity of the adsorbent, q_e ($\mu\text{g g}^{-1}$ or mg g^{-1}) is calculated according to the Equation 5.76.

$$q_e = \frac{(C_i - C_e) \times V}{w} \quad (5.76)$$

where C_i and C_e are the influent and effluent concentrations of adsorbates in the eluate ($\mu\text{g L}^{-1}$ or mg L^{-1}), respectively, V is the volume of the sample (L) and w is the weight of the adsorbent (g), respectively.

The values of q_m and K_L can be obtained by plotting $1/q_e$ versus $1/C_e$ in Equation 5.75. The value of K_L can then be calculated from intercept of the straight line while q_m can be obtained from the slope of the line.

5.9.2 Freundlich Isotherm

The Freundlich isotherm represents an empirical model. The Freundlich equation can be mathematically represented by in Equation 5.77.

$$q_e = K_f \times C_e^{\frac{1}{n}} \quad (5.77)$$

where q_e is the concentration of the adsorbate on the adsorbent ($\mu\text{g g}^{-1}$ or mg g^{-1}), K_f is the constant (function of energy of adsorption and temperature) ($\text{L } \mu\text{g}^{-1}$ or L mg^{-1}), C_e is the effluent concentrations of adsorbates ($\mu\text{g L}^{-1}$ or mg L^{-1}) and n is the constant (unitless), respectively.

Linearization of the Freundlich equation can be expressed as Equation 5.78;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5.78)$$

The values of $1/n$ and K_F can be obtained by plotting $\ln C_e$ versus $\ln q_e$ in Equation 5.78. The value of K_F can then be calculated from intercept of the straight line while $1/n$ can be obtained from the slope of the line.

5.10 Instrumental Characterization for the Nanoparticles Used in Photocatalytic and Ultrasound Treatment Processes

5.10.1 Scanning Electron Microscopy (SEM)

Field emission scanning electron microscopy (SEM) with 20.0 kV was used to study the morphology of the nanoparticles used in the photocatalytic experiments. The morphological and structural observation was made on a scanning electron microscope VegaII/LMU (Tescan, Czech Republic) for the nanoparticles.

5.10.2 Fourier Transform Infrared (FT-IR)

The optical properties of absorption for the nanoparticles were measured by Fourier transform infrared spectroscopy (FT-IR) Perkin Elmer Spectrum BX using the KBr method.

5.10.3 X-Ray Diffraction (XRD)

XRD analysis was used to identify the phase composition of the nanoparticles by means of a X-ray diffractometer with the D/max-2200 PC (Rigaku, Japan) using a Cu-K α radiation source ($\lambda = 1.541 \text{ \AA}$) at 40.0 kV and 200 mA.

5.11 Statistical Analysis

The regression (R^2) analysis between y (dependent) and x (independent) variables was carried out using Microsoft Excel 2010. An ANOVA (one-way) test was performed in order to determine the statistical significance between x and y variables. Each data are the mean of triplicate sampling with standard deviation (SD) values.

ANOVA (one-way) statistical program was used for the 95% confidence intervals with a significance level of $\alpha = 0.05$.

The data given in all tables are the mean of triplicate measurements with standard deviations (SD) while the data given in figures are the mean of triplicate measurements.

5.12 Cost Analysis

5.12.1 Cost Analysis for Biological Treatment Process

Cost analysis was done for the biological treatment of all studied micropollutants from 1 m³ raw hospital wastewater in continuous operated anaerobic/aerobic sequential biological reactor system. The overall costs are included chemical costs, investment costs (anaerobic UASB, aerobic CSTR, feeding tank, air pump, peristaltic pump, heater), electricity costs and biogas income.

5.12.2 Cost Analysis for Photocatalytic Treatment Process

A cost analysis was carried out for the photocatalytic treatment of all studied micropollutants from 1 m³ raw hospital wastewater with nanoparticles. The overall costs are included UV lamps, investment costs (photocatalytic reactor, isolated cabin and magnetic stirrer), electricity costs, nanoparticle costs and regeneration cost of nanoparticles.

5.12.3 Cost Analysis for Ultrasound Treatment Process

The total cost of the ultrasound treatment of all studied micropollutants from 1 m³ raw hospital wastewater was calculated considering the price of the chemical for pH adjustment, investment cost (sonicator), electricity consumption, purchase price of the nanoparticles and regeneration cost of the nanoparticles.

5.12.4 Cost Analysis for Membrane Treatment Process

Cost analysis were determined for the membrane treatment of all studied micropollutants from 1 m³ raw hospital wastewater with UF and RO. The investment cost (membrane, feeding tank, pump, store equipments and montage), electricity consumption and purchase price of the chemicals used for membrane cleaning were considered.

5.13 Properties of Chemicals Used in This Study

5.13.1 Standard Chemicals

Standard chemicals used in this study were shown in Table 5.19 including the information of name, purity, CAS number, MDL number, EC number, molecular weight, trade name and intended purpose.

Table 5.19 Standard chemicals used in this study

Name	Purity	CAS number	MDL number	EC number	Molecular weight (g mol ⁻¹)	Trade name	Intended purpose
Ammonium chloride (NH ₄ Cl)	≥99.5% (ACS reagent)	12125-02-9	MFCD00011420	235-186-4	53.49	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Magnesium sulfate heptahydrate (MgSO ₄ ·7H ₂ O)	≥98.0% (ACS reagent)	10034-99-8	MFCD00149785	231-298-2	46.47	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Potassium chloride (KCl)	≥99.0% (anhydrous, free-flowing, Redi-Dri™, ReagentPlus®)	7447-40-7	MFCD00011360	231-211-8	74.55	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium sulfide nonahydrate (Na ₂ S·9H ₂ O)	≥ 98.0% (ACS reagent)	1313-84-4	MFCD00149184	215-211-5	240.18	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Ammonium phosphate dibasic ((NH ₄) ₂ HPO ₄)	≥ 98.0% (ACS reagent)	7783-28-0	MFCD00010891	231-987-8	132.06	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Calcium chloride dihydrate (CaCl ₂ ·2H ₂ O)	ACS reagent	10035-04-08	--	233-140-8	147.01	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Iron (III) chloride hexahydrate (FeCl ₃ ·4H ₂ O)	97.0% (ACS reagent)	10025-77-1	MFCD00149712	231-729-4	270.30	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Cobalt (II) chloride hexahydrate (CoCl ₂ ·6H ₂ O)	98.0% (ACS reagent)	7791-13-1	MFCD00149652	231-589-4	237.93	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Potassium iodide (KI)	≥ 99.0%	7681-11-0	MFCD00011405	231-659-4	166.00	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium hexametaphosphate ((NaPO ₃) ₆)	65.0-70.0% (P ₂ O ₅ basis)	68915-31-1	MFCD00134118	272-808-3	611.77	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
L-Cysteine (HSCH ₂ CH(NH ₂)CO ₂ H)	≥ 97.0% (FG)	52-90-4	MFCD00064306	200-158-2	121.16	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Aluminum chloride hexahydrate (AlCl ₃ ·6H ₂ O)	meets EP, BP, USP testing specifications	7784-13-6	MFCD00149134	231-208-1	241.43	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Manganese (II) chloride tetrahydrate (MnCl ₂ ·4H ₂ O)	≥ 98.0% (ACS reagent)	13446-34-9	MFCD00149792	231-869-6	197.91	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Copper (II) chloride (CuCl ₂)	97.0%	7447-39-4	MFCD00010972	231-210-2	134.45	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Zinc chloride (ZnCl ₂)	≥ 97.0% (anhydrous, free-flowing, Redi-Dri™, ACS reagent)	7646-85-7	MFCD00011295	231-592-0	136.30	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Ammonium metavanadate (NH ₄ VO ₃)	≥ 99.0% (ACS reagent)	7803-55-6	MFCD00011430	232-261-3	116.98	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium

Table 5.19 continues

Name	Purity	CAS number	MDL number	EC number	Molecular weight (g mol ⁻¹)	Trade name	Intended purpose
Sodium molybdate dihydrate (Na ₂ MoO ₄ ·2H ₂ O)	≥ 99.5% (plant cell culture tested)	10102-40-6	MFCD00149170	231-551-7	241.95	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Boric acid (H ₃ BO ₃)	≥ 99.5%	10043-35-3	MFCD00011337	233-139-2	61.83	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Nickel (II) chloride hexahydrate (NiCl ₂ ·6H ₂ O)	BioReagent, suitable for cell culture	7791-20-0	MFCD00149809	231-743-0	237.69	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium tungstate dihydrate (Na ₂ WO ₄ ·2H ₂ O)	≥ 99.0% (ACS reagent)	10213-10-2	MFCD00149190	236-743-4	329.85	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium selenite (Na ₂ SeO ₃)	≥ 95.0% (RT)	10102-18-8	MFCD00003489	233-267-9	172.94	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium thioglycollate (C ₂ H ₃ O ₂ SNa)	≥ 96.5% (iodometric)	367-51-1	MFCD00043386	206-696-4	114.10	Sigma-Aldrich (Germany)	chemical in vanderbilt mineral medium
Sodium bicarbonate (NaHCO ₃)	≥ 99.7% (ACS reagent)	144-55-8	MFCD00003528	205-633-8	84.01	Sigma-Aldrich (Germany)	chemical in the anaerobic UASB and aerobic CSTR reactors to control alkalinity
Sodium hydroxide (NaOH)	≥ 97.0% (ACS reagent)	1310-73-2	MFCD00003548	215-185-5	40.00	Sigma-Aldrich (Germany)	-chemical in the anaerobic UASB and aerobic CSTR reactors to control pH level - used for methane (CH ₄) gas measurements - used for the cleaning of UF and RO
Hydrochloric acid (HCl)	37.0% (ACS reagent)	7647-01-0	MFCD00011324	231-595-7	36.46	Sigma-Aldrich (Germany)	-used as a chemical in the anaerobic UASB and aerobic CSTR reactors to control pH level - used for regeneration of the nanoparticles used in the photocatalytic treatment
Ethanol (CH ₃ CH ₂ OH)	≥ 99.8% (GC grade)	64-17-5	MFCD00003568	200-578-6	46.07	Sigma-Aldrich (Germany)	- used for regeneration of the nanoparticles used in the photocatalytic treatment - used for the instrumental analysis
Sulfuric acid (H ₂ SO ₄)	95.0-98.0% (ACS reagent)	7664-93-9	MFCD00064589	231-639-5	98.08	Sigma-Aldrich (Germany)	- used for bicarbonate (HCO ₃ ⁻) alkalinity and TVFA measurements - used for the extraction of micropollutants before the instrumental analysis
N-Allylthiourea	--	109-57-9	MFCD00004940	203-683-5	116.18	Sigma-Aldrich (Germany)	used for BOD ₅ measurements

Table 5.19 continues

Name	Purity	CAS number	MDL number	EC number	Molecular weight (g mol ⁻¹)	Trade name	Intended purpose
Potassium dichromate (K ₂ Cr ₂ O ₇)	≥ 99.0% (ACS reagent)	7778-50-9	MFCD00011367	231-906-6	294.19	Sigma-Aldrich (Germany)	used for COD measurements
Mercury (II) sulfate (HgSO ₄)	≥ 99.0% (ACS reagent)	7783-35-9	MFCD00011047	231-992-5	296.65	Sigma-Aldrich (Germany)	used for COD measurements
Silver sulfate (Ag ₂ SO ₄)	≥ 99.5% (ACS reagent)	10294-26-5	MFCD00003407	233-653-7	311.80	Sigma-Aldrich (Germany)	used for COD measurements
Sodium sulfate (Na ₂ SO ₄)	≥ 99.0% (ACS reagent)	7757-82-6	MFCD00003504	231-820-9	142.04	Sigma-Aldrich (Germany)	used for adsorption tests
Methanol (CH ₃ OH)	LiChrosolv®	67-56-1	MFCD00004595	200-659-6	32.04	Sigma-Aldrich (Germany)	-used for adsorption tests - used for the extraction of micropollutants before the instrumental analysis
Acetone (CH ₃ COCH ₃)	≥ 99.9% (LC and GC grade)	67-64-1	MFCD00008765	200-662-2	58.08	Sigma-Aldrich (Germany)	used for volatilization tests
Hexane (CH ₃ (CH ₂) ₄ CH ₃)	≥ 95.0% (LC and GC grade)	110-54-3	MFCD00009520	203-777-6	86.18	Sigma-Aldrich (Germany)	-used for volatilization tests - used for the extraction of micropollutants before the instrumental analysis
Nitrogen gas (N ₂)	99.999%	7727-37-9	--	231-783-9	--	Linde Group (Turkey)	used for the extraction of micropollutants before the instrumental analysis
Triethylamine ((C ₂ H ₅) ₃ N)	≥ 99.0%	121-44-8	MFCD00009051	204-469-4	101.19	Sigma-Aldrich (Germany)	used for the extraction of micropollutants before the instrumental analysis
Acetonitrile (CH ₃ CN)	≥ 99.9% (LC grade)	75-05-8	MFCD00001878	200-835-2	41.05	Sigma-Aldrich (Germany)	used for the extraction of micropollutants before the instrumental analysis
Dichloromethane (CH ₂ Cl ₂)	≥ 99.9% (LC and GC grade)	75-09-2	MFCD00000881	200-838-9	84.93	Sigma-Aldrich (Germany)	used for the extraction of micropollutants before the instrumental analysis
Sodium phosphate dibasic (Na ₂ HPO ₄)	≥ 99.0% (ACS reagent)	7558-79-4	MFCD00003496	231-448-7	141.96	Sigma-Aldrich (Germany)	used for the instrumental analysis
Potassium dihydrogen phosphate (KH ₂ PO ₄)	≥ 99.0% (ACS reagent)	7778-77-0	MFCD00011401	231-913-4	136.08	Sigma-Aldrich (Germany)	used for the instrumental analysis
Ammonium dihydrogen phosphate (NH ₄ H ₂ PO ₄)	≥ 98.0% (ACS reagent)	7722-76-1	MFCD00003396	231-764-5	115.03	Sigma-Aldrich (Germany)	used for the instrumental analysis
Helium gas (He)	99.999%	7440-59-7	--	231-168-5	--	Linde Group (Turkey)	used for the instrumental analysis
Ammonium acetate (CH ₃ COONH ₄)	≥ 98.0% (ACS reagent)	631-61-8	MFCD00013066	211-162-9	77.08	Sigma-Aldrich (Germany)	used for the instrumental analysis

Table 5.19 continues

Name	Purity	CAS number	MDL number	EC number	Molecular weight (g mol ⁻¹)	Trade name	Intended purpose
Sodium bisulfite (NaHSO ₃)	ACS reagent	7631-90-5	--	--	104.06	Sigma-Aldrich (Germany)	used for the cleaning of UF and RO
Nitric acid (HNO ₃)	70.0% (ACS reagent)	7697-37-2	MFCD00011349	231-714-2	63.01	Sigma-Aldrich (Germany)	used for the cleaning of UF and RO

5.13.2 Analytical Standards

Analytical standards used for the micropollutant measurements in the content of this study were shown in Table 5.20 including the information of name, purity, CAS number, MDL number, molecular weight and trade name.



Table 5.20 Analytical standards used in this study

Name	Purity	CAS number	MDL number	Molecular weight (g mol ⁻¹)	Trade name
Pentabromotoluene (PBT)	> 98.0%	87-83-2	MFCD00000060	486.62	TCI (Japan)
4-Methylbromobenzene (4-MBB)	> 98.0%	106-38-7	MFCD00000109	171.03	Sigma-Aldrich (Germany)
2,3,4,5,6-Pentabromoethylbenzene (PBEB)	97.0%	85-22-3	MFCD00000061	500.65	Dr Ehrenstorfer (Germany)
(Bromomethyl)benzene (BMB)	> 98.0%	100-39-0	MFCD00000172	171.03	Sigma-Aldrich (Germany)
3,3',5,5'-Tetrabromobisphenol A (TBBPA)	≥ 97.0%	79-94-7	MFCD00013962	543.88	Sigma-Aldrich (Germany)
2,2-Bis(4-hydroxyphenyl)propane (BPA)	≥ 99.0%	80-05-7	MFCD00002366	228.29	Sigma-Aldrich (Germany)
α-Hexabromocyclododecane (α-HBCDD)	≥ 98.0%	134237-50-6	MFCD28118917	641.70	Sigma-Aldrich (Germany)
2-Bromocyclododecan-1-ol (2-BCD)	--	83602-77-1	--	263.22	DayangChem (China)
Perfluorooctanesulfonic acid (PFOS)	--	1763-23-1	MFCD00042454	500.13	Fluka (Germany)
2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decanol (FTA)	98.0%	307-37-9	MFCD00153234	500.10	Sigma-Aldrich (Germany)
Perfluorooctanoic acid (PFOA)	≥ 95.0%	335-67-1	MFCD00004174	414.07	Sigma-Aldrich (Germany)
Perfluoroheptanoic Acid (PFHpA)	≥ 99.0%	375-85-9	MFCD00039604	364.06	Sigma-Aldrich (Germany)
6-Acetyl-1,1,2,4,4,7-hexamethyl-tetralin (AHTN)	--	21145-77-7	MFCD00437355	258.41	Fluka (Germany)
3-Ethyl-5,6,7,8-tetrahydro-5,8,8-tetramethyl-2-naphthaldehyde (3-ETTN)	--	58243-85-9	MFCD00156900	244.38	Sigma-Aldrich (Germany)
N-Nitrosodimethylamine (NDMA)	--	62-75-9	MFCD00002053	74.08	Supelco (Germany)
Dimethylamine (DMA)	--	124-40-3	MFCD00008288	45.08	Sigma-Aldrich (Germany)
Ciprofloxacin (CIP)	≥ 98.0%	85721-33-1	MFCD00185755	331.35	Fluka (Germany)
Sulfociprofloxacin (SCP)	--	105093-21-8	Catalog number: NVIP04497	413.43	Novachemistry (UK)
Oxociprofloxacin (OCP)	> 95.0%	103237-52-1	Catalog number: NVC170363	345.33	Novachemistry (UK)
Formylciprofloxacin (FCP)	> 97.0%	93594-39-9	Catalog number: NVC031824	359.35	Novachemistry (UK)
Triclosan (TCS)	≥ 98.0%	3380-34-5	MFCD00800992	289.55	Fluka (Germany)
Methyl triclosan (MTCS)	98.9%	4640-01-1	Product number: DRE-C17803300	303.57	LGC Standards (Germany)
Ibuprofen (IBU)	≥ 98.0%	15687-27-1	MFCD00010393	206.29	Fluka (Germany)
1-hydroxyibuprofen (1-OH IBU)	≥ 98.0%	53949-53-4	MFCD08275586	222.28	Fluka (Germany)
2-hydroxyibuprofen (2-OH IBU)	≥ 98.0%	51146-55-5	MFCD08275592	222.28	Fluka (Germany)
Ibuprofen carboxylic acid (CBX IBU)	≥ 98.0%	15935-54-3	MFCD08063737	236.26	Fluka (Germany)
Gemfibrozil (GFZ)	≥ 98.0%	25812-30-0	MFCD00079335	250.34	Fluka (Germany)
2-Hydroxy-5-methylbenzaldehyde (2,H-5,MBA)	≥ 98.0%	613-84-3	MFCD00274297	136.15	Sigma-Aldrich (Germany)

5.13.2 Nanoparticles

Nanoparticles used in the photocatalytic and ultrasound experiments were shown in Table 5.21 including the information of name, purity, CAS number, MDL number, EC number, molecular weight and trade name.

Table 5.21 Nanoparticles used in this study

Name	Purity	CAS number	MDL number	EC number	Molecular weight (g mol ⁻¹)	Trade name
Silicon dioxide (SiO ₂)	99.50%	7631-86-9	MFCD00011232	231-545-4	60.08	Sigma-Aldrich (Germany)
Zinc oxide (ZnO)	--	1314-13-2	MFCD00011300	215-222-5	81.39	Sigma-Aldrich (Germany)
Graphene (SiC _x H _y O _z)	--	--	--	--	--	Ege Nanotek Kimya Sanayi Ltd. Şti. (Turkey)
Titanium (IV) oxide (TiO ₂)	≥ 99.50%	13463-67-7	MFCD00011269	236-675-5	79.87	Sigma-Aldrich (Germany)
Cerium (IV) oxide (CeO ₂)	--	1306-38-3	MFCD00010933	215-150-4	172.11	Sigma-Aldrich (Germany)

CHAPTER SIX

RESULTS AND DISCUSSION

6.1 Biological Treatment Process

6.1.1 Start-up Period of Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The anaerobic/aerobic sequential biological reactor system was operated for 50 days with synthetic wastewater at a SRT of 5 days corresponding to an organic loading rate of $0.18 \text{ g COD L}^{-1} \text{ day}^{-1}$ to reach steady-state conditions by providing the acclimation of the anaerobic and aerobic biomass in the reactors (Figure 6.1). The maximum COD yields were recorded as 93% and 96% in anaerobic and aerobic biological reactors, respectively, after the system reached steady state conditions at 55 days SRT (Figure 6.1.a). The maximum sCOD yields were recorded as 95% and 98% in anaerobic and aerobic biological reactors, respectively, after the system reached steady state conditions at 55 days SRT (Figure 6.1.b). The steady-state conditions for the anaerobic/aerobic sequential biological reactor system were defined with around 92% and 95% COD yields and 94% and 97% sCOD yields for anaerobic and aerobic reactors, respectively for the consecutive five days (data not shown). After this period, the continuous studies with raw hospital wastewater were begun. Biological reactor systems started to fed with raw hospital wastewater through 80, 140, 210 and 250 days at SRTs of 5, 30, 45 and 55 days, respectively. The anaerobic/aerobic sequential biological reactor system was operated through 45 days before changing the SRT with the new biomass to provide the acclimation of the bacterial population in the anaerobic and aerobic biological sludges. Thus, the anaerobic/aerobic sequential biological reactor system was operated through 815 days with the raw hospital wastewater for the whole study.

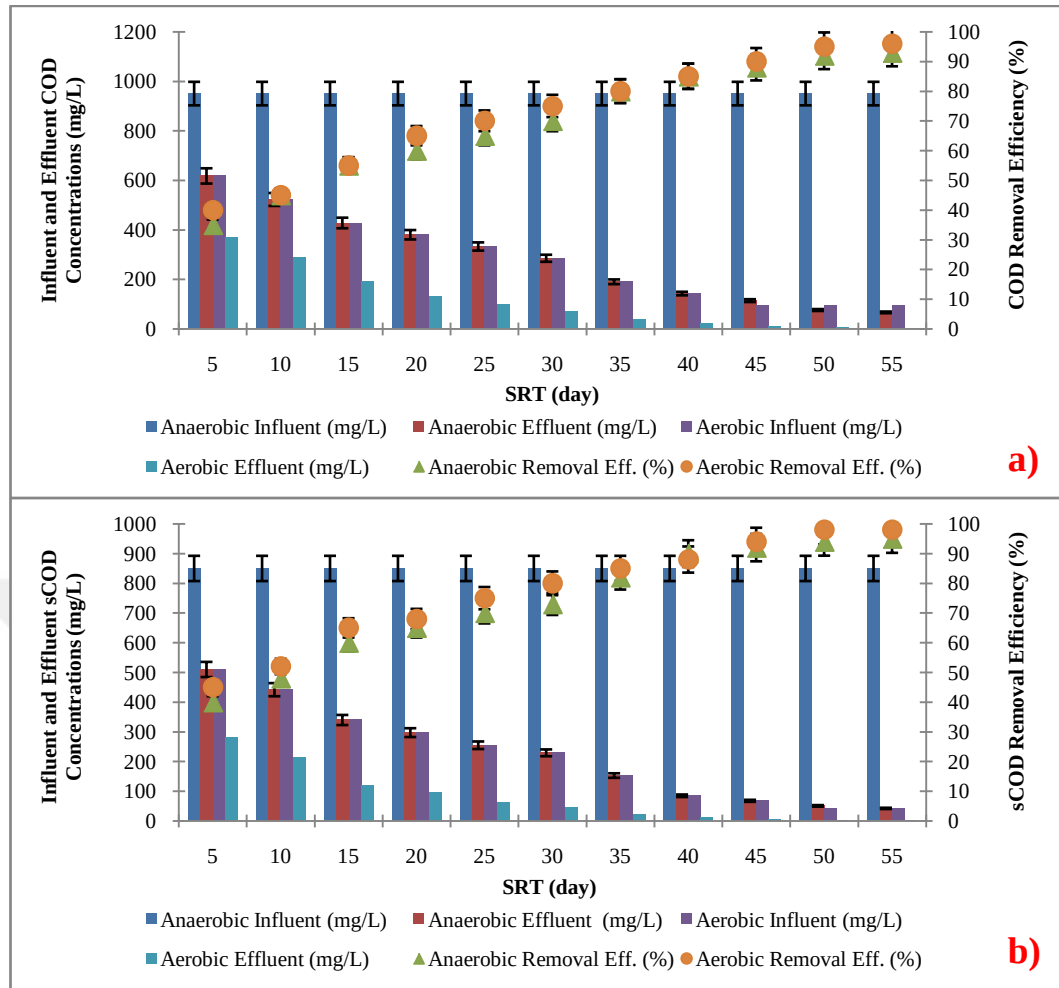


Figure 6.1 Removal efficiencies versus operation times for anaerobic and aerobic reactors in start-up period (a) COD removal efficiencies (b) sCOD removal efficiencies (n = 3, mean)

The mixture of solids with influent wastewater in the bioreactor is termed as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). The MLSS concentrations were measured as 3950, 4000, 4450 and 4980 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively in the aerobic reactor (Table 6.1). The MLSS concentrations were determined as 18000, 23900, 25650 and 34500 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively in the anaerobic reactor (Table 6.1). In the anaerobic/aerobic sequential biological reactor system, the MLSS concentrations were calculated as 21950, 27900, 30100 and 39480 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.1). The portion of the MLSS that is actually eating the incoming food/substrate (COD, BOD or TOC) is referred as MLVSS. This shows the active bacteria concentration. As the SRT increases, so that MLVSS concentration increases with SRT (Metcalf & Eddy, 2004). For the MLVSS

concentrations, the aerobic reactor had 3160, 3200, 3560 and 3984 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.1). For the anaerobic reactor, the MLVSS concentrations were determined as 14400, 19120, 20520 and 27600 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.1). The MLVSS concentrations were measured as 17560, 22320, 24080 and 31584 mg L⁻¹ at SRTs of 5, 30, 45 and 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.1). Theoretically, the aerobic reactor MLSS level is fixed by selecting a number between 1500 to 5000 mg L⁻¹. Nevertheless, anaerobic UASB reactor MLSS level can be higher than 10000 mg L⁻¹ (Jimenez, La Motta, & Parker, 2007). In this study, MLSS and MLVSS are the major suspended solids present during anaerobic and aerobic treatment and their concentrations provide a useful measure of reactor performance.

Table 6.1 MLSS and MLVSS alterations at different SRTs (n = 3, mean ± SD)

SRT (day)	OLR (g COD L ⁻¹ day ⁻¹)	MLSS (mg L ⁻¹)			MLVSS (mg L ⁻¹)		
		Aerobic Reactor	Anaerobic Reactor	Sequential Reactor	Aerobic Reactor	Anaerobic Reactor	Sequential Reactor
5	0.186	3950 ± 0.5	18000 ± 0.5	21950 ± 0.5	3160 ± 0.5	14400 ± 0.5	17560 ± 0.5
30	0.031	4000 ± 0.5	23900 ± 0.5	27900 ± 0.5	3200 ± 0.5	19120 ± 0.5	22320 ± 0.5
45	0.021	4450 ± 0.5	25650 ± 0.5	30100 ± 0.5	3560 ± 0.5	20520 ± 0.5	24080 ± 0.5
55	0.017	4980 ± 0.5	34500 ± 0.5	39480 ± 0.5	3984 ± 0.5	27600 ± 0.5	31584 ± 0.5

During the anaerobic and aerobic phases, 0 and 2 mg L⁻¹ dissolved oxygen (DO) concentrations were observed and the oxidation reduction potentials (ORPs) were around -610 and +145 mV for anaerobic and aerobic reactors, respectively (data not shown).

6.1.2 Total COD and sCOD Removals

6.1.2.1 Total COD and sCOD Removals in Anaerobic Biological Reactor

During 5 days of SRT operation, the maximum COD removal efficiency of the anaerobic reactor was obtained as 44.5% with a COD effluent of 527.30 mg L⁻¹ at a COD influent of 950.00 mg L⁻¹ (Figure 6.2.a). The 5 days SRT operation did not provide sufficient COD removal efficiency. However, 30 days SRT operation

enhanced the COD removal efficiency. The maximum COD removal efficiency reached 66.9% with a COD effluent of 314.88 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ at 30 days SRT (Figure 6.2.a). A slight increase in the COD removal efficiency from 66.9% to 74.8% was observed after 45 days SRT operation. For 45 days SRT operation, the maximum COD removal efficiency was found as 74.8% with a COD effluent of 239.01 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ (Figure 6.2.a). However, 55 days SRT operation in the anaerobic reactor increased the COD removal efficiency and the maximum level was obtained between four different SRT operations. Finally, the maximum COD removal efficiency was determined as 80.6% with a COD effluent of 184.20 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ at 55 days SRT (Figure 6.2.a). As a result of the study, the increased COD removal at the highest SRT (55 days) is mainly due to the increasing bacteria concentration as MLVSS (Table 6.1), anaerobic reducing reactions, bacterial adaptability and utilization of COD as carbon/energy source.

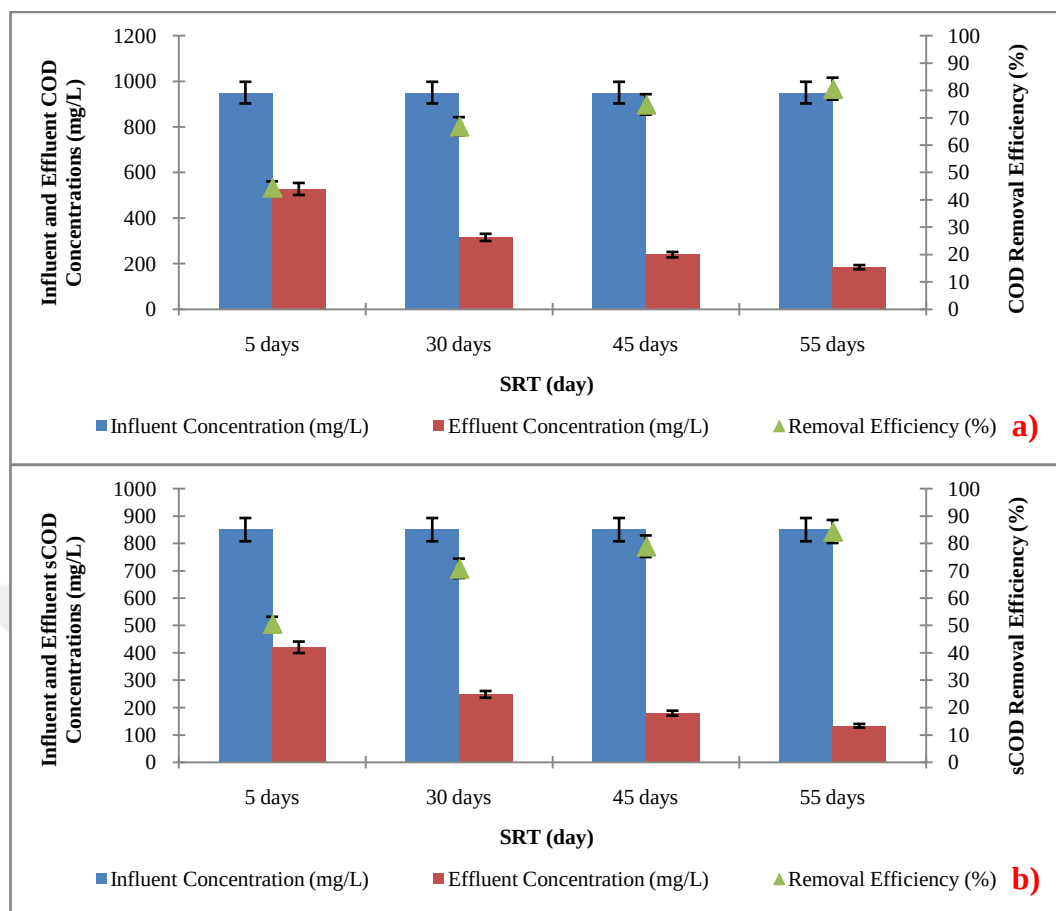


Figure 6.2 COD and sCOD concentrations and yields for anaerobic reactor during the 5, 30, 45 and 55 days of SRT operations (a) COD concentrations and (b) sCOD concentrations (n = 3, mean)

The maximum sCOD removal efficiency of the anaerobic reactor was measured as 50.6% with an sCOD effluent of 419.78 mg L⁻¹ at an sCOD influent of 850.00 mg L⁻¹ for 5 days SRT operation (Figure 6.2.b). Increasing the SRT from 5 days to 30 days increased the sCOD removal efficiency and the maximum sCOD removal efficiency reached 70.9% with an sCOD effluent of 247.75 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ at 30 days SRT (Figure 6.2.b). After 45 days SRT operation, the maximum sCOD removal efficiency was found as 78.9% with an sCOD effluent of 179.10 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ (Figure 6.2.b). As expected, the highest sCOD removal efficiency was achieved at the longest SRT of 55 days in the anaerobic reactor. The maximum sCOD removal efficiency was determined as 84.3% with an sCOD effluent of 133.20 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ at 55 days SRT (Figure 6.2.b).

6.1.2.2 Total COD and sCOD Removals in Aerobic Biological Reactor

The aerobic reactor was operated as a post-treatment to anaerobic effluent and the performance of the aerobic reactor is shown in Figure 6.3. During 5 days of SRT operation, the maximum COD removal efficiency of the aerobic reactor was obtained as 52.1% with a COD effluent of 252.35 mg L⁻¹ at a COD influent of 527.30 mg L⁻¹ (Figure 6.3.a). Long term operation of more than 5 days SRT was required to achieve higher COD removal efficiencies. The maximum COD removal efficiency reached 77.6% with a COD effluent of 70.60 mg L⁻¹ for a COD influent of 314.88 mg L⁻¹ at 30 days SRT (Figure 6.3.a). A slight increase in the COD removal efficiency from 77.6% to 80.7% was observed after 45 days of SRT operation. For 45 days SRT operation, the maximum COD removal efficiency was found as 80.7% with a COD effluent of 46.22 mg L⁻¹ for a COD influent of 239.01 mg L⁻¹ (Figure 6.3.a). Aerobic biomass growth enhanced with increased MLVSS concentration (Table 6.1) at higher SRT operation indicates the adaptability of aerobic bacteria to the COD as a carbon/energy source and greatly influences the reactor performance. As a result, the maximum COD removal efficiency reached 90.0% with a COD effluent of 18.50 mg L⁻¹ for a COD influent of 184.20 mg L⁻¹ at 55 days SRT (Figure 6.3.a).

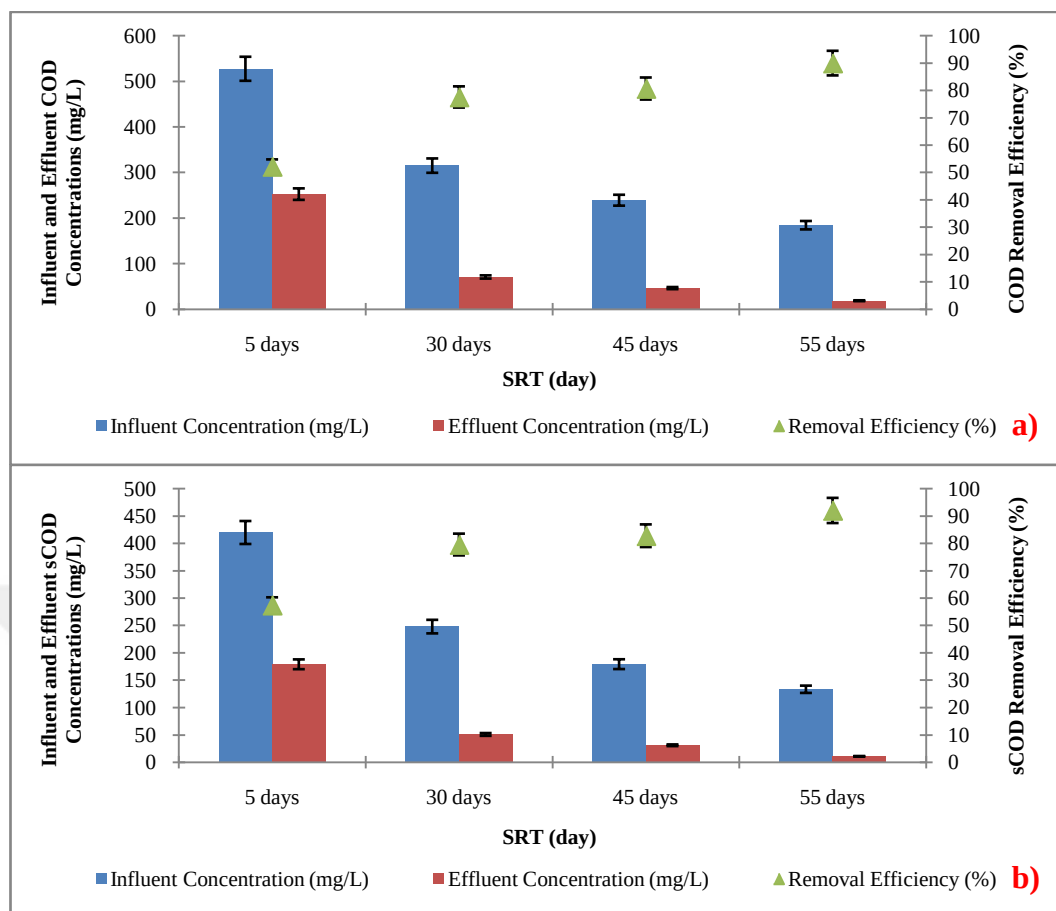


Figure 6.3 COD and sCOD concentrations and yields for aerobic reactor during the 5, 30, 45 and 55 days of SRT operations (a) COD concentrations and (b) sCOD concentrations (n = 3, mean)

The COD removal in the aerobic reactor (90.0%) (Figure 6.3.a) exhibited better efficiency than the anaerobic reactor (80.6%) (Figure 6.2.a) at 55 days SRT. This could be attributed to the aerobic treatment provides improvement in the COD removal and acts as a post-treatment step after anaerobic treatment. COD was treated firstly in the anaerobic reactor and after anaerobic treatment, aerobic microorganisms were treated COD by further removing in the aerobic reactor more easily than anaerobic ones (Kumar, Srikantaswamy, Abhilash, & Nagaraju, 2015). In addition, anaerobic bacteria have low specific growth rates in comparison with aerobic ones.

At 5 days SRT, the maximum sCOD removal efficiency of the aerobic reactor was obtained as 57.4% with an sCOD effluent of 178.87 mg L^{-1} at an sCOD influent of 419.78 mg L^{-1} (Figure 6.3.b). The aerobic reactor could not able to remove sufficient sCOD at 5 days SRT and the SRT was increased to 30 days. The maximum sCOD

removal efficiency reached 79.6% with an sCOD effluent of 50.64 mg L⁻¹ for an sCOD influent of 247.75 mg L⁻¹ at 30 days SRT (Figure 6.3.b). Aerobic reactor increased the sCOD removal efficiency slightly as the SRT was increased to 45 days. For 45 days SRT operation, the maximum sCOD removal efficiency was found as 82.8% with an sCOD effluent of 30.84 mg L⁻¹ for an sCOD influent of 179.10 mg L⁻¹ (Figure 6.3.b). The maximum yield of sCOD was obtained at the highest SRT of 55 days. Finally, the maximum sCOD removal efficiency was determined as 92.0% with an sCOD effluent of 10.64 mg L⁻¹ for an sCOD influent of 133.20 mg L⁻¹ at 55 days SRT (Figure 6.3.b). This could be attributed to the good acclimation of the aerobic microorganisms to the hospital wastewater characteristics at longer SRT operation of 55 days.

The sCOD removals was found to be high in the aerobic reactor (92.0%) (Figure 6.3.b) than the anaerobic reactor (84.3%) (Figure 6.2.b). This could be attributed to the anaerobic bacteria were more sensitive to the hospital wastewater than the aerobic bacteria and have low specific growth rates and low yields based on the ratio of produced biomass to the consumed-removed sCOD.

6.1.2.3 Total COD and sCOD Removals in Anaerobic/Aerobic Sequential Biological Reactor System

The maximum COD removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 73.4% with a COD effluent of 252.35 mg L⁻¹ at a COD influent of 950.00 mg L⁻¹ at 5 days SRT (Figure 6.4.a). After the SRT increased to 30 days, the COD removal efficiency was affected positively and reached 92.6% with a COD effluent of 70.60 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ at 30 days SRT (Figure 6.4.a). A slight increase for COD removal was observed for 45 days SRT operation in comparison with 30 days SRT operation. For 45 days SRT, the maximum COD removal efficiency was found as 95.1% with a COD effluent of 46.22 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ (Figure 6.4.a). For 55 days SRT, the COD removal efficiency reached the highest level both for the contributions of enhanced anaerobic and aerobic biomass growth with increased

MLVSS concentrations (Table 6.1) at the highest SRT (55 days) resulting the utilization of COD as carbon/energy source effectively. Finally, the maximum COD removal efficiency was determined as 98.1% with a COD effluent of 18.50 mg L⁻¹ for a COD influent of 950.00 mg L⁻¹ at 55 days SRT (Figure 6.4.a). These results showed that as the SRT was increased from 5 days to 55 days the COD removal efficiency increased from 73.4% to 98.1%. A linear correlation between COD yields and SRTs was found for the anaerobic/aerobic sequential biological reactor system and this regression was significant ($R^2 = 0.92$, $P = 0.004$, $\alpha = 0.05$, $F = 21.05$).

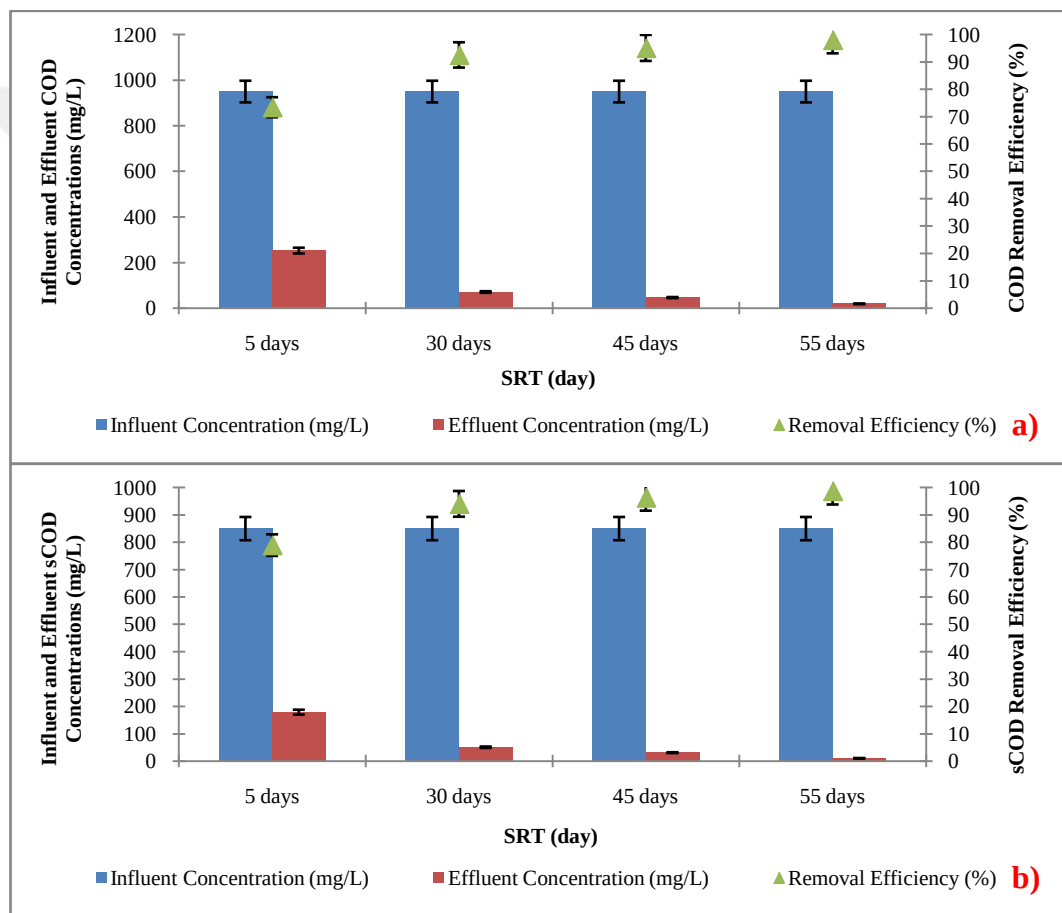


Figure 6.4 COD and sCOD concentrations and yields for anaerobic/aerobic sequential biological reactor system during the 5, 30, 45 and 55 days of SRT operations (a) COD concentrations and (b) sCOD concentrations (n = 3, mean)

The maximum sCOD removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 79.0% with an sCOD effluent of 178.87 mg L⁻¹ at an sCOD influent of 850.00 mg L⁻¹ during 5 days of SRT operation

(Figure 6.4.b). 30 days SRT operation enhanced the sCOD removal efficiency of the anaerobic/aerobic sequential biological reactor system. The maximum sCOD removal efficiency reached 94.0% with an sCOD effluent of 50.64 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ at 30 days SRT (Figure 6.4.b). sCOD removal efficiency increased slightly after 45 days SRT operation. For 45 days SRT operation, the maximum sCOD removal efficiency was found as 96.4% with an sCOD effluent of 30.84 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ (Figure 6.4.b). As it is expected, 55 days of SRT operation in anaerobic/aerobic sequential biological reactor system enhanced the sCOD removal efficiency and the highest yield achieved via the improved treatment conditions both for anaerobic and aerobic reactors. Finally, the maximum sCOD removal efficiency was determined as 98.7% with an sCOD effluent of 10.64 mg L⁻¹ for an sCOD influent of 850.00 mg L⁻¹ at 55 days SRT (Figure 6.4.b). These results showed that as the SRT was increased from 5 days to 55 days the sCOD removal efficiency increased from 79.0% to 98.7%. A linear correlation between sCOD yields and SRTs was found for the anaerobic/aerobic sequential biological reactor system and this regression was statistically important ($R^2 = 0.92$, $P = 0.003$, $\alpha = 0.05$, $F = 24.59$).

The high COD (98.1%) and sCOD (98.7%) performances in the anaerobic/aerobic sequential biological treatment system at 55 days SRT for the raw hospital wastewater can be attributed to the utilisation of anaerobic pre-treatment in order to biodegrade the already low COD and sCOD content prior to the aerobic stage. Zhang, Liu, & Zhang (2012) reported that the removals of COD and sCOD parameters gradually increased with increasing SRT in hospital wastewater (Zhang et al., 2012). This could be attributed to the good acclimation of the microorganisms to the hospital wastewater characteristics at high SRT (55 days). The reason for the slight decrease in COD and sCOD yields at the lowest SRT of 5 days is the low contact time of hospital wastewater with sludge granules as reported by Al-Hashimi & Abbas (2007) and Chelliapan & Sallis (2011). The maximum removal efficiencies found for COD (98.1%) and sCOD (98.7%) from the raw hospital wastewater in the anaerobic/aerobic sequential biological reactor system at 55 days SRT in this study were higher than the results obtained by several authors studying with the hospital

wastewater. Pirsahab et al. (2015) determined 96.6% COD removal efficiency in a continuous feeding and intermittent discharge (CFID) bioreactor including aerobic, anoxic and anaerobic conditions for an initial concentration of 586 mg L⁻¹ at a HRT of 4 h and 6000 mg L⁻¹ MLSS concentration treating real hospital wastewater (Pirsahab et al., 2015). Chiarello, Minetto, Giustina, Beal, & Moura (2016) found 85.4% and 76.7% COD and sCOD removal efficiencies using biological system with an anoxic (HRT = 3 h) and an aerobic (HRT = 10 h) bioreactor for initial COD and sCOD concentrations of 685.0 and 212.1 mg L⁻¹, respectively in a hospital wastewater treatment plant at 24 °C and at pH 7.5 (Chiarello et al., 2016). Qarni, Collier, O'Keeffe, & Akunna (2016) reached 83.0% of COD removal efficiency using activated sludge process for an initial COD concentration of 376 mg L⁻¹ at a hospital wastewater treatment plant under a high ambient temperature (>26 °C) and normal pH (7-8) conditions (Qarni et al., 2016). Shokoohi et al. (2017) measured 95.6% COD removal efficiency in a moving bed biofilm reactor system for 800 mg L⁻¹ initial COD concentration at a HRT of 24 h at 25 °C at pH 7.8 and at 3000 mg L⁻¹ MLSS concentration treating real hospital wastewater (Shokoohi et al., 2017). Hamjinda et al. (2018) obtained 70% COD removal efficiency in a conventional activated sludge system for 371 mg L⁻¹ initial COD concentration treating hospital wastewater (Hamjinda et al., 2018).

6.1.3 Removal Mechanisms of COD and sCOD in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

In order to detect the main removal mechanisms of COD and sCOD; biodegradation, sorption, adsorption and volatilization tests were performed. The biodegraded, adsorbed, sorbed and volatilized COD and sCOD masses were calculated. Furthermore, the biodegraded, adsorbed, sorbed and volatilized COD and sCOD percentages were detected in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations.

6.1.3.1 Removed Masses and Removal Efficiencies of COD

An example for the calculations relevant to the removed masses of COD and the removal efficiencies of COD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.1 to 6.18, respectively (Section 5.6.12.2) at a SRT of 5 days (Table 6.2). Calculated COD masses exposed to biodegradation, sorption, adsorption and volatilization during 5, 30, 45 and 55 days of SRT operations were shown in Table 6.2.



Table 6.2 The total removal percentages for COD throughout biodegradation, adsorption, sorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	1056.75	0.380	17.08	0.118	5.32	0.00	0.00	44.49	0.72	0.22	0.00
30	1587.80	0.563	25.34	0.158	7.12	0.00	0.00	66.85	1.07	0.30	0.00
45	1777.48	0.670	30.16	0.227	10.22	0.00	0.00	74.84	1.27	0.43	0.00
55	1914.50	0.730	32.85	0.285	12.82	0.00	0.00	80.61	1.38	0.54	0.00
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	549.90	0.499	7.49	0.073	1.10	0.00	0.00	52.14	0.71	0.10	0.00
30	732.84	0.705	10.57	0.155	2.32	0.00	0.00	69.49	1.00	0.22	0.00
45	809.72	0.840	12.60	0.223	3.34	0.00	0.00	76.78	1.19	0.32	0.00
55	911.35	0.941	14.12	0.224	3.36	0.00	0.00	86.42	1.34	0.32	0.00
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	3139.43	--	24.57	--	6.42	--	0.00	73.44	0.57	0.15	0.00
30	3957.30	--	35.91	--	9.44	--	0.00	92.57	0.84	0.22	0.00
45	4067.01	--	42.76	--	13.56	--	0.00	95.13	1.00	0.32	0.00
55	4191.75	--	46.57	--	16.18	--	0.00	98.05	1.10	0.38	0.00

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

The biodegradation masses were calculated from the removed COD concentrations. The removed COD concentrations were calculated by taking the difference between the influent and effluent concentrations for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors. The removed COD concentrations were multiplied by the reactor volumes in Equations 6.1, 6.2 and 6.3 for the anaerobic (2.5 L), aerobic (2.0 L) and anaerobic/aerobic sequential biological reactors (4.5 L), respectively at 5 days SRT. The total biodegradation masses for COD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined in Equations 6.1, 6.2 and 6.3, respectively at 5 days SRT.

$$M_{\text{BIO,Anaerobic}} = (422.70 \text{ mg L}^{-1}) \times (2.5 \text{ L}) = 1056.75 \text{ mg} \quad (6.1)$$

$$M_{\text{BIO,Aerobic}} = (274.95 \text{ mg L}^{-1}) \times (2.0 \text{ L}) = 549.90 \text{ mg} \quad (6.2)$$

$$M_{\text{BIO,Sequential}} = (697.65 \text{ mg L}^{-1}) \times (4.5 \text{ L}) = 3139.43 \text{ mg} \quad (6.3)$$

The biodegradation removal efficiencies at 5 days of SRT operation in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated using the total biodegradation masses and influent concentrations according to the Equation 6.4, 6.5 and 6.6, respectively (Table 6.2).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (1056.75 \times 100)/(950 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 44.49\% \quad (6.4)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (549.90 \times 100)/(527.30 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 52.14\% \quad (6.5)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (3139.43 \times 100)/(950 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 73.44\% \quad (6.6)$$

The adsorption masses onto the anaerobic and aerobic biological sludges of COD were calculated using the eluate concentration prepared from the sludge for the adsorption experiments, the extracted sample volume, the sludge weight used in the eluate preparation and the sludge weight in the biological reactor according to the Equation 6.7 and Equation 6.8, respectively at a SRT operation of 5 days (Table 6.2). The total adsorption mass for COD in the anaerobic/aerobic sequential biological reactor system was determined by adding the masses from the anaerobic and aerobic reactors at 5 days SRT (Equation 6.9).

$$M_{ADS,Anaerobic} = [(0.380 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 17.08 \text{ mg} \quad (6.7)$$

$$M_{ADS,Aerobic} = [(0.499 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 7.49 \text{ mg} \quad (6.8)$$

$$M_{ADS,Sequential} = 17.08 + 7.49 = 24.57 \text{ mg} \quad (6.9)$$

The adsorption removal efficiencies at 5 days of SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.10, 6.11 and 6.12, respectively (Table 6.2).

$$Ads(\%),_{Anaerobic} = (17.08 \times 100)/(950 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 0.72\% \quad (6.10)$$

$$Ads(\%),_{Aerobic} = (7.49 \times 100)/(527.30 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 0.71\% \quad (6.11)$$

$$Ads(\%),_{Sequential} = (24.57 \times 100)/(950 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 0.57\% \quad (6.12)$$

The sorption masses into the anaerobic and aerobic biological sludges of COD were calculated using the eluate concentration prepared from the killed biomass for the sorption experiments, the extracted sample volume, the sludge weight used in the eluate preparation and the sludge weight in the biological reactor according to the Equation 6.13 and Equation 6.14, respectively at a SRT operation of 5 days (Table 6.2). The total sorption mass for COD in the anaerobic/aerobic sequential biological reactor system was determined by adding the masses from the anaerobic and aerobic reactors at 5 days SRT (Equation 6.15).

$$M_{SORP,Anaerobic} = [(0.118 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 5.32 \text{ mg} \quad (6.13)$$

$$M_{SORP,Aerobic} = [(0.073 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 1.10 \text{ mg} \quad (6.14)$$

$$M_{SORP,Sequential} = 5.32 + 1.10 = 6.42 \text{ mg} \quad (6.15)$$

The sorption removal efficiencies at 5 days of SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.16, 6.17 and 6.18, respectively (Table 6.2).

$$Sorp(\%),_{Anaerobic} = (5.32 \times 100)/(950 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 0.22\% \quad (6.16)$$

$$\text{Sorp}(\%),_{\text{Aerobic}} = (1.10 \times 100)/(527.30 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 0.10\% \quad (6.17)$$

$$\text{Sorp}(\%),_{\text{Sequential}} = (6.42 \times 100)/(950 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 0.15\% \quad (6.18)$$

In order to determine the volatilization masses PUF disks were used. No COD concentrations (0.00 mg L^{-1}) were determined after 5, 30, 45 and 55 days of SRTs in the PUF disks under anaerobic and aerobic conditions, respectively. Because of the concentrations were measured as zero (0.00 mg L^{-1}), volatilization masses ($(0.00 \text{ mg L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00 \text{ mg}$) and volatilization removal efficiencies for COD calculated zero in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days SRTs (Table 6.2).

6.1.3.1.1 Removed Masses and Removal Efficiencies of COD in Anaerobic Reactor. As is shown in Table 6.2 the biodegraded COD masses increased from 1056.75 mg to 1914.50 mg as the SRT was increased from 5 up to 55 days in the anaerobic reactor. The biodegradation percentages of COD also increased from 44.49% to 80.61% with the increasing of SRTs from 5 days up to 55 days (Table 6.2). At long sludge retention times (55 days) the anaerobic bacteria can be metabolized COD effectively. The less COD biodegradation removal efficiencies could be related to the shorter contact time between the biomass and organic matter at low SRTs. Biodegraded COD removal efficiency decreased with the decrease in SRT - increase in OLR (Table 6.1). At low SRTs (5, 30 and 45 days), the decrease in biodegraded COD removal efficiency might also be due to the fact that some bacteria were washed out from the anaerobic reactor when the SRT duration was less than generation time of the methanogenic bacteria (Wang et al., 2015). The COD removal via biodegradation in the anaerobic reactor was found significant according to the ANOVA (one-way) test statistics results ($P = 0.050$, $\alpha = 0.05$, $F = 6.00$). The sorption masses (5.32 – 12.82 mg) were low and the volatilization masses were measured as zero for COD at all SRTs in the anaerobic reactor (Table 6.2). The sorbed and volatilized COD removal percentages also were low (between 0.22% and 0.54% for sorption and 0.00% for volatilization, respectively) in the anaerobic reactor (Table 6.2). The ANOVA (one-way) test statistics results showed that removal of COD via sorption ($P = 0.082$, $\alpha = 0.05$, $F = 4.35$) and volatilization ($P = 0.084$, $\alpha = 0.05$, $F =$

4.28) were not significant in the anaerobic reactor. Therefore, COD removal via sorption and volatilization were found insignificant in the anaerobic reactor. The adsorption of COD to the anaerobic sludge had no important change in the anaerobic reactor since the adsorbed COD masses varies between 17.08 mg and 32.85 mg (Table 6.2). It is important to note that the adsorbed COD percentages were changed between 0.72% and 1.38% as the SRTs were increased from 5 to 55 days, respectively (Table 6.2). The ANOVA (one-way) test statistics results showed that the removal of COD via adsorption was not significant ($P = 0.080$, $\alpha = 0.05$, $F = 4.41$). As a result, adsorption has not a significant contribution to the removal of COD in the anaerobic reactor at all SRTs.

6.1.3.1.2 Removed Masses and Removal Efficiencies of COD in Aerobic Reactor.

In the aerobic reactor, the biodegraded COD masses increased from 549.90 mg to 911.35 mg resulting an increase in the COD removal percentages from 52.14% to 86.42% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.2). The maximum biodegradation yield of COD (86.42%) was obtained at 55 days SRT (Table 6.2). This can be explained by the increase in COD removal efficiencies at increasing SRTs due to a higher biomass concentration (MLVSS) for longer SRTs as mentioned by Hajiabadi, Moghaddam, & Hashemi (2009) (Table 6.1). MLVSS concentration in the aerobic reactor plays a major role in the biological degradation process. Enough active biomass must be available in the system to oxidize COD for getting benefits from observing energy and carbon released during biodegradation (Zheng et al., 2013). The ANOVA (one-way) test statistics results showed that removal of COD via biodegradation was statistically important in the aerobic reactor ($P = 0.029$, $\alpha = 0.05$, $F = 8.22$). The sorption masses (1.10 – 3.36 mg) were low and the volatilization masses were measured as zero for COD at all SRTs in the aerobic reactor (Table 6.2). The sorbed and volatilized COD removal percentages also were low (between 0.10% and 0.32% for sorption and 0.00% for volatilization, respectively) in the aerobic reactor (Table 6.2). The ANOVA (one-way) test statistics results showed that removal of COD via sorption ($P = 0.055$, $\alpha = 0.05$, $F = 5.63$) and volatilization ($P = 0.057$, $\alpha = 0.05$, $F = 5.55$) had no statistical significance in the aerobic reactor. The adsorption of COD masses to the aerobic sludge was changed

between 7.49 mg and 14.12 mg as the SRT increased from 5 days to 55 days, respectively (Table 6.2). This attributed to the COD adsorption yields of 0.71% and 1.34% at 5 days and 55 days SRT, respectively (Table 6.2). Moreover, the ANOVA (one-way) test statistics results showed that the removal of COD via adsorption was not important statistically ($P = 0.072$, $\alpha = 0.05$, $F = 4.76$). As a result, adsorption was not found to be significant for the removal of COD in the aerobic reactor at all SRTs.

Removal of COD via biodegradation was higher in the aerobic reactor (86.42%) than the anaerobic reactor (80.61%) at 55 days of SRT (Table 6.2). This could be attributed to the organic compounds were preliminary oxidized in the anaerobic treatment and then more easily oxidized in the aerobic treatment (Rezaee, Ansari, Khavanin, Sabzali, & Aryan, 2005).

6.1.3.1.3 Removed Masses and Removal Efficiencies of COD in Anaerobic/Aerobic Sequential Biological Reactor System. From the Table 6.2, it can be said that the total biodegraded masses of COD increased from 3139.43 mg to 4191.75 mg resulting in the COD removal percentages of 73.44% and 98.05% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor. Biodegradation yield of COD reached the highest level (98.05%) at 55 days SRT (Table 6.2). Biodegradation of COD in the anaerobic/aerobic sequential biological reactor system was found significant according to the ANOVA (one-way) test statistics results ($P = 0.004$, $\alpha = 0.05$, $F = 21.05$). The sorption masses were ranged from 6.42 to 16.18 mg at SRTs varying between 5 days and 55 days, respectively (Table 6.2). The volatilization masses were measured as zero for COD at all SRTs in the anaerobic/aerobic sequential biological reactor (Table 6.2). The sorbed and volatilized COD removal percentages also were low (between 0.15% and 0.38% for sorption and 0.00% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor (Table 6.2). The ANOVA (one-way) test statistics results showed that removal of COD via sorption ($P = 0.162$, $\alpha = 0.05$, $F = 2.54$) and volatilization ($P = 0.165$, $\alpha = 0.05$, $F = 2.51$) were not important in the anaerobic/aerobic sequential biological reactor. The total adsorption of COD masses to the anaerobic and aerobic sludges

increased from 24.57 mg to 46.97 mg while the COD adsorption yields were measured as 0.57% and 1.10% as the SRT increased from 5 days to 55 days, respectively (Table 6.2). The ANOVA (one-way) test statistics results showed that the removal of COD via adsorption had no statistical importance in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.099$, $\alpha = 0.05$, $F = 3.81$).

The results from this study showed that COD can not be effectively removed via adsorption (1.10%), sorption (0.38%) and volatilization (0.00%) at a SRT of 55 days (Figure 6.5). In this study we found that biodegradation (98.05%) is the main removal mechanism of COD removal at 55 days SRT (Figure 6.5). Therefore, it can be concluded that the removal of COD with biodegradation is major (98.05%), adsorption is low (1.10%), sorption is minor (0.38%) and volatilization is negligible (0.00%) at a SRT of 55 days (Figure 6.5). Rajakumar, Meenambal, Banu, & Yeom (2011) also found that biodegradation is the major pathway for COD removal (78.0%) in an upflow anaerobic filter and the contribution of the other mechanisms were less than 10.0% at an OLR of $10.05 \text{ kg m}^{-3} \text{ day}^{-1}$ at the end of 147 days SRT operation at 35°C and at a pH of 7.30 for an initial COD concentration of 3900 mg L^{-1} (Rajakumar et al., 2011).

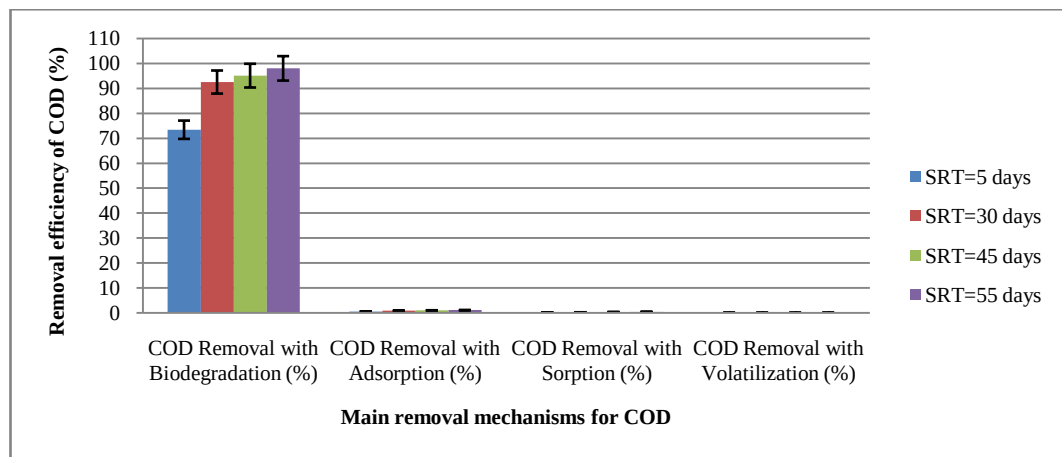


Figure 6.5 The removal efficiencies of COD with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.3.2 Removed Masses and Removal Efficiencies of sCOD

An example for the calculations relevant to the removed masses of sCOD and the removal efficiencies of sCOD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.19 to 6.36, respectively (Section 5.6.12.2) at a SRT of 5 days (Table 6.3). Calculated sCOD masses exposed to biodegradation, sorption, adsorption and volatilization during 5, 30, 45 and 55 days of SRT operations were shown in Table 6.3.



Table 6.3 The total removal percentages for sCOD throughout biodegradation, adsorption, sorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Bio-degraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	1056.75	0.294	13.22	0.092	4.15	0.00	0.00	49.73	0.62	0.20	0.00
30	1587.80	0.370	16.67	0.180	8.12	0.00	0.00	74.72	0.78	0.38	0.00
45	1777.48	0.445	20.01	0.209	9.40	0.00	0.00	83.65	0.94	0.44	0.00
55	1914.50	0.582	26.20	0.222	10.00	0.00	0.00	90.09	1.23	0.47	0.00
AEROBIC REACTOR											
SRT	Bio-degraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	481.82	0.219	3.29	0.058	0.87	0.00	0.00	57.39	0.39	0.10	0.00
30	630.75	0.417	6.26	0.123	1.85	0.00	0.00	75.13	0.75	0.22	0.00
45	711.65	0.512	7.68	0.150	2.25	0.00	0.00	84.76	0.91	0.27	0.00
55	796.64	0.687	10.30	0.167	2.50	0.00	0.00	94.89	1.23	0.30	0.00
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Bio-degraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(mg)	(mg L ⁻¹)	(mg)	(mg L ⁻¹)	(µg)	(mg L ⁻¹)	(mg)	(%)	(%)	(%)	(%)
5	3020.09	--	16.51	--	5.02	--	0.00	78.96	0.43	0.13	0.00
30	3597.12	--	22.93	--	9.97	--	0.00	94.04	0.60	0.26	0.00
45	3686.22	--	27.69	--	11.65	--	0.00	96.37	0.72	0.30	0.00
55	3777.12	--	36.50	--	12.50	--	0.00	98.75	0.95	0.33	0.00

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

The biodegradation masses for sCOD were calculated in Equations 6.19, 6.20 and 6.21 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.3).

$$M_{\text{BIO,Anaerobic}} = (422.70 \text{ mg L}^{-1}) \times (2.5 \text{ L}) = 1056.75 \text{ mg} \quad (6.19)$$

$$M_{\text{BIO,Aerobic}} = (240.91 \text{ mg L}^{-1}) \times (2.0 \text{ L}) = 481.82 \text{ mg} \quad (6.20)$$

$$M_{\text{BIO,Sequential}} = (671.13 \text{ mg L}^{-1}) \times (2.0 \text{ L}) = 3020.09 \text{ mg} \quad (6.21)$$

The biodegradation removal efficiencies at 5 days SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.22, 6.23 and 6.24, respectively (Table 6.3).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (1056.75 \times 100) / (850.00 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 49.73\% \quad (6.22)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (481.82 \times 100) / (419.78 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 57.39\% \quad (6.23)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (3020.09 \times 100) / (850.00 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 78.96\% \quad (6.24)$$

The adsorption masses for sCOD were calculated according to the Equation 6.25, 6.26 and 6.27 at a SRT operation of 5 days in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors (Table 6.3).

$$M_{\text{ADS,Anaerobic}} = [(0.294 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 13.22 \text{ mg} \quad (6.25)$$

$$M_{\text{ADS,Aerobic}} = [(0.219 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 3.29 \text{ mg} \quad (6.26)$$

$$M_{\text{ADS,Sequential}} = 13.22 + 3.29 = 16.51 \text{ mg} \quad (6.27)$$

The adsorption removal efficiencies at 5 days of SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.28, 6.29 and 6.30, respectively (Table 6.3).

$$\text{Ads}(\%)_{\text{Anaerobic}} = (13.22 \times 100) / (850.00 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 0.62\% \quad (6.28)$$

$$\text{Ads}(\%)_{\text{Aerobic}} = (3.29 \times 100) / (419.78 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 0.39\% \quad (6.29)$$

$$Ads(\%),_{\text{Sequential}} = (16.51 \times 100) / (850.00 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 0.43\% \quad (6.30)$$

The sorption masses for sCOD were calculated using Equation 6.31, 6.32 and 6.33 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at a SRT operation of 5 days (Table 6.3).

$$M_{\text{SORP,Anaerobic}} = [(0.092 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 4.15 \text{ mg} \quad (6.31)$$

$$M_{\text{SORP,Aerobic}} = [(0.058 \text{ mg L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.87 \text{ mg} \quad (6.32)$$

$$M_{\text{SORP,Sequential}} = 4.15 + 0.87 = 5.02 \text{ mg} \quad (6.33)$$

The sorption removal efficiencies at 5 days of SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.34, 6.35 and 6.36, respectively (Table 6.3).

$$\text{Sorp}(\%),_{\text{Anaerobic}} = (4.15 \times 100) / (850.00 \text{ mg L}^{-1} \times 2.5 \text{ L}) = 0.20\% \quad (6.34)$$

$$\text{Sorp}(\%),_{\text{Aerobic}} = (0.87 \times 100) / (419.78 \text{ mg L}^{-1} \times 2.0 \text{ L}) = 0.10\% \quad (6.35)$$

$$\text{Sorp}(\%),_{\text{Sequential}} = (5.02 \times 100) / (850.00 \text{ mg L}^{-1} \times 4.5 \text{ L}) = 0.13\% \quad (6.36)$$

In order to determine the volatilization masses PUF disks were used. No COD concentrations (0.00 mg L^{-1}) were determined after 5, 30, 45 and 55 days of SRTs in the PUF disks under anaerobic and aerobic conditions, respectively. Because of the concentrations were measured as zero (0.00 mg L^{-1}), volatilization masses ($(0.00 \text{ mg L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00 \text{ mg}$) and volatilization removal efficiencies for COD calculated zero in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days SRTs (Table 6.3).

6.1.3.2.1 Removed Masses and Removal Efficiencies of sCOD in Anaerobic Reactor. sCOD masses exposed to biodegradation increased from 1056.75 mg to 1914.50 mg as the SRT was increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.3). An increase in the biodegraded sCOD masses caused an increase in the biodegradation percentages of sCOD from 49.73% to 90.09% with the increasing of SRTs from 5 days up to 55 days, respectively in the anaerobic

reactor (Table 6.3). When the SRT is not sufficient, organic substances could not be hydrolysed effectively in hydrolysis step of the anaerobic treatment. At long sludge retention times (55 days) the anaerobic bacteria can be metabolized sCOD effectively. This was a general agreement with sCOD removal efficiencies were increased with time of operation due to an increase in SRTs – decrease in OLRs (Table 6.1) (Rajakumar & Meenambal, 2008). The biodegraded sCOD masses in the anaerobic reactor were found statistically meaningful according to the ANOVA (one-way) test statistics results ($P = 0.027$, $\alpha = 0.05$, $F = 8.47$). Low sorption (accumulation inside the anaerobic biological sludge granules) masses were calculated between 4.15 mg and 10.00 mg corresponding to low sorption percentages between 0.20% and 0.47% for sCOD varying between 5 days and 55 days SRTs, respectively in the anaerobic reactor (Table 6.3). The volatilization masses and volatilization percentages were measured as zero for sCOD at all SRTs in the anaerobic reactor (Table 6.3). The ANOVA (one-way) test statistics results showed that removal of sCOD via sorption ($P = 0.076$, $\alpha = 0.05$, $F = 4.57$) and volatilization ($P = 0.078$, $\alpha = 0.05$, $F = 4.51$) were negligible in the anaerobic reactor. The adsorbed (onto the anaerobic biological sludge) sCOD masses varies between 13.22 mg and 26.20 mg related to the adsorbed sCOD percentages between 0.62% and 1.23% for sCOD varying between 5 days and 55 days SRTs, respectively in the anaerobic reactor (Table 6.3). Because of the anaerobic bacteria can be metabolized the adsorbed sCOD, the adsorption of sCOD to the anaerobic sludge was insignificant in the anaerobic reactor. Also, ANOVA (one-way) test statistics results showed that the removal of sCOD via adsorption was not significant ($P = 0.051$, $\alpha = 0.05$, $F = 5.95$). As a result, adsorption has not an important contribution to the removal of sCOD in the anaerobic reactor at all SRTs.

6.1.3.2.2 Removed Masses and Removal Efficiencies of sCOD in Aerobic Reactor.

The biodegraded sCOD masses increased from 481.82 mg to 796.64 mg corresponding an increase in the biodegradation percentages of sCOD from 57.39% to 94.89% depending on SRT increase from 5 days to 55 days, respectively in the aerobic reactor (Table 6.3). The maximum biodegradation yield of sCOD (94.89%) was obtained at 55 days SRT (Table 6.3). Increasing of the removal efficiencies at

higher SRTs can be attributed to providing more contact time between the secreted enzymes from aerobic bacteria and the sCOD. In other words, increase in contact time between aerobic bacteria and sCOD facilitates the bacterial adaption to the environment and the sCOD degradation would be enhanced (Shokoohi et al., 2017). The ANOVA (one-way) test statistics results supported that removal of sCOD via biodegradation was significant in the aerobic reactor ($P = 0.017$, $\alpha = 0.05$, $F = 10.79$). Low sorption masses were calculated between 0.87 mg and 2.50 mg resulting in low sorption percentages from 0.10% to 0.30% for sCOD varying between 5 days and 55 days SRTs, respectively in the aerobic reactor (Table 6.3). The volatilization masses and volatilization percentages were measured as zero for sCOD at all SRTs in the aerobic reactor (Table 6.3). The ANOVA (one-way) test statistics results showed that removal of sCOD via sorption ($P = 0.099$, $\alpha = 0.05$, $F = 3.81$) and volatilization ($P = 0.100$, $\alpha = 0.05$, $F = 3.77$) were not meaningful statistically in the aerobic reactor. The adsorbed sCOD masses to the aerobic sludge ranged from 3.29 mg to 10.30 mg resulting in the adsorbed sCOD percentages between 0.39% to 1.23% for sCOD varying between 5 days and 55 days SRTs, respectively in the aerobic reactor (Table 6.3). The ANOVA (one-way) test statistics results showed that the removal of sCOD via adsorption was not significant ($P = 0.083$, $\alpha = 0.05$, $F = 4.32$). As a result, adsorption was not found to be important for the removal of sCOD in the aerobic reactor at all SRTs.

The results showed that the removal percentage of sCOD via biodegradation was higher in the aerobic reactor (94.89%) than the anaerobic reactor (90.09%) at 55 days of SRT (Table 6.3). Anaerobic degradation processes have always been considered to be slow in comparison to aerobic degradation (Zheng et al., 2013). sCOD consisted of simple molecules able to pass through the cell wall and they are used for energy and synthesis in biodegradation process by the anaerobic and aerobic microorganisms at a SRT of 55 days in this study. The anaerobic and aerobic microorganisms used COD as a sole source of carbon and energy in biodegradation process (Zheng et al., 2013).

6.1.3.2.3 *Removed Masses and Removal Efficiencies of sCOD in Anaerobic/Aerobic Sequential Biological Reactor System.* Total biodegraded masses of sCOD increased from 3020.09 mg to 3777.12 mg corresponding to an increase for sCOD removal percentages of 78.96% to 98.75% depending on SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.3). The biodegradation yield of sCOD reached the highest level (98.75%) at 55 days SRT (Table 6.3). The removal of sCOD via biodegradation was found significant in the ANOVA (one-way) test statistics ($P = 0.003$, $\alpha = 0.05$, $F = 24.59$). Low sorption masses obtained (5.02 – 12.50 mg) and the volatilization masses were measured as zero for sCOD between 5 days and 55 days SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.3). Low sorption masses equaled to low sorption percentages resulting between 0.13% and 0.33% for sCOD between 5 days and 55 days SRTs, while the volatilization percentages calculated zero at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.3). The ANOVA (one-way) test statistics results showed that removal of sCOD via sorption ($P = 0.174$, $\alpha = 0.05$, $F = 2.38$) and volatilization ($P = 0.177$, $\alpha = 0.05$, $F = 2.34$) had no statistical significance in the anaerobic/aerobic sequential biological reactor system. The total adsorption of sCOD masses measured between 16.51 mg and 36.50 mg related to the adsorption percentages from 0.43% to 0.95% as the SRT increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.3). The ANOVA (one-way) test statistics results showed that the removal of sCOD via adsorption has not a significant contribution and accepted as negligible in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.058$, $\alpha = 0.05$, $F = 5.47$).

Low adsorption (0.95%), sorption (0.33%) and volatilization (0.00%) percentages showed that sCOD can not be effectively removed via these three mechanisms at 55 days SRT (Figure 6.6). This study proved that biodegradation (98.75%) was the main removal mechanism of sCOD removal at 55 days SRT (Figure 6.6). As a result of the study, the removal of sCOD via biodegradation (98.75%) can be accepted as the major removal mechanism at 55 days SRT (Figure 6.6). Some researchers also confirmed that biodegradation is the main removal mechanism for sCOD removal

(83.5%) in an upflow anaerobic filter treating hospital wastewaters and the other mechanisms supported the sCOD removal less than 10.0% for an initial sCOD concentration of 2015 mg L⁻¹ at 10.05 kg m⁻³ day⁻¹ OLR, at 147 days SRT, at 35 °C and at a pH of 7.30 (Rajakumar et al., 2011).

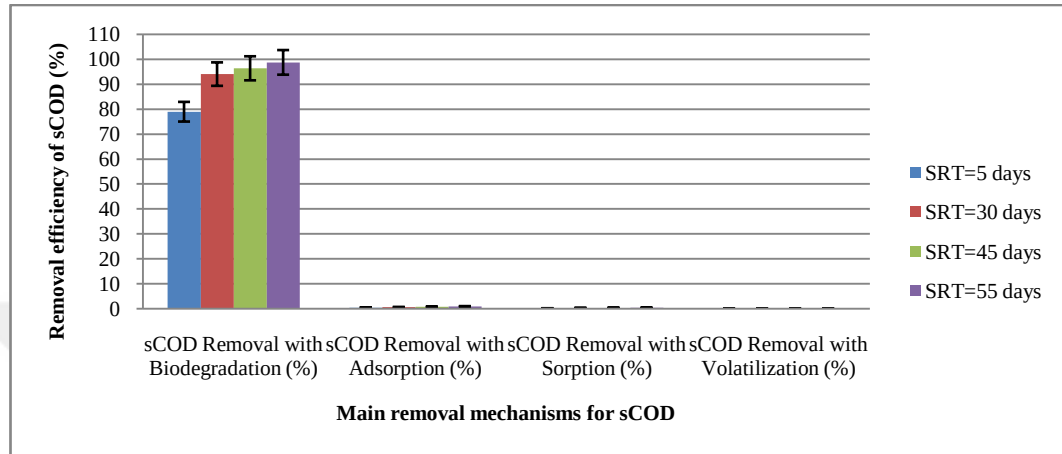


Figure 6.6 The removal efficiencies of sCOD with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.4 TOC Removals in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

TOC removal efficiencies were monitored through experimental periods in order to evaluate the feasibility of anaerobic/aerobic sequential biological reactor system. The TOC removal efficiencies obtained at different SRT operations were summarized in Table 6.4.

Table 6.4 TOC yields at different SRTs (n = 3, mean ± SD)

SRT (day)	Anaerobic Reactor			Aerobic Reactor			Anaerobic/Aerobic Sequential Biological Reactor		
	Influent TOC conc. (mg L ⁻¹)	Effluent TOC conc. (mg L ⁻¹)	TOC Rem. Eff. (%)	Influent TOC conc. (mg L ⁻¹)	Effluent TOC conc. (mg L ⁻¹)	TOC Rem. Eff. (%)	Influent TOC conc. (mg L ⁻¹)	Effluent TOC conc. (mg L ⁻¹)	TOC Rem. Eff. (%)
5	525.00 ± 1.00	504.00 ± 1.00	4.0	504.00 ± 1.00	473.26 ± 1.00	6.1	525.00 ± 1.00	473.26 ± 1.00	9.8
30	525.00 ± 1.00	381.15 ± 1.00	27.4	381.15 ± 1.00	193.62 ± 1.00	49.2	525.00 ± 1.00	193.62 ± 1.00	63.1
45	525.00 ± 1.00	347.55 ± 1.00	33.8	347.55 ± 1.00	129.29 ± 1.00	62.8	525.00 ± 1.00	129.29 ± 1.00	75.4
55	525.00 ± 1.00	315.00 ± 1.00	40.0	315.00 ± 1.00	116.24 ± 1.00	63.1	525.00 ± 1.00	116.24 ± 1.00	77.9

The maximum TOC removal efficiencies of the anaerobic reactor was measured as 4.0%, 27.4%, 33.8% and 40.0% at SRTs of 5, 30, 45 and 55 days, respectively while the TOC yields in the aerobic reactor obtained as 6.1%, 49.2%, 62.8% and 63.1% at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.4). Therefore, in the anaerobic/aerobic sequential biological reactor system 9.8%, 63.1%, 75.4% and 77.9% of TOC removal efficiencies were achieved at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.4). The TOC removal efficiencies increased with increasing SRTs and the maximum removal efficiency (77.9%) obtained at the maximum SRT of 55 days (Table 6.4).

Changotra, Rajput, Guin, Varshney, & Dhir (2019) achieved a maximum value of 56.7% TOC removal in an aerobic biological treatment for low organic strength pharmaceutical wastewater at an initial TOC concentration of 11840 mg L⁻¹ with 3.6 g L⁻¹ MLSS concentration at 27 °C and 120 h HRT (Changotra et al., 2019). In this study, the maximum TOC removal efficiency of the anaerobic reactor was obtained as 40.0% with a TOC effluent of 315.00 mg L⁻¹ at a TOC influent of 525.00 mg L⁻¹ at 55 days SRT (Table 6.4). On the other hand, the aerobic reactor achieved better maximum TOC removal efficiency than that in anaerobic reactor (40.0%) and obtained 63.1% maximum TOC removal efficiency with an effluent TOC of 116.24 mg L⁻¹ at a TOC influent of 315.00 mg L⁻¹ at 55 days SRT (Table 6.4). For this study, the aerobic reactor achieved better maximum TOC removal efficiency (63.1%) than Changotra et al. (2019) who found 56.7% of TOC removal efficiency in an aerobic reactor treating pharmaceutical wastewater. The aerobic reactor showed better removal performances than anaerobic reactor due to its enhanced bacterial adaptability for the utilization of COD, sCOD and TOC as carbon/energy source. For the anaerobic/aerobic sequential reactor system, it can be concluded that the maximum TOC removal efficiency reached 77.9% with an effluent of 116.24 mg L⁻¹ at a TOC influent of 525.00 mg L⁻¹ at 55 days SRT (Table 6.4). In this study, the increased TOC removal efficiency at 55 days SRT supported that the organic substances was exposed to mineralization and the organic substances might have transformed to small molecule intermediates (Kajitvichyanukul & Suntronvipart, 2006).

6.1.5 pH Variations in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

pH is the one of the most important operating parameters to control biological system stability. Therefore, during the experimental studies, pH values of raw hospital wastewater, anaerobic and aerobic biological reactor effluents were monitored regularly. pH alterations during the experimental studies are given in Figure 6.7.



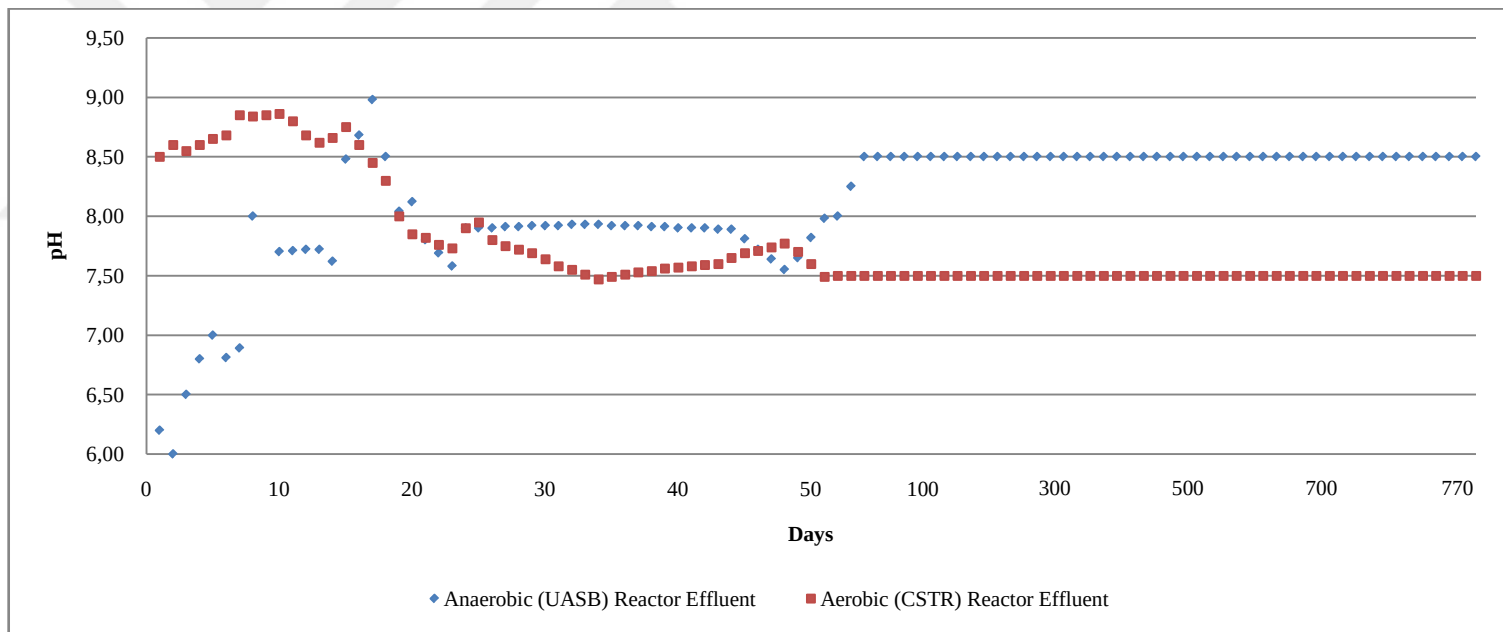


Figure 6.7 pH variations of anaerobic/aer

The raw hospital wastewater pH was almost stable at pH 8.00 and changed between 7.50 and 8.50 (Figure 6.7). The anaerobic reactor effluent pH did not fall to below 6.00, which is lower than the adequate value for the growth of methanogenic bacteria. The highest pH value was measured as 8.50 for the anaerobic reactor effluent (Figure 6.7). The optimum pH range for methanogenic bacteria growth is between 7.80 and 8.50. The pH in the anaerobic reactor must be kept in this range because of methanogenic bacteria that is the most sensitive group in the anaerobic biological treatment. Methanogenesis are more sensitive than acidogenesis, nevertheless, acidogenesis are inhibited when the pH decreases under the value of 5.50 (Yüceer, 2006). The anaerobic reactor effluent had an average pH value of 8.50 throughout the study (Figure 6.7). pH value of the aerobic reactor effluent showed an alteration from 7.47 to 8.86 and kept approximately 7.50 in the aerobic reactor effluent (Figure 6.7). During the start-up period with synthetic wastewater the desired pH levels were provided by the addition of diluted NaOH or HCl to the feeding of the biological reactors in case of need. As seen from the figure, at the end of the start-up period there was no significant pH fluctuations for the experiments with raw hospital wastewater showing that the biological reactor operations were stable.

6.1.6 Methane Gas (CH₄) Variations in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

In this study, average CH₄ gas volumes of the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system were determined as 161.60, 243.20, 266.30 and 284.10 mL CH₄ day⁻¹ for 5, 30, 45 and 55 days of SRT operations, respectively (Table 6.5). As a consequence, increasing the SRT from 5 to 55 days positively affected the CH₄ gas production. CH₄ gas production at 55 days of SRT was better than the productions at 5, 30 and 45 days of SRT conditions. This could be due to the high CH₄ gas production at high retention time from the low TVFA without any accumulation in the anaerobic UASB reactor.

Table 6.5 CH₄ gas, TVFA and HCO₃⁻ alkalinity alterations at different SRTs (n=3, mean ± SD)

SRT (day)	CH ₄ gas (mL day ⁻¹)	TVFA (mg L ⁻¹)	HCO ₃ ⁻ Alkalinity (mg CaCO ₃ L ⁻¹)	TVFA/Alkalinity Ratio
5	161.60 ± 0.50	180.00 ± 0.50	1500.00 ± 0.50	0.12
30	243.20 ± 0.50	92.00 ± 0.50	3250.00 ± 0.50	0.03
45	266.30 ± 0.50	64.00 ± 0.50	3700.00 ± 0.50	0.02
55	284.10 ± 0.50	46.00 ± 0.50	2300.00 ± 0.50	0.02

6.1.7 Variations of TVFA and Bicarbonate (HCO₃⁻) Alkalinity Concentrations in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The TVFA concentration of the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system reached 180.00 mg acetic acid L⁻¹ at the end of the 5 days of SRT operation (Table 6.5). The TVFA concentrations were determined as 92.00 and 64.00 mg acetic acid L⁻¹ at the end of the 30 and 45 days of SRT operations, respectively (Table 6.5). When the SRT was increased to 55 days, the TVFA concentration of the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system decreased to 46.00 mg acetic acid L⁻¹ (Table 6.5). Sánchez, Borja, Travieso, Martin, & Colmenarejo (2005) suggested that when the values for TVFA/Bicarbonate alkalinity ratio are lower than 0.3–0.4 the system is under steady-state conditions (Sánchez et al., 2005). In this study, TVFA to bicarbonate alkalinity ratios during the experimental studies were 0.12, 0.03, 0.02 and 0.02 at 5, 30, 45 and 55 days of SRT operations, respectively (Table 6.5). It could be concluded that the anaerobic reactor operations were stable during the experimental studies at 5, 30, 45 and 55 days of SRTs.

6.1.8 TS, TDS and TSS Removals in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

In the raw hospital wastewater influent TS, TDS and TSS concentrations were 380.00, 130.00 and 250.00 mg L⁻¹, respectively. The effect of increasing SRT from 5 days to 55 days on TS, TDS and TSS removals in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactor systems were shown in Table 6.6.

Table 6.6 TS, TDS and TSS removal efficiencies at different SRTs (n = 3, mean $\pm$ SD)

Anaerobic (UASB) Biological Reactor									
Influent (mg L⁻¹)			Effluent (mg L⁻¹)			Removal Efficiency (%)			
SRT (day)	TS	TDS	TSS	TS	TDS	TSS	TS	TDS	TSS
5	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	340.47 $\pm$ 0.50	119.47 $\pm$ 0.50	221.00 $\pm$ 0.50	10.4 $\pm$ 0.50	8.1 $\pm$ 0.50	11.6 $\pm$ 0.50
30	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	299.85 $\pm$ 0.50	100.10 $\pm$ 0.50	199.75 $\pm$ 0.50	21.1 $\pm$ 0.50	23.0 $\pm$ 0.50	20.1 $\pm$ 0.50
45	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	286.85 $\pm$ 0.50	93.60 $\pm$ 0.50	193.25 $\pm$ 0.50	24.5 $\pm$ 0.50	28.0 $\pm$ 0.50	22.7 $\pm$ 0.50
55	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	268.30 $\pm$ 0.50	89.05 $\pm$ 0.50	179.25 $\pm$ 0.50	29.4 $\pm$ 0.50	31.5 $\pm$ 0.50	28.3 $\pm$ 0.50
Aerobic (CSTR) Biological Reactor									
Influent (mg L⁻¹)			Effluent (mg L⁻¹)			Removal Efficiency (%)			
SRT (day)	TS	TDS	TSS	TS	TDS	TSS	TS	TDS	TSS
5	340.47 $\pm$ 0.50	119.47 $\pm$ 0.50	221.00 $\pm$ 0.50	210.09 $\pm$ 0.50	82.79 $\pm$ 0.50	127.30 $\pm$ 0.50	38.3 $\pm$ 0.50	30.7 $\pm$ 0.50	42.4 $\pm$ 0.50
30	299.85 $\pm$ 0.50	100.10 $\pm$ 0.50	199.75 $\pm$ 0.50	161.21 $\pm$ 0.50	50.15 $\pm$ 0.50	111.06 $\pm$ 0.50	46.2 $\pm$ 0.50	49.9 $\pm$ 0.50	44.4 $\pm$ 0.50
45	286.85 $\pm$ 0.50	93.60 $\pm$ 0.50	193.25 $\pm$ 0.50	136.66 $\pm$ 0.50	37.72 $\pm$ 0.50	98.94 $\pm$ 0.50	52.4 $\pm$ 0.50	59.7 $\pm$ 0.50	48.8 $\pm$ 0.50
55	268.30 $\pm$ 0.50	89.05 $\pm$ 0.50	179.25 $\pm$ 0.50	121.78 $\pm$ 0.50	32.33 $\pm$ 0.50	89.45 $\pm$ 0.50	54.6 $\pm$ 0.50	63.7 $\pm$ 0.50	50.1 $\pm$ 0.50
Anaerobic/Aerobic Sequential Biological Reactor System									
Influent (mg L⁻¹)			Effluent (mg L⁻¹)			Removal Efficiency (%)			
SRT (day)	TS	TDS	TSS	TS	TDS	TSS	TS	TDS	TSS
5	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	210.09 $\pm$ 0.50	82.79 $\pm$ 0.50	127.30 $\pm$ 0.50	44.7 $\pm$ 0.50	36.3 $\pm$ 0.50	49.1 $\pm$ 0.50
30	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	161.21 $\pm$ 0.50	50.15 $\pm$ 0.50	111.06 $\pm$ 0.50	57.6 $\pm$ 0.50	61.4 $\pm$ 0.50	55.6 $\pm$ 0.50
45	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	136.66 $\pm$ 0.50	37.72 $\pm$ 0.50	98.94 $\pm$ 0.50	64.0 $\pm$ 0.50	71.0 $\pm$ 0.50	60.4 $\pm$ 0.50
55	380.00 $\pm$ 0.50	130.00 $\pm$ 0.50	250.00 $\pm$ 0.50	121.78 $\pm$ 0.50	32.33 $\pm$ 0.50	89.45 $\pm$ 0.50	68.0 $\pm$ 0.50	75.1 $\pm$ 0.50	64.2 $\pm$ 0.50

The maximum TS removal efficiencies of the anaerobic reactor were measured as 10.4%, 21.1%, 24.5% and 29.4% at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6). The aerobic reactor enhanced the TS removal efficiencies. 38.3%, 46.2%, 52.4% and 54.6% of maximum TS removals at SRTs of 5, 30, 45 and 55 days, respectively were measured in the aerobic reactor (Table 6.6). Therefore, in the anaerobic/aerobic sequential biological reactor system, 44.7%, 57.6%, 64.0% and 68.0% of maximum TS removal efficiencies were achieved at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6).

The maximum TDS removal efficiencies of the anaerobic reactor were determined as 8.1%, 23.0%, 28.0% and 31.5% at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6). In the aerobic reactor, the maximum TDS removal efficiencies increased to 30.7%, 49.9%, 59.7% and 63.7% at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6). Moreover, in the anaerobic/aerobic sequential biological reactor system, 36.3%, 61.4%, 71.0% and 75.1% of maximum TDS removal efficiencies were obtained at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6).

The anaerobic reactor showed 11.6%, 20.1%, 22.7% and 28.3% of maximum TSS removal efficiencies at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6). TSS removals increased in the aerobic reactor. 42.4%, 44.4%, 48.8% and 50.1% of maximum TSS removal efficiencies were detected at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6). As a consequence, in the anaerobic/aerobic sequential biological reactor system, 49.1%, 55.6%, 60.4% and 64.2% of maximum TSS removal efficiencies were calculated at SRTs of 5, 30, 45 and 55 days, respectively (Table 6.6).

TDS exhibits the dissolved of all inorganic and organic substances contained in the wastewater which are present in a molecular, ionized or micro-granular (colloidal solution) suspended form. These solids are metabolised directly by the microorganisms (MLVSS) in the wastewater. High TDS concentrations inhibit the growth of microorganisms by osmotic shocks of microbial cell which results in the lower rates of elimination of dissolved organic components regarding COD and

decrease the oxygen uptake rates in the aerobic processes. In this study, the aerobic TDS and TSS yields are higher than that the anaerobic reactor since the yields of the aerobic microorganisms to uptake the solids are high compared to anaerobic ones.

Khan & Mostafa (2011) operated an aerobic biological reactor treating pharmaceutical wastewater at a HRT of 15 days under mesophilic (30 ± 1 °C) temperature conditions. The maximum TSS removal efficiency of the aerobic biological reactor reached 50.0% at an influent TSS concentration of 300 mg L^{-1} (Khan & Mostafa, 2011). Chiarello et al. (2016) found 63.7% TSS removal efficiency for an initial TSS concentration of 155.0 mg L^{-1} in a hospital wastewater treatment plant using biological system with an anoxic (HRT = 3 h) and an aerobic (HRT = 10 h) bioreactor at 24 °C and at pH 7.5 (Chiarello et al., 2016). In a continuous biological process, it is expected that solids removal rates would be increased with time. The results from this study showed that TS, TDS and TSS effluent concentrations decreased with increasing SRTs in both reactors (Table 6.6). In this study, in the anaerobic/aerobic sequential biological reactor system the higher TSS removal efficiencies (64.2%) were obtained than the study performed by Khan & Mostafa (2011) (50.0%) and Chiarello et al. (2016) (63.7%).

6.1.9 Total α -Hexabromocyclododecane (α -HBCDD) Removals

6.1.9.1 Total α -HBCDD Removals in Anaerobic Biological Reactor

α -HBCDD removal efficiency of the anaerobic reactor was obtained as 1.7% with an α -HBCDD effluent of $0.0113 \text{ } \mu\text{g L}^{-1}$ at an α -HBCDD influent of $0.0115 \text{ } \mu\text{g L}^{-1}$ during the 5 days of SRT operation (Table 6.7). α -HBCDD removal efficiency was measured as 2.6% with an α -HBCDD effluent of $0.0112 \text{ } \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \text{ } \mu\text{g L}^{-1}$ at 30 days SRT (Table 6.7). For 45 days SRT operation, α -HBCDD removal efficiency was found as 5.2% with an α -HBCDD effluent of $0.0109 \text{ } \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \text{ } \mu\text{g L}^{-1}$ (Table 6.7). For 55 days SRT operation, α -HBCDD removal efficiency was calculated as 7.0% with an α -

HBCDD effluent of $0.0107 \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \mu\text{g L}^{-1}$ (Table 6.7).



Table 6.7 α -HBCDD and its metabolite 2-Bromocyclododecan-1-ol (2-BCD) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent α -HBCDD ($\mu\text{g L}^{-1}$)	Effluent α -HBCDD ($\mu\text{g L}^{-1}$)	metabolite of α -HBCDD namely 2-BCD			Removed α -HBCDD ($\mu\text{g L}^{-1}$)	α -HBCDD Rem. Eff. (%)	Influent α -HBCDD ($\mu\text{g L}^{-1}$)	Effluent α -HBCDD ($\mu\text{g L}^{-1}$)	metabolite of α -HBCDD namely 2-BCD			Removed α -HBCDD ($\mu\text{g L}^{-1}$)	α -HBCDD Rem. Eff. (%)
			Influent 2-BCD ($\mu\text{g L}^{-1}$)	Effluent 2-BCD ($\mu\text{g L}^{-1}$)	2-BCD Rem. Eff. (%)					Influent 2-BCD ($\mu\text{g L}^{-1}$)	Effluent 2-BCD ($\mu\text{g L}^{-1}$)	2-BCD Rem. Eff. (%)		
5	0.0115 $\pm$ 0.001	0.0113 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.00 $\pm$ 5.0	0.0002 $\pm$ 0.001	1.7 $\pm$ 5.0	0.0113 $\pm$ 0.001	0.0109 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0012 $\pm$ 0.001	20.0 $\pm$ 5.0	0.0004 $\pm$ 0.001	3.5 $\pm$ 5.0
30	0.0115 $\pm$ 0.001	0.0112 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.00 $\pm$ 5.0	0.0003 $\pm$ 0.001	2.6 $\pm$ 5.0	0.0112 $\pm$ 0.001	0.0105 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0010 $\pm$ 0.001	33.3 $\pm$ 5.0	0.0007 $\pm$ 0.001	6.3 $\pm$ 5.0
45	0.0115 $\pm$ 0.001	0.0109 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.00 $\pm$ 5.0	0.0006 $\pm$ 0.001	5.2 $\pm$ 5.0	0.0109 $\pm$ 0.001	0.0100 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.0008 $\pm$ 0.001	38.5 $\pm$ 5.0	0.0009 $\pm$ 0.001	8.3 $\pm$ 5.0
55	0.0115 $\pm$ 0.001	0.0107 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0011 $\pm$ 0.001	0.00 $\pm$ 5.0	0.0008 $\pm$ 0.001	7.0 $\pm$ 5.0	0.0107 $\pm$ 0.001	0.0094 $\pm$ 0.001	0.0011 $\pm$ 0.001	0.0004 $\pm$ 0.001	63.6 $\pm$ 5.0	0.0013 $\pm$ 0.001	12.1 $\pm$ 5.0

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent α -HBCDD ($\mu\text{g L}^{-1}$)	Effluent α -HBCDD ($\mu\text{g L}^{-1}$)	metabolite of α -HBCDD namely 2-BCD			Removed α -HBCDD ($\mu\text{g L}^{-1}$)	α -HBCDD Rem. Eff. (%)
			Influent 2-BCD ($\mu\text{g L}^{-1}$)	Effluent 2-BCD ($\mu\text{g L}^{-1}$)	2-BCD Rem. Eff. (%)		
5	0.0115 $\pm$ 0.001	0.0109 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0012 $\pm$ 0.001	20.0 $\pm$ 5.0	0.0006 $\pm$ 0.001	5.2 $\pm$ 5.0
30	0.0115 $\pm$ 0.001	0.0105 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0010 $\pm$ 0.001	33.3 $\pm$ 5.0	0.0010 $\pm$ 0.001	8.7 $\pm$ 5.0
45	0.0115 $\pm$ 0.001	0.0100 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.0008 $\pm$ 0.001	38.5 $\pm$ 5.0	0.0015 $\pm$ 0.001	13.0 $\pm$ 5.0
55	0.0115 $\pm$ 0.001	0.0094 $\pm$ 0.001	0.0011 $\pm$ 0.001	0.0004 $\pm$ 0.001	63.6 $\pm$ 5.0	0.0021 $\pm$ 0.001	18.3 $\pm$ 5.0

The results showed that as the SRT was increased from 5 days to 55 days α -HBCDD removal efficiency increased slightly from 1.7% to 7.0% in the anaerobic reactor (Table 6.7). However, the ANOVA (one-way) statistical analysis results showed that it was not observed a significant regression between α -HBCDD removal and SRT increase ($P = 0.052$, $\alpha = 0.05$, $F = 5.86$). The α -HBCDD is slightly removed in the anaerobic step.

In this study, the presence of 2-Bromocyclododecan-1-ol (2-BCD) which is the main metabolite of α -HBCDD was monitored in the effluents of the anaerobic reactor at all SRTs. 2-BCD was a less hydrophobic ($\log K_{OW} = 4.90$) micropollutant than its parent compound of α -HBCDD ($\log K_{OW} = 7.74$) based on its $\log K_{OW}$ value. The effluent concentrations of 2-BCD were determined as 0.0015, 0.0015, 0.0013 and 0.0011 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.7). Based on Davis et al. (2004), dehalogenation is caused by breaking off the bromines from α -HBCDD and as a result, 2-BCD formed in the anaerobic conditions (Davis et al., 2004).

6.1.9.2 Total α -HBCDD Removals in Aerobic Biological Reactor

During 5 days of SRT operation, α -HBCDD removal efficiency of the aerobic biological reactor was found as 3.5% with an α -HBCDD effluent of 0.0109 $\mu\text{g L}^{-1}$ at an α -HBCDD influent of 0.0113 $\mu\text{g L}^{-1}$ (Table 6.7). α -HBCDD removal efficiency reached to 6.3% with an α -HBCDD effluent of 0.0105 $\mu\text{g L}^{-1}$ for an α -HBCDD influent of 0.0112 $\mu\text{g L}^{-1}$ at 30 days SRT (Table 6.7). For 45 days SRT operation, α -HBCDD removal efficiency was obtained as 8.3% with an α -HBCDD effluent of 0.0100 $\mu\text{g L}^{-1}$ for an α -HBCDD influent of 0.0109 $\mu\text{g L}^{-1}$ (Table 6.7). When the SRT was reached to the highest value of 55 days, α -HBCDD removal efficiency was determined as 12.1% with an α -HBCDD effluent of 0.0094 $\mu\text{g L}^{-1}$ for an α -HBCDD influent of 0.0107 $\mu\text{g L}^{-1}$ (Table 6.7).

Total removal of α -HBCDD was higher in the aerobic reactor (12.1%) than the anaerobic reactor (7.0%) at 55 days of SRT (Table 6.7). The low removals of α -

HBCDD in both reactors showed that this micropollutant is partially resistant to biodegradation due to its physicochemical properties (low water solubility = $2.09 \times 10^{-5} \text{ g L}^{-1}$ and high octanol/water partition coefficient = 7.74) in both reactors.

α -HBCDD removal efficiency in the aerobic reactor was calculated between 3.5% and 12.1% as the SRT was increased from 5 days to 55 days, respectively (Table 6.7). According to the ANOVA (one-way) statistical test results α -HBCDD could not be treated effectively biologically in the aerobic reactor at all SRTs ($P = 0.055$, $\alpha = 0.05$, $F = 5.65$).

In the presence of 2-BCD (0.0015, 0.0015, 0.0013 and 0.0011 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively) produced from the reductive dehalogenation in the anaerobic reactor, the 2-BCD was analysed in the samples taken from the effluent of the aerobic reactor at all SRTs (Table 6.7). The effluent concentrations of 2-BCD were found as 0.0012, 0.0010, 0.0008 and 0.0004 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor effluents (Table 6.7). Aerobic microorganisms could degrade 20.0% of 2-BCD with an effluent concentration of 0.0012 $\mu\text{g L}^{-1}$ at an influent 2-BCD concentration of 0.0015 $\mu\text{g L}^{-1}$ at 5 days SRT in the aerobic reactor (Table 6.7). When the SRT was increased to 30 days, the removal efficiency of 2-BCD was obtained as 33.3% with an effluent concentration of 0.0010 $\mu\text{g L}^{-1}$ at an influent 2-BCD concentration of 0.0015 $\mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.7). The 2-BCD removal efficiency was found as 38.5% with an effluent concentration of 0.0008 $\mu\text{g L}^{-1}$ at an influent 2-BCD concentration of 0.0013 $\mu\text{g L}^{-1}$ at 45 days SRT in the aerobic reactor (Table 6.7). Finally, 2-BCD removal efficiency increased to 63.6% with an effluent concentration of 0.0004 $\mu\text{g L}^{-1}$ at an influent 2-BCD concentration of 0.0011 $\mu\text{g L}^{-1}$ at the highest SRT of 55 days in the aerobic reactor (Table 6.7). As the SRT was increased from 5 days to 55 days, 2-BCD yields increased from 20.0% to 63.6%, respectively in the aerobic reactor (Table 6.7). The ANOVA (one-way) test statistics results showed that there was a linear correlation between SRTs and the removals of 2-BCD remaining from the anaerobic reactor and this regression was significant ($R^2 = 0.93$, $P = 0.007$, $\alpha = 0.05$, $F = 15.78$).

6.1.9.3 Total α -HBCDD Removals in Anaerobic/Aerobic Sequential Biological Reactor System

Firstly, α -HBCDD removal efficiency of the anaerobic/aerobic sequential biological reactor system was measured as 5.2% with an α -HBCDD effluent of $0.0109 \mu\text{g L}^{-1}$ at an α -HBCDD influent of $0.0115 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.7). After 30 days SRT, α -HBCDD removal efficiency was determined as 8.7% with an α -HBCDD effluent of $0.0105 \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \mu\text{g L}^{-1}$ at 30 days SRT (Table 6.7). When the SRT was increased to 45 days, α -HBCDD removal efficiency reached to 13.0% with an α -HBCDD effluent of $0.0100 \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \mu\text{g L}^{-1}$ (Table 6.7). At the highest SRT of 55 days, α -HBCDD removal efficiency was calculated as 18.3% with an α -HBCDD effluent of $0.0094 \mu\text{g L}^{-1}$ for an α -HBCDD influent of $0.0115 \mu\text{g L}^{-1}$ at 55 days SRT (Table 6.7). In this study, total α -HBCDD removal efficiency (18.3%) calculated in the anaerobic/aerobic sequential biological reactor system was higher than the results obtained by other researchers. Davis et al. (2004) also studied the aerobic treatability of α -HBCDD and reported that this micropollutant was not removed (0.00% removal efficiency) in the aerobic activated sludge process for an initial concentration of 3.6 mg L^{-1} at 56 days HRT and at $22 \pm 3^\circ\text{C}$ (Davis et al., 2004).

The influent concentrations of 2-BCD were determined as 0.0015, 0.0015, 0.0013 and $0.0011 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor (Table 6.7). The effluent concentrations of 2-BCD were detected as 0.0012, 0.0010, 0.0008 and $0.0004 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor (Table 6.7). The anaerobic/aerobic sequential biological reactor system achieved 20.0%, 33.3%, 38.5% and 63.6% removal efficiencies for 2-BCD at 5, 30 45 and 55 days SRTs, respectively (Table 6.7). 2-BCD removal efficiency increased with the increasing SRT and the maximum 2-BCD yield was obtained as 63.6% in the anaerobic/aerobic sequential biological reactor system at the highest SRT of 55 days (Table 6.7). The maximum 2-BCD removal efficiency (63.6%) found in the anaerobic/aerobic sequential biological reactor system was higher than

the study performed by Kassotaki, Buttiglieri, Ferrando-Climent, Rodriguez-Roda, & Pijuan (2016). They found 6.5% of 2-BCD removal efficiency in a sequencing batch reactor having a volume of 8 L treating synthetic wastewater at 24 h HRT and at 30 °C for 100 µg L⁻¹ initial α-HBCDD concentration (Kassotaki et al., 2016).

6.1.9.4 Removal Mechanisms of α-HBCDD in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to decide the main removal mechanisms for α-HBCDD. The biodegraded, adsorbed, sorbed and volatilized α-HBCDD masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.8).

Table 6.8 The total removal percentages for α -HBCDD throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	0.0005	0.00014	0.0062	0.000002	0.0001	0.000023	0.000000023	1.74	21.57	0.35	0.00008
30	0.0008	0.00032	0.0146	0.000004	0.0002	0.000025	0.000000025	2.61	50.78	0.70	0.00009
45	0.0015	0.00054	0.0245	0.000007	0.0003	0.000025	0.000000025	5.22	85.22	1.04	0.00009
55	0.0020	0.00055	0.0248	0.000007	0.0003	0.000025	0.000000025	6.96	86.09	1.04	0.00009
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	0.0008	0.00031	0.0046	0.000005	0.00007	0.000020	0.000000020	3.54	20.35	0.31	0.00009
30	0.0014	0.00060	0.0090	0.000009	0.00014	0.000022	0.000000022	6.25	40.18	0.63	0.00010
45	0.0018	0.00107	0.0160	0.000011	0.00017	0.000022	0.000000022	8.26	73.39	0.78	0.00010
55	0.0026	0.00114	0.0171	0.000013	0.00020	0.000023	0.000000023	12.15	79.91	0.93	0.00011
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	0.0027	--	0.011	--	0.0002	--	0.000000043	5.22	20.87	0.33	0.00008
30	0.0045	--	0.024	--	0.0003	--	0.000000047	8.70	45.60	0.66	0.00009
45	0.0067	--	0.041	--	0.0005	--	0.000000047	13.04	78.26	0.91	0.00009
55	0.0095	--	0.042	--	0.0005	--	0.000000048	18.26	80.87	0.97	0.00009

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.9.4.1 *Removed Masses and Removal Efficiencies of α -HBCDD*. An example for the calculations relevant to the removed masses and the removal efficiencies of α -HBCDD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.37 to 6.59, respectively at a SRT of 5 days (Table 6.8).

The biodegraded masses of α -HBCDD were calculated from Equations 6.37, 6.38 and 6.39 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.8).

$$M_{\text{BIO,Anaerobic}} = (0.0002 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 0.0005 \mu\text{g} \quad (6.37)$$

$$M_{\text{BIO,Aerobic}} = (0.0004 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 0.0008 \mu\text{g} \quad (6.38)$$

$$M_{\text{BIO,Sequential}} = (0.0006 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 0.0027 \mu\text{g} \quad (6.39)$$

The biodegradation removal efficiencies of α -HBCDD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.40, 6.41 and 6.42, respectively at 5 days SRT (Table 6.8).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (0.0005 \mu\text{g} \times 100) / (0.0115 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 1.74\% \quad (6.40)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (0.0008 \mu\text{g} \times 100) / (0.0113 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 3.54\% \quad (6.41)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (0.0027 \mu\text{g} \times 100) / (0.0115 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 5.22\% \quad (6.42)$$

The adsorbed masses of α -HBCDD were determined from Equation 6.43, 6.44 and 6.45 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.8).

$$M_{\text{ADS,Anaerobic}} = [(0.00014 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.0062 \mu\text{g} \quad (6.43)$$

$$M_{\text{ADS,Aerobic}} = [(0.00031 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.0046 \mu\text{g} \quad (6.44)$$

$$M_{\text{ADS,Sequential}} = 0.0062 + 0.0046 = 0.011 \mu\text{g} \quad (6.45)$$

The adsorption removal efficiencies for α -HBCDD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were detected from Equation 6.46, 6.47 and 6.48, respectively at 5 days SRT (Table 6.8).

$$\text{Ads}(\%)_{\text{An}} = (0.0062 \mu\text{g} \times 100)/(0.0115 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 21.57\% \quad (6.46)$$

$$\text{Ads}(\%)_{\text{Aerobic}} = (0.0046 \mu\text{g} \times 100)/(0.0113 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 20.35\% \quad (6.47)$$

$$\text{Ads}(\%)_{\text{Sequential}} = (0.011 \mu\text{g} \times 100)/(0.0115 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 20.87\% \quad (6.48)$$

The sorbed masses for α -HBCDD in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated from Equation 6.49, 6.50 and 6.51, respectively at 5 days SRT (Table 6.8).

$$M_{\text{SORP,Anaerobic}} = [(0.000002 \mu\text{g L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 0.0001 \mu\text{g} \quad (6.49)$$

$$M_{\text{SORP,Aerobic}} = [(0.000005 \mu\text{g L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 0.00007 \mu\text{g} \quad (6.50)$$

$$M_{\text{SORP,Sequential}} = 0.0001 + 0.00007 = 0.0002 \mu\text{g} \quad (6.51)$$

The sorption removal efficiencies in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.52, 6.53 and 6.54, respectively at 5 days SRT for α -HBCDD (Table 6.8).

$$\text{Sorp}(\%)_{\text{Anaerobic}} = (0.0001 \mu\text{g} \times 100)/(0.0115 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.35\% \quad (6.52)$$

$$\text{Sorp}(\%)_{\text{Aerobic}} = (0.00007 \mu\text{g} \times 100)/(0.0113 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.31\% \quad (6.53)$$

$$\text{Sorp}(\%)_{\text{Sequential}} = (0.0002 \mu\text{g} \times 100)/(0.0115 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.33\% \quad (6.54)$$

The volatilized masses of α -HBCDD were calculated using Equation 6.55, 6.56 and 6.57 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at a SRT operation of 5 days (Table 6.8).

$$M_{\text{VOL,Anaerobic}} = (2.3 \times 10^{-5} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 2.3 \times 10^{-8} \mu\text{g} \quad (6.55)$$

$$M_{\text{VOL,Aerobic}} = (2.0 \times 10^{-5} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 2.0 \times 10^{-8} \mu\text{g} \quad (6.56)$$

$$M_{VOL, Sequential} = 2.3 \times 10^{-8} + 2.0 \times 10^{-8} = 4.3 \times 10^{-8} \mu\text{g} \quad (6.57)$$

The volatilization removal efficiencies for α -HBCDD were determined according to the Equation 6.58, 6.59 and 6.60 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.8).

$$\text{Vol}(\%)_{\text{Anaerobic}} = (2.3 \times 10^{-8} \mu\text{g} \times 100) / (0.0115 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00008\% \quad (6.58)$$

$$\text{Vol}(\%)_{\text{Aerobic}} = (2.0 \times 10^{-8} \mu\text{g} \times 100) / (0.0113 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00009\% \quad (6.59)$$

$$\text{Vol}(\%)_{\text{Sequential}} = (4.3 \times 10^{-8} \mu\text{g} \times 100) / (0.0115 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00008\% \quad (6.60)$$

6.1.9.4.2 Removed Masses and Removal Efficiencies of α -HBCDD in Anaerobic Reactor. As is shown in Table 6.8 there was an increase for the biodegraded α -HBCDD masses from 0.0005 μg to 0.0020 μg as the SRT was increased from 5 up to 55 days in the anaerobic reactor. The biodegradation percentages of α -HBCDD also increased from 1.74% to 6.96% with the increasing of SRTs from 5 days up to 55 days, respectively (Table 6.8). At long sludge retention times (55 days) the anaerobic bacteria can co-metabolized only 6.96% of α -HBCDD together COD and sCOD in the anaerobic reactor. α -HBCDD can be used as co-metabolite together COD and its components (sCOD). Usually, halogenated compounds can serve as electron acceptors in the co-metabolic processes. A small quantity of α -HBCDD can be degraded with reductive dehalogenation (substitution of Br by a hydrogen atom) during biodegradation process under anaerobic conditions (Peng et al., 2018). Recently, it was reported that the bromides released from α -HBCDD by debromination process and bromides generated during α -HBCDD degradation (Yamada, Takahama, & Yamada, 2009 and Zhong et al., 2018). Long retention times are required to achieve efficient α -HBCDD biodegradation in the co-metabolic pathways. Peng et al. (2018) reported that α -HBCDD can be biodegraded 92.4% in a downflow batch anaerobic reactor at 300 days SRT for 500 $\mu\text{g L}^{-1}$ initial α -HBCDD concentration at pH 7.00 at 30 °C together with the carbon source (glucose) from a synthetic wastewater (Peng et al., 2018). The solubility ($2.089 \times 10^{-5} \text{ g L}^{-1}$) and Henry's Law constants of α -HBCDD ($1.72 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$) were quite low, however, the octanol/water partition coefficient ($\log K_{OW} = 7.74$) of α -HBCDD was

quite high. Therefore, this micropollutant is quite hydrophobic in the anaerobic reactor and can not be effectively biodegraded at 55 days SRT by the anaerobic bacteria in this study. Zhong et al. (2018) also reported that α -HBCDD could not biodegraded (0.00% removal efficiency) in an anaerobic batch reactor after 42 days SRT from synthetic wastewater for an initial α -HBCDD concentration of 38 μM at neutral pH because of being a quite hydrophobic micropollutant (Zhong et al., 2018). The removal of α -HBCDD with biodegradation in this study was not found to be meaningful statistically at all SRTs according to the ANOVA (one-way) test statistic results ($P = 0.052$, $\alpha = 0.05$, $F = 5.86$). The sorbed masses for α -HBCDD were calculated between 0.0001 and 0.0003 μg corresponding to a slight increase in the sorption removal percentages from 0.35% to 1.04% at SRTs varying from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.8). The volatilized masses (2.3×10^{-8} – 2.5×10^{-8} μg) and volatilization removal percentages (0.00008% – 0.00009%) of α -HBCDD were low at all SRTs in the anaerobic reactor (Table 6.8). The ANOVA (one-way) test statistics results showed that the removal of α -HBCDD via sorption ($P = 0.085$, $\alpha = 0.05$, $F = 4.24$) and volatilization ($P = 0.088$, $\alpha = 0.05$, $F = 4.15$) were insignificant in the anaerobic reactor at all SRTs. The adsorption of α -HBCDD to the anaerobic sludge was found to be important in the anaerobic reactor since the adsorbed α -HBCDD masses varies between 0.0062 μg and 0.0248 μg at SRTs from 5 days to 55 days (Table 6.8). It is important to note that the adsorbed α -HBCDD percentages increased from 21.57% to 86.09% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.8). As a result of the study, adsorption has a significant effect on the removal of α -HBCDD in the anaerobic reactor at all SRTs ($P = 0.0003$, $\alpha = 0.05$, $F = 14.63$).

6.1.9.4.3 Removed Masses and Removal Efficiencies of α -HBCDD in Aerobic Reactor. In the aerobic reactor, the biodegraded masses of α -HBCDD increased from 0.0008 μg to 0.0026 μg as the SRT increased from 5 days to 55 days, respectively (Table 6.8). This attributed to α -HBCDD biodegradation yields of 3.54% and 12.15% at 5 days and 55 days SRT, respectively (Table 6.8). The maximum biodegradation yield of α -HBCDD was obtained as 12.15% at 55 days SRT (Table 6.8). Davis et al. (2004) also studied the aerobic treatability of α -HBCDD and

reported that it was not possible to treat this micropollutant (0.00% removal efficiency) and did not follow further degradation to CO₂ and H₂O because of its physicochemical properties like low solubility (2.089×10^{-5} g L⁻¹) and high hydrophobicity (log K_{OW} = 7.74) (Davis et al., 2004). The ANOVA (one-way) test statistic results supported that the removal of α -HBCDD via biodegradation was not significant at all SRTs in the aerobic reactor (P = 0.055, α = 0.05, F = 5.65). The sorbed masses for α -HBCDD were measured between 0.00007 μ g and 0.00020 μ g at SRTs increasing from 5 days to 55 days, respectively in the aerobic reactor (Table 6.8). The sorption removal percentages were calculated between 0.31% and 0.93% for α -HBCDD at SRTs increasing from 5 days to 55 days, respectively in the aerobic reactor (Table 6.8). The volatilized masses were found as 2.0×10^{-8} and 2.3×10^{-8} μ g at 5 days and 55 days of SRTs, respectively for α -HBCDD in the aerobic reactor (Table 6.8). This attributed to α -HBCDD volatilization yields of 0.00009% and 0.00011% at 5 days and 55 days SRT, respectively in the aerobic reactor (Table 6.8). The ANOVA (one-way) test statistics results showed that removal of α -HBCDD via sorption (P = 0.051, α = 0.05, F = 5.92) and volatilization (P = 0.052, α = 0.05, F = 5.82) were not important in the aerobic reactor at all SRTs. The adsorbed masses of α -HBCDD to the aerobic sludge increased from 0.0046 μ g to 0.0171 μ g resulting in α -HBCDD adsorption removal percentages of 20.35% and 79.91% depending on the SRT increase from 5 days to 55 days, respectively in the aerobic reactor (Table 6.8). Low solubility (2.089×10^{-5} g L⁻¹), high hydrophobicity (log K_{OW} = 7.74) and low Henry's Law constant (1.72×10^{-6} atm m³ mol⁻¹) makes α -HBCDD quite hydrophobic in the aerobic reactor and adsorption (79.91%) becomes more dominant than biodegradation (12.15%) at 55 days SRT. Moreover, removal via adsorption has a significant contribution to the removal of α -HBCDD in the aerobic reactor at all SRTs (P = 0.0004, α = 0.05, F = 13.05). Kim, Guerra, Alaei, & Smyth (2014) found a median value of 78% α -HBCDD adsorption on aerobic sludges in the aerobic reactors of fifteen wastewater treatment plants (Kim et al., 2014).

Removal of α -HBCDD via biodegradation was slightly higher in the aerobic reactor (12.15%) than the anaerobic reactor (6.96%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table

6.8). Removal of α -HBCDD via adsorption was higher in the anaerobic reactor (86.09%) than the aerobic reactor (79.91%) at 55 days of SRT (Table 6.8) because α -HBCDD found more sludge surface to be adsorbed in the anaerobic reactor (MLVSS concentration of 27600 mg L^{-1}) than the aerobic reactor (MLVSS concentration of 3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.9.4.4 Removed Masses and Removal Efficiencies of α -HBCDD in Anaerobic/Aerobic Sequential Biological Reactor System. It can be said that the total biodegraded masses of α -HBCDD increased from $0.0027 \text{ }\mu\text{g}$ to $0.0095 \text{ }\mu\text{g}$ resulting in the α -HBCDD biodegradation removal percentages of 5.22% and 18.26% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor (Table 6.8). The biodegradation yield of α -HBCDD reached 18.26% as the maximum level at 55 days SRT (Table 6.8). The ANOVA (one-way) test statistic results showed that the removal of α -HBCDD via biodegradation was insignificant at all SRTs in the anaerobic/aerobic sequential biological reactor ($P = 0.093$, $\alpha = 0.05$, $F = 3.99$). A slight increase for α -HBCDD were observed from $0.0002 \text{ }\mu\text{g}$ to $0.0005 \text{ }\mu\text{g}$ regarding a negligible increase in the sorption removal percentages from 0.33% to 0.97% as the SRT was increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor (Table 6.8). The volatilized masses ($4.3 \times 10^{-8} - 4.8 \times 10^{-8} \text{ }\mu\text{g}$) and volatilization removal percentages (0.00008% – 0.00009%) were quite low at all SRTs for α -HBCDD in the anaerobic/aerobic sequential biological reactor (Table 6.8). The ANOVA (one-way) test statistics results showed that removal of α -HBCDD via sorption ($P = 0.112$, $\alpha = 0.05$, $F = 3.46$) and volatilization ($P = 0.115$, $\alpha = 0.05$, $F = 3.40$) were not important statistically in the anaerobic/aerobic sequential biological reactor at all SRTs. The total adsorbed masses of α -HBCDD to the anaerobic (from $0.0062 \text{ }\mu\text{g}$ to $0.0248 \text{ }\mu\text{g}$) and aerobic (from $0.0046 \text{ }\mu\text{g}$ to $0.0171 \text{ }\mu\text{g}$) sludge increased from $0.011 \text{ }\mu\text{g}$ ($0.0062 \text{ }\mu\text{g} + 0.0046 \text{ }\mu\text{g}$) to $0.042 \text{ }\mu\text{g}$ ($0.0248 \text{ }\mu\text{g} + 0.0171 \text{ }\mu\text{g}$) as the SRT increased from 5 days to 55 days, respectively (Table 6.8). The raise in the adsorbed masses also increased the α -HBCDD adsorption yields from 20.87% to 80.87% at SRTs from 5 days to 55 days, respectively (Table 6.8). As a result, adsorption was found to be statistically important for the removal of α -HBCDD in

the anaerobic/aerobic sequential biological reactor at all SRTs ($P = 0.0004$, $\alpha = 0.05$, $F = 13.42$). α -HBCDD is a hydrophobic micropollutant with its low water solubility ($2.089 \times 10^{-5} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 7.74$) and low Henry's Law constant ($1.72 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$) properties. Based on these properties α -HBCDD was biodegraded with low yields since the bacteria can not metabolise effectively this micropollutant at all SRTs. As a result, adsorption plays an important role for the removal of α -HBCDD at all SRTs.

Our results were in accordance with the literature showing that α -HBCDD is considered to be not readily biodegradable (18.26%) but highly adsorbed (80.87%) onto the sludge in the anaerobic/aerobic sequential biological reactor system at 55 days SRT due to its physicochemical properties such as low water solubility ($2.089 \times 10^{-5} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 7.74$) and low Henry's Law constant ($1.72 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$) (Figure 6.8) (TemaNord, 2008).

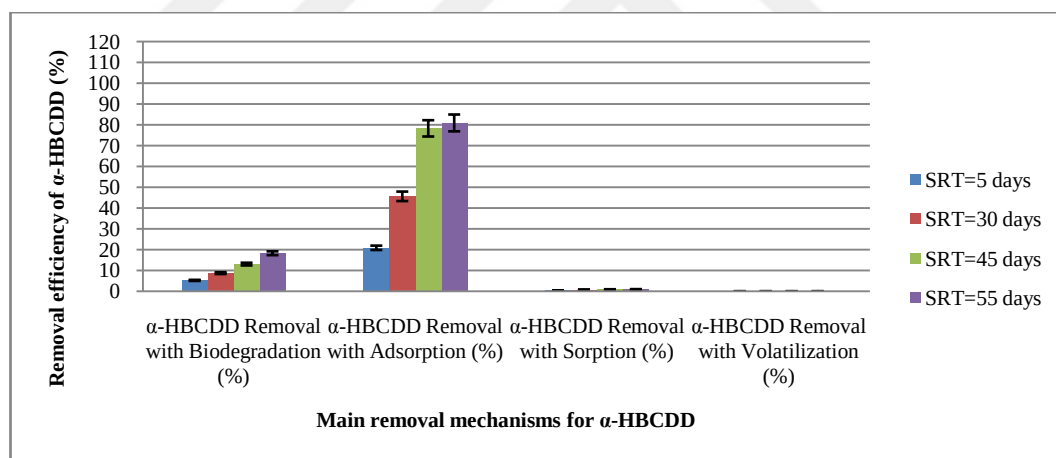


Figure 6.8 The removal efficiencies of α -HBCDD with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.10 Total Pentabromoethylbenzene (PBEB) removals

6.1.10.1 Total PBEB Removals in Anaerobic Biological Reactor

In the anaerobic reactor, the maximum PBEB removal efficiency was calculated as 2.7% with a PBEB effluent of 3.19 ng L^{-1} at a PBEB influent of 3.28 ng L^{-1} at 5 days SRT (Table 6.9). The maximum PBEB removal efficiency was achieved as 3.8% at 30 days SRT with a PBEB effluent of 3.15 ng L^{-1} for a PBEB influent of 3.28 ng L^{-1} in the anaerobic reactor (Table 6.9). After 45 days SRT operation, the maximum PBEB removal efficiency was determined as 5.8% with a PBEB effluent of 3.09 ng L^{-1} for a PBEB influent of 3.28 ng L^{-1} in the anaerobic reactor (Table 6.9). When the SRT was increased to 55 days, the maximum PBEB removal efficiency was obtained as 7.6% with a PBEB effluent of 3.03 ng L^{-1} for a PBEB influent of 3.28 ng L^{-1} in the anaerobic reactor (Table 6.9).

Table 6.9 PBEB and its metabolite (Bromomethyl)benzene (BMB) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent PBEB (ng L ⁻¹)	Effluent PBEB (ng L ⁻¹)	metabolite of PBEB namely BMB			Removed PBEB (ng L ⁻¹)	PBEB Rem. Eff. (%)	Influent PBEB (ng L ⁻¹)	Effluent PBEB (ng L ⁻¹)	metabolite of PBEB namely BMB			Removed PBEB (ng L ⁻¹)	PBEB Rem. Eff. (%)
			Influent BMB (ng L ⁻¹)	Effluent BMB (ng L ⁻¹)	BMB Rem. Eff. (%)					Influent BMB (ng L ⁻¹)	Effluent BMB (ng L ⁻¹)	BMB Rem. Eff. (%)		
5	3.28 $\pm$ 0.02	3.19 $\pm$ 0.02	0.00 $\pm$ 0.02	0.421 $\pm$ 0.02	0.00 $\pm$ 0.5	0.089 $\pm$ 0.02	2.7 $\pm$ 0.5	3.19 $\pm$ 0.02	3.06 $\pm$ 0.02	0.421 $\pm$ 0.02	0.327 $\pm$ 0.02	22.3 $\pm$ 0.5	0.134 $\pm$ 0.02	4.2 $\pm$ 0.5
30	3.28 $\pm$ 0.02	3.15 $\pm$ 0.02	0.00 $\pm$ 0.02	0.404 $\pm$ 0.02	0.00 $\pm$ 0.5	0.126 $\pm$ 0.02	3.8 $\pm$ 0.5	3.15 $\pm$ 0.02	2.95 $\pm$ 0.02	0.404 $\pm$ 0.02	0.266 $\pm$ 0.02	34.2 $\pm$ 0.5	0.208 $\pm$ 0.02	6.6 $\pm$ 0.5
45	3.28 $\pm$ 0.02	3.09 $\pm$ 0.02	0.00 $\pm$ 0.02	0.381 $\pm$ 0.02	0.00 $\pm$ 0.5	0.189 $\pm$ 0.02	5.8 $\pm$ 0.5	3.09 $\pm$ 0.02	2.80 $\pm$ 0.02	0.381 $\pm$ 0.02	0.230 $\pm$ 0.02	39.6 $\pm$ 0.5	0.295 $\pm$ 0.02	9.5 $\pm$ 0.5
55	3.28 $\pm$ 0.02	3.03 $\pm$ 0.02	0.00 $\pm$ 0.02	0.332 $\pm$ 0.02	0.00 $\pm$ 0.5	0.248 $\pm$ 0.02	7.6 $\pm$ 0.5	3.03 $\pm$ 0.02	2.66 $\pm$ 0.02	0.332 $\pm$ 0.02	0.115 $\pm$ 0.02	65.4 $\pm$ 0.5	0.377 $\pm$ 0.02	12.4 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent PBEB (ng L ⁻¹)	Effluent PBEB (ng L ⁻¹)	metabolite of PBEB namely BMB			Removed PBEB (ng L ⁻¹)	PBEB Rem. Eff. (%)
			Influent BMB (ng L ⁻¹)	Effluent BMB (ng L ⁻¹)	BMB Rem. Eff. (%)		
5	3.28 $\pm$ 0.02	3.06 $\pm$ 0.02	0.421 $\pm$ 0.02	0.327 $\pm$ 0.02	22.3 $\pm$ 0.5	0.22 $\pm$ 0.02	6.8 $\pm$ 0.5
30	3.28 $\pm$ 0.02	2.95 $\pm$ 0.02	0.404 $\pm$ 0.02	0.266 $\pm$ 0.02	34.2 $\pm$ 0.5	0.33 $\pm$ 0.02	10.2 $\pm$ 0.5
45	3.28 $\pm$ 0.02	2.80 $\pm$ 0.02	0.381 $\pm$ 0.02	0.230 $\pm$ 0.02	39.6 $\pm$ 0.5	0.48 $\pm$ 0.02	14.8 $\pm$ 0.5
55	3.28 $\pm$ 0.02	2.66 $\pm$ 0.02	0.332 $\pm$ 0.02	0.115 $\pm$ 0.02	65.4 $\pm$ 0.5	0.63 $\pm$ 0.02	19.1 $\pm$ 0.5

PBEB removal efficiency was found as 2.7% and 7.6% at 5 days and 55 days SRTs, respectively in the anaerobic reactor (Table 6.9). The relationship between PBEB yields and SRTs was not found to be important statistically according to the ANOVA (one-way) statistical analysis results ($P = 0.057$, $\alpha = 0.05$, $F = 5.53$) at all SRTs in the anaerobic reactor.

In the anaerobic reactor, the presence of (Bromomethyl)benzene (BMB) which is the main metabolite of PBEB was monitored in the effluents of the anaerobic reactor at all SRTs. Previous researchers supported that PBEB was reductively debrominated to BMB under anaerobic conditions (Agüera, Martínez Bueno, & Fernández-Alba, 2013). BMB has a log K_{OW} value (2.88) between 2.5 and 4.0 and accepted as a moderately hydrophobic micropollutant. Also BMB has higher solubility value ($1.95 \times 10^{-3} \text{ g L}^{-1}$) than PBEB ($2.90 \times 10^{-7} \text{ g L}^{-1}$) in water. The effluent concentrations of BMB were determined as 0.421, 0.404, 0.381 and 0.332 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.9).

6.1.10.2 Total PBEB Removals in Aerobic Biological Reactor

The maximum PBEB removal efficiency of the aerobic biological reactor was found as 4.2% with a PBEB effluent of 3.06 ng L^{-1} at a PBEB influent of 3.19 ng L^{-1} at 5 days SRT (Table 6.9). At 30 days SRT, the maximum PBEB removal efficiency increased slightly to 6.6% with a PBEB effluent of 2.95 ng L^{-1} for a PBEB influent of 3.15 ng L^{-1} in the aerobic reactor (Table 6.9). At 45 days SRT, in the aerobic reactor, the maximum PBEB removal efficiency was found as 9.5% with a PBEB effluent of 2.80 ng L^{-1} for a PBEB influent of 3.09 ng L^{-1} (Table 6.9). For the maximum SRT of 55 days, the maximum PBEB removal efficiency was determined as 12.4% with a PBEB effluent of 2.66 ng L^{-1} for a PBEB influent of 3.03 ng L^{-1} in the aerobic reactor (Table 6.9).

Total removal of PBEB was higher in the aerobic reactor (12.4%) than the anaerobic reactor (7.6%) at 5 days of SRT (Table 6.9). The low removals of PBEB in both reactors showed that this micropollutant is partially resistant to biodegradation

due its physicochemical properties (low water solubility = 2.90×10^{-7} g L⁻¹ and high octanol/water partition coefficient = 7.48) in both reactors.

In the aerobic reactor, PBEB removal efficiency was determined as 4.2% and 12.4% at SRTs changing from 5 days to 55 days, respectively (Table 6.9). The regression between PBEB yields and SRTs was insignificant according to the ANOVA (one-way) statistical analysis results ($P = 0.059$, $\alpha = 0.05$, $F = 5.38$). These results proved that PBEB could not be treated effectively biologically in the aerobic reactor at all SRTs.

0.421, 0.404, 0.381 and 0.332 ng L⁻¹ effluent BMB concentrations were measured in the anaerobic reactor at 5, 30, 45 and 55 days SRTs, respectively and they were occurred from the reductive dehalogenation reactions during the anaerobic treatment (Table 6.9). The effluent concentrations of BMB were found as 0.327, 0.266, 0.230 and 0.115 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor effluents (Table 6.9). Therefore, in the aerobic step 22.3%, 34.2%, 39.6% and 65.4% BMB removal efficiencies were achieved at 5, 30, 45 and 55 days SRTs in the aerobic reactor (Table 6.9). The increase in the SRTs from 5 days to 55 days affected positively the removal efficiencies of BMB from 22.3% to 65.4%, respectively in the aerobic reactor (Table 6.9). The aerobic reactor showed an important contribution to the removal of BMB remaining from the anaerobic reactor and the ANOVA (one-way) test statistics results supported the linear relationship between BMB yields and SRTs and the correlation is significant ($R^2 = 0.92$, $P = 0.006$, $\alpha = 0.05$, $F = 17.31$).

6.1.10.3 Total PBEB Removals in Anaerobic/Aerobic Sequential Biological Reactor System

For 5 days SRT, the maximum PBEB removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 6.8% with a PBEB effluent of 3.06 ng L⁻¹ at a PBEB influent of 3.28 ng L⁻¹ (Table 6.9). The maximum PBEB removal efficiency was found as 10.2% with a PBEB effluent of 2.95 ng L⁻¹ for a PBEB influent of 3.28 ng L⁻¹ at 30 days SRT in the anaerobic/aerobic sequential

biological reactor system (Table 6.9). The maximum PBEB removal efficiency was calculated as 14.8% with a PBEB effluent of 2.80 ng L^{-1} for a PBEB influent of 3.28 ng L^{-1} for 45 days SRT operation in the anaerobic/aerobic sequential (Table 6.9). At the highest SRT of 55 days, the anaerobic/aerobic sequential biological reactor achieved 19.1% of maximum PBEB removal efficiency with a PBEB effluent of 2.66 ng L^{-1} for a PBEB influent of 3.28 ng L^{-1} (Table 6.9).

The influent concentrations of BMB were found as 0.421, 0.404, 0.381 and 0.332 ng L^{-1} while the effluent concentrations of BMB were obtained as 0.327, 0.266, 0.230 and 0.115 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.9). The anaerobic/aerobic sequential biological reactor system obtained 22.3%, 34.2%, 39.6% and 65.4% removal efficiencies for BMB at 5, 30 45 and 55 days SRTs, respectively (Table 6.9). BMB removal efficiency increased with the increasing SRT and the maximum BMB yield was measured as 65.4% in the anaerobic/aerobic sequential biological reactor system at the highest SRT of 55 days (Table 6.9).

6.1.10.4 Removal Mechanisms of PBEB in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegraded, adsorbed, sorbed and volatilized PBEB masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.10).

Table 6.10 The total removal percentages for PBEB throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	0.22	0.039	1.75	0.0006	0.025	0.000	0.000	2.71	21.34	0.30	0.00
30	0.32	0.091	4.11	0.0012	0.054	0.000	0.000	3.84	50.12	0.66	0.00
45	0.47	0.150	6.74	0.0015	0.066	0.000	0.000	5.76	82.20	0.80	0.00
55	0.62	0.156	7.02	0.0017	0.077	0.000	0.000	7.56	85.56	0.94	0.00
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	0.27	0.082	1.23	0.001	0.018	0.000	0.000	4.20	19.27	0.28	0.00
30	0.42	0.165	2.47	0.003	0.038	0.000	0.000	6.59	39.16	0.60	0.00
45	0.59	0.284	4.26	0.003	0.046	0.000	0.000	9.54	68.91	0.74	0.00
55	0.75	0.350	4.80	0.004	0.054	0.000	0.000	12.43	79.16	0.89	0.00
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	1.00	--	2.98	--	0.04	--	0.000	6.80	20.19	0.29	0.00
30	1.50	--	6.58	--	0.09	--	0.000	10.18	44.58	0.62	0.00
45	2.18	--	11.00	--	0.11	--	0.000	14.76	74.53	0.76	0.00
55	2.81	--	11.82	--	0.13	--	0.000	19.05	80.05	0.89	0.00

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.10.4.1 *Removed Masses and Removal Efficiencies of PBEB.* An example for the calculations relevant to the removed masses and the removal efficiencies of PBEB in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.61 to 6.78, respectively at a SRT of 5 days (Table 6.10).

The biodegraded masses of PBEB in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were shown in Equations 6.61, 6.62 and 6.63, respectively at 5 days SRT (Table 6.10).

$$M_{\text{BIO,Anaerobic}} = (0.09 \text{ ng L}^{-1}) \times (2.5 \text{ L}) = 0.22 \text{ ng} \quad (6.61)$$

$$M_{\text{BIO,Aerobic}} = (0.13 \text{ ng L}^{-1}) \times (2.0 \text{ L}) = 0.27 \text{ ng} \quad (6.62)$$

$$M_{\text{BIO,Sequential}} = (0.22 \text{ ng L}^{-1}) \times (4.5 \text{ L}) = 1.00 \text{ ng} \quad (6.63)$$

The biodegradation removal efficiencies of PBEB were determined according to the Equation 6.64, 6.65 and 6.66 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.10).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (0.22 \times 100) / (3.28 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 2.71\% \quad (6.64)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (0.27 \times 100) / (3.19 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 4.20\% \quad (6.65)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (1.00 \times 100) / (3.28 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 6.80\% \quad (6.66)$$

The adsorbed masses onto the anaerobic and aerobic biological sludges of PBEB were determined according to the Equation 6.67 and Equation 6.68, respectively while the total adsorbed mass for PBEB was calculated in Equation 6.69 for the anaerobic/aerobic sequential biological reactor system at 5 days SRT (Table 6.10).

$$M_{\text{ADS,Anaerobic}} = [(0.039 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 1.75 \text{ ng} \quad (6.67)$$

$$M_{\text{ADS,Aerobic}} = [(0.082 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 1.23 \text{ ng} \quad (6.68)$$

$$M_{\text{ADS,Sequential}} = 1.75 + 1.23 = 2.98 \text{ ng} \quad (6.69)$$

The adsorption removal efficiencies of PBEB were calculated according to the Equation 6.70, 6.71 and 6.72 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.10).

$$\text{Adsorption (\%)}_{\text{Anaerobic}} = (1.75 \times 100)/(3.28 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 21.34\% \quad (6.70)$$

$$\text{Adsorption (\%)}_{\text{Aerobic}} = (1.23 \times 100)/(3.19 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 19.27\% \quad (6.71)$$

$$\text{Adsorption (\%)}_{\text{Sequential}} = (2.98 \times 100)/(3.28 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 20.19\% \quad (6.72)$$

The sorbed masses into the anaerobic and aerobic biological sludges of PBEB were calculated in Equation 6.73 and Equation 6.74, respectively while the total sorbed mass for PBEB was determined in Equation 6.75 for the anaerobic/aerobic sequential biological reactor system at 5 days SRT (Table 6.10).

$$M_{\text{SORP,Anaerobic}} = [(0.0006 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 0.025 \text{ ng} \quad (6.73)$$

$$M_{\text{SORP,Aerobic}} = [(0.001 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 0.018 \text{ ng} \quad (6.74)$$

$$M_{\text{SORP,Sequential}} = 0.025 + 0.018 = 0.04 \text{ ng} \quad (6.75)$$

The sorption removal efficiencies of PBEB were calculated according to the Equation 6.76, 6.77 and 6.78 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.10).

$$\text{Sorption (\%)}_{\text{Anaerobic}} = (0.025 \times 100)/(3.28 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.30\% \quad (6.76)$$

$$\text{Sorption (\%)}_{\text{Aerobic}} = (0.018 \times 100)/(3.19 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.28\% \quad (6.77)$$

$$\text{Sorption (\%)}_{\text{Sequential}} = (0.04 \times 100)/(3.28 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.29\% \quad (6.78)$$

PUF disks were used in order to determine the volatilization masses. No PBEB concentrations (0.00 ng L^{-1}) were determined after 5, 30, 45 and 55 days of SRTs in the PUF disks under anaerobic and aerobic conditions, respectively. Because of the concentrations were measured as zero (0.00 ng L^{-1}), volatilization masses ($(0.00 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00 \text{ ng}$) and volatilization removal efficiencies

for PBEB calculated zero in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days SRTs (Table 6.10).

6.1.10.4.2 Removed Masses and Removal Efficiencies of PBEB in Anaerobic Reactor. The biodegraded PBEB masses increased from 0.22 ng to 0.62 ng as the SRT was increased from 5 up to 55 days in the anaerobic reactor (Table 6.10). The biodegradation percentages of PBEB in the anaerobic reactor also increased from 2.71% to 7.56% with the increasing of SRTs from 5 days up to 55 days (Table 6.10). The anaerobic bacteria can co-metabolized only 7.56% of PBEB together COD and sCOD at the highest SRT of 55 days. PBEB can be used as co-metabolite together COD and its components (sCOD). Co-metabolism describes the ability of microorganisms to remove non-growth supporting substrates (secondary substrate), typically in the presence of a growth supporting substrate (primary substrate), in other words, a simultaneous degradation of two compounds (Peng & Jia, 2013). Although the influent COD (950 mg L^{-1}) and sCOD (850 mg L^{-1}) concentrations as primary substrates were high (Table 5.1), the influent concentration of 3.28 ng L^{-1} for PBEB as the electron acceptor was too low to sustain the growth of dehalogenation performing bacteria at 55 days SRT (Table 5.1), therefore, the biodegradation efficiency did not go further than 7.56% for PBEB as a secondary substrate (Table 6.10). Having low water solubility value ($2.90 \times 10^{-7} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 7.48$) and low Henry's Law constant ($7.92 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) of PBEB makes it quite hydrophobic in the anaerobic reactor and can not be effectively biodegraded at 55 days SRT by the anaerobic bacteria in this study. The removal of PBEB with biodegradation in the anaerobic reactor was not found to be significant at all SRTs according to the ANOVA (one-way) test statistic results ($P = 0.057$, $\alpha = 0.05$, $F = 5.53$). The sorbed masses (0.025 – 0.077 ng) and the sorption removal percentages also were low (0.30% – 0.94%) for PBEB at all SRTs in the anaerobic reactor (Table 6.10). The volatilized masses and the volatilization percentages were measured as zero for PBEB at all SRTs in the anaerobic reactor (Table 6.10). The ANOVA (one-way) test statistics results showed that removal of PBEB via sorption ($P = 0.076$, $\alpha = 0.05$, $F = 4.60$) and volatilization ($P = 0.078$, $\alpha = 0.05$, $F = 4.52$) were not significant in the anaerobic reactor. The adsorption of PBEB

to the anaerobic sludge was found to be high in the anaerobic reactor since the adsorbed PBEB masses varies between 1.75 ng and 7.02 ng (Table 6.10). The adsorbed PBEB percentages increased from 21.34% to 85.56% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.10). It is important to note that the adsorption has an important effect on the removal of PBEB in the anaerobic reactor at all SRTs ($P = 0.0003$, $\alpha = 0.05$, $F = 14.71$). PBEB is a quite hydrophobic micropollutant with its relatively low water solubility value ($2.90 \times 10^{-7} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 7.48$) and low Henry's Law constant ($7.92 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$). These physicochemical properties makes PBEB easily sorb on the anaerobic sludge granules due its hydrophobic structure. As a result, PBEB can be effectively removed (85.56%) by adsorption in the anaerobic reactor at 55 days SRT.

6.1.10.4.3 Removed Masses and Removal Efficiencies of PBEB in Aerobic Reactor. In the aerobic reactor, the biodegraded PBEB masses increased from 0.27 ng to 0.75 ng resulting in PBEB biodegradation removal percentages of 4.20% and 12.43% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.10). The maximum biodegradation yield of PBEB was obtained as 12.43% at the highest SRT of 55 days in the aerobic reactor (Table 6.10). The maximum biodegradation removal efficiency of PBEB (12.43%) at 55 days SRT in the aerobic reactor found in this study was in accordance with the other results previously obtained by other researchers. Shen, Smyth, Droste, & Delâge (2018) studied the aerobic treatability of PBEB and obtained less than 30% of PBEB removal efficiency in an activated sludge process treating municipal wastewater for an initial PBEB concentration of 0.002 ng L^{-1} with 2000 mg L^{-1} MLSS concentration at 10 h HRT and at 9 days SRT (Shen et al., 2018). The removal of PBEB via biodegradation was not found to be important according to the ANOVA (one-way) test statistic results at all SRTs in the aerobic reactor ($P = 0.060$, $\alpha = 0.05$, $F = 5.38$). The sorbed PBEB masses increased from 0.018 ng to 0.054 ng resulting in PBEB sorption removal percentages of 0.28% and 0.89% depending on the SRT increase from 5 days to 55 days, respectively in the aerobic reactor (Table 6.10). The volatilized masses and volatilization removal efficiencies were measured as zero for PBEB at all SRTs in

the aerobic reactor (Table 6.10). The ANOVA (one-way) test statistics results showed that removal of PBEB via sorption ($P = 0.051$, $\alpha = 0.05$, $F = 5.88$) and volatilization ($P = 0.053$, $\alpha = 0.05$, $F = 5.79$) were not meaningful statistically in the aerobic reactor. The adsorbed masses of PBEB to the aerobic sludge increased from 1.23 ng to 4.80 ng as the SRT increased from 5 days to 55 days, respectively (Table 6.10). This attributed to the adsorption yields of PBEB from 19.27% to 79.16% at SRTs ranging from 5 days to 55 days, respectively (Table 6.10). Because of PBEB is a quite hydrophobic micropollutant with its physicochemical properties like low water water solubility ($2.90 \times 10^{-7} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 7.48$) and low Henry's Law constant ($7.92 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$), PBEB has resistance to extensive biodegradation and adsorption has a significant contribution to the removal of PBEB in the aerobic reactor at all SRTs ($P = 0.0005$, $\alpha = 0.05$, $F = 12.67$).

Removal of PBEB via biodegradation was slightly higher in the aerobic reactor (12.43%) than the anaerobic reactor (7.56%) at 55 days SRT because the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.10). The removal of PBEB via adsorption was higher in the anaerobic reactor (85.56%) than the aerobic reactor (79.16%) at 55 days of SRT (Table 6.10). This could be attributed to the better adsorption conditions for PBEB in the anaerobic reactor than the aerobic reactor. PBEB found more sludge surface to be adsorbed in the anaerobic reactor than the aerobic reactor due to the anaerobic reactor had much more MLVSS concentration (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.10.4.4 Removed Masses and Removal Efficiencies of PBEB in Anaerobic/Aerobic Sequential Biological Reactor System. As the SRT increased from 5 days to 55 days, the total biodegraded masses of PBEB increased from 1.00 ng to 2.81 ng resulting in PBEB biodegradation removal percentages of 6.80% and 19.05%, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.10). The biodegradation yield of PBEB reached the highest level as 19.05% at 55 days SRT in the anaerobic/aerobic sequentials (Table 6.10). The removal of

PBEB via biodegradation was insignificant at all SRTs in the anaerobic/aerobic sequential biological reactor according to the ANOVA (one-way) test statistic results ($P = 0.109$, $\alpha = 0.05$, $F = 3.53$). The sorbed masses were measured between 0.04 ng and 0.13 ng at SRTs between 5 days and 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.10). The sorption removal percentages of PBEB were calculated between 0.29% and 0.89% at SRTs between 5 days and 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.10). The volatilized masses and volatilization removal percentages were measured as zero for PBEB at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.10). The ANOVA (one-way) test statistics results showed that removal of PBEB via sorption ($P = 0.102$, $\alpha = 0.05$, $F = 3.71$) and volatilization ($P = 0.105$, $\alpha = 0.05$, $F = 3.65$) were insignificant in the anaerobic/aerobic sequential biological reactor system. The adsorbed PBEB masses to the anaerobic (from 1.75 ng to 7.02 ng) and aerobic (from 1.23 ng to 4.80 ng) sludge increased from 2.98 ng (1.75 ng + 1.23 ng) to 11.82 ng (7.02 ng + 4.80 ng) as the SRT increased from 5 days to 55 days, respectively (Table 6.10). The raise in the adsorbed masses also increased the adsorption yields of PBEB from 20.19% to 80.05% at SRTs between 5 days and 55 days, respectively (Table 6.10). It can be concluded that the adsorption was an important mechanism for the removal of PBEB in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.0004$, $\alpha = 0.05$, $F = 13.29$) because PBEB is a quite hydrophobic micropollutant and shows a tendency to sorb on sludge due to its physicochemical properties (low water water solubility = 2.90×10^{-7} g L⁻¹, high log $K_{OW} = 7.48$ and low Henry's Law constant = 7.92×10^{-5} atm m³ mol⁻¹).

The adsorption degree of a micropollutant can be indicated by the octanol-water partition coefficient (log K_{OW}), a measure for hydrophobicity (Wells, 2006). The high octanol-water partition coefficient (log $K_{OW} = 7.48$), low water water solubility (2.90×10^{-7} g L⁻¹) and low Henry's Law constant (7.92×10^{-5} atm m³ mol⁻¹) of PBEB indicates high hydrophobicity or adsorption to sludge (Shen et al., 2018). The results from this study proved that PBEB can be effectively removed via adsorption (80.05%) and the contributon of the other mechanisms were not important such as

biodegradation (19.05%) and sorption (0.89%) or even negligible like volatilization (0.00%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Figure 6.9).

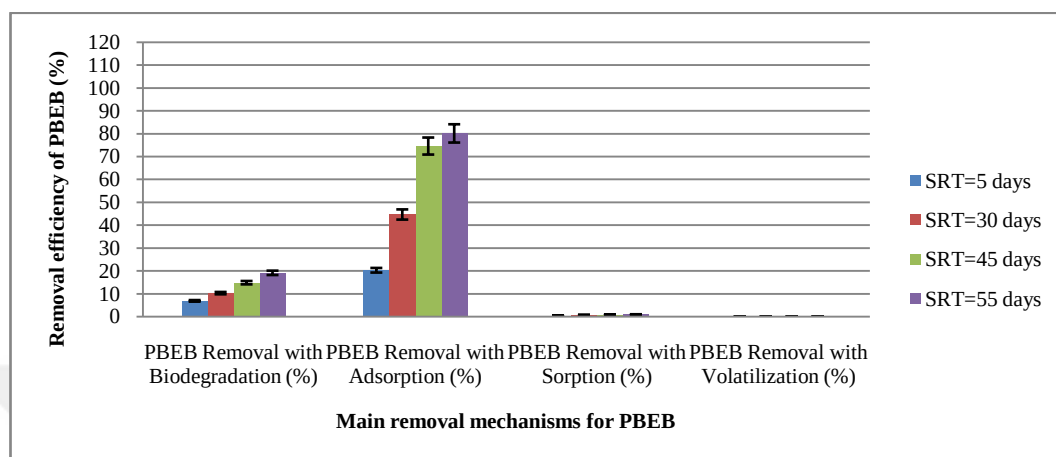


Figure 6.9 The removal efficiencies of PBEB with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.11 Total Pentabromotoluene (PBT) removals

6.1.11.1 Total PBT Removals in Anaerobic Biological Reactor

At the beginning of the study, the maximum PBT removal efficiency of the anaerobic reactor was obtained as 3.5% with a PBT effluent of 2.23 ng L^{-1} at a PBT influent of 2.31 ng L^{-1} at 5 days SRT (Table 6.11). The maximum PBT removal efficiency was determined as 4.8% with a PBT effluent of 2.20 ng L^{-1} for a PBT influent of 2.31 ng L^{-1} at 30 days SRT in the anaerobic reactor (Table 6.11). For 45 days SRT operation, the maximum PBT removal efficiency was found as 6.3% with a PBT effluent of 2.17 ng L^{-1} for a PBT influent of 2.31 ng L^{-1} in the anaerobic reactor (Table 6.11). After 55 days of SRT operation, the maximum PBT removal efficiency was achieved as 7.9% with a PBT effluent of 2.13 ng L^{-1} for a PBT influent of 2.31 ng L^{-1} in the anaerobic reactor (Table 6.11).

Table 6.11 PBT and its metabolite 4-Methylbromobenzene (4-MBB) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent PBT (ng L ⁻¹)	Effluent PBT (ng L ⁻¹)	metabolite of PBT namely 4-MBB			Removed PBT (ng L ⁻¹)	PBT Rem. Eff. (%)	Influent PBT (ng L ⁻¹)	Effluent PBT (ng L ⁻¹)	metabolite of PBT namely 4-MBB			Removed PBT (ng L ⁻¹)	PBT Rem. Eff. (%)
			Influent 4-MBB (ng L ⁻¹)	Effluent 4-MBB (ng L ⁻¹)	4-MBB Rem. Eff. (%)					Influent 4-MBB (ng L ⁻¹)	Effluent 4-MBB (ng L ⁻¹)	4-MBB Rem. Eff. (%)		
5	2.31 $\pm$ 0.02	2.23 $\pm$ 0.02	0.00 $\pm$ 0.02	0.230 $\pm$ 0.02	0.00 $\pm$ 0.5	0.08 $\pm$ 0.02	3.5 $\pm$ 0.5	2.23 $\pm$ 0.02	2.11 $\pm$ 0.02	0.230 $\pm$ 0.02	0.171 $\pm$ 0.02	25.7 $\pm$ 0.5	0.12 $\pm$ 0.02	5.4 $\pm$ 0.5
30	2.31 $\pm$ 0.02	2.20 $\pm$ 0.02	0.00 $\pm$ 0.02	0.200 $\pm$ 0.02	0.00 $\pm$ 0.5	0.11 $\pm$ 0.02	4.8 $\pm$ 0.5	2.20 $\pm$ 0.02	2.04 $\pm$ 0.02	0.200 $\pm$ 0.02	0.131 $\pm$ 0.02	34.5 $\pm$ 0.5	0.16 $\pm$ 0.02	7.3 $\pm$ 0.5
45	2.31 $\pm$ 0.02	2.17 $\pm$ 0.02	0.00 $\pm$ 0.02	0.195 $\pm$ 0.02	0.00 $\pm$ 0.5	0.15 $\pm$ 0.02	6.3 $\pm$ 0.5	2.17 $\pm$ 0.02	1.96 $\pm$ 0.02	0.195 $\pm$ 0.02	0.117 $\pm$ 0.02	40.0 $\pm$ 0.5	0.21 $\pm$ 0.02	9.7 $\pm$ 0.5
55	2.31 $\pm$ 0.02	2.13 $\pm$ 0.02	0.00 $\pm$ 0.02	0.188 $\pm$ 0.02	0.00 $\pm$ 0.5	0.18 $\pm$ 0.02	7.9 $\pm$ 0.5	2.13 $\pm$ 0.02	1.86 $\pm$ 0.02	0.188 $\pm$ 0.02	0.064 $\pm$ 0.02	66.0 $\pm$ 0.5	0.27 $\pm$ 0.02	12.7 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent PBT (ng L ⁻¹)	Effluent PBT (ng L ⁻¹)	metabolite of PBT namely 4-MBB			Removed PBT (ng L ⁻¹)	PBT Rem. Eff. (%)
			Influent 4-MBB (ng L ⁻¹)	Effluent 4-MBB (ng L ⁻¹)	4- MBB Rem. Eff. (%)		
5	2.31 $\pm$ 0.02	2.11 $\pm$ 0.02	0.230 $\pm$ 0.02	0.08 $\pm$ 0.02	25.7 $\pm$ 0.5	0.20 $\pm$ 0.02	8.7 $\pm$ 0.5
30	2.31 $\pm$ 0.02	2.04 $\pm$ 0.02	0.200 $\pm$ 0.02	0.11 $\pm$ 0.02	34.5 $\pm$ 0.5	0.27 $\pm$ 0.02	11.7 $\pm$ 0.5
45	2.31 $\pm$ 0.02	1.96 $\pm$ 0.02	0.195 $\pm$ 0.02	0.15 $\pm$ 0.02	40.0 $\pm$ 0.5	0.36 $\pm$ 0.02	15.4 $\pm$ 0.5
55	2.31 $\pm$ 0.02	1.86 $\pm$ 0.02	0.188 $\pm$ 0.02	0.18 $\pm$ 0.02	66.0 $\pm$ 0.5	0.45 $\pm$ 0.02	19.6 $\pm$ 0.5

PBT removal efficiency changed in a range between 3.5% and 7.9% as the SRT was increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.11). The ANOVA (one-way) statistical analysis results showed that the relationship between PBT yields and SRTs was not meaningful statistically in the anaerobic reactor ($P = 0.061$, $\alpha = 0.05$, $F = 5.29$).

According to the literature, PBT is reductively debrominated to 4-MBB under anaerobic conditions (Agüera et al., 2013). 4-MBB is a moderately hydrophobic micropollutant with its $\log K_{OW}$ value (3.43) and has higher water solubility ($7.29 \times 10^{-2} \text{ g L}^{-1}$) in the comparison with PBT ($9.35 \times 10^{-7} \text{ g L}^{-1}$). Therefore, the presence of 4-Methylbromobenzene (4-MBB) which is the main metabolite of PBT was monitored in the effluents of the anaerobic reactor at all SRTs. The effluent concentrations of 4-MBB were determined as 0.230, 0.200, 0.195 and 0.188 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.11).

6.1.11.2 Total PBT Removals in Aerobic Biological Reactor

The maximum PBT removal efficiency of the aerobic biological reactor was obtained as 5.4% with a PBT effluent of 2.11 ng L^{-1} at a PBT influent of 2.23 ng L^{-1} at 5 days SRT (Table 6.11). When the SRT was increased to 30 days, the maximum PBT removal efficiency was found as 7.3% with a PBT effluent of 2.04 ng L^{-1} for a PBT influent of 2.20 ng L^{-1} in the aerobic reactor (Table 6.11). In the aerobic reactor, the maximum PBT removal efficiency was measured as 9.7% with a PBT effluent of 1.96 ng L^{-1} for a PBT influent of 2.17 ng L^{-1} for 45 days SRT operation (Table 6.11). At the highest SRT of 55 days, the maximum PBT removal efficiency was obtained as 12.7% with a PBT effluent of 1.86 ng L^{-1} for a PBT influent of 2.13 ng L^{-1} at 55 days SRT in the aerobic reactor (Table 6.11).

Total removal yields of PBT were low both in the anaerobic (7.9%) and aerobic (12.7%) reactors at 55 days SRT (Table 6.11) because the physicochemical properties of PBT such as low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$) and high

hydrophobicity (octanol/water partition coefficient = 6.99) makes PBT a partially biodegradable micropollutant in both reactors.

PBT removal efficiencies increased from 5.4% to 12.7% as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.11). However, the raise in PBT yields with increasing SRTs was not found to be important statistically in the aerobic reactor according to the ANOVA (one-way) statistical analysis results ($P = 0.063$, $\alpha = 0.05$, $F = 5.17$). It can be concluded that the PBEB could not biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the 4-MBB remaining from the anaerobic reactor. The effluent concentrations of the anaerobic reactor were the influent concentrations of the aerobic reactor and they were detected as 0.230, 0.200, 0.195 and 0.188 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor influents (Table 6.11). The effluent concentrations of 4-MBB were found as 0.171, 0.131, 0.117 and 0.064 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor effluents (Table 6.11). 4-MBB removal efficiencies were calculated as 25.7%, 34.5%, 40.0% and 66.0% at 5, 30, 45 and 55 days SRTs in the aerobic reactor (Table 6.11). There was a linear relationship between 4-MBB yields and SRTs and the aerobic reactor had significant contribution to the removal of 4-MBB remaining from the anaerobic reactor according to the ANOVA (one-way) test statistics results at all SRTs ($R^2 = 0.90$, $P = 0.004$, $\alpha = 0.05$, $F = 20.18$).

6.1.11.3 Total PBT Removals in Anaerobic/Aerobic Sequential Biological Reactor System

At 5 days SRT, the maximum PBT removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 8.7% with a PBT effluent of 2.11 ng L⁻¹ at a PBT influent of 2.31 ng L⁻¹ (Table 6.11). The maximum PBT removal efficiency was detected as 11.7% with a PBT effluent of 2.04 ng L⁻¹ for a PBT influent of 2.31 ng L⁻¹ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.11). For 45 days SRT operation, the maximum

PBT removal efficiency was found as 15.4% with a PBT effluent of 1.96 ng L^{-1} for a PBT influent of 2.31 ng L^{-1} anaerobic/aerobic sequential biological reactor system (Table 6.11). In the anaerobic/aerobic sequential biological reactor system, the maximum PBT removal efficiency was determined as 19.6% with a PBT effluent of 1.86 ng L^{-1} for a PBT influent of 2.31 ng L^{-1} for the highest SRT of 55 days (Table 6.11).

In the anaerobic/aerobic sequential biological reactor system, the influent concentrations of 4-MBB were determined as 0.230, 0.200, 0.195 and 0.188 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively (Table 6.11). For the anaerobic/aerobic sequential biological reactor system, the effluent 4-MBB concentrations were obtained as 0.171, 0.131, 0.117 and 0.064 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively (Table 6.11). The anaerobic/aerobic sequential biological reactor system achieved 25.7%, 34.5%, 40.0% and 66.0% removal efficiencies for 4-MBB at 5, 30, 45 and 55 days SRTs, respectively (Table 6.11). 4-MBB removal efficiency increased with the increasing SRT and the maximum 4-MBB yield was measured as 66.0% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.11).

6.1.11.4 Removal Mechanisms of PBT in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

In order to decide the main removal mechanism of PBT; biodegradation, sorption, adsorption and volatilization tests were performed. The biodegraded, adsorbed, sorbed and volatilized PBT masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.12).

Table 6.12 The total removal percentages for PBT throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	0.20	0.027	1.22	0.0004	0.019	0.000	0.000	3.46	21.13	0.33	0.00
30	0.28	0.063	2.85	0.0009	0.039	0.000	0.000	4.76	49.35	0.68	0.00
45	0.36	0.104	4.70	0.0011	0.050	0.000	0.000	6.28	81.39	0.87	0.00
55	0.46	0.109	4.92	0.0013	0.057	0.000	0.000	7.88	85.19	0.99	0.00
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	0.24	0.057	0.85	0.0009	0.013	0.000	0.000	5.38	19.06	0.29	0.00
30	0.32	0.114	1.71	0.0018	0.027	0.000	0.000	7.27	38.86	0.61	0.00
45	0.42	0.197	2.95	0.0022	0.033	0.000	0.000	9.70	68.13	0.76	0.00
55	0.54	0.223	3.35	0.0025	0.038	0.000	0.000	12.69	78.71	0.89	0.00
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	0.90	--	2.07	--	0.03	--	0.000	8.66	19.91	0.31	0.00
30	1.22	--	4.56	--	0.07	--	0.000	11.69	43.87	0.63	0.00
45	1.60	--	7.65	--	0.08	--	0.000	15.37	73.59	0.80	0.00
55	2.03	--	8.27	--	0.10	--	0.000	19.57	79.56	0.91	0.00

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.11.4.1 Removed Masses and Removal Efficiencies of PBT. An example for the calculations relevant to the removed masses and the removal efficiencies of PBT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.79 to 6.96, respectively at a SRT of 5 days (Table 6.12).

The biodegraded masses of PBT were calculated from Equations 6.79, 6.80 and 6.81 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.12).

$$M_{\text{BIO,Anaerobic}} = (0.08 \text{ ng L}^{-1}) \times (2.5 \text{ L}) = 0.20 \text{ ng} \quad (6.79)$$

$$M_{\text{BIO,Aerobic}} = (0.12 \text{ ng L}^{-1}) \times (2.0 \text{ L}) = 0.24 \text{ ng} \quad (6.80)$$

$$M_{\text{BIO,Sequential}} = (0.20 \text{ ng L}^{-1}) \times (4.5 \text{ L}) = 0.90 \text{ ng} \quad (6.81)$$

The biodegradation removal efficiencies for PBT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.82, 6.83 and 6.84, respectively at 5 days SRT (Table 6.12).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (0.20 \times 100)/(2.31 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 3.46\% \quad (6.82)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (0.24 \times 100)/(2.23 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 5.38\% \quad (6.83)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (0.90 \times 100)/(2.31 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 8.66\% \quad (6.84)$$

The adsorbed masses of PBT were calculated using Equation 6.85, 6.86 and 6.87 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.12).

$$M_{\text{ADS,Anaerobic}} = [(0.027 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 1.22 \text{ ng} \quad (6.85)$$

$$M_{\text{ADS,Aerobic}} = [(0.057 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 0.85 \text{ ng} \quad (6.86)$$

$$M_{\text{ADS,Sequential}} = 1.22 + 0.85 = 2.07 \text{ ng} \quad (6.87)$$

The total adsorption removal efficiencies of PBT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.88, 6.89 and 6.90, respectively at 5 days SRT (Table 6.12).

$$\text{Adsorption (\%)}_{\text{Anaerobic}} = (1.22 \times 100)/(2.31 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 21.13\% \quad (6.88)$$

$$\text{Adsorption (\%)}_{\text{Aerobic}} = (0.85 \times 100)/(2.23 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 19.06\% \quad (6.89)$$

$$\text{Adsorption (\%)}_{\text{Sequential}} = (2.07 \times 100)/(2.31 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 19.91\% \quad (6.90)$$

The sorbed masses into the anaerobic and aerobic biological sludges of PBT were calculated according to the Equation 6.91 and 6.92, respectively while the total sorbed mass for PBT in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.93 at 5 days SRT (Table 6.12).

$$M_{\text{SORP,Anaerobic}} = [(0.0004 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 0.019 \text{ ng} \quad (6.91)$$

$$M_{\text{SORP,Aerobic}} = [(0.0009 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 0.013 \text{ ng} \quad (6.92)$$

$$M_{\text{SORP,Sequential}} = 0.019 + 0.013 = 0.03 \text{ ng} \quad (6.93)$$

The total sorption removal efficiencies of PBT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.94, 6.95 and 6.96, respectively at 5 days SRT (Table 6.12).

$$\text{Sorption (\%)}_{\text{Anaerobic}} = (0.019 \times 100)/(2.31 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.33\% \quad (6.94)$$

$$\text{Sorption (\%)}_{\text{Aerobic}} = (0.013 \times 100)/(2.23 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.29\% \quad (6.95)$$

$$\text{Sorption (\%)}_{\text{Sequential}} = (0.03 \times 100)/(2.31 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.31\% \quad (6.96)$$

PUF disks were used in order to determine the volatilization masses. No PBT concentrations (0.00 ng L^{-1}) were determined after 5, 30, 45 and 55 days of SRTs in the PUF disks under anaerobic and aerobic conditions, respectively. Because of the concentrations were measured as zero (0.00 ng L^{-1}), volatilization masses ($(0.00 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00 \text{ ng}$) and volatilization removal efficiencies

for PBT calculated zero in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days SRTs (Table 6.12).

6.1.11.4.2 Removed Masses and Removal Efficiencies of PBT in Anaerobic Reactor. As is shown in Table 6.12 the biodegraded PBT masses increased from 0.20 ng to 0.46 ng as the SRT was increased from 5 up to 55 days in the anaerobic reactor. The biodegradation removal percentages of PBT also increased from 3.46% to 7.88% with the increasing of SRTs from 5 days up to 55 days (Table 6.12). PBT can be used as co-metabolite together COD and sCOD. PBT served as an electron acceptor in this co-metabolic process and was reductively debrominated during the anaerobic treatment. Although the influent COD (950 mg L^{-1}) and sCOD (850 mg L^{-1}) concentrations as primary substrates were high (Table 5.1), the influent concentration of 2.31 ng L^{-1} for PBT as the electron acceptor was too low to sustain the growth of dehalogenating bacteria at 55 days SRT (Table 5.1). Only 7.88% of PBT can be degraded with reductive dehalogenation where halogens acted as terminal acceptors of electrons during biodegradation process under anaerobic condition at 55 days SRT (Table 6.12). Therefore, this micropollutant is quite hydrophobic ($9.35 \times 10^{-7} \text{ g L}^{-1}$ of water solubility and $\log K_{OW}$ of 6.99) in the anaerobic reactor and can not be effectively biodegraded by the anaerobic bacteria (Peng et al., 2018). The ANOVA (one-way) test statistic results also proved that PBT can not be effectively removed via biodegradation in the anaerobic reactor at all SRTs ($P = 0.061$, $\alpha = 0.05$, $F = 5.29$). The sorbed masses of PBT were calculated between 0.019 ng and 0.057 ng at SRTs increasing from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.12). The sorption removal percentages of PBT were detected between 0.33% and 0.99% at SRTs varying from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.12). The volatilized masses and the volatilization removal percentages were measured as zero for PBT at all SRTs in the anaerobic reactor (Table 6.12). The ANOVA (one-way) test statistics results showed that removal of PBT via sorption ($P = 0.074$, $\alpha = 0.05$, $F = 4.66$) and volatilization ($P = 0.076$, $\alpha = 0.05$, $F = 4.58$) were not significant in the anaerobic reactor. The adsorbed masses of PBT to the anaerobic sludge were increased from 1.22 ng to 4.92 ng with the increasing adsorption removal percentages from 21.13% to 85.19% as the SRTs were increased from 5 to

55 days, respectively in the anaerobic reactor (Table 6.12). Because of the PBT was a hydrophobic micropollutant with its relatively low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$), low Henry's Law constant ($5.97 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) and high octanol/water partition coefficient ($\log K_{OW}$ of 6.99), the adsorption becomes an important removal mechanism for PBT at all SRTs in the anaerobic reactor. Also the ANOVA (one-way) test statistics results supported that the adsorption has a significant contribution to the removal of PBT in the anaerobic reactor at all SRTs ($P = 0.0003$, $\alpha = 0.05$, $F = 14.49$).

6.1.11.4.3 Removed Masses and Removal Efficiencies of PBT in Aerobic Reactor.

In the aerobic reactor, the biodegraded PBT masses increased from 0.24 ng to 0.54 ng resulting in PBT removal percentages of 5.38% and 12.69% depending on the SRT increase from 5 days to 55 days (Table 6.12). The maximum biodegradation yield of PBT (12.69%) was obtained at the highest SRT of 55 days (Table 6.12). Biodegradation could not play a major role on the removal of PBT during aerobic treatment, since the influent concentration of PBT in the aerobic reactor at different SRTs were too low to serve as a direct growth substrate (Table 5.1). Co-metabolic biodegradation mechanism allows only 12.69% of PBT removal at the highest SRT of 55 days (Table 6.12), because of this micropollutant is quite hydrophobic with its low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$) and high sorption capacity ($\log K_{OW} = 6.99$) (Grandclément et al., 2017). Besides, the removal of PBT via biodegradation was not found to be important according to the ANOVA (one-way) test statistic results at all SRTs in the aerobic reactor ($P = 0.063$, $\alpha = 0.05$, $F = 5.17$). The sorbed masses were measured as 0.013 ng and 0.038 ng, furthermore, the sorption removal efficiencies were obtained as 0.29% and 0.89% at SRTs varying between 5 days and 55 days, respectively in the aerobic reactor (Table 6.12). The volatilized masses and volatilization removal efficiencies were measured as zero for PBT at all SRTs in the aerobic reactor (Table 6.12). The ANOVA (one-way) test statistics results showed that removal of PBT via sorption ($P = 0.064$, $\alpha = 0.05$, $F = 5.15$) and volatilization ($P = 0.065$, $\alpha = 0.05$, $F = 5.06$) were not important statistically in the aerobic reactor. The adsorbed masses of PBT to the aerobic sludge increased from 0.85 ng to 3.35 ng as the SRT increased from 5 days to 55 days, respectively in the aerobic reactor

(Table 6.12). This attributed to PBT adsorption yields of 19.06% and 78.71% at 5 days and 55 days SRT, respectively (Table 6.12). The ANOVA (one-way) test statistics results supported that the adsorption was found to be an important removal mechanism for PBT in the aerobic reactor at all SRTs ($P = 0.0005$, $\alpha = 0.05$, $F = 12.61$). Low solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$), high hydrophobicity ($\log K_{OW} = 6.99$) and low Henry's Law constant ($5.97 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) makes PBT quite hydrophobic in the aerobic reactor and adsorption becomes more dominant than the other removal mechanisms (biodegradation, sorption and volatilization) at all SRTs.

Removal of PBT via biodegradation was slightly higher in the aerobic reactor (12.69%) than the anaerobic reactor (7.88%) at 55 days SRT because of the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.12). Removal of PBT via adsorption was higher in the anaerobic reactor (85.19%) than the aerobic reactor (78.71%) at 55 days of SRT (Table 6.12). It was possible that there were much sludge surfaces to be adsorbed for PBT in the anaerobic reactor than that in the aerobic reactor owing to the high MLVSS concentration in the anaerobic reactor (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.11.4.4 Removed Masses and Removal Efficiencies of PBT in Anaerobic/Aerobic Sequential Biological Reactor System. From the Table 6.12, it can be said that the total biodegraded masses of PBT increased from 0.90 ng to 2.03 ng resulting in PBT removal percentages of 8.66% and 19.57% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system. The maximum biodegradation yield of PBT was achieved as 19.57% at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.12). The ANOVA (one-way) test statistic results supported that the removal of PBT via biodegradation was insignificant at all SRTs in the anaerobic/aerobic sequential biological reactor system ($P = 0.123$, $\alpha = 0.05$, $F = 3.21$). The sorbed masses changed between 0.03 ng and 0.10 ng corresponding to the sorption removal percentages of 0.31% and 0.91% at 5 days and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table

6.12). The volatilized masses and volatilization removal percentages were calculated as zero for PBT at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.12). The ANOVA (one-way) test statistics results showed that removal of PBT via sorption ($P = 0.100$, $\alpha = 0.05$, $F = 3.77$) and volatilization ($P = 0.102$, $\alpha = 0.05$, $F = 3.71$) were not significant in the anaerobic/aerobic sequential biological reactor system. The total adsorbed masses of PBT to the anaerobic (from 1.22 ng to 4.92 ng) and aerobic (from 0.85 ng to 3.35 ng) sludge increased from 2.07 ng (1.22 ng + 0.85 ng) to 8.27 ng (4.92 ng + 3.35 ng) as the SRT increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.12). The raise in the total adsorbed masses of PBT also increased the total adsorption removal percentages from 19.91% to 79.56% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.12). The adsorption mechanism has an important statistical contribution on the removal of PBT in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.0004$, $\alpha = 0.05$, $F = 13.19$). The physicochemical properties of PBT (low water solubility = 9.35×10^{-7} g L⁻¹, high log $K_{OW} = 6.99$ and low Henry's Law constant = 5.97×10^{-5} atm m³ mol⁻¹) makes PBT suitable to adsorb on anaerobic and aerobic sludges.

The results from this study showed that PBT can not be effectively removed via biodegradation (19.57%), sorption (0.91%) and volatilization (0.00) at 55 days SRT. In this study, we found that adsorption (79.56%) is the main removal mechanism for PBT at 55 days SRT (Figure 6.10). PBT is a hydrophobic micropollutant due to its low water solubility (9.35×10^{-7} g L⁻¹), high octanol/water partition coefficient (log $K_{OW} = 6.99$) and low Henry's Law constant (5.97×10^{-5} atm m³ mol⁻¹) values. These properties makes PBT resistant to biodegradation, as a result, adsorption plays an important role for its removal.

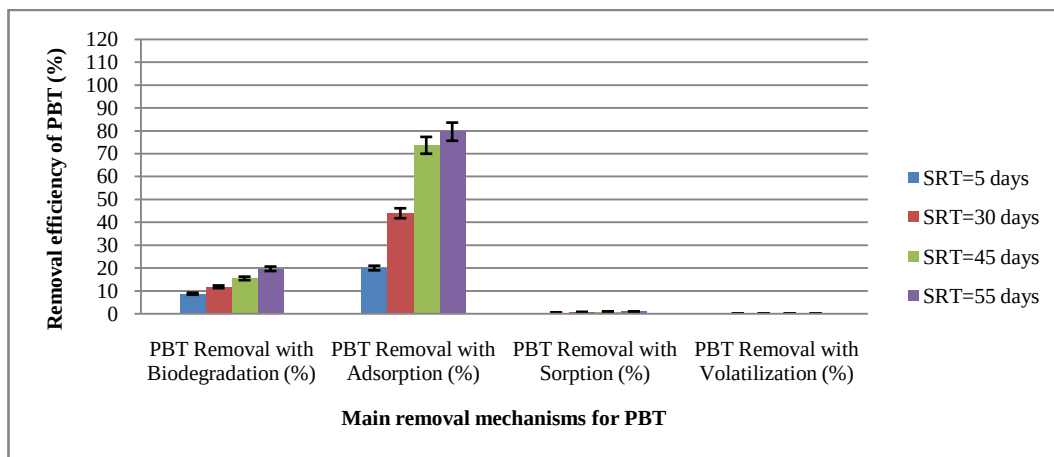


Figure 6.10 The removal efficiencies of PBT with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.12 Total Tetrabromobisphenol A (TBBPA) Removals

6.1.12.1 Total TBBPA Removals in Anaerobic Biological Reactor

In the anaerobic reactor, the maximum TBBPA removal efficiency was calculated as 4.1% with a TBBPA effluent of $0.0163 \mu\text{g L}^{-1}$ at a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.13). The maximum TBBPA removal efficiency was achieved as 5.3% with a TBBPA effluent of $0.0161 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic reactor (Table 6.13). After 45 days SRT operation, the maximum TBBPA removal efficiency was determined as 7.1% with a TBBPA effluent of $0.0158 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.13). In the anaerobic reactor, the maximum TBBPA removal efficiency was obtained as 8.2% with a TBBPA effluent of $0.0156 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ at the highest SRT of 55 days (Table 6.13).

Table 6.13 TBBPA and its metabolite 2,2-Bis(4-hydroxyphenyl)propane (BPA) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent TBBPA ($\mu\text{g L}^{-1}$)	Effluent TBBPA ($\mu\text{g L}^{-1}$)	metabolite of TBBPA namely BPA			Removed TBBPA ($\mu\text{g L}^{-1}$)	TBBPA Rem. Eff. (%)	Influent TBBPA ($\mu\text{g L}^{-1}$)	Effluent TBBPA ($\mu\text{g L}^{-1}$)	metabolite of TBBPA namely BPA			Removed TBBPA ($\mu\text{g L}^{-1}$)	TBBPA Rem. Eff. (%)
			Influent BPA ($\mu\text{g L}^{-1}$)	Effluent BPA ($\mu\text{g L}^{-1}$)	BPA Rem. Eff. (%)					Influent BPA ($\mu\text{g L}^{-1}$)	Effluent BPA ($\mu\text{g L}^{-1}$)	BPA Rem. Eff. (%)		
5	0.017 $\pm$ 0.001	0.0163 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0017 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0007 $\pm$ 0.001	4.1 $\pm$ 0.5	0.0163 $\pm$ 0.001	0.0153 $\pm$ 0.001	0.0017 $\pm$ 0.001	0.0012 $\pm$ 0.001	29.4 $\pm$ 0.5	0.0010 $\pm$ 0.001	6.1 $\pm$ 0.5
30	0.017 $\pm$ 0.001	0.0161 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0009 $\pm$ 0.001	5.3 $\pm$ 0.5	0.0161 $\pm$ 0.001	0.0149 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0010 $\pm$ 0.001	33.3 $\pm$ 0.5	0.0012 $\pm$ 0.001	7.5 $\pm$ 0.5
45	0.017 $\pm$ 0.001	0.0158 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0014 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0012 $\pm$ 0.001	7.1 $\pm$ 0.5	0.0158 $\pm$ 0.001	0.0142 $\pm$ 0.001	0.0014 $\pm$ 0.001	0.0008 $\pm$ 0.001	42.9 $\pm$ 0.5	0.0016 $\pm$ 0.001	10.1 $\pm$ 0.5
55	0.017 $\pm$ 0.001	0.0156 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0014 $\pm$ 0.001	8.2 $\pm$ 0.5	0.0156 $\pm$ 0.001	0.0135 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.0004 $\pm$ 0.001	69.2 $\pm$ 0.5	0.0021 $\pm$ 0.001	13.5 $\pm$ 0.5

SRT (day)	Anaerobic/Aerobic Sequential Biological Reactor System						
	Influent TBBPA ($\mu\text{g L}^{-1}$)	Effluent TBBPA ($\mu\text{g L}^{-1}$)	metabolite of TBBPA namely BPA			Removed TBBPA ($\mu\text{g L}^{-1}$)	TBBPA Rem. Eff. (%)
			Influent BPA ($\mu\text{g L}^{-1}$)	Effluent BPA ($\mu\text{g L}^{-1}$)	BPA Rem. Eff. (%)		
5	0.017 $\pm$ 0.001	0.0153 $\pm$ 0.001	0.0017 $\pm$ 0.001	0.0012 $\pm$ 0.001	29.4 $\pm$ 0.5	0.0017 $\pm$ 0.001	10.0 $\pm$ 0.5
30	0.017 $\pm$ 0.001	0.0149 $\pm$ 0.001	0.0015 $\pm$ 0.001	0.0010 $\pm$ 0.001	33.3 $\pm$ 0.5	0.0021 $\pm$ 0.001	12.4 $\pm$ 0.5
45	0.017 $\pm$ 0.001	0.0142 $\pm$ 0.001	0.0014 $\pm$ 0.001	0.0008 $\pm$ 0.001	42.9 $\pm$ 0.5	0.0028 $\pm$ 0.001	16.5 $\pm$ 0.5
55	0.017 $\pm$ 0.001	0.0135 $\pm$ 0.001	0.0013 $\pm$ 0.001	0.0004 $\pm$ 0.001	69.2 $\pm$ 0.5	0.0035 $\pm$ 0.001	20.6 $\pm$ 0.5

TBBPA removal efficiency increased slightly from 4.1% to 8.2% as the SRT was increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.13). TBBPA was partially biodegraded in the anaerobic reactor because of the physicochemical properties like low water solubility (7.65×10^{-6} g L⁻¹) and high octanol/water partition coefficient (log K_{OW} of 5.90). Moreover, the ANOVA (one-way) statistical analysis results showed that the biodegradation of TBBPA at increasing SRTs was not found to be important statistically in the anaerobic reactor at all SRTs ($P = 0.065$, $\alpha = 0.05$, $F = 5.07$).

Some researchers have demonstrated that TBBPA is reductively debrominated to the 2,2-Bis(4-hydroxyphenyl)propane (BPA) or in other words to bisphenol A (BPA) under anaerobic conditions (McAvoy et al., 2016). The main degradation pathway was a reductive debromination of TBBPA to BPA following the degradation order of TBBPA to 3,3',5-tribromobisphenol (tri-BBPA), to 3,3'-dibromobisphenol (di-BBPA), to 3-bromobisphenol A (mono-BBPA) and to BPA (Lefevre et al., 2016). In this study, the presence of 2,2-Bis(4-hydroxyphenyl)propane (BPA) which is the main metabolite of TBBPA was monitored in the effluents of the anaerobic reactor at all SRTs. BPA accepted as a moderately hydrophobic micropollutant because of having a log K_{OW} value (3.64) between 2.5 and 4.0, besides, BPA has higher solubility value (1.73×10^{-3} g L⁻¹) than TBBPA (7.65×10^{-6} g L⁻¹) in water. The effluent concentrations of BPA were determined as 0.0017, 0.0015, 0.0014 and 0.0013 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.13).

6.1.12.2 Total TBBPA Removals in Aerobic Biological Reactor

The maximum TBBPA removal efficiency of the aerobic biological reactor was found as 6.1% with a TBBPA effluent of 0.0153 µg L⁻¹ at a TBBPA influent of 0.0163 µg L⁻¹ at 5 days SRT (Table 6.13). At 30 days SRT, the maximum TBBPA removal efficiency increased slightly to 7.5% with a TBBPA effluent of 0.0149 µg L⁻¹ for a TBBPA influent of 0.0161 µg L⁻¹ in the aerobic reactor (Table 6.13). At 45 days SRT, the maximum TBBPA removal efficiency was found as 10.1% with a

TBBPA effluent of $0.0142 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0158 \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.13). For the maximum SRT of 55 days, the maximum TBBPA removal efficiency was determined as 13.5% with a TBBPA effluent of $0.0135 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0156 \mu\text{g L}^{-1}$ in aerobic reactor (Table 6.13).

Total removal yields of TBBPA were low both in the anaerobic (8.2%) and aerobic (13.5%) reactors at 55 days SRT (Table 6.13). The low removals of TBBPA in both reactors showed that this micropollutant is partially resistant to biodegradation due to its physicochemical properties like low water solubility ($7.65 \times 10^{-6} \text{ g L}^{-1}$) and high hydrophobicity ($\log K_{\text{OW}}$ of 5.90) in both reactors.

TBBPA removal efficiencies increased from 6.1% to 13.5% as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.13). The increase in TBBPA yields with increasing SRTs was examined with the ANOVA (one-way) statistical analysis and the relationship between TBBPA yields and SRTs was not significant in the aerobic reactor ($P = 0.068$, $\alpha = 0.05$, $F = 4.95$). It can be concluded that the TBBPA could not biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the BPA remaining from the anaerobic reactor and the influent concentrations of BPA were detected as 0.0017, 0.0015, 0.0014 and $0.0013 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.13). The effluent concentrations of BPA were measured as 0.0012, 0.0010, 0.0008 and $0.0004 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.13). BPA removal efficiencies were found as 29.4%, 33.3%, 42.9% and 69.2% at 5, 30, 45 and 55 days SRTs in the aerobic reactor (Table 6.13). A linear correlation between BPA yields and SRTs was found for the aerobic reactor and this regression was found to be significant according to the ANOVA (one-way) test statistics results at all SRTs ($R^2 = 0.86$, $P = 0.004$, $\alpha = 0.05$, $F = 21.03$). The ANOVA (one-way) test statistics results proved that the aerobic reactor had a significant contribution to the removal of BPA remaining from the anaerobic reactor at all SRTs.

6.1.12.3 Total TBBPA Removals in Anaerobic/Aerobic Sequential Biological Reactor System

For 5 days SRT operation, the maximum TBBPA removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 10.0% with a TBBPA effluent of $0.0153 \mu\text{g L}^{-1}$ at a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ (Table 6.13). The maximum TBBPA removal efficiency was calculated as 12.4% with a TBBPA effluent of $0.0149 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.13). The maximum TBBPA removal efficiency was found as 16.5% with a TBBPA effluent of $0.0142 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ for 45 days SRT operation in the anaerobic/aerobic sequential biological reactor system (Table 6.13). Finally, the maximum TBBPA removal efficiency was determined as 20.6% with a TBBPA effluent of $0.0135 \mu\text{g L}^{-1}$ for a TBBPA influent of $0.0170 \mu\text{g L}^{-1}$ at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.13).

In the anaerobic/aerobic sequential biological reactor system, influent concentrations of BPA were determined as 0.0017, 0.0015, 0.0014 and $0.0013 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively (Table 6.13). The effluent BPA concentrations were obtained as 0.0012, 0.0010, 0.0008 and $0.0004 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.13). The anaerobic/aerobic sequential biological reactor system achieved 29.4%, 33.3%, 42.9% and 69.2% removal efficiencies for BPA at 5, 30, 45 and 55 days SRTs, respectively (Table 6.13). BPA removal efficiency increased with the increasing SRT and the maximum BPA yield was calculated as 69.2% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.13).

6.1.12.4 Removal Mechanisms of TBBPA in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

In order to detect the main removal mechanisms of TBBPA; biodegradation, sorption, adsorption and volatilization tests were performed. The biodegraded, adsorbed, sorbed and volatilized TBBPA masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.14).



Table 6.14 The total removal percentages for TBBPA throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.002	0.00019	0.0087	0.000003	0.000145	0.000042	0.000000042	4.12	20.47	0.34	0.00010
30	0.002	0.00044	0.0200	0.000007	0.000293	0.000044	0.000000044	5.29	47.06	0.69	0.00010
45	0.003	0.00077	0.0345	0.000009	0.000383	0.000047	0.000000047	7.06	81.18	0.90	0.00011
55	0.004	0.00080	0.0360	0.000009	0.000420	0.000047	0.000000047	8.24	84.71	0.99	0.00011
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.002	0.00041	0.0061	0.000006	0.000097	0.000028	0.000000028	6.13	18.71	0.30	0.00009
30	0.002	0.00081	0.0122	0.000013	0.000198	0.000031	0.000000031	7.45	37.89	0.61	0.00010
45	0.003	0.00143	0.0214	0.000016	0.000242	0.000031	0.000000031	10.13	67.72	0.77	0.00010
55	0.004	0.00161	0.0241	0.000019	0.000283	0.000033	0.000000033	13.46	77.24	0.91	0.00011
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.008	--	0.0148	--	0.000242	--	0.000000070	10.00	19.35	0.32	0.00009
30	0.009	--	0.0322	--	0.000491	--	0.000000075	12.35	42.09	0.64	0.00010
45	0.013	--	0.0559	--	0.000625	--	0.000000078	16.47	73.07	0.82	0.00010
55	0.016	--	0.0601	--	0.000703	--	0.000000080	20.59	78.56	0.92	0.00010

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.12.4.1 *Removed Masses and Removal Efficiencies of TBBPA.* An example for the calculations relevant to the removed masses and the removal efficiencies of TBBPA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.97 to 6.120, respectively at a SRT of 5 days (Table 6.14).

The biodegraded masses of TBBPA were calculated from Equations 6.97, 6.98 and 6.99 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.14).

$$M_{\text{BIO,Anaerobic}} = (0.0007 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 0.002 \mu\text{g} \quad (6.97)$$

$$M_{\text{BIO,Aerobic}} = (0.0010 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 0.002 \mu\text{g} \quad (6.98)$$

$$M_{\text{BIO,Sequential}} = (0.0017 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 0.008 \mu\text{g} \quad (6.99)$$

The biodegradation removal efficiencies for TBBPA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.100, 6.101 and 6.102, respectively at 5 days SRT (Table 6.14).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (0.002 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 4.12\% \quad (6.100)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (0.002 \times 100)/(0.0163 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 6.13\% \quad (6.101)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (0.008 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 10.00\% \quad (6.102)$$

The adsorbed masses of TBBPA were calculated using Equation 6.103, 6.104 and 6.105 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.14).

$$M_{\text{ADS,Anaerobic}} = [(0.00019 \mu\text{g L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 0.0087 \mu\text{g} \quad (6.103)$$

$$M_{\text{ADS,Aerobic}} = [(0.00041 \mu\text{g L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 0.0061 \mu\text{g} \quad (6.104)$$

$$M_{\text{ADS,Sequential}} = 0.0087 + 0.0061 = 0.0148 \mu\text{g} \quad (6.105)$$

The total adsorption removal efficiencies for TBBPA at 5 days of SRT in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.106, 6.107 and 6.108, respectively (Table 6.14).

$$\text{Adsorption (\%)}_{\text{An}} = (0.0087 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 20.47\% \quad (6.106)$$

$$\text{Adsorption (\%)}_{\text{Ae}} = (0.0061 \times 100)/(0.0163 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 18.71\% \quad (6.107)$$

$$\text{Adsorption (\%)}_{\text{Seq}} = (0.0148 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 19.35\% \quad (6.108)$$

The sorbed masses into the anaerobic and aerobic biological sludges of TBBPA were calculated according to the Equation 6.109 and 6.110, respectively while the total sorbed mass for TBBPA in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.111 at 5 days SRT (Table 6.14).

$$M_{\text{SORP,An}} = [(0.000003 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.000145 \mu\text{g} \quad (6.109)$$

$$M_{\text{SORP,Ae}} = [(0.000006 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.000097 \mu\text{g} \quad (6.110)$$

$$M_{\text{SORP,Sequential}} = 0.000145 + 0.000097 = 0.000242 \mu\text{g} \quad (6.111)$$

The total sorption removal efficiencies of TBBPA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.112, 6.113 and 6.114, respectively at 5 days of SRT (Table 6.14).

$$\text{Sorption (\%)}_{\text{An}} = (0.000145 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.34\% \quad (6.112)$$

$$\text{Sorption (\%)}_{\text{Ae}} = (0.000097 \times 100)/(0.0163 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.30\% \quad (6.113)$$

$$\text{Sorption (\%)}_{\text{Seq}} = (0.000242 \times 100)/(0.0170 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.32\% \quad (6.114)$$

The volatilized masses of TBBPA were calculated using Equation 6.115, 6.116 and 6.117 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at a SRT operation of 5 days (Table 6.14).

$$M_{\text{VOL,An}} = (4.2 \times 10^{-5} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 4.2 \times 10^{-8} \mu\text{g} \quad (6.115)$$

$$M_{VOL,Ae} = (2.8 \times 10^{-5} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 2.8 \times 10^{-8} \mu\text{g} \quad (6.116)$$

$$M_{VOL,Sequential} = 4.2 \times 10^{-8} + 2.8 \times 10^{-8} = 7.0 \times 10^{-8} \mu\text{g} \quad (6.117)$$

The volatilization removal efficiencies were determined according to the Equation 6.118, 6.119 and 6.120 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days of SRT (Table 6.14).

$$\text{Vol}(\%),_{An} = (4.2 \times 10^{-8} \mu\text{g} \times 100) / (0.0170 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00010\% \quad (6.118)$$

$$\text{Vol}(\%),_{Ae} = (2.8 \times 10^{-8} \mu\text{g} \times 100) / (0.0163 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00009\% \quad (6.119)$$

$$\text{Vol}(\%),_{Seq} = (7.0 \times 10^{-8} \mu\text{g} \times 100) / (0.0170 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00009\% \quad (6.120)$$

6.1.12.4.2 Removed Masses and Removal Efficiencies of TBBPA in Anaerobic Reactor. The biodegraded TBBPA masses increased from 0.002 μg to 0.004 μg as the SRT was increased from 5 up to 55 days in the anaerobic reactor (Table 6.14). The biodegradation removal percentages of TBBPA also increased from 4.12% to 8.24% with the increasing of SRTs from 5 days up to 55 days (Table 6.14). TBBPA can be used as co-metabolite together COD and sCOD by the anaerobic bacteria, however, the influent concentration of TBBPA ($0.0170 \mu\text{g L}^{-1}$) as the electron acceptor in co-metabolic process was not enough to sustain the growth of dehalogenating bacteria at 55 days SRT in the anaerobic reactor (Table 5.1). Therefore, only 8.24% of TBBPA was co-metabolized together COD and sCOD by the anaerobic bacteria at the highest SRT of 55 days (Table 6.14). Having low water solubility value ($7.65 \times 10^{-6} \text{ g L}^{-1}$) and high octanol/water partition coefficient ($\log K_{OW} = 5.90$) of TBBPA makes it quite hydrophobic in the anaerobic reactor and can not be effectively biodegraded at 55 days SRT by the anaerobic bacteria in this study. Lower removal efficiencies for TBBPA were also obtained by other researchers. McAvoy et al. (2016) found less than 10% of TBBPA yield in an anaerobic reactor (UASB) having a volume of 500 mL at 120 days SRT at a pH of 7.10 at 35 °C for $0.445 \mu\text{g L}^{-1}$ initial TBBPA concentration (McAvoy et al., 2016). The ANOVA (one-way) test statistic results showed that TBBPA can not be effectively removed via biodegradation in the anaerobic reactor at all SRTs ($P = 0.065$, $\alpha = 0.05$, $F = 5.07$). The sorbed masses ($0.000145 - 0.000420 \mu\text{g}$) and volatilized masses ($4.2 \times 10^{-8} -$

4.7×10^{-8} μg) were low at all SRTs for TBBPA in the anaerobic reactor (Table 6.14). The sorption and volatilization removal percentages also were low (between 0.34% and 0.99% for sorption and between 0.00010% and 0.00011% for volatilization, respectively) in the anaerobic reactor (Table 6.14). The ANOVA (one-way) test statistics results showed that the removal of TBBPA via sorption ($P = 0.074$, $\alpha = 0.05$, $F = 4.65$) and volatilization ($P = 0.076$, $\alpha = 0.05$, $F = 4.57$) were not significant in the anaerobic reactor. The adsorption of TBBPA to the anaerobic sludge was found to be important in the anaerobic reactor since the adsorbed TBBPA masses varies between 0.0087 μg and 0.0360 μg (Table 6.14). It is important to note that the adsorption removal percentages of TBBPA increased from 20.47% to 84.71% as the SRTs were increased from 5 to 55 days, respectively (Table 6.14). The ANOVA (one-way) test statistics results supported that the adsorption has a significant effect on the removal of TBBPA in the anaerobic reactor at all SRTs ($P = 0.0004$, $\alpha = 0.05$, $F = 13.65$). Having low water solubility value (7.65×10^{-6} g L^{-1}), high octanol/water partition coefficient ($\log K_{OW} = 5.90$) and low Henry's Law constant (1.47×10^{-5} $\text{atm m}^3 \text{mol}^{-1}$) of TBBPA makes it quite hydrophobic in the anaerobic reactor, therefore, TBBPA can be effectively removed by adsorption (84.71%) in the anaerobic reactor at 55 days SRT (Table 6.14).

6.1.12.4.3 Removed Masses and Removal Efficiencies of TBBPA in Aerobic Reactor. In the aerobic reactor, the biodegraded TBBPA masses increased from 0.002 μg to 0.004 μg resulting in TBBPA removal percentages of 6.13% and 13.46% depending on SRT increase from 5 days to 55 days (Table 6.14). The maximum biodegradation yield of TBBPA was obtained as 13.46% at 55 days SRT in the aerobic reactor (Table 6.14). The low TBBPA biodegradation yield (13.46%) has been observed in the aerobic reactor because of the physicochemical properties of TBBPA such as low water solubility (7.65×10^{-6} g L^{-1}) and high hydrophobicity ($\log K_{OW} = 5.90$). The removal of TBBPA via biodegradation was not found to be significant according to the ANOVA (one-way) test statistic results at all SRTs in the aerobic reactor ($P = 0.068$, $\alpha = 0.05$, $F = 4.95$). The sorbed masses ($0.000097 - 0.000283$ μg) and volatilized masses ($2.8 \times 10^{-8} - 3.3 \times 10^{-8}$ μg) were low at all SRTs for TBBPA in the aerobic reactor (Table 6.14). The TBBPA removal percentages

also were low (between 0.30% and 0.91% for sorption and between 0.00009% and 0.00011% for volatilization, respectively) in the aerobic reactor (Table 6.14). The ANOVA (one-way) test statistics results showed that removal of TBBPA via sorption ($P = 0.061$, $\alpha = 0.05$, $F = 5.32$) and volatilization ($P = 0.062$, $\alpha = 0.05$, $F = 5.23$) were not significant in the aerobic reactor. The adsorption of TBBPA masses to the aerobic sludge increased from $0.0061 \mu\text{g}$ to $0.0241 \mu\text{g}$ as the SRT increased from 5 days to 55 days, respectively (Table 6.14). This attributed to the TBBPA adsorption yields of 18.71% and 77.24% at 5 days and 55 days SRT, respectively (Table 6.14). Because of TBBPA is a quite hydrophobic micropollutant with its physicochemical properties like low water water solubility ($7.65 \times 10^{-6} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 5.90$) and low Henry's Law constant ($1.47 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$), TBBPA has resistance to extensive biodegradation. Therefore, adsorption has a significant contribution on the removal of TBBPA in the aerobic reactor at all SRTs according to the ANOVA (one-way) test statistics results ($P = 0.0005$, $\alpha = 0.05$, $F = 12.41$).

Removal of TBBPA via biodegradation was slightly higher in the aerobic reactor (13.46%) than the anaerobic reactor (8.24%) at 55 days SRT owing to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.14). Removal of TBBPA via adsorption was higher in the anaerobic reactor (84.71%) than the aerobic reactor (77.24%) at 55 days SRT (Table 6.14) due to the TBBPA found more sludge surface to be adsorbed in the anaerobic reactor (MLVSS concentration of 27600 mg L^{-1}) than the aerobic reactor (MLVSS concentration of 3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.12.4.4 Removed Masses and Removal Efficiencies of TBBPA in Anaerobic/Aerobic Sequential Biological Reactor System. From the Table 6.14, it can be said that the total biodegraded masses of TBBPA increased from $0.008 \mu\text{g}$ to $0.016 \mu\text{g}$ resulting in TBBPA removal percentages of 10.00% and 20.59% depending on SRT increase from 5 days to 55 days in the anaerobic/aerobic sequential biological reactor system. Biodegradation yield of TBBPA reached the highest level (20.59%) at 55 days SRT (Table 6.14). However, the ANOVA (one-way) test

statistic results showed that the raise in the biodegradation yields of TBBPA was not important statistically at all SRTs in the anaerobic/aerobic sequential biological reactor system ($P = 0.140$, $\alpha = 0.05$, $F = 2.89$). The sorbed masses ($0.000242 - 0.000703 \mu\text{g}$) and volatilized masses ($7.00 \times 10^{-8} - 8.00 \times 10^{-8} \mu\text{g}$) were low at all SRTs for TBBPA in the anaerobic/aerobic sequential biological reactor system (Table 6.14). The TBBPA removal percentages also were low (between 0.32% and 0.92% for sorption and between 0.00009% and 0.00010% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system (Table 6.14). The ANOVA (one-way) test statistics results showed that the removal of TBBPA via sorption ($P = 0.101$, $\alpha = 0.05$, $F = 3.75$) and volatilization ($P = 0.103$, $\alpha = 0.05$, $F = 3.70$) were not significant in the anaerobic/aerobic sequential biological reactor system. The total adsorption of TBBPA masses to the anaerobic (from $0.0087 \mu\text{g}$ to $0.0360 \mu\text{g}$) and aerobic (from $0.0061 \mu\text{g}$ to $0.0241 \mu\text{g}$) sludge in the anaerobic/aerobic sequential biological reactor system increased from $0.0148 \mu\text{g}$ to $0.0601 \mu\text{g}$ as the SRT increased from 5 days to 55 days, respectively (Table 6.14). The raise in adsorbed masses also increased the TBBPA adsorption yields from 19.35% to 78.56% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.14). The hydrophobic structure of TBBPA (low water water solubility = $7.65 \times 10^{-6} \text{ g L}^{-1}$, high $\log K_{OW} = 5.90$ and low Henry's Law constant = $1.47 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) makes TBBPA easily adsorbed on anaerobic and aerobic sludges. The ANOVA (one-way) test statistics results supported that the removal of TBBPA via adsorption was significant in the anaerobic/aerobic sequential biological reactor at all SRTs ($P = 0.0005$, $\alpha = 0.05$, $F = 12.64$).

The high octanol-water partition coefficient ($\log K_{OW} = 5.90$), low water water solubility ($7.65 \times 10^{-6} \text{ g L}^{-1}$) and low Henry's Law constant ($1.47 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) of TBBPA indicates high hydrophobicity or adsorption to sludge. Therefore, it can be concluded that the removal of TBBPA with adsorption is major (78.56%), biodegradation is low (20.59%), sorption is minor (0.92%) and volatilization is negligible (0.00010%) at 55 days SRT (Figure 6.11).

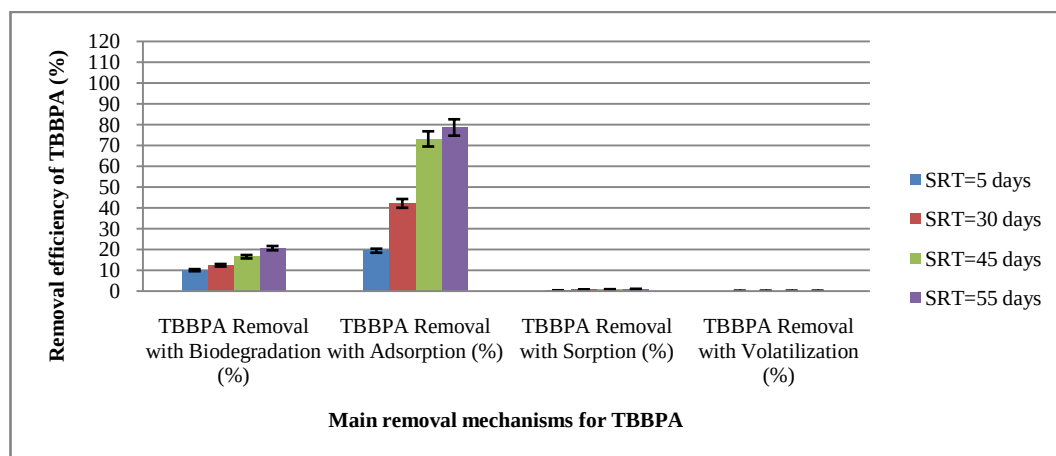


Figure 6.11 The removal efficiencies of TBBPA with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.13 Total Musk Tonalide (AHTN) Removals

6.1.13.1 Total AHTN Removals in Anaerobic Biological Reactor

The maximum AHTN removal efficiency of the anaerobic reactor was obtained as 5.1% with an AHTN effluent of 195.59 ng L^{-1} at an AHTN influent of 206.00 ng L^{-1} during the 5 days of SRT operation (Table 6.15). The maximum AHTN removal efficiency was determined as 8.4% with an AHTN effluent of 188.64 ng L^{-1} for an AHTN influent of 206.00 ng L^{-1} at 30 days SRT in the anaerobic reactor (Table 6.15). For 45 days SRT operation, the maximum AHTN removal efficiency was found as 9.0% with an AHTN effluent of 187.37 ng L^{-1} for an AHTN influent of 206.00 ng L^{-1} in the anaerobic reactor (Table 6.15). Finally, the maximum AHTN removal efficiency was calculated as 11.1% with an AHTN effluent of 183.16 ng L^{-1} for an AHTN influent of 206.00 ng L^{-1} at 55 days SRT in the anaerobic reactor (Table 6.15).

Table 6.15 AHTN and its metabolite 3-Ethyl-5,6,7,8-Tetrahydro-5,5,8,8-Tetramethyl-2-Naphthaldehyde (3-ETTN) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent AHTN (ng L ⁻¹)	Effluent AHTN (ng L ⁻¹)	metabolite of AHTN namely 3-ETTN			Removed AHTN (ng L ⁻¹)	AHTN Rem. Eff. (%)	Influent AHTN (ng L ⁻¹)	Effluent AHTN (ng L ⁻¹)	metabolite of AHTN namely 3-ETTN			Removed AHTN (ng L ⁻¹)	AHTN Rem. Eff. (%)
			Influent 3-ETTN (ng L ⁻¹)	Effluent 3-ETTN (ng L ⁻¹)	3-ETTN Rem. Eff. (%)					Influent 3-ETTN (ng L ⁻¹)	Effluent 3-ETTN (ng L ⁻¹)	3-ETTN Rem. Eff. (%)		
5	206.00 $\pm$ 0.02	195.59 $\pm$ 0.02	0.00 $\pm$ 0.02	29.47 $\pm$ 0.02	0.00 $\pm$ 0.5	10.41 $\pm$ 0.02	5.1 $\pm$ 0.5	195.59 $\pm$ 0.02	179.65 $\pm$ 0.02	29.47 $\pm$ 0.02	19.67 $\pm$ 0.02	33.3 $\pm$ 0.5	15.94 $\pm$ 0.02	8.1 $\pm$ 0.5
30	206.00 $\pm$ 0.02	188.64 $\pm$ 0.02	0.00 $\pm$ 0.02	22.50 $\pm$ 0.02	0.00 $\pm$ 0.5	17.36 $\pm$ 0.02	8.4 $\pm$ 0.5	188.64 $\pm$ 0.02	169.44 $\pm$ 0.02	22.50 $\pm$ 0.02	13.73 $\pm$ 0.02	39.0 $\pm$ 0.5	19.20 $\pm$ 0.02	10.2 $\pm$ 0.5
45	206.00 $\pm$ 0.02	187.37 $\pm$ 0.02	0.00 $\pm$ 0.02	19.47 $\pm$ 0.02	0.00 $\pm$ 0.5	18.63 $\pm$ 0.02	9.0 $\pm$ 0.5	187.37 $\pm$ 0.02	164.43 $\pm$ 0.02	19.47 $\pm$ 0.02	11.34 $\pm$ 0.02	41.8 $\pm$ 0.5	22.94 $\pm$ 0.02	12.2 $\pm$ 0.5
55	206.00 $\pm$ 0.02	183.16 $\pm$ 0.02	0.00 $\pm$ 0.02	17.00 $\pm$ 0.02	0.00 $\pm$ 0.5	22.84 $\pm$ 0.02	11.1 $\pm$ 0.5	183.16 $\pm$ 0.02	155.74 $\pm$ 0.02	17.00 $\pm$ 0.02	9.52 $\pm$ 0.02	44.0 $\pm$ 0.5	27.42 $\pm$ 0.02	15.0 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent AHTN (ng L ⁻¹)	Effluent AHTN (ng L ⁻¹)	metabolite of AHTN namely 3-ETTN			Removed AHTN (ng L ⁻¹)	AHTN Rem. Eff. (%)
			Influent 3-ETTN (ng L ⁻¹)	Effluent 3-ETTN (ng L ⁻¹)	3-ETTN Rem. Eff. (%)		
5	206.00 $\pm$ 0.02	179.65 $\pm$ 0.02	29.47 $\pm$ 0.02	19.67 $\pm$ 0.02	33.3 $\pm$ 0.5	26.35 $\pm$ 0.02	12.8 $\pm$ 0.5
30	206.00 $\pm$ 0.02	169.44 $\pm$ 0.02	22.50 $\pm$ 0.02	13.73 $\pm$ 0.02	39.0 $\pm$ 0.5	36.56 $\pm$ 0.02	17.7 $\pm$ 0.5
45	206.00 $\pm$ 0.02	164.43 $\pm$ 0.02	19.47 $\pm$ 0.02	11.34 $\pm$ 0.02	41.8 $\pm$ 0.5	41.57 $\pm$ 0.02	20.2 $\pm$ 0.5
55	206.00 $\pm$ 0.02	155.74 $\pm$ 0.02	17.00 $\pm$ 0.02	9.52 $\pm$ 0.02	44.0 $\pm$ 0.5	50.26 $\pm$ 0.02	24.4 $\pm$ 0.5

AHTN removal efficiency increased from 5.1% to 11.1% as the SRT was increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.15). The physicochemical properties of AHTN enables the partial biodegradation in the anaerobic reactor at all SRTs (low water solubility = 1.25×10^{-3} g L⁻¹ and high log K_{OW} = 5.70). The ANOVA (one-way) statistical analysis results showed that the biodegradation of AHTN at increasing SRTs was not found to be important statistically in the anaerobic reactor at all SRTs (P = 0.060, α = 0.05, F = 5.36).

It was reported that the AHTN (parent compound) was biodegraded through metabolic pathways into 3-Ethyl-5,6,7,8-Tetrahydro-5,5,8,8-Tetramethyl-2-Naphthaldehyde (3-ETTN) (metabolite) under anaerobic conditions (Gabriel, Mora, Kolvenbach, Corvini, & Kohler, 2012). AHTN was exposed to monohydroxylation and 3-ETTN occurred by the characteristic fragmentation of the parent compound (AHTN) showing the unspecific loss of -CH₃ and subsequent elimination of the ethanone substituent from the aromatic ring of AHTN (Martin et al., 2007). Starting from this point of view, the presence of 3-ETTN which is the main metabolite of AHTN was monitored in the effluents of the anaerobic reactor at all SRTs. 3-ETTN accepted as a quite hydrophobic micropollutant because of having a log K_{OW} value (6.46) higher than 4.00, in addition to this, 3-ETTN has lower water solubility value (7.80×10^{-5} g L⁻¹) than the parent compound of AHTN (1.25×10^{-3} g L⁻¹). The effluent concentrations of 3-ETTN were determined as 29.47, 22.50, 19.47 and 17.00 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.15).

6.1.13.2 Total AHTN Removals in Aerobic Biological Reactor

During 5 days of SRT operation, the maximum AHTN removal efficiency of the aerobic biological reactor was obtained as 8.1% with an AHTN effluent of 179.65 ng L⁻¹ at an AHTN influent of 195.59 ng L⁻¹ (Table 6.15). The maximum AHTN removal efficiency was calculated as 10.2% with an AHTN effluent of 169.44 ng L⁻¹ for an AHTN influent of 188.64 ng L⁻¹ at 30 days SRT in the aerobic reactor (Table 6.15). For 45 days SRT operation, the maximum AHTN removal efficiency was found as 12.2% with an AHTN effluent of 164.43 ng L⁻¹ for an AHTN influent of

187.37 ng L⁻¹ in the aerobic reactor (Table 6.15). At the end of the study, the maximum AHTN removal efficiency was determined as 15.0% with an AHTN effluent of 155.74 ng L⁻¹ for an AHTN influent of 183.16 ng L⁻¹ at 55 days SRT in the aerobic reactor (Table 6.15).

Total removal of AHTN was slightly higher in the aerobic reactor (15.0%) than the anaerobic reactor (11.1%) at 55 days of SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.15). Although having a high octanol/water partition coefficient ($\log K_{OW} = 5.70$), AHTN has relatively higher water solubility (1.25×10^{-3} g L⁻¹) and could be partly biodegraded in both reactors because of its physicochemical properties.

AHTN removal efficiencies increased from 8.1% to 15.0% as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.15). The increase in AHTN yields with increasing SRTs was not found to be meaningful statistically according to the ANOVA (one-way) statistical analysis results in the aerobic reactor ($P = 0.088$, $\alpha = 0.05$, $F = 4.16$). The statistical results showed that the AHTN could not be biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the 3-ETTN remaining from the anaerobic reactor and the influent concentrations of 3-ETTN were detected as 29.47, 22.50, 19.47 and 17.00 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.15). The effluent concentrations of 3-ETTN were measured as 19.67, 13.73, 11.34 and 9.52 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.15). 3-ETTN removal efficiencies were calculated as 33.3%, 39.0%, 41.8% and 44.0% at 5, 30, 45 and 55 days SRTs in the aerobic reactor (Table 6.15). A linear correlation between 3-ETTN yields and SRTs was found for the aerobic reactor and this regression was found to be important according to the ANOVA (one-way) test statistics results at all SRTs ($R^2 = 0.95$, $P = 4.81 \times 10^{-6}$, $\alpha = 0.05$, $F = 235.91$).

6.1.13.3 Total AHTN Removals in Anaerobic/Aerobic Sequential Biological Reactor System

In the first step, AHTN removal efficiency of the anaerobic/aerobic sequential biological reactor system was measured as 12.8% with an AHTN effluent of 179.65 ng L⁻¹ at an AHTN influent of 206.00 ng L⁻¹ at 5 days SRT (Table 6.15). After 30 days SRT, AHTN removal efficiency was determined as 17.7% with an AHTN effluent of 169.44 ng L⁻¹ for an AHTN influent of 206.00 ng L⁻¹ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.15). When the SRT was increased to 45 days, AHTN removal efficiency was calculated as 20.2% with an AHTN effluent of 164.43 ng L⁻¹ for an AHTN influent of 206.00 ng L⁻¹ in the anaerobic/aerobic sequential biological reactor system (Table 6.15). At the highest SRT of 55 days, AHTN removal efficiency was obtained as 24.4% with an AHTN effluent of 155.74 ng L⁻¹ for an AHTN influent of 206.00 ng L⁻¹ at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.15).

In the anaerobic/aerobic sequential biological reactor system, influent concentrations of 3-ETTN were obtained as 29.47, 22.50, 19.47 and 17.00 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively (Table 6.15). The effluent 3-ETTN concentrations were found as 19.67, 13.73, 11.34 and 9.52 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.15). In the anaerobic/aerobic sequential biological reactor system obtained 33.3%, 39.0%, 41.8% and 44.0% removal efficiencies for 3-ETTN were obtained at 5, 30, 45 and 55 days SRTs, respectively (Table 6.15). 3-ETTN removal efficiencies increased slightly with the increasing SRTs because of being a hydrophobic micropollutant (low water solubility = 7.80×10^{-5} g L⁻¹ and high log K_{OW} = 6.46). The maximum 3-ETTN yield was calculated as 44.0% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.15).

6.1.13.4 Removal Mechanisms of AHTN in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of AHTN. The biodegraded, adsorbed, sorbed and volatilized AHTN masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.16).



Table 6.16 The total removal percentages for AHTN throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	26.03	2.143	96.42	0.057	2.55	0.88	0.00088	5.05	18.72	0.50	0.00017
30	43.40	5.275	237.38	0.094	4.22	1.05	0.00105	8.43	46.09	0.82	0.00020
45	46.58	9.180	413.10	0.118	5.32	1.11	0.00111	9.04	80.21	1.03	0.00022
55	57.10	9.259	416.65	0.138	6.20	1.32	0.00132	11.09	80.90	1.20	0.00026
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	31.88	4.30	64.55	0.117	1.75	0.68	0.00068	8.15	16.50	0.45	0.00017
30	38.39	9.06	135.86	0.202	3.03	0.63	0.00063	10.18	36.01	0.80	0.00017
45	45.89	16.34	245.11	0.249	3.74	0.63	0.00063	12.24	65.41	1.00	0.00017
55	54.84	18.25	273.75	0.279	4.19	0.72	0.00072	14.97	74.73	1.14	0.00020
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	118.57	--	160.98	--	4.30	--	0.00156	12.79	17.37	0.46	0.00017
30	164.50	--	373.24	--	7.25	--	0.00168	17.75	40.26	0.78	0.00018
45	187.08	--	658.22	--	9.06	--	0.00174	20.18	71.01	0.98	0.00019
55	226.17	--	690.40	--	10.39	--	0.00204	24.40	74.48	1.12	0.00022

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.13.4.1 *Removed Masses and Removal Efficiencies of AHTN.* An example for the calculations relevant to the removed masses and the removal efficiencies of AHTN in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.121 to 6.144, respectively at a SRT of 5 days (Table 6.16).

The biodegraded masses of AHTN were calculated from Equations 6.121, 6.122 and 6.123 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.16).

$$M_{\text{BIO,Anaerobic}} = (10.41 \text{ ng L}^{-1}) \times (2.5 \text{ L}) = 26.03 \text{ ng} \quad (6.121)$$

$$M_{\text{BIO,Aerobic}} = (15.94 \text{ ng L}^{-1}) \times (2.0 \text{ L}) = 31.88 \text{ ng} \quad (6.122)$$

$$M_{\text{BIO,Sequential}} = (26.35 \text{ ng L}^{-1}) \times (4.5 \text{ L}) = 118.57 \text{ ng} \quad (6.123)$$

The biodegradation removal efficiencies for AHTN in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.124, 6.125 and 6.126, respectively at 5 days SRT (Table 6.16).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (26.03 \times 100)/(206.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 5.05\% \quad (6.124)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (31.88 \times 100)/(195.59 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 8.15\% \quad (6.125)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (118.57 \times 100)/(206.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 12.79\% \quad (6.126)$$

The adsorbed masses of AHTN were calculated using Equation 6.127, 6.128 and 6.129 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.16).

$$M_{\text{ADS,Anaerobic}} = [(4.303 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 96.42 \text{ ng} \quad (6.127)$$

$$M_{\text{ADS,Aerobic}} = [(0.057 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 64.55 \text{ ng} \quad (6.128)$$

$$M_{\text{ADS,Sequential}} = 96.42 + 64.55 = 160.98 \text{ ng} \quad (6.129)$$

The total adsorption removal efficiencies of AHTN in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.130, 6.131 and 6.132, respectively at 5 days SRT (Table 6.16).

$$\text{Adsorption (\%)}_{\text{An}} = (96.42 \times 100)/(206.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 18.72\% \quad (6.130)$$

$$\text{Adsorption (\%)}_{\text{Ae}} = (64.55 \times 100)/(195.59 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 16.50\% \quad (6.131)$$

$$\text{Adsorption (\%)}_{\text{Seq}} = (160.98 \times 100)/(206.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 17.37\% \quad (6.132)$$

The sorbed masses into the anaerobic and aerobic biological sludges of AHTN were calculated according to the Equation 6.133 and 6.134, respectively while the total sorbed mass for AHTN in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.135 at 5 days SRT (Table 6.16).

$$M_{\text{SORP,Anaerobic}} = [(0.057 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (450 \text{ g}) = 2.55 \text{ ng} \quad (6.133)$$

$$M_{\text{SORP,Aerobic}} = [(0.117 \text{ ng L}^{-1}) \times (1 \text{ L})/(10 \text{ g})] \times (150 \text{ g}) = 1.75 \text{ ng} \quad (6.134)$$

$$M_{\text{SORP,Sequential}} = 2.55 + 1.75 = 4.30 \text{ ng} \quad (6.135)$$

The total sorption removal efficiencies of AHTN in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.136, 6.137 and 6.138, respectively at 5 days SRT (Table 6.16).

$$\text{Sorption (\%)}_{\text{Anaerobic}} = (2.55 \times 100)/(206.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.50\% \quad (6.136)$$

$$\text{Sorption (\%)}_{\text{Aerobic}} = (1.75 \times 100)/(195.59 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.45\% \quad (6.137)$$

$$\text{Sorption (\%)}_{\text{Sequential}} = (4.30 \times 100)/(206.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.46\% \quad (6.138)$$

Volatilized masses of AHTN were calculated according to the Equation 6.139, 6.140 and 6.141 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.16).

$$M_{\text{VOL,An}} = (0.88 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00088 \text{ ng} \quad (6.139)$$

$$M_{VOL,Aerobic} = (0.68 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00068 \text{ ng} \quad (6.140)$$

$$M_{VOL,Sequential} = 0.00088 + 0.00068 = 0.00156 \text{ ng} \quad (6.141)$$

The total volatilization removal efficiencies of AHTN were determined according to the Equation 6.142, 6.143 and 6.144 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.16).

$$Vol(\%)_{Anaerobic} = (0.00088 \times 100)/(206.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.00017\% \quad (6.142)$$

$$Vol(\%)_{Aerobic} = (0.00068 \times 100)/(195.59 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.00017\% \quad (6.143)$$

$$Vol(\%)_{Sequential} = (0.00156 \times 100)/(206.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.00017\% \quad (6.144)$$

6.1.13.4.2 Removed Masses and Removal Efficiencies of AHTN in Anaerobic Reactor. In the anaerobic reactor, the biodegraded AHTN masses increased from 26.03 ng to 57.10 ng as the SRT was increased from 5 up to 55 days (Table 6.16). The biodegradation percentages of AHTN also increased from 5.05% to 11.09% with the increasing of SRTs from 5 days up to 55 days (Table 6.16). The anaerobic bacteria can co-metabolized only 11.09% of AHTN together COD and sCOD at the highest SRT of 55 days. In the co-metabolic approach, AHTN was utilized by the corresponding anaerobic organisms in the obligatory presence of the growth substrates (COD and sCOD). Co-metabolic strategy can particularly depend on the nature and amount of the growth substrates (Kumwimba & Meng, 2019). Therefore, the removal of AHTN is inherently connected to that of growth substrates (COD and sCOD) in this study. Although COD (950.00 mg L⁻¹) and sCOD (850.00 mg L⁻¹) concentrations were enough to serve as growth substrates in the anaerobic reactor, AHTN concentration (206.00 ng L⁻¹) was detected too low for the electron acceptor in the anaerobic reactor at all SRTs (Table 5.1). The low AHTN concentration (206.00 ng L⁻¹) in the co-metabolic process was not enough to sustain the growth of anaerobic bacteria in the anaerobic reactor at all SRTs (Table 5.1). Furthermore, the ANOVA (one-way) test statistic results showed that AHTN can not be effectively removed via biodegradation in the anaerobic reactor at all SRTs ($P = 0.060$, $\alpha = 0.05$, $F = 5.36$) because of being a hydrophobic micropollutant (low water solubility

$=1.25 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 5.70$, and low Henry's Law constant $= 1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$). The sorbed masses (2.55 – 6.20 ng) and volatilized masses (0.00088 – 0.00132 ng) were low for AHTN at SRTs varying between 5 days and 55 days, respectively in the anaerobic reactor (Table 6.16). The sorption and volatilization removal percentages of AHTN also were low (between 0.50% and 1.20% for sorption and between 0.00017% and 0.00026% for volatilization, respectively) in the anaerobic reactor at all SRTs (Table 6.16). The ANOVA (one-way) test statistics results showed that removal of AHTN via sorption ($P = 0.078$, $\alpha = 0.05$, $F = 4.50$) and volatilization ($P = 0.080$, $\alpha = 0.05$, $F = 4.41$) were not significant in the anaerobic reactor. The adsorbed mass of AHTN was determined as 96.42 ng and 416.65 ng corresponding to the adsorption yields of 16.50% and 74.73% at 5 days and 55 days SRT, respectively (Table 6.16). The relationship between adsorption yields and SRTs was studied with the ANOVA (one-way) test statistics and the results revealed that the adsorption has a significant effect on the removal of AHTN in the anaerobic reactor at all SRTs ($P = 0.0005$, $\alpha = 0.05$, $F = 12.86$).

6.1.13.4.3 Removed Masses and Removal Efficiencies of AHTN in Aerobic Reactor. In the aerobic reactor, the biodegraded masses of AHTN increased from 31.88 ng to 54.84 ng resulting in AHTN removal percentages of 8.15% and 14.97% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.16). The maximum biodegradation yield of AHTN was obtained as 14.97% at 55 days SRT in the aerobic reactor (Table 6.16). The maximum biodegradation removal efficiency of AHTN in the conventional activated sludge processes was about 50% depending on the operational parameters of the wastewater treatment plants because adsorption plays a considerable role than biodegradation in the removal of AHTN due to its physicochemical properties like low water solubility ($1.25 \times 10^{-3} \text{ g L}^{-1}$) and high hydrophobicity ($\log K_{OW} = 5.70$) (Carballa et al., 2005, Zeng et al., 2007 and Lee, Lee, & Oh, 2010). Also, the ANOVA (one-way) test statistic results supported that the removal of AHTN via biodegradation was not important in the aerobic reactor at all SRTs ($P = 0.088$, $\alpha = 0.05$, $F = 4.16$). The sorbed masses (1.75 – 4.19 ng) and volatilized masses (0.00068 – 0.00072 ng) were low for AHTN in the aerobic reactor at all SRTs (Table 6.16). The AHTN removal percentages also were

low (between 0.45% and 1.14% for sorption and between 0.00017% and 0.00020% for volatilization, respectively) in the aerobic reactor at all SRTs (Table 6.16). The ANOVA (one-way) test statistics results showed that removal of AHTN via sorption ($P = 0.058$, $\alpha = 0.05$, $F = 5.46$) and volatilization ($P = 0.060$, $\alpha = 0.05$, $F = 5.35$) were insignificant in the aerobic reactor at all SRTs. The adsorbed AHTN masses to the aerobic sludge increased from 64.55 ng to 273.75 ng corresponding to the adsorption yields from 16.50% to 74.73% at SRTs from 5 days to 55 days, respectively (Table 6.16). Low solubility ($1.25 \times 10^{-3} \text{ g L}^{-1}$), high hydrophobicity ($\log K_{OW} = 5.70$) and low Henry's Law constant ($1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$) makes AHTN a hydrophobic micropollutant and adsorption becomes more dominant than biodegradation in the aerobic reactor at all SRTs. The ANOVA (one-way) test statistics results supported that the removal of AHTN via adsorption was important statistically in the aerobic reactor at all SRTs ($P = 0.0008$, $\alpha = 0.05$, $F = 11.29$).

Removal of AHTN via biodegradation was slightly higher in the aerobic reactor (14.97%) than the anaerobic reactor (11.09%) at 55 days SRT owing to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.16). The removal of AHTN via adsorption was slightly higher in the anaerobic reactor (80.90%) than the aerobic reactor (74.73%) at 55 days of SRT (Table 6.16). This could be attributed to the better adsorption conditions for AHTN in the anaerobic reactor than the aerobic reactor. AHTN found more sludge surface to be adsorbed in the anaerobic reactor than the aerobic reactor because the anaerobic reactor had much more MLVSS concentration (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.13.4.4 Removed Masses and Removal Efficiencies of AHTN in Anaerobic/Aerobic Sequential Biological Reactor System. The total biodegraded masses of AHTN increased from 118.57 ng to 226.17 ng resulting in AHTN removal percentages of 12.79% and 24.40% depending on SRT increase from 5 days to 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.16). The maximum biodegradation yield of AHTN was achieved as 24.40% at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.16). The

ANOVA (one-way) test statistic results showed that the relationship between AHTN biodegradation yields and SRTs was negligible in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.228$, $\alpha = 0.05$, $F = 1.81$). The sorbed masses (4.30 – 10.39 ng) and volatilized masses (0.00156 – 0.00204 ng) were low for AHTN in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.16). The AHTN removal percentages also were low (between 0.46% and 1.12% for sorption and between 0.00017% and 0.00022% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.16). The ANOVA (one-way) test statistics results showed that removal of AHTN via sorption ($P = 0.111$, $\alpha = 0.05$, $F = 3.49$) and volatilization ($P = 0.113$, $\alpha = 0.05$, $F = 3.43$) were not significant in anaerobic/aerobic sequential biological reactor system at all SRTs. The total adsorbed masses of AHTN to the anaerobic (from 96.42 ng to 416.65 ng) and aerobic (from 64.55 ng to 273.75 ng) sludge increased from 160.98 ng to 690.40 ng as the SRT was increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.16). The raise in the adsorbed masses also increased the adsorption yields of AHTN from 17.37% to 74.48% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.16). AHTN has a hydrophobic structure (low water solubility $= 1.25 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 5.70$, and low Henry's Law constant $= 1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$), therefore, the adsorption has a significant contribution on the removal of AHTN in the anaerobic/aerobic sequential biological reactor system at all SRTs according to the ANOVA (one-way) test statistics results ($P = 0.0006$, $\alpha = 0.05$, $F = 11.94$).

The results from this study showed that AHTN can not be effectively removed via biodegradation (24.40%), sorption (1.12%) and volatilization (0.00022%) at 55 days SRT. It is important to note that the adsorption (74.48%) is the main removal mechanism of AHTN at 55 days SRT (Figure 6.12). The adsorption of AHTN onto the biological sludges also confirmed by Yang & Metcalfe (2006) and they reported that the AHTN is most likely to accumulate onto the activated sludge of the secondary treatment in the wastewater treatment plants because of its hydrophobicity

(log K_{OW} = 5.70), low water solubility (1.25×10^{-3} g L⁻¹) and low Henry's Law constant (1.40×10^{-4} atm m³ mol⁻¹) values (Yang & Metcalfe, 2006).

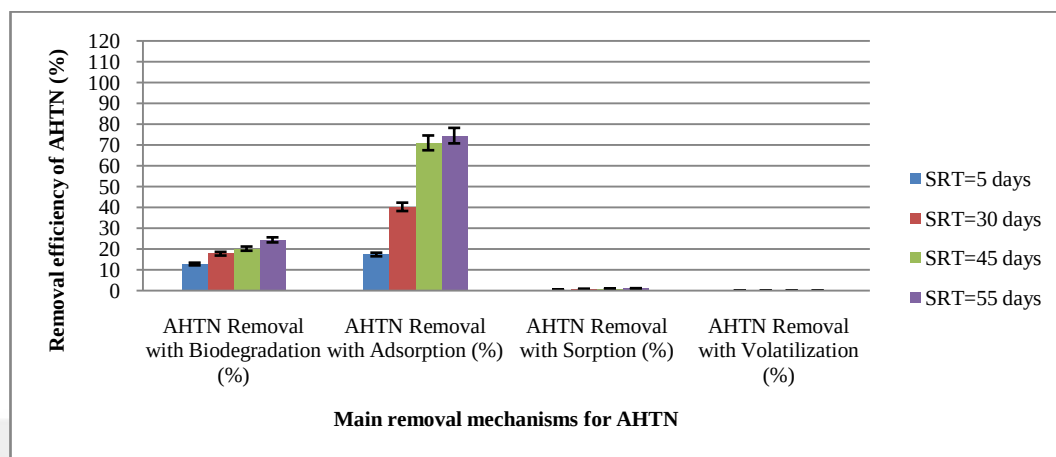


Figure 6.12 The removal efficiencies of AHTN with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.14 Total Perfluorooctanic Acid (PFOA) Removals

6.1.14.1 Total PFOA Removals in Anaerobic Biological Reactor

In the anaerobic reactor, the maximum PFOA removal efficiency was calculated as 6.7% with a PFOA effluent of $0.1652 \mu\text{g L}^{-1}$ at a PFOA influent of $0.1770 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.17). The maximum PFOA removal efficiency was achieved as 9.4% at 30 days SRT with a PFOA effluent of $0.1604 \mu\text{g L}^{-1}$ for a PFOA influent of $0.1770 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.17). After 45 days of SRT operation, the maximum PFOA removal efficiency was determined as 10.9% with a PFOA effluent of $0.1577 \mu\text{g L}^{-1}$ for a PFOA influent of $0.1770 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.17). When the SRT was increased to 55 days, the maximum PFOA removal efficiency was obtained as 12.0% with a PFOA effluent of $0.1557 \mu\text{g L}^{-1}$ for a PFOA influent of $0.1770 \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.17).

Table 6.17 PFOA and its metabolite Perfluoroheptanoic Acid (PFHpA) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent PFOA ($\mu\text{g L}^{-1}$)	Effluent PFOA ($\mu\text{g L}^{-1}$)	metabolite of PFOA namely PFHpA			Removed PFOA ($\mu\text{g L}^{-1}$)	PFOA Rem. Eff. (%)	Influent PFOA ($\mu\text{g L}^{-1}$)	Effluent PFOA ($\mu\text{g L}^{-1}$)	metabolite of PFOA namely PFHpA			Removed PFOA ($\mu\text{g L}^{-1}$)	PFOA Rem. Eff. (%)
			Influent PFHpA ($\mu\text{g L}^{-1}$)	Effluent PFHpA ($\mu\text{g L}^{-1}$)	PFHpA Rem. Eff. (%)					Influent PFHpA ($\mu\text{g L}^{-1}$)	Effluent PFHpA ($\mu\text{g L}^{-1}$)	PFHpA Rem. Eff. (%)		
5	0.1770 $\pm$ 0.001	0.1652 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0094 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0118 $\pm$ 0.001	6.7 $\pm$ 0.5	0.1652 $\pm$ 0.001	0.1483 $\pm$ 0.001	0.0094 $\pm$ 0.001	0.0077 $\pm$ 0.001	18.1 $\pm$ 0.5	0.0169 $\pm$ 0.001	10.2 $\pm$ 0.5
30	0.1770 $\pm$ 0.001	0.1604 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0062 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0166 $\pm$ 0.001	9.4 $\pm$ 0.5	0.1604 $\pm$ 0.001	0.1396 $\pm$ 0.001	0.0062 $\pm$ 0.001	0.0047 $\pm$ 0.001	24.2 $\pm$ 0.5	0.0208 $\pm$ 0.001	13.0 $\pm$ 0.5
45	0.1770 $\pm$ 0.001	0.1577 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0055 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0193 $\pm$ 0.001	10.9 $\pm$ 0.5	0.1577 $\pm$ 0.001	0.1326 $\pm$ 0.001	0.0055 $\pm$ 0.001	0.0040 $\pm$ 0.001	27.3 $\pm$ 0.5	0.0251 $\pm$ 0.001	15.9 $\pm$ 0.5
55	0.1770 $\pm$ 0.001	0.1557 $\pm$ 0.001	0.00 $\pm$ 0.001	0.0050 $\pm$ 0.001	0.00 $\pm$ 0.5	0.0213 $\pm$ 0.001	12.0 $\pm$ 0.5	0.1557 $\pm$ 0.001	0.1275 $\pm$ 0.001	0.0050 $\pm$ 0.001	0.0035 $\pm$ 0.001	30.0 $\pm$ 0.5	0.0282 $\pm$ 0.001	18.1 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent PFOA ($\mu\text{g L}^{-1}$)	Effluent PFOA ($\mu\text{g L}^{-1}$)	metabolite of PFOA namely PFHpA			Removed PFOA ($\mu\text{g L}^{-1}$)	PFOA Rem. Eff. (%)
			Influent PFHpA ($\mu\text{g L}^{-1}$)	Effluent PFHpA ($\mu\text{g L}^{-1}$)	PFHpA Rem. Eff. (%)		
5	0.1770 $\pm$ 0.001	0.1483 $\pm$ 0.001	0.0094 $\pm$ 0.001	0.0077 $\pm$ 0.001	18.1 $\pm$ 0.5	0.029 $\pm$ 0.001	16.2 $\pm$ 0.5
30	0.1770 $\pm$ 0.001	0.1396 $\pm$ 0.001	0.0062 $\pm$ 0.001	0.0047 $\pm$ 0.001	24.2 $\pm$ 0.5	0.037 $\pm$ 0.001	21.1 $\pm$ 0.5
45	0.1770 $\pm$ 0.001	0.1326 $\pm$ 0.001	0.0055 $\pm$ 0.001	0.0040 $\pm$ 0.001	27.3 $\pm$ 0.5	0.044 $\pm$ 0.001	25.1 $\pm$ 0.5
55	0.1770 $\pm$ 0.001	0.1275 $\pm$ 0.001	0.0050 $\pm$ 0.001	0.0035 $\pm$ 0.001	30.0 $\pm$ 0.5	0.049 $\pm$ 0.001	28.0 $\pm$ 0.5

The raise in the SRTs from 5 days to 55 days was increased the PFOA removal efficiencies from 6.7% to 12.0%, respectively in the anaerobic reactor (Table 6.17). The physicochemical properties of PFOA such as low water solubility (4.81×10^{-4} g L⁻¹) and high hydrophobicity ($\log K_{OW} = 4.81$) enables the partial biodegradation in the anaerobic reactor at all SRTs. However, the ANOVA (one-way) statistical analysis results showed that the partial biodegradation of PFOA at increasing SRTs was not significant in the anaerobic reactor at all SRTs ($P = 0.071$, $\alpha = 0.05$, $F = 4.82$).

In this study, the presence of Perfluoroheptanoic Acid (PFHpA) which is the main metabolite of PFOA was monitored in the effluents of the anaerobic reactor at all SRTs. Although PFHpA has slightly less octanol/water partition coefficient ($\log K_{OW} = 4.15$) and higher water solubility (3.65×10^{-3} g L⁻¹) than its parent compound of PFOA ($\log K_{OW} = 4.81$ and water solubility = 4.81×10^{-4} g L⁻¹), PFHpA was accepted as a hydrophobic micropollutant due to having a higher $\log K_{OW}$ than 4.00. The effluent concentrations of PFHpA were determined as 0.0094, 0.0062, 0.0055 and 0.0050 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.17).

6.1.14.2 Total PFOA Removals in Aerobic Biological Reactor

The maximum PFOA removal efficiency of the aerobic biological reactor was measured as 10.2% with a PFOA effluent of 0.1483 $\mu\text{g L}^{-1}$ at a PFOA influent of 0.1652 $\mu\text{g L}^{-1}$ at 5 days SRT (Table 6.17). At 30 days SRT, the maximum PFOA removal efficiency did not change considerably and found as 13.0% with a PFOA effluent of 0.1396 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1604 $\mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.17). At 45 days SRT, the maximum PFOA removal efficiency was calculated as 15.9% with a PFOA effluent of 0.1326 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1577 $\mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.17). For the maximum SRT of 55 days, the maximum PFOA removal efficiency was determined as 18.1% with a PFOA effluent of 0.1275 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1557 $\mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.17).

Total removal of PFOA was slightly higher in the aerobic reactor (18.1%) than the anaerobic reactor (12.0%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.17). Although PFOA is a hydrophobic micropollutant and resistant to extensive biodegradation due its physicochemical properties (low water solubility = $4.81 \times 10^{-4} \text{ g L}^{-1}$ and high $\log K_{ow} = 4.81$), PFOA was partially biodegraded in both reactors.

PFOA removal efficiencies increased from 10.2% to 18.1% as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.17). However, the increase in PFOA yields with increasing SRTs was insignificant according to the ANOVA (one-way) statistical analysis results in the aerobic reactor ($P = 0.128$, $\alpha = 0.05$, $F = 3.12$). It can be concluded that the PFOA could not biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the PFHpA remaining from the anaerobic reactor and the influent concentrations of PFHpA were measured as 0.0094, 0.0062, 0.0055 and $0.0050 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.17). The effluent concentrations of PFHpA were determined as 0.0077, 0.0047, 0.0040 and $0.0035 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.17). PFHpA removal efficiencies were found as 18.1%, 24.2%, 27.3% and 30.0% at 5, 30, 45 and 55 days SRTs in the aerobic reactor (Table 6.17). In general, the metabolite yield increases due to the enhanced metabolism capacity of the microorganisms at longer operation times (Evangelista, Cooper, & Yargeau, 2010). The PFHpA yield of the aerobic reactor increased at increasing SRTs and the maximum PFHpA yield was obtained as 30.0% at the highest SRT of 55 days (Table 6.17). A linear correlation between PFHpA yields and SRTs was observed for the aerobic reactor and this regression was meaningful statistically according to the ANOVA (one-way) test statistics results at all SRTs ($R^2 = 0.96$, $P = 0.00015$, $\alpha = 0.05$, $F = 71.96$).

6.1.14.3 Total PFOA Removals in Anaerobic/Aerobic Sequential Biological Reactor System

For 5 days SRT, the maximum PFOA removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 16.2% with a PFOA effluent of 0.1483 $\mu\text{g L}^{-1}$ at a PFOA influent of 0.1770 $\mu\text{g L}^{-1}$ (Table 6.17). The maximum PFOA removal efficiency was achieved as 21.1% with a PFOA effluent of 0.1396 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1770 $\mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.17). The maximum PFOA removal efficiency was found as 25.1% with a PFOA effluent of 0.1326 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1770 $\mu\text{g L}^{-1}$ for 45 days SRT operation in the anaerobic/aerobic sequential biological reactor system (Table 6.17). The maximum PFOA removal efficiency was determined as 28.0% with a PFOA effluent of 0.1275 $\mu\text{g L}^{-1}$ for a PFOA influent of 0.1770 $\mu\text{g L}^{-1}$ at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.17).

In the anaerobic/aerobic sequential biological reactor system, the influent concentrations of PFHpA were measured as 0.0094, 0.0062, 0.0055 and 0.0050 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively (Table 6.17). The effluent PFHpA concentrations were determined as 0.0077, 0.0047, 0.0040 and 0.0035 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.17). In the anaerobic/aerobic sequential biological reactor system 18.1%, 24.2%, 27.3% and 30.0% removal efficiencies for PFHpA were found at 5, 30, 45 and 55 days SRTs, respectively (Table 6.17). PFHpA removal efficiencies increased with the increasing SRTs although PFHpA is a hydrophobic micropollutant (low water solubility = $0.481 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.81$). This can be attributed to the 18.1%, 24.2%, 27.3% and 30.0% medium biodegradation yields of PFHpA at 5, 30, 45 and 55 days SRTs, respectively due to the enhanced metabolism capacity of the microorganisms at longer operation times (Evangelista et al., 2010). The maximum PFHpA yield was obtained as 30.0% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.17).

6.1.14.4 Removal Mechanisms of PFOA in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of PFOA. The biodegraded, adsorbed, sorbed and volatilized PFOA masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.18).



Table 6.18 The total removal percentages for PFOA throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.029	0.0016	0.071	0.00004	0.002	0.000773	0.000000773	6.66	16.05	0.45	0.00017
30	0.042	0.0044	0.198	0.00007	0.003	0.001100	0.000001100	9.40	44.73	0.68	0.00025
45	0.048	0.0076	0.340	0.00009	0.004	0.001225	0.000001225	10.90	76.89	0.90	0.00028
55	0.053	0.0077	0.348	0.00011	0.005	0.001372	0.000001372	12.03	78.64	1.13	0.00031
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.034	0.003	0.045	0.00009	0.0013	0.000655	0.000000655	10.21	13.59	0.40	0.00020
30	0.042	0.007	0.110	0.00016	0.0024	0.000892	0.000000892	12.96	34.21	0.75	0.00028
45	0.050	0.013	0.201	0.00017	0.0026	0.000883	0.000000883	15.94	63.68	0.82	0.00028
55	0.056	0.015	0.218	0.00022	0.0033	0.000999	0.000000999	18.12	70.00	1.06	0.00032
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	0.129	--	0.116	--	0.0033	--	0.000001428	16.19	14.56	0.42	0.00018
30	0.168	--	0.308	--	0.0054	--	0.000001992	21.14	38.62	0.68	0.00025
45	0.200	--	0.541	--	0.0066	--	0.000002108	25.11	67.94	0.83	0.00026
55	0.223	--	0.566	--	0.0083	--	0.000002371	27.96	71.06	1.04	0.00030

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.14.4.1 Removed Masses and Removal Efficiencies of PFOA. An example for the calculations relevant to the removed masses and the removal efficiencies of PFOA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.145 to 6.168, respectively at a SRT of 5 days (Table 6.18).

The biodegraded masses of PFOA were calculated from Equations 6.145, 6.146 and 6.147 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.18).

$$M_{\text{BIO,Anaerobic}} = (0.0118 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 0.029 \mu\text{g} \quad (6.145)$$

$$M_{\text{BIO,Aerobic}} = (0.0169 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 0.034 \mu\text{g} \quad (6.146)$$

$$M_{\text{BIO,Sequential}} = (0.0290 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 0.129 \mu\text{g} \quad (6.147)$$

The biodegradation removal efficiencies for PFOA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.148, 6.149 and 6.150, respectively at 5 days SRT (Table 6.18).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (0.029 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 6.66\% \quad (6.148)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (0.034 \times 100) / (0.1652 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 10.21\% \quad (6.149)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (0.129 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 16.19\% \quad (6.150)$$

The adsorbed masses of PFOA were calculated using Equation 6.151, 6.152 and 6.153 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.18).

$$M_{\text{ADS,Anaerobic}} = [(0.0016 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.071 \mu\text{g} \quad (6.151)$$

$$M_{\text{ADS,Aerobic}} = [(0.003 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.045 \mu\text{g} \quad (6.152)$$

$$M_{\text{ADS,Sequential}} = 0.071 + 0.045 = 0.116 \mu\text{g} \quad (6.153)$$

The total adsorption removal efficiencies of PFOA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.154, 6.155 and 6.156, respectively at 5 days SRT (Table 6.18).

$$\text{Ads}(\%),_{\text{Anaerobic}} = (0.071 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 16.05\% \quad (6.154)$$

$$\text{Ads}(\%),_{\text{Aerobic}} = (0.045 \times 100) / (0.1652 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 13.59\% \quad (6.155)$$

$$\text{Ads}(\%),_{\text{Sequential}} = (0.116 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 14.56\% \quad (6.156)$$

The sorbed masses into the anaerobic and aerobic biological sludges of PFOA were calculated according to the Equation 6.157 and 6.158, respectively while the total sorbed mass for PFOA in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.159 at 5 days SRT (Table 6.18).

$$M_{\text{SORP,Anaerobic}} = [(0.00004 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.0020 \mu\text{g} \quad (6.157)$$

$$M_{\text{SORP,Aerobic}} = [(0.00009 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.0013 \mu\text{g} \quad (6.158)$$

$$M_{\text{SORP,Sequential}} = 0.0020 + 0.0013 = 0.0033 \mu\text{g} \quad (6.159)$$

The total sorption removal efficiencies of PFOA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.160, 6.161 and 6.162, respectively at 5 days SRT (Table 6.18).

$$\text{Sorp}(\%),_{\text{Anaerobic}} = (0.0020 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.45\% \quad (6.160)$$

$$\text{Sorp}(\%),_{\text{Aerobic}} = (0.0013 \times 100) / (0.1652 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.40\% \quad (6.161)$$

$$\text{Sorp}(\%),_{\text{Sequential}} = (0.0033 \times 100) / (0.1770 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.42\% \quad (6.162)$$

Volatilized masses of PFOA were calculated according to the Equation 6.163, 6.164 and 6.165 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.18).

$$M_{\text{VOL,An}} = (7.73 \times 10^{-4} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 7.73 \times 10^{-7} \mu\text{g} \quad (6.163)$$

$$M_{VOL,Ae} = (6.55 \times 10^{-4} \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 6.55 \times 10^{-7} \mu\text{g} \quad (6.164)$$

$$M_{VOL,Sequential} = 7.73 \times 10^{-7} + 6.55 \times 10^{-7} = 1.428 \times 10^{-6} \mu\text{g} \quad (6.165)$$

The total volatilization removal efficiencies of PFOA were determined according to the Equation 6.166, 6.167 and 6.168 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.18).

$$\text{Vol}(\%)_{\text{Anaerobic}} = (7.73 \times 10^{-7} \times 100) / (0.1770 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00017\% \quad (6.166)$$

$$\text{Vol}(\%)_{\text{Aerobic}} = (6.55 \times 10^{-7} \times 100) / (0.1652 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00020\% \quad (6.167)$$

$$\text{Vol}(\%)_{\text{Sequential}} = (1.428 \times 10^{-6} \times 100) / (0.1770 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00018\% \quad (6.168)$$

6.1.14.4.2 Removed Masses and Removal Efficiencies of PFOA in Anaerobic Reactor. The biodegraded PFOA masses increased from 0.029 μg to 0.053 μg as the SRT was increased from 5 up to 55 days in the anaerobic reactor (Table 6.18). The biodegradation removal percentages of PFOA also increased from 6.66% to 12.03% with the increasing of SRTs from 5 days up to 55 days (Table 6.18). The anaerobic bacteria can co-metabolized only 12.03% of PFOA together COD and sCOD at the highest SRT operation of 55 days. The microbial cleavage of fluorinated alkyl compounds requires at least one hydrogen atom in the alkyl chain for primary attack to occur (Kucharzyk, Darlington, Benotti, Deeb, & Hawley, 2017). The additional difficulty to oxidatively replace fluorine atoms lies in their ability to form a dense hydrophobic layer surrounding carbon-carbon bonds, preventing oxidative degradation (Kucharzyk et al., 2017). This characteristic fluorine-saturated carbon chain element provides some resistance from utilization by microorganisms as carbon and energy sources (Kucharzyk et al., 2017). Due to the PFOA contains a hydrophobic perfluorinated chain, the biodegradation of PFOA becomes difficult for the anaerobic microorganisms in this study. PFOA is accepted as a hydrophobic micropollutant (low water solubility = $4.81 \times 10^{-4} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.81$) and can not be effectively biodegraded by the anaerobic bacteria. The ANOVA (one-way) test statistic results also showed that there is no significant relationship between PFOA yields and SRTs in the anaerobic reactor ($P = 0.071$, $\alpha = 0.05$, $F = 4.82$). The

sorbed masses ($0.0020 - 0.0050 \mu\text{g}$) and volatilized masses ($7.73 \times 10^{-7} - 1.372 \times 10^{-6} \mu\text{g}$) were low for PFOA in the anaerobic reactor at all SRTs (Table 6.18). The sorption and volatilization removal percentages of PFOA also were low (between 0.45% and 1.13% for sorption and between 0.00017% and 0.00031% for volatilization, respectively) in the anaerobic reactor at all SRTs (Table 6.18). The ANOVA (one-way) test statistics results showed that removal of PFOA via sorption ($P = 0.069$, $\alpha = 0.05$, $F = 4.88$) and volatilization ($P = 0.071$, $\alpha = 0.05$, $F = 4.79$) were not significant in the anaerobic reactor. The adsorbed PFOA masses to the anaerobic sludge increased from $0.071 \mu\text{g}$ to $0.348 \mu\text{g}$ as the SRTs were increased from 5 days to 55 days, respectively (Table 6.18). The PFOA adsorption removal percentages also increased from 16.05% to 78.64% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.18). PFOA shows tendency to be adsorbed on the surface of anaerobic sludge at all SRTs due to its physicochemical properties like having low water solubility ($4.81 \times 10^{-4} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 4.81$) and low Henry's Law constant ($9.08 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$). Moreover, the ANOVA (one-way) test statistics results supported that there was an important relationship between adsorption removal efficiencies and SRTs for PFOA in the anaerobic reactor at all SRTs ($P = 0.0007$, $\alpha = 0.05$, $F = 11.83$).

6.1.14.4.3 Removed Masses and Removal Efficiencies of PFOA in Aerobic Reactor. In the aerobic reactor, the biodegraded PFOA masses increased from $0.034 \mu\text{g}$ to $0.056 \mu\text{g}$ resulting in PFOA biodegradation removal percentages of 10.21% and 18.12% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.18). The maximum biodegradation yield of PFOA (18.12%) was obtained at 55 days SRT (Table 6.18). The ANOVA (one-way) test statistic results showed that the removal of PFOA via biodegradation was not important statistically in the aerobic reactor at all SRTs ($P = 0.128$, $\alpha = 0.05$, $F = 3.12$). The sorbed masses ($0.0013 - 0.0033 \mu\text{g}$) and volatilized masses ($6.55 \times 10^{-7} - 9.99 \times 10^{-7} \mu\text{g}$) were low for PFOA at all SRTs in the aerobic reactor (Table 6.18). The PFOA removal percentages also were low (between 0.40% and 1.06% for sorption and between 0.00020% and 0.00032% for volatilization, respectively) in the aerobic reactor

(Table 6.18). The ANOVA (one-way) test statistics results showed that the removal of PFOA via sorption ($P = 0.059$, $\alpha = 0.05$, $F = 5.41$) and volatilization ($P = 0.061$, $\alpha = 0.05$, $F = 5.32$) were not significant in the aerobic reactor. The adsorption of PFOA masses to the aerobic sludge increased from $0.045 \mu\text{g}$ to $0.218 \mu\text{g}$ as the SRTs were increased from 5 days to 55 days, respectively (Table 6.18). This attributed to the PFOA adsorption yields of 13.59% and 70.00% at 5 days and 55 days SRT, respectively in the aerobic reactor (Table 6.18). Because of PFOA is a hydrophobic micropollutant with its physicochemical properties such as low water water solubility ($4.81 \times 10^{-4} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 4.81$) and low Henry's Law constant ($9.08 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$), PFOA has resistance to extensive biodegradation and adsorption has a significant effect on the removal of PFOA in the aerobic reactor at all SRTs ($P = 0.001$, $\alpha = 0.05$, $F = 10.23$).

Removal of PFOA via biodegradation was slightly higher in the aerobic reactor (18.12%) than the anaerobic reactor (12.03%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.18). Removal of PFOA via adsorption was slightly higher in the anaerobic reactor (78.64%) than the aerobic reactor (70.00%) at 55 days SRT (Table 6.18). It was possible that there were much sludge surfaces to be adsorbed for PFOA in the anaerobic reactor than that in the aerobic reactor owing to the high MLVSS concentration in the anaerobic reactor (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.14.4.4 Removed Masses and Removal Efficiencies of PFOA in Anaerobic/Aerobic Sequential Biological Reactor System. From the Table 6.18, it can be said that the total biodegraded masses of PFOA increased from $0.129 \mu\text{g}$ to $0.223 \mu\text{g}$ resulting in the PFOA removal percentages of 16.19% and 27.96% depending on the SRT increases from 5 days to 55 days in the anaerobic/aerobic sequential biological reactor system. The highest biodegradation yield of PFOA was calculated as 27.96% at 55 days SRT (Table 6.18). However, the ANOVA (one-way) test statistic results showed that the relationship between PFOA biodegradation yields and SRTs was not important statistically in the anaerobic/aerobic sequential

biological reactor system at all SRTs ($P = 0.357$, $\alpha = 0.05$, $F = 1.00$). The sorbed masses ($0.0033 - 0.0083 \mu\text{g}$) and volatilized masses ($1.428 \times 10^{-6} - 2.371 \times 10^{-6} \mu\text{g}$) were low for PFOA at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.18). The PFOA removal percentages also were low (between 0.42% and 1.04% for sorption and between 0.00018% and 0.00030% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.18). The ANOVA (one-way) test statistics results showed that the removal of PFOA via sorption ($P = 0.121$, $\alpha = 0.05$, $F = 3.26$) and volatilization ($P = 0.124$, $\alpha = 0.05$, $F = 3.20$) were negligible in the anaerobic/aerobic sequential biological reactor system. The total adsorbed PFOA masses to the anaerobic (from $0.071 \mu\text{g}$ to $0.348 \mu\text{g}$) and aerobic (from $0.045 \mu\text{g}$ to $0.218 \mu\text{g}$) sludge increased from $0.116 \mu\text{g}$ to $0.566 \mu\text{g}$ as the SRTs increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.18). The raise in the adsorbed masses also increased the PFOA adsorption yields from 14.56% to 71.06% at SRTs varying from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.18). The physicochemical properties such as high octanol-water partition coefficient ($\log K_{OW} = 4.81$), low water water solubility ($4.81 \times 10^{-4} \text{ g L}^{-1}$) and low Henry's Law constant ($9.08 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$) indicates that PFOA has an ability for adsorption on the anaerobic and aerobic sludges. The ANOVA (one-way) test statistics results revealed that there is a strong relationship between adsorption yields and SRTs for PFOA in the anaerobic/aerobic sequential biological reactor system ($P = 0.0009$, $\alpha = 0.05$, $F = 11.17$).

The high octanol-water partition coefficient ($\log K_{OW} = 4.81$), low water water solubility ($4.81 \times 10^{-4} \text{ g L}^{-1}$) and low Henry's Law constant ($9.08 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$) of PFOA indicates high hydrophobicity and resistance to extensive biodegradation. PFOA have been recognized as favorable to adsorption, due to its hydrophobic carbon-fluorine bonds on its molecule (Dombrowski et al., 2018). In this study we found that adsorption (71.06%) is the main removal mechanism for PFOA at 55 days SRT (Figure 6.13). The other removal mechanisms such as biodegradation (27.96%),

sorption (1.04%), and volatilization (0.00030%) could be accepted as negligible for PFOA removal at 55 days SRT (Figure 6.13).

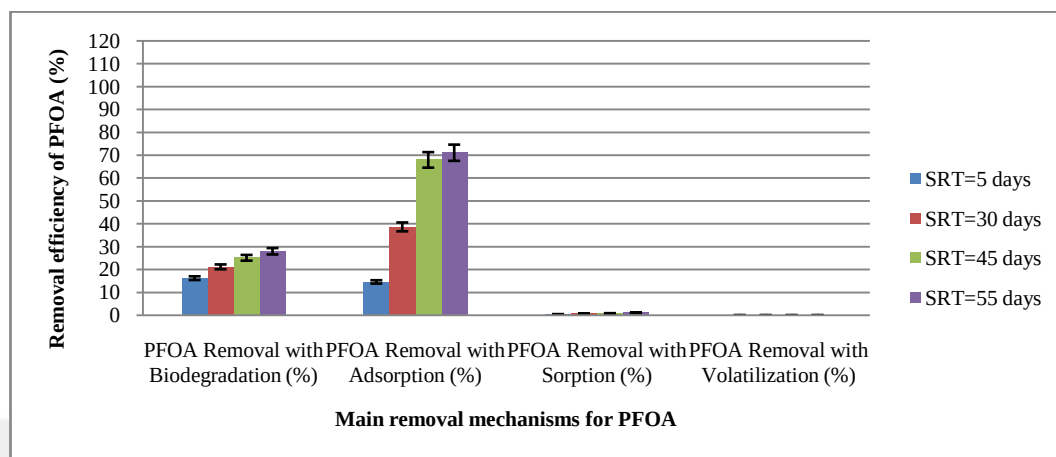


Figure 6.13 The removal efficiencies of PFOA with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.15 Total Perfluorooctanesulfonic Acid (PFOS) Removals

6.1.15.1 Total PFOS Removals in Anaerobic Biological Reactor

At the beginning of the study, the maximum PFOS removal efficiency of the anaerobic reactor was obtained as 11.7% with a PFOS effluent of 15.89 ng L^{-1} at a PFOS influent of 18.00 ng L^{-1} at 5 days SRT (Table 6.19). The maximum PFOS removal efficiency was calculated as 15.3% with a PFOS effluent of 15.25 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} at 30 days SRT in the anaerobic reactor (Table 6.19). For 45 days of SRT operation, the maximum PFOS removal efficiency was found as 15.9% with a PFOS effluent of 15.14 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} in the anaerobic reactor (Table 6.19). When the SRT was increased to the highest level of 55 days, the maximum PFOS removal efficiency did not change considerably and it was determined as 16.4% with a PFOS effluent of 15.05 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} in the anaerobic reactor (Table 6.19).

Table 6.19 PFOS and its metabolite 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decanol (FTA) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent PFOS (ng L ⁻¹)	Effluent PFOS (ng L ⁻¹)	metabolite of PFOS namely FTA			Removed PFOS (ng L ⁻¹)	PFOS Rem. Eff. (%)	Influent PFOS (ng L ⁻¹)	Effluent PFOS (ng L ⁻¹)	metabolite of PFOS namely FTA			Removed PFOS (ng L ⁻¹)	PFOS Rem. Eff. (%)
			Influent FTA (ng L ⁻¹)	Effluent FTA (ng L ⁻¹)	FTA Rem. Eff. (%)					Influent FTA (ng L ⁻¹)	Effluent FTA (ng L ⁻¹)	FTA Rem. Eff. (%)		
5	18.00 $\pm$ 0.001	15.89 $\pm$ 0.001	0.00 $\pm$ 0.001	0.389 $\pm$ 0.001	0.00 $\pm$ 0.5	2.11 $\pm$ 0.001	11.7 $\pm$ 0.5	15.89 $\pm$ 0.001	13.39 $\pm$ 0.001	0.389 $\pm$ 0.001	0.281 $\pm$ 0.001	27.8 $\pm$ 0.5	2.50 $\pm$ 0.001	15.7 $\pm$ 0.5
30	18.00 $\pm$ 0.001	15.25 $\pm$ 0.001	0.00 $\pm$ 0.001	0.368 $\pm$ 0.001	0.00 $\pm$ 0.5	2.75 $\pm$ 0.001	15.3 $\pm$ 0.5	15.25 $\pm$ 0.001	12.15 $\pm$ 0.001	0.368 $\pm$ 0.001	0.239 $\pm$ 0.001	35.1 $\pm$ 0.5	3.10 $\pm$ 0.001	20.3 $\pm$ 0.5
45	18.00 $\pm$ 0.001	15.14 $\pm$ 0.001	0.00 $\pm$ 0.001	0.310 $\pm$ 0.001	0.00 $\pm$ 0.5	2.86 $\pm$ 0.001	15.9 $\pm$ 0.5	15.14 $\pm$ 0.001	10.64 $\pm$ 0.001	0.310 $\pm$ 0.001	0.175 $\pm$ 0.001	43.5 $\pm$ 0.5	4.50 $\pm$ 0.001	29.7 $\pm$ 0.5
55	18.00 $\pm$ 0.001	15.05 $\pm$ 0.001	0.00 $\pm$ 0.001	0.304 $\pm$ 0.001	0.00 $\pm$ 0.5	2.95 $\pm$ 0.001	16.4 $\pm$ 0.5	15.05 $\pm$ 0.001	9.48 $\pm$ 0.001	0.304 $\pm$ 0.001	0.149 $\pm$ 0.001	51.0 $\pm$ 0.5	5.57 $\pm$ 0.001	37.0 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent PFOS (ng L ⁻¹)	Effluent PFOS (ng L ⁻¹)	metabolite of PFOS namely FTA			Removed PFOS (ng L ⁻¹)	PFOS Rem. Eff. (%)
			Influent FTA (ng L ⁻¹)	Effluent FTA (ng L ⁻¹)	FTA Rem. Eff. (%)		
5	18.00 $\pm$ 0.001	13.39 $\pm$ 0.001	0.389 $\pm$ 0.001	0.281 $\pm$ 0.001	27.8 $\pm$ 0.5	4.61 $\pm$ 0.001	25.6 $\pm$ 0.5
30	18.00 $\pm$ 0.001	12.15 $\pm$ 0.001	0.368 $\pm$ 0.001	0.239 $\pm$ 0.001	35.1 $\pm$ 0.5	5.85 $\pm$ 0.001	32.5 $\pm$ 0.5
45	18.00 $\pm$ 0.001	10.64 $\pm$ 0.001	0.310 $\pm$ 0.001	0.175 $\pm$ 0.001	43.5 $\pm$ 0.5	7.36 $\pm$ 0.001	40.9 $\pm$ 0.5
55	18.00 $\pm$ 0.001	9.48 $\pm$ 0.001	0.304 $\pm$ 0.001	0.149 $\pm$ 0.001	51.0 $\pm$ 0.5	8.52 $\pm$ 0.001	47.3 $\pm$ 0.5

The PFOS removal efficiencies increased slightly from 11.7% to 16.4% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.19). The hydrophobic structure of PFOS (low water solubility = 1.04×10^{-4} g L⁻¹ and high log K_{OW} = 4.49) allows only partial biodegradation in the anaerobic reactor at all SRTs. On the other hand, the ANOVA (one-way) statistical analysis results showed that the partial biodegradation of PFOS at increasing SRTs was not important statistically in the anaerobic reactor at all SRTs ($P = 0.134$, $\alpha = 0.05$, $F = 3.00$).

In this study, the presence of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluoro-1-decanol (FTA) which is the main metabolite of PFOS was monitored in the effluents of the anaerobic reactor at all SRTs. FTA was more hydrophobic (log K_{OW} = 6.00) than its parent compound of PFOS (log K_{OW} = 4.49). The effluent concentrations of FTA were determined as 0.389, 0.368, 0.310 and 0.304 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.19).

6.1.15.2 Total PFOS Removals in Aerobic Biological Reactor

For the 5 days SRT, the maximum PFOS removal efficiency of the aerobic biological reactor was obtained as 15.7% with a PFOS effluent of 13.39 ng L⁻¹ at a PFOS influent of 15.89 ng L⁻¹ (Table 6.19). When the SRT was increased to 30 days, the maximum PFOS removal efficiency was found as 20.3% with a PFOS effluent of 12.15 ng L⁻¹ for a PFOS influent of 15.25 ng L⁻¹ in the aerobic reactor (Table 6.19). For 45 days SRT, the maximum PFOS removal efficiency was achieved as 29.7% with a PFOS effluent of 10.64 ng L⁻¹ for a PFOS influent of 15.14 ng L⁻¹ in the aerobic reactor (Table 6.19). At the highest SRT of 55 days, the maximum PFOS removal efficiency reached to 37.0% with a PFOS effluent of 9.48 ng L⁻¹ for a PFOS influent of 15.05 ng L⁻¹ at 55 days SRT in the aerobic reactor (Table 6.19). PFOS removal efficiency of 37.0% at 55 days SRT in the aerobic reactor was higher than the results previously obtained by the other authors (Table 6.19). Yu et al. (2009) obtained 34.0% of maximum PFOS removal efficiency in a real scale sewage

treatment plant for an influent PFOS concentration of $25.3 \pm 4.2 \text{ ng L}^{-1}$ at a SRT of 15 days and at a HRT of 8 h in dry season (September) (Yu et al., 2009).

Total removal of PFOS was higher in the aerobic reactor (37.0%) than the anaerobic reactor (16.4%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.19). On the other hand, previous researchers reported that the aerobic microorganisms could remove a fair amount of multiple $-\text{CF}_2-$ groups from fluorotelomer alcohols in the molecular structure of PFOS (Ross et al., 2018). Although PFOS was accepted as a hydrophobic micropollutant and resistant to extensive biodegradation due its physicochemical properties (low water solubility = $1.04 \times 10^{-4} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.49$), PFOS could be partially biodegraded in both reactors.

An increase was observed for the PFOS removal efficiencies from 15.7% to 37.0% as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.19). However, the increase in PFOS removal efficiencies with increasing SRTs was not important statistically according to the ANOVA (one-way) statistical analysis results in the aerobic reactor ($P = 0.523$, $\alpha = 0.05$, $F = 0.46$). It is important to note that the PFOS could not biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the FTA remaining from the anaerobic reactor and the influent concentrations of FTA were detected as 0.389, 0.368, 0.310 and 0.304 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.19). The effluent concentrations of FTA were measured as 0.281, 0.239, 0.175 and 0.149 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.19). FTA removal efficiencies were obtained as 27.8%, 35.1%, 43.5% and 51.0% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.19). The maximum FTA yield of 51.0% was achieved at the highest SRT of 55 days in the aerobic reactor (Table 6.19). The microorganisms enhanced their metabolism capacities at longer operation times and an increase was observed for the metabolite yields in biological treatment processes (Evangelista et al., 2010). As a result, there was an

increase in FTA yields at increasing SRTs and this raise was significant according to the ANOVA (one-way) test statistics results ($P = 0.0004$, $\alpha = 0.05$, $F = 52.41$).

6.1.15.3 Total PFOS Removals in Anaerobic/Aerobic Sequential Biological Reactor System

At 5 days SRT, the maximum PFOS removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 25.6% with a PFOS effluent of 13.39 ng L^{-1} at a PFOS influent of 18.00 ng L^{-1} (Table 6.19). The maximum PFOS removal efficiency was measured as 32.5% with a PFOS effluent of 12.15 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.19). When the SRT was increased from 30 days to 45 days, the maximum PFOS removal efficiency was found as 40.9% with a PFOS effluent of 10.64 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} in the anaerobic/aerobic sequential biological reactor system (Table 6.19). The maximum PFOS removal efficiency was determined as 47.3% with a PFOS effluent of 9.48 ng L^{-1} for a PFOS influent of 18.00 ng L^{-1} at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.19).

In the anaerobic/aerobic sequential biological reactor system, the influent concentrations of FTA were detected as 0.389, 0.368, 0.310 and 0.304 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively (Table 6.19). The effluent FTA concentrations were obtained as 0.281, 0.239, 0.175 and 0.149 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.19). In the anaerobic/aerobic sequential biological reactor system 27.8%, 35.1%, 43.5% and 51.0% removal efficiencies for FTA were achieved at 5, 30, 45 and 55 days SRTs, respectively (Table 6.19). The maximum FTA yield was obtained as 51.0% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.19).

6.1.15.4 Removal Mechanisms of PFOS in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of PFOS. The biodegraded, adsorbed, sorbed and volatilized PFOS masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.20).



Table 6.20 The total removal percentages for PFOS throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	5.28	0.141	6.34	0.004	0.18	0.075	0.00008	11.73	14.09	0.40	0.00017
30	6.88	0.376	16.91	0.008	0.35	0.100	0.00010	15.28	37.59	0.78	0.00022
45	7.15	0.497	22.35	0.011	0.48	0.111	0.00011	15.89	49.68	1.07	0.00025
55	7.38	0.581	26.15	0.011	0.49	0.120	0.00012	16.39	58.11	1.09	0.00027
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	5.00	0.231	3.47	0.007	0.11	0.061	0.00006	15.73	10.91	0.35	0.00019
30	6.20	0.630	9.45	0.013	0.20	0.071	0.00007	20.33	30.98	0.66	0.00023
45	9.00	0.902	13.53	0.019	0.29	0.075	0.00008	29.72	44.70	0.96	0.00025
55	11.14	1.049	15.73	0.021	0.32	0.087	0.00009	37.01	52.26	1.06	0.00029
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	20.75	--	9.81	--	0.29	--	0.00014	25.62	12.11	0.36	0.00017
30	26.33	--	26.36	--	0.55	--	0.00017	32.50	32.55	0.68	0.00021
45	33.12	--	35.89	--	0.77	--	0.00019	40.89	44.31	0.95	0.00023
55	38.34	--	41.88	--	0.81	--	0.00021	47.33	51.70	1.00	0.00026

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.15.4.1 *Removed Masses and Removal Efficiencies of PFOS.* An example for the calculations relevant to the removed masses and the removal efficiencies of PFOS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.169 to 6.192, respectively at a SRT of 5 days (Table 6.20).

The biodegraded masses of PFOS were calculated from Equations 6.169, 6.170 and 6.171 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.20).

$$M_{\text{BIO,Anaerobic}} = (2.11 \text{ ng L}^{-1}) \times (2.5 \text{ L}) = 5.28 \text{ ng} \quad (6.169)$$

$$M_{\text{BIO,Aerobic}} = (2.50 \text{ ng L}^{-1}) \times (2.0 \text{ L}) = 5.00 \text{ ng} \quad (6.170)$$

$$M_{\text{BIO,Sequential}} = (4.61 \text{ ng L}^{-1}) \times (4.5 \text{ L}) = 20.75 \text{ ng} \quad (6.171)$$

The biodegradation removal efficiencies for PFOS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.172, 6.173 and 6.174, respectively at 5 days SRT (Table 6.20).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (5.28 \times 100) / (18.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 11.73\% \quad (6.172)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (5.00 \times 100) / (15.89 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 15.73\% \quad (6.173)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (20.75 \times 100) / (18.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 25.62\% \quad (6.174)$$

The adsorbed masses of PFOS were calculated using Equation 6.175, 6.176 and 6.177 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.20).

$$M_{\text{ADS,Anaerobic}} = [(0.141 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 6.34 \text{ ng} \quad (6.175)$$

$$M_{\text{ADS,Aerobic}} = [(0.231 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 3.47 \text{ ng} \quad (6.176)$$

$$M_{\text{ADS,Sequential}} = 6.34 + 3.47 = 9.81 \text{ ng} \quad (6.177)$$

The total adsorption removal efficiencies of PFOS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.178, 6.179 and 6.180, respectively at 5 days SRT (Table 6.20).

$$\text{Ads}(\%),_{\text{Anaerobic}} = (6.34 \times 100) / (18.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 14.09\% \quad (6.178)$$

$$\text{Ads}(\%),_{\text{Aerobic}} = (3.47 \times 100) / (15.89 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 10.91\% \quad (6.179)$$

$$\text{Ads}(\%),_{\text{Sequential}} = (9.81 \times 100) / (18.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 12.11\% \quad (6.180)$$

The sorbed masses into the anaerobic and aerobic biological sludges of PFOS were calculated according to the Equation 6.181 and 6.182, respectively while the total sorbed mass for PFOS in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.183 at 5 days SRT (Table 6.20).

$$M_{\text{SORP,Anaerobic}} = [(0.004 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.18 \text{ ng} \quad (6.181)$$

$$M_{\text{SORP,Aerobic}} = [(0.007 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.11 \text{ ng} \quad (6.182)$$

$$M_{\text{SORP,Sequential}} = 0.18 + 0.11 = 0.29 \text{ ng} \quad (6.183)$$

The total sorption removal efficiencies of PFOS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.184, 6.185 and 6.186, respectively at 5 days SRT (Table 6.20).

$$\text{Sorp}(\%),_{\text{Anaerobic}} = (0.18 \times 100) / (18.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.40\% \quad (6.184)$$

$$\text{Sorp}(\%),_{\text{Aerobic}} = (0.11 \times 100) / (15.89 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.35\% \quad (6.185)$$

$$\text{Sorp}(\%),_{\text{Sequential}} = (0.29 \times 100) / (18.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.36\% \quad (6.186)$$

Volatilized masses of PFOS were calculated according to the Equation 6.187, 6.188 and 6.189 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.20).

$$M_{\text{VOL,An}} = (0.075 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00008 \text{ ng} \quad (6.187)$$

$$M_{VOL,Ae} = (0.061 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00006 \text{ ng} \quad (6.188)$$

$$M_{VOL,Sequential} = 0.00008 + 0.00006 = 0.00014 \text{ ng} \quad (6.189)$$

The total volatilization removal efficiencies of PFOS were determined according to the Equation 6.190, 6.191 and 6.192 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.20).

$$\text{Vol}(\%)_{An} = (0.00008 \times 100) / (18.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.00017\% \quad (6.190)$$

$$\text{Vol}(\%)_{Ae} = (0.00006 \times 100) / (15.89 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.00019\% \quad (6.191)$$

$$\text{Vol}(\%)_{Seq} = (0.00014 \times 100) / (18.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.00017\% \quad (6.192)$$

6.1.15.4.2 Removed Masses and Removal Efficiencies of PFOS in Anaerobic Reactor. The biodegraded PFOS masses increased from 5.28 ng to 7.38 ng as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor (Table 6.20). This attributed to an increase in the biodegradation removal percentages of PFOS from 11.73% to 16.39% at SRTs ranging from 5 days to 55 days, respectively (Table 6.20). The anaerobic bacteria can co-metabolized only 16.39% of PFOS together COD and sCOD at the highest SRT of 55 days (Table 6.20). The ANOVA (one-way) test statistic results showed that there is no significant relationship between PFOS yields and SRTs in the anaerobic reactor ($P = 0.134$, $\alpha = 0.05$, $F = 3.00$). Arvaniti & Stasinakis (2015) also reported that PFOS is resistant to extensive biodegradation under anaerobic conditions due to the physicochemical properties (low water solubility = $1.04 \times 10^{-4} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.49$) (Arvaniti & Stasinakis, 2015). The sorbed masses (0.18 – 0.49 ng) and volatilized masses (0.00008 – 0.00012 ng) were low for PFOS at all SRTs in the anaerobic reactor (Table 6.20). The sorption and volatilization removal percentages also were low (between 0.40% and 1.09% for sorption and between 0.00017% and 0.00027% for volatilization, respectively) in the anaerobic reactor at all SRTs (Table 6.20). The ANOVA (one-way) test statistics results showed that the removal of PFOS via sorption ($P = 0.060$, $\alpha = 0.05$, $F = 5.33$) and volatilization ($P = 0.063$, $\alpha = 0.05$, $F = 5.18$) were not significant in the anaerobic reactor at all SRTs. The adsorbed PFOS

masses increased from 6.34 ng to 26.15 ng as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor (Table 6.20). The adsorption removal percentages of PFOS were found between 14.09% and 58.11% at 5 days and 55 days SRTs, respectively (Table 6.20). The adsorbed masses of PFOS on the anaerobic sludge were found to be important in the anaerobic reactor since PFOS was a hydrophobic micropollutant (low solubility = 1.04×10^{-4} g L⁻¹, high log K_{OW} = 4.49 and low Henry's Law constant = 1.10×10^{-2} atm m³ mol⁻¹). The ANOVA (one-way) test statistics results showed that there is a significant relationship between PFOS yields and SRTs in the anaerobic reactor (P = 0.0002, α = 0.05, F = 14.95).

6.1.15.4.3 Removed Masses and Removal Efficiencies of PFOS in Aerobic Reactor. In the aerobic reactor, the biodegraded PFOS masses increased from 5.00 ng to 11.14 ng resulting in PFOS biodegradation removal percentages of 15.73% and 37.01% depending on SRT increase from 5 days to 55 days, respectively (Table 6.20). The maximum biodegradation yield of PFOS was calculated as 37.01% at 55 days SRT (Table 6.20). The perfluorinated chains in the molecular structure of PFOS are accepted as recalcitrant to extensive biodegradation (Kucharzyk et al., 2017). However, the recent studies have shown that the aerobic microorganisms could remove a fair amount of multiple –CF₂– groups from fluorotelomer alcohols in the molecular structure of PFOS (Ross et al., 2018). The fragmentation of the multiple –CF₂– groups leads to the formation of the perfluorinated acids, furthermore, the α - and/or β -oxidation mechanisms were involved in the degradation pathway (Sun et al., 2013). PFOS was accepted as a hydrophobic micropollutant and resistant to extensive biodegradation due its physicochemical properties (low water solubility = 1.04×10^{-4} g L⁻¹ and high log K_{OW} = 4.49), therefore, PFOS was partially biodegraded (37.01%) in the aerobic reactor at 55 days SRT. The ANOVA (one-way) test statistics also supported that the biodegradation of PFOS was not important statistically in the aerobic reactor at all SRTs (P = 0.523, α = 0.05, F = 0.46). The sorbed masses (0.11 – 0.32 ng) and volatilized masses (0.00006 – 0.00009 ng) were low for PFOS at all SRTs in the aerobic reactor (Table 6.20). The PFOS removal percentages also were low (between 0.35% and 1.06% for sorption and between 0.00019% and 0.00029% for volatilization, respectively) in the aerobic reactor at all

SRTs (Table 6.20). The ANOVA (one-way) test statistics results showed that removal of PFOS via sorption ($P = 0.080$, $\alpha = 0.05$, $F = 4.43$) and volatilization ($P = 0.083$, $\alpha = 0.05$, $F = 4.33$) were insignificant in the aerobic reactor at all SRTs. The adsorbed PFOS masses to the aerobic sludge increased from 3.47 ng to 15.73 ng as the SRTs were increased from 5 days to 55 days, respectively (Table 6.20). This attributed to the PFOS adsorption yields of 10.91% and 52.26% at 5 days and 55 days SRTs, respectively (Table 6.20). The ANOVA (one-way) test statistics results showed that there was a significant relationship between the PFOS adsorption yields and increasing SRTs in the aerobic reactor ($P = 0.0007$, $\alpha = 0.05$, $F = 11.81$). As a result of the study, it can be concluded that the adsorption has a significant effect on the removal of PFOS in the aerobic reactor at all SRTs because of being a hydrophobic micropollutant with its low solubility ($0.104 \times 10^{-3} \text{ g L}^{-1}$), high hydrophobicity ($\log K_{OW} = 4.49$) and low Henry's Law constant ($1.10 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$).

Removal of PFOS via biodegradation was higher in the aerobic reactor (37.01%) than the anaerobic reactor (16.39%) at 55 days SRT because of the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.20). Removal of PFOS via adsorption was higher in the anaerobic reactor (58.11%) than the aerobic reactor (52.26%) at 55 days SRT (Table 6.20) since PFOS found more sludge surface to be adsorbed in the anaerobic reactor (MLVSS concentration of 27600 mg L^{-1}) than the aerobic reactor (MLVSS concentration of 3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.15.4.4 Removed Masses and Removal Efficiencies of PFOS in Anaerobic/Aerobic Sequential Biological Reactor System. From the Table 6.20, it can be said that the total biodegraded masses of PFOS increased from 20.75 ng to 38.34 ng resulting in the PFOS removal percentages of 25.62% and 47.33% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system. The highest level of the PFOS biodegradation yield was achieved as 47.33% at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.20). However, the

ANOVA (one-way) test statistic results showed that the relationship between PFOS biodegradation yields and SRTs was not significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.819$, $\alpha = 0.05$, $F = 0.06$). The sorbed masses (0.29 – 0.81 ng) and volatilized masses (0.00014 – 0.00021 ng) were low for PFOS at all SRTs in the anaerobic/aerobic sequential biological reactor (Table 6.20). The PFOS removal percentages also were low (between 0.36% and 1.00% for sorption and between 0.00017% and 0.00026% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.20). The ANOVA (one-way) test statistics results showed that removal of PFOS via sorption ($P = 0.084$, $\alpha = 0.05$, $F = 4.26$) and volatilization ($P = 0.087$, $\alpha = 0.05$, $F = 4.17$) were negligible in the anaerobic/aerobic sequential biological reactor system at all SRTs. The total adsorbed PFOS masses to the anaerobic (from 6.34 ng to 26.15 ng) and aerobic (from 3.47 ng to 15.73 ng) sludge increased from 9.81 ng to 41.88 ng as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.20). The increase in the total adsorption masses also increased the total adsorption yields from 12.11% to 51.70% from 5 days to 55 days, respectively for PFOS in the anaerobic/aerobic sequential biological reactor system (Table 6.20). The ANOVA (one-way) test statistics results supported that the removal of PFOS via adsorption was significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.0001$, $\alpha = 0.05$, $F = 17.30$) due to the hydrophobicity of PFOS (low solubility = 1.04×10^{-4} g L⁻¹, high log $K_{OW} = 4.49$ and low Henry's Law constant = 1.10×10^{-2} atm m³ mol⁻¹).

The micropollutants with log K_{OW} values lower than 4.0 are preferably dissolved in the water matrix, whereas the more hydrophobic ones with log K_{OW} values higher than 4.0 tend to be adsorbed on the surface of the solids (sludge/sediment/soil) (López, Brandsma, Leonards, & De Boer, 2009). PFOS was a hydrophobic micropollutant with its low water solubility (1.04×10^{-4} g L⁻¹), high octanol/water partition coefficient (log $K_{OW} = 4.49$) and low Henry's Law constant (1.10×10^{-2} atm m³ mol⁻¹). Therefore, the main removal mechanism was found as adsorption (51.70%) for PFOS at 55 days SRT (Figure 6.14).

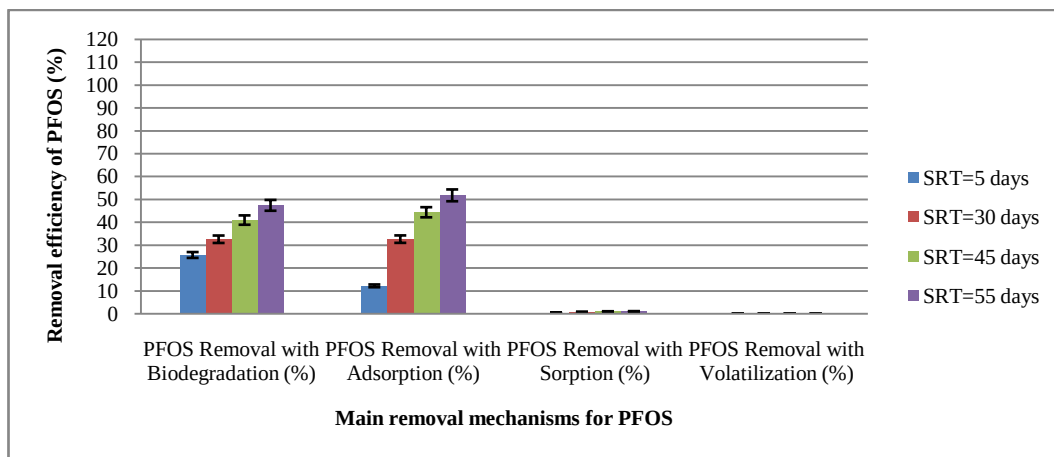


Figure 6.14 The removal efficiencies of PFOS with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.16 Total Gemfibrozil (GFZ) Removals

6.1.16.1 Total GFZ Removals in Anaerobic Biological Reactor

In the anaerobic reactor, the maximum GFZ removal efficiency was calculated as 9.1% with a GFZ effluent of $48.44 \mu\text{g L}^{-1}$ at a GFZ influent of $53.30 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.21). The maximum GFZ removal efficiency was achieved as 12.0% with a GFZ effluent of $46.89 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic reactor (Table 6.21). After 45 days of SRT operation, the maximum GFZ removal efficiency was determined as 12.9% with a GFZ effluent of $46.41 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.21). When the SRT was increased to 55 days, the maximum GFZ removal efficiency was obtained as 14.5% with a GFZ effluent of $45.56 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.21).

Table 6.21 GFZ and its metabolite 2-Hydroxy-5-Methylbenzaldehyde (2,H-5,MBA) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent GFZ ($\mu\text{g L}^{-1}$)	Effluent GFZ ($\mu\text{g L}^{-1}$)	metabolite of GFZ namely 2,H-5,MBA			Removed GFZ ($\mu\text{g L}^{-1}$)	GFZ Rem. Eff. (%)	Influent GFZ ($\mu\text{g L}^{-1}$)	Effluent GFZ ($\mu\text{g L}^{-1}$)	metabolite of GFZ namely 2,H-5,MBA			Removed GFZ ($\mu\text{g L}^{-1}$)	GFZ Rem. Eff. (%)
			Influent 2,H-5,MBA ($\mu\text{g L}^{-1}$)	Effluent 2,H- 5,MBA ($\mu\text{g L}^{-1}$)	2,H-5,MBA Rem. Eff. (%)					Influent 2,H-5,MBA ($\mu\text{g L}^{-1}$)	Effluent 2,H- 5,MBA ($\mu\text{g L}^{-1}$)	2,H- 5,MBA Rem. Eff. (%)		
5	53.30±0.05	48.44±0.05	0.00 ±0.05	2.61 ±0.05	0.00 ±0.5	4.86±0.05	9.1±0.5	48.44±0.05	42.37±0.05	2.61 ±0.05	0.65 ±0.05	75.1 ±0.5	6.07±0.05	12.5±0.5
30	53.30±0.05	46.89±0.05	0.00 ±0.05	1.97 ±0.05	0.00 ±0.5	6.41±0.05	12.0±0.5	46.89±0.05	39.27±0.05	1.97 ±0.05	0.30 ±0.05	84.8 ±0.5	7.61±0.05	16.2±0.5
45	53.30±0.05	46.41±0.05	0.00 ±0.05	1.90 ±0.05	0.00 ±0.5	6.89±0.05	12.9±0.5	46.41±0.05	38.38±0.05	1.90 ±0.05	0.19 ±0.05	90.0 ±0.5	8.02±0.05	17.3±0.5
55	53.30±0.05	45.56±0.05	0.00 ±0.05	1.70 ±0.05	0.00 ±0.5	7.74±0.05	14.5±0.5	45.56±0.05	36.41±0.05	1.70 ±0.05	0.09 ±0.05	94.7 ±0.5	9.15±0.05	20.1±0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent GFZ ($\mu\text{g L}^{-1}$)	Effluent GFZ ($\mu\text{g L}^{-1}$)	metabolite of GFZ namely 2,H-5,MBA			Removed GFZ ($\mu\text{g L}^{-1}$)	GFZ Rem. Eff. (%)
			Influent 2,H-5,MBA ($\mu\text{g L}^{-1}$)	Effluent 2,H- 5,MBA ($\mu\text{g L}^{-1}$)	2,H- 5,MBA Rem. Eff. (%)		
5	53.30±0.05	42.37±0.05	2.61±0.05	0.65±0.05	75.1±0.5	10.93±0.05	20.5±0.5
30	53.30±0.05	39.27±0.05	1.97±0.05	0.30±0.05	84.8±0.5	14.03±0.05	26.3±0.5
45	53.30±0.05	38.38±0.05	1.90±0.05	0.19±0.05	90.0±0.5	14.92±0.05	28.0±0.5
55	53.30±0.05	36.41±0.05	1.70±0.05	0.09±0.05	94.7±0.5	16.89±0.05	31.7±0.5

The total GFZ removal efficiencies increased slightly from 9.1% to 14.5% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.21). The hydrophobic structure of GFZ (low water solubility = 4.964×10^{-3} g L⁻¹ and high log K_{OW} = 4.77) allows the partial biodegradation in the anaerobic reactor at all SRTs. The increase in the GFZ yields at increasing SRTs was studied with the ANOVA (one-way) statistical analysis and the results showed that the increased GFZ yields at increasing SRTs was not significant in the anaerobic reactor at all SRTs (P = 0.096, α = 0.05, F = 3.90).

In this study, 2-Hydroxy-5-Methylbenzaldehyde (2,H-5,MBA) which is the main metabolite of GFZ was monitored in the effluents of the anaerobic reactor at all SRTs. Although GFZ was a hydrophobic micropollutant (low water solubility = 4.964×10^{-3} g L⁻¹ and high log K_{OW} = 4.77), 2,H-5,MBA accepted as a hydrophilic micropollutant with its high water solubility (2.18 g L⁻¹) and low log K_{OW} (2.55) values. The effluent concentrations of 2,H-5,MBA were measured as 2.61, 1.97, 1.90 and 1.70 μ g L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.21).

6.1.16.2 Total GFZ Removals in Aerobic Biological Reactor

The maximum GFZ removal efficiency of the aerobic biological reactor was found as 12.5% with a GFZ effluent of 42.37 μ g L⁻¹ at a GFZ influent of 48.44 μ g L⁻¹ at 5 days SRT (Table 6.21). At 30 days SRT, the maximum GFZ removal efficiency was determined as 16.2% with a GFZ effluent of 39.27 μ g L⁻¹ for a GFZ influent of 46.89 μ g L⁻¹ (Table 6.21). At 45 days SRT, the maximum GFZ removal efficiency did not change considerably and was calculated as 17.3% with a GFZ effluent of 38.38 μ g L⁻¹ for a GFZ influent of 46.41 μ g L⁻¹ in the aerobic reactor (Table 6.21). For the maximum SRT of 55 days, the maximum GFZ removal efficiency was obtained as 20.1% with a GFZ effluent of 36.41 μ g L⁻¹ for a GFZ influent of 45.56 μ g L⁻¹ in the aerobic reactor (Table 6.21).

Total removal of GFZ was slightly higher in the aerobic reactor (20.1%) than the anaerobic reactor (14.5%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.21). Although GFZ is a hydrophobic micropollutant and resistant to extensive biodegradation due its physicochemical properties (low water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1}$ and high log $K_{OW} = 4.77$), GFZ was partially biodegraded in both reactors.

The increase in the SRTs from 5 days to 55 days was increased the GFZ yields from 12.5% to 20.1%, respectively in the aerobic reactor (Table 6.21). However, the increase in GFZ yields with increasing SRTs was not significant according to the ANOVA (one-way) statistical analysis results in the aerobic reactor ($P = 0.168$, $\alpha = 0.05$, $F = 2.45$). It can be concluded that the GFZ could not biodegraded effectively in the aerobic reactor at all SRTs.

The aerobic reactor received the 2,H-5,MBA remaining from the anaerobic reactor and the influent concentrations of 2,H-5,MBA were detected as 2.61, 1.97, 1.90 and $1.70 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.21). The effluent concentrations of 2,H-5,MBA were obtained as 0.65, 0.30, 0.19 and $0.09 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.21). 2,H-5,MBA removal efficiencies were determined as 75.1%, 84.8%, 90.0% and 94.7% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.21). GFZ was eliminated to 2,H-5,MBA biologically and increasing SRT had a positive effect on the removal of 2,H-5,MBA under aerobic conditions. Kosjek, Heath, Pérez, Petrović, & Barceló, 2009 studied the removal of the 2,H-5,MBA at different HRTs (12, 24 and 48 h) and found 30% of removal efficiency at the highest HRT of 48 h in an activated sludge bioreactor having a volume of 4 L treating synthetic wastewater for an initial 2,H-5,MBA concentration of $5.00 \text{ } \mu\text{g L}^{-1}$ (Kosjek et al., 2009). The maximum 2,H-5,MBA yield was calculated as 94.7% at the highest SRT of 55 days in this study (Table 6.21). A linear correlation between 2,H-5,MBA yields and SRTs was observed for the aerobic reactor and this regression was significant according to the ANOVA (one-way) test statistics results at all SRTs ($R^2 = 0.99$, $P = 0.004$, $\alpha = 0.05$, $F = 20.20$).

6.1.16.3 Total GFZ Removals in Anaerobic/Aerobic Sequential Biological Reactor System

For 5 days of SRT operation, the maximum GFZ removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 20.5% with a GFZ effluent of $42.37 \mu\text{g L}^{-1}$ at a GFZ influent of $53.30 \mu\text{g L}^{-1}$ (Table 6.21). The maximum GFZ removal efficiency was calculated as 26.3% with a GFZ effluent of $39.27 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.21). The maximum GFZ removal efficiency was found as 28.0% with a GFZ effluent of $38.38 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ at 45 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.21). The maximum GFZ removal efficiency was determined as 31.7% with a GFZ effluent of $36.41 \mu\text{g L}^{-1}$ for a GFZ influent of $53.30 \mu\text{g L}^{-1}$ at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.21).

In the anaerobic/aerobic sequential biological reactor system, the influent concentrations of 2,H-5,MBA were obtained as 2.61, 1.97, 1.90 and $1.70 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively (Table 6.21). The effluent 2,H-5,MBA concentrations were found as 0.65, 0.30, 0.19 and $0.09 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.21). The 2,H-5,MBA removal efficiencies were calculated as 75.1%, 84.8%, 90.0% and 94.7% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.21). 2,H-5,MBA removal efficiencies increased with the increasing SRTs because 2,H-5,MBA was an appropriate micropollutant to be removed via biodegradation in both reactors due to its physicochemical properties (high water solubility = 2.18 g L^{-1} and low $\log K_{OW} = 2.55$). The maximum 2,H-5,MBA yield was found as 94.7% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.21).

6.1.16.4 Removal Mechanisms of GFZ in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of GFZ. The biodegraded, adsorbed, sorbed and volatilized GFZ masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.22).



Table 6.22 The total removal percentages for GFZ throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	12.16	0.450	20.26	0.018	0.83	0.071	0.00007	9.12	15.21	0.62	0.00005
30	16.03	1.252	56.34	0.025	1.13	0.073	0.00007	12.03	42.28	0.85	0.00006
45	17.23	1.888	84.94	0.032	1.44	0.074	0.00007	12.93	63.74	1.08	0.00006
55	19.35	2.221	99.95	0.037	1.66	0.092	0.00009	14.52	75.01	1.25	0.00007
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	12.14	0.814	12.20	0.035	0.53	0.054	0.00005	12.53	12.60	0.55	0.00006
30	15.23	2.010	30.14	0.053	0.80	0.074	0.00007	16.24	32.15	0.85	0.00008
45	16.05	3.736	56.05	0.067	1.00	0.074	0.00007	17.29	60.39	1.08	0.00008
55	18.30	4.077	61.16	0.072	1.08	0.077	0.00008	20.08	67.11	1.19	0.00008
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	49.20	--	32.46	--	1.36	--	0.00013	20.51	13.54	0.57	0.00005
30	63.13	--	86.48	--	1.93	--	0.00015	26.32	36.06	0.80	0.00006
45	67.12	--	140.98	--	2.44	--	0.00015	27.99	58.78	1.02	0.00006
55	76.00	--	161.11	--	2.74	--	0.00017	31.69	67.17	1.14	0.00007

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.16.4.1 Removed Masses and Removal Efficiencies of GFZ. An example for the calculations relevant to the removed masses and the removal efficiencies of GFZ in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.193 to 6.216, respectively at a SRT of 5 days (Table 6.22).

The biodegraded masses of GFZ were calculated from Equations 6.193, 6.194 and 6.195 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.22).

$$M_{\text{BIO,Anaerobic}} = (4.86 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 12.16 \mu\text{g} \quad (6.193)$$

$$M_{\text{BIO,Aerobic}} = (6.07 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 12.14 \mu\text{g} \quad (6.194)$$

$$M_{\text{BIO,Sequential}} = (10.93 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 49.20 \mu\text{g} \quad (6.195)$$

The biodegradation removal efficiencies for GFZ in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.196, 6.197 and 6.198, respectively at 5 days SRT (Table 6.22).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (12.16 \times 100) / (53.30 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 9.12\% \quad (6.196)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (12.14 \times 100) / (48.44 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 12.53\% \quad (6.197)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (49.20 \times 100) / (53.30 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 20.51\% \quad (6.198)$$

The adsorbed masses of GFZ were calculated using Equation 6.199, 6.200 and 6.201 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.22).

$$M_{\text{ADS,Anaerobic}} = [(0.450 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 20.26 \mu\text{g} \quad (6.199)$$

$$M_{\text{ADS,Aerobic}} = [(0.814 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 12.20 \mu\text{g} \quad (6.200)$$

$$M_{\text{ADS,Sequential}} = 20.26 + 12.20 = 32.46 \mu\text{g} \quad (6.201)$$

The total adsorption removal efficiencies of GFZ in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.202, 6.203 and 6.204, respectively at 5 days SRT (Table 6.22).

$$\text{Ads}(\%)_{\text{Anaerobic}} = (20.26 \times 100) / (53.30 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 15.21\% \quad (6.202)$$

$$\text{Ads}(\%)_{\text{Aerobic}} = (12.20 \times 100) / (48.44 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 12.60\% \quad (6.203)$$

$$\text{Ads}(\%)_{\text{Sequential}} = (32.46 \times 100) / (53.30 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 13.54\% \quad (6.204)$$

The sorbed masses into the anaerobic and aerobic biological sludges of GFZ were calculated according to the Equation 6.205 and 6.206, respectively while the total sorbed mass for GFZ in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.207 at 5 days SRT (Table 6.22).

$$M_{\text{SORP,Anaerobic}} = [(0.018 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.83 \mu\text{g} \quad (6.205)$$

$$M_{\text{SORP,Aerobic}} = [(0.035 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.53 \mu\text{g} \quad (6.206)$$

$$M_{\text{SORP,Sequential}} = 0.83 + 0.53 = 1.36 \mu\text{g} \quad (6.207)$$

The total sorption removal efficiencies of GFZ in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.208, 6.209 and 6.210, respectively at 5 days SRT (Table 6.22).

$$\text{Sorp}(\%)_{\text{Anaerobic}} = (0.83 \times 100) / (53.30 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.62\% \quad (6.208)$$

$$\text{Sorp}(\%)_{\text{Aerobic}} = (0.53 \times 100) / (48.44 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.55\% \quad (6.209)$$

$$\text{Sorp}(\%)_{\text{Sequential}} = (1.36 \times 100) / (53.30 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.57\% \quad (6.210)$$

Volatilized masses of GFZ were calculated according to the Equation 6.211, 6.212 and 6.213 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.22).

$$M_{\text{VOL,Anaerobic}} = (0.071 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00007 \mu\text{g} \quad (6.211)$$

$$M_{VOL,Aerobic} = (0.054 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00005 \mu\text{g} \quad (6.212)$$

$$M_{VOL,Sequential} = 0.00007 + 0.00005 = 0.00013 \mu\text{g} \quad (6.213)$$

The total volatilization removal efficiencies of GFZ were determined according to the Equation 6.214, 6.215 and 6.216 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.22).

$$\text{Vol}(\%),_{Anaerobic} = (0.00007 \times 100) / (53.30 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00005\% \quad (6.214)$$

$$\text{Vol}(\%),_{Aerobic} = (0.00005 \times 100) / (48.44 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00006\% \quad (6.215)$$

$$\text{Vol}(\%),_{Sequential} = (0.00013 \times 100) / (53.30 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00005\% \quad (6.216)$$

6.1.16.4.2 Removed Masses and Removal Efficiencies of GFZ in Anaerobic Reactor. The biodegraded GFZ masses increased from 12.16 μg to 19.35 μg as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor (Table 6.22). The biodegradation percentages of GFZ also increased from 9.12% to 14.52% with the increasing of SRTs from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.22). GFZ can be used as co-metabolite together COD (950.00 mg L^{-1}) and sCOD (850.00 mg L^{-1}) because its influent concentration (53.30 $\mu\text{g L}^{-1}$) was low to serve as a direct growth substrate (Table 5.1). The anaerobic bacteria can co-metabolized only 14.52% of GFZ together COD and sCOD at the highest SRT of 55 days (Table 6.22). GFZ is accepted as a hydrophobic micropollutant (high $\log K_{OW} = 4.77$, low water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1} \text{ g L}^{-1}$ and low Henry's Law constant = $1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$) and can not be effectively biodegraded by the anaerobic bacteria. The ANOVA (one-way) test statistics results confirmed that the relationship between GFZ yields and SRTs were insignificant in the anaerobic reactor ($P = 0.096$, $\alpha = 0.05$, $F = 3.90$). The sorbed masses (0.83 – 1.66 μg) and volatilized masses (0.00007 – 0.00009 μg) were low for GFZ at all SRTs in the anaerobic reactor (Table 6.22). The sorption and volatilization removal percentages of GFZ also were low (between 0.62% and 1.25% for sorption and between 0.00005% and 0.00007% for volatilization, respectively) in the anaerobic reactor (Table 6.22). The ANOVA (one-way) test statistics results showed that the removal of GFZ via sorption ($P = 0.061$, $\alpha = 0.05$, $F = 5.28$) and volatilization ($P =$

0.063, $\alpha = 0.05$, $F = 5.19$) were negligible in the anaerobic reactor. The adsorbed masses of GFZ to the anaerobic sludge increased from 20.26 μg to 99.95 μg corresponding to an increase in the adsorbed GFZ percentages from 15.21% to 75.01% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.22). Having low water solubility ($4.964 \times 10^{-3} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 4.77$) and low Henry's Law constant ($1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$) values makes GFZ a hydrophobic micropollutant in the anaerobic reactor, therefore GFZ was effectively removed via adsorption (75.01%) in the anaerobic reactor at 55 days SRT. Previous researches suggest that the increased adsorption of a micropollutant in sludges, soils or sediments is due to the effect of "aging". It is commonly believed that as the contact time increases, in other words as the SRT increases, the adsorbed masses of the micropollutants on sludges, soils or sediments increased (Conkle, Gan, & Anderson, 2012). In this study, the ANOVA (one-way) test statistics results also confirmed that an important relationship between adsorption removal efficiencies and SRTs was found for GFZ in the anaerobic reactor ($P = 0.0006$, $\alpha = 0.05$, $F = 12.13$).

6.1.16.4.3 Removed Masses and Removal Efficiencies of GFZ in Aerobic Reactor.

In the aerobic reactor, the biodegraded GFZ masses increased from 12.14 μg to 18.30 μg resulting in the GFZ removal percentages of 12.53% and 20.08% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.22). The maximum biodegradation yield of GFZ was obtained as 20.08% at 55 days SRT in the aerobic reactor (Table 6.22). The ANOVA (one-way) test statistic results showed that the removal of GFZ via biodegradation was not significant in the aerobic reactor at all SRTs ($P = 0.168$, $\alpha = 0.05$, $F = 2.45$). The sorbed masses (0.53 – 1.08 μg) and volatilized masses (0.00005 – 0.00008 μg) were low for GFZ at all SRTs in the aerobic reactor (Table 6.22). The GFZ removal percentages also were low for sorption and volatilization (between 0.55% and 1.19% for sorption and between 0.00006% and 0.00008% for volatilization, respectively) in the aerobic reactor (Table 6.22). The ANOVA (one-way) test statistics results showed that the removal of GFZ via sorption ($P = 0.051$, $\alpha = 0.05$, $F = 5.94$) and volatilization ($P = 0.052$, $\alpha = 0.05$, $F = 5.83$) were insignificant in the aerobic reactor. The adsorbed GFZ masses

to the aerobic sludge increased from 12.20 μg to 61.16 μg as the SRT increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.22). This attributed to the GFZ adsorption yields of 12.60% and 67.11% at 5 days and 55 days SRT, respectively in the aerobic reactor (Table 6.22). GFZ has resistance to extensive biodegradation due to the physicochemical properties (low water water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.77$ and low Henry's Law constant = $1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$) and adsorption has a significant effect on the removal of GFZ in the aerobic reactor at all SRTs according to the ANOVA (one-way) test statistics results ($P = 0.001$, $\alpha = 0.05$, $F = 9.93$). Therefore, adsorption played an important role for GFZ removal (67.11%) at 55 days SRT in the aerobic reactor (Table 6.22).

Removal of GFZ via biodegradation was slightly higher in the aerobic reactor (20.08%) than the anaerobic reactor (14.52%) at 55 days SRT because of the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.22). Removal of GFZ via adsorption was higher in the anaerobic reactor (75.01%) than the aerobic reactor (67.11%) at 55 days SRT (Table 6.22). This could be attributed to the better adsorption conditions for GFZ in the anaerobic reactor than that in the aerobic reactor. GFZ found more sludge surface to be adsorbed in the anaerobic reactor than the aerobic reactor because the anaerobic reactor had much more MLVSS concentration (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.16.4.4 Removed Masses and Removal Efficiencies of GFZ in Anaerobic/Aerobic Sequential Biological Reactor System. The total biodegraded masses of GFZ increased from 49.20 μg to 76.00 μg resulting an increase in the GFZ biodegradation removal percentages of 20.51% and 31.69% at SRTs varying from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.22). The maximum biodegradation yield of GFZ was calculated as 31.69% at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.22). The ANOVA (one-way) test statistic results showed that the relationship between GFZ biodegradation yields and SRTs was not significant in the anaerobic/aerobic sequential biological reactor system ($P = 0.545$, $\alpha = 0.05$, $F =$

0.41). The sorbed masses (1.36 – 2.74 µg) and volatilized masses (0.00013 – 0.00017 µg) were low for GFZ in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.22). The GFZ removal percentages also were low for sorption and volatilization (between 0.57% and 1.14% for sorption and between 0.00005% and 0.00007% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.22). The ANOVA (one-way) test statistics results showed that the removal of GFZ via sorption ($P = 0.093$, $\alpha = 0.05$, $F = 3.99$) and volatilization ($P = 0.095$, $\alpha = 0.05$, $F = 3.92$) were not significant in the anaerobic/aerobic sequential biological reactor system at all SRTs. The total adsorbed GFZ masses to the anaerobic (from 20.26 µg to 99.95 µg) and aerobic (from 12.20 µg to 61.16 µg) sludge increased from 32.46 µg to 161.11 µg as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.22). The increase in the adsorption masses also increased the GFZ adsorption yields from 13.54% to 67.17% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.22). The increase in the SRTs showed positive effect on the GFZ adsorption yields because of being a hydrophobic micropollutant (low water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.77$ and low Henry's Law constant = $1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$). The ANOVA (one-way) test statistics results supported that there was a significant relationship between GFZ adsorption yields and SRTs in the anaerobic/aerobic sequential biological reactor system ($P = 0.0006$, $\alpha = 0.05$, $F = 12.02$).

GFZ was a hydrophobic micropollutant due to its physicochemical properties (low water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.77$ and low Henry's Law constant = $1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$) and the results from this study supported that the GFZ can not be effectively removed via biodegradation (31.69%), sorption (1.14%) and volatilization (0.00007%) at 55 days SRT (Figure 6.15). In this study, we found that adsorption (67.17%) was the main removal mechanism of the hydrophobic GFZ at 55 days SRT (Figure 6.15).

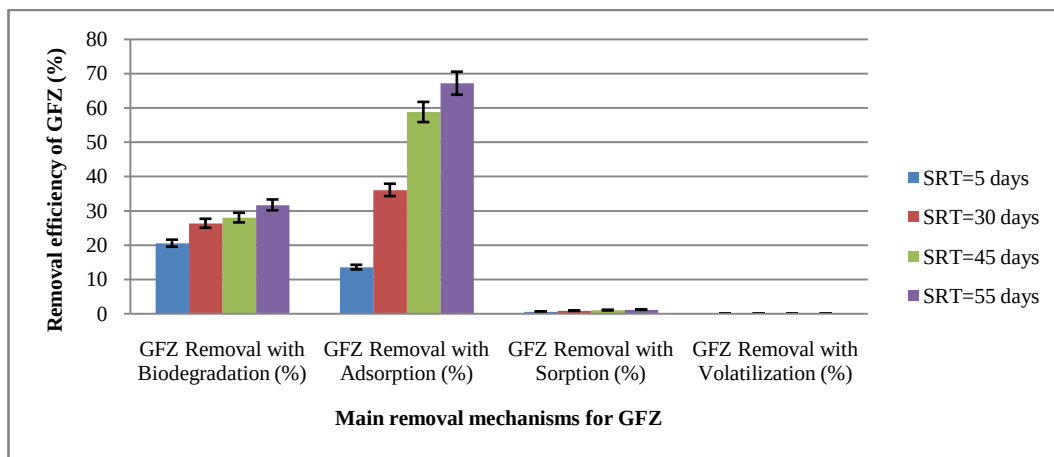


Figure 6.15 The removal efficiencies of GFZ with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.17 Total Triclosan (TCS) Removals

6.1.17.1 Total TCS Removals in Anaerobic Biological Reactor

The maximum TCS removal efficiency of the anaerobic reactor was obtained as 9.0% with a TCS effluent of $328.42 \mu\text{g L}^{-1}$ at a TCS influent of $361.00 \mu\text{g L}^{-1}$ during 5 days of SRT operation (Table 6.23). The maximum TCS removal efficiency was calculated as 12.0% with a TCS effluent of $317.50 \mu\text{g L}^{-1}$ for a TCS influent of $361.00 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic reactor (Table 6.23). For 45 days of SRT operation, the maximum TCS removal efficiency did not change considerably and was found as 12.4% with a TCS effluent of $316.40 \mu\text{g L}^{-1}$ for a TCS influent of $361.00 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.23). Finally, the maximum TCS removal efficiency was determined as 14.3% with a TCS effluent of $309.50 \mu\text{g L}^{-1}$ for a TCS influent of $361.00 \mu\text{g L}^{-1}$ at 55 days SRT in the anaerobic reactor (Table 6.23).

Table 6.23 TCS and its metabolite Methyl triclosan (MTCS) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent TCS ($\mu\text{g L}^{-1}$)	Effluent TCS ($\mu\text{g L}^{-1}$)	metabolite of TCS namely MTCS			Removed TCS ($\mu\text{g L}^{-1}$)	TCS Rem. Eff. (%)	Influent TCS ($\mu\text{g L}^{-1}$)	Effluent TCS ($\mu\text{g L}^{-1}$)	metabolite of TCS namely MTCS			Removed TCS ($\mu\text{g L}^{-1}$)	TCS Rem. Eff. (%)
			Influent MTCS ($\mu\text{g L}^{-1}$)	Effluent MTCS ($\mu\text{g L}^{-1}$)	MTCS Rem. Eff. (%)					Influent MTCS ($\mu\text{g L}^{-1}$)	Effluent MTCS ($\mu\text{g L}^{-1}$)	MTCS Rem. Eff. (%)		
5	361.00 $\pm$ 0.05	328.42 $\pm$ 0.05	0.00 $\pm$ 0.05	14.06 $\pm$ 0.05	0.00 $\pm$ 0.5	32.58 $\pm$ 0.05	9.0 $\pm$ 0.5	328.42 $\pm$ 0.05	288.37 $\pm$ 0.05	14.06 $\pm$ 0.05	10.75 $\pm$ 0.05	23.5 $\pm$ 0.5	40.05 $\pm$ 0.05	12.2 $\pm$ 0.5
30	361.00 $\pm$ 0.05	317.50 $\pm$ 0.05	0.00 $\pm$ 0.05	10.95 $\pm$ 0.05	0.00 $\pm$ 0.5	43.50 $\pm$ 0.05	12.0 $\pm$ 0.5	317.50 $\pm$ 0.05	266.62 $\pm$ 0.05	10.95 $\pm$ 0.05	7.81 $\pm$ 0.05	28.7 $\pm$ 0.5	50.89 $\pm$ 0.05	16.0 $\pm$ 0.5
45	361.00 $\pm$ 0.05	316.40 $\pm$ 0.05	0.00 $\pm$ 0.05	8.65 $\pm$ 0.05	0.00 $\pm$ 0.5	44.60 $\pm$ 0.05	12.4 $\pm$ 0.5	316.40 $\pm$ 0.05	260.95 $\pm$ 0.05	8.65 $\pm$ 0.05	5.91 $\pm$ 0.05	31.7 $\pm$ 0.5	55.45 $\pm$ 0.05	17.5 $\pm$ 0.5
55	361.00 $\pm$ 0.05	309.50 $\pm$ 0.05	0.00 $\pm$ 0.05	5.47 $\pm$ 0.05	0.00 $\pm$ 0.5	51.50 $\pm$ 0.05	14.3 $\pm$ 0.5	309.50 $\pm$ 0.05	246.33 $\pm$ 0.05	5.47 $\pm$ 0.05	3.55 $\pm$ 0.05	35.1 $\pm$ 0.5	63.18 $\pm$ 0.05	20.4 $\pm$ 0.5

Anaerobic/Aerobic Sequential Biological Reactor System							
SRT (day)	Influent TCS ($\mu\text{g L}^{-1}$)	Effluent TCS ($\mu\text{g L}^{-1}$)	metabolite of TCS namely MTCS			Removed TCS ($\mu\text{g L}^{-1}$)	TCS Rem. Eff. (%)
			Influent MTCS ($\mu\text{g L}^{-1}$)	Effluent MTCS ($\mu\text{g L}^{-1}$)	MTCS Rem. Eff. (%)		
5	361.00 $\pm$ 0.05	288.37 $\pm$ 0.05	14.06 $\pm$ 0.05	10.75 $\pm$ 0.05	23.5 $\pm$ 0.5	72.63 $\pm$ 0.05	20.1 $\pm$ 0.5
30	361.00 $\pm$ 0.05	266.62 $\pm$ 0.05	10.95 $\pm$ 0.05	7.81 $\pm$ 0.05	28.7 $\pm$ 0.5	94.38 $\pm$ 0.05	26.1 $\pm$ 0.5
45	361.00 $\pm$ 0.05	260.95 $\pm$ 0.05	8.65 $\pm$ 0.05	5.91 $\pm$ 0.05	31.7 $\pm$ 0.5	100.05 $\pm$ 0.05	27.7 $\pm$ 0.5
55	361.00 $\pm$ 0.05	246.33 $\pm$ 0.05	5.47 $\pm$ 0.05	3.55 $\pm$ 0.05	35.1 $\pm$ 0.5	114.68 $\pm$ 0.05	31.8 $\pm$ 0.5

The total TCS removal efficiencies increased slightly from 9.0% to 14.3% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.23). TCS was partially biodegraded in the anaerobic reactor because of its hydrophobicity (low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.76$). Besides, the ANOVA (one-way) statistical analysis results showed that the increased TCS yields at increasing SRTs was not significant in the anaerobic reactor at all SRTs ($P = 0.093$, $\alpha = 0.05$, $F = 3.99$).

In this study, Methyl triclosan (MTCS) which is the main metabolite of TCS was monitored in the effluents of the anaerobic reactor at all SRTs. TCS was biodegraded with subsequent breakdown steps and the MTCS was occurred in this reactions as mentioned by Veetil et al., 2012. MTCS accepted as a hydrophobic micropollutant because of having a $\log K_{OW}$ value (5.50) higher than 4.00. The effluent concentrations of MTCS were measured as 14.06, 10.95, 8.65 and $5.47 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic reactor (Table 6.23).

6.1.17.2 Total TCS Removals in Aerobic Biological Reactor

At 5 days SRT, the maximum TCS removal efficiency of the aerobic biological reactor was obtained as 12.2% with a TCS effluent of $288.37 \mu\text{g L}^{-1}$ at a TCS influent of $328.42 \mu\text{g L}^{-1}$ (Table 6.23). The maximum TCS removal efficiency was measured as 16.0% with a TCS effluent of $266.62 \mu\text{g L}^{-1}$ for a TCS influent of $317.50 \mu\text{g L}^{-1}$ at 30 days SRT in the aerobic reactor (Table 6.23). At 45 days SRT, the maximum TCS removal efficiency was found as 17.5% with a TCS effluent of $260.95 \mu\text{g L}^{-1}$ for a TCS influent of $316.40 \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.23). When the SRT was increased to 55 days, the maximum TCS removal efficiency was determined as 20.4% with a TCS effluent of $246.33 \mu\text{g L}^{-1}$ for a TCS influent of $309.50 \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.23).

Total removal of TCS was slightly higher in the aerobic reactor (20.4%) than the anaerobic reactor (14.3%) at 55 days of SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.23). Although TCS is

resistant to extensive biodegradation due its physicochemical properties (low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.76$), it was partially biodegraded in both reactors.

The GFZ yields increased from 12.2% to 20.4% at SRTs varying from 5 days to 55 days, respectively in the aerobic reactor (Table 6.23). It is important to note that the TCS could not biodegraded effectively due its physicochemical properties (low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{OW} = 4.76$) in the aerobic reactor at all SRTs. The increase in TCS yields with increasing SRTs was not found to be significant according to the ANOVA (one-way) statistical analysis results in the aerobic reactor ($P = 0.169$, $\alpha = 0.05$, $F = 2.44$).

The aerobic reactor received the MTCS remaining from the anaerobic reactor and the influent concentrations of MTCS were found as 14.06, 10.95, 8.65 and $5.47 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.23). The effluent concentrations of MTCS were determined as 10.75, 7.81, 5.91 and $3.55 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.23). MTCS removal efficiencies were calculated as 23.5%, 28.7%, 31.7% and 35.1% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.23). The results showed that as the SRT was increased from 5 days to 55 days, MTCS removal efficiency increased from 23.5% to 35.1% in the aerobic reactor (Table 6.23). A linear correlation between MTCS yields and SRTs was found for the aerobic reactor and this regression was significant according to the ANOVA (one-way) statistical analysis results ($R^2 = 0.99$, $P = 3.82 \times 10^{-5}$, $\alpha = 0.05$, $F = 115.66$).

6.1.17.3 Total TCS Removals in Anaerobic/Aerobic Sequential Biological Reactor System

At the beginning of the study, TCS removal efficiency of the anaerobic/aerobic sequential biological reactor system was measured as 20.1% with a TCS effluent of $288.37 \mu\text{g L}^{-1}$ at a TCS influent of $361.00 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.23). At 30 days SRT, TCS removal efficiency was determined as 26.1% with a TCS effluent of

266.62 $\mu\text{g L}^{-1}$ for a TCS influent of 361.00 $\mu\text{g L}^{-1}$ in the anaerobic/aerobic sequential biological reactor system (Table 6.23). TCS removal efficiency did not change considerably and was found as 27.7% with a TCS effluent of 260.95 $\mu\text{g L}^{-1}$ for a TCS influent of 361.00 $\mu\text{g L}^{-1}$ at 45 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.23). At the highest SRT of 55 days, TCS removal efficiency was calculated as 31.8% with a TCS effluent of 246.33 $\mu\text{g L}^{-1}$ for a TCS influent of 361.00 $\mu\text{g L}^{-1}$ in the anaerobic/aerobic sequential biological reactor system (Table 6.23).

In the anaerobic/aerobic sequential biological reactor system, the influent concentrations of MTCS were obtained as 14.06, 10.95, 8.65 and 5.47 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively (Table 6.23). The effluent MTCS concentrations were found as 10.75, 7.81, 5.91 and 3.55 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.23). The MTCS removal efficiencies were achieved as 23.5%, 28.7%, 31.7% and 35.1% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.23). MTCS removal efficiencies increased with the increasing SRTs and the maximum MTCS yield was calculated as 35.1% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.23).

6.1.17.4 Removal Mechanisms of TCS in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of TCS. The biodegraded, adsorbed, sorbed and volatilized TCS masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.24).

Table 6.24 The total removal percentages for TCS throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	81.45	3.05	137.12	0.110	4.97	0.300	0.0003	9.02	15.19	0.55	0.00003
30	108.74	8.45	380.28	0.166	7.48	0.422	0.0004	12.05	42.14	0.83	0.00005
45	111.51	12.47	561.32	0.215	9.67	0.453	0.0005	12.36	62.20	1.07	0.00005
55	128.75	15.02	675.69	0.246	11.06	0.454	0.0005	14.27	74.87	1.23	0.00005
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	80.11	5.36	80.42	0.221	3.31	0.251	0.0003	12.20	12.24	0.50	0.00004
30	101.77	13.19	197.89	0.356	5.34	0.281	0.0003	16.03	31.16	0.84	0.00004
45	110.90	25.35	380.31	0.439	6.59	0.281	0.0003	17.52	60.10	1.04	0.00004
55	126.35	27.63	414.45	0.484	7.26	0.283	0.0003	20.41	66.95	1.17	0.00005
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	326.85	--	217.54	--	8.28	--	0.0006	20.12	13.39	0.51	0.00003
30	424.72	--	578.17	--	12.82	--	0.0007	26.14	35.59	0.79	0.00004
45	450.23	--	941.63	--	16.26	--	0.0007	27.72	57.96	1.00	0.00005
55	516.04	--	1090.14	--	18.32	--	0.0007	31.77	67.11	1.13	0.00005

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.17.4.1 Removed Masses and Removal Efficiencies of TCS. An example for the calculations relevant to the removed masses and the removal efficiencies of TCS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.217 to 6.240, respectively at a SRT of 5 days (Table 6.24).

The biodegraded masses of TCS were calculated from Equations 6.217, 6.218 and 6.219 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.24).

$$M_{\text{BIO,Anaerobic}} = (32.58 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 81.45 \mu\text{g} \quad (6.217)$$

$$M_{\text{BIO,Aerobic}} = (40.05 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 80.11 \mu\text{g} \quad (6.218)$$

$$M_{\text{BIO,Sequential}} = (72.63 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 326.85 \mu\text{g} \quad (6.219)$$

The biodegradation removal efficiencies for TCS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.220, 6.221 and 6.222, respectively at 5 days SRT (Table 6.24).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (81.45 \times 100) / (361.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 9.02\% \quad (6.220)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (80.11 \times 100) / (328.42 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 12.20\% \quad (6.221)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (326.85 \times 100) / (361.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 20.12\% \quad (6.222)$$

The adsorbed masses of TCS were calculated using Equation 6.223, 6.224 and 6.225 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.24).

$$M_{\text{ADS,Anaerobic}} = [(3.05 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 137.12 \mu\text{g} \quad (6.223)$$

$$M_{\text{ADS,Aerobic}} = [(5.36 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 80.42 \mu\text{g} \quad (6.224)$$

$$M_{\text{ADS,Sequential}} = 137.12 + 80.42 = 217.54 \mu\text{g} \quad (6.225)$$

The total adsorption removal efficiencies of TCS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.226, 6.227 and 6.228, respectively at 5 days SRT (Table 6.24).

$$\text{Ads}(\%)_{\text{Anaerobic}} = (137.12 \times 100) / (361.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 15.19\% \quad (6.226)$$

$$\text{Ads}(\%)_{\text{Aerobic}} = (80.42 \times 100) / (328.42 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 12.24\% \quad (6.227)$$

$$\text{Ads}(\%)_{\text{Sequential}} = (217.54 \times 100) / (361.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 13.39\% \quad (6.228)$$

The sorbed masses into the anaerobic and aerobic biological sludges of TCS were calculated according to the Equation 6.229 and 6.230, respectively while the total sorbed mass for TCS in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.231 at 5 days SRT (Table 6.24).

$$M_{\text{SORP,Anaerobic}} = [(0.110 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 4.97 \mu\text{g} \quad (6.229)$$

$$M_{\text{SORP,Aerobic}} = [(0.221 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 3.31 \mu\text{g} \quad (6.230)$$

$$M_{\text{SORP,Sequential}} = 4.97 + 3.31 = 8.28 \mu\text{g} \quad (6.231)$$

The total sorption removal efficiencies of TCS in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.232, 6.233 and 6.234, respectively at 5 days SRT (Table 6.24).

$$\text{Sorp}(\%)_{\text{Anaerobic}} = (4.97 \times 100) / (361.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.55\% \quad (6.232)$$

$$\text{Sorp}(\%)_{\text{Aerobic}} = (3.31 \times 100) / (328.42 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.50\% \quad (6.233)$$

$$\text{Sorp}(\%)_{\text{Sequential}} = (8.28 \times 100) / (361.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.51\% \quad (6.234)$$

Volatilized masses of TCS were calculated according to the Equation 6.235, 6.236 and 6.237 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.24).

$$M_{\text{VOL,Anaerobic}} = (0.300 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.0003 \mu\text{g} \quad (6.235)$$

$$M_{VOL,Aerobic} = (0.251 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.0003 \mu\text{g} \quad (6.236)$$

$$M_{VOL,Sequential} = 0.0003 + 0.0003 = 0.0006 \mu\text{g} \quad (6.237)$$

The total volatilization removal efficiencies of TCS were determined according to the Equation 6.238, 6.239 and 6.240 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.24).

$$\text{Vol}(\%)_{An} = (0.0003 \times 100) / (361.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00003\% \quad (6.238)$$

$$\text{Vol}(\%)_{Ae} = (0.0003 \times 100) / (328.42 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00004\% \quad (6.239)$$

$$\text{Vol}(\%)_{Seq} = (0.0006 \times 100) / (361.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00003\% \quad (6.240)$$

6.1.17.4.2 Removed Masses and Removal Efficiencies of TCS in Anaerobic Reactor. As is shown in Table 6.24, the biodegraded TCS masses increased from 81.45 μg to 128.75 μg as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor. The biodegradation removal percentages of TCS also increased from 9.02% to 14.27% with the increasing of SRTs from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.24). The anaerobic bacteria could co-metabolized 14.27% of TCS together COD and sCOD at 55 days SRT (Table 6.24). Because of being a hydrophobic micropollutant (high $\log K_{OW} = 4.76$, low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1} \text{ g L}^{-1}$ and low Henry's Law constant = $4.99 \times 10^{-9} \text{ atm m}^3 \text{ mol}^{-1}$) TCS was partially biodegraded in the anaerobic reactor. The ANOVA (one-way) test statistics results also proved that the increasing TCS yields at increasing SRTs were not significant in the anaerobic reactor ($P = 0.093$, $\alpha = 0.05$, $F = 3.99$). The sorbed masses (4.97 – 11.06 μg) and volatilization masses (0.0003 – 0.0005 μg) were low for TCS at all SRTs in the anaerobic reactor (Table 6.24). The sorption and volatilization removal percentages also were low (between 0.55% and 1.23% for sorption and between 0.00003% and 0.00005% for volatilization, respectively) for TCS in the anaerobic reactor (Table 6.24). The ANOVA (one-way) test statistics results showed that removal of TCS via sorption ($P = 0.054$, $\alpha = 0.05$, $F = 5.69$) and volatilization ($P = 0.056$, $\alpha = 0.05$, $F = 5.58$) were negligible in the anaerobic reactor. The adsorbed TCS masses to the anaerobic sludge was calculated between 137.12 μg and 675.69 μg at SRTs between 5 days and 55 days, respectively

in the anaerobic reactor (Table 6.24). The adsorption yields of TCS increased from 15.19% to 74.87% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.24). TCS was removed with high adsorption yield (74.87%) at 55 days SRT in the anaerobic reactor because of having a hydrophobic structure (low water solubility = 4.621×10^{-3} g L⁻¹, high log K_{OW} = 4.76 and low Henry's Law constant = 4.99×10^{-9} atm m³ mol⁻¹). The ANOVA (one-way) test statistics results showed that the removal of TCS via adsorption was significant in the anaerobic reactor at all SRTs ($P = 0.0006$, $\alpha = 0.05$, $F = 12.20$).

6.1.17.4.3 Removed Masses and Removal Efficiencies of TCS in Aerobic Reactor.

In the aerobic reactor, the biodegraded TCS masses increased from 80.11 µg to 126.35 µg resulting in the TCS biodegradation removal percentages of 12.20% and 20.41% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.24). The maximum biodegradation yield of TCS was obtained as 20.41% at 55 days SRT in the aerobic reactor (Table 6.24). TCS was partly biodegraded (20.41%) at 55 days SRT due its hydrophobicity (low water solubility = 4.621×10^{-3} g L⁻¹ and high log K_{OW} = 4.76) and the ANOVA (one-way) test statistic results showed that the removal of TCS via biodegradation was not significant in the aerobic reactor at all SRTs ($P = 0.169$, $\alpha = 0.05$, $F = 2.44$). The sorbed masses (3.31 – 7.26 µg) and volatilized masses (0.0003 – 0.0003 µg) were low for TCS at all SRTs in the aerobic reactor (Table 6.24). The TCS removal percentages also were low for sorption (0.50% – 1.17%) and volatilization (0.00004% – 0.00005%) in the aerobic reactor at all SRTs (Table 6.24). The ANOVA (one-way) test statistics results showed that the removal of TCS via sorption ($P = 0.051$, $\alpha = 0.05$, $F = 5.90$) and volatilization ($P = 0.053$, $\alpha = 0.05$, $F = 5.78$) were not important statistically in the aerobic reactor at all SRTs. The adsorbed TCS masses to the aerobic sludge increased from 80.42 µg to 414.45 µg as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.24). This attributed to the TCS adsorption yields of 12.24% and 66.95% at 5 days and 55 days SRT, respectively in the aerobic reactor (Table 6.24). The ANOVA (one-way) test statistics results showed that the removal of TCS via adsorption was significant in the aerobic reactor at all SRTs ($P = 0.002$, $\alpha = 0.05$, $F = 9.57$). Due to the TCS was a hydrophobic

micropollutant with its low water solubility ($4.621 \times 10^{-3} \text{ g L}^{-1}$), high hydrophobicity ($\log K_{OW} = 4.76$) and low Henry's Law constant ($4.99 \times 10^{-9} \text{ atm m}^3 \text{ mol}^{-1}$), adsorption has an important contribution to the removal of TCS in the aerobic reactor at all SRTs. Chen et al. (2011) obtained 75% of TCS adsorption on aerobic sludge in an aerobic reactor having a volume of 5 L treating municipal wastewater for an influent TCS concentration of $30 \mu\text{g L}^{-1}$ at a HRT of 150 hours and at a SRT of 30 days with a MLVSS concentration of 2500 mg L^{-1} (Chen et al., 2011).

Removal of TCS via biodegradation was slightly higher in the aerobic reactor (20.41%) than the anaerobic reactor (14.27%) at 55 days of SRT because of the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.24). Removal of TCS via adsorption was higher in the anaerobic reactor (74.87%) than the aerobic reactor (66.95%) at 55 days SRT (Table 6.24). It was possible that there were much sludge surfaces to be adsorbed for TCS in the anaerobic reactor than that in the aerobic reactor owing to the high MLVSS concentration in the anaerobic reactor (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.17.4.4 Removed Masses and Removal Efficiencies of TCS in Anaerobic/Aerobic Sequential Biological Reactor System. The total biodegraded masses of TCS increased from $326.85 \mu\text{g}$ to $516.04 \mu\text{g}$ as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.24). The increase in the total biodegraded masses of TCS also increased the biodegradation yields of TCS from 20.12% to 31.77% at SRTs varying from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.24). The biodegradation yield of TCS reached to the highest level as 31.77% at 55 days SRT (Table 6.24). However, the raise in the TCS biodegradation yields at increasing SRTs was not found to be significant in the anaerobic/aerobic sequential biological reactor system according to the ANOVA (one-way) test statistic results ($P = 0.536$, $\alpha = 0.05$, $F = 0.43$). The sorbed masses ($8.28 - 18.32 \mu\text{g}$) and volatilized masses ($0.0006 - 0.0007 \mu\text{g}$) were low for TCS at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.24).

The TCS removal percentages also were low for sorption (0.51% – 1.13%) and volatilization (0.00003% – 0.00005%) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.24). The ANOVA (one-way) test statistics results showed that the removal of TCS via sorption ($P = 0.089$, $\alpha = 0.05$, $F = 4.12$) and volatilization ($P = 0.091$, $\alpha = 0.05$, $F = 4.05$) were not significant in the anaerobic/aerobic sequential biological reactor system at all SRTs. The total adsorbed TCS masses to the anaerobic (from 137.12 μg to 675.69 μg) and aerobic (from 80.42 μg to 414.45 μg) sludge increased from 217.54 μg to 1090.14 μg as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.24). The TCS adsorption yields also increased from 13.39% to 67.11% at SRTs from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.24). TCS was removed with high adsorption yield (67.11%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.24) due to its hydrophobic structure (low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.76$ and low Henry's Law constant = $4.99 \times 10^{-9} \text{ atm m}^3 \text{ mol}^{-1}$). The ANOVA (one-way) test statistics results also showed that the removal of TCS via adsorption was significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.0007$, $\alpha = 0.05$, $F = 11.87$).

The results from this study showed that TCS could not be effectively removed via biodegradation (31.77%), sorption (1.13%) and volatilization (0.00005%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Figure 6.16). TCS was a quite hydrophobic micropollutant with its physicochemical properties (low water solubility = $4.621 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.76$ and low Henry's Law constant = $4.99 \times 10^{-9} \text{ atm m}^3 \text{ mol}^{-1}$), therefore, we found that adsorption (67.11%) was the main removal mechanism of TCS at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Figure 6.16). The results obtained from this study were in accordance with the literature. McAvoy, Schatowitz, Jacob, Hauk, & Eckhoff (2009) found 35.1% of TCS biodegradation removal efficiency in a real scale wastewater treatment plant using an activated sludge system working at a

flowrate of 213 megaliters per day at a HRT of 18 h for an influent TCS concentration of $5.21 \mu\text{g L}^{-1}$ (McAvoy et al., 2009).

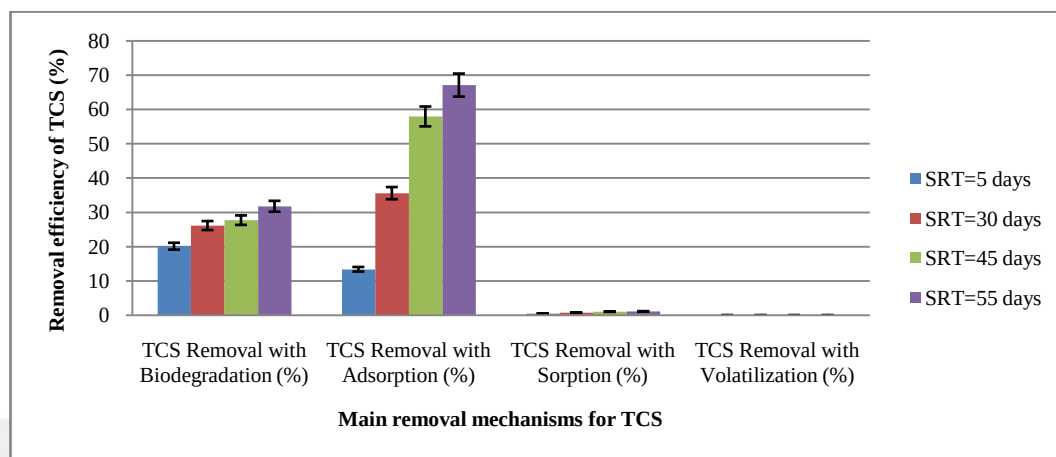


Figure 6.16 The removal efficiencies of TCS with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.18 Total Ibuprofen (IBU) Removals

6.1.18.1 Total IBU Removals in Anaerobic Biological Reactor

In the anaerobic reactor, the maximum IBU removal efficiency was calculated as 26.2% with an IBU effluent of $31.37 \mu\text{g L}^{-1}$ at an IBU influent of $42.50 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.25). The maximum IBU removal efficiency was achieved as 34.0% at 30 days SRT with an IBU effluent of $28.07 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.25). After 45 days of SRT operation, the maximum IBU removal efficiency was determined as 40.0% with an IBU effluent of $25.52 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.25). When the SRT was increased to 55 days, the maximum IBU removal efficiency was obtained as 45.5% with an IBU effluent of $23.16 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.25).

Table 6.25 IBU and its metabolites namely 1-OH IBU, 2-OH IBU and CBX IBU concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

Anaerobic Reactor													
SRT (day)	Influent IBU ($\mu\text{g L}^{-1}$)	Effluent IBU ($\mu\text{g L}^{-1}$)	Metabolites of IBU namely 1-OH IBU, 2-OH IBU and CBX IBU									Removed IBU ($\mu\text{g L}^{-1}$)	IBU Removal Eff. (%)
			Influent 1-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 1-OH IBU ($\mu\text{g L}^{-1}$)	1-OH IBU Removal Eff. (%)	Influent 2-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 2-OH IBU ($\mu\text{g L}^{-1}$)	2-OH IBU Removal Eff. (%)	Influent CBX IBU ($\mu\text{g L}^{-1}$)	Effluent CBX IBU ($\mu\text{g L}^{-1}$)	CBX IBU Removal Eff. (%)		
5	42.50	31.37	0.00	0.77	0.00	0.00	0.82	0.00	0.00	0.86	0.00	11.13	26.2
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
30	42.50	28.07	0.00	0.75	0.00	0.00	0.79	0.00	0.00	0.82	0.00	14.43	34.0
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
45	42.50	25.52	0.00	0.72	0.00	0.00	0.75	0.00	0.00	0.78	0.00	16.98	40.0
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
55	42.50	23.16	0.00	0.70	0.00	0.00	0.70	0.00	0.00	0.74	0.00	19.34	45.5
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
Aerobic Reactor													
SRT (day)	Influent IBU ($\mu\text{g L}^{-1}$)	Effluent IBU ($\mu\text{g L}^{-1}$)	Metabolites of IBU namely 1-OH IBU, 2-OH IBU and CBX IBU									Removed IBU ($\mu\text{g L}^{-1}$)	IBU Removal Eff. (%)
			Influent 1-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 1-OH IBU ($\mu\text{g L}^{-1}$)	1-OH IBU Removal Eff. (%)	Influent 2-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 2-OH IBU ($\mu\text{g L}^{-1}$)	2-OH IBU Removal Eff. (%)	Influent CBX IBU ($\mu\text{g L}^{-1}$)	Effluent CBX IBU ($\mu\text{g L}^{-1}$)	CBX IBU Removal Eff. (%)		
5	31.37	15.05	0.77	0.22	71.4	0.82	0.18	78.0	0.86	0.22	74.4	16.33	52.0
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
30	28.07	10.15	0.75	0.13	82.7	0.79	0.10	87.3	0.82	0.13	84.1	17.92	63.8
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
45	25.52	7.22	0.72	0.11	84.7	0.75	0.07	90.7	0.78	0.10	87.2	18.30	71.7
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
55	23.16	5.12	0.70	0.09	87.1	0.70	0.04	94.3	0.74	0.07	90.5	18.04	77.9
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5

Table 6.25 continues

Anaerobic/Aerobic Sequential Biological Reactor System													
SRT (day)	Influent IBU ($\mu\text{g L}^{-1}$)	Effluent IBU ($\mu\text{g L}^{-1}$)	Metabolites of IBU namely 1-OH IBU, 2-OH IBU and CBX IBU									Removed IBU ($\mu\text{g L}^{-1}$)	IBU Removal Eff. (%)
			Influent 1-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 1-OH IBU ($\mu\text{g L}^{-1}$)	1-OH IBU Removal Eff. (%)	Influent 2-OH IBU ($\mu\text{g L}^{-1}$)	Effluent 2-OH IBU ($\mu\text{g L}^{-1}$)	2-OH IBU Removal Eff. (%)	Influent CBX IBU ($\mu\text{g L}^{-1}$)	Effluent CBX IBU ($\mu\text{g L}^{-1}$)	CBX IBU Removal Eff. (%)		
5	42.50	15.05	0.77	0.22	71.4	0.82	0.18	78.0	0.86	0.22	74.4	27.45	64.6
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
30	42.50	10.15	0.75	0.13	82.7	0.79	0.10	87.3	0.82	0.13	84.1	32.35	76.1
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
45	42.50	7.22	0.72	0.11	84.7	0.75	0.07	90.7	0.78	0.10	87.2	35.28	83.0
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5
55	42.50	5.12	0.70	0.09	87.1	0.70	0.04	94.3	0.74	0.07	90.5	37.38	88.0
	± 0.05	± 0.05	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.05	± 0.5	± 0.05	± 0.5

The IBU removal efficiencies increased from 26.2% to 45.5% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.25). The maximum IBU removal efficiency was achieved as 45.5% at 55 days SRT (Table 6.25) due to the physicochemical properties of IBU (low water solubility = 4.105×10^{-4} g L⁻¹ and moderate high log K_{OW} = 3.79) in the anaerobic reactor. Moreover, the ANOVA (one-way) statistical analysis results showed that the IBU yields at increasing SRTs was insignificant in the anaerobic reactor at all SRTs ($P = 0.827$, $\alpha = 0.05$, $F = 0.05$).

In this study, 1-hydroxylated ibuprofen (1-OH IBU), 2-hydroxylated ibuprofen (2-OH IBU) and ibuprofen carboxylic acid (CBX IBU) which are the main metabolites of IBU were monitored in the effluents of the anaerobic reactor at all SRTs. 1-OH IBU (2.40), 2-OH IBU (2.10) and CBX IBU (2.20) were hydrophilic micropollutants based on their log K_{OW} values lower than 2.50. The effluent concentrations of 1-OH IBU were determined as 0.77, 0.75, 0.72 and 0.70 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.25). The effluent concentrations of 2-OH IBU were measured as 0.82, 0.79, 0.75 and 0.70 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.25). The effluent concentrations of CBX IBU were obtained as 0.86, 0.82, 0.78 and 0.74 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.25).

6.1.18.2 Total IBU Removals in Aerobic Biological Reactor

The maximum IBU removal efficiency of the aerobic biological reactor was found as 52.0% with an IBU effluent of 15.05 µg L⁻¹ at an IBU influent of 31.37 µg L⁻¹ at 5 days SRT (Table 6.25). At 30 days SRT, the maximum IBU removal efficiency was calculated as 63.8% with an IBU effluent of 10.15 µg L⁻¹ for an IBU influent of 28.07 µg L⁻¹ in the aerobic reactor (Table 6.25). At 45 days SRT, the maximum IBU removal efficiency was measured as 71.7% with an IBU effluent of 7.22 µg L⁻¹ for an IBU influent of 25.52 µg L⁻¹ in the aerobic reactor (Table 6.25). For the maximum SRT of 55 days, the maximum IBU removal efficiency was determined as 77.9%

with an IBU effluent of $5.12 \mu\text{g L}^{-1}$ for an IBU influent of $23.16 \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.25).

Total removal of IBU was higher in the aerobic reactor (77.9%) than the anaerobic reactor (45.5%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.25). Although IBU was accepted as a moderate hydrophobic micropollutant due its physicochemical properties (low water solubility = $4.105 \times 10^{-4} \text{ g L}^{-1}$ and high $\log K_{OW} = 3.79$), more satisfactory IBU removal achieved in the aerobic reactor. IBU was a moderate hydrophobic micropollutant with its $\log K_{ow}$ value (3.79) but its lower K_d value ($pK_a = 4.91$) made IBU mainly dissolved in the aqueous phase if the wastewater had an average pH value at 7.50 (Yan et al., 2014). The anaerobic reactor had an average pH value of 8.50 ± 0.50 while the aerobic reactor had an average pH value of 7.50 ± 0.50 in this study. Consequently, the IBU tends to be more dissolved in the aerobic reactor than the anaerobic reactor depending on its ionized form as reported by Yan et al. (2014).

An increase in IBU removal efficiencies was observed (from 52.0% to 77.9%) as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.25). The increase in IBU removal efficiencies with increasing SRTs was studied with the ANOVA (one-way) test statistics and found to be a significant regression in the aerobic reactor ($P = 2.80 \times 10^{-5}$, $\alpha = 0.05$, $F = 129.50$).

The aerobic reactor received the 1-OH IBU remaining from the anaerobic reactor and the influent concentrations of 1-OH IBU were detected as 0.77, 0.75, 0.72 and $0.70 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). The effluent concentrations of 1-OH IBU were measured as 0.22, 0.13, 0.11 and $0.09 \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). 1-OH IBU removal efficiencies were obtained as 71.4%, 82.7%, 84.7% and 87.1% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). In a similar way, the aerobic reactor received the 2-OH IBU remaining from the anaerobic reactor and the influent concentrations of 2-OH IBU were measured as

0.82, 0.79, 0.75 and 0.70 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). The effluent concentrations of 2-OH IBU were obtained as 0.18, 0.10, 0.07 and 0.04 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). 2-OH IBU removal efficiencies were calculated as 78.0%, 87.3%, 90.7% and 94.3% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). Finally, the influent concentrations of CBX IBU were found as 0.86, 0.82, 0.78 and 0.74 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). The effluent concentrations of CBX IBU were detected as 0.22, 0.13, 0.10 and 0.07 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). CBX removal efficiencies were obtained as 74.4%, 84.1%, 87.2% and 90.5% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.25). The results obtained from this study showed that the increasing SRTs increased the removal efficiencies of 1-OH IBU (87.1%), 2-OH IBU (94.3%) and CBX IBU (90.5%) and the maximum yields were obtained at the highest SRT of 55 days in the aerobic reactor (Table 6.25). The ANOVA (one-way) test statistics showed that the removals of 1-OH IBU ($P = 0.006$, $\alpha = 0.05$, $F = 17.49$), 2-OH IBU ($P = 0.003$, $\alpha = 0.05$, $F = 22.24$) and CBX IBU ($P = 0.005$, $\alpha = 0.05$, $F = 19.44$) at increasing SRTs were significant in the aerobic reactor. Because of the 1-OH IBU ($\log K_{OW} = 2.40$), 2-OH IBU ($\log K_{OW} = 2.10$) and CBX IBU ($\log K_{OW} = 2.20$) were hydrophilic micropollutants, the increase in 1-OH IBU, 2-OH IBU and CBX IBU yields were found to be important statistically. These results were higher than the other studies previously reported by the other researchers. The CBX IBU, 2-OH IBU and 1-OH IBU were eliminated approximately 72%, 77% and 58% for the initial CBX IBU, 2-OH IBU and 1-OH IBU concentrations of 38.4, 94.0 and 5.8 $\mu\text{g L}^{-1}$, respectively in a batch operated activated sludge system having a total volume of 2 L with 50 mg L^{-1} TSS concentration and at 48 h HRT (Ferrando-Climent et al., 2012).

6.1.18.3 Total IBU Removals in Anaerobic/Aerobic Sequential Biological Reactor System

For 5 days of SRT operation, the maximum IBU removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 64.6% with an IBU effluent of $15.05 \mu\text{g L}^{-1}$ at an IBU influent of $42.50 \mu\text{g L}^{-1}$ (Table 6.25). The maximum IBU removal efficiency was detected as 76.1% with an IBU effluent of $10.15 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.25). The maximum IBU removal efficiency was found as 83.0% with an IBU effluent of $7.22 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ at 45 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.25). The maximum IBU removal efficiency was determined as 88.0% with an IBU effluent of $5.12 \mu\text{g L}^{-1}$ for an IBU influent of $42.50 \mu\text{g L}^{-1}$ at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.25).

In the anaerobic/aerobic sequential biological reactor system 1-OH IBU removal efficiencies were calculated as 71.4%, 82.7%, 84.7% and 87.1% at 5, 30, 45 and 55 days SRTs, respectively (Table 6.25). The 2-OH IBU removal efficiencies were found as 78.0%, 87.3%, 90.7% and 94.3% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.25). Finally, the CBX IBU removal efficiencies were achieved as 74.4%, 84.1%, 87.2% and 90.5% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.25). Quintana, Weiss, & Reemtsma (2005) studied IBU and its metabolite 1-OH IBU removals in a membrane bioreactor treating municipal wastewater having a total volume of 21 L with 25 g L^{-1} MLSS concentration for an initial IBU concentration of $5.70 \mu\text{g L}^{-1}$ and for an initial 1-OH IBU concentration of $0.50 \mu\text{g L}^{-1}$. When the SRT was increased from 22 days to 26 days, they reported that the IBU and 1-OH IBU removals reached to 96% and 100%, respectively in their study (Quintana et al., 2005). In this study, increasing SRT showed positive effect on the removals of 1-OH IBU, 2-OH IBU and CBX IBU. The maximum 1-OH IBU, 2-OH IBU and CBX IBU yields were

calculated as 87.1%, 94.3% and 90.5%, respectively at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.25).

6.1.18.4 Removal Mechanisms of IBU in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of IBU. The biodegraded, adsorbed, sorbed and volatilized IBU masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.26).

Table 6.26 The total removal percentages for IBU throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	27.83	0.167	7.52	0.009	0.40	0.053	0.00005	26.19	7.08	0.38	0.00005
30	36.08	0.252	11.32	0.018	0.80	0.070	0.00007	33.95	10.65	0.75	0.00007
45	42.45	0.300	13.50	0.025	1.12	0.070	0.00007	39.95	12.71	1.05	0.00007
55	48.35	0.361	16.25	0.026	1.15	0.081	0.00008	45.51	15.29	1.08	0.00008
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	32.65	0.157	2.35	0.014	0.21	0.025	0.00003	52.04	3.75	0.33	0.00004
30	35.84	0.233	3.50	0.024	0.36	0.036	0.00004	63.84	6.23	0.64	0.00006
45	36.60	0.296	4.44	0.029	0.43	0.037	0.00004	71.71	8.70	0.84	0.00007
55	36.08	0.316	4.74	0.032	0.48	0.044	0.00004	77.89	10.23	1.04	0.00009
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(µg L ⁻¹)	(µg)	(%)	(%)	(%)	(%)
5	123.55	--	9.87	--	0.61	--	0.00008	64.60	5.16	0.32	0.00004
30	145.58	--	14.82	--	1.16	--	0.00011	76.12	7.75	0.61	0.00006
45	158.76	--	17.94	--	1.55	--	0.00011	83.01	9.38	0.81	0.00006
55	168.21	--	20.99	--	1.63	--	0.00013	87.95	10.98	0.85	0.00007

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.18.4.1 Removed Masses and Removal Efficiencies of IBU. An example for the calculations relevant to the removed masses and the removal efficiencies of IBU in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.241 to 6.264, respectively at a SRT of 5 days (Table 6.26).

The biodegraded masses of IBU were calculated from Equations 6.241, 6.242 and 6.243 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.26).

$$M_{\text{BIO,Anaerobic}} = (11.13 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 27.83 \mu\text{g} \quad (6.241)$$

$$M_{\text{BIO,Aerobic}} = (16.33 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 32.65 \mu\text{g} \quad (6.242)$$

$$M_{\text{BIO,Sequential}} = (27.45 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 123.55 \mu\text{g} \quad (6.243)$$

The biodegradation removal efficiencies for IBU in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.244, 6.245 and 6.246, respectively at 5 days SRT (Table 6.26).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (27.83 \times 100) / (42.50 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 26.19\% \quad (6.244)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (32.65 \times 100) / (31.37 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 52.04\% \quad (6.245)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (123.55 \times 100) / (42.50 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 64.60\% \quad (6.246)$$

The adsorbed masses of IBU were calculated using Equation 6.247, 6.248 and 6.249 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.26).

$$M_{\text{ADS,Anaerobic}} = [(0.167 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 7.52 \mu\text{g} \quad (6.247)$$

$$M_{\text{ADS,Aerobic}} = [(0.157 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 2.35 \mu\text{g} \quad (6.248)$$

$$M_{\text{ADS,Sequential}} = 7.52 + 2.35 = 9.87 \mu\text{g} \quad (6.249)$$

The total adsorption removal efficiencies of IBU in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.250, 6.251 and 6.252, respectively at 5 days SRT (Table 6.26).

$$\text{Ads}(\%),_{\text{Anaerobic}} = (7.52 \times 100) / (42.50 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 7.08\% \quad (6.250)$$

$$\text{Ads}(\%),_{\text{Aerobic}} = (2.35 \times 100) / (31.37 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 3.75\% \quad (6.251)$$

$$\text{Ads}(\%),_{\text{Sequential}} = (9.87 \times 100) / (42.50 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 5.16\% \quad (6.252)$$

The sorbed masses into the anaerobic and aerobic biological sludges of IBU were calculated according to the Equation 6.253 and 6.254, respectively while the total sorbed mass for IBU in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.255 at 5 days SRT (Table 6.26).

$$M_{\text{SORP,Anaerobic}} = [(0.009 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 0.40 \mu\text{g} \quad (6.253)$$

$$M_{\text{SORP,Aerobic}} = [(0.014 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.21 \mu\text{g} \quad (6.254)$$

$$M_{\text{SORP,Sequential}} = 0.40 + 0.21 = 0.61 \mu\text{g} \quad (6.255)$$

The total sorption removal efficiencies of IBU in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 2.256, 2.257 and 2.258, respectively at 5 days SRT (Table 6.26).

$$\text{Sorp}(\%),_{\text{Anaerobic}} = (0.40 \times 100) / (42.50 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.38\% \quad (6.256)$$

$$\text{Sorp}(\%),_{\text{Aerobic}} = (0.21 \times 100) / (31.37 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.33\% \quad (6.257)$$

$$\text{Sorp}(\%),_{\text{Sequential}} = (0.61 \times 100) / (42.50 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.32\% \quad (6.258)$$

Volatilized masses of IBU were calculated according to the Equation 6.259, 6.260 and 6.261 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.26).

$$M_{\text{VOL,An}} = (0.053 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 5.00 \times 10^{-5} \mu\text{g} \quad (6.259)$$

$$M_{VOL,Ae} = (0.025 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 3.00 \times 10^{-5} \mu\text{g} \quad (6.260)$$

$$M_{VOL,Sequential} = 5.00 \times 10^{-5} + 3.00 \times 10^{-5} = 8.00 \times 10^{-5} \mu\text{g} \quad (6.261)$$

The total volatilization removal efficiencies of IBU were determined according to the Equation 6.262, 6.263 and 6.264 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.26).

$$\text{Vol}(\%),_{\text{Anaerobic}} = (5.00 \times 10^{-5} \times 100) / (42.50 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.00005\% \quad (6.262)$$

$$\text{Vol}(\%),_{\text{Aerobic}} = (3.00 \times 10^{-5} \times 100) / (31.37 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.00005\% \quad (6.263)$$

$$\text{Vol}(\%),_{\text{Sequential}} = (8.00 \times 10^{-5} \times 100) / (42.50 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.00004\% \quad (6.264)$$

6.1.18.4.2 Removed Masses and Removal Efficiencies of IBU in Anaerobic Reactor. As is shown in Table 6.26, the biodegraded IBU masses increased from 27.83 μg to 48.35 μg as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor. The biodegradation removal percentages of IBU also increased from 26.19% to 45.51% with the increasing of SRTs from 5 days up to 55 days, respectively in the anaerobic reactor (Table 6.26). The anaerobic bacteria can co-metabolized 45.51% of IBU together COD and sCOD at the highest SRT of 55 days (Table 6.26). The ANOVA (one-way) test statistic results showed that there is no significant relationship between IBU yields and SRTs in the anaerobic reactor ($P = 0.827$, $\alpha = 0.05$, $F = 0.05$). The physicochemical properties of IBU (low water solubility = $4.105 \times 10^{-4} \text{ g L}^{-1}$, moderate high $\log K_{OW} = 3.79$ and low Henry's Law constant = $1.52 \times 10^{-7} \text{ atm m}^3 \text{ mol}^{-1}$) makes IBU resistant to extensive biodegradation under anaerobic conditions (Smook, Zho, & Zytner, 2008 and Matamoros, Hijosa, & Bayona, 2009). The sorbed masses (0.40 – 1.15 μg) and volatilized masses (0.00005 – 0.00008 μg) were low for IBU in the anaerobic reactor at all SRTs (Table 6.26). The sorption and volatilization removal percentages also were low (between 0.38% and 1.08% for sorption and between 0.00005% and 0.00008% for volatilization, respectively) in the anaerobic reactor at all SRTs (Table 6.26). The ANOVA (one-way) test statistics results showed that the removal of IBU via sorption ($P = 0.102$, $\alpha = 0.05$, $F = 3.73$) and volatilization ($P = 0.109$, $\alpha = 0.05$, $F = 3.54$) were insignificant in the anaerobic reactor at all SRTs. The adsorbed IBU

masses to the anaerobic sludge increased from 7.52 μg to 16.25 μg at SRTs varying from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.26). The increase in adsorbed IBU masses also increased the IBU adsorption yields from 7.08% to 15.29% at SRTs 5 days and 55 days, respectively in the anaerobic reactor (Table 6.26). The ANOVA (one-way) test statistics results showed that the removal of IBU via adsorption was significant ($P = 2.24 \times 10^{-7}$, $\alpha = 0.05$, $F = 57.12$). It can be noted that the adsorption has an important contribution to the removal of IBU in the anaerobic reactor at all SRTs because IBU was a moderate hydrophobic micropollutant with its physicochemical properties (low water solubility = $4.105 \times 10^{-4} \text{ g L}^{-1}$, low Henry's Law constant = $1.52 \times 10^{-7} \text{ atm m}^3 \text{ mol}^{-1}$ and moderate $\log K_{OW} = 3.79$).

6.1.18.4.3 Removed Masses and Removal Efficiencies of IBU in Aerobic Reactor.

In the aerobic reactor, the biodegraded IBU masses increased from 32.65 μg to 36.08 μg resulting in the IBU removal percentages of 52.04% and 77.89% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.26). The maximum biodegradation yield of IBU was obtained as 77.89% at 55 days SRT (Table 6.26). Regarding biodegradation, the co-metabolic biodegradation of IBU during aerobic treatment occurred (Li et al., 2016b) since the influent concentration of IBU as 42.50 $\mu\text{g L}^{-1}$ was too low to serve as a direct growth substrate (Table 6.26). In the co-metabolic approach, IBU may be utilized by the corresponding aerobic organisms in the obligatory presence of growth substrate (COD and sCOD) (Kumwimba & Meng, 2019). In this study, COD (950.00 mg L^{-1}) and sCOD (850.00 mg L^{-1}) were used as the sole energy and carbon to sustain aerobic biomass and generate the relevant enzymes resulting in the biodegradation of IBU in the aerobic reactor (Table 5.1). IBU could be co-metabolized via hydroxylation of aliphatic chain and then aromatic ring, respectively (Marchlewicz, Guzik, Smulek, & Wojcieszynska, 2017). The biodegradation of IBU was found to be significant according to the ANOVA (one-way) test statistics in the aerobic reactor at all SRTs ($P = 0.037$, $\alpha = 0.05$, $F = 7.13$). The sorbed masses (0.21 – 0.48 μg) and volatilized masses (0.00003 – 0.00004 μg) were low for IBU in the aerobic reactor at all SRTs (Table 6.26). The IBU removal percentages also were low (between 0.33% and 1.04% for sorption and

between 0.00004% and 0.00009% for volatilization, respectively) in the aerobic reactor at all SRTs (Table 6.26). The ANOVA (one-way) test statistics results showed that the removal of IBU via sorption ($P = 0.443$, $\alpha = 0.05$, $F = 0.67$) and volatilization ($P = 0.367$, $\alpha = 0.05$, $F = 0.95$) were not significant in the aerobic reactor. The adsorbed IBU masses to the aerobic sludge increased from 2.35 μg to 4.74 μg as the SRTs were increased from 5 days to 55 days, respectively (Table 6.26). This attributed to the IBU adsorption yields of 3.75% and 10.23% at 5 days and 55 days SRT, respectively (Table 6.26). However, the ANOVA (one-way) test statistics results showed that the removal of IBU via adsorption was not significant ($P = 0.052$, $\alpha = 0.05$, $F = 5.85$). As a result, adsorption has not a significant contribution to the removal of IBU in the aerobic reactor at all SRTs. Yan et al. (2014) also reported that IBU removed mainly by biodegradation (75.00%) in comparison with adsorption onto sludge (0.00%) in a wastewater treatment plant treating municipal wastewater. They concluded that the IBU was a moderate hydrophobic micropollutant with its $\log K_{ow}$ value (3.79) but its lower K_d value ($pK_a = 4.91$) made IBU mainly dissolved in the aqueous phase if the wastewater had an average pH value at 7.50 (Yan et al., 2014). In this study, IBU was removed mainly by biodegradation depending on its lower K_d value ($pK_a = 4.91$) and the contribution of the adsorption (10.23%) was lower than the biodegradation (77.89%) in the aerobic reactor at 55 days SRT and at a hospital wastewater pH of 7.50 ± 0.50 (Table 6.26).

Removal of IBU via biodegradation was higher in the aerobic reactor (77.89%) than the anaerobic reactor (45.51%) at 55 days SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.26). Preliminary studies suggested that the aerobic conditions are more energetically favorable and predominant for the co-metabolic biodegradation of IBU than that of the anaerobic conditions (Kumwimba & Meng, 2019). Removal of IBU via adsorption was higher in the anaerobic reactor (15.29%) than the aerobic reactor (10.23%) at 55 days SRT (Table 6.26). This could be attributed to that IBU found more sludge surface to be adsorbed in the anaerobic reactor (MLVSS concentration of 27600 mg L^{-1}) than the aerobic reactor (MLVSS concentration of 3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.18.4.4 *Removed Masses and Removal Efficiencies of IBU in Anaerobic/Aerobic Sequential Biological Reactor System.* The total biodegraded masses of IBU increased from 123.55 μg to 168.21 μg resulting in the IBU biodegradation removal percentages of 64.60% and 87.95% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.26). The maximum IBU biodegradation yield was obtained as 87.95% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.26). The ANOVA (one-way) test statistic results showed that the relationship between IBU biodegradation yields and SRTs was significant in the anaerobic/aerobic sequential biological reactor system ($P = 0.010$, $\alpha = 0.05$, $F = 13.56$). The sorbed masses (0.61 – 1.63 μg) and volatilized masses (0.00008 – 0.00013 μg) were low for IBU in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.26). The IBU removal percentages also found to be low (between 0.32% and 0.85% for sorption and between 0.00004% and 0.00007% for volatilization, respectively) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.26). The ANOVA (one-way) test statistics results showed that the removal of IBU via sorption ($P = 0.083$, $\alpha = 0.05$, $F = 4.33$) and volatilization ($P = 0.087$, $\alpha = 0.05$, $F = 4.17$) were negligible in the anaerobic/aerobic sequential biological reactor system. The total adsorbed IBU masses to the anaerobic (from 7.52 μg to 16.25 μg) and aerobic (from 2.35 μg to 4.74 μg) sludge increased from 9.87 μg to 20.99 μg as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.26). The increase in the total adsorbed masses also increased the total IBU adsorption yields from 5.16% to 10.98% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.26). However, the ANOVA (one-way) test statistics results showed that the removal of IBU via adsorption was not significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.059$, $\alpha = 0.05$, $F = 5.40$). IBU was a moderate hydrophobic micropollutant having a $\log K_{OW}$ value (3.79) between 2.50 - 4.00, besides, having lower K_d value ($pK_a = 4.91$) at a pH of 7.50 ± 0.50 allows IBU removing via biodegradation rather than adsorption in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.26).

Clara, Kreuzinger, Strenn, Gans, & Kroiss (2005) suggested that a critical value for the SRT can be determined to achieve IBU removals higher than 70.0% through the operation of the wastewater treatment plants and they reported that higher IBU removal efficiencies can be achieved at SRTs higher than 10 days (Clara et al., 2005). In this study, the increase in the SRTs showed positive effect on the biodegradation yields for IBU in the anaerobic/aerobic sequential biological reactor system. Total IBU biodegradation yields increased with the increasing SRTs and the highest removal efficiency was achieved as 87.95% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Figure 6.17). Being a moderate hydrophobic micropollutant (lower $pK_a = 4.91$ and moderate high $\log K_{ow} = 3.79$) makes IBU appropriate for biodegradation (Lishman et al., 2006). The maximum IBU biodegradation removal efficiency (87.95%) obtained in this study at 55 days SRT in the anaerobic/aerobic sequential biological reactor system was higher than the results previously obtained by the other authors. Verlicchi et al. (2013) studied IBU removal in a horizontal subsurface flow bed treating municipal wastewater and the maximum biodegradation removal efficiency of IBU was calculated as 28% for 1 day of HRT at a constant flowrate of $8 \text{ m}^3 \text{ day}^{-1}$ and at an average temperature of 10°C (Verlicchi et al., 2013). The IBU removal was also performed by Almeida et al. (2013) and they observed 50% of maximum IBU removal efficiency in an activated sludge system having a total volume of 500 mL for $250 \text{ } \mu\text{g L}^{-1}$ initial IBU concentration at 323 h HRT (Almeida et al., 2013). Zupanc et al. (2013) investigated the IBU removal in a suspended activated sludge reactor containing anoxic (0.725 L), aerated (2.55 L) and settlement (0.725 L) compartments havin a total volume of 4 L treating synthetic wastewater. The maximum IBU removal efficiency was measured as $86 \pm 10\%$ with an influent IBU concentration of $1.00 \text{ } \mu\text{g L}^{-1}$ at a HRT of 48 h (Zupanc et al., 2013).

The results from this study showed that IBU can not be effectively removed via adsorption (10.98%), sorption (0.85%) and volatilization (0.00007%) at 55 days SRT. In this study, we found that biodegradation (87.95%) was the main removal mechanism for IBU at 55 days SRT (Figure 6.17) due to the IBU was a moderate hydrophobic micropollutant with its physicochemical properties like moderate high

octanol/water partition coefficient ($\log K_{OW} = 3.79$) and lower K_d value ($pK_a = 4.91$). Other studies from the literature were in good agreement with our results. Previous studies have shown that IBU was commonly removed by biodegradation through removal studies. Also, they accepted the contribution of the volatilization is negligible (Ternes et al., 2004, Joss et al., 2006, Salgado et al., 2012).

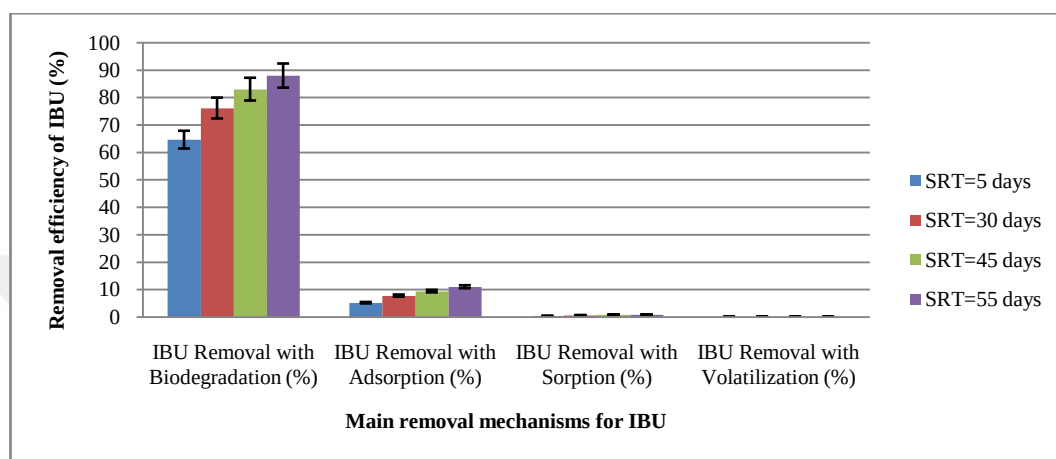


Figure 6.17 The removal efficiencies of IBU with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.19 Total Ciprofloxacin (CIP) Removals

6.1.19.1 Total CIP Removals in Anaerobic Biological Reactor

At the beginning of the study, the maximum CIP removal efficiency of the anaerobic reactor was obtained as 29.5% with a CIP effluent of $368.16 \mu\text{g L}^{-1}$ at a CIP influent of $522.00 \mu\text{g L}^{-1}$ at 5 days SRT (Table 6.27). The maximum CIP removal efficiency was detected as 41.2% with a CIP effluent of $307.11 \mu\text{g L}^{-1}$ for a CIP influent of $522.00 \mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic reactor (Table 6.27). For 45 days of SRT operation, the maximum CIP removal efficiency was found as 45.2% with a CIP effluent of $286.12 \mu\text{g L}^{-1}$ for a CIP influent of $522.00 \mu\text{g L}^{-1}$ in the anaerobic reactor (Table 6.27). When the SRT was increased to 55 days, the maximum CIP removal efficiency was determined as 50.0% with a CIP effluent of

261.01 $\mu\text{g L}^{-1}$ for a CIP influent of 522.00 $\mu\text{g L}^{-1}$ at 55 days SRT in the anaerobic reactor (Table 6.27).



Table 6.27 CIP and its metabolites; FCP, OCP and SCP concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor												
	Influent CIP ($\mu\text{g L}^{-1}$)	Effluent CIP ($\mu\text{g L}^{-1}$)	Metabolites of CIP namely FCP, OCP and SCP									Removed CIP ($\mu\text{g L}^{-1}$)	CIP Removal Eff. (%)
			Influent FCP ($\mu\text{g L}^{-1}$)	Effluent FCP ($\mu\text{g L}^{-1}$)	FCP Removal Eff. (%)	Influent OCP ($\mu\text{g L}^{-1}$)	Effluent OCP ($\mu\text{g L}^{-1}$)	OCP Removal Eff. (%)	Influent SCP ($\mu\text{g L}^{-1}$)	Effluent SCP ($\mu\text{g L}^{-1}$)	SCP Removal Eff. (%)		
5	522.00 $\pm$ 0.05	368.16 $\pm$ 0.05	0.00 $\pm$ 0.05	18.27 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	17.23 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	15.66 $\pm$ 0.05	0.00 $\pm$ 0.5	153.84 $\pm$ 0.05	29.5 $\pm$ 0.5
30	522.00 $\pm$ 0.05	307.11 $\pm$ 0.05	0.00 $\pm$ 0.05	8.62 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	7.09 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	5.53 $\pm$ 0.05	0.00 $\pm$ 0.5	214.89 $\pm$ 0.05	41.2 $\pm$ 0.5
45	522.00 $\pm$ 0.05	286.12 $\pm$ 0.05	0.00 $\pm$ 0.05	6.12 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	6.00 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	5.00 $\pm$ 0.05	0.00 $\pm$ 0.5	235.88 $\pm$ 0.05	45.2 $\pm$ 0.5
55	522.00 $\pm$ 0.05	261.01 $\pm$ 0.05	0.00 $\pm$ 0.05	5.75 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	5.05 $\pm$ 0.05	0.00 $\pm$ 0.5	0.00 $\pm$ 0.05	4.40 $\pm$ 0.05	0.00 $\pm$ 0.5	260.99 $\pm$ 0.05	50.0 $\pm$ 0.5

SRT (day)	Aerobic Reactor												
	Influent CIP ($\mu\text{g L}^{-1}$)	Effluent CIP ($\mu\text{g L}^{-1}$)	Metabolites of CIP namely FCP, OCP and SCP									Removed CIP ($\mu\text{g L}^{-1}$)	CIP Removal Eff. (%)
			Influent FCP ($\mu\text{g L}^{-1}$)	Effluent FCP ($\mu\text{g L}^{-1}$)	FCP Removal Eff. (%)	Influent OCP ($\mu\text{g L}^{-1}$)	Effluent OCP ($\mu\text{g L}^{-1}$)	OCP Removal Eff. (%)	Influent SCP ($\mu\text{g L}^{-1}$)	Effluent SCP ($\mu\text{g L}^{-1}$)	SCP Removal Eff. (%)		
5	368.16 $\pm$ 0.05	150.58 $\pm$ 0.05	18.27 $\pm$ 0.05	3.53 $\pm$ 0.05	80.7 $\pm$ 0.5	17.23 $\pm$ 0.05	3.07 $\pm$ 0.05	82.2 $\pm$ 0.5	15.66 $\pm$ 0.05	2.35 $\pm$ 0.05	85.0 $\pm$ 0.5	217.57 $\pm$ 0.05	59.1 $\pm$ 0.5
30	307.11 $\pm$ 0.05	85.75 $\pm$ 0.05	8.62 $\pm$ 0.05	0.84 $\pm$ 0.05	90.3 $\pm$ 0.5	7.09 $\pm$ 0.05	0.56 $\pm$ 0.05	92.1 $\pm$ 0.5	5.53 $\pm$ 0.05	0.36 $\pm$ 0.05	93.5 $\pm$ 0.5	221.35 $\pm$ 0.05	72.1 $\pm$ 0.5
45	286.12 $\pm$ 0.05	60.90 $\pm$ 0.05	6.12 $\pm$ 0.05	0.32 $\pm$ 0.05	94.8 $\pm$ 0.5	6.00 $\pm$ 0.05	0.25 $\pm$ 0.05	95.8 $\pm$ 0.5	5.00 $\pm$ 0.05	0.15 $\pm$ 0.05	97.0 $\pm$ 0.5	225.23 $\pm$ 0.05	78.7 $\pm$ 0.5
55	261.01 $\pm$ 0.05	35.71 $\pm$ 0.05	5.75 $\pm$ 0.05	0.16 $\pm$ 0.05	97.2 $\pm$ 0.5	5.05 $\pm$ 0.05	0.12 $\pm$ 0.05	97.6 $\pm$ 0.5	4.40 $\pm$ 0.05	0.00 $\pm$ 0.05	100.0 $\pm$ 0.5	225.30 $\pm$ 0.05	86.3 $\pm$ 0.5

Table 27. continues

SRT (day)	Anaerobic/Aerobic Sequential Biological Reactor System												
	Metabolites of CIP namely FCP, OCP and SCP											Removed CIP ($\mu\text{g L}^{-1}$)	CIP Removal Eff. (%)
	Influent CIP ($\mu\text{g L}^{-1}$)	Effluent CIP ($\mu\text{g L}^{-1}$)	Influent FCP ($\mu\text{g L}^{-1}$)	Effluent FCP ($\mu\text{g L}^{-1}$)	FCP Removal Eff. (%)	Influent OCP ($\mu\text{g L}^{-1}$)	Effluent OCP ($\mu\text{g L}^{-1}$)	OCP Removal Eff. (%)	Influent SCP ($\mu\text{g L}^{-1}$)	Effluent SCP ($\mu\text{g L}^{-1}$)	SCP Removal Eff. (%)		
5	522.00 ± 0.05	150.58 ± 0.05	18.27 ± 0.05	3.53 ± 0.05	80.7 ± 0.5	17.23 ± 0.05	3.07 ± 0.05	82.2 ± 0.5	15.66 ± 0.05	2.35 ± 0.05	85.0 ± 0.5	371.42 ± 0.05	71.2 ± 0.5
30	522.00 ± 0.05	85.75 ± 0.05	8.62 ± 0.05	0.84 ± 0.05	90.3 ± 0.5	7.09 ± 0.05	0.56 ± 0.05	92.1 ± 0.5	5.53 ± 0.05	0.36 ± 0.05	93.5 ± 0.5	436.25 ± 0.05	83.6 ± 0.5
45	522.00 ± 0.05	60.90 ± 0.05	6.12 ± 0.05	0.32 ± 0.05	94.8 ± 0.5	6.00 ± 0.05	0.25 ± 0.05	95.8 ± 0.5	5.00 ± 0.05	0.15 ± 0.05	97.0 ± 0.5	461.10 ± 0.05	88.3 ± 0.5
55	522.00 ± 0.05	35.71 ± 0.05	5.75 ± 0.05	0.16 ± 0.05	97.2 ± 0.5	5.05 ± 0.05	0.12 ± 0.05	97.6 ± 0.5	4.40 ± 0.05	0.00 ± 0.05	100.0 ± 0.5	486.29 ± 0.05	93.2 ± 0.5

The CIP removal efficiencies increased from 29.5% to 50.0% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.27). The maximum CIP yield was achieved as 50.0% at 55 days SRT in the anaerobic reactor (Table 6.27) owing to the hydrophilic structure of CIP (high water solubility = $1.148 \times 10^4 \text{ g L}^{-1}$ and low $\log K_{OW} = 0.28$). The ANOVA (one-way) statistical analysis results also confirmed that there was a significant relationship between the CIP yields and SRTs in the anaerobic reactor ($P = 0.00012$, $\alpha = 0.05$, $F = 77.30$).

In this study, Formylciprofloxacin (FCP), Oxociprofloxacin (OCP) and Sulfociprofloxacin (SCP) which are the main metabolites of CIP were monitored in the effluents of the anaerobic reactor at all SRTs. FCP (1.10), OCP (1.00) and SCP (0.40) were quite hydrophilic micropollutants based on their $\log K_{OW}$ values lower than 2.50. The effluent concentrations of FCP were measured as 18.27, 8.62, 6.12 and $5.75 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.27). The effluent concentrations of OCP were found as 17.23, 7.09, 6.00 and $5.05 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.27). The effluent concentrations of SCP were determined as 15.66, 5.53, 5.00 and $4.40 \text{ } \mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.27).

6.1.19.2 Total CIP Removals in Aerobic Biological Reactor

For the 5 days of SRT, the maximum CIP removal efficiency of the aerobic biological reactor was obtained as 59.1% with a CIP effluent of $150.58 \text{ } \mu\text{g L}^{-1}$ at a CIP influent of $368.16 \text{ } \mu\text{g L}^{-1}$ (Table 6.27). When the SRT was increased to 30 days, the maximum CIP removal efficiency was calculated as 72.1% with a CIP effluent of $85.75 \text{ } \mu\text{g L}^{-1}$ for a CIP influent of $307.11 \text{ } \mu\text{g L}^{-1}$ at 30 days SRT in the aerobic reactor (Table 6.27). The maximum CIP removal efficiency was found as 78.7% with a CIP effluent of $60.90 \text{ } \mu\text{g L}^{-1}$ for a CIP influent of $286.12 \text{ } \mu\text{g L}^{-1}$ in the aerobic reactor (Table 6.27). At the highest SRT of 55 days, the maximum CIP removal efficiency was determined as 86.3% with a CIP effluent of $35.71 \text{ } \mu\text{g L}^{-1}$ for a CIP influent of $261.01 \text{ } \mu\text{g L}^{-1}$ at 55 days SRT in the aerobic reactor (Table 6.27).

Total removal of CIP was higher in the aerobic reactor (86.3%) than the anaerobic reactor (50.0%) at 55 days of SRT (Table 6.27). This could be attributed to the aerobic conditions are more energetically favorable and predominant for the co-metabolic biodegradation than under anaerobic conditions (Kumwimba & Meng, 2019). In addition, CIP shows tendency to biodegradation with its physicochemical properties (high water solubility = 1.148×10^4 g L⁻¹ and low octanol/water partition coefficient log K_{OW} = 0.28). Also, the aerobic treatment provides improvement in the CIP removal and acts as a post-treatment step after anaerobic treatment in this study.

An increase in CIP removal efficiencies was obtained (from 59.1% to 86.3%) as the SRTs were increased from 5 days to 55 days, respectively in the aerobic reactor (Table 6.27). The increase in CIP removal efficiencies with increasing SRTs was found to be significant at all SRTs in the aerobic reactor according to the ANOVA (one-way) test statistics results ($P = 0.017$, $\alpha = 0.05$, $F = 10.72$).

The aerobic reactor received the FCP remaining from the anaerobic reactor and the influent concentrations of FCP were found as 18.27, 8.62, 6.12 and 5.75 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). The effluent concentrations of FCP were determined as 3.53, 0.84, 0.32 and 0.16 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). FCP removal efficiencies were calculated as 80.7%, 90.3%, 94.8% and 97.2% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). For the other metabolite of CIP namely OCP it could be said that the aerobic reactor received the OCP remaining from the anaerobic reactor and the influent concentrations of OCP were obtained as 17.23, 7.09, 6.00 and 5.05 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). The effluent concentrations of OCP were measured as 3.07, 0.56, 0.25 and 0.12 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). OCP removal efficiencies were determined as 82.2%, 92.1%, 95.8% and 97.6% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). Finally, the influent concentrations of SCP were detected as 15.66, 5.53, 5.00 and 4.40 µg L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). The effluent concentrations of

SCP were found as 2.35, 0.36, 0.15 and 0.00 $\mu\text{g L}^{-1}$ at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). SCP removal efficiencies were calculated as 85.0%, 93.5%, 97.0% and 100.0% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.27). The results from this study indicated that the maximum yields for FCP (97.2%), OCP (97.6%) and SCP (100.0%) were achieved at the highest SRT of 55 days in the aerobic reactor (Table 6.27). The ANOVA (one-way) test statistics results showed that there were linear correlations between the SRTs and the removal yields of FCP ($R^2 = 0.99$, $P = 0.0025$, $\alpha = 0.05$, $F = 24.68$), OCP ($R^2 = 0.98$, $P = 0.0022$, $\alpha = 0.05$, $F = 26.02$) and SCP ($R^2 = 0.99$, $P = 0.0018$, $\alpha = 0.05$, $F = 28.07$), and these regressions were significant in the aerobic reactor at all SRTs. The increases in FCP, OCP and SCP yields at increasing SRTs had significance because of the FCP ($\log K_{OW} = 1.10$), OCP ($\log K_{OW} = 1.00$) and SCP ($\log K_{OW} = 0.40$) were quite hydrophilic micropollutants.

6.1.19.3 Total CIP Removals in Anaerobic/Aerobic Sequential Biological Reactor System

At 5 days SRT, the maximum CIP removal efficiency of the anaerobic/aerobic sequential biological reactor system was obtained as 71.2% with a CIP effluent of 150.58 $\mu\text{g L}^{-1}$ at a CIP influent of 522.00 $\mu\text{g L}^{-1}$ (Table 6.27). The maximum CIP removal efficiency was calculated as 83.6% with a CIP effluent of 85.75 $\mu\text{g L}^{-1}$ for a CIP influent of 522.00 $\mu\text{g L}^{-1}$ at 30 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.27). For 45 days of SRT operation, the maximum CIP removal efficiency was found as 88.3% with a CIP effluent of 60.90 $\mu\text{g L}^{-1}$ for a CIP influent of 522.00 $\mu\text{g L}^{-1}$ in the anaerobic/aerobic sequential biological reactor system (Table 6.27). For the highest SRT of 55 days, the maximum CIP removal efficiency was determined as 93.2% with a CIP effluent of 35.71 $\mu\text{g L}^{-1}$ for a CIP influent of 522.00 $\mu\text{g L}^{-1}$ in the anaerobic/aerobic sequential biological reactor system (Table 6.27).

In the anaerobic/aerobic sequential biological reactor system FCP removal efficiencies were achieved as 80.7%, 90.3%, 94.8% and 97.2% at 5, 30, 45 and 55

days SRTs, respectively (Table 6.27). The OCP removal efficiencies were calculated as 82.2%, 92.1%, 95.8% and 97.6% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.27). Finally, the SCP removal efficiencies were obtained as 85.0%, 93.5%, 97.0% and 100.0% at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.27). The maximum FCP, OCP and SCP yields were obtained as 97.2%, 97.6% and 100.0%, respectively at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.27). It can be concluded that the increasing SRT showed positive effect on the removals of FCP, OCP and SCP in the anaerobic/aerobic sequential biological reactor system.

6.1.19.4 Removal Mechanisms of CIP in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of CIP. The biodegraded, adsorbed, sorbed and volatilized CIP masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.28).

Table 6.28 The total removal percentages for CIP throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	384.61	1.614	72.62	0.106	4.77	0.00	0.0000	29.47	5.56	0.37	0.0000
30	537.23	2.048	92.18	0.158	7.09	0.00	0.0000	41.17	7.06	0.54	0.0000
45	589.70	2.225	100.14	0.215	9.66	0.00	0.0000	45.19	7.67	0.74	0.0000
55	652.49	2.377	106.95	0.282	12.67	0.00	0.0000	50.00	8.20	0.97	0.0000
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	435.15	0.837	12.56	0.107	1.60	0.00	0.0000	59.10	1.71	0.22	0.0000
30	442.71	1.254	18.82	0.179	2.69	0.00	0.0000	72.08	3.06	0.44	0.0000
45	450.45	1.364	20.47	0.181	2.72	0.00	0.0000	78.72	3.58	0.48	0.0000
55	450.60	1.493	22.40	0.195	2.93	0.00	0.0000	86.32	4.29	0.56	0.0000
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	($\mu\text{g L}^{-1}$)	(μg)	(%)	(%)	(%)	(%)
5	1671.38	--	85.18	--	6.37	--	0.0000	71.15	3.63	0.27	0.0000
30	1963.10	--	110.99	--	9.78	--	0.0000	83.57	4.73	0.42	0.0000
45	2074.97	--	120.61	--	12.38	--	0.0000	88.33	5.13	0.53	0.0000
55	2188.32	--	129.35	--	15.60	--	0.0000	93.16	5.51	0.66	0.0000

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.19.4.1 Removed Masses and Removal Efficiencies of CIP. An example for the calculations relevant to the removed masses and the removal efficiencies of CIP in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.265 to 6.282, respectively at a SRT of 5 days (Table 6.28).

The biodegraded masses of CIP were calculated from Equations 6.265, 6.266 and 6.267 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.28).

$$M_{\text{BIO,Anaerobic}} = (153.84 \mu\text{g L}^{-1}) \times (2.5 \text{ L}) = 384.61 \mu\text{g} \quad (6.265)$$

$$M_{\text{BIO,Aerobic}} = (217.57 \mu\text{g L}^{-1}) \times (2.0 \text{ L}) = 435.15 \mu\text{g} \quad (6.266)$$

$$M_{\text{BIO,Sequential}} = (371.42 \mu\text{g L}^{-1}) \times (4.5 \text{ L}) = 1671.38 \mu\text{g} \quad (6.267)$$

The biodegradation removal efficiencies for CIP in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 2.268, 2.269 and 2.270, respectively at 5 days SRT (Table 6.28).

$$\text{Bio}(\%)_{\text{Anaerobic}} = (384.61 \times 100) / (522.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 29.47\% \quad (6.268)$$

$$\text{Bio}(\%)_{\text{Aerobic}} = (435.15 \times 100) / (368.16 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 59.10\% \quad (6.269)$$

$$\text{Bio}(\%)_{\text{Sequential}} = (1671.38 \times 100) / (522.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 71.15\% \quad (6.270)$$

The adsorbed masses of CIP were calculated using Equation 2.271, 2.272 and 2.273 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.28).

$$M_{\text{ADS,Anaerobic}} = [(1.614 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 72.62 \mu\text{g} \quad (6.271)$$

$$M_{\text{ADS,Aerobic}} = [(0.837 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 12.56 \mu\text{g} \quad (6.272)$$

$$M_{\text{ADS,Sequential}} = 72.62 + 12.56 = 85.18 \mu\text{g} \quad (6.273)$$

The total adsorption removal efficiencies of CIP in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.274, 6.275 and 6.276, respectively at 5 days SRT (Table 6.28).

$$\text{Ads}(\%)_{\text{Anaerobic}} = (72.62 \times 100) / (522.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 5.56\% \quad (6.274)$$

$$\text{Ads}(\%)_{\text{Aerobic}} = (12.56 \times 100) / (368.16 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 1.71\% \quad (6.275)$$

$$\text{Ads}(\%)_{\text{Sequential}} = (85.18 \times 100) / (522.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 3.63\% \quad (6.276)$$

The sorbed masses into the anaerobic and aerobic biological sludges of CIP were calculated according to the Equation 6.277 and 6.278, respectively while the total sorbed mass for CIP in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.279 at 5 days SRT (Table 6.28).

$$M_{\text{SORP,Anaerobic}} = [(0.106 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 4.77 \mu\text{g} \quad (6.277)$$

$$M_{\text{SORP,Aerobic}} = [(0.107 \mu\text{g L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 1.60 \mu\text{g} \quad (6.278)$$

$$M_{\text{SORP,Sequential}} = 4.77 + 1.60 = 6.37 \mu\text{g} \quad (6.279)$$

The total sorption removal efficiencies of CIP in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.280, 6.281 and 6.282, respectively at 5 days SRT (Table 6.28).

$$\text{Sorp}(\%)_{\text{Anaerobic}} = (4.77 \times 100) / (522.00 \mu\text{g L}^{-1} \times 2.5 \text{ L}) = 0.37\% \quad (6.280)$$

$$\text{Sorp}(\%)_{\text{Aerobic}} = (1.60 \times 100) / (368.16 \mu\text{g L}^{-1} \times 2.0 \text{ L}) = 0.22\% \quad (6.281)$$

$$\text{Sorp}(\%)_{\text{Sequential}} = (6.37 \times 100) / (522.00 \mu\text{g L}^{-1} \times 4.5 \text{ L}) = 0.27\% \quad (6.282)$$

PUF disks were used in order to determine the volatilization masses. No CIP concentrations ($0.00 \mu\text{g L}^{-1}$) were determined after 5, 30, 45 and 55 days of SRTs in the PUF disks under anaerobic and aerobic conditions, respectively. Because of the concentrations were measured as zero ($0.00 \mu\text{g L}^{-1}$), volatilization masses ($(0.00 \mu\text{g L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.00 \mu\text{g}$) and volatilization removal efficiencies

for CIP calculated zero in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days SRTs (Table 6.28).

6.1.19.4.2 Removed Masses and Removal Efficiencies of CIP in Anaerobic Reactor. As is shown in Table 6.28, the biodegraded CIP masses increased from 384.61 μg to 652.49 μg as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor. The biodegradation percentages of CIP also increased from 29.47% to 50.00% with the increasing of SRTs from 5 days up to 55 days, respectively in the anaerobic reactor (Table 6.28). The anaerobic bacteria can co-metabolized 50.00% of CIP together COD and sCOD at the highest SRT of 55 days (Table 6.28). In this study, it was expected that the easily biodegradable substances such as COD (influent concentration of 950.00 mg L^{-1}) and sCOD (influent concentration of 850.00 mg L^{-1}) might be served as the direct growth substrates in the co-metabolic removal of CIP (influent concentration of 522.00 $\mu\text{g L}^{-1}$) (Table 5.1). It was possible a competition between CIP-degrading bacteria and anaerobic bacteria in terms of COD and sCOD. The microorganisms used COD and sCOD as the direct growth substrates to support CIP removal as co-substrate also mentioned by Yang et al., 2018b. CIP was a hydrophilic micropollutant with its physicochemical properties (high water solubility = $1.148 \times 10^4 \text{ g L}^{-1}$, low $\log K_{\text{OW}} = 0.28$ and low Henry's Law constant = $5.09 \times 10^{-19} \text{ atm m}^3 \text{ mol}^{-1}$), therefore, biodegradation played an important role for the CIP removal in the anaerobic reactor at all SRTs. The ANOVA (one-way) test statistic results also supported that there was a significant relationship between CIP yields and SRTs in the anaerobic reactor ($P = 0.00012$, $\alpha = 0.05$, $F = 77.30$). The sorbed masses (4.77 – 12.67 μg) and sorption removal percentages (0.37% – 0.97%) were low for CIP at all SRTs in the anaerobic reactor (Table 6.28). The volatilized masses and the volatilization removal percentages were measured as zero for CIP at all SRTs in the anaerobic reactor (Table 6.28). The ANOVA (one-way) test statistics results also showed that the removal of CIP via sorption ($P = 0.073$, $\alpha = 0.05$, $F = 4.72$) and volatilization ($P = 0.078$, $\alpha = 0.05$, $F = 4.50$) were not significant in the anaerobic reactor. The adsorbed masses of CIP to the anaerobic sludge was measured between 72.62 μg and 106.95 μg corresponding to the adsorption removal percentages between 5.56% and

8.20% as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic reactor (Table 6.28). Although there was an increase in the CIP adsorption yields at increasing SRTs, this increase was not found to be significant according to the ANOVA (one-way) test statistics results ($P = 0.050$, $\alpha = 0.05$, $F = 5.98$). As a result, adsorption has not a significant contribution to the removal of CIP in the anaerobic reactor at all SRTs due to the hydrophilic structure of CIP (high water solubility = $1.148 \times 10^4 \text{ g L}^{-1}$, low $\log K_{OW} = 0.28$ and low Henry's Law constant = $5.09 \times 10^{-19} \text{ atm m}^3 \text{ mol}^{-1}$). Yang et al. (2018b) found 75.1% and 18.3% of CIP removals via biodegradation and adsorption, respectively suggesting that the biodegradation played a key role for the CIP removal in serum bottles having a total volume of 60 mL operating under anaerobic conditions for 50 mg L^{-1} initial CIP concentration in the presence of $20 \text{ mM Fe}_3\text{O}_4$ nanoparticles with 1200 mg L^{-1} MLVSS concentration at 30°C and at a pH of 7.00 from sewage wastewater (Yang et al., 2018b).

6.1.19.4.3 Removed Masses and Removal Efficiencies of CIP in Aerobic Reactor.

In the aerobic reactor, the biodegraded CIP masses increased from $435.15 \text{ }\mu\text{g}$ to $450.60 \text{ }\mu\text{g}$ resulting an increase in the CIP removal percentages from 59.10% to 86.32% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.28). The maximum biodegradation yield of CIP was obtained as 86.32% at 55 days SRT in the aerobic reactor (Table 6.28). The COD (influent concentration of 950.00 mg L^{-1}) and sCOD (influent concentration of 850.00 mg L^{-1}) served as the direct growth substrates, therefore, the co-metabolic biodegradation of CIP was occurred during aerobic treatment since the influent concentration of CIP as $522.00 \text{ }\mu\text{g L}^{-1}$ was too low to serve as a direct growth substrate (Table 5.1). The removal of CIP via biodegradation was found to be significant according to the ANOVA (one-way) test statistic results at all SRTs in the aerobic reactor ($P = 0.017$, $\alpha = 0.05$, $F = 10.72$). High water solubility ($1.148 \times 10^4 \text{ g L}^{-1}$), high hydrophilicity ($\log K_{OW} = 0.28$) and low Henry's Law constant ($5.09 \times 10^{-19} \text{ atm m}^3 \text{ mol}^{-1}$) makes CIP quite hydrophilic in the aerobic reactor and the biodegradation has an important contribution on the removal of CIP at all SRTs. The sorbed masses ($1.60 - 2.93 \text{ }\mu\text{g}$) and sorption removal efficiencies ($0.22\% - 0.56\%$) were low for CIP at all SRTs in the aerobic

reactor (Table 6.28). The volatilization masses and volatilization removal efficiencies were measured as zero for PBEB at all SRTs in the aerobic reactor (Table 6.28). The ANOVA (one-way) test statistics results showed that removal of CIP via sorption ($P = 0.098$, $\alpha = 0.05$, $F = 3.83$) and volatilization ($P = 0.101$, $\alpha = 0.05$, $F = 3.75$) were insignificant in the aerobic reactor. The adsorbed CIP masses to the aerobic sludge increased from 12.56 μg to 22.40 μg as the SRTs were increased from 5 days to 55 days, respectively (Table 6.28). This attributed to the CIP adsorption yields from 1.71% to 4.29% at 5 days and 55 days SRTs, respectively in the aerobic reactor (Table 6.28). However, the ANOVA (one-way) test statistics results showed that the removal of CIP via adsorption was not significant in the aerobic reactor ($P = 0.465$, $\alpha = 0.05$, $F = 0.61$). Low hydrophobicity or high hydrophilicity (high water solubility = $1.148 \times 10^4 \text{ g L}^{-1}$ and $\log K_{\text{OW}} = 0.28$) prevents CIP to be adsorbed on the aerobic sludge surface.

Removal of CIP via biodegradation was higher in the aerobic reactor (86.32%) than the anaerobic reactor (50.00%) at 55 days of SRT due to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.28). The aerobic conditions are more energetically favorable and predominant for co-metabolic biodegradation than under anaerobic conditions (Kumwimba & Meng, 2019). Removal of CIP via adsorption was higher in the anaerobic reactor (8.20%) than the aerobic reactor (4.29%) at 55 days SRT (Table 6.28). CIP found more sludge surface to be adsorbed in the anaerobic reactor than the aerobic reactor because the anaerobic reactor had much more MLVSS concentration (27600 mg L^{-1}) than the aerobic reactor (3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.19.4.4 Removed Masses and Removal Efficiencies of CIP in Anaerobic/Aerobic Sequential Biological Reactor System. The total biodegraded masses of CIP increased from 1671.38 μg to 2188.32 μg resulting in the CIP yields from 71.15% to 93.16% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.28). The maximum biodegradation yield of CIP was obtained as 93.16% at the maximum SRT of 55 days in the anaerobic/aerobic sequential biological reactor

system (Table 6.28). The ANOVA (one-way) test statistic results showed that the relationship between CIP biodegradation yields and SRTs was found to be significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.005$, $\alpha = 0.05$, $F = 18.00$). The sorbed masses ($6.37 - 15.60 \mu\text{g}$) and sorption removal efficiencies ($0.27\% - 0.66\%$) were low for CIP at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.28). The volatilized masses and volatilization removal percentages were measured as zero for CIP at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.28). The ANOVA (one-way) test statistics results showed that the removal of CIP via sorption ($P = 0.082$, $\alpha = 0.05$, $F = 4.37$) and volatilization ($P = 0.085$, $\alpha = 0.05$, $F = 4.24$) were negligible at all SRTs in the anaerobic/aerobic sequential biological reactor system. The total adsorbed CIP masses to the anaerobic (from $72.62 \mu\text{g}$ to $106.95 \mu\text{g}$) and aerobic (from $12.56 \mu\text{g}$ to $22.40 \mu\text{g}$) sludge increased from $85.18 \mu\text{g}$ to $129.35 \mu\text{g}$ as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.28). The increase in the adsorbed masses of CIP also increased the adsorption yields from 3.63% to 5.51% from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.28). The hydrophilic structure of CIP like high water solubility ($1.148 \times 10^4 \text{ g L}^{-1}$) and low octanol/water partition coefficient ($\log K_{OW} = 0.28$) makes the CIP hardly removed via adsorption but easily removed via biodegradation. Consequently, the ANOVA (one-way) test statistics results showed that the removal of CIP via adsorption was not significant in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.055$, $\alpha = 0.05$, $F = 5.66$).

CIP is a hydrophilic micropollutant due to its high water solubility ($1.148 \times 10^4 \text{ g L}^{-1}$), low octanol/water partition coefficient ($\log K_{OW} = 0.28$) and low Henry's Law constant ($5.09 \times 10^{-19} \text{ atm m}^3 \text{ mol}^{-1}$). These physicochemical properties makes CIP easily biodegraded and as a result, biodegradation plays an important role for its removal in the anaerobic/aerobic sequential biological reactor system. Therefore, it can be concluded that the removal of CIP with biodegradation is major (93.16%), adsorption is low (5.51%), sorption is minor (0.66%) and volatilization is negligible (0.00%) at 55 days SRT (Figure 6.18). Qarni et al. (2016) found higher than 90% of

CIP removal efficiency and indicated that its removal was as a result of biodegradation more than adsorption in a hospital wastewater treatment plant using tertiary treatment process for an initial CIP concentration of 5600 ng L⁻¹ under a high ambient temperature (>26 °C) and normal pH (7-8) conditions (Qarni et al., 2016).

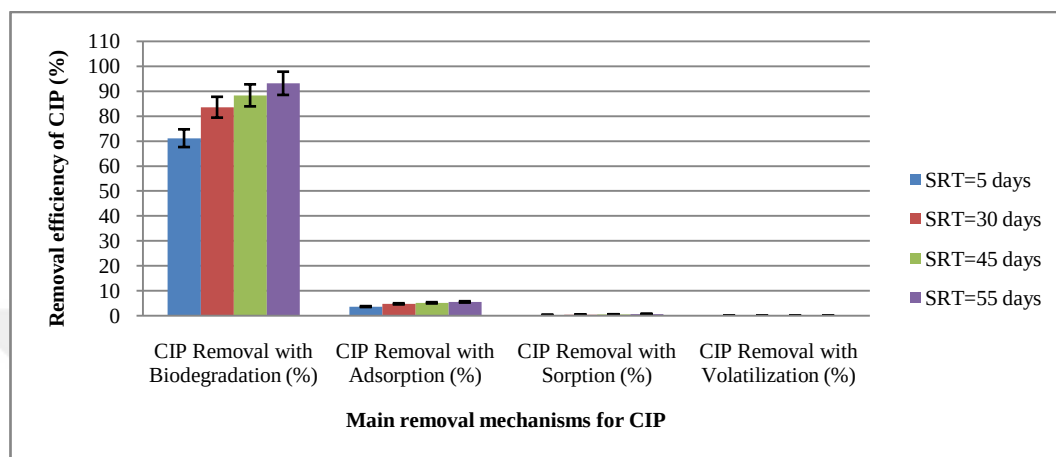


Figure 6.18 The removal efficiencies of CIP with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.20 Total *N*-Nitrosodimethylamine (NDMA) Removals

6.1.20.1 Total NDMA Removals in Anaerobic Biological Reactor

The maximum NDMA removal efficiency of the anaerobic reactor was obtained as 44.4% with a NDMA effluent of 91.75 ng L⁻¹ at a NDMA influent of 165.00 ng L⁻¹ at 5 days SRT (Table 6.29). At 30 days SRT, the maximum NDMA removal efficiency was calculated as 57.5% with a NDMA effluent of 70.21 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic reactor (Table 6.29). When the SRT was increased to 45 days, the maximum NDMA removal efficiency was found as 60.7% with a NDMA effluent of 64.84 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic reactor (Table 6.29). At the end of the study, when the SRT was increased to 55 days, the maximum NDMA removal efficiency was determined as 64.8% with a NDMA effluent of 58.02 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic reactor (Table 6.29).

Table 6.29 NDMA and its metabolite Dimethylamine (DMA) concentrations and total removal efficiencies in the effluents of the continuous operated anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 5, 30, 45 and 55 days SRTs ($n=3$, mean $\pm$ SD)

SRT (day)	Anaerobic Reactor							Aerobic Reactor						
	Influent NDMA (ng L ⁻¹)	Effluent NDMA (ng L ⁻¹)	metabolite of NDMA namely DMA			Removed NDMA (ng L ⁻¹)	NDMA Rem. Eff. (%)	Influent NDMA (ng L ⁻¹)	Effluent NDMA (ng L ⁻¹)	metabolite of NDMA namely DMA			Removed NDMA (ng L ⁻¹)	NDMA Rem. Eff. (%)
			Influent DMA (ng L ⁻¹)	Effluent DMA (ng L ⁻¹)	DMA Rem. Eff. (%)					Influent DMA (ng L ⁻¹)	Effluent DMA (ng L ⁻¹)	DMA Rem. Eff. (%)		
5	165.00 $\pm$ 0.02	91.75 $\pm$ 0.02	0.00 $\pm$ 0.02	16.61 $\pm$ 0.02	0.00 $\pm$ 0.5	73.25 $\pm$ 0.02	44.4 $\pm$ 0.5	91.75 $\pm$ 0.02	40.55 $\pm$ 0.02	16.61 $\pm$ 0.02	1.70 $\pm$ 0.02	89.8 $\pm$ 0.5	51.20 $\pm$ 0.02	55.8 $\pm$ 0.5
30	165.00 $\pm$ 0.02	70.21 $\pm$ 0.02	0.00 $\pm$ 0.02	11.57 $\pm$ 0.02	0.00 $\pm$ 0.5	94.80 $\pm$ 0.02	57.5 $\pm$ 0.5	70.21 $\pm$ 0.02	18.96 $\pm$ 0.02	11.57 $\pm$ 0.02	0.52 $\pm$ 0.02	95.5 $\pm$ 0.5	51.25 $\pm$ 0.02	73.0 $\pm$ 0.5
45	165.00 $\pm$ 0.02	64.84 $\pm$ 0.02	0.00 $\pm$ 0.02	8.03 $\pm$ 0.02	0.00 $\pm$ 0.5	100.17 $\pm$ 0.02	60.7 $\pm$ 0.5	64.84 $\pm$ 0.02	13.08 $\pm$ 0.02	8.03 $\pm$ 0.02	0.16 $\pm$ 0.02	98.0 $\pm$ 0.5	51.75 $\pm$ 0.02	79.8 $\pm$ 0.5
55	165.00 $\pm$ 0.02	58.02 $\pm$ 0.02	0.00 $\pm$ 0.02	5.10 $\pm$ 0.02	0.00 $\pm$ 0.5	106.98 $\pm$ 0.02	64.8 $\pm$ 0.5	58.02 $\pm$ 0.02	5.90 $\pm$ 0.02	5.10 $\pm$ 0.02	0.00 $\pm$ 0.02	100.0 $\pm$ 0.5	52.12 $\pm$ 0.02	89.8 $\pm$ 0.5

SRT (day)	Anaerobic/Aerobic Sequential Biological Reactor System						
	Influent NDMA (ng L ⁻¹)	Effluent NDMA (ng L ⁻¹)	metabolite of NDMA namely DMA			Removed NDMA (ng L ⁻¹)	NDMA Rem. Eff. (%)
			Influent DMA (ng L ⁻¹)	Effluent DMA (ng L ⁻¹)	DMA Rem. Eff. (%)		
5	165.00 $\pm$ 0.02	40.55 $\pm$ 0.02	16.61 $\pm$ 0.02	1.70 $\pm$ 0.02	89.8 $\pm$ 0.5	124.45 $\pm$ 0.02	75.4 $\pm$ 0.5
30	165.00 $\pm$ 0.02	18.96 $\pm$ 0.02	11.57 $\pm$ 0.02	0.52 $\pm$ 0.02	95.5 $\pm$ 0.5	146.04 $\pm$ 0.02	88.5 $\pm$ 0.5
45	165.00 $\pm$ 0.02	13.08 $\pm$ 0.02	8.03 $\pm$ 0.02	0.16 $\pm$ 0.02	98.0 $\pm$ 0.5	151.92 $\pm$ 0.02	92.1 $\pm$ 0.5
55	165.00 $\pm$ 0.02	5.90 $\pm$ 0.02	5.10 $\pm$ 0.02	0.00 $\pm$ 0.02	100.0 $\pm$ 0.5	159.10 $\pm$ 0.02	96.4 $\pm$ 0.5

The NDMA removal efficiencies were obtained as 44.4% and 64.8% at 5 days and 55 days SRTs, respectively in the anaerobic reactor (Table 6.29). The increase in SRTs also increased the NDMA removal efficiencies and the ANOVA (one-way) statistical analysis results showed that the increase in NDMA yields at increasing SRTs was found to be significant in the anaerobic reactor ($P = 0.00002$, $\alpha = 0.05$, $F = 148.19$) due to the hydrophilic structure of NDMA (high water solubility = $4.104 \times 10^5 \text{ g L}^{-1}$ and low octanol/water partition coefficient $\log K_{OW} = -0.57$).

In the effluents of the anaerobic reactor, Dimethylamine (DMA) which is the main metabolite of NDMA was monitored at all SRTs. DMA was considered as a quite hydrophilic micropollutant with its high water solubility ($1 \times 10^3 \text{ g L}^{-1}$) and quite low $\log K_{OW}$ (-0.17) values. The effluent concentrations of DMA were found as 16.61, 11.57, 8.03 and 5.10 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively, in the anaerobic reactor (Table 6.29).

6.1.20.2 Total NDMA Removals in Aerobic Biological Reactor

The maximum NDMA removal efficiency of the aerobic biological reactor was obtained as 55.8% with a NDMA effluent of 40.55 ng L^{-1} at a NDMA influent of 91.75 ng L^{-1} during 5 days of SRT operation (Table 6.29). At 30 days SRT, the maximum NDMA removal efficiency reached to 73.0% with a NDMA effluent of 18.96 ng L^{-1} for a NDMA influent of 70.21 ng L^{-1} in the aerobic reactor (Table 6.29). When the SRT was increased to 45 days, the maximum NDMA removal efficiency was found as 79.8% with a NDMA effluent of 13.08 ng L^{-1} for a NDMA influent of 64.84 ng L^{-1} in the aerobic reactor (Table 6.29). At 55 days SRT, the maximum NDMA removal efficiency was determined as 89.8% with a NDMA effluent of 5.90 ng L^{-1} for a NDMA influent of 58.02 ng L^{-1} in the aerobic reactor (Table 6.29).

Total removal of NDMA was higher in the aerobic reactor (89.8%) than the anaerobic reactor (64.8%) at 55 days of SRT (Table 6.29). This could be attributed to the aerobic treatment provides improvement in the NDMA removal because the aerobic bacteria have higher growth yields than anaerobic ones and acts as a post-

treatment step after anaerobic treatment in this study. Because of its highly hydrophilic structure (high water solubility = $4.104 \times 10^5 \text{ g L}^{-1}$ and low $\log K_{OW} = -0.57$), NDMA can be easily treated by anaerobic and aerobic microorganisms (Venkatesan, Pycke, & Halden, 2014).

When the SRT was increased from 5 days to 55 days an increase in the NDMA removal efficiencies was observed from 55.8% to 89.8%, respectively in the aerobic reactor (Table 6.29). The increase in NDMA removal efficiencies with increasing SRTs was found to be significant at all SRTs in the aerobic reactor according to the ANOVA (one-way) test statistics results ($P = 0.020$, $\alpha = 0.05$, $F = 9.85$).

The aerobic reactor received the DMA remaining from the anaerobic reactor and the influent concentrations of DMA were measured as 16.61, 11.57, 8.03 and 5.10 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.29). The effluent concentrations of DMA were determined as 1.70, 0.52, 0.16 and 0.00 ng L^{-1} at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.29). DMA removal efficiencies were found as 89.8%, 95.5%, 98.0% and 100.0% at 5, 30, 45 and 55 days SRTs, respectively in the aerobic reactor (Table 6.29). The results showed that as the SRT was increased from 5 days to 55 days, DMA removal efficiency increased from 89.8% to 100.0% in the aerobic reactor (Table 6.29). A linear correlation between DMA yields and SRTs was found for the aerobic reactor and this regression was significant ($R^2 = 0.99$, $P = 0.0014$, $\alpha = 0.05$, $F = 31.28$). The ANOVA (one-way) statistical analysis results showed that the DMA could be treated effectively in the aerobic reactor at all SRTs. The obtained biodegradation yield for DMA (100.0%) at 55 days SRT in this study was higher than the results previously obtained by other researchers. Wang et al. (2014) found 97% of DMA biodegradation yield in an anoxic (2 L) – aerobic (6 L) activated sludge system having a volume of 8 L for an influent DMA concentration of 10 ng L^{-1} at 8 h HRT, at 20 days SRT and at $23 \pm 2^\circ\text{C}$ with 3990 mg L^{-1} MLSS concentration (Wang et al., 2014).

6.1.20.3 Total NDMA Removals in Anaerobic/Aerobic Sequential Biological Reactor System

The NDMA removal efficiency of the anaerobic/aerobic sequential biological reactor system was measured as 75.4% with a NDMA effluent of 40.55 ng L⁻¹ at a NDMA influent of 165.00 ng L⁻¹ at 5 days SRT (Table 6.29). After 30 days of SRT operation, NDMA removal efficiency was determined as 88.5% with a NDMA effluent of 18.96 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic/aerobic sequential biological reactor system (Table 6.29). When the SRT was increased to 45 days, NDMA removal efficiency was calculated as 92.1% with a NDMA effluent of 13.08 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic/aerobic sequential biological reactor system (Table 6.29). At the highest SRT of 55 days, NDMA removal efficiency was found as 96.4% with a NDMA effluent of 5.90 ng L⁻¹ for a NDMA influent of 165.00 ng L⁻¹ in the anaerobic/aerobic sequential biological reactor system (Table 6.29).

The influent concentrations of DMA were determined as 16.61, 11.57, 8.03 and 5.10 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.29). The effluent concentrations of DMA were detected as 1.70, 0.52, 0.16 and 0.00 ng L⁻¹ at 5, 30, 45 and 55 days SRTs, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.29). In the anaerobic/aerobic sequential biological reactor system DMA removal efficiencies were obtained as 89.8%, 95.5%, 98.0% and 100.0% at 5, 30, 45 and 55 days SRTs, respectively (Table 6.29). The maximum DMA yield was calculated as 100.0% at the highest SRT of 55 days in the anaerobic/aerobic sequential biological reactor system (Table 6.29). It is important to note that the increasing SRT showed positive effect on the removal of DMA in the anaerobic/aerobic sequential biological reactor system.

6.1.20.4 Removal Mechanisms of NDMA in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The biodegradation, sorption, adsorption and volatilization tests were performed to investigate the main removal mechanisms of NDMA. The biodegraded, adsorbed, sorbed and volatilized NDMA masses and removal percentages were calculated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations (Table 6.30).



Table 6.30 The total removal percentages for NDMA throughout biodegradation, adsorption and volatilization for anaerobic, aerobic and anaerobic/aerobic sequential biological reactors during 5, 30, 45 and 55 days of SRT operations

ANAEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	183.13	0.271	12.21	0.022	1.00	0.234	0.000234	44.39	2.96	0.24	0.00006
30	236.99	0.368	16.54	0.053	2.37	0.287	0.000287	57.45	4.01	0.57	0.00007
45	250.41	0.406	18.26	0.061	2.73	0.300	0.000300	60.71	4.43	0.66	0.00007
55	267.45	0.427	19.20	0.066	2.97	0.390	0.000390	64.84	4.65	0.72	0.00009
AEROBIC REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	102.40	0.167	2.50	0.015	0.22	0.095	0.000095	55.80	1.36	0.12	0.00005
30	102.49	0.249	3.74	0.026	0.39	0.110	0.000110	72.99	2.66	0.28	0.00008
45	103.51	0.253	3.80	0.033	0.49	0.114	0.000114	79.82	2.93	0.38	0.00009
55	104.24	0.257	3.85	0.035	0.52	0.120	0.000120	89.83	3.32	0.45	0.00010
ANAEROBIC/AEROBIC SEQUENTIAL REACTOR											
SRT	Biodegraded mass	Eluate conc. ^a	Adsorbed mass	Eluate conc. ^b	Sorbed mass	PUF disc conc.	Volatilized mass	Bio-degradation	Adsorption	Sorption	Volatilization
(day)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(ng L ⁻¹)	(ng)	(%)	(%)	(%)	(%)
5	560.03	--	14.72	--	1.22	--	0.0003	75.42	1.98	0.16	0.00004
30	657.18	--	20.28	--	2.76	--	0.0004	88.51	2.73	0.37	0.00005
45	683.63	--	22.06	--	3.22	--	0.0004	92.07	2.97	0.43	0.00006
55	715.95	--	23.05	--	3.49	--	0.0005	96.42	3.10	0.47	0.00007

^a: Eluate prepared from sludge for adsorption experiments

^b: Eluate prepared from biomass for sorption experiments

6.1.20.4.1 *Removed Masses and Removal Efficiencies of NDMA.* An example for the calculations relevant to the removed masses and the removal efficiencies of NDMA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were given in Equations 6.283 to 6.306, respectively at a SRT of 5 days (Table 6.30).

The biodegraded masses of NDMA were calculated from Equations 6.284, 6.285 and 6.286 for the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.30).

$$M_{\text{BIO,Anaerobic}} = (73.25 \text{ ng L}^{-1}) \times (2.5 \text{ L}) = 183.13 \text{ ng} \quad (6.283)$$

$$M_{\text{BIO,Aerobic}} = (51.20 \text{ ng L}^{-1}) \times (2.0 \text{ L}) = 102.40 \text{ ng} \quad (6.284)$$

$$M_{\text{BIO,Sequential}} = (124.45 \text{ ng L}^{-1}) \times (4.5 \text{ L}) = 560.03 \text{ ng} \quad (6.285)$$

The biodegradation removal efficiencies for NDMA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were calculated according to the Equation 6.286, 6.287 and 6.288, respectively at 5 days SRT (Table 6.30).

$$\text{Bio}(\%),_{\text{Anaerobic}} = (183.13 \times 100) / (165.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 44.39\% \quad (6.286)$$

$$\text{Bio}(\%),_{\text{Aerobic}} = (102.40 \times 100) / (91.75 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 55.80\% \quad (6.287)$$

$$\text{Bio}(\%),_{\text{Sequential}} = (560.03 \times 100) / (165.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 75.42\% \quad (6.288)$$

The adsorbed masses of NDMA were calculated using Equation 6.289, 6.290 and 6.291 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.30).

$$M_{\text{ADS,Anaerobic}} = [(0.271 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 12.21 \text{ ng} \quad (6.289)$$

$$M_{\text{ADS,Aerobic}} = [(0.167 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 2.50 \text{ ng} \quad (6.290)$$

$$M_{\text{ADS,Sequential}} = 12.21 + 2.50 = 14.72 \text{ ng} \quad (6.291)$$

The total adsorption removal efficiencies of NDMA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.292, 6.293 and 6.294, respectively at 5 days SRT (Table 6.30).

$$\text{Adsorption (\%)}_{\text{Anaerobic}} = (12.21 \times 100) / (165.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 2.96\% \quad (6.292)$$

$$\text{Adsorption (\%)}_{\text{Aerobic}} = (2.50 \times 100) / (91.75 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 1.36\% \quad (6.293)$$

$$\text{Adsorption (\%)}_{\text{Sequential}} = (14.72 \times 100) / (165.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 1.98\% \quad (6.294)$$

The sorbed masses into the anaerobic and aerobic biological sludges of NDMA were calculated according to the Equation 6.295 and 6.296, respectively while the total sorbed mass for NDMA in the anaerobic/aerobic sequential biological reactor system was determined using Equation 6.297 at 5 days SRT (Table 6.30).

$$M_{\text{SORP,Anaerobic}} = [(0.022 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (450 \text{ g}) = 1.00 \text{ ng} \quad (6.295)$$

$$M_{\text{SORP,Aerobic}} = [(0.015 \text{ ng L}^{-1}) \times (1 \text{ L}) / (10 \text{ g})] \times (150 \text{ g}) = 0.22 \text{ ng} \quad (6.296)$$

$$M_{\text{SORP,Sequential}} = 1.00 + 0.22 = 1.22 \text{ ng} \quad (6.297)$$

The total sorption removal efficiencies of NDMA in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors were determined according to the Equation 6.298, 6.299 and 6.300, respectively at 5 days SRT (Table 6.30).

$$\text{Sorp(\%)}_{\text{Anaerobic}} = (1.00 \times 100) / (165.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.24\% \quad (6.298)$$

$$\text{Sorp(\%)}_{\text{Aerobic}} = (0.22 \times 100) / (91.75 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.12\% \quad (6.299)$$

$$\text{Sorp(\%)}_{\text{Sequential}} = (1.22 \times 100) / (165.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.16\% \quad (6.300)$$

Volatilized masses of NDMA were calculated according to the Equation 6.301, 6.302 and 6.303 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.30).

$$M_{\text{VOL,An}} = (0.234 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.000234 \text{ ng} \quad (6.301)$$

$$M_{VOL,Ae} = (0.095 \text{ ng L}^{-1}) \times (1.00 \text{ mL}) \times 10^{-3} (\text{L mL}^{-1}) = 0.000095 \text{ ng} \quad (6.302)$$

$$M_{VOL,Sequential} = 0.000234 + 0.000095 = 0.0003 \text{ ng} \quad (6.303)$$

The total volatilization removal efficiencies of NDMA were determined according to the Equation 6.304, 6.305 and 6.306 in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 5 days SRT (Table 6.30).

$$\text{Vol}(\%)_{\text{Anaerobic}} = (0.000234 \times 100) / (165.00 \text{ ng L}^{-1} \times 2.5 \text{ L}) = 0.00006\% \quad (6.304)$$

$$\text{Vol}(\%)_{\text{Aerobic}} = (0.000095 \times 100) / (91.75 \text{ ng L}^{-1} \times 2.0 \text{ L}) = 0.00005\% \quad (6.305)$$

$$\text{Vol}(\%)_{\text{Sequential}} = (0.0003 \times 100) / (165.00 \text{ ng L}^{-1} \times 4.5 \text{ L}) = 0.00004\% \quad (6.306)$$

6.1.20.4.2 Removed Masses and Removal Efficiencies of NDMA in Anaerobic Reactor. The biodegraded NDMA masses increased from 183.13 ng to 267.45 ng as the SRTs were increased from 5 up to 55 days, respectively in the anaerobic reactor (Table 6.30). The biodegradation percentages of NDMA also increased from 44.39% to 64.84% with the increasing of SRTs from 5 days up to 55 days, respectively in the anaerobic reactor (Table 6.30). The anaerobic bacteria could co-metabolized 64.84% of NDMA using COD and sCOD as the direct growth substrates at the highest SRT of 55 days in the anaerobic reactor (Table 6.30). The NDMA was removed via co-metabolic biodegradation due to the influent NDMA concentration was too low (165.00 ng L^{-1}) but the influent COD (950.00 mg L^{-1}) and sCOD (850.00 mg L^{-1}) concentrations were enough to serve as direct growth substrates in the anaerobic reactor (Table 5.1). The main biodegradation pathway of NDMA was followed the degradation order of NDMA to DMA and to N_2 under anaerobic conditions (Friedrich, Shapley, & Strathmann, 2008). The presence of strong electron donating functional groups (with two methyl functional groups) in the molecular structure of NDMA makes the anaerobic biodegradation of NDMA possible as mentioned by Wijekoon et al. (2013). The anaerobic biodegradation had a strong effect on the removal of NDMA due to being a quite hydrophilic micropollutant (high water solubility = $4.104 \times 10^5 \text{ g L}^{-1}$ and low $\log K_{OW} = -0.57$) (Sipma et al., 2010). The ANOVA (one-way) test statistics results confirmed that the biodegradation of

NDMA in the anaerobic reactor was significant at all SRTs ($P = 1.87 \times 10^{-5}$, $\alpha = 0.05$, $F = 148.19$). The sorbed masses (1.00 – 2.97 ng) and volatilized masses (0.000234 – 0.000390 ng) were low for NDMA at all SRTs in the anaerobic reactor (Table 6.30). The sorption and volatilization removal percentages also were low (between 0.24% and 0.72% for sorption and between 0.00006% and 0.00009% for volatilization, respectively) for NDMA in the anaerobic reactor (Table 6.30). The ANOVA (one-way) test statistics results showed that removal of NDMA via sorption ($P = 0.210$, $\alpha = 0.05$, $F = 1.97$) and volatilization ($P = 0.144$, $\alpha = 0.05$, $F = 2.83$) were not significant in the anaerobic reactor. The adsorbed masses of NDMA to the anaerobic sludge were measured between 12.21 ng and 19.20 ng at 5 days and 55 days SRTs, respectively (Table 6.30). The adsorbed NDMA percentages increased from 2.96% to 4.65% as the SRTs were increased from 5 to 55 days, respectively in the anaerobic reactor (Table 6.30). However, the ANOVA (one-way) test statistics results showed that the relationship between NDMA adsorption yields and increasing SRTs was not significant in the anaerobic reactor ($P = 0.089$, $\alpha = 0.05$, $F = 4.11$). NDMA shows hydrophilic properties such as high water solubility ($4.104 \times 10^5 \text{ g L}^{-1}$), low octanol/water partition coefficient ($\log K_{OW} = -0.57$) and low Henry's Law constant ($2.06 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$). Based on its hydrophilic properties, although NDMA was adsorbed with low yields (4.65%) however it was biodegraded with high yields (64.84%) in the anaerobic reactor at 55 days SRT (Table 6.30).

6.1.20.4.3 Removed Masses and Removal Efficiencies of NDMA in Aerobic Reactor. In the aerobic reactor, the biodegraded NDMA masses increased from 102.40 ng to 104.24 ng resulting in the NDMA biodegradation removal percentages of 55.80% and 89.83% depending on the SRT increase from 5 days to 55 days, respectively (Table 6.30). The maximum biodegradation yield of NDMA was obtained as 89.83% at 55 days SRT in the aerobic reactor (Table 6.30). NDMA is highly miscible in water ($4.104 \times 10^5 \text{ g L}^{-1}$) and it is not expected to sorb onto sludge because of its high hydrophilicity ($\log K_{OW} = -0.57$), therefore, it could be easily treated by aerobic microorganisms (Venkatesan et al., 2014). The ANOVA (one-way) test statistic results supported that the removal of NDMA via biodegradation was significant in the aerobic reactor at all SRTs ($P = 0.020$, $\alpha = 0.05$, $F = 9.85$). The

sorbed masses (0.22 – 0.52 ng) and volatilized masses (0.000095 – 0.000120 ng) were low for NDMA in the aerobic reactor at all SRTs (Table 6.30). Depending on the calculated masses, the NDMA removal percentages were found low for sorption (0.12% – 0.45%) and volatilization (0.00005% – 0.00010%) in the aerobic reactor at all SRTs (Table 6.30). The ANOVA (one-way) test statistics results showed that the removal of NDMA via sorption ($P = 0.183$, $\alpha = 0.05$, $F = 2.26$) and volatilization ($P = 0.192$, $\alpha = 0.05$, $F = 2.16$) were negligible in the aerobic reactor. The adsorbed NDMA masses to the aerobic sludge increased from 2.50 ng to 3.85 ng as the SRTs were increased from 5 days to 55 days, respectively (Table 6.30). This attributed to the NDMA adsorption yields of 1.36% and 3.32% at 5 days and 55 days SRT, respectively in the aerobic reactor (Table 6.30). The ANOVA (one-way) test statistics results showed that the removal of NDMA via adsorption was not important statistically in the aerobic reactor at all SRTs ($P = 0.932$, $\alpha = 0.05$, $F = 0.01$). NDMA is considered to be not readily adsorbed onto the aerobic sludge (3.32%) but highly biodegradable (89.83%) in the aerobic reactor at 55 days SRT due to its physicochemical properties such as high water solubility ($4.104 \times 10^5 \text{ g L}^{-1}$), high hydrophilicity ($\log K_{OW} = -0.57$) and low Henry's Law constant ($2.06 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$).

Removal of NDMA via biodegradation was higher in the aerobic reactor (89.83%) than the anaerobic reactor (64.84%) at 55 days of SRT owing to the aerobic bacteria have higher growth yields compared to the anaerobic bacteria (Table 6.30). Also, the aerobic conditions are accepted as more energetically favorable and predominant for the co-metabolic biodegradation than under anaerobic conditions (Kumwimba & Meng, 2019). Removal of NDMA via adsorption was higher in the anaerobic reactor (4.65%) than the aerobic reactor (3.32%) at 55 days SRT (Table 6.30) because NDMA found more sludge surfaces to be adsorbed in the anaerobic reactor (MLVSS = 27600 mg L^{-1}) than the aerobic reactor (MLVSS = 3984 mg L^{-1}) at 55 days SRT (Table 6.1).

6.1.20.4.4 *Removed Masses and Removal Efficiencies of NDMA in Anaerobic/Aerobic Sequential Biological Reactor System.* It can be said that the total biodegraded masses of NDMA increased from 560.03 ng to 715.95 ng resulting in the NDMA removal percentages of 75.42% and 96.42% depending on the SRT increase from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.30). The maximum biodegradation yield of NDMA was achieved as 96.42% at 55 days SRT (Table 6.30). The biodegradation of NDMA was found to be significant according to the ANOVA (one-way) test statistics in the anaerobic/aerobic sequential biological reactor system at all SRTs ($P = 0.004$, $\alpha = 0.05$, $F = 21.30$). The sorbed masses (1.22 – 3.49 ng) and volatilized masses (0.0003 – 0.0005 ng) were low for NDMA at all SRTs in the anaerobic/aerobic sequential biological reactor system (Table 6.30). The NDMA removal percentages also were low for sorption (0.16% – 0.47%) and volatilization (0.00004% – 0.00007%) in the anaerobic/aerobic sequential biological reactor system at all SRTs (Table 6.30). The ANOVA (one-way) test statistics results confirmed that the removal of NDMA via sorption ($P = 0.114$, $\alpha = 0.05$, $F = 3.42$) and volatilization ($P = 0.118$, $\alpha = 0.05$, $F = 3.33$) were not meaningful statistically in the anaerobic/aerobic sequential biological reactor system. The total adsorbed NDMA masses to the anaerobic (from 12.21 ng to 19.20 ng) and aerobic (from 2.50 ng to 3.85 ng) sludge increased from 14.72 ng to 23.05 ng as the SRTs were increased from 5 days to 55 days, respectively in the anaerobic/aerobic sequential biological reactor system (Table 6.30). The NDMA adsorption yields were calculated between 1.98% and 3.10% at 5 days and 55 days SRTs, respectively (Table 6.30). The relationship between NDMA adsorption yields and SRTs was not found to be important statistically according to the ANOVA (one-way) test statistics results in the anaerobic/aerobic sequential biological reactor system ($P = 0.785$, $\alpha = 0.05$, $F = 0.08$). It can be concluded that the adsorption has not a significant contribution to the removal of NDMA in the anaerobic/aerobic sequential biological reactor system at all SRTs because NDMA was a quite hydrophilic micropollutant with its physicochemical properties (high water solubility = $4.104 \times 10^5 \text{ g L}^{-1}$, low $\log K_{OW} = -0.57$ and low Henry's Law constant = $1.52 \times 10^{-7} \text{ atm m}^3 \text{ mol}^{-1}$).

Since NDMA is highly miscible in water ($4.104 \times 10^5 \text{ g L}^{-1}$), has a quite low octanol/water partition coefficient ($\log K_{OW} = -0.57$) and has a low volatility (Henry's Law constant = $1.52 \times 10^{-7} \text{ atm m}^3 \text{ mol}^{-1}$), it is not likely to adsorbed onto particles (sludge/soil/sediment) or volatilized to any significant level (WHO, 2002). In this study, we found that the biodegradation (96.42%) was the main removal mechanism of NDMA at 55 days SRT (Figure 6.19). Therefore, it can be concluded that the removal of NDMA via biodegradation is major (96.42%), adsorption is low (3.10%), sorption is minor (0.47%) and volatilization is negligible (0.00007%) at the highest SRT of 55 days (Figure 6.19).

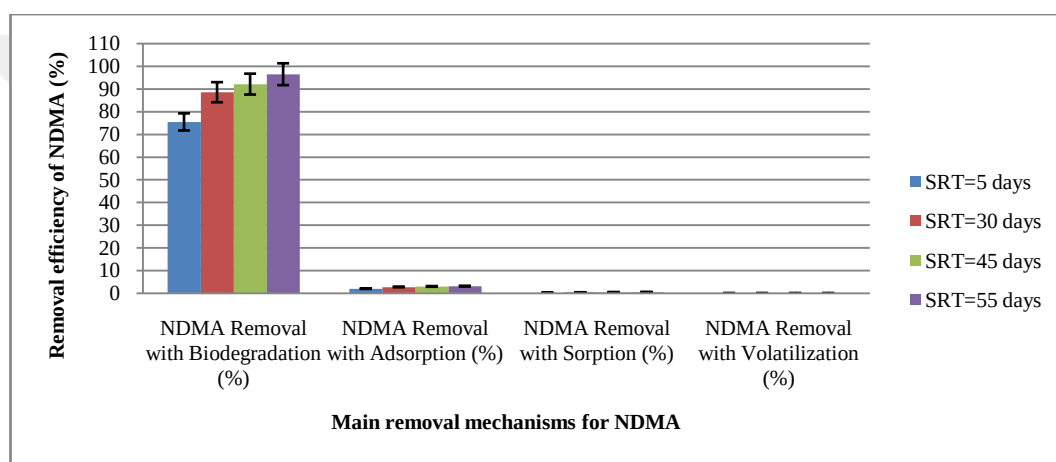


Figure 6.19 The removal efficiencies of NDMA with biodegradation, adsorption, sorption and volatilization during 5, 30, 45 and 55 days of SRT operations in the anaerobic/aerobic sequential biological reactor system

6.1.21 Comparison of Main Removal Mechanisms of All Studied Micropollutants in Anaerobic, Aerobic and Anaerobic/Aerobic Sequential Biological Reactors

In this study, biodegradation, adsorption, sorption and volatilization removal mechanisms of brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) micropollutants were investigated in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors. The sorption and volatilization had no any considerable effect on the removals of all studied micropollutants at 5, 30, 45 and 55 days SRTs.

The main removal mechanism of brominated micropollutants namely α -HBCDD, PBEB, PBT and TBBPA were adsorption on the anaerobic sludge with yields of 86.09%, 85.56%, 85.19% and 84.71%, respectively in the anaerobic reactor at 55 days SRT (Table 6.31). α -HBCDD, PBEB, PBT and TBBPA were removed with adsorption yields of 79.91%, 79.16%, 78.71% and 77.24%, respectively in the aerobic reactor at 55 days SRT and it can be concluded that the main removal mechanism was adsorption in the aerobic reactor for these brominated micropollutants (Table 6.31). The main removal mechanism of α -HBCDD, PBEB, PBT and TBBPA were also found adsorption in the whole reactor system and adsorption yields of α -HBCDD, PBEB, PBT and TBBPA were calculated as 80.87%, 80.05%, 79.56% 78.56%, respectively in the anaerobic/aerobic sequential biological reactor system at 55 days SRT (Table 6.31).

Table 6.31 The biodegradation, adsorption, sorption and volatilization removal efficiencies of all studied micropollutants in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactor system at 55 days SRT

Micro-pollutant	Anerobic Reactor				Aerobic Reactor				Anaerobic/Aerobic Sequential Biological Reactor System			
	Bio-degradation (%)	Adsorption (%)	Sorption (%)	Volatilization (%)	Bio-degradation (%)	Adsorption (%)	Sorption (%)	Volatilization (%)	Bio-degradation (%)	Adsorption (%)	Sorption (%)	Volatilization (%)
α -HBCDD	6.96±0.5	86.09±0.5	1.04±0.1	0.00009±0.00005	12.15±0.5	79.91±0.5	0.93±0.1	0.00011±0.00005	18.26±0.5	80.87±0.5	0.97±0.1	0.00009±0.00005
PBEB	7.56±0.5	85.56±0.5	0.94±0.1	0.00000±0.00005	12.43±0.5	79.16±0.5	0.89±0.1	0.00000±0.00005	19.05±0.5	80.05±0.5	0.89±0.1	0.00000±0.00005
PBT	7.88±0.5	85.19±0.5	0.99±0.1	0.00000±0.00005	12.69±0.5	78.71±0.5	0.89±0.1	0.00000±0.00005	19.57±0.5	79.56±0.5	0.91±0.1	0.00000±0.00005
TBBPA	8.24±0.5	84.71±0.5	0.99±0.1	0.00011±0.00005	13.46±0.5	77.24±0.5	0.91±0.1	0.00011±0.00005	20.59±0.5	78.56±0.5	0.92±0.1	0.00010±0.00005
AHTN	11.09±0.5	80.90±0.5	1.20±0.1	0.00026±0.00005	14.97±0.5	74.73±0.5	1.14±0.1	0.00020±0.00005	24.40±0.5	74.48±0.5	1.12±0.1	0.00022±0.00005
PFOA	12.03±0.5	78.64±0.5	1.13±0.1	0.00031±0.00005	18.12±0.5	70.00±0.5	1.06±0.1	0.00032±0.00005	27.96±0.5	71.06±0.5	1.04±0.1	0.00030±0.00005
PFOS	16.39±0.5	58.11±0.5	1.09±0.1	0.00027±0.00005	37.01±0.5	52.26±0.5	1.06±0.1	0.00029±0.00005	47.33±0.5	51.70±0.5	1.00±0.1	0.00026±0.00005
GFZ	14.52±0.5	75.01±0.5	1.25±0.1	0.00007±0.00005	20.08±0.5	67.11±0.5	1.19±0.1	0.00008±0.00005	31.69±0.5	67.17±0.5	1.14±0.1	0.00007±0.00005
TCS	14.27±0.5	74.87±0.5	1.23±0.1	0.00005±0.00005	20.41±0.5	66.95±0.5	1.17±0.1	0.00005±0.00005	31.77±0.5	67.11±0.5	1.13±0.1	0.00005±0.00005
IBU	45.51±0.5	15.29±0.5	1.08±0.1	0.00008±0.00005	77.89±0.5	10.23±0.5	1.04±0.1	0.00009±0.00005	87.95±0.5	10.98±0.5	0.85±0.1	0.00007±0.00005
CIP	50.00±0.5	8.20±0.5	0.97±0.1	0.00000±0.00005	86.32±0.5	4.29±0.5	0.56±0.1	0.00000±0.00005	93.16±0.5	5.51±0.5	0.66±0.1	0.00000±0.00005
NDMA	64.84±0.5	4.65±0.5	0.72±0.1	0.00009±0.00005	89.83±0.5	3.32±0.5	0.45±0.1	0.00010±0.00005	96.42±0.5	3.10±0.5	0.47±0.1	0.00007±0.00005

The main removal mechanism was adsorption for all brominated micropollutants (α -HBCDD, PBEB, PBT and TBBPA) in all reactors at 55 days SRT because of being hydrophobic micropollutants with low water solubilities, high log K_{OW} values and low Henry's Law constants. The most adsorbed brominated micropollutant was α -HBCDD with adsorption yields of 86.09%, 79.91% and 80.87% in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT because it was the most hydrophobic one due to its physicochemical properties (high log K_{OW} = 7.74, low water solubility = 2.089×10^{-5} g L⁻¹, low Henry's Law constant = 1.72×10^{-6} atm m³ mol⁻¹).

α -HBCDD, PBEB, PBT and TBBPA were biodegraded with yields of 6.96%, 7.56%, 7.88% and 8.24%, respectively in the anaerobic reactor at 55 days SRT (Table 6.31). α -HBCDD, PBEB, PBT and TBBPA biodegradation yields were detected as 12.15%, 12.43%, 12.69% and 13.46%, respectively in the aerobic reactor at 55 days SRT (Table 6.31). In the anaerobic/aerobic sequential biological reactor system, α -HBCDD, PBEB, PBT and TBBPA were biodegraded with yields of 18.26%, 19.05%, 19.57% and 20.59%, respectively at 55 days SRT (Table 6.31).

α -HBCDD, PBEB, PBT and TBBPA could be partially biodegraded due to their hydrophobic properties (high octanol/water partition coefficients, low water solubilities and low Henry's Law constants) in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors at 55 days SRT.

The most biodegraded brominated micropollutant was TBBPA with higher biodegradation yields of 8.24%, 13.46% and 20.59% in the comparison with the other brominated micropollutants in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT because it has lower hydrophobicity (log K_{OW} = 5.90) than the other brominated micropollutants (log $K_{OW,\alpha\text{-HBCDD}}$ = 7.74, log $K_{OW,\text{PBEb}}$ = 7.48 and log $K_{OW,\text{PBT}}$ = 6.99).

The main removal mechanism of AHTN from the aromatic group was found to be adsorption with higher adsorption yields of 80.90%, 74.73% and 74.48% in the

anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT (Table 6.31) because of its physicochemical properties (low water solubility $=1.25 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 5.70$, and low Henry's Law constant $= 1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$). The biodegradation yields of AHTN were 11.09%, 14.97% and 24.40% in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT (Table 6.31). The biodegradation removal percentages were found low because AHTN was resistant to extensive biodegradation due to being a hydrophobic micropollutant (low water solubility $=1.25 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 5.70$, and low Henry's Law constant $= 1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$).

The main removal mechanisms of the fluoro micropollutants (PFOA and PFOS) were adsorption on the anaerobic sludge both for PFOA (78.64%) and PFOS (58.11%) in the anaerobic reactor at 55 days SRT (Table 6.31). PFOA and PFOS were mainly removed with adsorption onto the aerobic sludge with yields of 70.00% and 52.26%, respectively in the aerobic reactor at 55 days SRT (Table 6.31). In the anaerobic/aerobic sequential biological reactor system, PFOA and PFOS were removed mainly with adsorption with adsorption yields of 71.06% and 51.70%, respectively at 55 days SRT (Table 6.31). The main removal mechanism was adsorption both for PFOA ($\log K_{OW} = 4.81$) and PFOS ($\log K_{OW} = 4.49$) in all reactors at 55 days SRT because of being hydrophobic micropollutants with low water solubilities, high $\log K_{OW}$ values and low Henry's Law constants. The biodegradation yields of PFOA and PFOS were 12.03% and 16.39%, respectively in the anaerobic reactor at 55 days SRT (Table 6.31). PFOA and PFOS were biodegraded with yields of 18.12% and 37.01%, respectively in the aerobic reactor at 55 days SRT (Table 6.31). The biodegradation yields of PFOA and PFOS were calculated as 27.96% and 47.33%, respectively in the anaerobic/aerobic sequential biological reactor system at 55 days SRT (Table 6.31). PFOS has lower hydrophobicity ($\log K_{OW} = 4.49$) than PFOA ($\log K_{OW} = 4.81$), therefore, PFOS was more biodegraded than PFOA in all three reactors at 55 days SRT.

From the phenolic micropollutants, GFZ and TCS were removed mainly via adsorption with yields of 75.01% and 74.87%, respectively in the anaerobic reactor at 55 days SRT (Table 6.31). The main removal mechanisms were found adsorption both for GFZ (67.11%) and TCS (66.95%) in the aerobic reactor at 55 days SRT (Table 6.31). In the anaerobic/aerobic sequential biological reactor system, the main removal mechanisms were adsorption both for GFZ (67.17%) and TCS (67.11%) at 55 days SRT (Table 6.31). GFZ and TCS are quite hydrophobic micropollutants due to their low water solubilities, high octanol/water partition coefficients and low Henry's Law constants, therefore, the main removal mechanisms both for GFZ and TCS were adsorption in all reactors at 55 days SRT. The biodegradation yields of GFZ and TCS were obtained as 14.52% and 14.27%, respectively in the anaerobic reactor at 55 days SRT (Table 6.31). GFZ and TCS were biodegraded as 20.08% and 20.41%, respectively in the aerobic reactor at 55 days SRT (Table 6.31). GFZ and TCS were biodegraded with biodegradation yields of 31.69% and 31.77%, respectively in the anaerobic/aerobic sequential biological reactor system at 55 days SRT (Table 6.31). The biodegradation removal percentages of GFZ and TCS were found low because they were partly biodegraded in all reactors at 55 days SRT due to their hydrophobic structures.

Although IBU from the phenolic micropollutant group was a hydrophobic micropollutant owing to its physicochemical properties (low water solubility = 4.105×10^{-4} g L⁻¹, moderate high log K_{OW} = 3.79 and low Henry's Law constant = 1.52×10^{-7} atm m³ mol⁻¹), the main removal mechanism was biodegradation for IBU both in the anaerobic (45.51%) and aerobic (77.89%) reactors at 55 days SRT (Table 6.31). IBU is mainly dissolved in the aqueous phase due to its lower K_d value (pK_a = 4.91) if the wastewater has an average pH value at 7.50. IBU was more dissolved in the aerobic reactor (pH = 7.50 ± 0.50) than the anaerobic reactor (pH = 8.50 ± 0.50) in this study. For this reason, IBU was more biodegraded (77.89%) in the aerobic reactor than the anaerobic reactor (45.51%) at 55 days SRT (Table 6.31). As a result, the main removal mechanism was found biodegradation with a yield of 87.95% in the anaerobic/aerobic sequential biological reactor system at 55 days SRT (Table 6.31).

CIP from the phenolic micropollutants was removed mainly with the biodegradation and the biodegradation yields reached 50.00%, 86.32% and 93.16% in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT (Table 6.31). CIP is a quite hydrophilic micropollutant due to its physicochemical properties (high water solubility = 1.148×10^4 g L⁻¹, low log K_{OW} = 0.28 and low Henry's Law constant = 5.09×10^{-19} atm m³ mol⁻¹), therefore, the main removal mechanism was biodegradation in all reactors at 55 days SRT. The adsorption yields of CIP were 8.20%, 4.29% and 5.51% in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT (Table 6.31). The adsorption yields were found low because CIP did not tend to be adsorbed on anaerobic and aerobic sludges due to its hydrophilic structure such as high water solubility (1.148×10^4 g L⁻¹), low octanol/water partition coefficient (log K_{OW} = 0.28) and low Henry's Law constant (5.09×10^{-19} atm m³ mol⁻¹).

The most adsorbed phenolic micropollutant was GFZ with adsorption yields of 75.01%, 67.11% and 67.17% in the anaerobic, aerobic and anaerobic/aerobic sequential biological reactors, respectively at 55 days SRT (Table 6.31) because it has more hydrophobic properties (high log K_{OW} = 4.77, low water solubility = 4.964×10^{-3} g L⁻¹, low Henry's Law constant = 1.19×10^{-8} atm m³ mol⁻¹) than the other phenolic micropollutants. The most biodegraded phenolic micropollutant was CIP in the anaerobic (50.00%), aerobic (86.32%) and anaerobic/aerobic sequential biological reactors (93.16%), respectively at 55 days SRT because it was the most hydrophilic one (log K_{OW} = 0.28) in the comparison with the other phenolic micropollutants (log K_{OW,GFZ} = 4.77, log K_{OW,TCS} = 4.76 and log K_{OW,IBU} = 3.79).

NDMA in the nitroso group was removed mainly with biodegradation in the anaerobic (64.84%), aerobic (89.83%) and anaerobic/aerobic sequential biological reactors (96.42%) at 55 days SRT (Table 6.31). NDMA has physicochemical properties such as very high water solubility (4.104×10^5 g L⁻¹), quite low hydrophobicity (log K_{OW} = -0.57) and low Henry's Law constant (1.52×10^{-7} atm m³ mol⁻¹). Because of having a quite hydrophilic structure, the main removal mechanism was found to be biodegradation for NDMA in all reactors at 55 days SRT. NDMA

was removed with lower adsorption yields in the anaerobic (4.65%), aerobic (3.32%) and anaerobic/aerobic sequential biological reactors (3.10%) at 55 days SRT due to its quite low hydrophobic properties (Table 6.31).

NDMA was removed with the highest biodegradation yield (96.42%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.31) because it was the most hydrophilic one in all studied micropollutants (too high water solubility = $4.104 \times 10^5 \text{ g L}^{-1}$, quite low $\log K_{OW} = -0.57$ and low Henry's Law constant = $1.52 \times 10^{-7} \text{ atm m}^3 \text{ mol}^{-1}$). α -HBCDD was removed with the lowest biodegradation yield (18.26%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system (Table 6.31) due to its quite high hydrophobic structure (too low water solubility = $2.089 \times 10^{-5} \text{ g L}^{-1}$, quite high $\log K_{OW} = 7.74$ and low Henry's Law constant = $1.72 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$).

The highest adsorption yield was achieved for α -HBCDD (80.87%) at 55 days SRT in the anaerobic/aerobic sequential biological reactor system because α -HBCDD showed the highest hydrophobic properties in the comparison with the all studied micropollutants (Table 6.31). The lowest adsorption yield was obtained as 3.10% for NDMA at 55 days SRT in the anaerobic/aerobic sequential biological reactor system because of being a quite hydrophilic micropollutant (Table 6.31).

6.1.22 Fish Acute Toxicity Test Results in Continuous Operated Anaerobic/Aerobic Sequential Biological Reactor System

The toxicity dilution factor of the raw hospital wastewater was measured as 5 before the anaerobic treatment (Table 6.32). The toxicity dilution factor was not decreased below 4 after anaerobic and aerobic treatments at 5 days of SRT (Table 6.32). After 30 and 45 days of SRT, the toxicity dilution factor decreased to 3 in the effluent of the anaerobic/aerobic sequential biological reactor (Table 6.32). The toxicity dilution factor decreased from initial 5 to 2 in anaerobic/aerobic sequential biological reactor effluent after 55 days of SRT operation (Table 6.32). This means 55 days of SRT operation removed the acute toxicity by 60.0%. Increasing the SRT

in the anaerobic/aerobic sequential biological reactor system had a significant effect on decreasing the toxicity dilution factors of the all biological reactors treating raw hospital wastewater ($P = 0.002$, $\alpha = 0.05$, $F = 4.26$). In the anaerobic/aerobic sequential biological reactor system it was found that that the aerobic post treatment provided improvements about decreasing the toxicity dilution factors after anaerobic treatment. The main reason for this can be attributed to the decrease of toxicity of the raw hospital wastewater after aerobic step. The toxicity test results indicated that the toxicity decreased from the influent of the anaerobic UASB reactor to the effluent of the aerobic CSTR reactor.

Table 6.32 The toxicity dilution factors at different SRTs (n = 3, mean)

SRT (day)	Influent Hospital Wastewater	Anaerobic UASB Reactor Effluent	Aerobic CSTR Reactor Effluent
5	5	4	4
30	5	4	3
45	5	3	3
55	5	3	2

6.2 Photocatalytic Treatment Processes for Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

6.2.1 Physicochemical Properties of Nanoparticles [Titanium (IV) Oxide (Nano-TiO₂), Cerium (IV) Oxide (Nano-CeO₂), Silicon Dioxide (Nano-SiO₂), Zinc Oxide (Nano-ZnO) and Graphene] Used in This Study

6.2.1.1 Scanning Electron Microscope (SEM) Analysis Results

The SEM images of raw and utilized nanoparticles after photocatalytic treatment were obtained at the following experimental conditions: 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00.

6.2.1.1.1 SEM Analysis Results of Nano-TiO₂. The SEM image shows that the raw and utilized TiO₂ nanoparticle samples exhibit a spherical structure (Figure 6.20. a and b). Only a few nanoparticle samples showed irregular shapes (Figure 6.20. a and b). The raw and utilized nano-TiO₂ samples were uniformly distributed (Figure 6.20. a and b). The average particle sizes were measured about 20-25 nm for the raw and utilized nano-TiO₂ (Figure 6.20. a and b). Yuenyongsuwan, Nithiyakorn, Sabkird, O'Rear, & Pongprayoon (2018) and Cabello, Davoglio, & Pereira (2017) expressed the raw TiO₂ nanoparticles in spherical shapes from their experimental studies (Yuenyongsuwan et al., 2018 and Cabello et al., 2017).

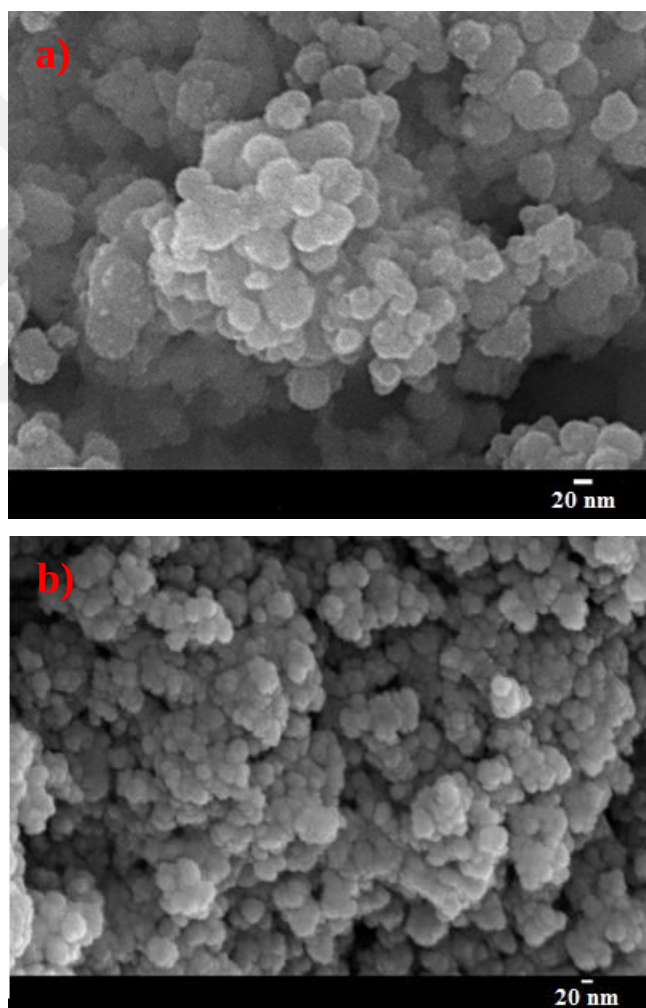


Figure 6.20 (a) SEM image of the raw nano-TiO₂ (b) SEM image of the utilized nano-TiO₂ after photocatalytic treatment at 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

6.2.1.1.2 *SEM Analysis Results of Nano-CeO₂*. The raw and utilized CeO₂ nanoparticles were spherical in shape according to the SEM analysis (Figure 6.21.a and b). The raw and utilized nano-CeO₂ samples showed a homogeneous structure (Figure 6.21. a and b). The average particle sizes were measured about 15-20 nm for the raw and utilized nano-CeO₂ (Figure 6.21.a and b). Several studies confirmed that CeO₂ nanoparticles had a well-defined spherical structure in its raw form (Zhang & Chen, 2016, Gnanam & Rajendran, 2018, Kallapa & Venkatarangaiah, 2018, and Saadati-Moshtaghin & Zonoz, 2019).

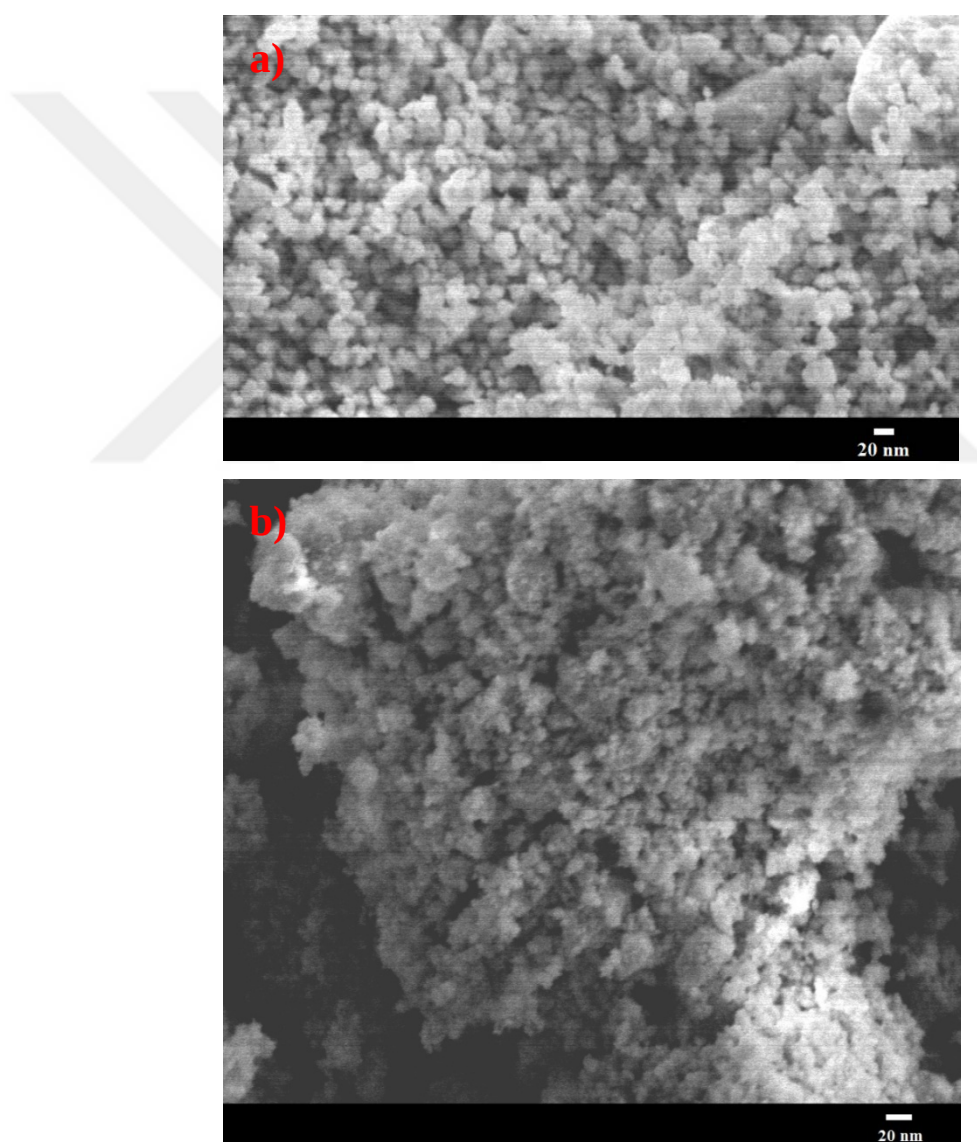


Figure 6.21 (a) SEM image of the raw nano-CeO₂ (b) SEM image of the utilized nano-CeO₂ after photocatalytic treatment at 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

6.2.1.1.3 SEM Analysis Results of Nano-SiO₂. The raw and utilized nano-SiO₂ samples depicted mostly in micro-flake shapes according to the SEM results (Figure 6.22.a and b). The raw and utilized nano-SiO₂ samples had a heterogeneous structure (Figure 6.22.a and b). The particle size was changed from 10 to 20 nm both for its raw and utilized forms (Figure 6.22.a and b).

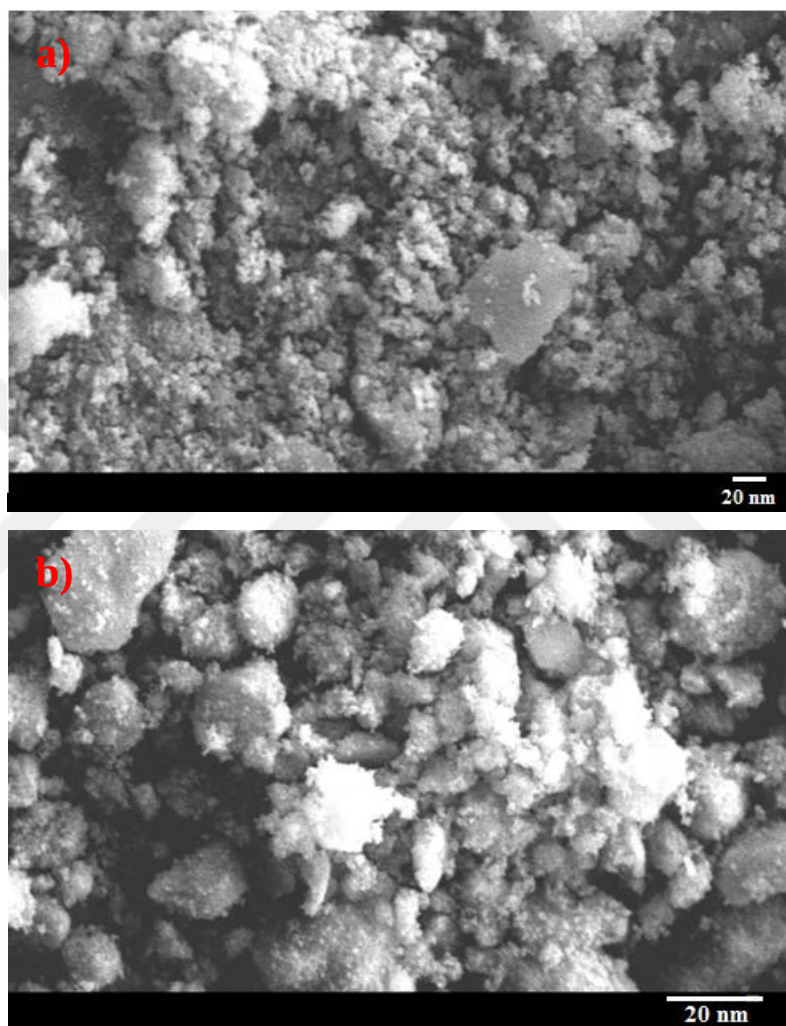


Figure 6.22 (a) SEM image of the raw silicon dioxide (b) SEM image of the utilized nano-SiO₂ after photocatalytic treatment at 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

6.2.1.1.4 SEM Analysis Results of Nano-ZnO. The raw and utilized nano-ZnO samples showed hexagonal shapes (Figure 6.23.a and b).). The raw and utilized nano-ZnO samples were uniformly distributed and had a homogeneous structure (Figure 6.23.a and b). The grain size of the raw and utilized nano-ZnO samples were

approximately 30 nm (Figure 6.23.a and b). Similar results were obtained for the raw nano-ZnO indicating that it was hexagonal in shape and the size distribution was uniform (Zak, Razali, Majid, & Darroudi, 2011 and Azizi, Ahmad, Namvar, & Mohamad, 2014).

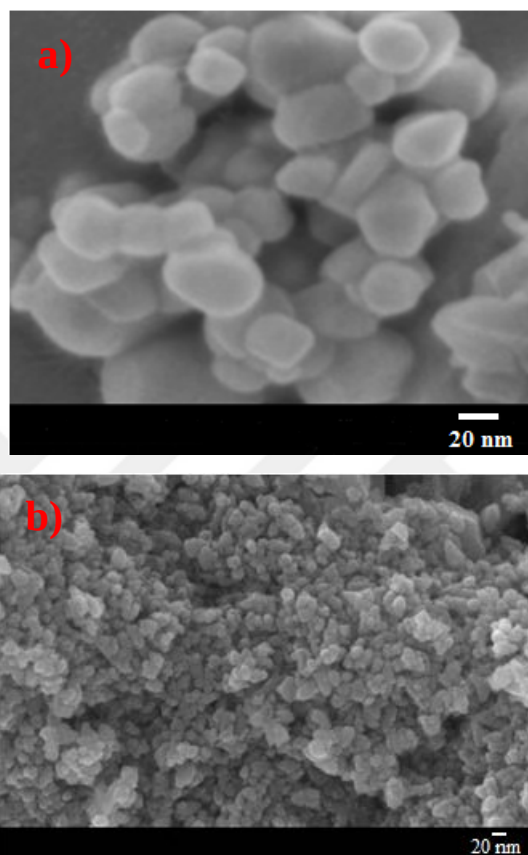


Figure 6.23 (a) SEM image of the raw zinc oxide (b) SEM image of the utilized nano-ZnO after photocatalytic treatment at 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60°C and a constant pH of 7.00

6.2.1.1.5 SEM Analysis Results of Graphene. The SEM image of raw and utilized graphene showed well separated platelets (Figure 6.24.a and b). The SEM images also revealed that the raw and utilized graphene consists of individual sheets closely associated with each other (Figure 6.24.a and b). The grain size of the raw and utilized graphene samples were approximately 100 nm (Figure 6.24.a and b). The results obtained from this study were in accordance with the literature. Grunathan, Han, Eppakayala, & Kim (2013) expressed the raw graphene in a wavy, folded shape and existed in thin layers (Grunathan et al., 2013).

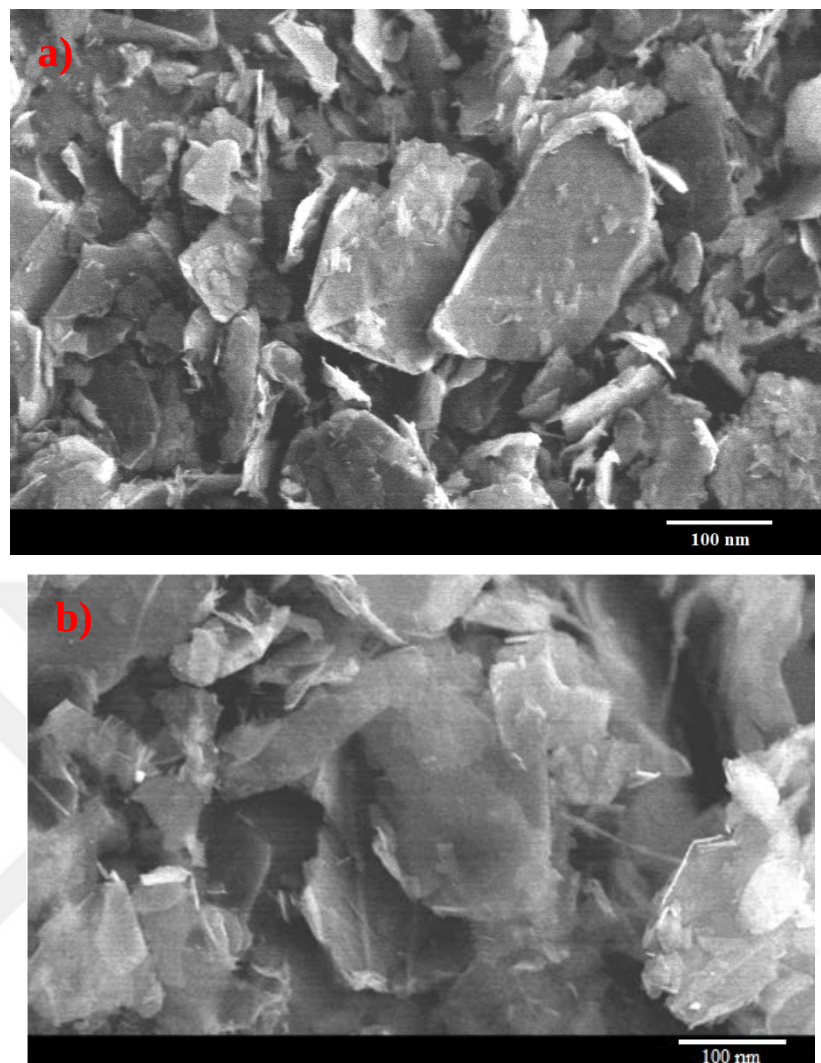


Figure 6.24 (a) SEM image of the raw graphene (b) SEM image of the utilized graphene after photocatalytic treatment at 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60°C and a constant pH of 7.00

6.2.1.2 Fourier Transform Infrared (FT-IR) Analyses Results

Fourier Transform Infrared (FT-IR) analysis were performed on the raw and utilized nanoparticles at the following experimental conditions: 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60°C and a constant pH of 7.00. The FT-IR peaks of the studied nanoparticles were plotted between wave number (cm^{-1}) and absorbance.

6.2.1.2.1 FT-IR Analyses Results of Nano-TiO₂. According to FT-IR analysis, the bonds in maximum absorption-diffraction peaks are determined at 3282, 2972, 2880, 2183, 1651, 1381, 1088, 1047 and 879 cm⁻¹ for the raw nano-TiO₂ (Figure 6.25.a). In this spectrum, the absorption band at 3282 and 1651 cm⁻¹ are related to the stretching and bending vibrations of O-H (δ -H₂O) respectively, representing the water as moisture (Figure 6.25.a) (Al-Amin, Dey, Rashid, Ashaduzzaman, & Shamsuddin, 2016). The absorption peaks at 2880 and 2972 cm⁻¹ can be attributed to the symmetric and asymmetric stretching bands of =C-H, respectively (Figure 6.25.a) (Bagheri, Shameli, & Hamid, 2013). The peak at 1381 cm⁻¹ is related to the aromatic -C=C stretching band where the peaks at 1088 and 1047 cm⁻¹ represent the C-O stretching band (Figure 6.25.a) (Huang et al., 2017). The peaks from 1800-2200 cm⁻¹ is assigned for bending vibrations of Ti-O (Figure 6.25.a). Therefore, the peak at 2183 cm⁻¹ represents the bending vibration of Ti-O (Figure 6.25.a) (Mulmi, Thapa, Dahal, Baral, & Solanki, 2016). Metal oxides generally give absorption bands in finger print region i.e. below 1000 cm⁻¹ arising from inter-atomic vibrations (Kumar & Rani, 2013). At 850–950 cm⁻¹ there is band, also common to all spectra, typical of TiO₂ material. This band peak shifts towards lower from higher wavenumbers for anatase from rutile phase transition. In this study the peak at 879 cm⁻¹ exhibited the triangular peroxy titanyl group (O-Ti-O) in fingerprint region as mentioned by Silva, 2008 (Figure 6.25.a). The polar groups, especially the surface hydroxyl groups, result in the formation of hydrogen bonds between nano-TiO₂ and water molecules. These properties explain the hydrophilic nature of nano-TiO₂ (Ye, Liu, Tang, & Zhai, 2007).

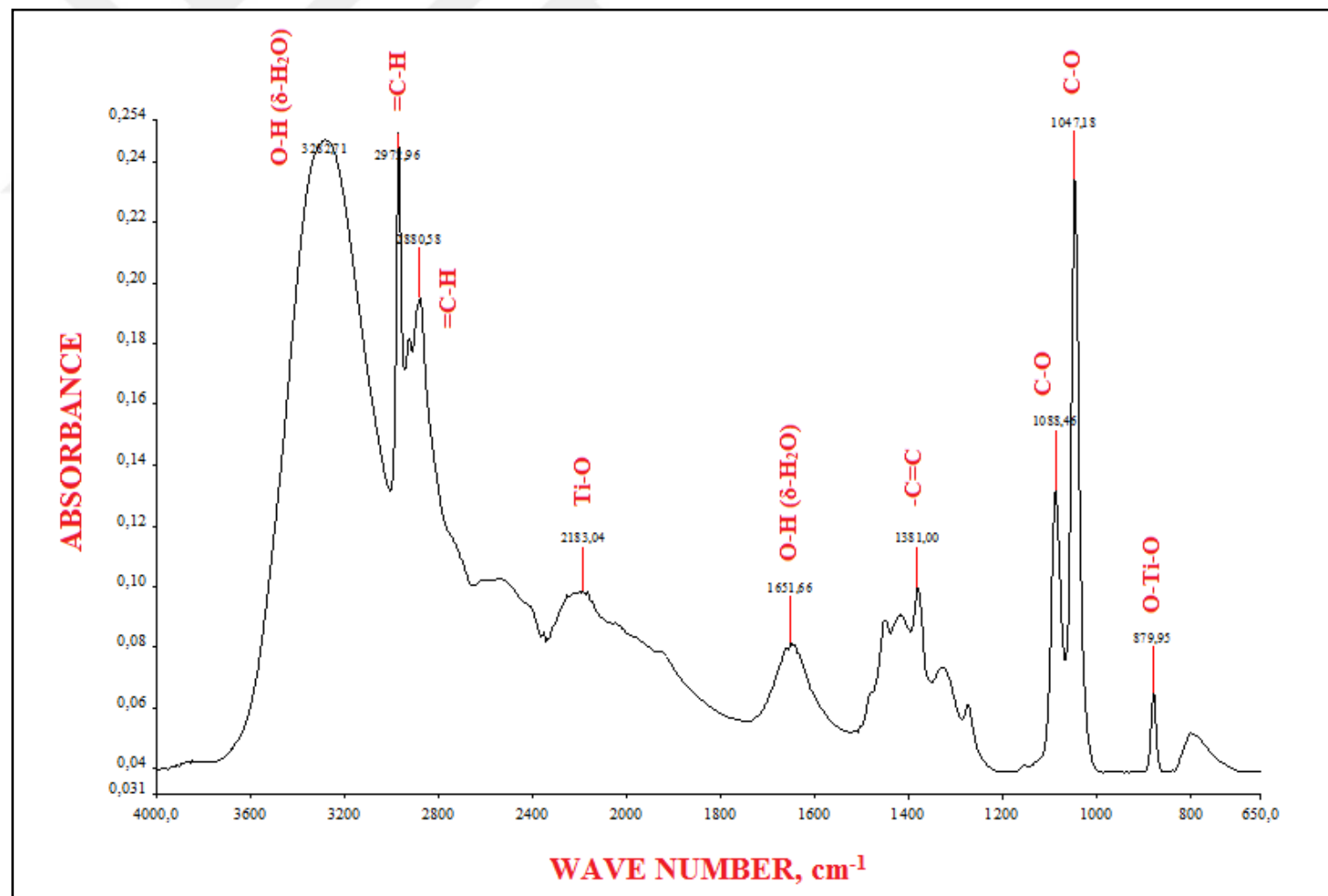


Figure 6.25 (a) FT-IR analysis of raw nano-TiO₂

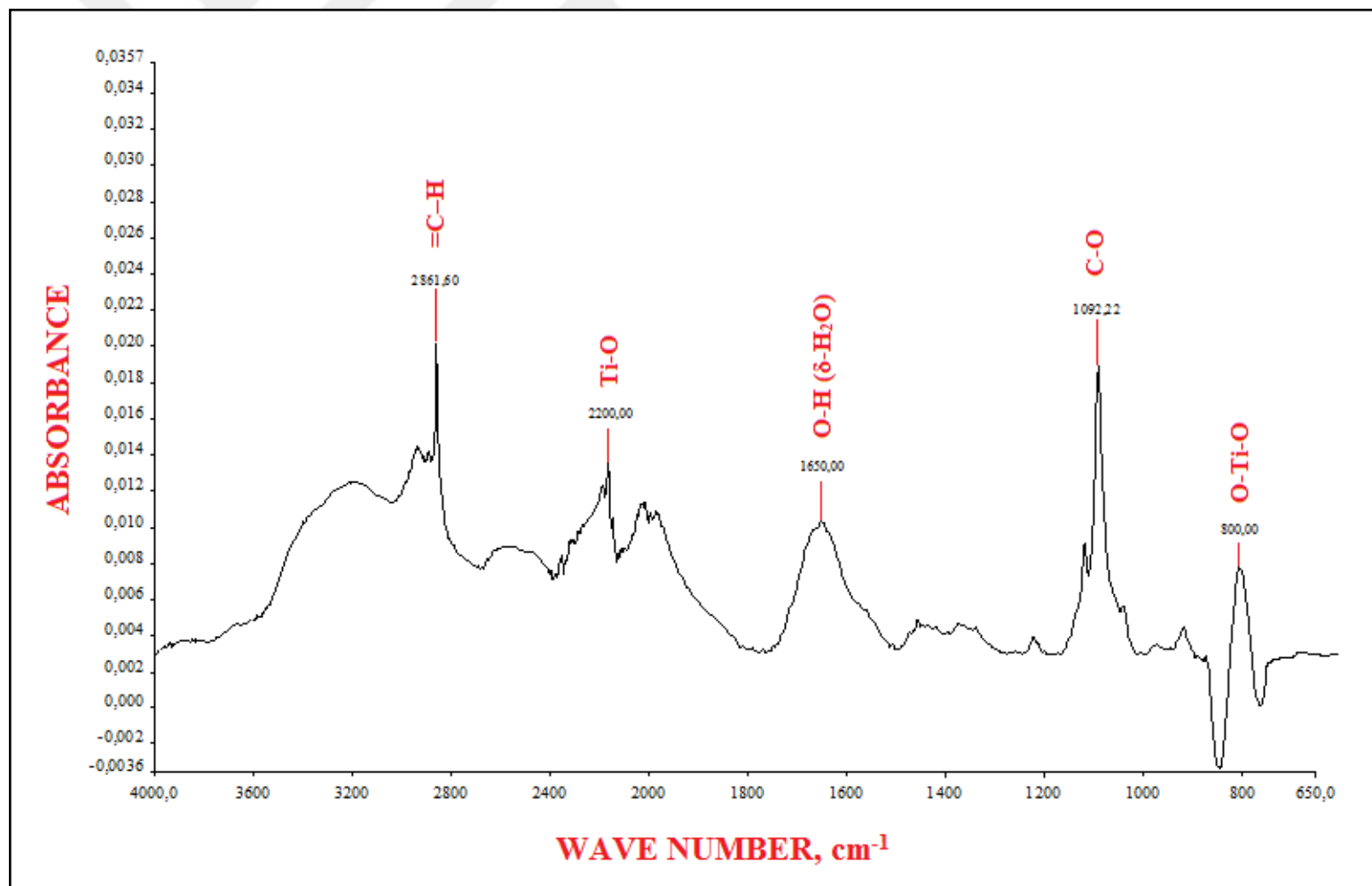


Figure 6.25 (b) FT-IR analysis of utilized TiO₂ nanoparticles after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The most characteristic features in the FT-IR spectrum of the utilized nano-TiO₂ after photocatalytic treatment at the aforementioned experimental conditions are the absorption bands corresponding to the =C–H stretching band at 2861 cm⁻¹ (Bagheri et al., 2013), the bending vibrations of Ti–O at 2200 cm⁻¹ (Mulmi et al., 2016), the bending vibrations of O–H (δ -H₂O) at 1650 cm⁻¹ (Al-Amin et al., 2016), the C–O stretching at 1092 cm⁻¹ (Huang et al., 2017) and the triangular peroxy titanyl group (O–Ti–O) at 800 cm⁻¹ (Silva, 2008) (Figure 6.25.b). The maximum peaks (2861, 2200, 1650, 1092 and 800 cm⁻¹) for the utilized nano-TiO₂ after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.25.b) are similar to the peaks of raw nano-TiO₂ (2880, 2183, 1651, 1088 and 879 cm⁻¹) (Figure 6.25.a).

6.2.1.2.2 FT-IR Analyses Results of Nano-CeO₂. According to FT-IR analysis, the bonds in maximum absorption-diffraction peaks were determined at 3626, 1635, 1457, 988 and 850 cm⁻¹ for the raw nano-CeO₂ (Figure 6.26.a). In this spectrum, the absorption band at 3626 cm⁻¹ is related to the stretching vibration of O–H (δ -H₂O) representing the water as moisture (Figure 6.26.a) (Babitha, Sreedevi, Priyanka, Sabu, & Varghese, 2015). The absorption peak at 1635 cm⁻¹ can be attributed to the scissor bending of H–O–H (Figure 6.26.a) (Liu, Zuo, Ren, & Yong, 2014). The peak at 1457 cm⁻¹ is related to the bending vibration of C–H stretching band (Figure 6.26.a) (Farahmandjou & Zarinkamar, 2015). The C–O stretching vibration peak appeared at 988 cm⁻¹ (Figure 6.26.a) (Farahmandjou, Zarinkamar, & Firoozabadi, 2016). Metal oxides generally give absorption bands in finger print region i.e. below 1000 cm⁻¹ arising from inter-atomic vibrations (Kumar & Rani, 2013). In this study the peak at 850 cm⁻¹ exhibited the Ce–O stretching in fingerprint region as reported by Babitha et al., 2015 (Figure 6.26.a).

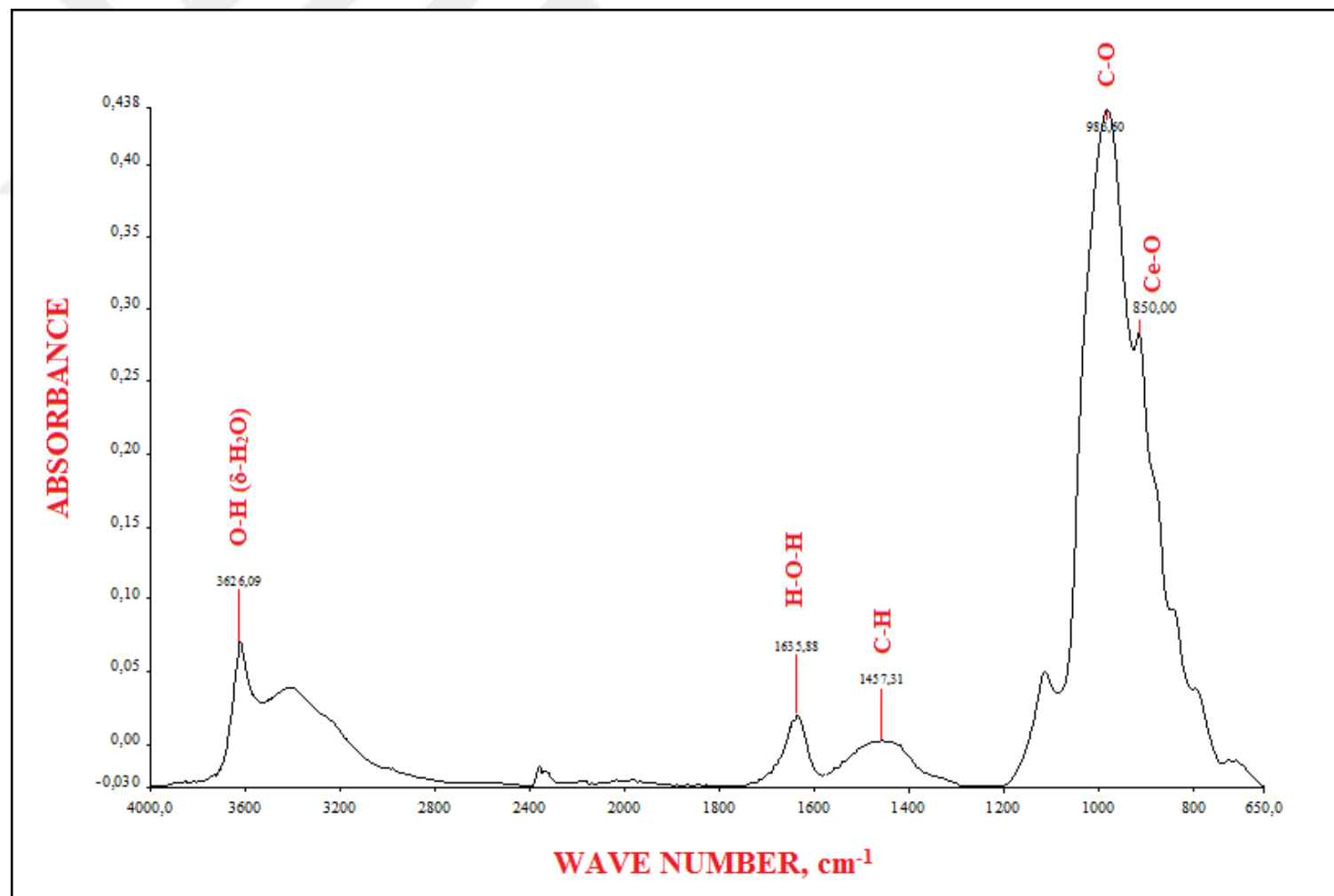


Figure 6.26 (a) FT-IR analysis of raw nano-CeO₂

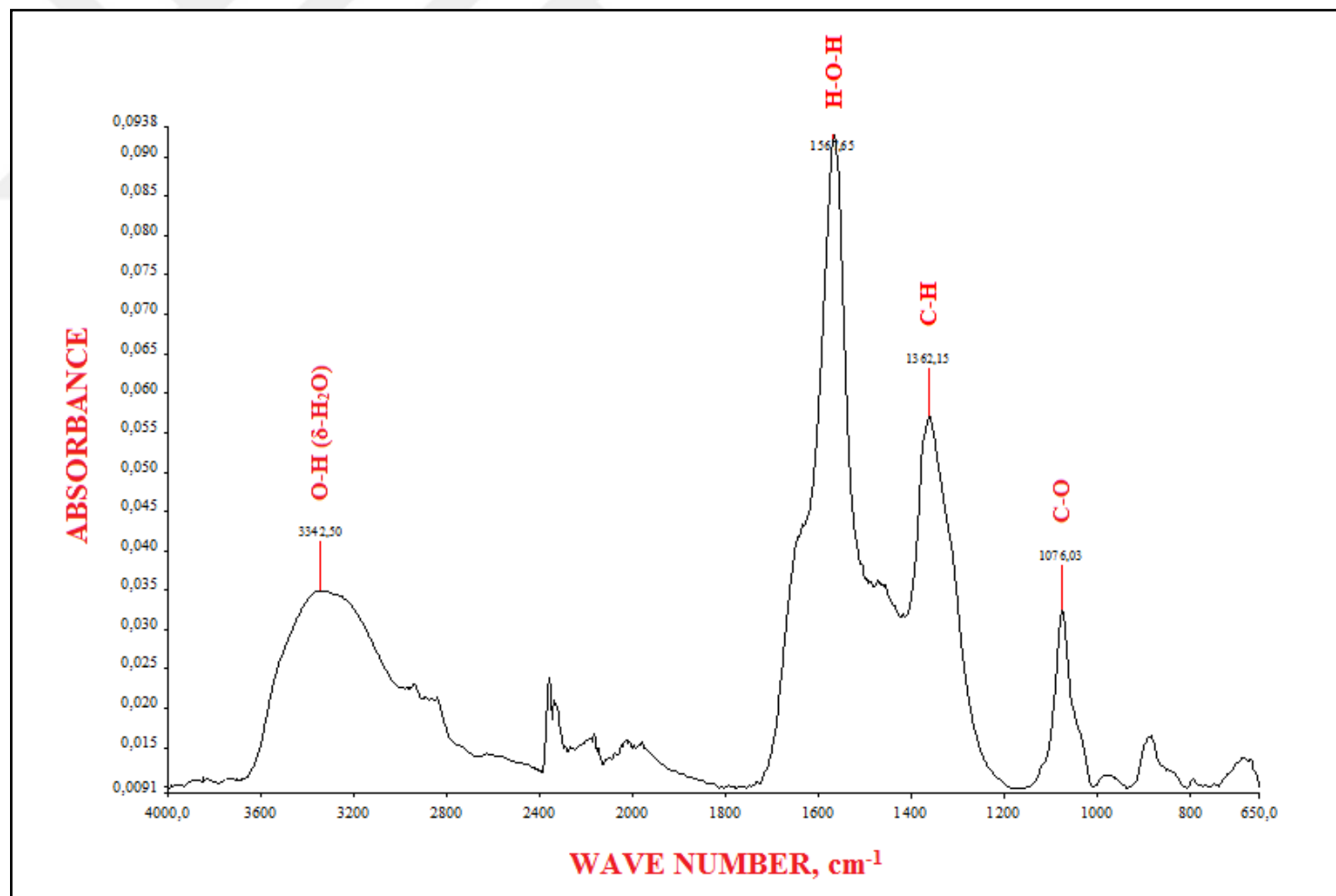


Figure 6.26 (b) FT-IR analysis of utilized CeO₂ nanoparticles after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The most characteristic features in the FT-IR spectrum of the utilized nano-CeO₂ after photocatalytic treatment at the aforementioned experimental conditions are the adsorption bands corresponding to the stretching vibration of O-H (δ -H₂O) at 3342 cm⁻¹ (Babitha et al., 2015), the scissor bending of H-O-H at 1567 cm⁻¹ (Liu et al., 2014), the bending vibration of C-H stretching band at 1362 cm⁻¹ (Farahmandjou & Zarinkamar, 2015) and the C-O stretching vibration at 1076 cm⁻¹ (Farahmandjou et al., 2016) (Figure 6.26.b). The maximum peaks (3342, 1567, 1362 and 1076 cm⁻¹) obtained in this figure (Figure 6.26.b) are similar to the peaks of raw nano-CeO₂ (3626, 1635, 1457 and 988 cm⁻¹) (Figure 6.26.a).

6.2.1.2.3 FT-IR Analyses Results of Nano-SiO₂. According to the FT-IR analysis, the bonds in maximum absorption-diffraction peaks are determined at 1063, 964 and 799 cm⁻¹ for the raw nano-SiO₂ (Figure 6.27.a). The characteristic bands at 1063, 964 and 799 cm⁻¹ are correspond to the Si-O-Si stretching, Si-OH stretching and Si-O bending bonds, respectively (Figure 6.27.a) (Shokri, Firouzjah, & Hosseini, 2009). The position and the shape of the main Si-O vibrational band at 1063 cm⁻¹ shows a stoichiometric silicon dioxide structure (Figure 6.27.a) (Shokri et al., 2009).

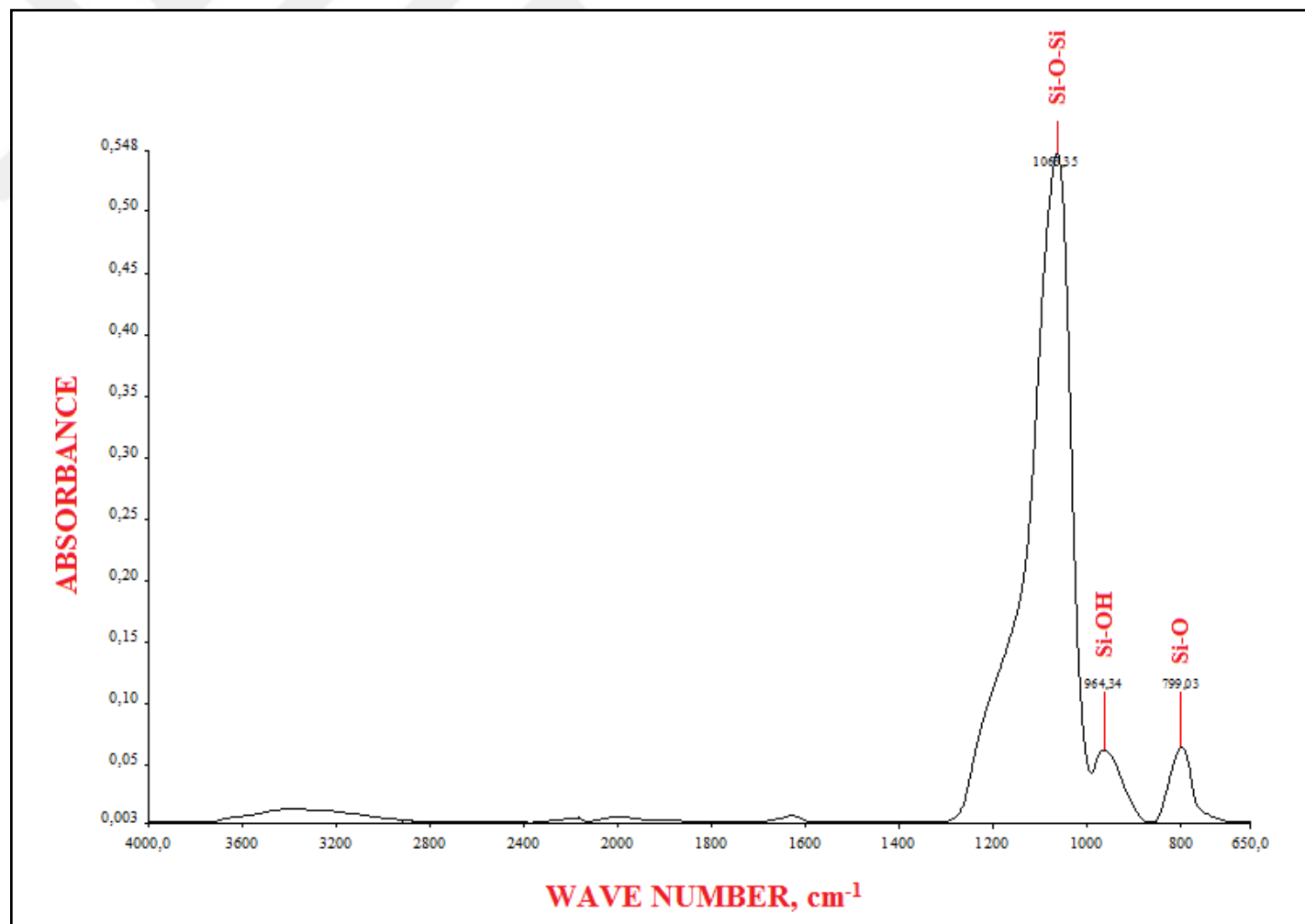


Figure 6.27 (a) FT-IR analysis of raw nano-SiO₂

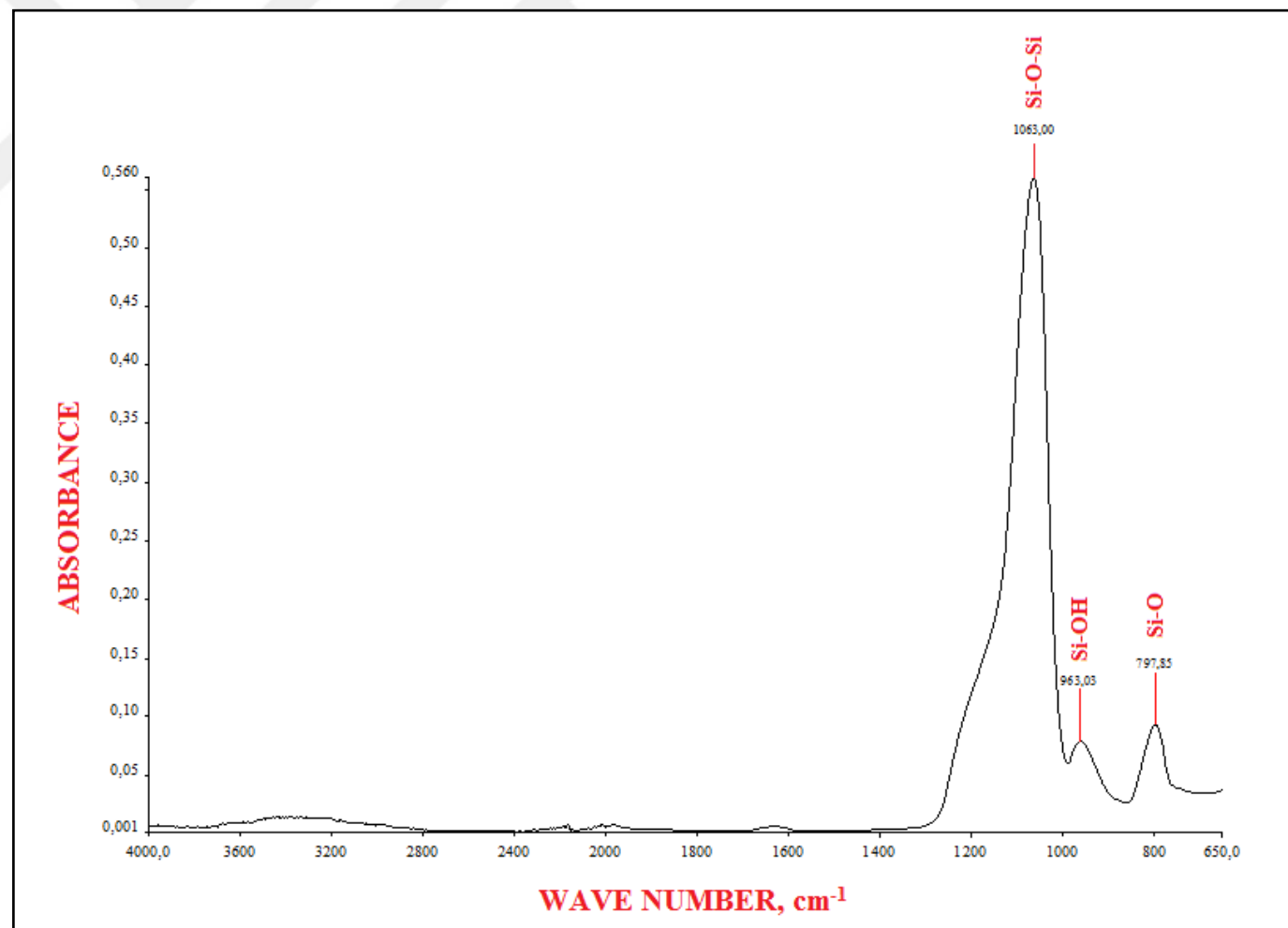


Figure 6.27 (b) FT-IR analysis of utilized nano-SiO₂ after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

From the Figure 6.27.b, it can be seen that the most characteristic features in the FT-IR spectrum of the utilized nano-SiO₂ after photocatalytic treatment at the aforementioned experimental conditions are the absorption bands corresponding to the Si-O-Si stretching band at 1063 cm⁻¹, the Si-OH stretching band at 963 cm⁻¹ and the Si-O bending bond at 797 cm⁻¹, respectively (Shokri et al., 2009). The maximum peaks of utilized nano-SiO₂ after photocatalytic treatment at the aforementioned experimental conditions (1063, 963 and 797 cm⁻¹) (Figure 6.27.b) are similar to the raw silicon dioxide (1063, 964 and 799 cm⁻¹) (Figure 6.27.a).

6.2.1.2.4 FT-IR Analyses Results of Nano-ZnO. According to the FT-IR analysis, the bonds in maximum absorption-diffraction peaks are determined at 3626, 1635, 1489 and 980 cm⁻¹ for the raw nano-ZnO (Figure 6.28.a). The band intensity at 3626 cm⁻¹ corresponded to the O-H stretching, while the Zn-O stretching detected at 1635 cm⁻¹ (Kumar & Rani, 2013) (Figure 6.28.a). The band at 1489 cm⁻¹ corresponds to the stretching vibration of CH₂ ethylene group and the band located at 980 cm⁻¹ corresponds to the stretching vibrations of the C-C groups (Anand & Muthuvel, 2017) (Figure 6.28.a).

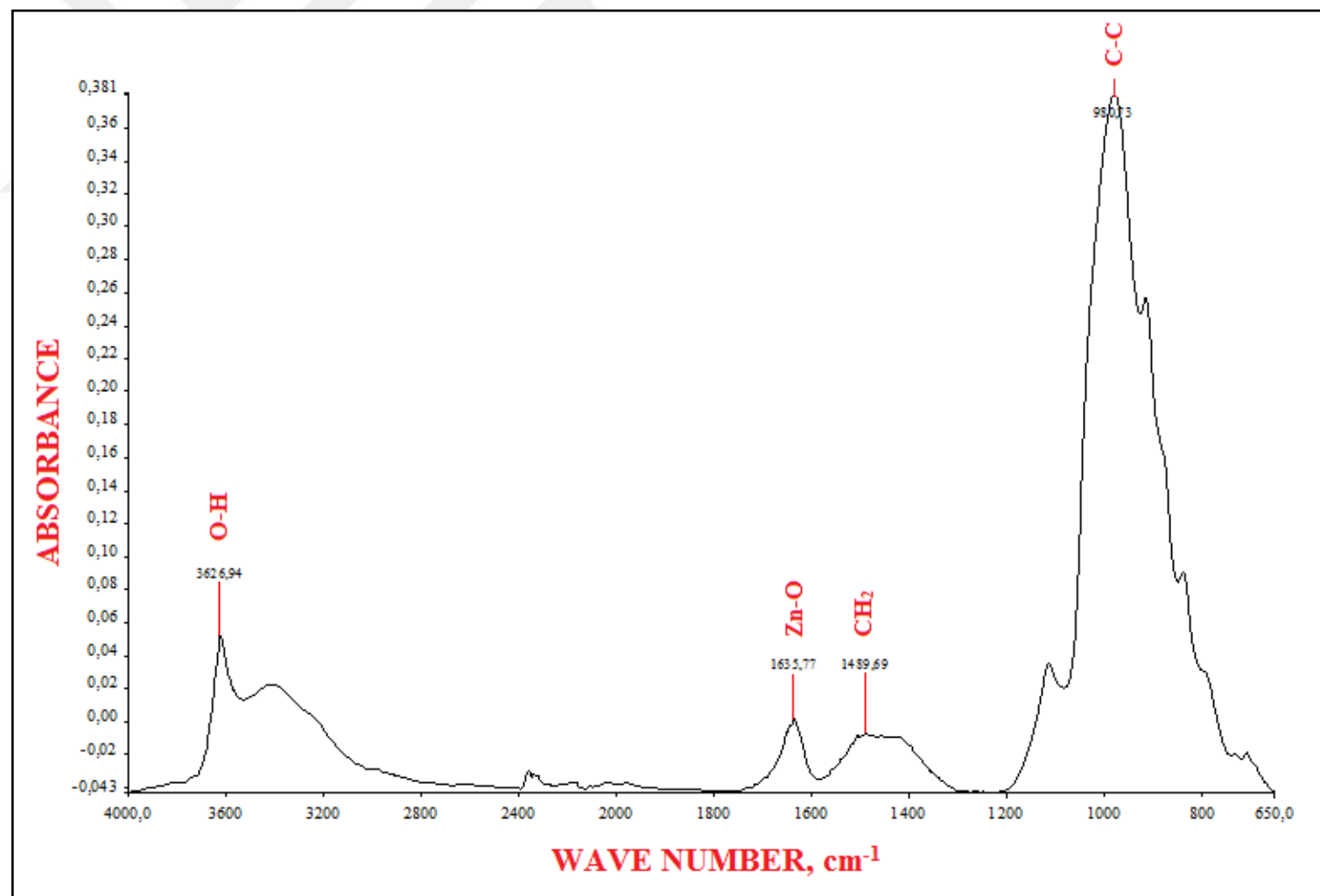


Figure 6.28 (a) FT-IR analysis of raw nano-ZnO

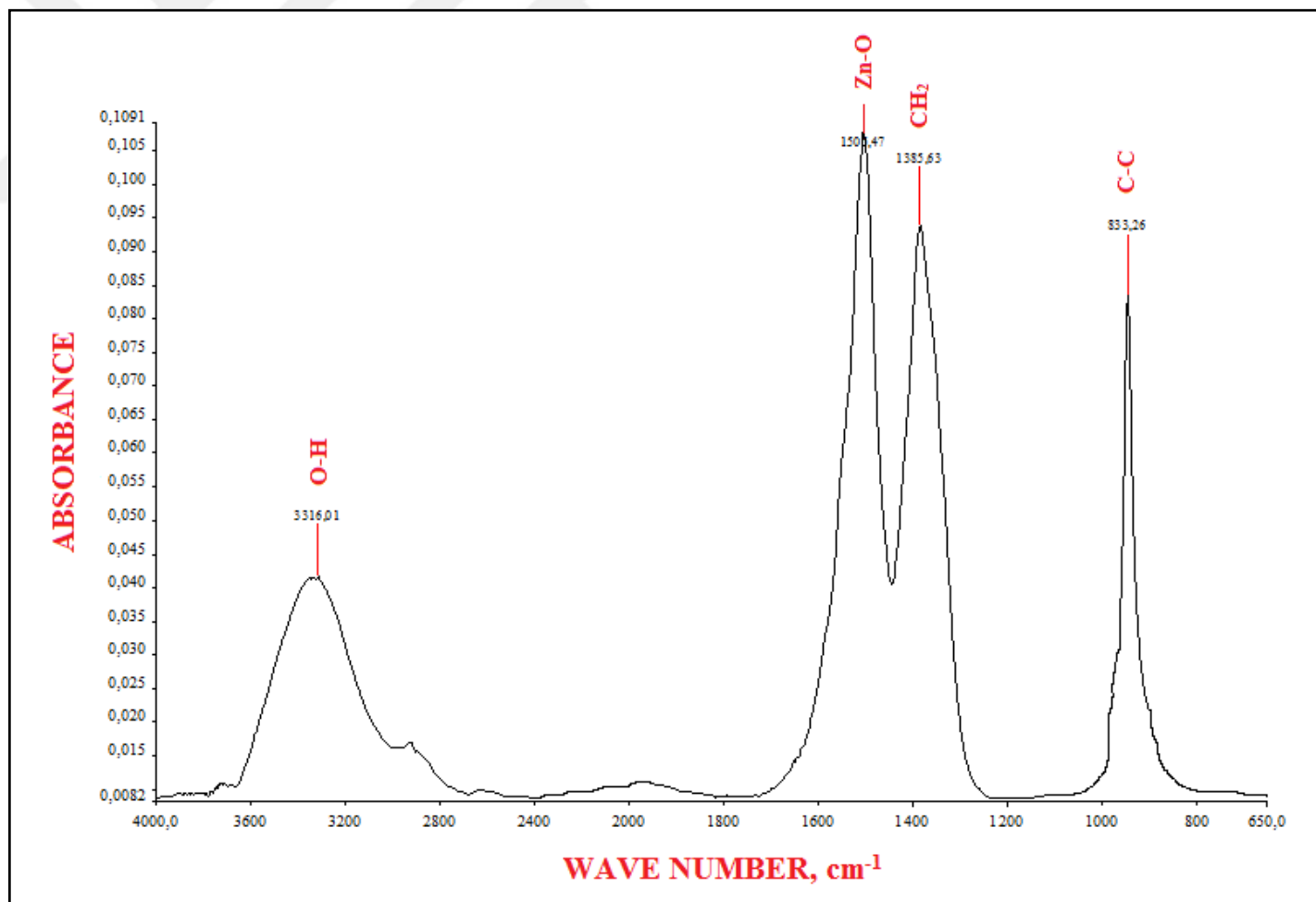


Figure 6.28 (b) FT-IR analysis of utilized nano-ZnO after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The O-H stretching and Zn-O stretching were detected at 3316 and 1505 cm^{-1} , respectively (Kumar & Rani, 2013), furthermore, the stretching vibration of CH_2 ethylene group and the the stretching vibrations of the C-C groups were located at 1385 and 833 cm^{-1} , respectively (Anand & Muthuvel, 2017) (Figure 6.28.b). The maximum peaks of utilized nano-ZnO after photocatalytic treatment at the aforementioned experimental conditions (3316, 1505, 1385 and 833 cm^{-1}) (Figure 6.28.b) are similar to the raw zinc oxide (3626, 1635, 1489 and 980 cm^{-1}) (Figure 6.28.a).

6.2.1.2.5 FT-IR Analyses Results of Graphene. According to the FT-IR analysis, the bonds in maximum absorption-diffraction peaks are determined at 3622, 1637, 1457 and 973 cm^{-1} for the raw graphene (Figure 6.29.a). The FT-IR spectrum of graphene shows a broad peak appeared at 3622 cm^{-1} attributed to the stretching mode of O-H bond, reveals the presence of hydroxyl groups in graphene (Figure 6.29.a) (Khalili, 2016). The peak found at 1637 cm^{-1} is a C=O group (Figure 6.29.a) (Kartick, Srivastava, & Srivastava, 2013). The peak at 1457 cm^{-1} arises from C-OH group and the peak at 973 cm^{-1} corresponds to the vibrational mode of the C-O group (Figure 6.29.a) (Khalili, 2016).

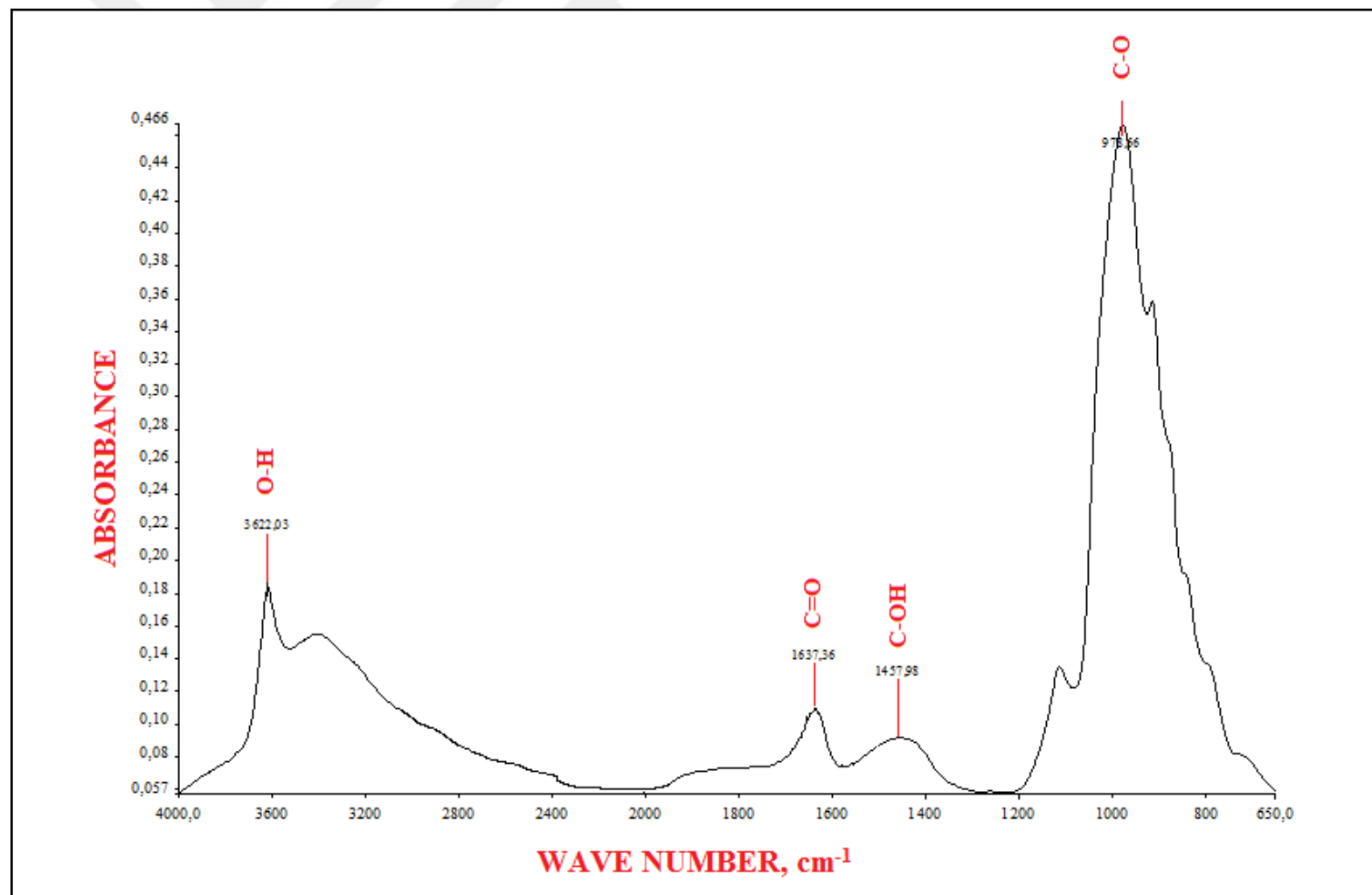


Figure 6.29 (a) FT-IR analysis of raw graphene

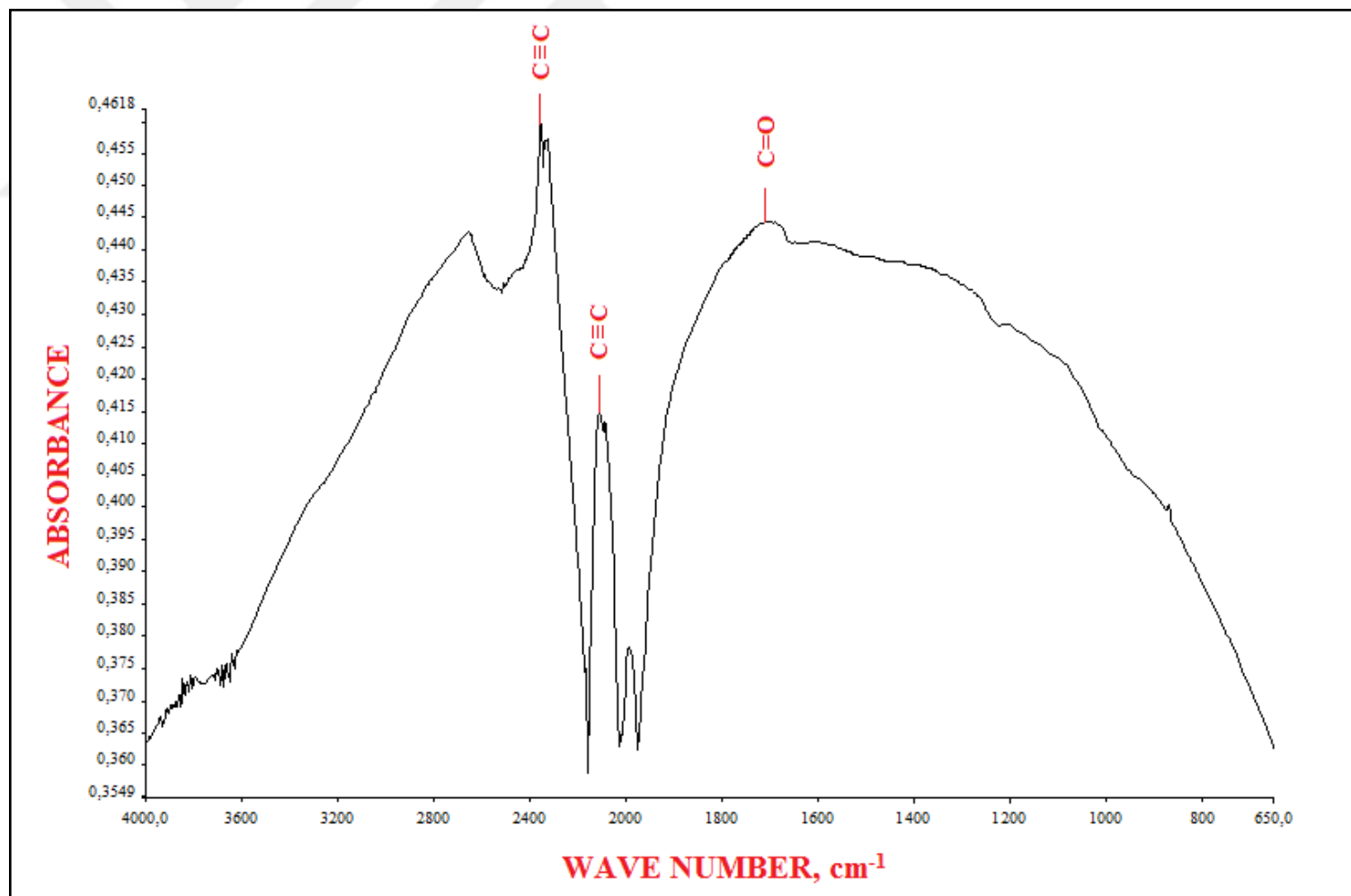


Figure 6.29 (b) FT-IR analysis of utilized graphene after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The peaks found in arange between 2200-2300 cm^{-1} are a $\text{C}\equiv\text{C}$ groups (Figure 6.29.b) (Khalili, 2016). The maximum peaks of utilized graphene (after photocatalytic treatment at the aforementioned experimental conditions) at approximately 2300, 2200 and 1700 cm^{-1} (Figure 6.29.b) were very different from the raw graphene (3622, 1637, 1457 and 973 cm^{-1}) (Figure 6.29.a). As a result, the graphene can not be used again for the photocatalytic treatment of micropollutants from the raw hospital wastewater with UV light according to the FT-IR spectrum results since the catalyst was not stable.

6.2.1.3 X-Ray Diffraction (XRD) Analysis Results

X-Ray Diffraction (XRD) analysis were performed on nano- TiO_2 , nano- CeO_2 , nano- SiO_2 , nano- ZnO and graphene to identify the structures of the nanoparticles. The raw nanoparticles and the utilized nanoparticles after photocatalytic treatment were characterized using XRD at the following experimental conditions: 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 $^{\circ}\text{C}$ and a constant pH of 7.00.

6.2.1.3.1 XRD Analyses Results of Nano- TiO_2 . The strongest and narrow peak was detected at $2\theta = 25^{\circ}$ for the raw nano- TiO_2 (Figure 6.30.a). As is shown in the figure, the main peaks of raw nano- TiO_2 appeared at 25° , 28° , 39° , 48° , 54° , 55° , 63° , 69° , 70° and 76° (Figure 6.30.a). High intensity sharp peak ($2\theta = 25^{\circ}$) and absence of unidentified peaks confirmed the crystallinity and higher purity of the raw nano- TiO_2 (Figure 6.30.a). The XRD analysis showed that, the raw TiO_2 nanoparticle originated completely from the pure anatase phase with a good crystallinity. The peaks of the raw nano- TiO_2 were in accordance with the peaks given by Hu et al. (2017) (at 25° , 28° , 38° and 48°) and Hassani et al. (2017) (54° , 55° , 63° , 69° , 70° , and 76°) (Hu et al., 2017 and Hassani et al., 2017). These results confirmed using Joint Committee on Powder Diffraction Standards (JCPDS card no 21-1272 for anatase TiO_2 nanoparticles) (Rosi & Kalyanasundaram, 2018). TiO_2 exists in three principal crystallographic forms (anatase, brookite and rutile) but only the anatase and rutile

form are photocatalytically active (Martínez, Morales-Mejía, Hernández, Santiago, & Almanza, 2014).



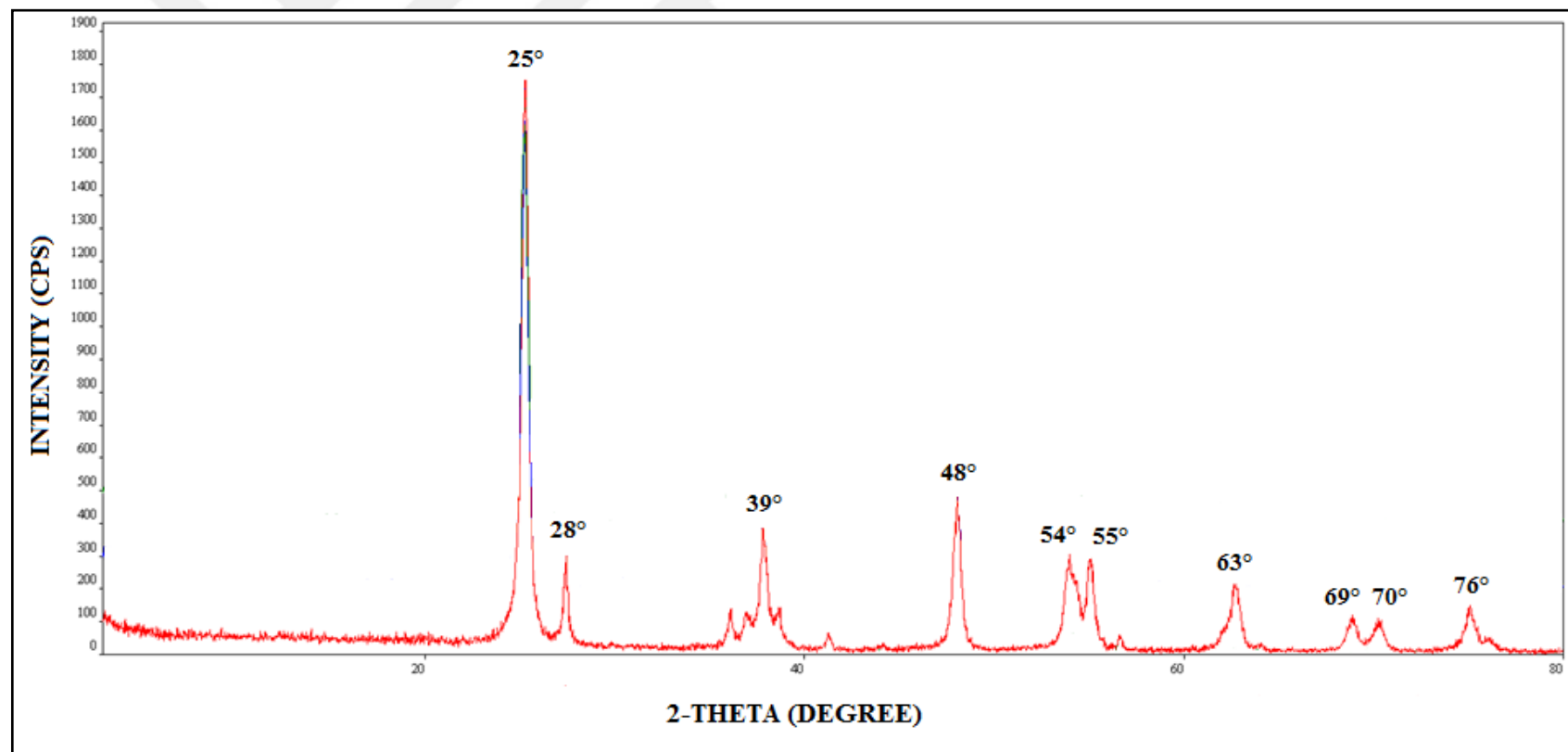


Figure 6.30 (a) XRD analysis of raw nano-TiO₂

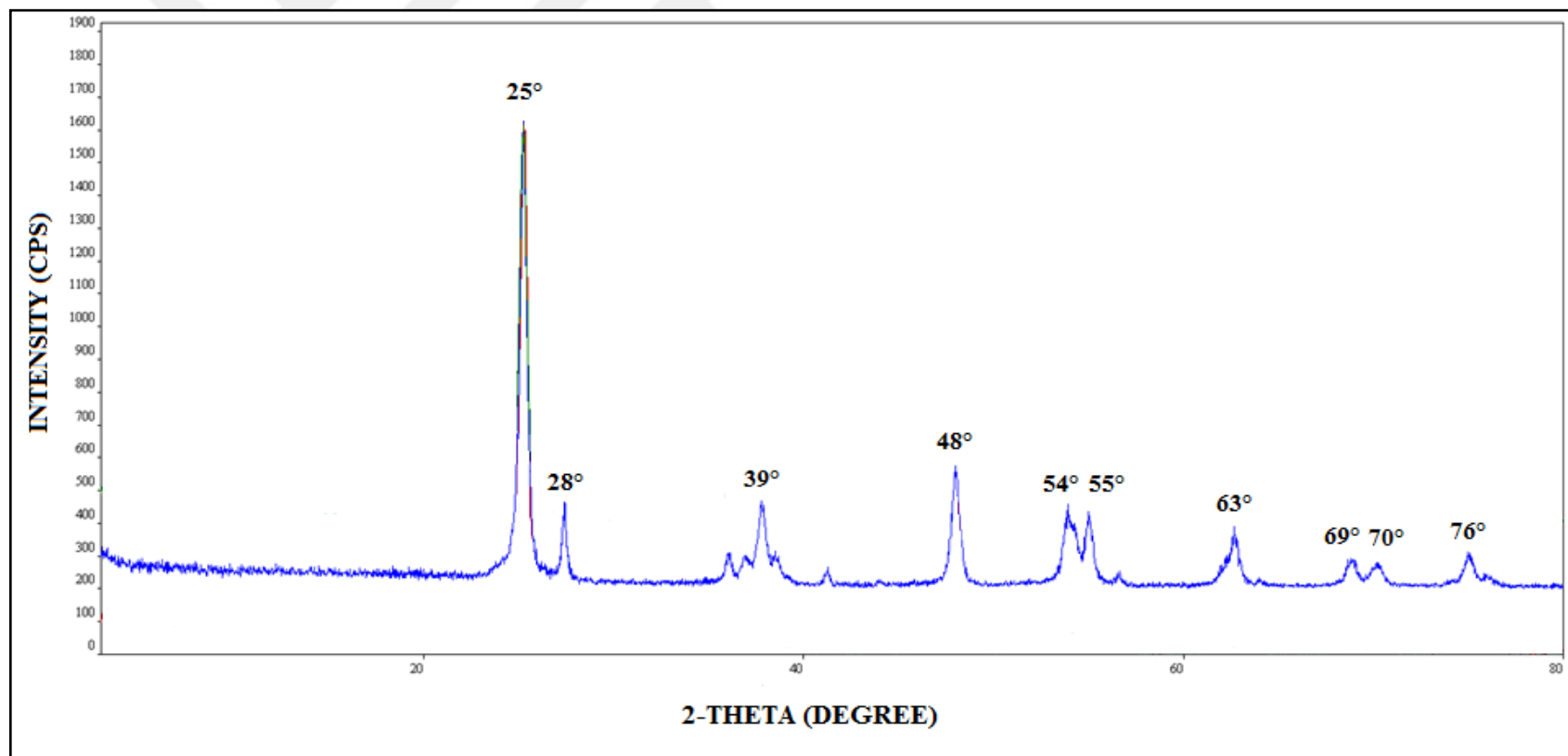


Figure 6.30 (b) XRD analysis of utilized nano-TiO₂ after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The strongest and narrow peak for the utilized nano-TiO₂ after photocatalytic treatment at the aforementioned experimental conditions was detected at $2\theta = 25^\circ$ (Figure 6.30.b). The characteristic peaks of the utilized nano-TiO₂ (25° , 28° , 39° , 48° , 54° , 55° , 63° , 69° , 70° and 76°) did not change after photocatalytic treatment (Figure 6.30.b).

6.2.1.3.2 XRD Analyses Results of Nano-CeO₂. The strongest and narrow peak was detected at $2\theta = 28^\circ$ for the raw nano-CeO₂ (Figure 6.31.a). From the XRD peaks it is evident that the crystallites were oriented along 28° , 33° , 48° , 56° , 59° and 69° , corresponding to the cubic fluorite structure of CeO₂ (Figure 6.31.a). These results confirmed using Joint Committee on Powder Diffraction Standards (JCPDS card no 34-0394 for CeO₂ nanoparticles). The XRD patterns reveal that the CeO₂ nanoparticles had a cubic fluorite structure. Similar peaks at 28° , 33° , 48° and 56° were reported by Phuruangrat, Thongtem, & Thongtem (2017) and Channei, Nakaruk, & Phanichphant (2017).

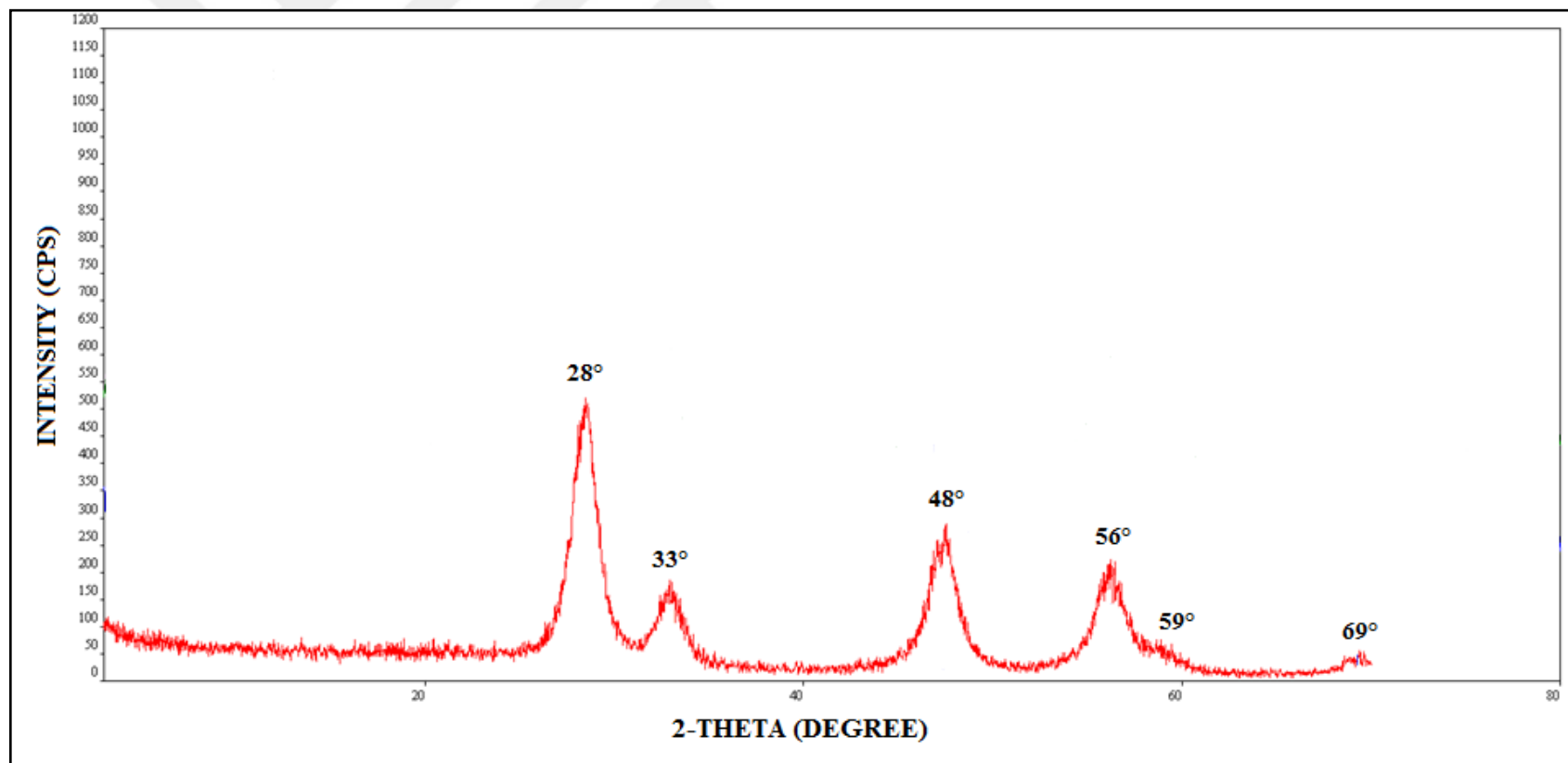


Figure 6.31 (a) XRD analysis of raw nano-CeO₂

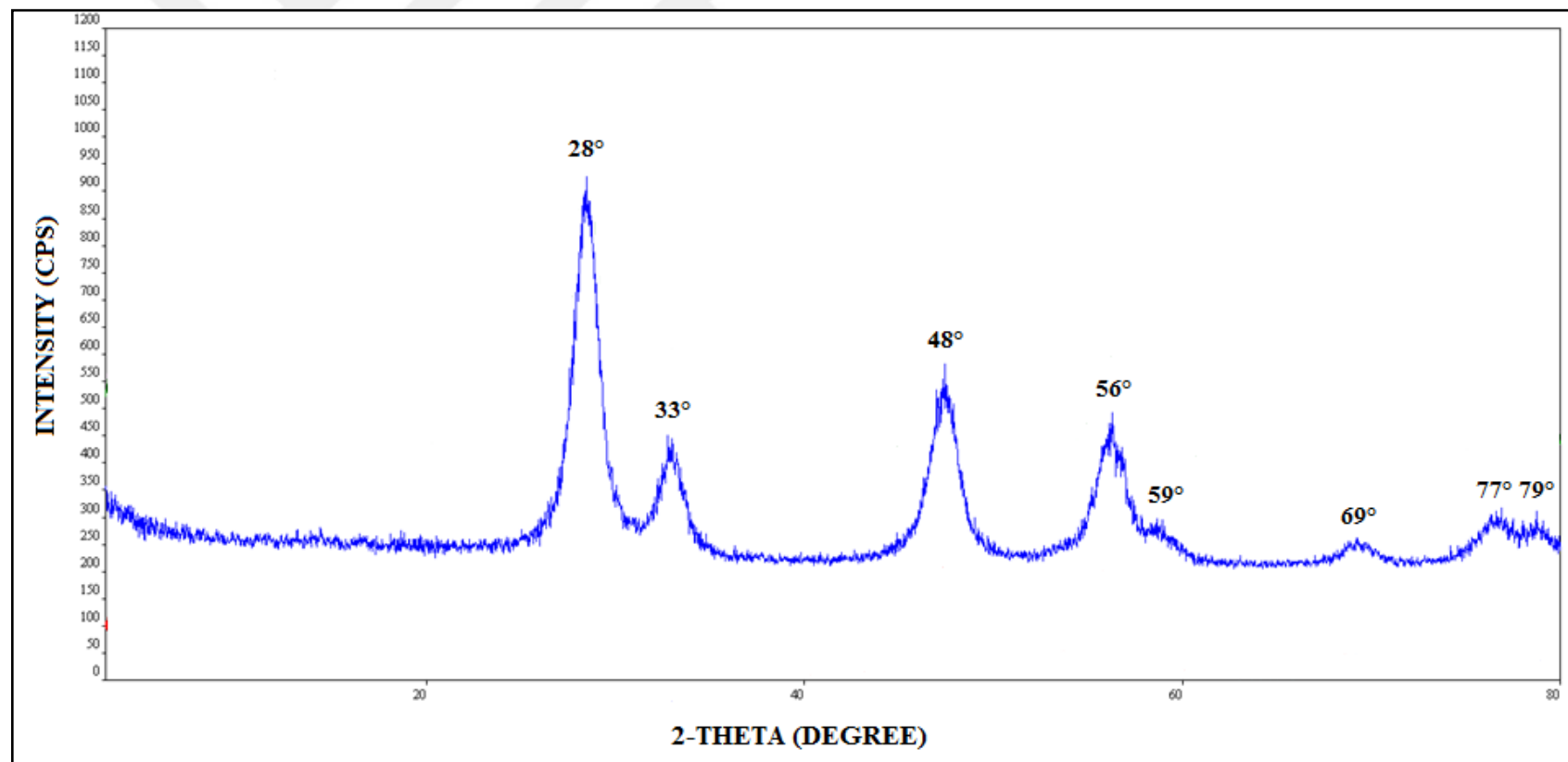


Figure 6.31 (b) XRD analysis of utilized nano-CeO₂ after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The strongest and narrow peak was detected at $2\theta = 28^\circ$ for the utilized nano-CeO₂ after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.31.b). The obtained peaks for the utilized nano-CeO₂ (28° , 33° , 48° , 56° , 59° , 69° , 77° and 79°) showing the characteristic cubic phase structure of nano-CeO₂ did not change considerably after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.31.b).

6.2.1.3.3 XRD Analyses Results of Nano-SiO₂. The strongest and narrow peak was detected at $2\theta = 22^\circ$ for the raw nano-SiO₂ (Figure 6.32.a). The only peak of raw nano-SiO₂ appeared at 22° (Figure 6.32.a) which is in good agreement with the only peak at 22° obtained by Joni, Nulhakim, Vanitha, & Panatarani, 2018. The results showed that the nano-SiO₂ exhibits a crystalline nature representing the cristobalite low type of SiO₂ (Joni et al., 2018).

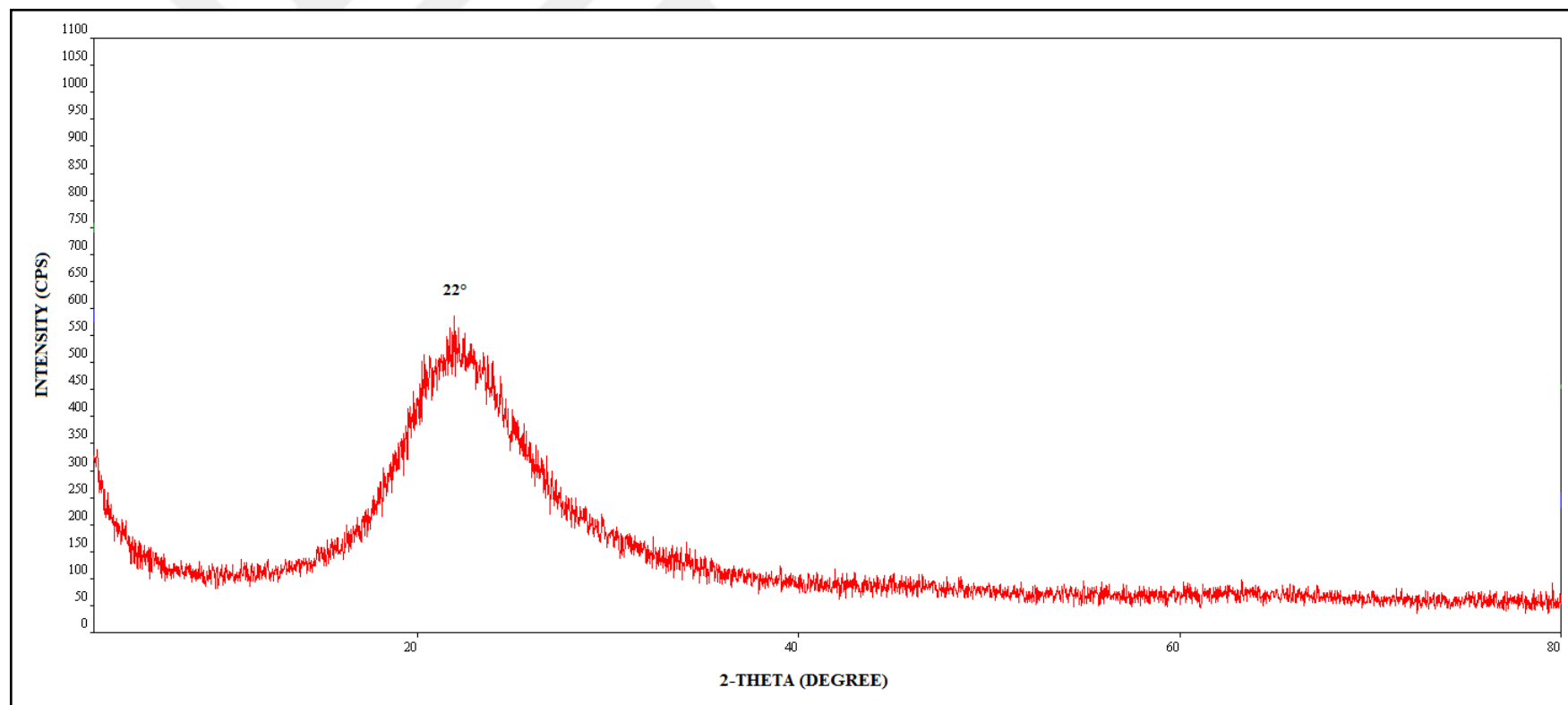


Figure 6.32 (a) XRD analysis of raw nano-SiO₂

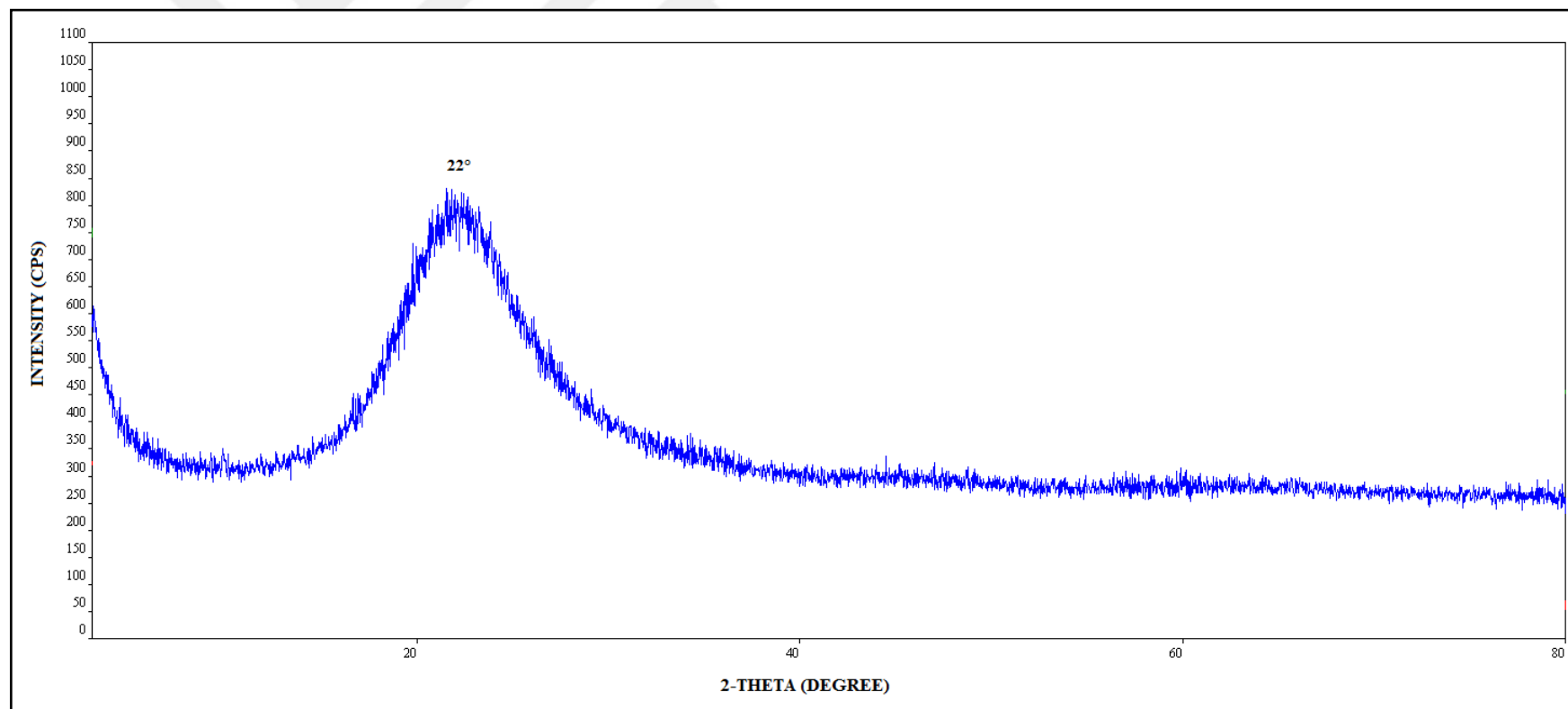


Figure 6.32 (b) XRD analysis of utilized nano-SiO₂ after photocatalytic treatment with 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

The strongest and narrow peak was detected at $2\theta = 22^\circ$ for the utilized nano-SiO₂ after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.32.b). The only peak of the utilized nano-SiO₂ at 22° did not change after photocatalytic treatment and remained the same (Figure 6.32.b).

6.2.1.3.4 XRD Analyses Results of Nano-ZnO. The strongest and narrow peak was detected at $2\theta = 36^\circ$ for the raw nano-ZnO (Figure 6.33.a). The main peaks of raw nano-ZnO appeared at 12° , 30° , 32° , 34° , 36° , 48° , 58° , 60° , 62° and 68° (Figure 6.33.a). These peaks of the raw nano-ZnO used in this study were in accordance with the peaks at 32° , 34° , 36° , 48° , 58° , 62° and 68° given by Arefi & Zarchi, 2012. The results showed that the nano-ZnO exhibits a wurtzite structure according to the detected peaks (Zak et al, 2011).

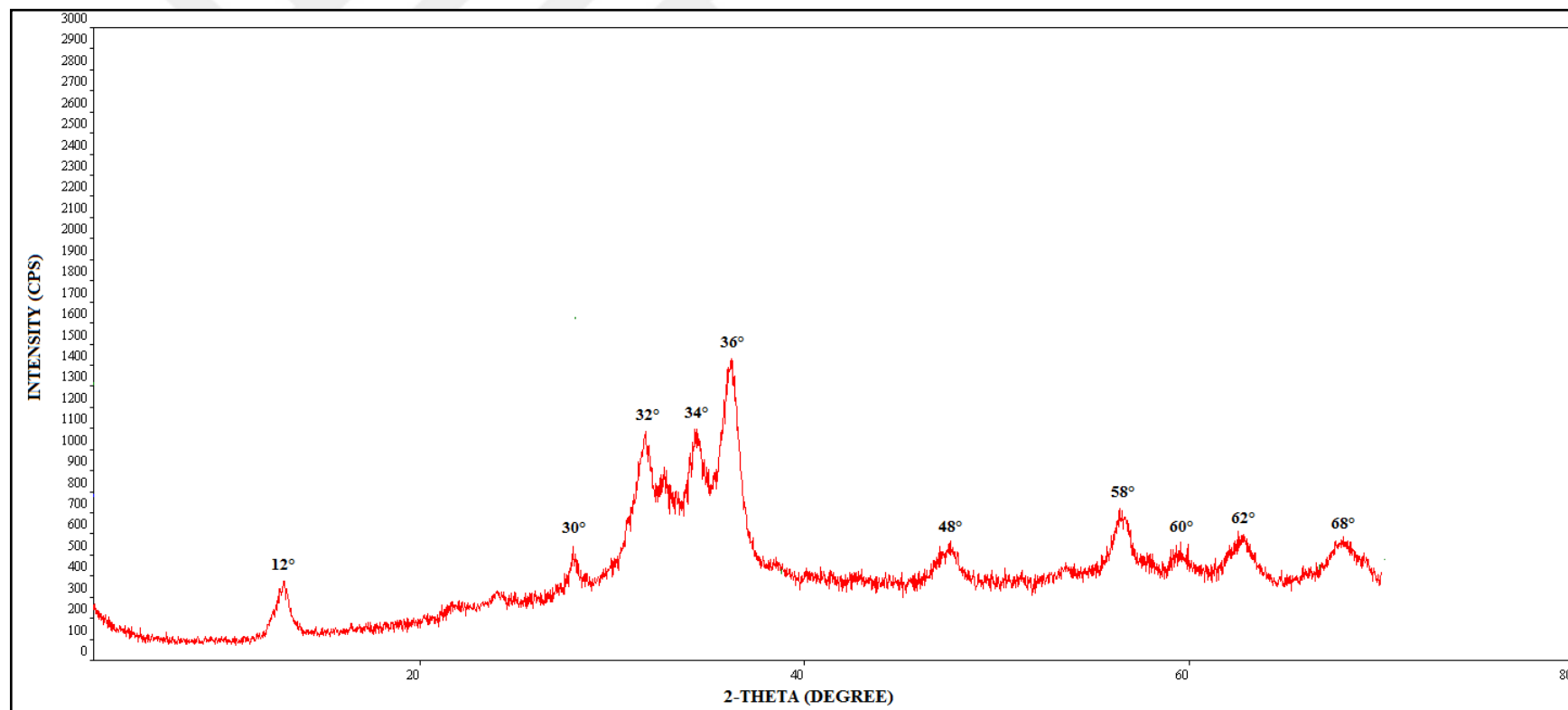


Figure 6.33 (a) XRD analysis of raw nano-ZnO

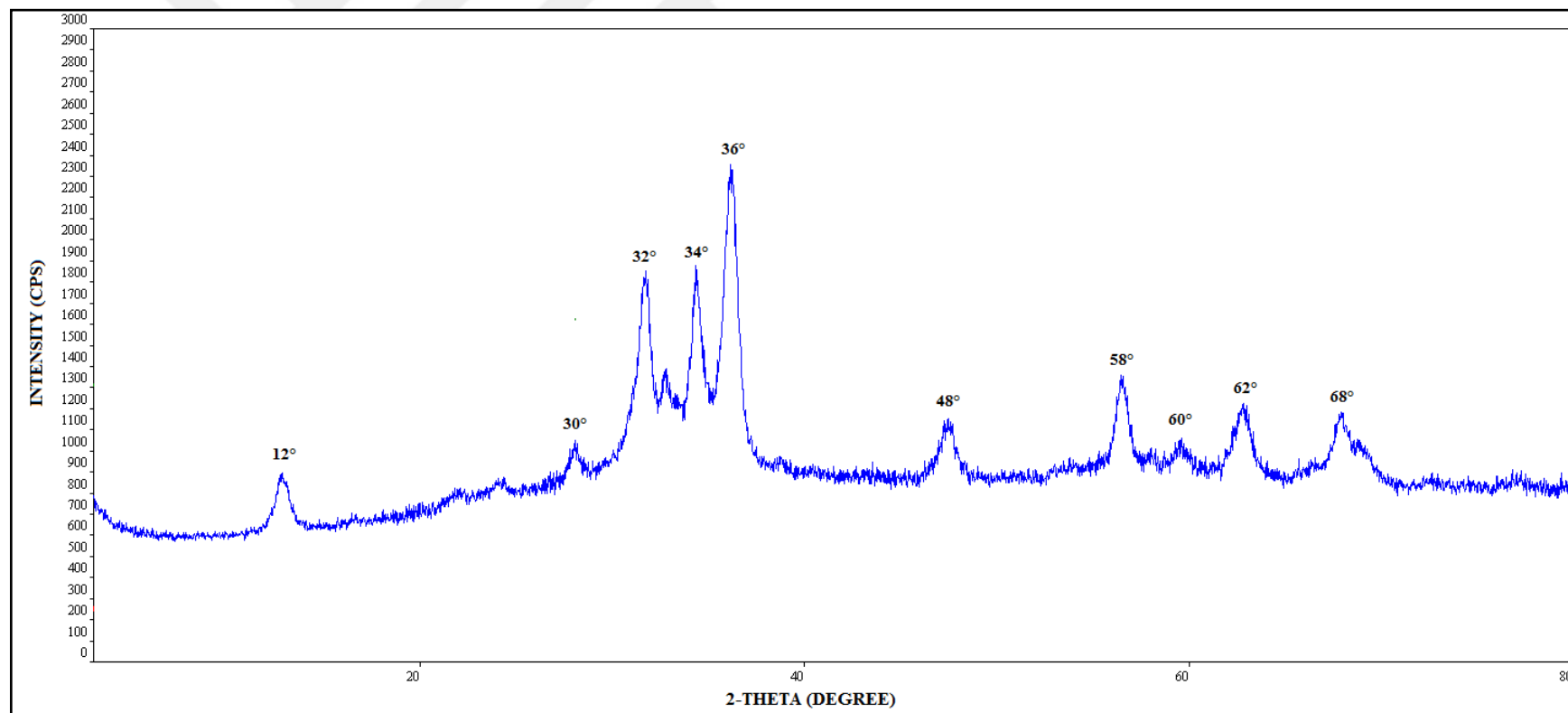


Figure 6.33 (b) XRD analysis of utilized nano-ZnO after photocatalytic treatment with 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60°C and a constant pH of 7.00

The strongest and narrow peak was detected at $2\theta = 36^\circ$ for the utilized nano-ZnO after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.33.b). The characteristic peaks of the utilized nano-ZnO did not change and remained the same at 12° , 30° , 32° , 34° , 36° , 48° , 58° , 60° , 62° and 68° after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.33.b).

6.2.1.3.5 XRD Analyses Results of Graphene. The strongest and narrow peak was detected at $2\theta = 27^\circ$ for the raw graphene (Figure 6.34.a). The main peaks of raw graphene appeared at 27° and 55° (Figure 6.34.a). Johra, Lee, & Jung (2014) also found the 2θ value at 27° for the raw graphene (Johra et al., 2014). The strong and sharp diffraction peak at $2\theta = 27^\circ$ (Figure 6.34.a) shows the (002) plane of hexagonal graphite structure of the raw graphene as mentioned by Khalili, 2016.

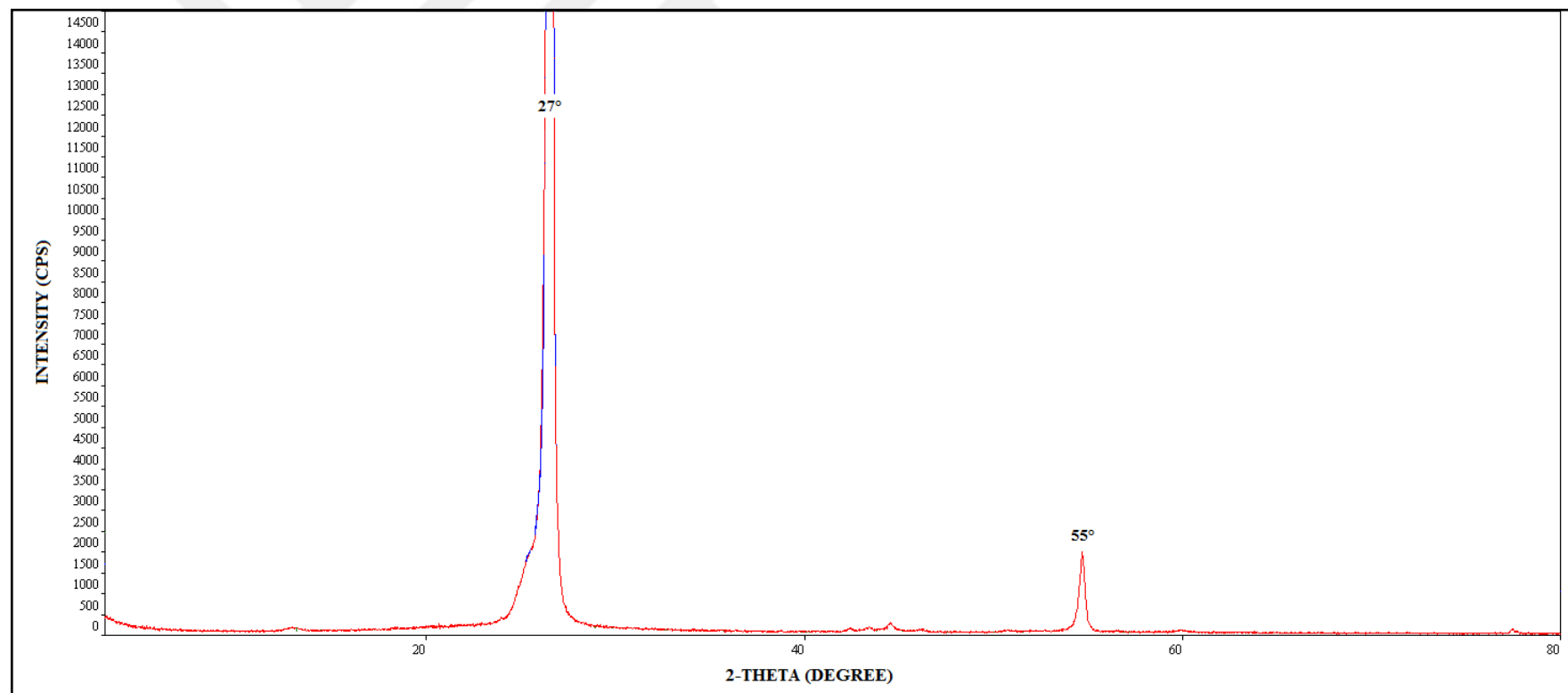


Figure 6.34 (a) XRD analysis of raw graphene

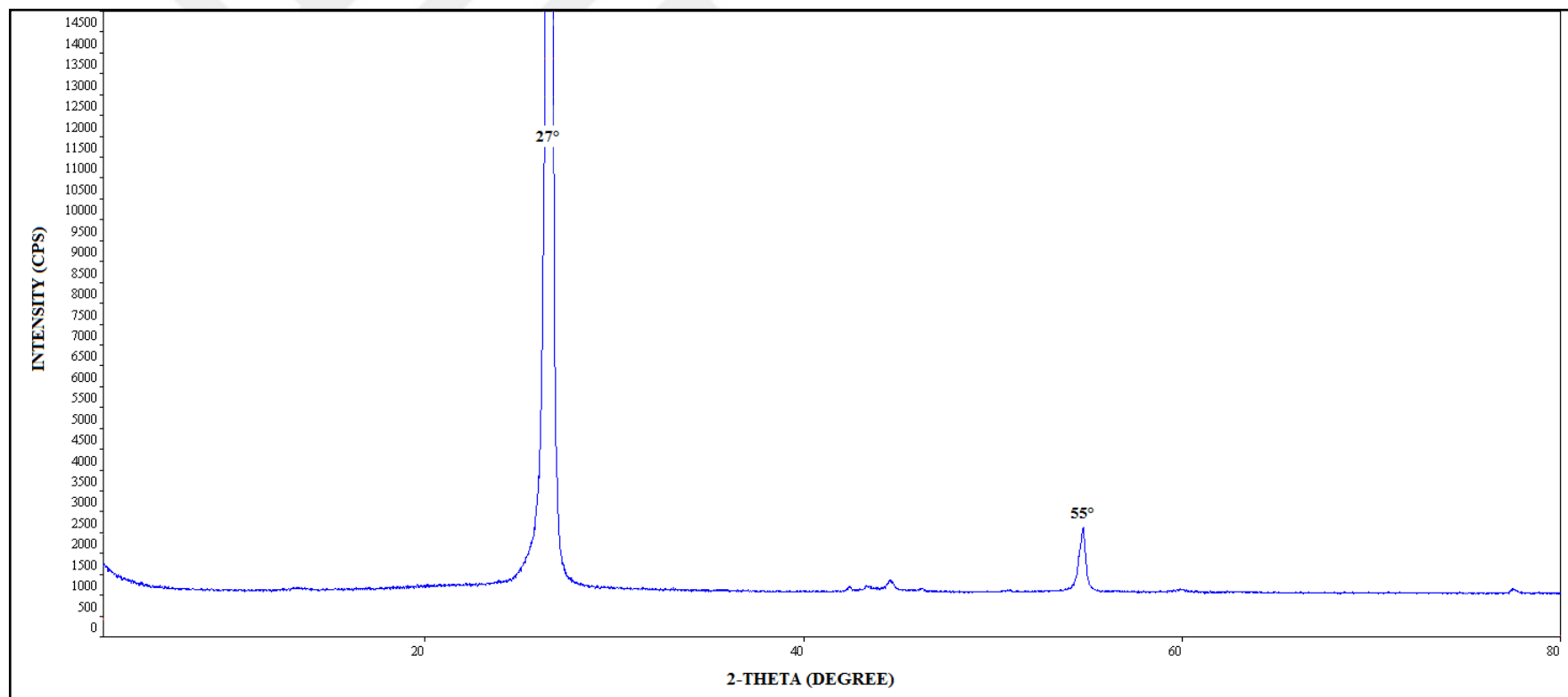


Figure 6.34 (b) XRD analysis of utilized graphene after photocatalytic treatment with 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60°C and a constant pH of 7.00

The strongest and narrow peak was detected at $2\theta = 27^\circ$ for the utilized graphene after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.34.b). The characteristic peaks of the utilized graphene were found at 27° and 55° after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.34.b). The characteristic peaks of the utilized graphene did not change and remained the same at 27° and 55° after photocatalytic treatment at the aforementioned experimental conditions (Figure 6.34.b).

6.2.2 Preliminary Studies on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

6.2.2.1 Effect of Different Nanoparticle Concentrations (0.25, 0.50 and 1.50 g L⁻¹) for Nano-SiO₂, Nano-ZnO, Graphene, Nano-TiO₂ and Nano-CeO₂ Used in This Study on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

Preliminary experiments were carried out with five different nanoparticles (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) to decide which nanoparticles give higher removal efficiencies for the photocatalytic treatment of the selected micropollutants. Preliminary experiments were carried out with PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group) from the raw hospital wastewater. According to the previous studies given in the literature (Cao et al., 2015), it was decided to use 0.25, 0.50 and 1.50 g L⁻¹ nanoparticle concentrations for nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ in this study. The experiments were carried out at a constant irradiation time (60 min) based on the study performed by Miranda-García et al. (2011), at a constant UV light power (120 W) based on the study performed by Guo et al. (2015), at a constant pH (7.00) based on the study performed by Van Doorslaer, Demeestere, Heynderickx, Van Langenhove, & Dewulf (2011) and at a constant temperature of 25 °C which was the original wastewater temperature for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations.

The photocatalytic removal efficiencies of selected micropollutants (PBT, CIP, NDMA, PFOA and AHTN) increased with the increasing nanoparticle concentrations (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) from 0.25 g L⁻¹ to 0.50 g L⁻¹, but, after the 0.50 g L⁻¹ nanoparticle concentration the photocatalytic removal efficiencies of the selected micropollutants (PBT, CIP, NDMA, PFOA and AHTN) decreased for the 1.50 g L⁻¹ nanoparticle concentration (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) at a constant irradiation time of 60 min at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Table 6.33). The increase in nanoparticle concentrations increases the amount of hydroxyl (OH[•]) radicals to degrade the micropollutants. Also, this increase supports more binding sites for the micropollutants to adsorb onto nanoparticles (Bethi, Sonawane, Bhanvase, & Gumfekar, 2016). However, increasing of nanoparticle concentrations cause turbidity in the wastewater. The penetration of UV light through turbidity becomes difficult and the photocatalytic removal efficiencies of the micropollutants decreases (Wang et al., 2017a). The optimum nano-TiO₂ and nano-CeO₂ concentrations were found as 0.50 g L⁻¹ and it was found higher removal efficiencies for PBT (81.8% for nano-TiO₂ and 83.4% for nano-CeO₂), CIP (82.0% for nano-TiO₂ and 84.4% for nano-CeO₂), NDMA (36.6% for nano-TiO₂ and 41.7% for nano-CeO₂) PFOA (42.7% for nano-TiO₂ and 50.1% for nano-CeO₂) and AHTN (78.1% for nano-TiO₂ and 83.3% for nano-CeO₂) than nano-SiO₂, nano-ZnO and graphene at the aforementioned experimental conditions (Table 6.33). The nano-SiO₂ ($P = 0.993$, $\alpha = 0.05$, $F = 0.25$), nano-ZnO ($P = 0.996$, $\alpha = 0.05$, $F = 0.23$) and graphene ($P = 0.990$, $\alpha = 0.05$, $F = 0.27$) showed no significant effect on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN with 0.50 g L⁻¹ nanoparticle concentration at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results. The ANOVA (one-way) test statistics results showed that 0.50 g L⁻¹ nano-TiO₂ ($P = 3.64 \times 10^{-6}$, $\alpha = 0.05$, $F = 22.27$) and nano-CeO₂ ($P = 4.22 \times 10^{-5}$, $\alpha = 0.05$, $F = 14.87$) had significant effects on the removals of PBT, CIP, NDMA, PFOA and AHTN at the aforementioned experimental conditions. If we compare the photocatalytic removal efficiencies of the micropollutants, NDMA and PFOA showed lower removal efficiencies than PBT, CIP and AHTN at the aforementioned

experimental conditions with nano-TiO₂ and nano-CeO₂. The main reason is the relationship between the operating pH value and the point of zero charge (pzc) values of the nanoparticles. This relationship was expressed in Subtitle of 6.2.2.5, furthermore, it was discussed in detail in Subtitle of 6.2.8.



Table 6.33 Effect of nanoparticle concentrations (0.25, 0.50 and 1.50 g L⁻¹) for nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ used in this study on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN (60 min constant irradiation time, 120 W constant UV light power, constant temperature of 25 °C and constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations) (n=3, mean ± SD)

Nanoparticle	Removal efficiency (%)														
	PBT			CIP			NDMA			PFOA			AHTN		
	0.25 g L ⁻¹	0.50 g L ⁻¹	1.50 g L ⁻¹	0.25 g L ⁻¹	0.50 g L ⁻¹	1.50 g L ⁻¹	0.25 g L ⁻¹	0.50 g L ⁻¹	1.50 g L ⁻¹	0.25 g L ⁻¹	0.50 g L ⁻¹	1.50 g L ⁻¹	0.25 g L ⁻¹	0.50 g L ⁻¹	1.50 g L ⁻¹
Nano-SiO₂	53.4±0.5	56.7±0.5	54.2±0.5	55.8±0.5	58.8±0.5	57.1±0.5	9.1±0.5	13.5±0.5	11.0±0.5	11.5±0.5	17.2±0.5	15.5±0.5	52.5±0.5	59.0±0.5	55.4±0.5
Nano-ZnO	60.5±0.5	66.6±0.5	62.1±0.5	66.8±0.5	72.7±0.5	70.5±0.5	13.6±0.5	20.0±0.5	17.3±0.5	15.0±0.5	22.3±0.5	19.3±0.5	60.0±0.5	68.8±0.5	65.3±0.5
Graphene	58.2±0.5	65.0±0.5	60.5±0.5	60.0±0.5	66.0±0.5	62.7±0.5	10.0±0.5	15.1±0.5	13.5±0.5	10.1±0.5	15.6±0.5	11.7±0.5	55.5±0.5	60.4±0.5	57.2±0.5
Nano-TiO₂	70.1±0.5	81.8±0.5	75.5±0.5	71.0±0.5	82.0±0.5	77.0±0.5	25.2±0.5	36.6±0.5	30.8±0.5	30.0±0.5	42.7±0.5	40.7±0.5	67.3±0.5	78.1±0.5	76.0±0.5
Nano-CeO₂	75.0±0.5	83.4±0.5	78.6±0.5	72.2±0.5	84.4±0.5	79.7±0.5	30.4±0.5	41.7±0.5	38.0±0.5	37.2±0.5	50.1±0.5	46.7±0.5	74.0±0.5	83.3±0.5	80.6±0.5

6.2.2.2 Effect of Irradiation Times (45, 60 and 90 min) for Nano-SiO₂, Nano-ZnO, Graphene, Nano-TiO₂ and Nano-CeO₂ Used in This Study on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

The effect of irradiation times (45, 60 and 90 min) were researched on the photocatalytic removals of PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group) from the raw hospital wastewater with nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ with the following starting conditions: at a constant nanoparticle concentration of 0.50 g L⁻¹ at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations (Table 6.34).

The photocatalytic removal efficiencies of selected micropollutants (PBT, CIP, NDMA, PFOA and AHTN) increased with the increasing irradiation time from 45 min to 90 min for all studied nanoparticles (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) (Table 6.34). However, the effect of irradiation time on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN for higher than 45 min (60 and 90 min) was not significant with nano-SiO₂ ($P = 0.752$, $\alpha = 0.05$, $F = 0.69$), nano-ZnO ($P = 0.542$, $\alpha = 0.05$, $F = 0.94$), graphene ($P = 0.668$, $\alpha = 0.05$, $F = 0.79$), nano-TiO₂ ($P = 0.327$, $\alpha = 0.05$, $F = 1.27$) and nano-CeO₂ ($P = 0.355$, $\alpha = 0.05$, $F = 1.22$) at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results. OH[•] radicals formation increases with the increasing irradiation time and increases the micropollutant removal efficiency. If the irradiation time continues longer than the optimum irradiation time, OH[•] radicals formation does not increase for the constant dose of nanoparticle (Miranda-García et al., 2011). The higher removal efficiencies for PBT (80.3% for nano-TiO₂ and 81.1% for nano-CeO₂), CIP (80.2% for nano-TiO₂ and 83.5% for nano-CeO₂), NDMA (33.9% for nano-TiO₂ and 40.0% for nano-CeO₂) PFOA (39.8% for nano-TiO₂ and 48.7% for nano-CeO₂) and AHTN (75.9% for nano-TiO₂ and 80.0% for nano-CeO₂) were achieved with nano-TiO₂ and nano-CeO₂ for the optimum irradiation time as 45 min at the aforementioned experimental conditions (Table 6.34). The ANOVA (one-way)

test statistics results showed that nano-TiO₂ ($P = 3.20 \times 10^{-6}$, $\alpha = 0.05$, $F = 22.74$) and nano-CeO₂ ($P = 5.00 \times 10^{-5}$, $\alpha = 0.05$, $F = 14.45$) had significant effects on the removals of PBT, CIP, NDMA, PFOA and AHTN for the optimum irradiation time of 45 min at the aforementioned experimental conditions. Lower photocatalytic removal efficiencies for NDMA and PFOA were observed in the comparison with PBT, CIP and AHTN at the aforementioned experimental conditions with nano-TiO₂ and nano-CeO₂. The main reason was the relationship between the operating pH value and the pzc values of the nanoparticles and the relationship was clarified in Subtitles of 6.2.2.5 and 6.2.8.



Table 6.34 Effect of irradiation times (45, 60 and 90 min) with nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ used in this study on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN (0.50 g L⁻¹ constant nanoparticle concentration at constant 120 W UV light power at constant temperature of 25 °C and at constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations) (*n*=3, mean ± SD)

Nanoparticle	Removal efficiency (%)														
	PBT			CIP			NDMA			PFOA			AHTN		
	45 min	60 min	90 min	45 min	60 min	90 min	45 min	60 min	90 min	45 min	60 min	90 min	45 min	60 min	90 min
Nano-SiO₂	55.1±0.5	56.7±0.5	57.7±0.5	56.0±0.5	58.8±0.5	60.0±0.5	11.8±0.5	13.5±0.5	15.0±0.5	15.2±0.5	18.2±0.5	19.6±0.5	56.0±0.5	59.0±0.5	61.6±0.5
Nano-ZnO	64.4±0.5	66.6±0.5	68.0±0.5	70.4±0.5	72.7±0.5	74.7±0.5	19.6±0.5	20.0±0.5	21.6±0.5	20.3±0.5	22.3±0.5	22.9±0.5	66.0±0.5	68.8±0.5	70.0±0.5
Graphene	64.5±0.5	65.0±0.5	66.0±0.5	66.0±0.5	66.0±0.5	67.0±0.5	13.0±0.5	15.1±0.5	16.8±0.5	15.0±0.5	15.6±0.5	17.0±0.5	57.3±0.5	60.4±0.5	62.2±0.5
Nano-TiO₂	80.3±0.5	81.8±0.5	83.0±0.5	80.2±0.5	82.0±0.5	84.8±0.5	33.9±0.5	36.6±0.5	38.7±0.5	39.8±0.5	42.7±0.5	44.9±0.5	75.9±0.5	78.1±0.5	80.2±0.5
Nano-CeO₂	81.1±0.5	83.4±0.5	85.1±0.5	83.5±0.5	84.4±0.5	85.0±0.5	40.0±0.5	41.7±0.5	43.3±0.5	48.7±0.5	50.1±0.5	52.7±0.5	80.0±0.5	83.3±0.5	84.1±0.5

6.2.2.3 Effect of UV Light Powers (120, 210 and 300 W) with Different Nanoparticle Types (Nano-SiO₂, Nano-ZnO, Graphene, Nano-TiO₂ and Nano-CeO₂) Used in This Study on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

The effect of UV light powers (120, 210 and 300 W) with different nanoparticle types (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) were determined on the photocatalytic removals of PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group) from the raw hospital wastewater with the following starting conditions: at a constant nanoparticle concentration of 0.50 g L⁻¹ at a constant irradiation time of 45 min at a constant temperature of 25 °C and at a constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations (Table 6.35).

The photocatalytic removals of all selected micropollutants (PBT, CIP, NDMA, PFOA and AHTN) increased when the UV light power was increased from 120 W to 210 W with nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ (Table 6.35). However, when the UV light power was increased to 300 W the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN decreased at the aforementioned experimental conditions (Table 6.35). The concentrations of hydroxyl (OH[•]) radicals increased at increased UV light powers and they increased the photocatalytic removal efficiencies of the micropollutants. However, at too high UV light powers, the amount of photons absorbed by the nanoparticle could not be increased for the constant nanoparticle dose and sufficient hydroxyl (OH[•]) radicals could not be formed and causes lower photocatalytic removal efficiencies (Bai & Acharya, 2016). The optimum UV light power was found as 210 W and the highest photocatalytic removal efficiencies were observed for the nano-TiO₂ and nano-CeO₂ for PBT (88.2% for nano-TiO₂ and 90.0% for nano-CeO₂), CIP (86.2% for nano-TiO₂ and 88.5% for nano-CeO₂), NDMA (40.5% for nano-TiO₂ and 47.8% for nano-CeO₂) PFOA (48.8% for nano-TiO₂ and 53.4% for nano-CeO₂) and AHTN (80.2% for nano-TiO₂ and 86.3% for nano-CeO₂) at the aforementioned experimental conditions

(Table 6.35). According to the ANOVA (one-way) test statistics results nano-SiO₂ ($P = 0.998$, $\alpha = 0.05$, $F = 0.19$), nano-ZnO ($P = 0.997$, $\alpha = 0.05$, $F = 0.21$) and graphene ($P = 0.997$, $\alpha = 0.05$, $F = 0.21$) showed no significant effect on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN for all studied UV light powers at the aforementioned experimental conditions. The ANOVA (one-way) test statistics results showed that the increasing UV light power increased the micropollutant photocatalytic removals significantly up to 210 W UV light power with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions ($P = 1.30 \times 10^{-5}$, $\alpha = 0.05$, $F = 18.18$ for nano-TiO₂ and $P = 0.0001$, $\alpha = 0.05$, $F = 12.77$ for nano-CeO₂). Lower removal efficiencies of NDMA and PFOA were related to the operating pH value, therefore, PBT, CIP and AHTN showed better photocatalytic removal efficiencies at the aforementioned experimental conditions with nano-TiO₂ and nano-CeO₂. The effect of pH on the photocatalytic removals of the micropollutants was described in Subtitles of 6.2.2.5 and 6.2.8.

Table 6.35 Effect of UV light powers (120, 210 and 300 W) with different nanoparticle types (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN (0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 25 °C constant temperature and constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations) (*n*=3, mean ± SD)

Nanoparticle	Removal efficiency (%)														
	PBT			CIP			NDMA			PFOA			AHTN		
	120 W	210 W	300 W	120 W	210 W	300 W	120 W	210 W	300 W	120 W	210 W	300 W	120 W	210 W	300 W
Nano-SiO₂	55.1±0.5	59.2±0.5	56.0±0.5	56.0±0.5	61.1±0.5	59.2±0.5	11.8±0.5	14.5±0.5	14.0±0.5	15.2±0.5	20.0±0.5	18.3±0.5	56.0±0.5	58.0±0.5	56.0±0.5
Nano-ZnO	64.4±0.5	70.9±0.5	65.8±0.5	70.4±0.5	76.6±0.5	72.2±0.5	19.6±0.5	28.3±0.5	20.5±0.5	20.3±0.5	28.2±0.5	25.3±0.5	66.0±0.5	72.5±0.5	70.1±0.5
Graphene	64.5±0.5	70.0±0.5	66.0±0.5	66.0±0.5	74.4±0.5	70.3±0.5	13.0±0.5	22.6±0.5	20.9±0.5	15.0±0.5	22.5±0.5	19.8±0.5	57.3±0.5	64.4±0.5	60.4±0.5
Nano-TiO₂	80.3±0.5	88.2±0.5	85.4±0.5	80.2±0.5	86.2±0.5	83.6±0.5	33.9±0.5	40.5±0.5	38.0±0.5	39.8±0.5	48.8±0.5	45.4±0.5	75.9±0.5	80.2±0.5	78.0±0.5
Nano-CeO₂	81.1±0.5	90.0±0.5	86.4±0.5	83.5±0.5	88.5±0.5	85.2±0.5	40.0±0.5	47.8±0.5	44.4±0.5	48.7±0.5	53.4±0.5	50.3±0.5	80.0±0.5	86.3±0.5	82.7±0.5

6.2.2.4 Effect of Temperatures (25, 35 and 45 °C) with Different Nanoparticle Types (Nano-SiO₂, Nano-ZnO, Graphene, Nano-TiO₂ and Nano-CeO₂) Used in This Study on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

The effect of temperatures (25, 35 and 45 °C) were examined on the photocatalytic removals of PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group) from the raw hospital wastewater with nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ with the following starting conditions: at a constant nanoparticle concentration of 0.50 g L⁻¹ at a constant irradiation time of 45 min at a constant UV light power of 210 W and at a constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations (Table 6.36).

The photocatalytic removals of all selected micropollutants (PBT, CIP, NDMA, PFOA and AHTN) increased with the increasing temperatures from 25 °C to 45 °C with nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions (Table 6.36). Higher temperature provides higher electron transfers in valance band of the nanoparticle to higher energy levels and increases the amount of hydroxyl radicals (OH[•]) to degrade micropollutants (Chatila et al., 2016). The optimum wastewater temperature was found as 45 °C and the highest photocatalytic removal efficiencies calculated for nano-TiO₂ and nano-CeO₂ for PBT (92.2% for nano-TiO₂ and 93.6% for nano-CeO₂), CIP (93.4% for nano-TiO₂ and 96.6% for nano-CeO₂), NDMA (47.6% for nano-TiO₂ and 53.7% for nano-CeO₂) PFOA (54.8% for nano-TiO₂ and 60.4% for nano-CeO₂) and AHTN (85.4% for nano-TiO₂ and 90.0% for nano-CeO₂) at the aforementioned experimental conditions (Table 6.36). According to the ANOVA (one-way) test statistics results nano-SiO₂ (P = 0.503, α = 0.05, F = 0.99), nano-ZnO (P = 0.818, α = 0.05, F = 0.61) and graphene (P = 0.698, α = 0.05, F = 0.75) showed no significant effect on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN for all studied temperatures (25, 35 and 45 °C) at the aforementioned experimental conditions. The ANOVA (one-way) test statistics results showed that the increasing temperature

increased the micropollutants photocatalytic removals significantly with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions ($P = 4.40 \times 10^{-5}$, $\alpha = 0.05$, $F = 14.78$ for nano-TiO₂ and $P = 0.00025$, $\alpha = 0.05$, $F = 10.78$ for nano-CeO₂). NDMA and PFOA showed lower photocatalytic removal efficiencies than PBT, CIP and AHTN at the aforementioned experimental conditions with nano-TiO₂ and nano-CeO₂. The main reason was the relationship between the operating pH value and pzc values of the nanoparticles and it was explained in Subtitles of 6.2.2.5 and 6.2.8.



Table 6.36 Effect of temperatures (25, 35 and 45 °C) with different nanoparticle types (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN (0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power and constant pH of 7.00 for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations) (*n*=3, mean ± SD)

Nanoparticle	Removal efficiency (%)														
	PBT			CIP			NDMA			PFOA			AHTN		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Nano-SiO₂	59.2±0.5	60.0±0.5	62.5±0.5	61.1±0.5	62.8±0.5	63.8±0.5	14.5±0.5	15.3±0.5	16.0±0.5	20.0±0.5	21.5±0.5	22.6±0.5	58.0±0.5	60.1±0.5	62.2±0.5
Nano-ZnO	70.9±0.5	72.8±0.5	73.6±0.5	76.6±0.5	80.7±0.5	81.1±0.5	28.3±0.5	29.8±0.5	30.2±0.5	28.2±0.5	30.9±0.5	32.0±0.5	72.5±0.5	75.5±0.5	77.8±0.5
Graphene	70.0±0.5	71.0±0.5	73.2±0.5	74.4±0.5	76.0±0.5	77.3±0.5	22.6±0.5	25.7±0.5	26.8±0.5	22.5±0.5	24.0±0.5	26.0±0.5	64.4±0.5	66.0±0.5	68.0±0.5
Nano-TiO₂	88.2±0.5	90.4±0.5	92.2±0.5	86.2±0.5	90.4±0.5	93.4±0.5	40.5±0.5	44.6±0.5	47.6±0.5	48.8±0.5	51.5±0.5	54.8±0.5	80.2±0.5	83.7±0.5	85.4±0.5
Nano-CeO₂	90.0±0.5	92.5±0.5	93.6±0.5	88.5±0.5	93.3±0.5	96.6±0.5	47.8±0.5	50.0±0.5	53.7±0.5	53.4±0.5	57.7±0.5	60.4±0.5	86.3±0.5	88.8±0.5	90.0±0.5

6.2.2.5 Effect of pHs (4.00, 7.00 and 8.50) with Different Nanoparticle Types (Nano-SiO₂, Nano-ZnO, Graphene, Nano-TiO₂ and Nano-CeO₂) Used in This Study on the Photocatalytic Removals of Selected Micropollutants (PBT, CIP, NDMA, PFOA and AHTN)

The effect of pHs (4.00, 7.00 and 8.50) with different nanoparticle types (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) used in this study were examined on the photocatalytic removals of PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group) from the raw hospital wastewater with the following starting conditions: at a constant nanoparticle concentration of 0.50 g L⁻¹ at a constant irradiation time of 45 min at a constant UV light power of 210 W and at a constant temperature of 45 °C for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations (Table 6.37).

The higher NDMA and PFOA photocatalytic removals were observed at pH 4.00 with nano-TiO₂ (90.1% for NDMA and 88.2% for PFOA) and nano-CeO₂ (92.0% for NDMA and 90.5% for PFOA) at the aforementioned experimental conditions (Table 6.37). The higher PBT and CIP photocatalytic removals were achieved at pH 7.00 with nano-TiO₂ (92.2% for PBT and 93.4% for CIP) and nano-CeO₂ (93.6% for PBT and 96.6% for CIP) at the aforementioned experimental conditions (Table 6.37). The higher AHTN photocatalytic removals were determined at pH 8.50 with nano-TiO₂ (89.0%) and nano-CeO₂ (94.6%) at the aforementioned experimental conditions (Table 6.37).

The surface of the nano-TiO₂ and nano-CeO₂ became positively (+) charged under acidic (pH = 4.00) conditions because their point of zero charge (pzc) values were 6.25 and 5.60 in water, respectively (Wang et al., 2017a). NDMA and PFOA were in their anionic forms (–) at pH 4.00 because their pzc values (3.52 for NDMA and 2.80 for PFOA) were lower than the acidic pH (4.00) value. The adsorption of the anionic negatively charged (–) micropollutants (NDMA and PFOA) on the positively (+) charged nanoparticle surfaces (nano-TiO₂ and nano-CeO₂) were accelerated due to

the electrostatic force between the micropollutants and the nanoparticles. The surface of the nano-TiO₂ and nano-CeO₂ became negatively (–) charged under neutral (pH = 7.00) conditions. PBT and CIP were in their cationic forms (+) at pH 7.00 because their pzc values (8.00 for PBT and 8.80 for CIP) were higher than the neutral pH (7.00) value. The adsorption of the cationic (+) micropollutants (PBT and CIP) on the negatively (–) charged nanoparticle surfaces (nano-TiO₂ and nano-CeO₂) were accelerated due to the electrostatic force between the micropollutants and the nanoparticles. Although the pzc value of AHTN is not available in the literature, it can be concluded that the photocatalytic removal efficiency of AHTN increased at alkaline (pH = 8.50) conditions comparing with the acidic (pH = 4.00) and neutral (pH = 7.00) conditions due to the more production of the hydroxyl (OH•) radicals at higher pH values. The ANOVA (one-way) test statistics results showed that effect of nano-TiO₂ at a pH of 4.00 ($P = 0.015$, $\alpha = 0.05$, $F = 4.02$ for NDMA and PFOA), at a pH of 7.00 ($P = 4.40 \times 10^{-5}$, $\alpha = 0.05$, $F = 14.78$ for PBT and CIP) and at a pH of 8.50 ($P = 0.00014$, $\alpha = 0.05$, $F = 12.05$ for AHTN) and effect of nano-CeO₂ at a pH of 4.00 ($P = 0.019$, $\alpha = 0.05$, $F = 3.76$ for NDMA and PFOA), at a pH of 7.00 ($P = 0.00025$, $\alpha = 0.05$, $F = 10.78$ for PBT and CIP) and at a pH of 8.50 ($P = 0.00173$, $\alpha = 0.05$, $F = 7.36$ for AHTN) on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN found to be significant at the aforementioned experimental conditions.

Table 6.37 Effect of pHs (4.00, 7.00 and 8.50) with different nanoparticle types (nano-SiO₂, nano-ZnO, graphene, nano-TiO₂ and nano-CeO₂) used in this study on the photocatalytic removals of PBT, CIP, NDMA, PFOA and AHTN (0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power and 45 °C constant temperature for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations) (*n*=3, mean ± SD)

Nanoparticle	Removal efficiency (%)														
	PBT			CIP			NDMA			PFOA			AHTN		
	pH=4.00	pH=7.00	pH=8.50	pH=4.00	pH=7.00	pH=8.50	pH=4.00	pH=7.00	pH=8.50	pH=4.00	pH=7.00	pH=8.50	pH=4.00	pH=7.00	pH=8.50
Nano-SiO₂	60.0±0.5	62.5±0.5	58.6±0.5	60.2±0.5	63.8±0.5	65.7±0.5	12.0±0.5	16.0±0.5	18.3±0.5	13.5±0.5	22.6±0.5	24.7±0.5	55.0±0.5	62.2±0.5	65.0±0.5
Nano-ZnO	70.5±0.5	73.6±0.5	74.0±0.5	78.8±0.5	81.1±0.5	82.9±0.5	24.4±0.5	30.2±0.5	35.7±0.5	25.9±0.5	32.0±0.5	37.0±0.5	73.2±0.5	77.8±0.5	82.6±0.5
Graphene	72.1±0.5	73.2±0.5	70.5±0.5	75.0±0.5	77.3±0.5	82.7±0.5	20.6±0.5	26.8±0.5	30.2±0.5	20.6±0.5	26.0±0.5	33.3±0.5	64.4±0.5	68.0±0.5	71.0±0.5
Nano-TiO₂	85.3±0.5	92.2±0.5	87.0±0.5	79.9±0.5	93.4±0.5	94.0±0.5	90.1±0.5	47.6±0.5	52.7±0.5	88.2±0.5	54.8±0.5	60.6±0.5	80.6±0.5	85.4±0.5	89.0±0.5
Nano-CeO₂	86.4±0.5	93.6±0.5	89.4±0.5	81.0±0.5	96.6±0.5	96.0±0.5	92.0±0.5	53.7±0.5	65.3±0.5	90.5±0.5	60.4±0.5	68.3±0.5	84.7±0.5	90.0±0.5	94.6±0.5

6.2.3 Effect of Adsorption and Photolysis on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

6.2.3.1 Effect of Adsorption on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

During the adsorption studies of all studied micropollutants on the surface of nano-TiO₂, the maximum removal efficiencies of α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, GFZ, TCS, PFOS, IBU, CIP and NDMA via adsorption were 10.0%, 9.6%, 9.0%, 8.6%, 8.4%, 7.9%, 7.7%, 7.6%, 7.2%, 6.7%, 2.6% and 1.6%, respectively without UV light and sunlight under dark conditions at a constant nano-TiO₂ concentration of 0.50 g L⁻¹ at a constant stirring time of 60 min at a constant temperature of 25 °C and at a constant pH of 7.00 (Table 6.38).

Table 6.38 Effect of adsorption on the photocatalytic removals of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants without UV light and sunlight under dark conditions at a constant nano-TiO₂ and nano-CeO₂ concentrations of 0.50 g L⁻¹ at a constant stirring time of 60 min at a constant temperature of 25 °C and at a constant pH of 7.00 ($n=3$, mean $\pm$ SD)

Micropollutant	Solubility in water, at 25 °C (g L ⁻¹)	log K _{ow} (unitless)	Adsorption removal efficiency (%)	
			nano-TiO ₂	nano-CeO ₂
α-HBCDD	2.09 $\times 10^{-5}$	7.74	10.0 $\pm$ 0.5	14.4 $\pm$ 0.5
PBEB	2.90 $\times 10^{-7}$	7.48	9.6 $\pm$ 0.5	13.8 $\pm$ 0.5
PBT	9.35 $\times 10^{-7}$	6.99	9.0 $\pm$ 0.5	13.2 $\pm$ 0.5
TBBPA	7.65 $\times 10^{-6}$	5.90	8.6 $\pm$ 0.5	11.5 $\pm$ 0.5
AHTN	1.25 $\times 10^{-3}$	5.70	8.4 $\pm$ 0.5	11.0 $\pm$ 0.5
PFOA	4.81 $\times 10^{-4}$	4.81	7.9 $\pm$ 0.5	9.8 $\pm$ 0.5
GFZ	4.964 $\times 10^{-3}$	4.77	7.7 $\pm$ 0.5	9.7 $\pm$ 0.5
TCS	4.621 $\times 10^{-3}$	4.76	7.6 $\pm$ 0.5	9.1 $\pm$ 0.5
PFOS	0.104 $\times 10^{-3}$	4.49	7.2 $\pm$ 0.5	8.9 $\pm$ 0.5
IBU	4.105 $\times 10^{-4}$	3.79	6.7 $\pm$ 0.5	7.3 $\pm$ 0.5
CIP	1.148 $\times 10^{-4}$	0.28	2.6 $\pm$ 0.5	3.25 $\pm$ 0.5
NDMA	4.104 $\times 10^{-5}$	-0.57	1.6 $\pm$ 0.5	1.9 $\pm$ 0.5

The adsorption removal percentages of α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, GFZ, TCS, PFOS, IBU, CIP and NDMA were 14.4%, 13.8%, 13.2%, 11.5%, 11.0%, 9.8%, 9.7%, 9.1%, 8.9%, 7.3%, 3.25% and 1.9%, respectively on the surface of nano-CeO₂ without UV light and sunlight under dark conditions at a constant nano-CeO₂ concentration of 0.50 g L⁻¹ at a constant stirring time of 60 min at a constant temperature of 25 °C and at a constant pH of 7.00 (Table 6.38).

It can be said that the adsorption of all studied micropollutants on the nano-TiO₂ and nano-CeO₂ without UV light and sunlight under dark conditions was not the primary mechanism for their removals according to the ANOVA (one-way) test statistics results ($P = 0.109$, $\alpha = 0.05$, $F = 2.79$ for nano-TiO₂ and nano-CeO₂). The micropollutants having higher adsorption removal efficiencies (α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, IBU and AHTN) than the other micropollutants (CIP and NDMA) may be explained by comparing their physicochemical properties. α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, IBU and AHTN have high adsorption capacities and accepted as hydrophobic micropollutants due to their low water solubility and high hydrophobicity (log K_{ow})

values (Table 6.38). However, CIP and NDMA have lower adsorption capacities and accepted as hydrophilic micropollutants because of their high water solubility and low hydrophobicity ($\log K_{ow}$) values (Table 6.38). It has been found that the hydrophobic micropollutants with lower water solubilities and higher hydrophobicities have greater adsorption capacities on the nanoparticle surfaces. The hydrophobic micropollutants with lower water solubilities and higher hydrophobicities are expected to have greater affinity for adsorption on the nanoparticle surface and are more readily oxidized (Alvarez-Corena et al., 2016).

The ANOVA (one-way) test statistics results showed that there was a linear relationship between adsorption removals of all studied micropollutants on nanoparticle surfaces and the hydrophobicity ($\log K_{ow}$) values ($R^2 = 0.98$ for nano-TiO₂ and $R^2 = 0.99$ for nano-CeO₂) without UV light and sunlight under dark conditions at the aforementioned experimental conditions. Also, the relationship between adsorption removals of all studied micropollutants on nanoparticle surfaces and the hydrophobicity ($\log K_{ow}$) values was found to be significant in the raw hospital wastewater without UV light and sunlight under dark conditions at the aforementioned experimental conditions ($P = 0.024$, $\alpha = 0.05$, $F = 5.91$ for nano-TiO₂ and $P = 0.002$, $\alpha = 0.05$, $F = 12.85$ for nano-CeO₂).

6.2.3.2 Effect of Photolysis on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

The experiments were also performed with the direct photolysis of all studied micropollutants in the absence of nano-TiO₂ and nano-CeO₂ at a constant irradiation time of 60 min at a constant UV light power of 210 W at a constant temperature of 25 °C and at a constant pH of 7.00. The removal efficiencies of α -HBCDD, TBBPA, PBEB, PBT, TCS, CIP, PFOS, PFOA, NDMA, GFZ, IBU and AHTN were calculated as 6.5%, 4.8%, 6.2%, 5.9%, 5.6%, 3.0%, 5.5%, 5.0%, 4.5%, 5.3%, 4.4% and 4.7%, respectively via photolysis without nanoparticle addition at a constant

irradiation time of 60 min at a constant UV light power of 210 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Table 6.39).

Table 6.39 Effect of photolysis on the photocatalytic removals of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants without nanoparticle addition at a constant irradiation time of 60 min at a constant UV light power of 210 W at a constant temperature of 25 °C and at a constant pH of 7.00 ($n=3$, mean $\pm$ SD)

Micropollutant	Photolysis removal efficiency (%)	Micropollutant	Photolysis removal efficiency (%)
α-HBCDD	6.5 $\pm$ 0.5	NDMA	4.5 $\pm$ 0.5
TBBPA	4.8 $\pm$ 0.5	TCS	5.6 $\pm$ 0.5
PBEB	6.2 $\pm$ 0.5	CIP	3.0 $\pm$ 0.5
PBT	5.9 $\pm$ 0.5	GFZ	5.3 $\pm$ 0.5
PFOS	5.5 $\pm$ 0.5	IBU	4.4 $\pm$ 0.5
PFOA	5.0 $\pm$ 0.5	AHTN	4.7 $\pm$ 0.5

For alone UV light exposure, it was found that the all studied micropollutants in the raw hospital wastewater were not easily photolyzed at 210 W UV light power. The main removal of all studied micropollutants were not the photolysis in this study. During photolysis only the photons were generated during UV light irradiation instead of generation of OH[•] radicals. The low removals of the micropollutants in photolysis were expected to be achieved mostly by the low photons from UV light irradiation (Son, Ko, & Zoh, 2009). The ANOVA (one-way) test statistics results showed that the photolysis had no significant effect on the removals of all studied micropollutants in the raw hospital wastewater in the absence of nano-TiO₂ and nano-CeO₂ at a constant irradiation time of 60 min at a constant UV light power of 210 W at a constant temperature of 25 °C and at a constant pH of 7.00 ($P = 0.585$, $\alpha = 0.05$, $F = 0.31$).

Low removal efficiencies were obtained for the photolysis of TCS and GFZ by Carlson, Stefan, Parnis, & Metcalfe (2015). TCS had $40 \times 10^{-5} \text{ sn}^{-1}$ pseudo-first order photolysis rate constant while the photolysis rate of GFZ was measured as zero at pH 7.2 for 250 $\mu\text{g L}^{-1}$ initial TCS and GFZ concentrations at 21 ± 1 °C for 0.15 m W cm^{-2} UV light intensity (Carlson et al., 2015). Stamatis, Antonopoulou, Hela, & Konstantinou (2014) also found that the removal of 1.0 mg L^{-1} TCS with adsorption

and photolysis was low (1.8% and 4.9%, respectively) with 550 mg L⁻¹ nano-TiO₂ at an irradiation intensity of 700 W m⁻² and at a pH of 6.60 (Stamatis et al., 2014). Fang, Li, Yao, Liang, & An (2017) indicated that the direct photolysis of AHTN was negligible (first order rate constant, $k_1 = 0.0017 \text{ min}^{-1}$) in the comparison with the photocatalytic degradation (first order rate constant, $k_1 = 0.0867 \text{ min}^{-1}$) with 2 g L⁻¹ nano-TiO₂ concentration for an initial AHTN concentration of 50 µ under 300 W UV light power for 20 min (Fang et al., 2017).

6.2.4 Effects of Nano-TiO₂ and Nano-CeO₂ Concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹) on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

The effect of nano-TiO₂ concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹) on the photocatalytic removals of all studied micropollutants were investigated at a constant irradiation time of 15 min at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Figure 6.35). These experimental conditions were obtained from the preliminary studies. Firstly, the maximum photocatalytic removals were obtained as 58%, 60%, 57%, 56%, 24%, 20%, 46%, 42%, 48%, 42%, 15% and 55% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively with 0.50 g L⁻¹ nano-TiO₂ at the aforementioned experimental conditions (Figure 6.35.a, b, c, d, e).

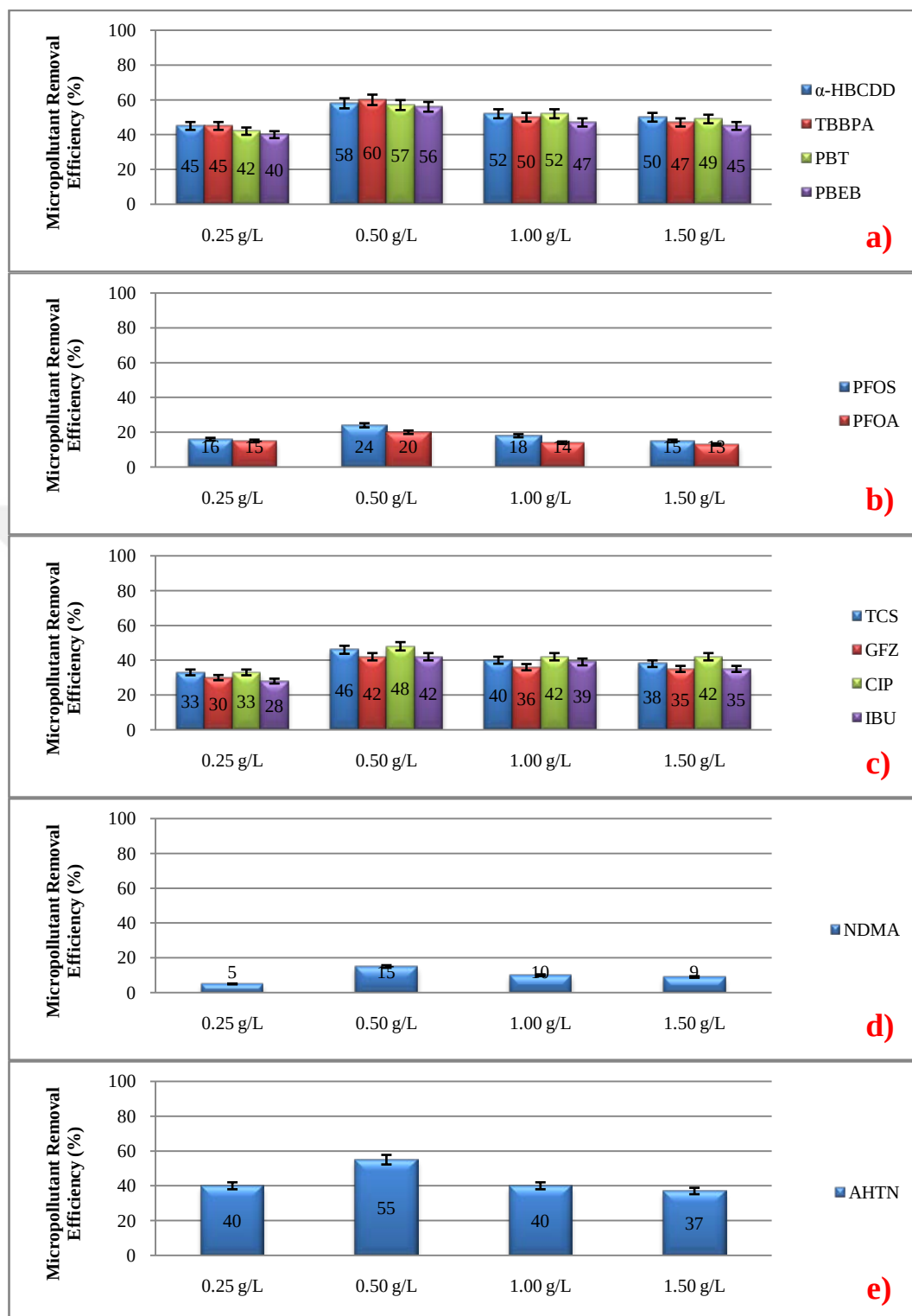


Figure 6.35 Effect of nano-TiO₂ concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹) on the photocatalytic removals of all studied micropollutants at constant irradiation time of 15 min at constant UV light power of 120 W at constant temperature of 25 °C and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

Thereafter, the effect of nano-CeO₂ concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹) on the photocatalytic removals of all studied micropollutants were investigated at a constant irradiation time of 15 min at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Figure 6.36). The optimum photocatalytic removals were found as 62%, 63%, 61%, 60%, 29%, 25%, 50%, 46%, 50%, 52%, 28% and 68% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively with 0.50 g L⁻¹ nano-CeO₂ at the aforementioned experimental conditions (Figure 6.36.a, b, c, d, e).



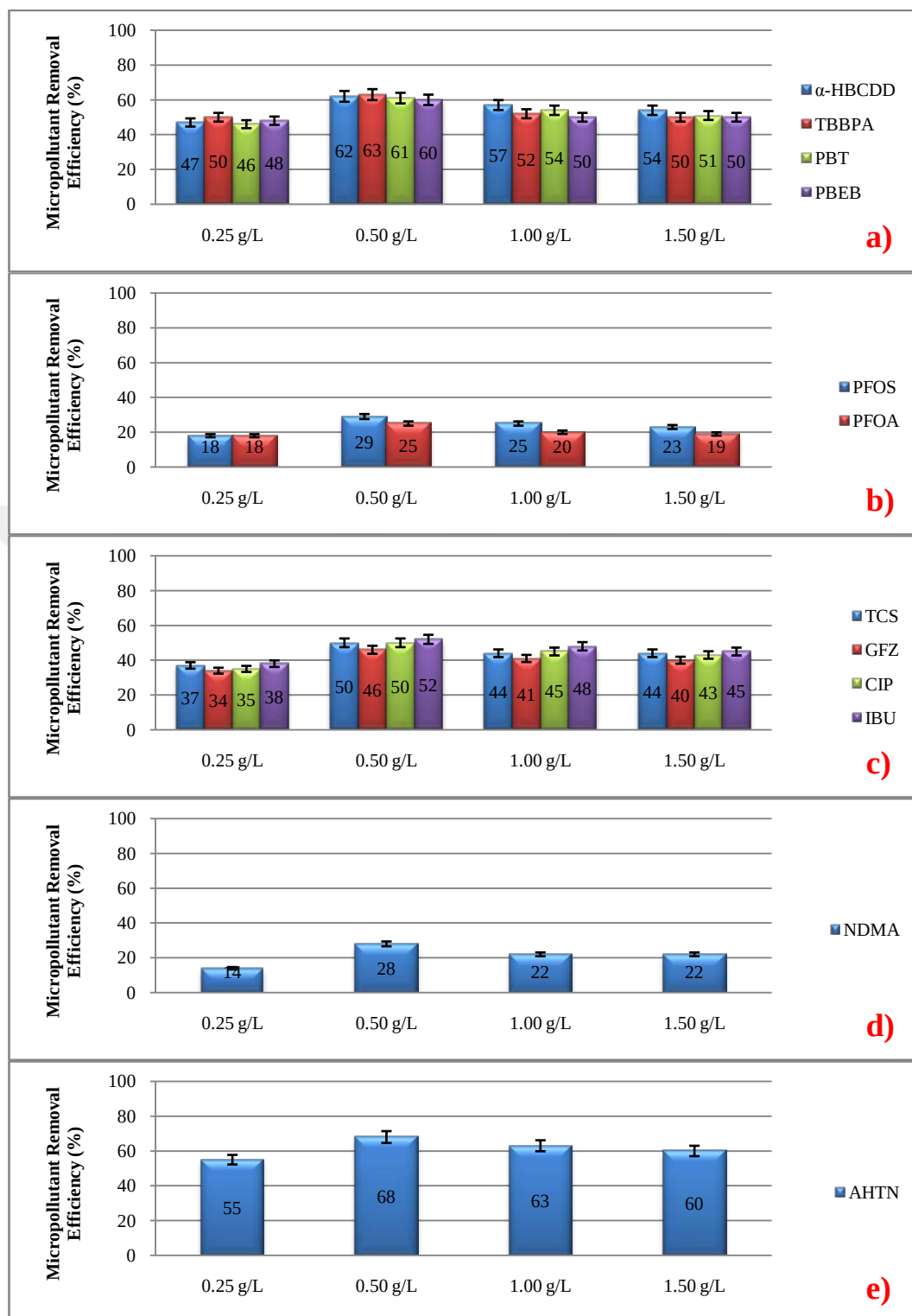


Figure 6.36 Effect of nano-CeO₂ concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹) on the photocatalytic removals of all studied micropollutants at constant irradiation time of 15 min at constant UV light power of 120 W at constant temperature of 25 °C and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

Increasing the amount of photocatalysts (nano-TiO₂ and nano-CeO₂) from 0.25 to 0.50 g L⁻¹ resulted in an increase in the photocatalytic removal efficiencies of all studied micropollutants from the raw hospital wastewater (Figure 6.35 and 6.36). The nano-TiO₂ and nano-CeO₂ concentrations higher than 0.50 g L⁻¹ were slightly decreased the photocatalytic removals of all studied micropollutants (Figure 6.35 and 6.36). Among 0.25, 0.50, 1.00 and 1.50 g L⁻¹ nanoparticle concentrations, 0.50 g L⁻¹ nano-TiO₂ and nano-CeO₂ concentrations were determined as the optimum nanoparticle concentrations to achieve the maximum photocatalytic removals of all studied micropollutants at the aforementioned experimental conditions in this study (Figure 6.35 and 6.36).

During the photocatalytic degradation of all studied micropollutants, semiconductor nano-TiO₂ and nano-CeO₂ were excited by photons (hν) and produced pairs of electrons (e⁻_{CB}) and holes (h⁺_{VB}) in the conduction and valance bands, respectively. The photogenerated electrons (e⁻_{CB}) and holes (h⁺_{VB}) were able to react with O₂ and OH⁻ to generate hydroxyl radicals (OH[•]). OH[•] radicals tended to attack the carbon atoms with the highest electron density (Yu, Kwong, Luo, & Cai, 2006). The increase in nano-TiO₂ and nano-CeO₂ concentrations from 0.25 g L⁻¹ to 0.50 g L⁻¹ provided more binding sites for the micropollutants to adsorb onto the nanoparticle surfaces. At low nanoparticle concentrations, the low photocatalytic removals were obtained for all studied micropollutants since the active sites on the surface of the nanoparticles were low and partially exposed to the micropollutants. With excessive nano-TiO₂ and nano-CeO₂ concentrations (1.00 and 1.50 g L⁻¹), it has been suggested that the nanoparticles in the centre of an irradiating vessel may be shielded from the incident UV by other nano-TiO₂ and nano-CeO₂ particles, and thus particles in the centre do not contribute significantly to the production of electron (e⁻_{CB}) – hole (h⁺_{VB}) pairs (Bethi et al., 2016). At higher nanoparticle concentrations (1.00 and 1.50 g L⁻¹) the contacting sites on the surface of the nanoparticles were not fully activated to bind to the micropollutants. Therefore, the photocatalytic removals decreased slightly in this study. The optimum concentrations of the nano-TiO₂ (0.50 g L⁻¹) and nano-CeO₂ (0.50 g L⁻¹) were useful both from the economic and the photocatalytic efficiency standpoints. Because an increase in opacity and light

scattering of the nanoparticles occurred at high concentrations, leading to the decreased passage of UV irradiation through the suspension (Bethi et al., 2016). By increasing the nanoparticle concentration to an optimum level, the surface area of the nanoparticle was increased, leading to an increase in the production of reactive species ($\text{OH}^\bullet$ radicals). However, more nanoparticle concentrations would also induce greater aggregation of the nanoparticle and decrease the total active surface area, thereby leading to a reduction in the photocatalytic removal efficiency. Wang et al. (2017a) also concluded that too high nanoparticle concentrations would induce nanoparticle aggregation to hinder the contact between micropollutants and the active surface sites of the nanoparticles, or make the reaction solution more turbid and the penetration of UV irradiation weaker, inducing a slight decrease in the photocatalytic removal efficiencies (Wang et al., 2017a).

The ANOVA (one-way) test statistics results showed that the increasing nanoparticle concentrations from 0.25 to 0.50 g L^{-1} had a significant effect on the photocatalytic removals of all studied micropollutants at the aforementioned experimental conditions ($P = 0.044$, $\alpha = 0.05$, $F = 4.56$ for nano- TiO_2 and $P = 0.038$, $\alpha = 0.05$, $F = 4.85$ for nano- CeO_2). Any further increase in the nano- TiO_2 and nano- CeO_2 concentrations (from 0.50 to 1.5 g L^{-1}) did not have a significant effect on the photocatalytic removals of all studied micropollutants at the aforementioned experimental conditions ($P = 0.729$, $\alpha = 0.05$, $F = 0.12$ for nano- TiO_2 and $P = 0.769$, $\alpha = 0.05$, $F = 0.09$ for nano- CeO_2).

Li et al. (2012) investigated the photocatalytic degradation of CIP with nano- TiO_2 under simulated solar light irradiation. The effect of nano- TiO_2 concentrations (0.10, 0.50, 1.00, and 1.50 g L^{-1}) on CIP removal were determined at 800 W UV light power at a temperature of 23 ± 2 °C for 150 min irradiation time. Maximum CIP removal efficiency was determined as 96% with 0.50 g L^{-1} nano- TiO_2 concentration at a pH of 9.00 for 0.030 mmol L^{-1} initial CIP concentration in a synthetic wastewater (Li et al., 2012). Sansotera et al. (2014) studied the photocatalytic degradation of PFOA with 0.66 g L^{-1} nano- TiO_2 and obtained 32% of PFOA removal efficiency under 95 W m^{-2} UV exposure for 4 h at 30 ± 5 °C for an initial PFOA

concentration of 0.004 M in a synthetic wastewater. Increasing the nano-TiO₂ concentration from 0.66 g L⁻¹ to 1.00 g L⁻¹ under the same experimental conditions leads to worse results, since in these conditions the phenomenon of scattering was increased, affecting the nanoparticle performance (Sansotera et al., 2014). Alvarez-Corena (2015) studied the effect of nano-TiO₂ concentrations (0.10, 0.50, 1.00, 1.50, 2.00 and 2.50 g L⁻¹) on the photocatalytic removal of GFZ for 30 min at a pH of 5.00 for an initial GFZ concentration of 2 mg L⁻¹ at 100W UV light power from the synthetic wastewater. The increase in nano-TiO₂ concentration from 0.10 g L⁻¹ to 1.50 g L⁻¹ affected the photocatalytic removal of GFZ (42%) positively because greater surface area and more active sites became available for nano-TiO₂. However, an increase in TiO₂ concentration from 1.50 g L⁻¹ to 2.50 g L⁻¹ decreased the ability of the UV irradiation to reach the nano-TiO₂ surface because a portion of the UV light was reduced and scattered by the TiO₂ nanoparticles (Alvarez-Corena, 2015). Alvarez-Corena et al. (2016) concluded that the optimum nano-TiO₂ concentration was found as 1.5 g L⁻¹ for the highest photocatalytic removal efficiency of NDMA (39%) among 0.10, 0.50, 1.00, 1.50, 2.00 and 2.50 g L⁻¹ nano-TiO₂ concentrations for 30 min at 20 ± 2 °C at a pH of 5.00 under 100 W UV light power for an initial NDMA concentration of 2 mg L⁻¹ from the synthetic wastewater (Alvarez-Corena et al., 2016). The photocatalytic degradation of IBU (initial concentration of 213 mg L⁻¹) in a pharmaceutical industry wastewater was researched using different concentrations of nano-TiO₂ (0.50, 1.00, 2.00, 2.50, 3.00 and 4.00 g L⁻¹) for 240 min at 10 W UV light power at 25 °C and at a pH of 5.30. The photocatalytic removal of IBU increased with the increasing nano-TiO₂ concentrations up to 2.50 g L⁻¹, moreover, IBU was below the detection limit with 2.50 g L⁻¹ nano-TiO₂ concentration for 240 min at 10 W UV light power at 25 °C and at a pH of 5.30. It can be concluded that the photocatalytic removal efficiency did not increase after 2.50 g L⁻¹ nano-TiO₂ concentration, mainly due to the light scattering phenomenon (Jallouli et al., 2018).

Using 0.50 g L⁻¹ nano-CeO₂ gave better results for the photocatalytic removal of α-HBCDD (62%), TBBPA (63%), PBT (61%), PBEB (60%), PFOS (29%), PFOA (25%), TCS (50%), GFZ (46%), CIP (50%), IBU (52%), NDMA (28%) and AHTN

(68%) (Figure 6.36) than using 0.50 g L⁻¹ nano-TiO₂ (58% for α -HBCDD, 60% for TBBPA, 57% for PBT, 56% for PBEB, 24% for PFOS, 20% for PFOA, 46% for TCS, 42% for GFZ, 48% for CIP, 42% for IBU, 15% for NDMA and 55% for AHTN) (Figure 6.35) at the aforementioned experimental conditions. This can be attributed to the higher specific surface area of nano-CeO₂ (302 m² g⁻¹) with lower particle size (20 nm) in the comparison with the surface area (205 m² g⁻¹) and particle size (25 nm) of nano-TiO₂.

6.2.5 Effect of Irradiation Times (15, 30, 45, 60 and 90 min) on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

The photocatalytic experiments performed with nano-TiO₂ at different irradiation times (15, 30, 45, 60 and 90 min) showed that 45 min was the optimum irradiation time for the maximum photocatalytic removals of α -HBCDD (81%), TBBPA (83%), PBT (80%), PBEB (79%), PFOS (43%), PFOA (40%), TCS (78%), GFZ (64%), CIP (80%), IBU (64%), NDMA (34%) and AHTN (76%) with 0.50 g L⁻¹ constant nano-TiO₂ concentration at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Figure 6.37.a, b, c, d, e).

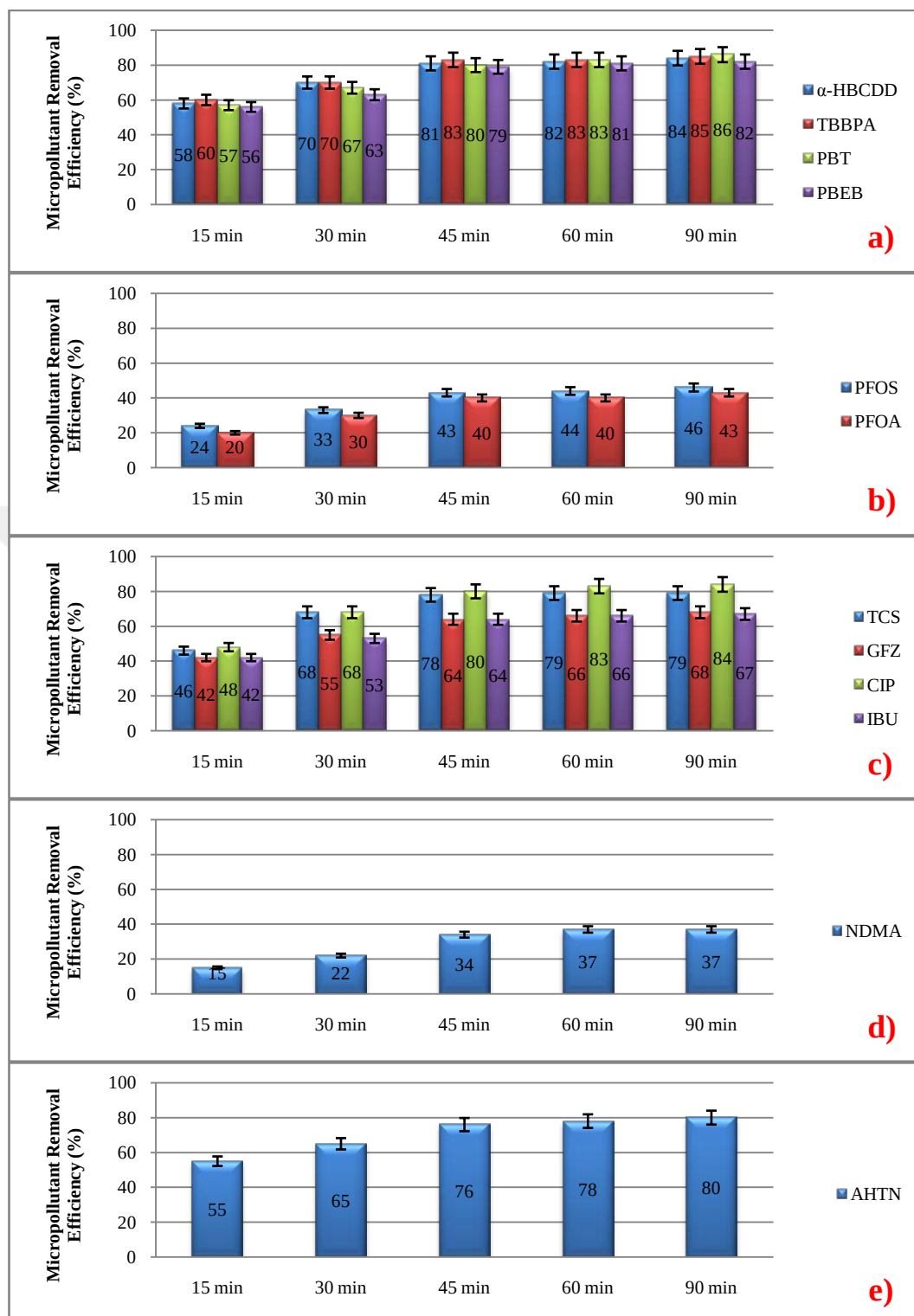


Figure 6.37 Effect of irradiation times (15, 30, 45, 60 and 90 min) on the photocatalytic removals of all studied micropollutants at constant nano-TiO₂ concentration of 0.50 g L⁻¹ at constant UV light power of 120 W at constant temperature of 25 °C and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

Also, the photocatalytic experiments performed with nano-CeO₂ at different irradiation times (15, 30, 45, 60 and 90 min) showed that 45 min was the optimum irradiation time for the maximum photocatalytic removals of α -HBCDD (85%), TBBPA (86%), PBT (83%) and PBEB (83%), PFOS (48%), PFOA (46%), TCS (81%), GFZ (72%), CIP (83%), IBU (74%), NDMA (40%) and AHTN (80%) with 0.50 g L⁻¹ constant nano-CeO₂ concentration at a constant UV light power of 120 W at a constant temperature of 25 °C and at a constant pH of 7.00 (Figure 6.38.a, b, c, d, e).



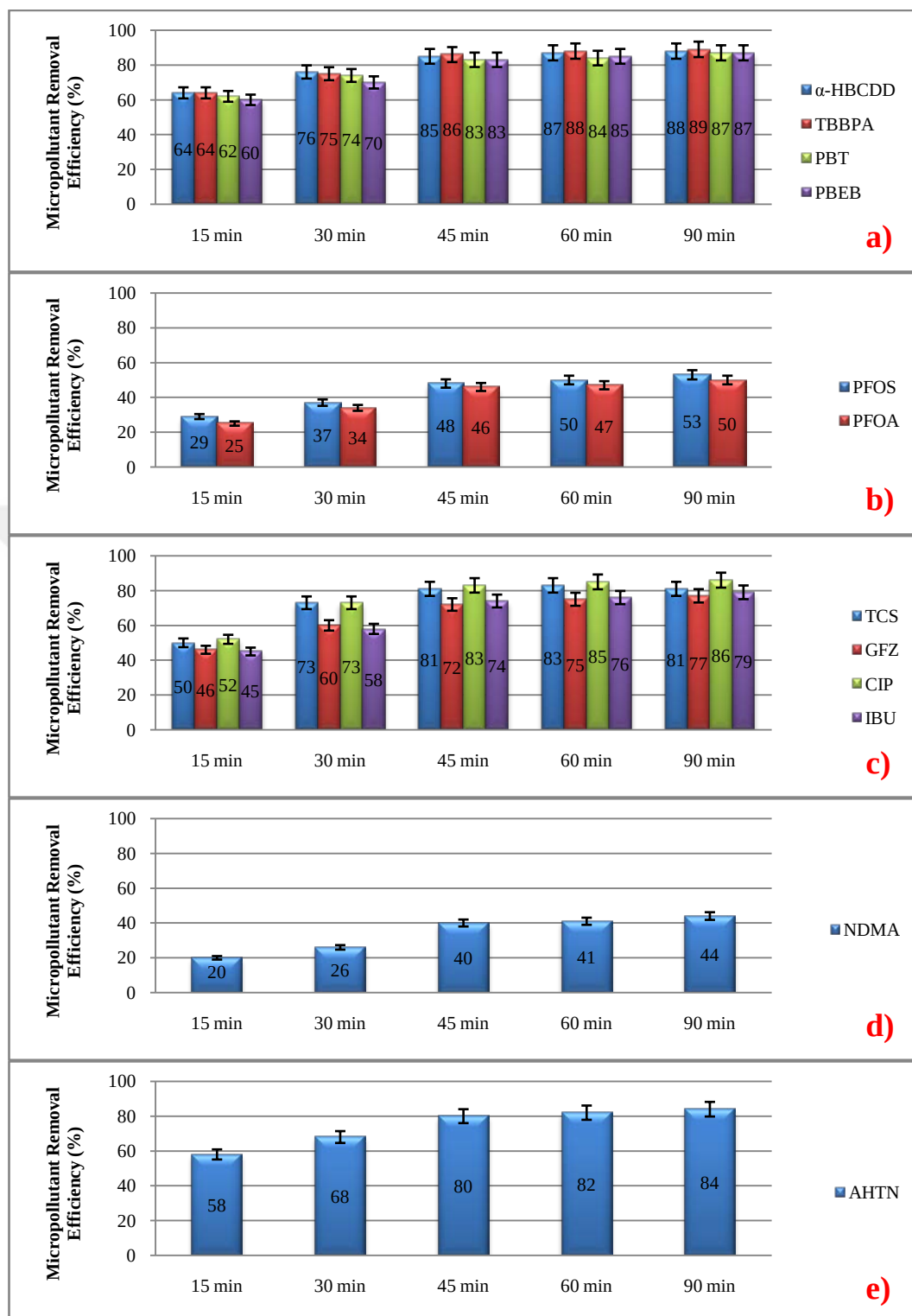


Figure 6.38 Effect of irradiation times (15, 30, 45, 60 and 90 min) on the photocatalytic removals of all studied micropollutants at constant nano-CeO₂ concentration of 0.50 g L⁻¹ at constant UV light power of 120 W at constant pH of 7.00 and at constant temperature of 25 °C for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

It is widely accepted that UV irradiation leads to the generation of electron (e^-_{CB}) – hole (h^+_{VB}) pairs on the nano-TiO₂ and nano-CeO₂ surfaces. These charges will react with water molecules and result in hydroxyl (OH $\cdot$) radicals. OH $\cdot$ radicals oxidize the micropollutant molecules and cause latter to decompose and mineralize to water and to carbon dioxide (Sponza & Guney, 2017). Any further increase from the optimum irradiation time (45 min) did not change considerably the photocatalytic removal efficiencies of all studied micropollutants with nano-TiO₂ and nano-CeO₂. As the irradiation time increases, OH $\cdot$ radicals formation increases and increasing OH $\cdot$ radicals increase the micropollutant removal efficiency. When the experimental conditions continue longer than the optimum irradiation time (45 min), OH $\cdot$ radicals formation do not increase significantly for the constant dose of nanoparticle (0.50 g L⁻¹ for nano-TiO₂ and nano-CeO₂) in this study. The ANOVA (one-way) test statistics showed that a linear regression between irradiation time and micropollutants photocatalytic removals were observed when the irradiation time was increased from 15 min to 45 min ($R^2 = 0.995$ for nano-TiO₂ and $R^2 = 0.993$ for nano-CeO₂) at the aforementioned experimental conditions. The ANOVA (one-way) test statistics showed that the increased length of time up to 45 min had a significant effect on the photocatalytic removals of all studied micropollutants at the aforementioned experimental conditions ($P = 0.008$, $\alpha = 0.05$, $F = 5.59$ for nano-TiO₂ and $P = 0.006$, $\alpha = 0.05$, $F = 6.02$ for nano-CeO₂). The effect of irradiation time on the photocatalytic removals of all studied micropollutants for higher than 45 min (60 and 90 min) was not significant ($P = 0.832$, $\alpha = 0.05$, $F = 0.05$ for nano-TiO₂ and $P = 0.792$, $\alpha = 0.05$, $F = 0.07$ for nano-CeO₂) at the aforementioned experimental conditions.

Miranda-García et al. (2011) studied the photocatalytic degradation of IBU and increased the irradiation time gradually from zero to 120 min at 30 W m⁻² UV light intensity in a synthetic wastewater having at a pH of 8.00 for an initial IBU concentration of 100 µg L⁻¹. Almost 90% of IBU was removed after 120 min of irradiation time with 0.335 g L⁻¹ nano-TiO₂ concentration (Miranda-García et al., 2011). Santiago-Morales et al. (2012) investigated the effect of irradiation time on AHTN removal with 200 mg L⁻¹ Ce-doped TiO₂ under 15 W UV light power for an

initial AHTN concentration of 438 ng L⁻¹ in raw wastewater effluents from the secondary sedimentation tank of a wastewater treatment plant. They found almost 70% of AHTN removal and determined the optimum irradiation time as 15 min and observed no significant increase after 30 min at 25 °C at a pH of 7.79 (Santiago-Morales et al., 2012). Neves (2014) reported that the increasing of the irradiation time from 1 h to 5 h positively affected the 0.01 g L⁻¹ TCS removal (from 68% to 78%) at a pH value of 7.00 with 0.50 g L⁻¹ nano-TiO₂ with 90 μW mm⁻² UV irradiation from a synthetic wastewater (Neves, 2014). Cao et al. (2015) researched the photocatalytic removal of TBBPA at different irradiation times (10-20-30-40-50-60 min) and they obtained 65.8% TBBPA removal efficiency with 0.25 g L⁻¹ graphene-TiO₂ nanocomposite after 60 min irradiation time at 230 W UV light power at a room temperature (20 °C) and at a neutral pH (7.00) for an initial TBBPA concentration of 10 mg L⁻¹ from a synthetic wastewater (Cao et al., 2015). The photocatalytic removal efficiencies of AHTN (76%) and TBBPA (83%) with nano-TiO₂ found in this study at the aforementioned experimental conditions were higher than Santiago-Morales et al. (2012) (70%) and Cao et al. (2015) (65.8%) cited above.

6.2.6 Effect of Light Powers (80, 120, 210 and 300 W) on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

The photocatalytic reactor system was operated at constant sunlight (80 W) and at increasing UV light powers (120, 210 and 300 W) in order to determine the optimum UV light power for the maximum micropollutants removals with 0.50 g L⁻¹ constant nano-TiO₂ (Figure 6.39) and 0.50 g L⁻¹ constant nano-CeO₂ concentrations (Figure 6.40) at a constant irradiation time of 45 min at a constant temperature of 25 °C and at a constant pH of 7.00. The maximum micropollutant photocatalytic removal efficiencies were obtained as 87%, 86%, 85%, 86%, 57%, 55%, 85%, 77%, 88%, 75%, 45% and 84%, respectively for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN at the optimum UV light power as

210 W with nano-TiO₂ at the aforementioned experimental conditions (Figure 6.39.a, b, c, d, e).



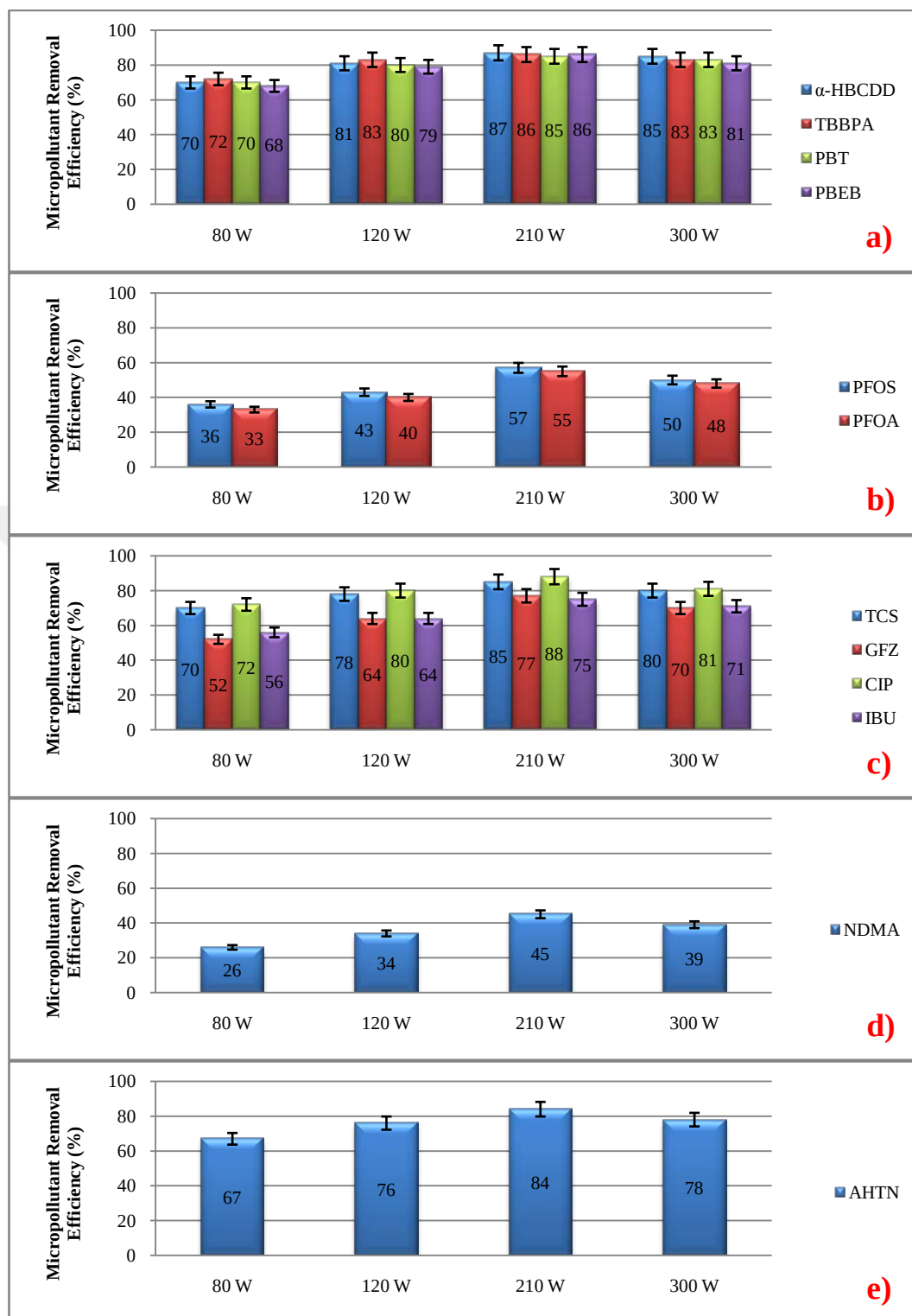


Figure 6.39 Effect of UV light powers (80, 120, 210 and 300 W) on the photocatalytic removals of all studied micropollutants at constant nano-TiO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant temperature of 25 °C and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

Similarly, the maximum micropollutant photocatalytic removal efficiencies were obtained as 93%, 92%, 94%, 90%, 64%, 61%, 90%, 80%, 92%, 79%, 51% and 90%, respectively for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN at the optimum UV light power as 210 W with nano-CeO₂ at the aforementioned experimental conditions (Figure 6.40.a, b, c, d, e).



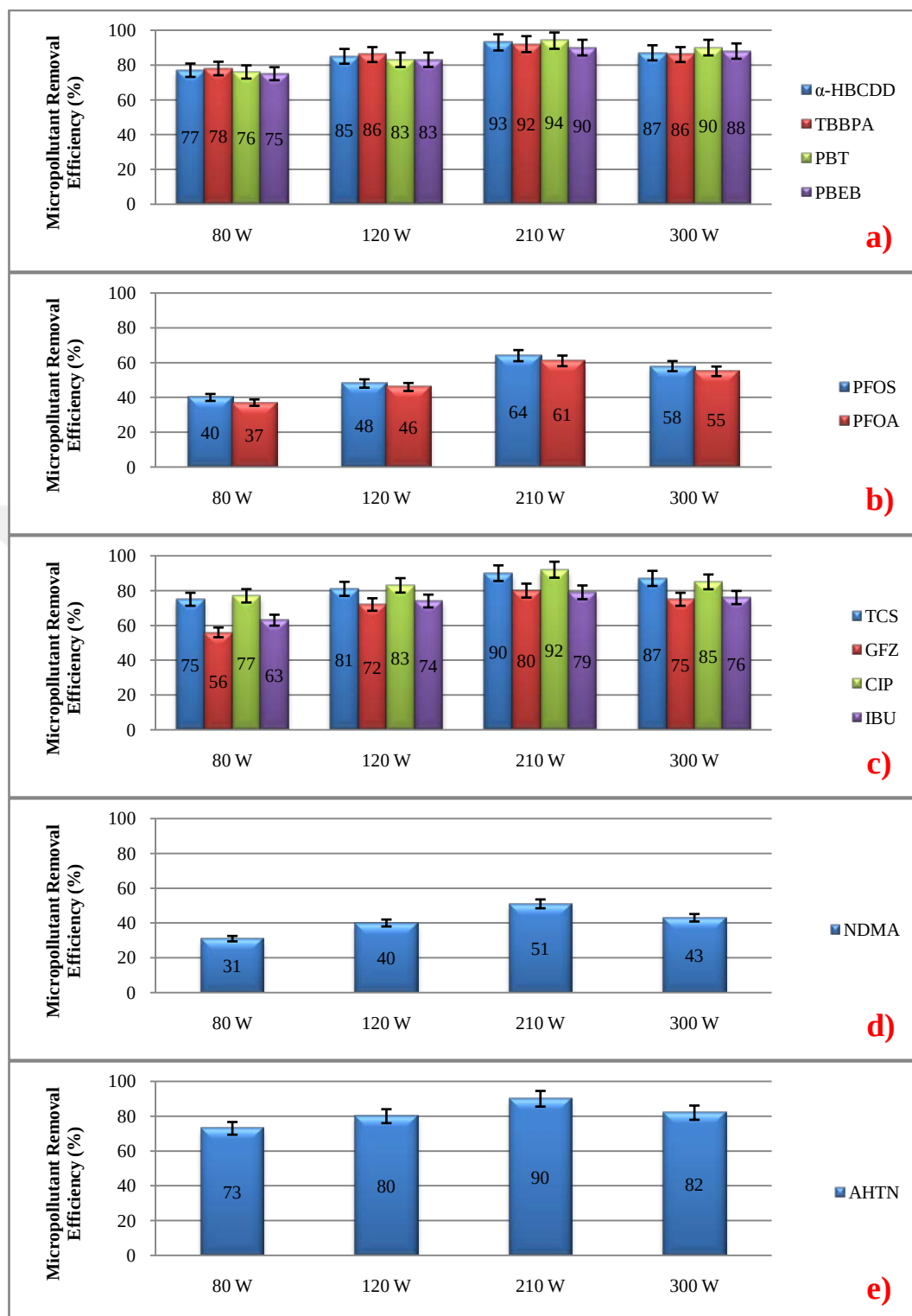


Figure 6.40 Effect of UV light powers (80, 120, 210 and 300 W) on the photocatalytic removals of all studied micropollutants at constant nano-CeO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant temperature of 25 °C and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

The photocatalytic removals of all studied micropollutants increased when the UV light power was increased from 80 W to 210 W with nano-TiO₂ (Figure 6.39) and nano-CeO₂ (Figure 6.40). Increased UV light power (210 W) was increased the photocatalytic removal efficiencies of all studied micropollutants because the nano-TiO₂ and nano-CeO₂ absorbed more photons, produced more electron (e^-_{CB}) – hole (h^+_{VB}) pairs on the catalyst surfaces and the concentrations of hydroxyl ($OH^\bullet$) radicals increased (Bai & Acharya, 2016). The optimum UV light power for the maximum micropollutant photocatalytic removals was found to be 210 W UV light power at the aforementioned experimental conditions with nano-TiO₂ (Figure 6.39) and nano-CeO₂ (Figure 6.40). However, when the UV light power was increased to 300 W the photocatalytic removals of all studied micropollutants decreased with nano-TiO₂ (Figure 6.39) and nano-CeO₂ (Figure 6.40) at the aforementioned experimental conditions. At 300 W UV light power, the amount of photons absorbed by the catalysts could not be increased for the constant dose of nano-TiO₂ and nano-CeO₂ and sufficient hydroxyl ($OH^\bullet$) radicals could not be formed. The ANOVA (one-way) test statistics results showed that the increasing UV light power increased the micropollutant photocatalytic removals significantly up to 210 W UV light power with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions ($R^2 = 0.991$, $P = 0.040$, $\alpha = 0.05$, $F = 3.56$ for nano-TiO₂ and $R^2 = 0.988$, $P = 0.037$, $\alpha = 0.05$, $F = 3.64$ for nano-CeO₂). The relationship between 300 W UV light power and the micropollutants photocatalytic removals was not significant both for nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions ($P = 0.429$, $\alpha = 0.05$, $F = 0.65$ for nano-TiO₂ and $P = 0.398$, $\alpha = 0.05$, $F = 0.74$ for nano-CeO₂).

Sansotera et al. (2014) increased the UV light intensity from 75 to 95 W m⁻² for the photocatalytic degradation of PFOA with 0.66 g L⁻¹ nano-TiO₂ concentration and the removal efficiency increased from 22% to 32% after 6 h UV irradiation at 0.004 M initial PFOA concentration (Sansotera et al., 2014). Guo et al. (2015) found approximately 47% of NDMA removal under 500 W UV light power with 0.50 g L⁻¹ nano-TiO₂ (Degussa P25 nanopowder) concentration for 240 min at pH = 7.00 for an initial NDMA concentration of 1.05 mM (Guo et al., 2015). Chen et al. (2017) achieved 70.5% GFZ photocatalytic removal with 0.5 g L⁻¹ nano-TiO₂ for 8 min for

an initial GFZ concentration of 2 mg L^{-1} at 350 W UV light power and at neutral pH (Chen et al., 2017). The photocatalytic degradation of AHTN was researched at 300 W UV light power by Fang et al. (2017) and they achieved a complete removal with 2.0 g L^{-1} nano-TiO₂ at 25 °C after 60 min for an initial AHTN concentration of 50 μM (Fang et al., 2017). Wang, Yin, & Wang (2017b) found that TCS was photodegraded with a removal efficiency of 60% under 1 kGy gamma irradiation while the photodegradation was enhanced to 95% with 5 kGy gamma for an initial TCS concentration of 10 mg L^{-1} at pH 5.60 (Wang et al., 2017b). The photocatalytic removal efficiencies of PFOA (55%) and GFZ (77%) at 210 W UV light power found in this study at the aforementioned experimental conditions were higher than the results in the comparison with the results previously obtained by Sansotera et al. (2014) (32%) and Chen et al. (2017) (70.5%).

6.2.7 Effect of Temperatures (25, 35, 45 and 60 °C) on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

The photocatalytic experiments carried out with nano-TiO₂ at different temperatures (25, 35, 45 and 60 °C) showed that 60 °C was the optimum temperature for the maximum photocatalytic removals of α -HBCDD (97%), TBBPA (96%), PBT (97%), PBEB (96%), PFOS (72%), PFOA (72%), TCS (97%), GFZ (89%), CIP (97%), IBU (90%), NDMA (60%) and AHTN (96%) with 0.50 g L^{-1} constant nano-TiO₂ concentration at a constant irradiation time of 45 min at a constant UV light power of 210 W and at a constant pH of 7.00 (Figure 6.41.a, b, c, d, e).

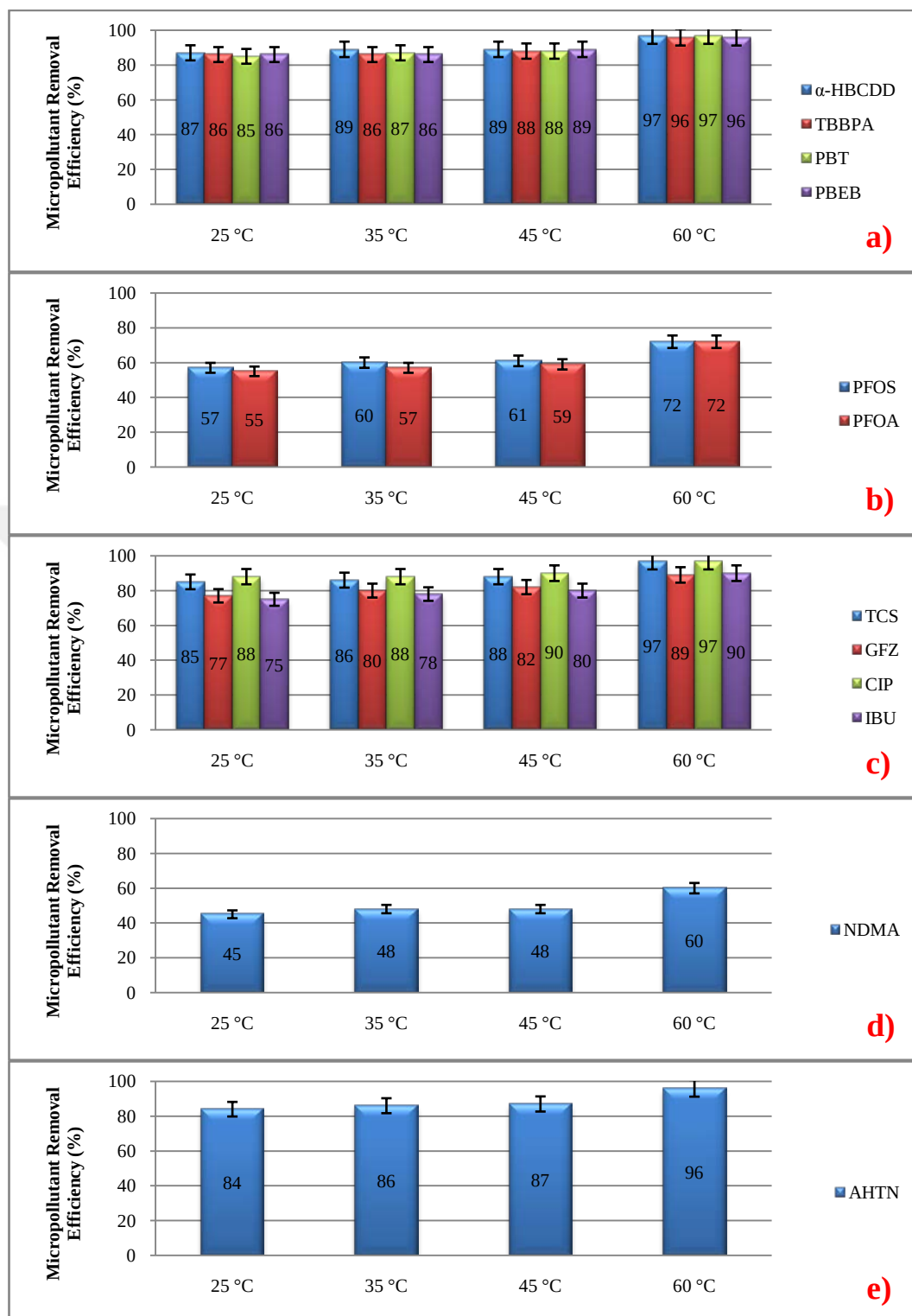


Figure 6.41 Effect of temperatures (25, 35, 45 and 60 °C) on the photocatalytic removals of all studied micropollutants at constant nano-TiO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant UV light power of 210 W and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants (n=3, mean)

The results showed that 60 °C was the optimum temperature from the studied temperature range (25, 35, 45 and 60 °C) for the maximum photocatalytic removals of α -HBCDD (98%), TBBPA (97%), PBT (97%), PBEB (96%), PFOS (76%), PFOA (75%), TCS (97%), GFZ (95%), CIP (98%), IBU (95%), NDMA (66%) and AHTN (97%) with 0.50 g L⁻¹ constant nano-CeO₂ concentration at a constant irradiation time of 45 min at a constant UV light power of 210 W and at a constant pH of 7.00 (Figure 6.42.a, b, c, d, e).



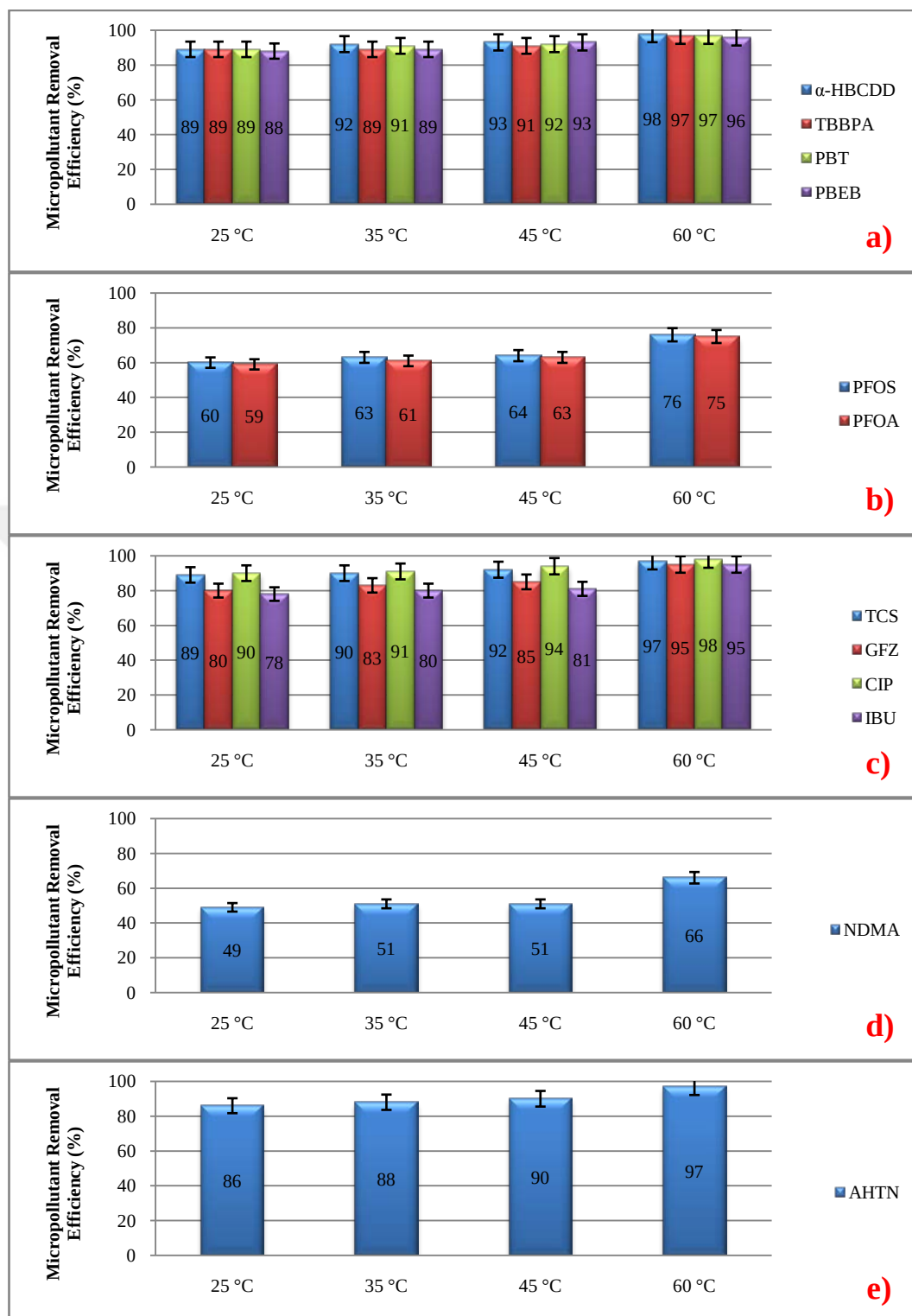


Figure 6.42 Effect of temperatures (25, 35, 45 and 60 °C) on the photocatalytic removals of all studied micropollutants at constant nano-CeO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant UV light power of 210 W and at constant pH of 7.00 for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants (n=3, mean)

It can be seen that the photocatalytic degradation of all studied micropollutants increased with increasing temperature both for the experiments conducted with nano-TiO₂ (Figure 6.41) and nano-CeO₂ (Figure 6.42). Higher temperature provides higher TiO₂ and CeO₂ electron transfers in valance band to higher energy levels and hence facilitates the electron (e^-_{CB}) – hole (h^+_{VB}) productions that could be utilized in initiating oxidation and reduction reactions, respectively (Fukahori and Fujiwara, 2015). The species of photon-generated holes (h^+_{VB}), electrons (e^-_{CB}) and hydroxyl radicals (OH $\cdot$) can thus degrade micropollutants to CO₂ and H₂O (Chatila et al., 2016). A linear regression between temperature and micropollutants photocatalytic removals was observed ($R^2 = 0.997$ for nano-TiO₂ and $R^2 = 0.982$ for nano-CeO₂), moreover, the temperature affected the photocatalytic removals of all studied micropollutants significantly ($P = 0.040$, $\alpha = 0.05$, $F = 4.76$ for nano-TiO₂ and $P = 0.037$, $\alpha = 0.05$, $F = 4.90$ for nano-CeO₂) for the optimum temperature of 60 °C at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results. The increase in the temperature from 25 °C to 45 °C had no significant effect on the photocatalytic removals of all studied micropollutants ($P = 0.861$, $\alpha = 0.05$, $F = 0.15$ for nano-TiO₂ and $P = 0.833$, $\alpha = 0.05$, $F = 0.18$ for nano-CeO₂) at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results.

6.2.8 Effect of pHs (4.00, 7.00 and 8.50) on the Photocatalytic Removals of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants with Nano-TiO₂ and Nano-CeO₂

In photocatalysis, pH can affect the reaction of OH $\cdot$ radical production from H₂O/OH $\cdot$ and the nanoparticle. The photocatalytic removals of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were researched under acidic (pH = 4.00), neutral (pH = 7.00) and alkaline (pH = 8.50) pH conditions with 0.50 g L⁻¹ constant nano-TiO₂ (Figure 6.43) and nano-CeO₂ (Figure 6.44) concentrations at a constant irradiation time of 45 min at a constant UV light power of 210 W and at a constant temperature of 60 °C. The pH was adjusted by the

addition of 1 N NaOH or 1 N HCl for the desired levels. Under neutral conditions (pH = 7.00); the micropollutants photocatalytic removals reached the maximum levels for α -HBCDD (97%), TBBPA (96%), PBT (97%), PBEB (96%), TCS (97%) and CIP (97%) with nano-TiO₂ at the aforementioned experimental conditions (Figure 6.43.a and c). On the other hand, the maximum photocatalytic removal efficiencies of PFOS, PFOA and NDMA were found as 96%, 93% and 95%, respectively under acidic conditions (pH = 4.00) with nano-TiO₂ at the aforementioned experimental conditions (Figure 6.43.b and d). The maximum photocatalytic removal efficiencies of GFZ (98%), IBU (96%) and AHTN (97%) were obtained at alkaline conditions (pH = 8.50) with nano-TiO₂ at the aforementioned experimental conditions (Figure 6.43.c and e).

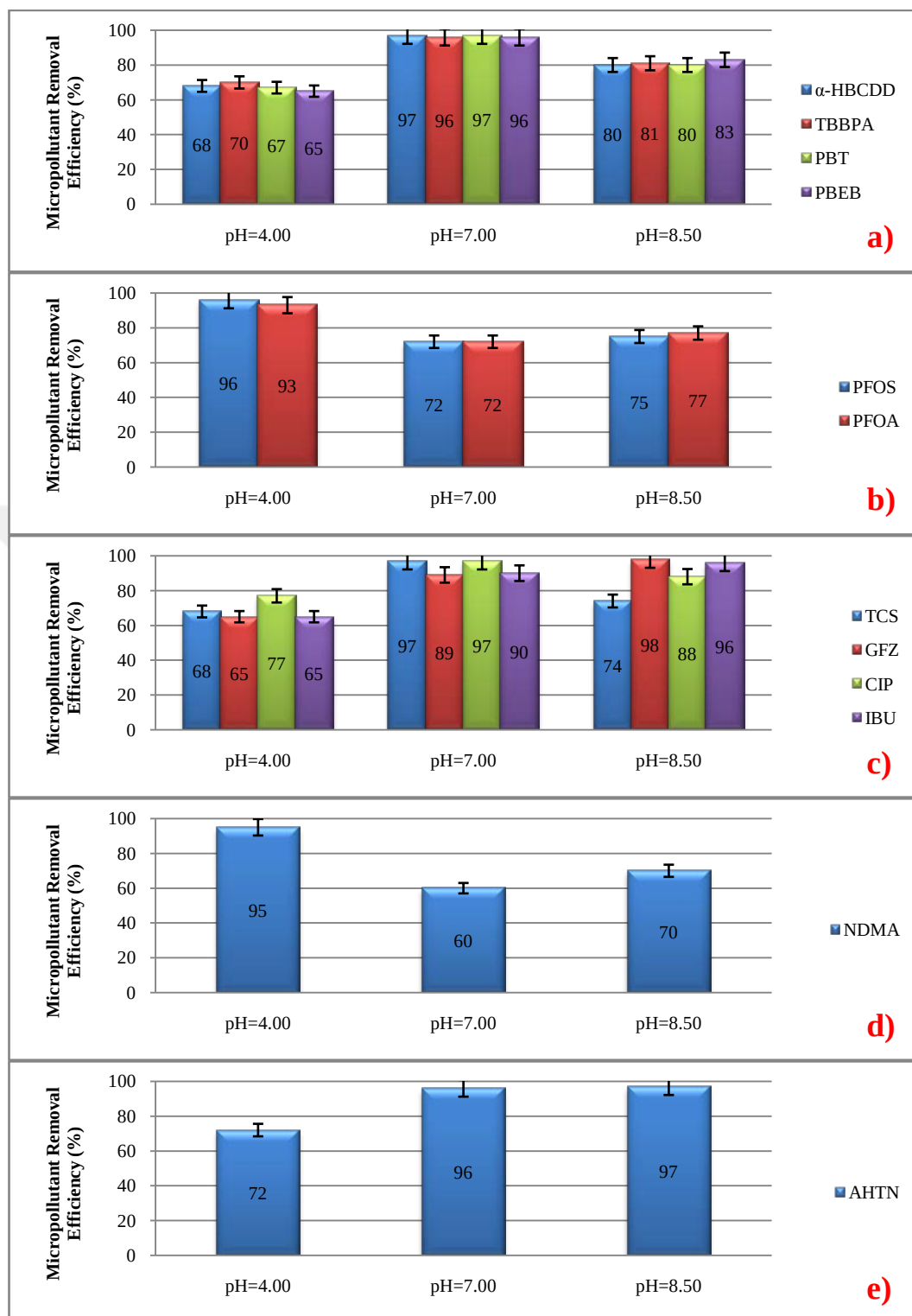


Figure 6.43 Effect of pHs (4.00, 7.00 and 8.50) on the photocatalytic removals of all studied micropollutants at constant nano-TiO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant UV light power of 210 W and at constant temperature of 60 °C for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

For the experiments carried out with nano-CeO₂, the maximum photocatalytic removal efficiencies were determined as 98%, 97%, 97%, 96%, 97% and 98% for α -HBCDD, TBBPA, PBT, PBEB, TCS and CIP, respectively under neutral conditions (pH = 7.00) at the aforementioned experimental conditions (Figure 6.44.a and c). The maximum PFOS, PFOA and NDMA photocatalytic removal efficiencies were obtained as 98%, 95% and 97%, respectively under acidic conditions (pH = 4.00) with nano-CeO₂ at the aforementioned experimental conditions (Figure 6.44.b and d). Under alkaline conditions (pH = 8.50); the micropollutants photocatalytic removals reached the maximum levels for GFZ (100%), IBU (98%) and AHTN (100%) with nano-CeO₂ at the aforementioned experimental conditions (Figure 6.44.c and e).

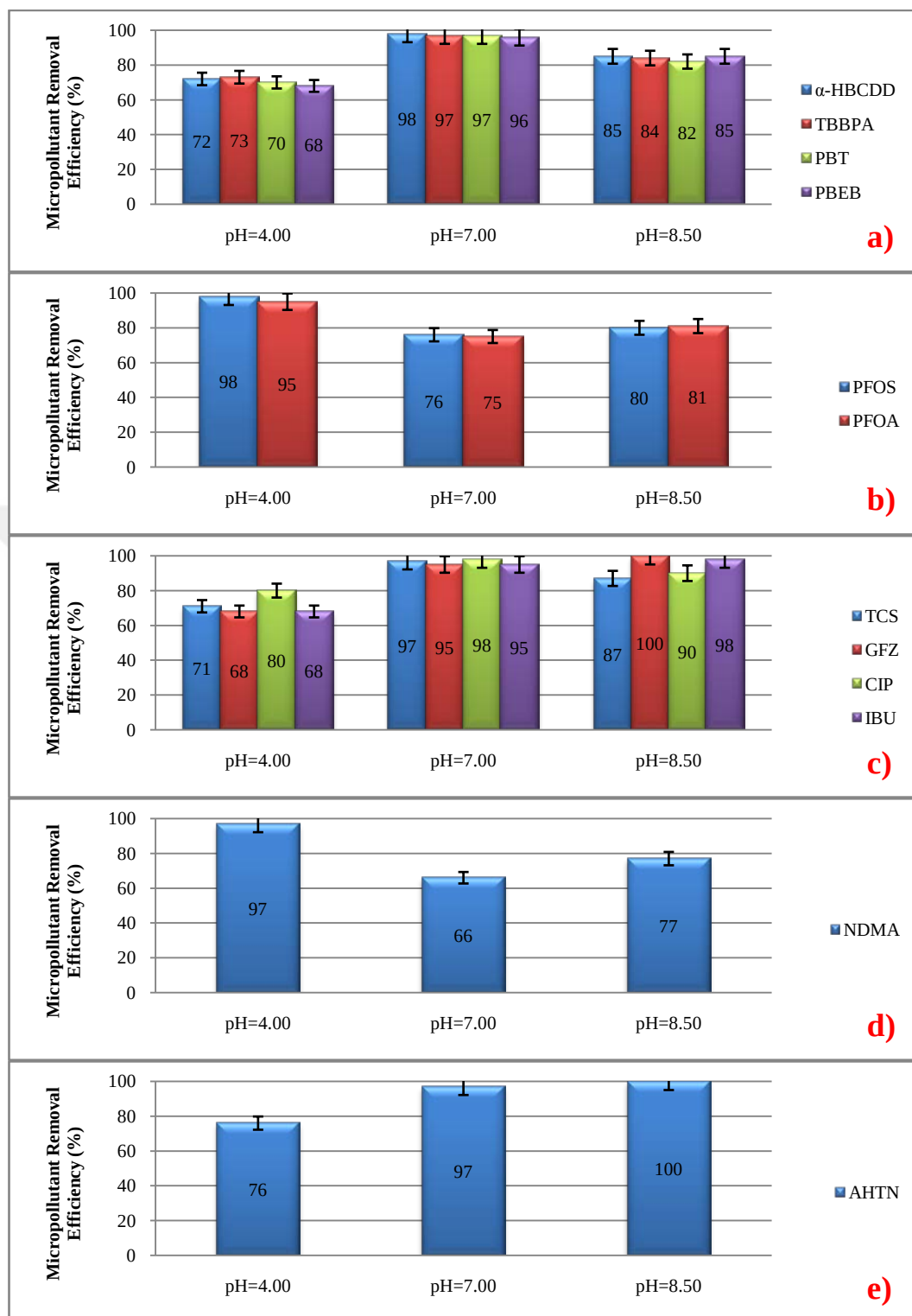


Figure 6.44 Effect of pHs (4.00, 7.00 and 8.50) on the photocatalytic removals of all studied micropollutants at constant nano-CeO₂ concentration of 0.50 g L⁻¹ at constant irradiation time of 45 min at constant UV light power of 210 W and at constant temperature of 60 °C for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants ($n=3$, mean)

The surface of the photocatalyst (nano-TiO₂ and nano-CeO₂) may become positively (+) or negatively (–) charged depending on the operating pH value. The nano-TiO₂ and nano-CeO₂ has a point of zero charge at pH = 6.25 and pH = 5.60 in water, respectively (Wang et al., 2017a and Barany, Bohacs, Chepurna, & Meszaros, 2016). Therefore, the surface of the nano-TiO₂ and nano-CeO₂ will be positively (+) charged in the raw hospital wastewater below these pHs (pH = 6.25 for nano-TiO₂ and pH = 5.60 for nano-CeO₂) and will be negatively (–) charged above them.

Also, the micropollutant may become positively (+) or negatively (–) charged depending on the operating pH value. The surface of the micropollutant will be positively (+) charged if the raw hospital wastewater has an operating pH value below the micropollutant's point of zero charge value ($pzc_{micropollutant} > pH_{wastewater}$). The surface of the micropollutant will be negatively (–) charged if the raw hospital wastewater has an operating pH value above the micropollutant's point of zero charge value ($pzc_{micropollutant} < pH_{wastewater}$).

For the acidic pH (4.00) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became positively (+) charged. However, α -HBCDD, TBBPA, PBT, PBEB, TCS, GFZ, CIP and IBU existed in the cationic (+) form at acidic pH (4.00) conditions, so the desired electrostatic force can not develop between the nanoparticles (nano-TiO₂ and nano-CeO₂) and the micropollutants (α -HBCDD, TBBPA, PBT, PBEB, TCS, GFZ, CIP and IBU).

For the acidic pH (4.00) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became positively (+) charged and PFOS, PFOA and NDMA existed in the anionic (–) form, so the adsorption of the anionic (–) micropollutants (PFOS, PFOA and NDMA) on the positively (+) charged nanoparticle surfaces (nano-TiO₂ and nano-CeO₂) were accelerated due to the electrostatic force between the micropollutants (PFOS, PFOA and NDMA) and the nanoparticles (nano-TiO₂ and nano-CeO₂).

For the neutral pH (7.00) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became negatively (–) charged, but also PFOS, PFOA, GFZ, IBU and NDMA

existed in the anionic (–) form, so the desired electrostatic force can not develop between the nanoparticles (nano-TiO₂ and nano-CeO₂) and the micropollutants (PFOS, PFOA, GFZ, IBU and NDMA).

Nevertheless, for the neutral pH (7.00) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became negatively (–) charged and α -HBCDD, TBBPA, PBT, PBEB, TCS and CIP existed in the cationic (+) form, so the adsorption of the cationic (+) micropollutants (α -HBCDD, TBBPA, PBT, PBEB, TCS and CIP) on the negatively (–) charged nanoparticle (nano-TiO₂ and nano-CeO₂) surfaces were accelerated due to the electrostatic force between the micropollutants (α -HBCDD, TBBPA, PBT, PBEB, TCS and CIP) and the nanoparticles (nano-TiO₂ and nano-CeO₂).

For the alkaline pH (8.50) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became negatively (–) charged but also α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, IBU and NDMA existed in the anionic (–) form, so the desired electrostatic force can not develop between the nanoparticles (nano-TiO₂ and nano-CeO₂) and the micropollutants (α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, IBU and NDMA).

In despite of, at the alkaline pH (8.50) conditions, the surface of the nano-TiO₂ and nano-CeO₂ became negatively (–) charged and CIP existed in the cationic (+) form, so the adsorption of the cationic (+) micropollutant (CIP) on the negatively (–) charged nanoparticle (nano-TiO₂ and nano-CeO₂) surfaces was accelerated due to the electrostatic force between CIP and the nano-TiO₂ and nano-CeO₂.

In this study, it was found that the most efficient pH was neutral (pH = 7.00) to remove the brominated micropollutants (α -HBCDD, TBBPA, PBT and PBEB) both for nano-TiO₂ (97% for α -HBCDD, 96% for TBBPA, 97% for PBT and 96% for PBEB) (Figure 6.43.a) and nano-CeO₂ (98% for α -HBCDD, 97% for TBBPA, 97% for PBT and 96% for PBEB) (Figure 6.44.a) from the raw hospital wastewater whereas more extreme pH conditions (acidic pH = 4.00 and alkaline pH = 8.50)

negatively affected the photocatalytic degradation removal efficiencies at the aforementioned experimental conditions. Therefore, because of the negative (–) surface charge of the nanoparticles (nano-TiO₂ and nano-CeO₂), the maximum photocatalytic removals occur based on the brominated micropollutants (α -HBCDD, TBBPA, PBT and PBEB) were in the cationic (+) form ($p_{ZC, \text{brominated micropollutants}} = 7.5\text{--}8.5$).

For the photocatalytic removals of the fluoro (PFOS and PFOA) and nitroso (NDMA) micropollutants, the most efficient pH was acidic (pH = 4.00) both for nano-TiO₂ (96% for PFOS, 93% for PFOA and 95% for NDMA) (Figure 6.43.b and d) and nano-CeO₂ (98% for PFOS, 95% for PFOA and 97% for NDMA) (Figure 6.44.b and d) because positively (+) charged nanoparticles and anionic (–) forms of PFOS, PFOA and NDMA enhanced the photocatalytic removal efficiencies at the aforementioned experimental conditions ($p_{ZC, \text{PFOS}} < 1.0$, $p_{ZC, \text{PFOA}} = 2.8$ and $p_{ZC, \text{NDMA}} = 3.52$).

The phenolic micropollutants (TCS and CIP) were in the cationic (+) forms while the nano-TiO₂ and nano-CeO₂ were negatively (–) charged under neutral pH (7.00) conditions, therefore, the maximum photocatalytic removal efficiencies were obtained at a pH of 7.00 for TCS (97% with nano-TiO₂ and 97% with nano-CeO₂) and CIP (97% with nano-TiO₂ and 98% with nano-CeO₂) at the aforementioned experimental conditions (Figure 6.43.c and Figure 6.44.c) ($p_{ZC, \text{TCS}} = 7.9$ and $p_{ZC, \text{CIP}} = 5.6, 6.2, 8.8$).

The other phenolic micropollutants GFZ and IBU were in the cationic (+) forms while the nano-TiO₂ and nano-CeO₂ were positively (+) charged under acidic pH (4.00) conditions. GFZ and IBU were in the anionic (–) forms while the nano-TiO₂ and nano-CeO₂ were negatively (–) charged under neutral (7.00) and alkaline (8.50) pH conditions. The most hydroxyl (OH•) radicals produced at the highest pH value of 8.50 (alkaline conditions) (Chow et al., 2012), therefore, the highest photocatalytic degradation removals of GFZ and IBU were achieved as 98% and 96%, respectively with nano-TiO₂, while the highest photocatalytic degradation removals of GFZ and

IBU were determined as 100% and 98%, respectively with nano-CeO₂ at the aforementioned experimental conditions (Figure 6.43.c and Figure 6.44.c) ($p_{zc,GFZ} = 4.75$ and $p_{zc,IBU} = 4.91$).

AHTN was removed with the highest removal efficiency of 97% at a pH of 8.50 with nano-TiO₂ at the aforementioned experimental conditions (Figure 6.43.e). The experiments carried out with the nano-CeO₂ showed that the photocatalytic removal efficiency of AHTN was determined as 100% at a pH of 8.50 at the aforementioned experimental conditions (Figure 6.44.e). AHTN was removed efficiently with nano-TiO₂ (97%) (Figure 6.43.e) and nano-CeO₂ (100%) (Figure 6.44.e) at alkaline (pH = 8.50) conditions. The p_{zc} value of AHTN is not available in the literature. The reason for the increase in the photocatalytic removal efficiencies of AHTN at alkaline (pH = 8.50) conditions comparing with the acidic (pH = 4.00) and neutral (pH = 7.00) conditions can be explained by the production of the hydroxyl (OH•) radicals are more readily at higher pH values. As a result, more hydroxyl (OH•) radicals produced at higher pH values and higher amount of OH• radicals increased the photocatalytic degradation removals of AHTN, as reported by Chow et al. (2012). Son et al. (2009) reported that the decreasing of photocatalytic removals under acidic conditions is due to the inhibition of hydroxyl radicals (OH•) generation (Son et al., 2009).

Van Doorslaer et al. (2011) found that the highest photocatalytic degradation of CIP (an initial concentration of 45.3 µM) with 0.50 g L⁻¹ nano-TiO₂ were achieved at pH 7.00 ($k_1 = 0.163 \text{ min}^{-1}$) than at pH 3.00 ($k_1 = 0.128 \text{ min}^{-1}$) and at pH 10.00 ($k_1 = 0.089 \text{ min}^{-1}$) at 25 °C with 389 µW cm⁻² UV light intensity (Van Doorslaer et al., 2011). Sturini et al. (2012) reported that CIP removal was very efficient at neutral pH on the basis of its point of zero charge value ($p_{zc,CIP} = 5.6, 6.2, 8.8$). They researched the photocatalytic degradation of CIP (an initial concentration of 50 µg L⁻¹) under natural sunlight at 27-30 °C corresponding to 20-31 W m⁻² UV light intensity with 0.50 g L⁻¹ nano-TiO₂ concentration at a pH of 7.7 ± 0.1 and found approximately 90% of CIP removal efficiency (Sturini et al., 2012). The highest photocatalytic removal efficiencies were above 70% for GFZ and NDMA at a pH of 5.00 ranging

from 3.00 to 9.00 with 1.50 g L^{-1} nano-TiO₂ concentration throughout 30 min under 100 W UV light power at $20 \pm 2 \text{ }^{\circ}\text{C}$ for the initial concentrations of 2 mg L^{-1} for GFZ and NDMA (Alvarez-Corena et al., 2016).

The ANOVA (one-way) test statistics results showed that the effect of acidic pH (4.00) on the photocatalytic removals of PFOS, PFOA and NDMA ($P = 0.0009$, $\alpha = 0.05$, $F = 27.81$ for nano-TiO₂ and $P = 0.0004$, $\alpha = 0.05$, $F = 38.17$ for nano-CeO₂), the effect of neutral pH (7.00) on the photocatalytic removals of α -HBCDD, TBBPA, PBT, PBEB, TCS and CIP ($P = 4.73 \times 10^{-9}$, $\alpha = 0.05$, $F = 89.12$ for nano-TiO₂ and $P = 1.05 \times 10^{-9}$, $\alpha = 0.05$, $F = 110.55$ for nano-CeO₂), the effect of alkaline pH (8.50) on the photocatalytic removals of GFZ, IBU and AHTN ($P = 6.64 \times 10^{-5}$, $\alpha = 0.05$, $F = 71.08$ for nano-TiO₂ and $P = 3.22 \times 10^{-5}$, $\alpha = 0.05$, $F = 91.26$ for nano-CeO₂) were found to be significant with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions.

6.2.9 Reusability of Nano-TiO₂ and Nano-CeO₂

In order to decrease the catalyst cost, reusability of nano-TiO₂ and nano-CeO₂ were researched throughout six sequential treatment steps in this study. The TiO₂ and CeO₂ nanoparticles were reused at the following experimental conditions: 0.50 g L^{-1} constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of $60 \text{ }^{\circ}\text{C}$ and a constant pH of 7.00 (Table 6.40).

Table 6.40 The utilization of nano-TiO₂ and nano-CeO₂ after first, second, third, fourth, fifth and sixth treatment sequentials for the photocatalytic removal efficiencies of all studied micropollutants at the following experimental conditions: 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00 (*n*=3, mean ± SD)

	α-HBCDD	TBBPA	PBT	PBEB	PFOS	PFOA	TCS	GFZ	CIP	IBU	NDMA	AHTN
Treatment step	Removal efficiencies (%) with nano-TiO₂											
1 st treatment	97±0.5	96±0.5	97±0.5	96±0.5	72±0.5	72±0.5	97±0.5	89±0.5	97±0.5	90±0.5	60±0.5	96±0.5
2 nd treatment	94±0.5	90±0.5	94±0.5	92±0.5	69±0.5	68±0.5	92±0.5	84±0.5	92±0.5	87±0.5	55±0.5	91±0.5
3 rd treatment	91±0.5	90±0.5	92±0.5	90±0.5	66±0.5	67±0.5	92±0.5	84±0.5	91±0.5	87±0.5	53±0.5	89±0.5
4 th treatment	90±0.5	89±0.5	87±0.5	89±0.5	66±0.5	67±0.5	90±0.5	83±0.5	89±0.5	85±0.5	50±0.5	86±0.5
5 th treatment	90±0.5	86±0.5	85±0.5	87±0.5	63±0.5	64±0.5	88±0.5	81±0.5	87±0.5	82±0.5	47±0.5	86±0.5
6 th treatment	75±0.5	73±0.5	74±0.5	75±0.5	48±0.5	50±0.5	77±0.5	66±0.5	75±0.5	68±0.5	37±0.5	72±0.5
Treatment step	Removal efficiencies (%) with nano-CeO₂											
1 st treatment	98±0.5	97±0.5	97±0.5	96±0.5	76±0.5	75±0.5	97±0.5	95±0.5	98±0.5	95±0.5	66±0.5	97±0.5
2 nd treatment	92±0.5	90±0.5	92±0.5	92±0.5	71±0.5	69±0.5	92±0.5	89±0.5	94±0.5	89±0.5	61±0.5	92±0.5
3 rd treatment	90±0.5	89±0.5	91±0.5	90±0.5	68±0.5	67±0.5	90±0.5	89±0.5	91±0.5	86±0.5	59±0.5	92±0.5
4 th treatment	87±0.5	87±0.5	88±0.5	88±0.5	68±0.5	66±0.5	90±0.5	87±0.5	90±0.5	86±0.5	55±0.5	89±0.5
5 th treatment	85±0.5	84±0.5	87±0.5	87±0.5	66±0.5	66±0.5	88±0.5	84±0.5	88±0.5	85±0.5	55±0.5	88±0.5
6 th treatment	73±0.5	71±0.5	74±0.5	74±0.5	54±0.5	53±0.5	75±0.5	71±0.5	75±0.5	72±0.5	43±0.5	75±0.5

The photocatalytic removal efficiencies of all studied micropollutants were taken into consideration to detect the reusability of nano-TiO₂ and nano-CeO₂ throughout six treatment sequentials. After the first treatment step with nano-TiO₂, the maximum photocatalytic removal efficiencies of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were determined as 97%, 96%, 97%, 96%, 72%, 72%, 97%, 89%, 97%, 90%, 60% and 96%, respectively at the aforementioned experimental conditions (Table 6.40). After the second, third, fourth and fifth treatment steps, the photocatalytic removal efficiencies of all studied micropollutants had no obvious change with nano-TiO₂. In the sixth treatment step, the photocatalytic removal efficiencies decreased and were calculated as 75%, 73%, 74%, 75%, 48%, 50%, 77%, 66%, 75%, 68%, 37% and 72% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively at the aforementioned experimental conditions (Table 6.40).

The maximum photocatalytic removal efficiencies of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were found as 98%, 97%, 97%, 96%, 76%, 75%, 97%, 95%, 98%, 95%, 66% and 97%, respectively after the first treatment step with nano-CeO₂ at the aforementioned experimental conditions (Table 6.40). After the second, third, fourth and fifth treatment steps, the photocatalytic removal efficiencies of all studied micropollutants did not change considerably with nano-CeO₂. In the sixth treatment step, the photocatalytic removal efficiencies decreased and were obtained as 73%, 71%, 74%, 74%, 54%, 53%, 75%, 71%, 75%, 72%, 43% and 75% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively with nano-CeO₂ at the aforementioned experimental conditions (Table 6.40).

Alvarez-Corena et al. (2016) examined the reusability of nano-TiO₂ for five cycles during 5 min at a pH of 5.00 with 1.5 g L⁻¹ nano-TiO₂ concentration for 2 mg L⁻¹ GFZ and NDMA concentrations at 100 W UV light power. The results indicated that some decreases in the removal efficiencies of nano-TiO₂ with increasing treatment cycles for GFZ (from 95% to 60%) and NDMA (from 90% to 55%) were observed at the end of five cycles (Alvarez-Corena et al., 2016).

The results showed that nano-TiO₂ and nano-CeO₂ can be reused effectively during five sequential times for the photocatalytic treatment of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants from the raw hospital wastewater in order to decrease the cost of treatment at the aforementioned experimental conditions (Table 6.40). The ANOVA (one-way) test statistics results proved that a linear regression between five sequential treatment steps and photocatalytic removals of all studied micropollutants ($R^2 = 0.998$ for nano-TiO₂ and $R^2 = 0.997$ for nano-CeO₂) was obtained, while five sequential treatment steps had no significant effect on the reusability of the nanoparticle at the aforementioned experimental conditions ($P = 0.475$, $\alpha = 0.05$, $F = 0.89$ for nano-TiO₂ and $P = 0.226$, $\alpha = 0.05$, $F = 1.46$ for nano-CeO₂). Moreover, the ANOVA (one-way) test statistics results showed that after six sequential treatment steps, the reuse of the nanoparticle affected significantly for the photocatalytic treatment of all studied micropollutants at the aforementioned experimental conditions ($P = 0.0025$, $\alpha = 0.05$, $F = 4.14$ for nano-TiO₂ and $P = 0.0003$, $\alpha = 0.05$, $F = 5.53$ for nano-CeO₂).

6.3 Ultrasound Treatment Processes for Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

In this study, effects of sonicator power (20, 70 and 120 W), sonication time (15, 30, 45, 60 and 90 min), pHs (4.00, 7.00 and 8.50), temperatures (25, 40, 50, 65 and 80 °C), nano-TiO₂ and nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) were investigated on the ultrasound removals of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants from the raw hospital wastewater at a constant sonicator frequency of 132 kHz. The influent concentrations of all studied micropollutants in the ultrasound treatment experiments were shown in Table 5.1. The reusability of the nano-TiO₂ and nano-CeO₂ were researched from the raw hospital wastewater after each treatment.

6.3.1 Physicochemical Properties of Nanoparticles [Titanium (IV) Oxide (Nano-TiO₂) and Cerium (IV) Oxide (Nano-CeO₂)] Used in This Study

6.3.1.1 Scanning Electron Microscope (SEM) Analysis Results

The SEM images of raw and utilized nanoparticles after ultrasound treatment were obtained at the following experimental conditions: 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz.

6.3.1.1.1 SEM Analysis Results of Nano-TiO₂. The SEM image showed that the raw and utilized TiO₂ nanoparticle samples exhibit spherical structure and uniform distribution (Figure 6.45. a and b). The average particle sizes were measured about 20-25 nm for the raw and utilized nano-TiO₂ (Figure 6.45. a and b).

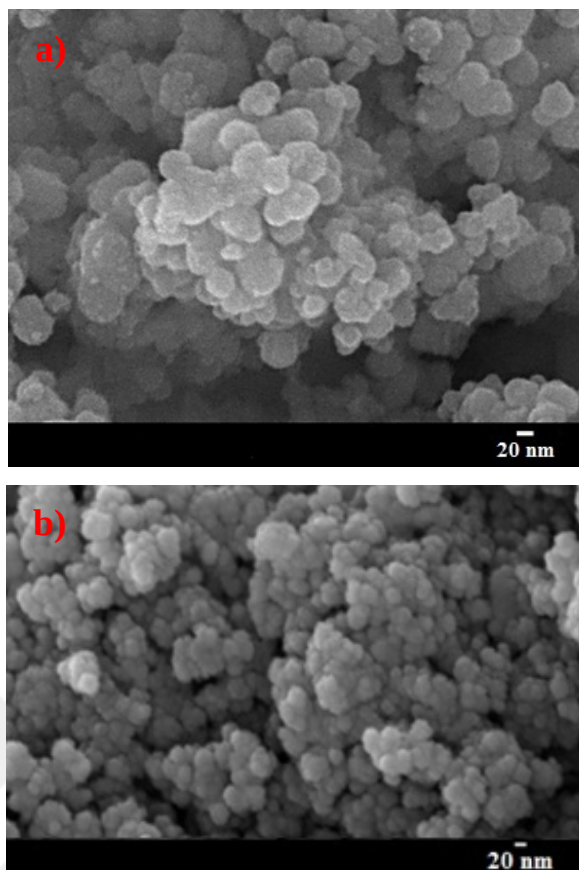


Figure 6.45 (a) SEM image of the raw nano-TiO₂ (b) SEM image of the utilized nano-TiO₂ after ultrasound treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

6.3.1.1.2 SEM Analysis Results of Nano-CeO₂. The raw and utilized CeO₂ nanoparticles showed spherical shapes and a homogeneous structure according to the SEM analysis (Figure 6.46.a and b). The average particle sizes were measured about 15-20 nm for the raw and utilized nano-CeO₂ (Figure 6.46.a and b).

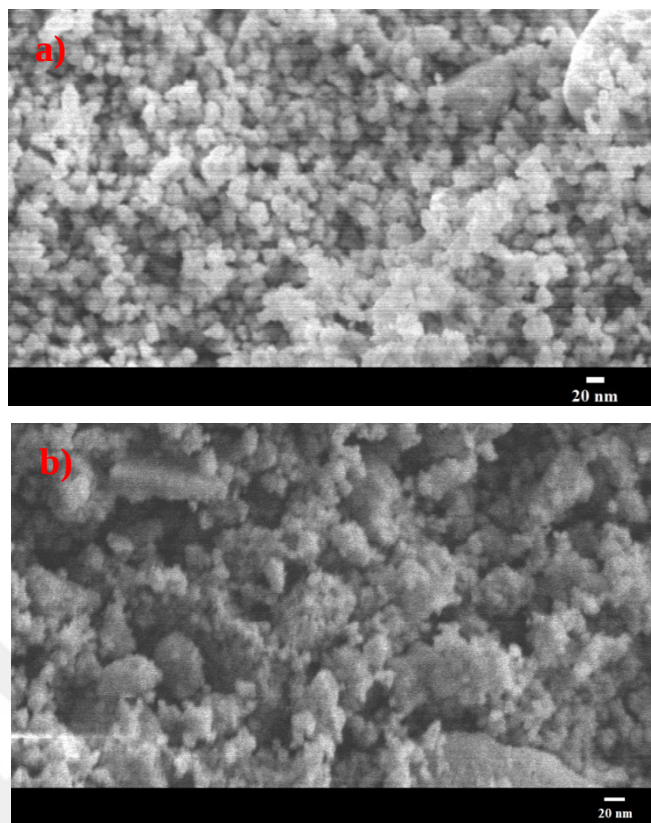


Figure 6.46 (a) SEM image of the raw nano-CeO₂ (b) SEM image of the utilized nano-CeO₂ after ultrasound treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

6.3.1.2 Fourier Transform Infrared (FT-IR) Analyses Results

Fourier Transform Infrared (FT-IR) analysis were performed on the raw and utilized nanoparticles at the following experimental conditions: 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz. The FT-IR peaks of the studied nanoparticles were plotted between wave number (cm⁻¹) and absorbance.

6.3.1.2.1 FT-IR Analyses Results of Nano-TiO₂. According to FT-IR analysis, the bonds in maximum absorption-diffraction peaks are determined at 3282, 2972, 2880, 2183, 1651, 1381, 1088, 1047 and 879 cm⁻¹ for the raw nano-TiO₂ (Figure 6.47.a). The absorption band at 3282 and 1651 cm⁻¹ are related to the stretching and bending

vibrations of O-H (δ -H₂O) respectively, (Figure 6.47.a) (Al-Amin et al., 2016). The absorption peaks at 2880 and 2972 cm⁻¹ are the symmetric and asymmetric stretching bands of =C-H, respectively (Figure 6.47.a) (Bagheri et al., 2013). The peaks at 1381, 1088 and 1047 cm⁻¹ are the aromatic -C=C stretching band and the C-O stretching bands, respectively (Figure 6.47.a) (Huang et al., 2017). The peak at 2183 cm⁻¹ shows the bending vibration of Ti-O (Figure 6.47.a) (Mulmi et al., 2016). The peak at 879 cm⁻¹ exhibited the triangular peroxy titanyl group (O-Ti-O) (Figure 6.47.a) (Silva, 2008).



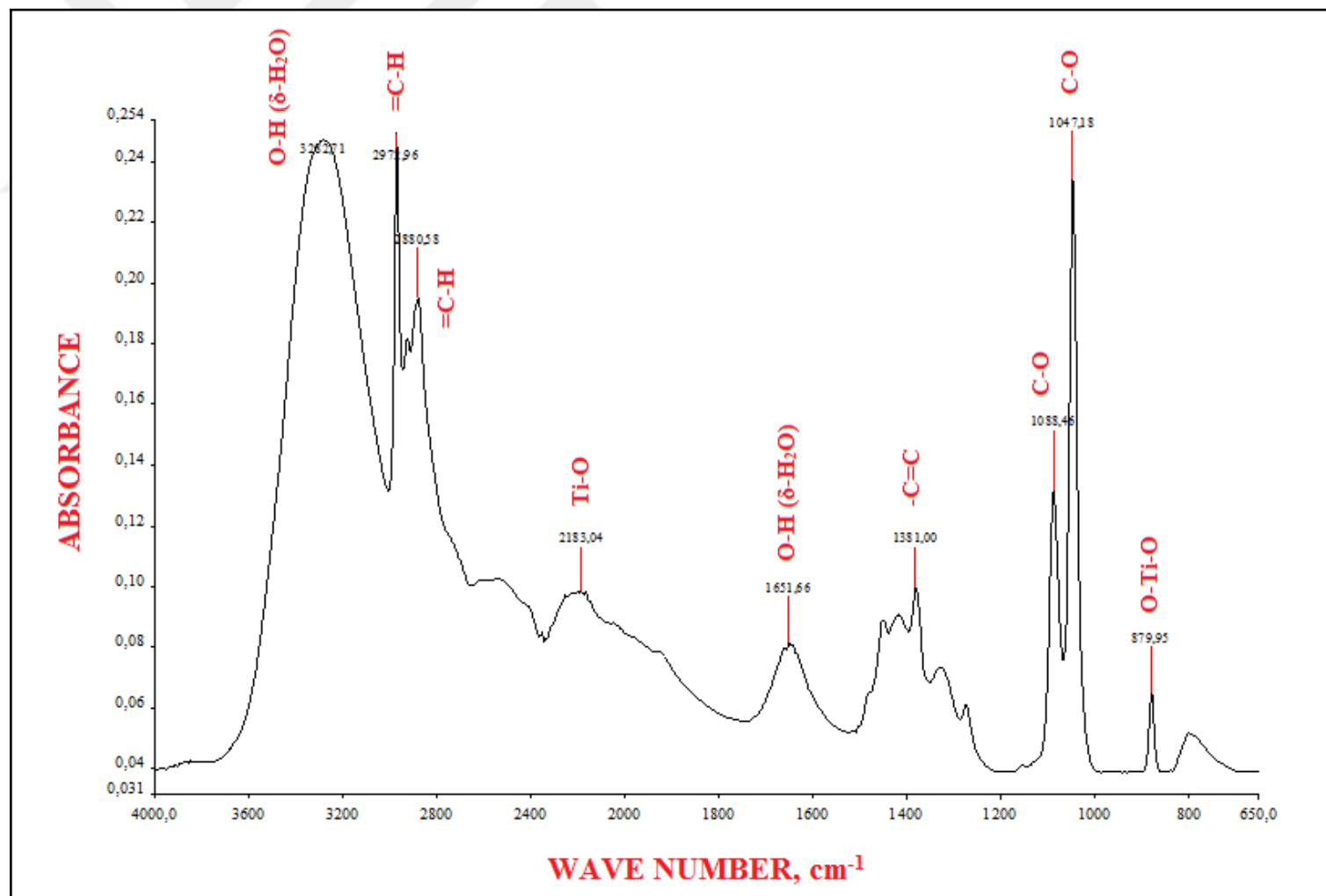


Figure 6.47 (a) FT-IR analysis of raw nano-TiO₂

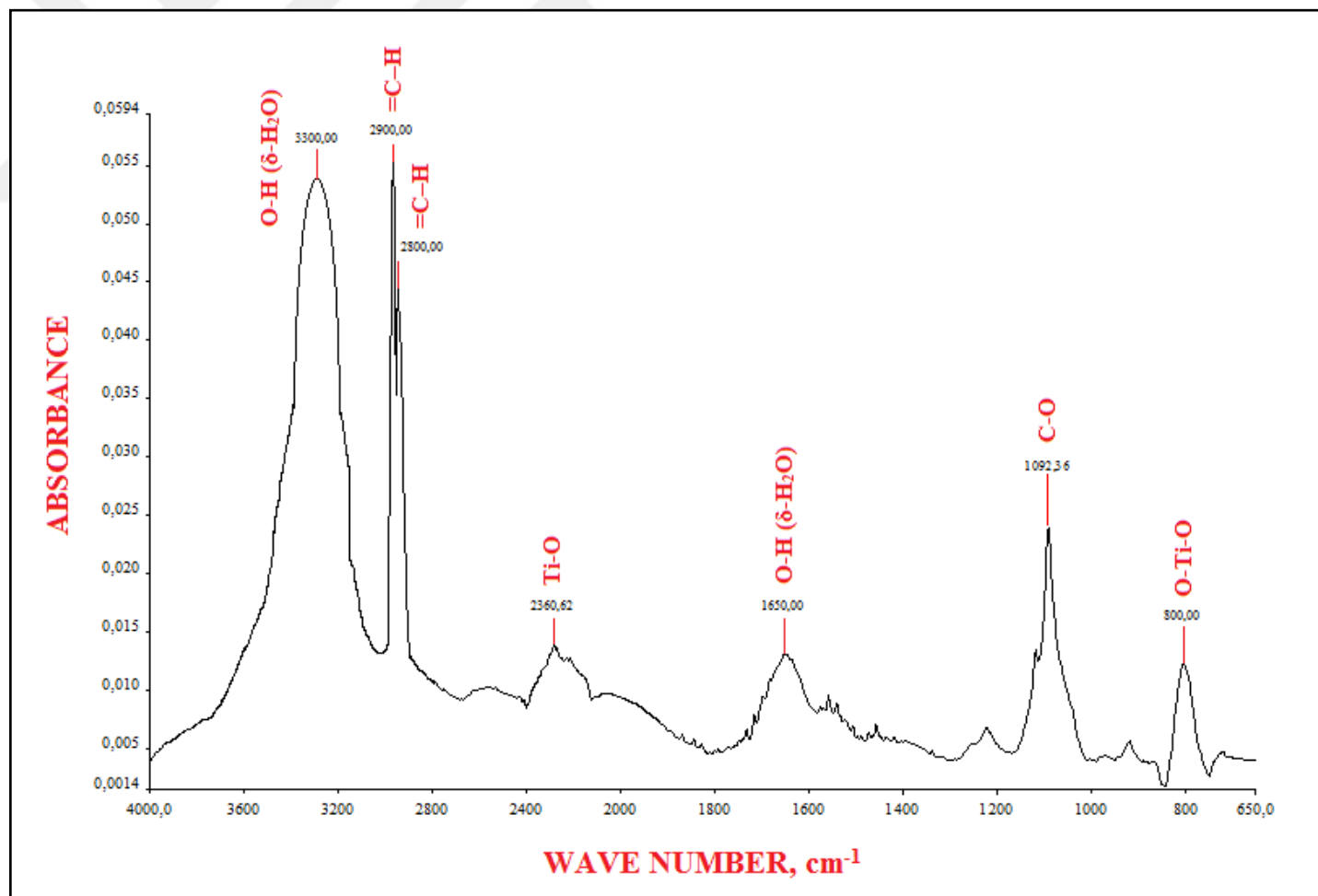


Figure 6.47 (b) FT-IR analysis of utilized TiO₂ nanoparticles after ultrasound treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

The most characteristic features in the FT-IR spectrum of the utilized nano-TiO₂ after ultrasound treatment at the aforementioned experimental conditions are the absorption bands corresponding to the =C–H stretching band at 2900 and 2800 cm⁻¹ (Bagheri et al., 2013), the bending vibrations of Ti-O at 2360 cm⁻¹ (Mulmi et al., 2016), the bending vibrations of O-H (δ-H₂O) at 3300 and 1650 cm⁻¹ (Al-Amin et al., 2016), the C-O stretching at 1092 cm⁻¹ (Huang et al., 2017) and the triangular peroxy titanyl group (O-Ti-O) at 800 cm⁻¹ (Silva, 2008) (Figure 6.47.b). The maximum peaks (3300, 2900, 2800, 2360, 1650, 1092 and 800 cm⁻¹) for the utilized nano-TiO₂ after ultrasound treatment at the aforementioned experimental conditions (Figure 6.47.b) are similar to the peaks of raw nano-TiO₂ (3282, 2972, 2880, 2183, 1651, 1088 and 879 cm⁻¹) (Figure 6.47.a).

6.3.1.2.2 FT-IR Analyses Results of Nano-CeO₂. The peaks at 3626, 1635, 1457, 988 and 850 cm⁻¹ for the raw nano-CeO₂ is related to the stretching vibration of O-H (δ-H₂O) representing the water as moisture (Babitha et al., 2015), the scissor bending of H-O-H (Liu et al., 2014), the bending vibration of C-H stretching band (Farahmandjou & Zarinkamar, 2015), the C-O stretching vibration (Farahmandjou et al., 2016) and the Ce-O stretching (Babitha et al., 2015), respectively according to FT-IR analysis (Figure 6.48.a).

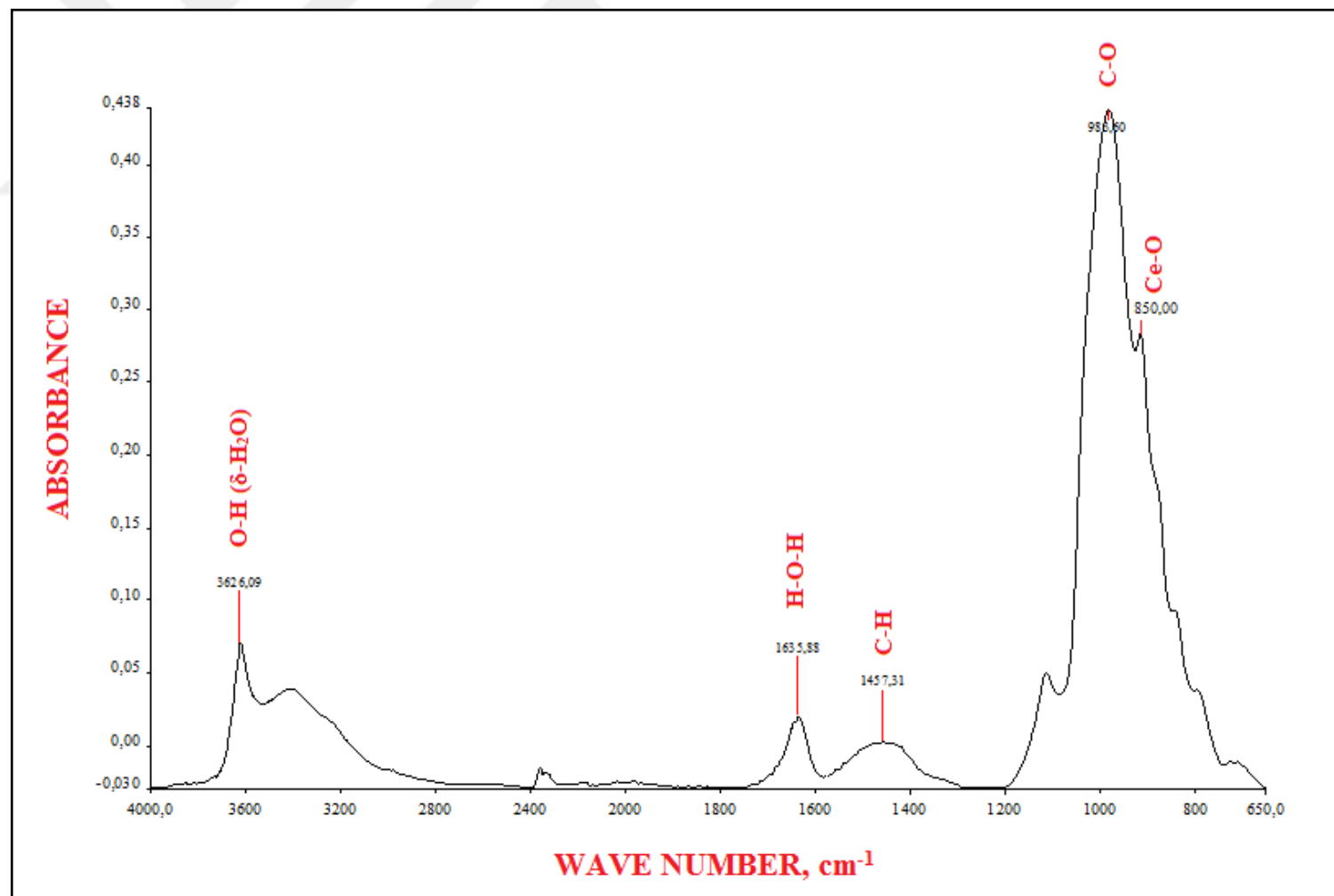


Figure 6.48 (a) FT-IR analysis of raw nano-CeO₂

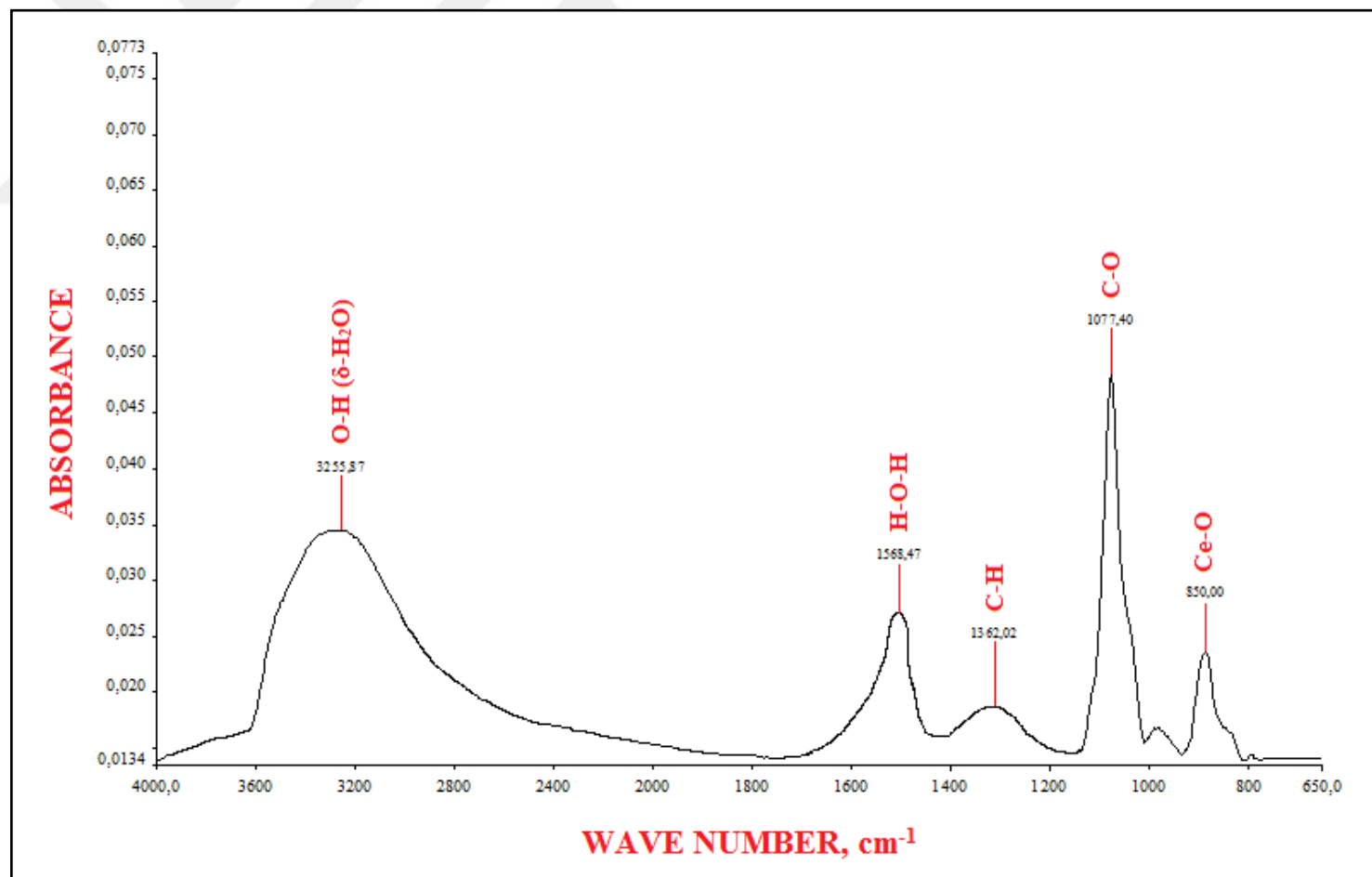


Figure 6.48 (b) FT-IR analysis of utilized CeO₂ nanoparticles after ultrasound treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

The FT-IR peaks of the utilized nano-CeO₂ after ultrasound treatment at the aforementioned experimental conditions are the stretching vibration of O-H (δ -H₂O) at 3255 cm⁻¹ (Babitha et al., 2015), the scissor bending of H-O-H at 1568 cm⁻¹ (Liu et al., 2014), the bending vibration of C-H stretching band at 1362 cm⁻¹ (Farahmandjou & Zarinkamar, 2015), the C-O stretching vibration at 1077 cm⁻¹ (Farahmandjou et al., 2016) and the Ce-O stretching at 850 cm⁻¹ (Babitha et al., 2015), respectively (Figure 6.48.b). The maximum peaks (3255, 1568, 1362, 1077 and 850 cm⁻¹) obtained for the utilized nano-CeO₂ (Figure 6.48.b) are similar to the peaks of raw nano-CeO₂ (3626, 1635, 1457, 988 and 850 cm⁻¹) (Figure 6.48.a).

6.3.1.3 X-Ray Diffraction (XRD) Analysis Results

The raw and utilized nanoparticles (nano-TiO₂ and nano-CeO₂) after ultrasound treatment were characterized using XRD to identify the structures of the nanoparticles at the following experimental conditions: at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz.

6.3.1.3.1 XRD Analyses Results of Nano-TiO₂. The main peaks of raw nano-TiO₂ appeared at 25°, 28°, 39°, 48°, 54°, 55°, 63°, 69°, 70° and 76° while the strongest and narrow peak was detected at $2\theta = 25^\circ$ (Figure 6.49.a). High intensity sharp peak ($2\theta = 25^\circ$) and absence of unidentified peaks confirmed the good crystallinity, higher purity and anatase phase of the raw nano-TiO₂ (Figure 6.49.a). The peaks of the raw nano-TiO₂ were in accordance with the literature data (Hu et al., 2017 and Hassani et al., 2017).

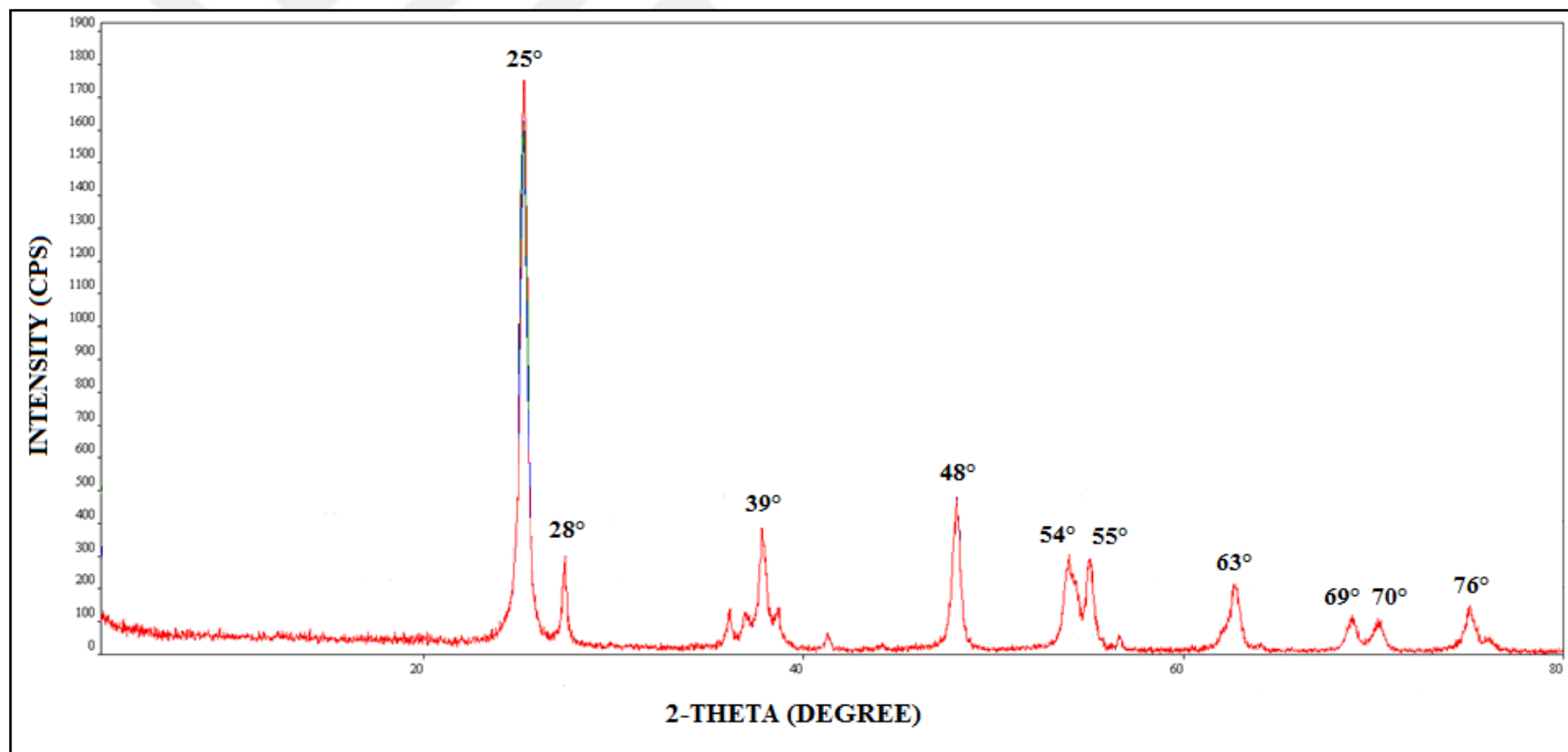


Figure 6.49 (a) XRD analysis of raw nano-TiO₂

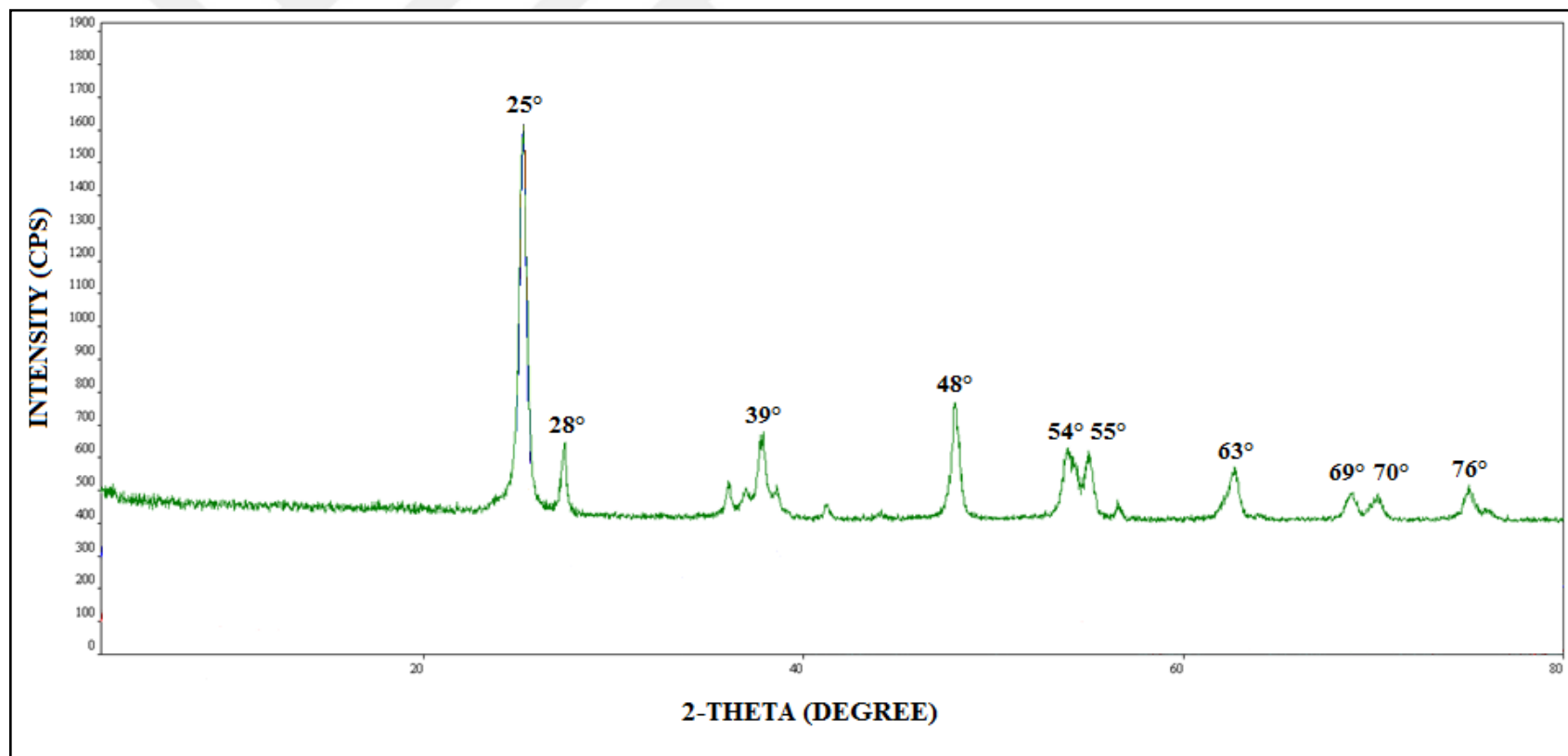


Figure 6.49 (b) XRD analysis of utilized nano-TiO₂ after ultrasound treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

The strongest and narrow peak for the utilized nano-TiO₂ after ultrasound treatment at the aforementioned experimental conditions was detected at $2\theta = 25^\circ$ (Figure 6.49.b). The characteristic peaks of the utilized nano-TiO₂ (25° , 28° , 39° , 48° , 54° , 55° , 63° , 69° , 70° and 76°) did not change after ultrasound treatment (Figure 6.49.b).

6.3.1.3.2 XRD Analyses Results of Nano-CeO₂. The XRD peaks were obtained at 28° , 33° , 48° , 56° , 59° and 69° , while the strongest and narrow peak was detected at $2\theta = 28^\circ$ for the raw nano-CeO₂ (Figure 6.50.a). These results confirmed using Joint Committee on Powder Diffraction Standards (JCPDS card no 34-0394 for CeO₂ nanoparticles) and also, these results showed that the CeO₂ nanoparticles had a cubic fluorite structure. Similar peaks were determined for nano-CeO₂ in the literature (Phuruangrat et al., 2017 and Channei et al., 2017).

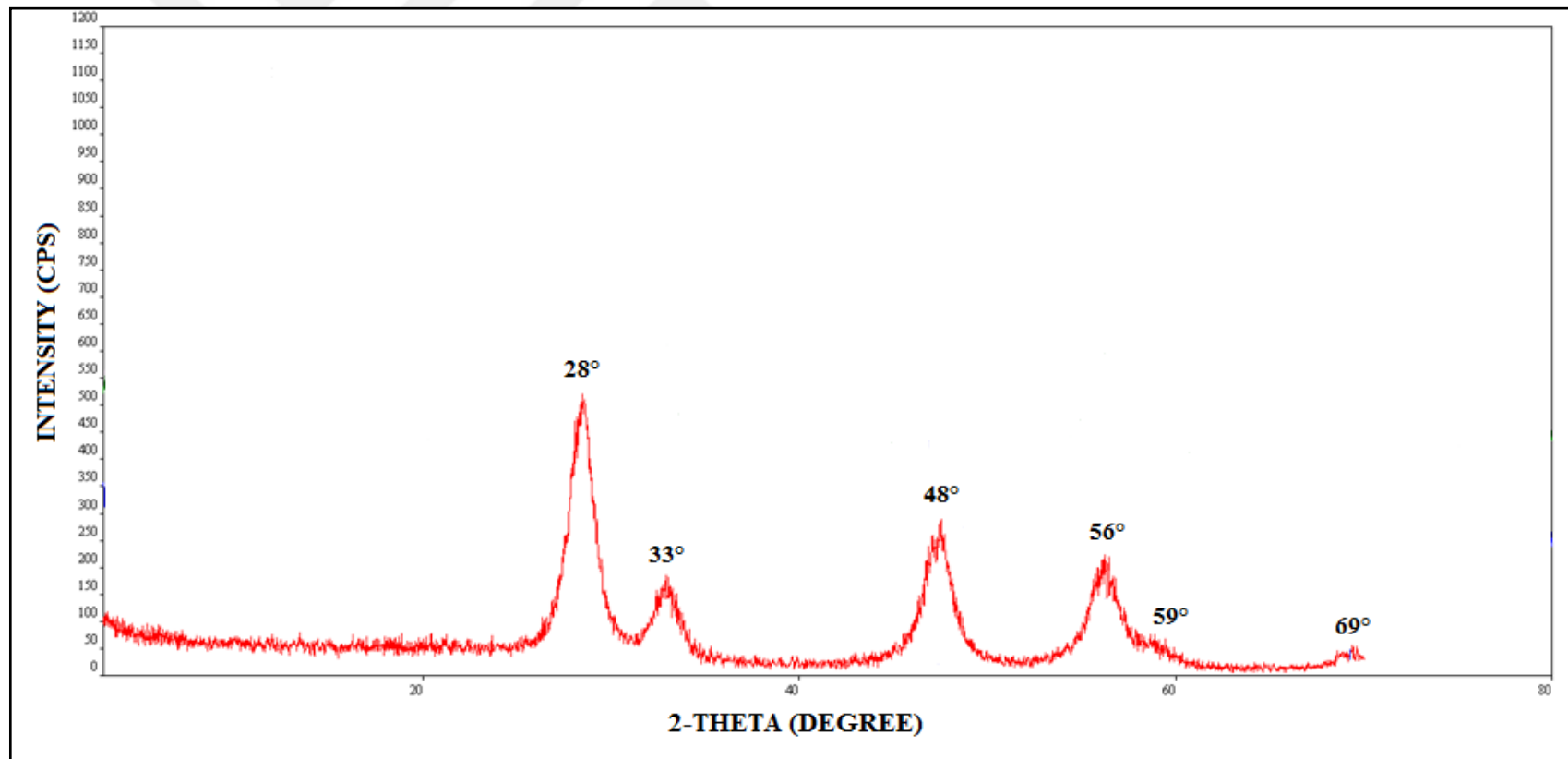


Figure 6.50 (a) XRD analysis of raw nano-CeO₂

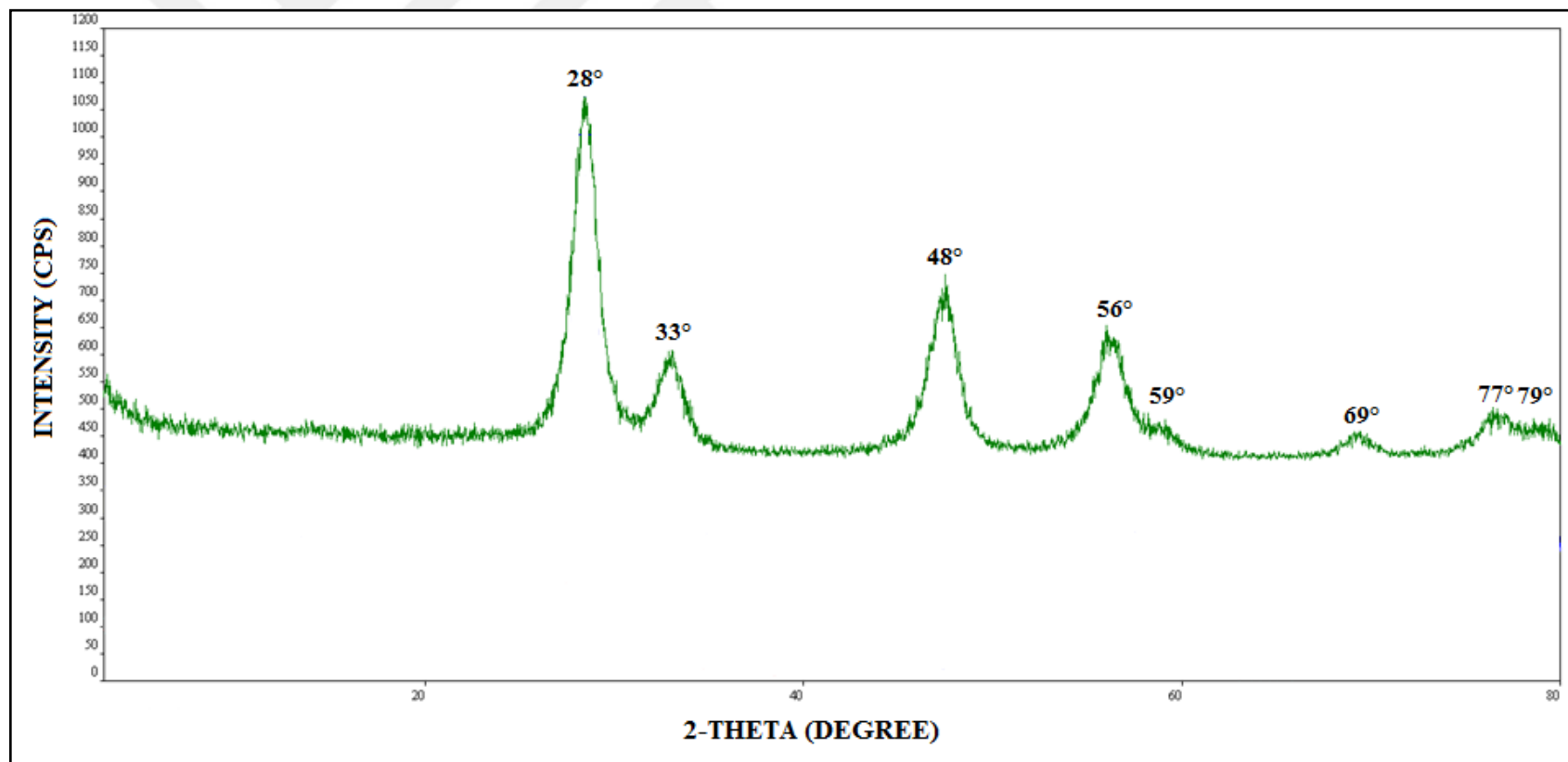


Figure 6.50 (b) XRD analysis of utilized nano-CeO₂ after ultrasoun treatment at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

The strongest and narrow peak was detected at $2\theta = 28^\circ$ for the utilized nano-CeO₂ after ultrasound treatment at the aforementioned experimental conditions (Figure 6.50.b). The detected peaks for the utilized nano-CeO₂ (28° , 33° , 48° , 56° , 59° , 69° , 77° and 79°) did not change after ultrasound treatment at the aforementioned experimental conditions (Figure 6.50.b).

6.3.2 Effect of Sonicator Power on the Ultrasonic Degradations of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

Effect of sonicator power (20, 70 and 120 W) was researched on the ultrasound removals of all studied micropollutants in this study. It was decided to use a sonicator power range between 20 and 120 W according to the experiments given by the recent literature (Méndez-Arriaga et al., 2008). The experiments were carried out at a constant sonication time (15 min) based on the study performed by Moriwaki et al. (2005), at a constant pH (7.00) based on the study tested by De Bel et al. (2009), at a constant temperature (25 °C) based on the study examined by Ren et al. (2014) and at a constant frequency (132 kHz) based on the study given by Adiyotosulindro et al (2017). Among the powers used in the ultrasonic degradation process (20, 70 and 120 W) it was found that a sonication power of 120 W was the optimum power for the maximum micropollutants removals in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.51). Higher sonicator power than 120 W did not increase the removals of micropollutants. Therefore, the maximum removals were illustrated only for 120 W power. The maximum ultrasonic degradations were followed the order of brominated (higher than 34%), phenolic (higher than 30%), aromatic (33%), nitroso (28%) and fluoro (higher than 23%) micropollutants at the optimum sonicator power of 120 W at the aforementioned experimental conditions (Figure 6.51).

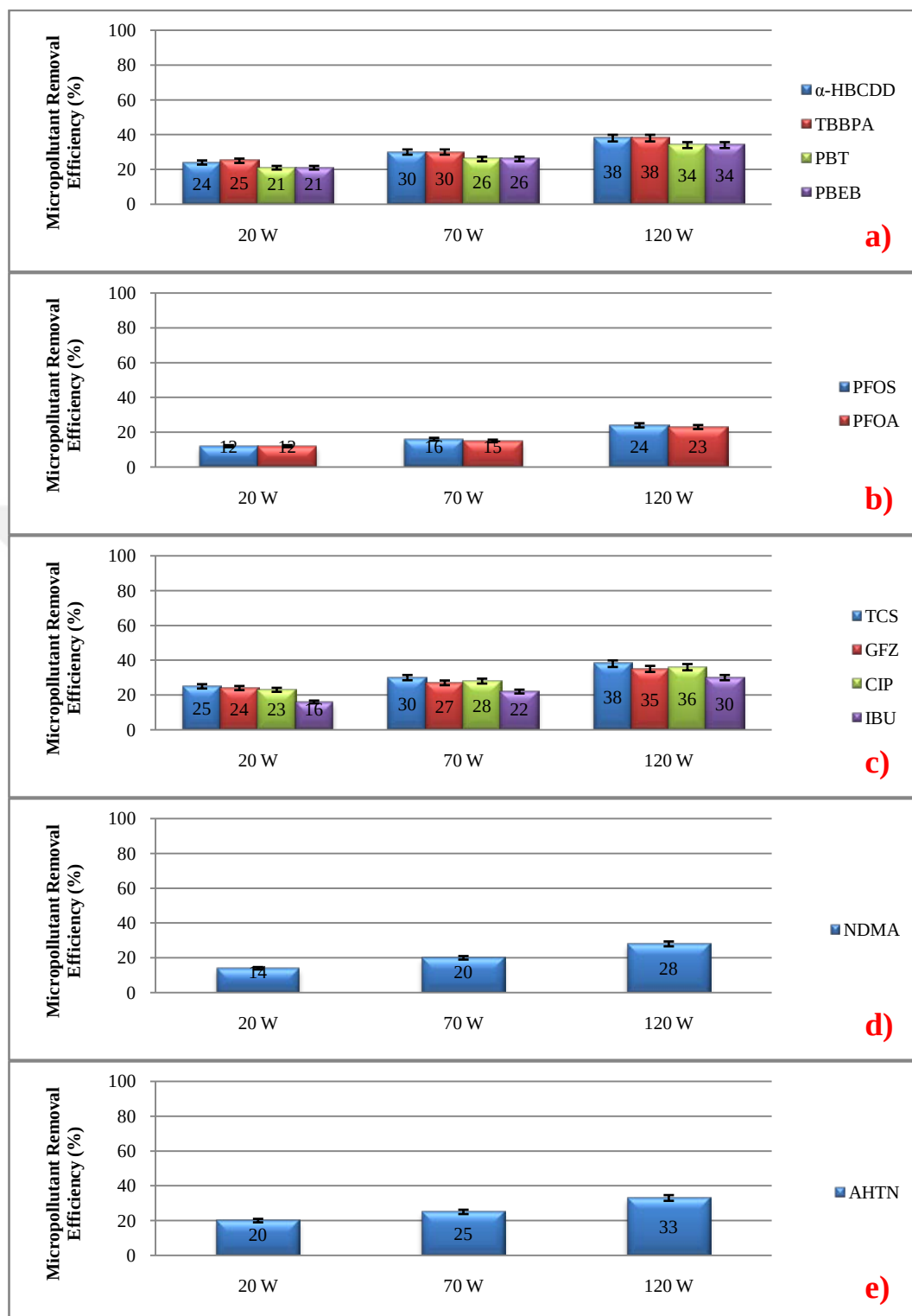


Figure 6.51 Effect of sonicator power (20, 70 and 120 W) on the ultrasound removals of all studied micropollutants at a constant sonication time (15 min), at a constant pH (7.00), at a constant temperature (25 °C) and at a constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

The removal efficiency increases with the increasing output power of the sonicator used in the ultrasound treatment. The ultrasonic degradation of the micropollutants increased with the increasing sonicator power from 20 W to 120 W at the aforementioned experimental conditions. Buseti, Heitz, Cuomo, Badoer, & Traverso (2006) reported that the number of collapsing cavities increase with increasing sonicator power and provides enhanced degradation rates (Busetti et al., 2006). The vibration of sound in the cavitation area was increased with increasing sonicator power and more cavitation bubbles were produced during the ultrasound treatment. When ultrasound is applied, cavitation bubbles form during the rarefaction (negative pressure) portion of sound waves. The cavitation bubbles will implode adiabatically, creating extreme temperatures ($> 9700\text{ }^{\circ}\text{C}$ in the vapor core) and pressures ($\approx 14000\text{ psi}$) within its cavity. Highly reactive intermediates and radicals, including hydroxyl radicals, hydrogen atom and oxygen atom form during cavitation bubble collapse. This combination of highly reactive species, high temperatures and pressures have made ultrasonic degradation of the micropollutants (Merino et al., 2016). Méndez-Arriaga et al. (2008) investigated the effect of sonicator power (20, 40, 60 and 80 W) on the ultrasonic degradation of IBU. A higher applied power (80 W) lead to a higher degradation rate ($6.1\text{ }\mu\text{mol L}^{-1}\text{ min}^{-1}$) for an initial IBU concentration of 21 mg L^{-1} at 300 kHz for 30 min sonication time at $25\text{ }^{\circ}\text{C}$ and at a pH of 3.00 (Méndez-Arriaga et al, 2008).

The ANOVA (one-way) test statistics results showed that there is a strong correlation between sonicator power and the removals of all studied micropollutants ($R^2 = 0.98$). Therefore, the sonicator power significantly increased the micropollutant removals at the optimum sonicator power of 120 W at the aforementioned experimental conditions ($P = 3.30 \times 10^{-6}$, $\alpha = 0.05$, $F = 18.95$).

6.3.3 Effect of Sonication Time on the Ultrasonic Degradations of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

Effect of sonication time (15, 30, 45, 60 and 90 min) was researched on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant pH (7.00), at a constant temperature (25 °C) and at a constant sonicator frequency of 132 kHz (Figure 6.52). It was decided to use a time interval between 15 min and 90 min based on the working time set up of the sonicator used in the experiments and a previous study taken from the literature (Moriwaki et al., 2005). Among the sonication times used in the ultrasound treatment process (15, 30, 45, 60 and 90 min) it was found that a sonication time of 60 min was the optimum sonication time for the maximum micropollutants removals in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.52). The maximum ultrasonic degradations were higher than 50% for brominated and phenolic micropollutants, in addition, removals were higher than 40% for fluoro, nitroso and aromatic micropollutants at the optimum sonication time of 60 min at the aforementioned experimental conditions (Figure 6.52).

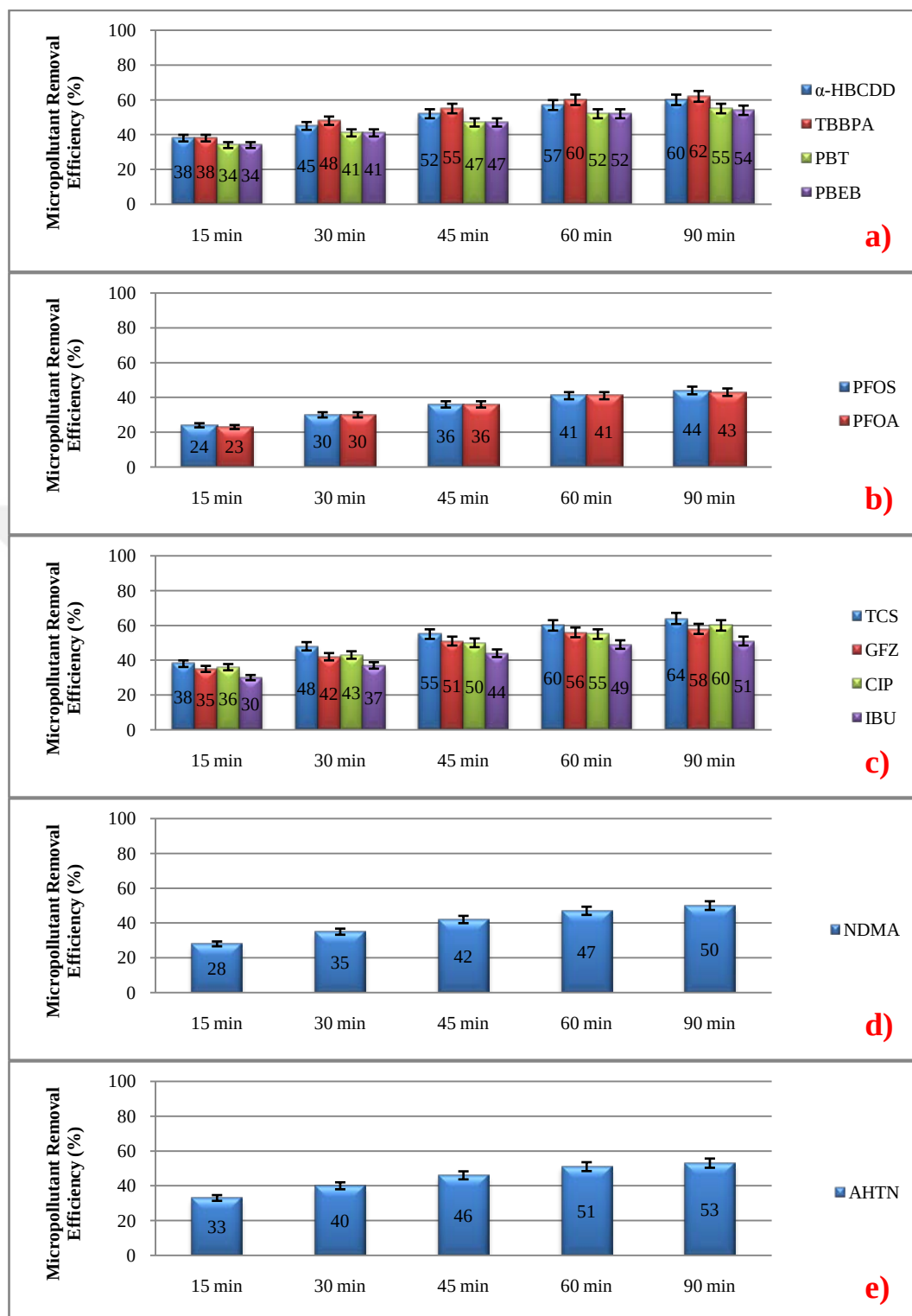


Figure 6.52 Effect of sonication time (15, 30, 45, 60 and 90 min) on the ultrasound removals of all studied micropollutants at constant sonicator power (120 W), at constant pH (7.00), at constant temperature (25 °C) and at constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

Shorter sonication times (15, 30 and 45 min) did not provide higher ultrasonic degradation removals for all studied micropollutants since they were not exposed to ultrasonic degradation for a long enough time. Higher sonication times (60 min) are needed to achieve a complete mineralization for all studied micropollutants having complex structures. This is due to the fact that the micropollutants have very low probabilities of making contact with hydroxyl radicals, which react mainly at the interface of the bubble (Karami, Mohammadi, Zinatizadeh, Falahi, & Aghamohammadi, 2018). Therefore, an increase in the removal efficiencies of micropollutants was expected at longer sonication times due to sufficient radical reactions through cavitation (Sponza & Oztekin, 2010). Any further increase in the sonication time (90 min) did not significantly affect the ultrasonic degradation removals of all studied micropollutants. Because more cavitation bubbles were not produced for the constant volume of the sample (250 mL) when the experimental conditions continue longer than the optimum sonication time (60 min) in this study. The ANOVA (one-way) test statistics results showed that a linear regression between sonication time and ultrasonic degradation removals of all studied micropollutants was observed with the increasing sonication time from 15 min to 60 min ($R^2 = 0.98$) and this correlation was significant at the aforementioned experimental conditions ($P = 5 \times 10^{-9}$, $\alpha = 0.05$, $F = 22.68$). The effect of sonication time on the ultrasonic degradation removals of all studied micropollutants for higher than 60 min (90 min) was not significant at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results ($P = 0.317$, $\alpha = 0.05$, $F = 1.05$).

6.3.4 Effect of pH on the Ultrasonic Degradations of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

The ultrasonic degradation rates of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were researched under acidic (pH = 4.00), neutral (pH = 7.00) and alkaline (pH = 8.50) pH conditions at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant temperature (25 °C) and at a constant sonicator frequency of 132 kHz (Figure 6.53).

It was decided to study at the pHs of 4.00, 7.00 and 8.50 based on a previous study from the literature (De Bel et al., 2009). The pH was adjusted by the addition of 1N NaOH or 1N HCl for the desired levels.

Among the pHs used in the ultrasound treatment process (4.00, 7.00 and 8.50) it was found that a pH of 4.00 is the optimum pH since all brominated (α -HBCDD, PBEB, PBT and TBBPA), phenolic (GFZ, TCS, IBU and CIP) and aromatic (AHTN) micropollutants reached the highest removal efficiencies (higher than 52%) in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.53.a, c and e). The fluoro (PFOA and PFOS) and nitroso (NDMA) micropollutants showed the highest removal efficiencies (higher than 40%) at the neutral pH of 7.00 at the aforementioned experimental conditions (Figure 6.53.b and d).

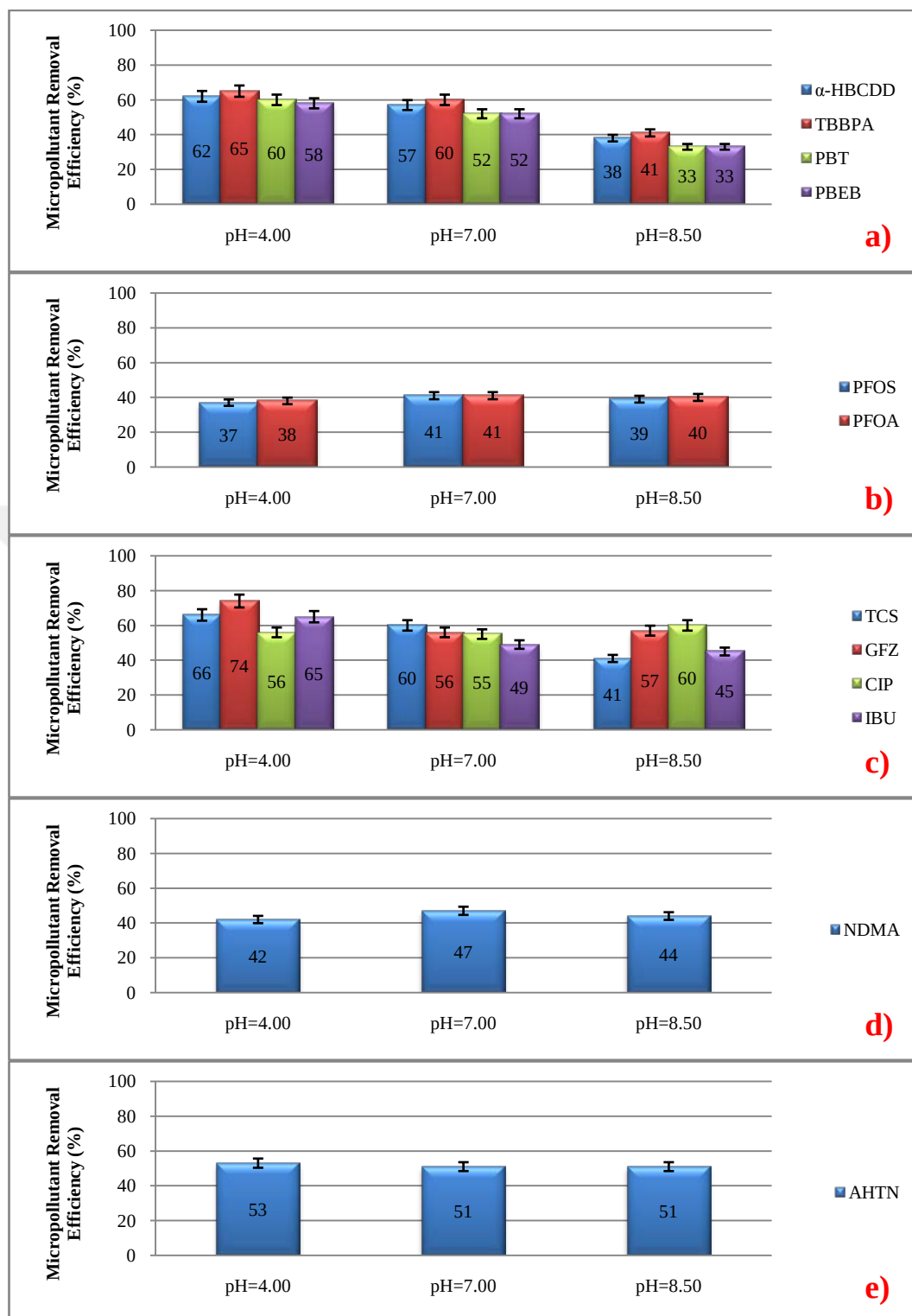


Figure 6.53 Effect of pH (4.00, 7.00 and 8.50) on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant temperature (25 °C) and at a constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

The removal efficiencies of all brominated (α -HBCDD, PBEB, PBT and TBBPA), phenolic (GFZ, TCS, IBU and CIP) and aromatic (AHTN) micropollutants increased at the gas–liquid interface of the bubbles with an increase of acidity of the raw hospital wastewater. The more hydrophobic micropollutants are found in their molecular form at lower pKa (acid dissociation constant or acid-ionization constant) values (under acidic conditions). As the molecular state of the micropollutants are more hydrophobic than the ionic one, the more hydrophobic micropollutants are expected to accumulate in the vicinity of the cavitation bubbles under acidic conditions. The reaction between the radicals generated and the micropollutants would be enhanced if their hydrophobicity is favored. The micropollutants have a hydrophobic character when their structure is in the molecular state which occurs at a pH value lower than pKa. All brominated (α -HBCDD, TBBPA, PBEB and PBT), phenolic (TCS, GFZ, CIP and IBU) and aromatic (AHTN) micropollutants have a hydrophobic character in this study because their pKa values were higher than acidic pH of 4.00 (for the numerical values see Table 5.2). Under this condition, the micropollutant is accumulated in the interface of the cavitation bubbles and the highest degradation efficiency is achieved (Méndez-Arriaga et al., 2008). The ANOVA (one-way) test statistics results showed that the effect of acidic pH (4.00) on the ultrasound removals of the brominated, phenolic and aromatic micropollutants were significant at the aforementioned experimental conditions ($P = 0.009$, $\alpha = 0.05$, $F = 5.52$). The removal efficiencies of fluoro (PFOA and PFOS) and nitroso (NDMA) micropollutants were lower at the acidic pH (4.00) because their pKa values were lower than the acidic pH of 4.00 (for the numerical values see Table 5.2). Therefore, they could not show hydrophobic properties in this study and their removal efficiencies were high at the neutral pH (7.00) in the comparison with the acidic pH (4.00).

Moriwaki et al. (2005) achieved 60% and 85% of PFOS and PFOA removals, respectively for the initial PFOS and PFOA concentrations of 10 mg L^{-1} at 20°C at 200 kHz for 1 h ultrasound treatment with a pH range of 3.5 to 4.8 (Moriwaki et al., 2005). De Bel et al. (2009) degraded 57% of CIP (15 mg L^{-1} initial CIP concentration) at pH 7.00 after 120 min sonication time at 520 kHz frequency and at

25 °C. Degradation at pH 3.00 ($k_1=0.021 \text{ min}^{-1}$) was almost four times faster than at pH 7.00 ($k_1=0.0058 \text{ min}^{-1}$). The degradation constant at pH 10 ($k_1=0.0069 \text{ min}^{-1}$) was also significantly higher than at pH 7.00 (De Bel et al., 2009). The results obtained from this study for CIP were similar to the findings of De Bel et al., (2009). This can be explained by the different CIP forms (CIP^{3+} , CIP^{2+} , CIP^+ , CIP and CIP^-) due to (de)protonation depending on the pzc values (De Bel et al., 2009) ($\text{pzc}_{\text{CIP}} = 3.6, 5.6, 6.2 \text{ and } 8.8$).

6.3.5 Effect of Temperature on the Ultrasonic Degradations of Brominated (α -HBCDD, TBBPA, PBT And PBEB), Fluoro (PFOS And PFOA), Phenolic (TCS, GFZ, CIP And IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

Effect of temperature (25, 40, 50, 65 and 80 °C) was researched on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant pH (4.00) and at a constant sonicator frequency of 132 kHz (Figure 6.54). It was decided to examine a temperature range between 25 °C and 80 °C based on the working temperature range of the sonicator used in the experiments and a previous study taken from the literature (Ren et al., 2014). Among the temperatures used in the ultrasound treatment process (25, 40, 50, 65 and 80 °C) it was found that a temperature of 40 °C was the optimum temperature for the maximum ultrasound removals of all studied micropollutants in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.54). The maximum ultrasonic degradations were followed the order of phenolic (higher than 72%), brominated (higher than 70%), aromatic (68%), nitroso (56%) and fluoro (higher than 52%) micropollutants at the optimum temperature of 40 °C at the aforementioned experimental conditions (Figure 6.54).

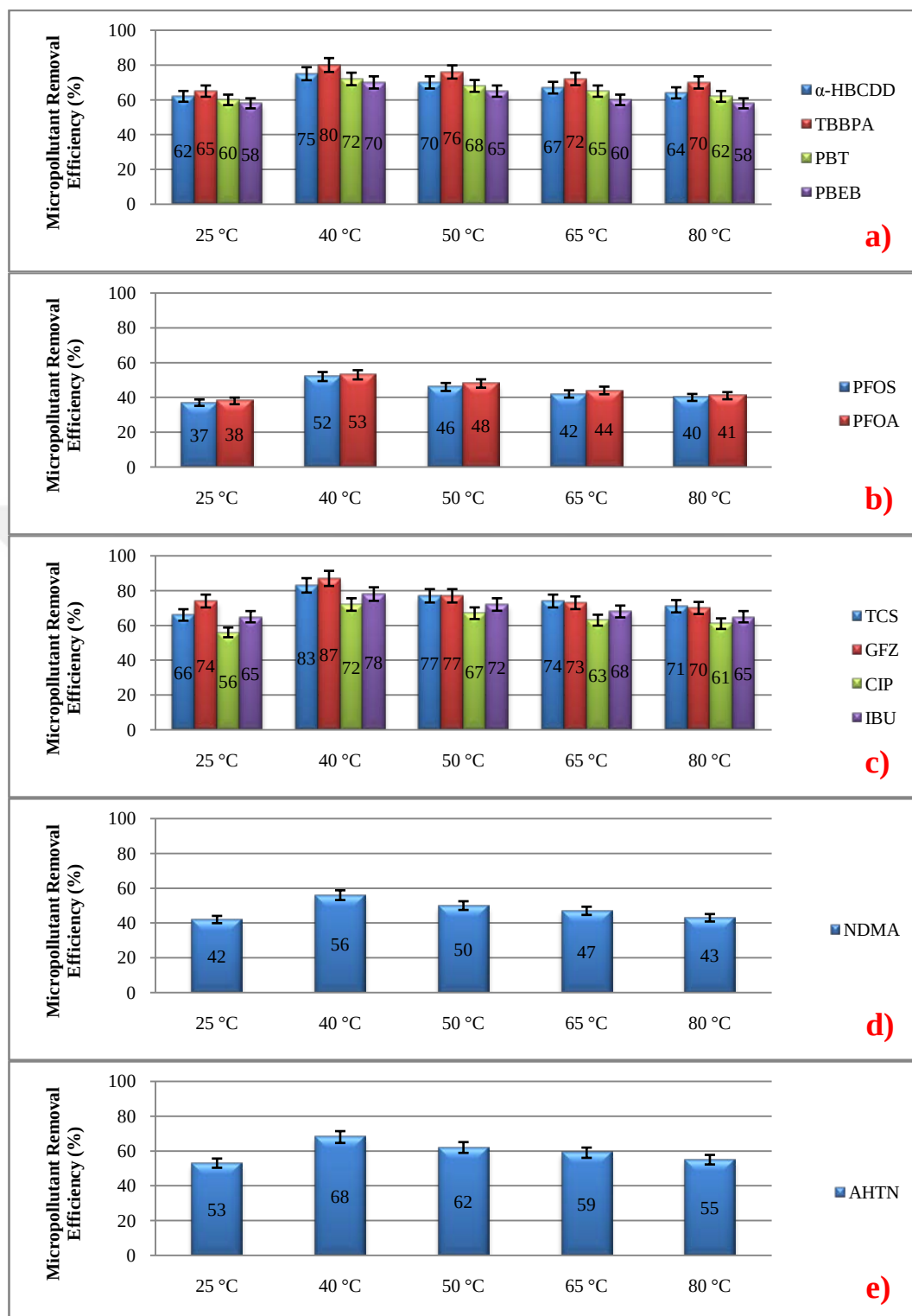


Figure 6.54 Effect of temperature (25, 40, 50, 65 and 80 °C) on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant pH (4.00) and at a constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

As is shown in Figure 6.54, the ultrasonic degradation removals of all studied micropollutants increased with the increasing temperature from 25 °C to 40 °C. The bulk phase temperature affects several factors such as the vapor pressure, viscosity, gas solubility and surface tension (Goel, Hu, Mujumdar, & Ray, 2004). So, it is expected that an increase in the temperature would lead to an increased number of cavitation bubbles, promoting the production of free radicals ($\text{OH}\cdot$ and $\text{OOH}\cdot$) that have a high oxidation potential (He, Song, Zhou, Ying, & Chen, 2007). At the same time, reactions of the hydroxyl ($\text{OH}\cdot$) radicals and other oxidative species in the bulk solution are facilitated by the increased temperature at a optimum value due to the higher mass transfer of different species at higher temperatures and this leads to an enhancement of the reaction rate of the radicals with micropollutant. An increase of bulk temperature generally seems to have a positive effect on the ultrasonic degradation removal up to an optimum value (De Bel et al., 2011). The ultrasonic degradation removals of all studied micropollutants decreased with the increasing temperature from 50 °C to 80 °C. However, an increase in the temperature increases the vapor pressure of the solvent. Consequently, the cavitation bubbles contain more water vapor. Because of this increased vapor content, the collapse of cavitation bubbles will be less violent (cushion effect). This causes a reduction in the collapse temperature and thus a reduced production of hydroxyl ($\text{OH}\cdot$) radicals. On the other hand, the increased temperature results in the reduction of the viscosity and the surface tension, lowering the threshold intensity required to produce cavitation (Mason & Lorimer, 2002).

The ultrasonic degradation constant of CIP increased from 0.0055 min^{-1} to 0.0105 min^{-1} as the temperature was increased from 15 °C to 45 °C for an initial CIP concentration of 15 mg L^{-1} at a frequency of 544 kHz and at a pH of 7.00 with 200 W sonicator power (De Bel et al., 2011). Ren et al. (2014) concluded that the optimum ultrasonic degradation degrees of the micropollutants could be found for the temperatures higher than 30 °C. They reported 88% of TCS removal at 35 °C at 170 W sonicator power after 15 min sonication time at 850 kHz frequency and at a pH of 2.50 for an initial TCS concentration of 5 mg L^{-1} (Ren et al., 2014).

The ANOVA (one-way) test statistics results showed that the increased temperature up to 40 °C had a significant effect on the ultrasound removals of all studied micropollutants at the aforementioned experimental conditions ($P = 0.007$, $\alpha = 0.05$, $F = 8.84$). The effect of temperature on the ultrasonic degradation removals of all studied micropollutants for higher than 40 °C (50, 65 and 80 °C) was not found to be significant at the aforementioned experimental conditions ($P = 0.377$, $\alpha = 0.05$, $F = 1.01$).

6.3.6 Effect of Nano-TiO₂ and Nano-CeO₂ Concentrations on the Ultrasonic Degradations of Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants

Effect of nano-TiO₂ and nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) were researched on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant pH (4.00), at a constant temperature (40 °C) and at a constant sonicator frequency of 132 kHz (Figure 6.55 and 6.56). It was decided to use a nanoparticle concentration range between 0.25 and 1.50 g L⁻¹ both for nano-TiO₂ and nano-CeO₂ based on a previous study from the literature (Anju, Yesodharan, & Yesodharan, 2012).

Among the nano-TiO₂ concentrations used in the ultrasound treatment process (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) it was found that a nano-TiO₂ concentration of 0.40 g L⁻¹ was the optimum nanoparticle concentration for the maximum ultrasound removals of all studied micropollutants in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.55). The maximum ultrasonic degradations were followed the order of phenolic (higher than 86%), brominated (higher than 82%), aromatic (80%), nitroso (70%) and fluoro (higher than 65%) micropollutants at the optimum nano-TiO₂ concentration of 0.40 g L⁻¹ at the aforementioned experimental conditions (Figure 6.55).

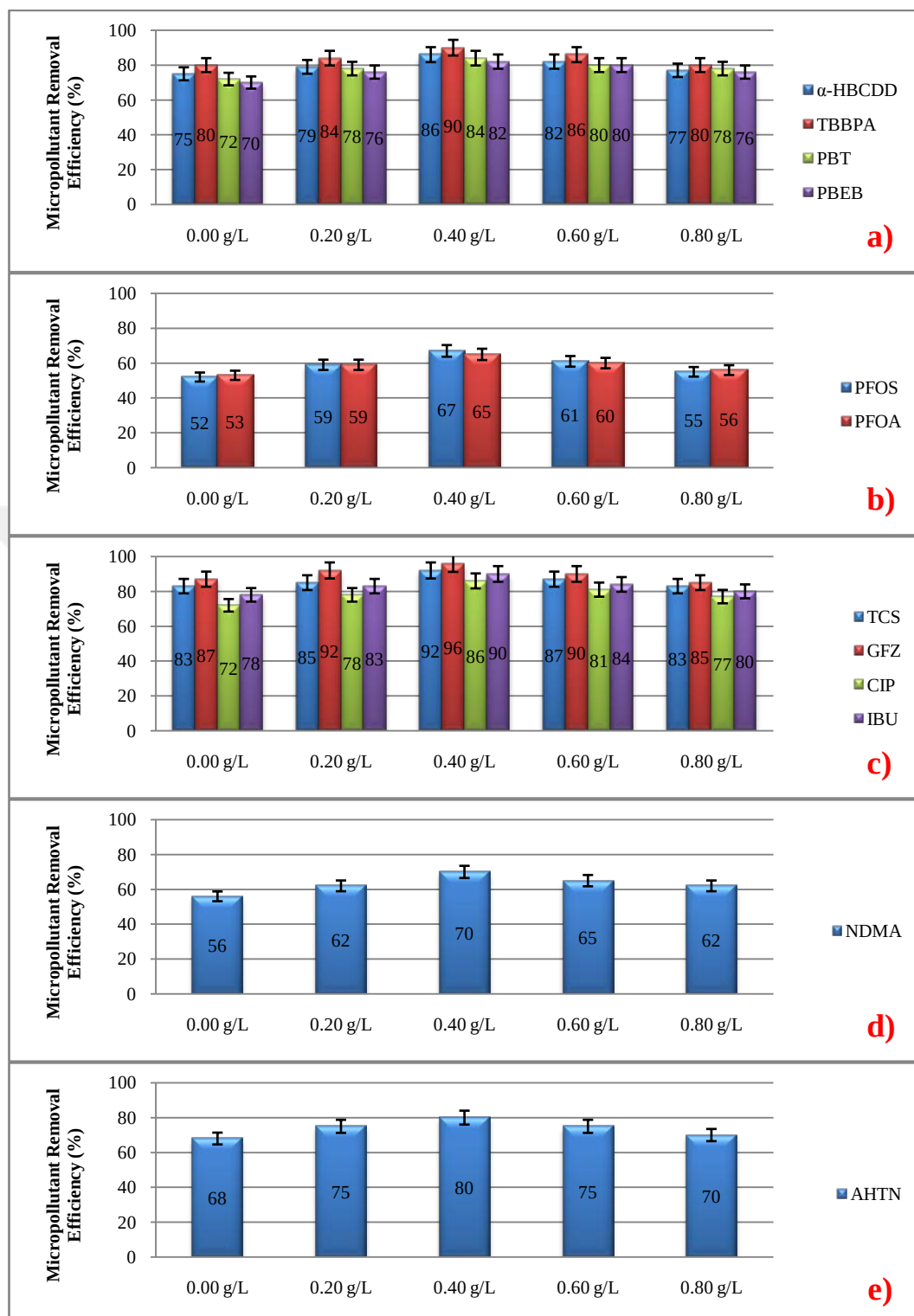


Figure 6.55 Effect of nano-TiO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant pH (4.00), at a constant temperature (40 °C) and at a constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

Effect of nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) was researched on the ultrasound removals of all studied micropollutants at the aforementioned experimental conditions (Figure 6.56). It was found that a nano-CeO₂ concentration of 0.40 g L⁻¹ was the optimum nanoparticle concentration for the maximum ultrasound removals of all studied micropollutants in the raw hospital wastewater at the aforementioned experimental conditions (Figure 6.56). The maximum ultrasonic degradations were followed the order of phenolic (higher than 90%), brominated (higher than 87%), aromatic (85%), nitroso (75%) and fluoro (higher than 70%) micropollutants at the optimum nano-CeO₂ concentration of 0.40 g L⁻¹ at the aforementioned experimental conditions (Figure 6.56).



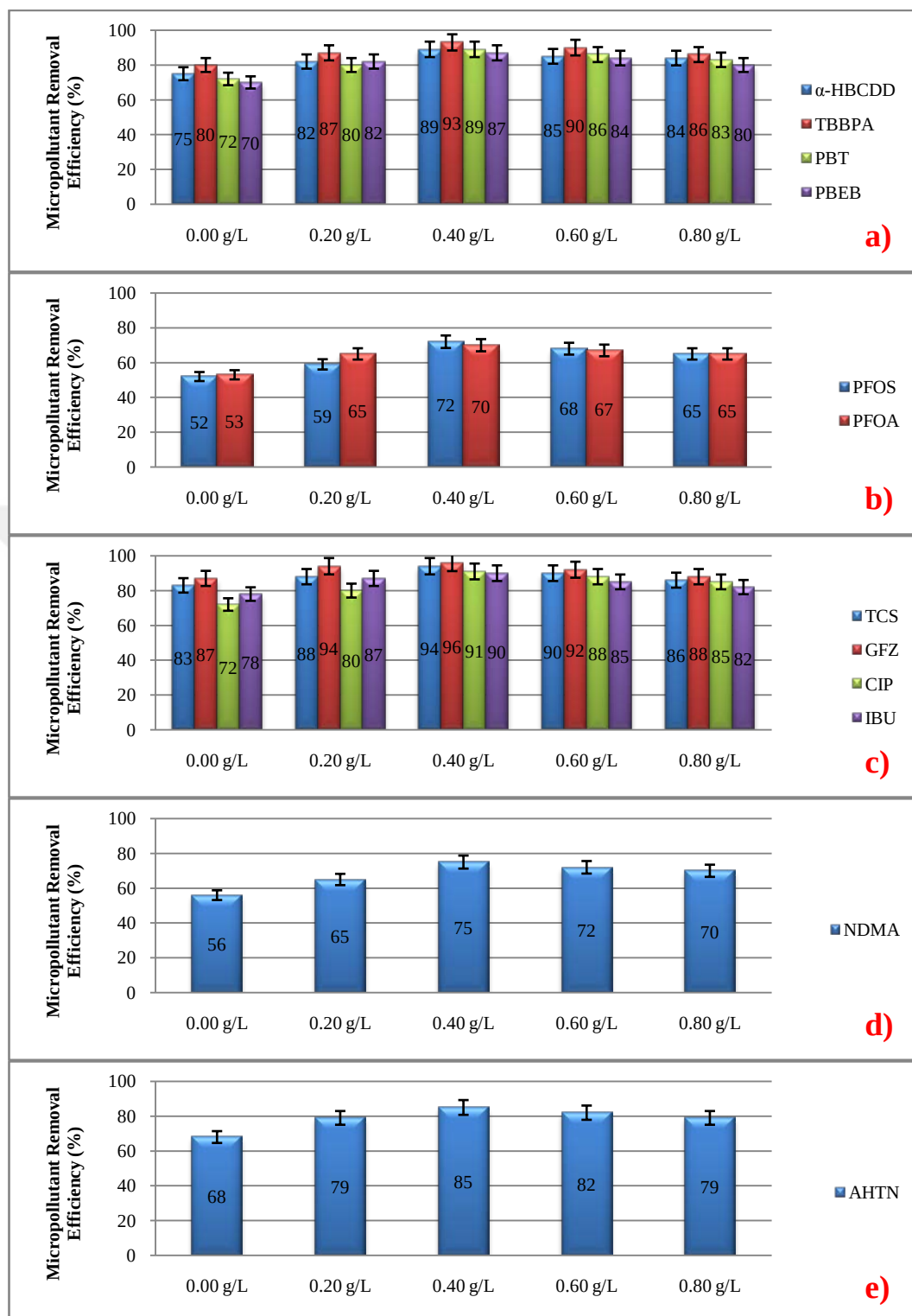


Figure 6.56 Effect of nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) on the ultrasound removals of all studied micropollutants at a constant sonicator power (120 W), at a constant sonication time (60 min), at a constant pH (4.00), at a constant temperature (40 °C) and at a constant sonicator frequency (132 kHz) for (a) brominated, (b) fluoro, (c) phenolic, (d) nitroso and (e) aromatic micropollutants

Ultrasonic degradation of water produces free radicals $\text{H}\cdot$ and $\text{OH}\cdot$ (Equation 6.307), which are capable of attacking the micropollutants in the raw hospital wastewater.



This process is facilitated in a heterogeneous environment in the presence of nano-TiO₂ or nano-CeO₂. The presence of the nanoparticles (nano-TiO₂ and nano-CeO₂) help to break up the microbubbles created by ultrasound into smaller ones, thus increasing the number of regions of high temperature and pressure. This leads to an increase in the number of hydroxyl ($\text{OH}\cdot$) radicals which will interact with the micropollutants present in the wastewater and oxidise them, resulting in eventual mineralization (Anju et al., 2012). The increase of nanoparticle concentrations from 0.00 g L⁻¹ up to 0.40 g L⁻¹ both for nano-TiO₂ and nano-CeO₂ increased the ultrasound removal efficiencies of all studied micropollutants at the aforementioned experimental conditions (Figure 6.55 and 6.56). The enhanced ultrasound removal efficiencies are probably due to the increased number of adsorption sites which lead to higher number of reactive hydroxyl ($\text{OH}\cdot$) radicals and their interactions (Anju et al., 2012). Slightly lower efficiencies were observed both for the nano-TiO₂ and nano-CeO₂ concentrations of 0.60 and 0.80 g L⁻¹ at the aforementioned experimental conditions (Figure 6.55 and 6.56). Wen, Zhao, Sheng, Fu, & Peng (2003) reported that excessive TiO₂ nanoparticles cause turbidity and this phenomenon decrease the sonication waves coming to the micropollutants (Wen et al., 2003). Anju et al. (2012) explained the lower removal efficiencies in the ultrasound treatment at increasing nanoparticle concentrations that the aggregation of the nanoparticles causing a decrease in the number of available active surface sites on the nanoparticles. The nanoparticles cannot be fully and effectively suspended in water which also leads to the reduced adsorption of micropollutant on the surface of the nanoparticles (Anju et al., 2012).

The ultrasonic degradations in the presence of nano-TiO₂ and nano-CeO₂ enhanced the ultrasound removal efficiencies of all studied micropollutants from the

raw hospital wastewater demonstrating a synergistic effect for the optimum nanoparticle concentration of 0.40 g L^{-1} (both for nano-TiO₂ and nano-CeO₂) at the aforementioned experimental conditions (Figure 6.55 and 6.56). The ANOVA (one-way) test statistics results showed that the increased nanoparticle concentrations up to 0.40 g L^{-1} had a significant effect on the ultrasound removals of all studied micropollutants at the aforementioned experimental conditions ($P = 0.037$, $\alpha = 0.05$, $F = 3.63$ for nano-TiO₂ and $P = 0.004$, $\alpha = 0.05$, $F = 6.64$ for nano-CeO₂). The effect of nanoparticle concentrations on the sonocatalytic degradation removals of all studied micropollutants for higher than 0.40 g L^{-1} (0.60 and 0.80 g L^{-1}) was not found to be significant at the aforementioned experimental conditions according to the ANOVA (one-way) test statistics results ($P = 0.310$, $\alpha = 0.05$, $F = 1.08$ for nano-TiO₂ and $P = 0.392$, $\alpha = 0.05$, $F = 0.76$ for nano-CeO₂).

6.3.7 Reusability of Nano-TiO₂ and Nano-CeO₂

In order to decrease the catalyst cost, reusability of nano-TiO₂ and nano-CeO₂ were researched in this study. Six sequential treatment steps were investigated in order to determine the possible reusability of the TiO₂ and CeO₂ nanoparticles. The TiO₂ and CeO₂ nanoparticles were reused at the following experimental conditions: 120 W constant sonicator power, 60 min constant sonication time, a constant pH of 4.00, a constant temperature of 40°C, a constant nanoparticle concentration of 0.40 g L^{-1} and a constant sonicator frequency of 132 kHz. The ultrasound removal efficiencies of all studied micropollutants were taken into consideration to detect the reusability of nano-TiO₂ and nano-CeO₂ throughout six treatment sequentials.

After the first treatment step with nano-TiO₂, the maximum ultrasound removal efficiencies of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were measured as 86%, 90%, 84%, 82%, 67%, 65%, 92%, 96%, 86%, 90%, 70% and 80%, respectively with 0.40 g L^{-1} constant nano-TiO₂ concentration at the aforementioned experimental conditions (Table 6.41). After the second, third, fourth and fifth treatment step, the ultrasound removal efficiencies of all studied micropollutants had no obvious change with 0.40 g L^{-1} nano-TiO₂ for the

aforementioned optimum experimental conditions (Table 6.41). In the sixth treatment step, the ultrasound removal efficiencies decreased significantly and were calculated as 74%, 78%, 75%, 71%, 54%, 52%, 73%, 80%, 72%, 76%, 55% and 68% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively with 0.40 g L⁻¹ constant nano-TiO₂ concentration at the aforementioned optimum experimental conditions (Table 6.41).



Table 6.41 The utilization of nano-TiO₂ and nano-CeO₂ after first, second, third, fourth, fifth and sixth times for the ultrasound removal efficiencies of all studied micropollutants at the following experimental conditions: 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

	α-HBCDD	TBBPA	PBT	PBEB	PFOS	PFOA	TCS	GFZ	CIP	IBU	NDMA	AHTN
Treatment step	Removal efficiencies (%) with nano-TiO₂											
1 st treatment	86±0.5	90±0.5	84±0.5	82±0.5	67±0.5	65±0.5	92±0.5	96±0.5	86±0.5	90±0.5	70±0.5	80±0.5
2 nd treatment	86±0.5	90±0.5	84±0.5	82±0.5	67±0.5	65±0.5	92±0.5	96±0.5	85±0.5	89±0.5	68±0.5	78±0.5
3 rd treatment	85±0.5	88±0.5	83±0.5	82±0.5	65±0.5	63±0.5	91±0.5	95±0.5	83±0.5	86±0.5	68±0.5	78±0.5
4 th treatment	84±0.5	87±0.5	83±0.5	81±0.5	65±0.5	62±0.5	89±0.5	93±0.5	83±0.5	86±0.5	66±0.5	77±0.5
5 th treatment	83±0.5	85±0.5	82±0.5	80±0.5	64±0.5	62±0.5	89±0.5	93±0.5	81±0.5	84±0.5	66±0.5	76±0.5
6 th treatment	74±0.5	78±0.5	75±0.5	71±0.5	54±0.5	52±0.5	73±0.5	80±0.5	72±0.5	76±0.5	55±0.5	68±0.5
Treatment step	Removal efficiencies (%) with nano-CeO₂											
1 st treatment	89±0.5	93±0.5	89±0.5	87±0.5	72±0.5	70±0.5	94±0.5	96±0.5	91±0.5	90±0.5	75±0.5	85±0.5
2 nd treatment	89±0.5	91±0.5	87±0.5	86±0.5	70±0.5	68±0.5	94±0.5	96±0.5	89±0.5	90±0.5	72±0.5	84±0.5
3 rd treatment	87±0.5	90±0.5	85±0.5	84±0.5	69±0.5	68±0.5	92±0.5	95±0.5	88±0.5	88±0.5	70±0.5	83±0.5
4 th treatment	84±0.5	88±0.5	84±0.5	84±0.5	66±0.5	65±0.5	91±0.5	93±0.5	88±0.5	86±0.5	67±0.5	80±0.5
5 th treatment	82±0.5	86±0.5	82±0.5	82±0.5	64±0.5	63±0.5	89±0.5	91±0.5	86±0.5	84±0.5	65±0.5	78±0.5
6 th treatment	77±0.5	80±0.5	76±0.5	79±0.5	60±0.5	58±0.5	85±0.5	83±0.5	80±0.5	78±0.5	59±0.5	71±0.5

The maximum ultrasound removal efficiencies of α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN were found as 89%, 93%, 89%, 87%, 72%, 70%, 94%, 96%, 91%, 90%, 75% and 85%, respectively after the first treatment step with 0.40 g L^{-1} constant nano-CeO₂ concentration at the aforementioned optimum experimental conditions (Table 6.41). After the second, third, fourth and fifth treatment steps, the ultrasound removal efficiencies of all studied micropollutants had no obvious change with nano-CeO₂ for the aforementioned optimum experimental conditions (Table 6.41). In the sixth treatment step, the ultrasound removal efficiencies decreased slightly and were calculated as 77%, 80%, 76%, 79%, 60%, 58%, 85%, 83%, 80%, 78%, 59% and 71% for α -HBCDD, TBBPA, PBT, PBEB, PFOS, PFOA, TCS, GFZ, CIP, IBU, NDMA and AHTN, respectively with 0.40 g L^{-1} constant nano-CeO₂ concentration at the aforementioned optimum experimental conditions (Table 6.41).

The results showed that nano-TiO₂ and nano-CeO₂ can be used effectively five sequential treatment steps for the sonocatalytic treatment of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants from raw hospital wastewater in order to decrease the cost of treatment with 0.40 g L^{-1} constant nanoparticle (both for nano-TiO₂ and nano-CeO₂) concentration at the aforementioned optimum experimental conditions (Table 6.41). The ANOVA (one-way) test statistics results showed that five sequential treatment steps had no significant effect on the reusability of both for nano-TiO₂ and nano-CeO₂ with 0.40 g L^{-1} constant nanoparticle concentration at the aforementioned optimum experimental conditions ($P = 0.904$, $\alpha = 0.05$, $F = 0.26$ for nano-TiO₂ and $P = 0.456$, $\alpha = 0.05$, $F = 0.93$ for nano-CeO₂). The ANOVA (one-way) test statistics results showed that after five sequential treatment steps, the reuse of the nanoparticles had significant effects on the ultrasound removals of all studied micropollutants both for nano-TiO₂ and nano-CeO₂ with 0.40 g L^{-1} constant nanoparticle concentration at the aforementioned optimum experimental conditions ($P = 0.021$, $\alpha = 0.05$, $F = 2.88$ for nano-TiO₂ and $P = 0.035$, $\alpha = 0.05$, $F = 2.57$ for nano-CeO₂).

6.4 Membrane Treatment Processes

The UF and RO membranes used separately and they were fed with the raw hospital wastewater in this study. The influent concentrations of all studied micropollutants in the raw hospital wastewater for UF and RO treatment experiments were shown in Table 5.1. The effects of operational parameters [transmembrane pressure (TMP), permeate flux (J_v) and cross-flow velocity (CFV)] on the removals of conventional pollutants (TSS, TOC, TDS, COD and sCOD) and micropollutants (brominated, aromatic, fluoro, phenolic and nitroso) were investigated for UF and RO at a constant pH (8.00) and temperature (25 °C) in this study.

6.4.1 Effects of Operational Parameters [Permeate Flux (J_v) and Cross-Flow Velocity (CFV)] on the Removals of Pollutants in UF

6.4.1.1 Effects of Different Permeate Fluxes (J_v) on the Removals of Conventional Pollutants (TOC, TSS, TDS, COD and sCOD), Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants in UF

The experiments were carried out at increasing permeate flux (J_v) values (78.13, 104.17 and 156.25 L m⁻² h⁻¹) based on the study given by Bunani et al. (2015), at a constant TMP (2.75 bar) based on the study performed by Tunc et al. (2014), at a constant pH (8.00) and temperature (25 °C) based on the study researched by Jadhao and Dawande (2012) in UF (Table 6.42). TMP of the UF was calculated by taking the arithmetic average of the operating pressure measured at the inlet (5 bar) and the outlet (0.5 bar), where the permeate side was open to the atmosphere (0 bar) (Equation 6.308).

$$\text{TMP}_{\text{UF}} = [(P_1 + P_2)/(2 - P_3)] = [(5 + 0.5)/(2 - 0)] = 2.75 \text{ bar} \quad (6.308)$$

At a constant TMP of 2.75 bar, for a constant raw hospital wastewater volume of 100 L and according to its constant membrane surface area of 0.64 m², the UF

showed permeate fluxes (J_v) up to 78.13 and 156.25 L m⁻² h⁻¹ during 1.0, 1.5 and 2.0 h membrane operation times at a constant temperature of 25 °C and at a constant pH of 8.00 (Equation 6.309, 6.310 and 6.311).

$$J_{v,UF \text{ at TMP}=2.75} = [V/(S \times t)] = [100 \text{ L}/(0.64 \text{ m}^2 \times 1.0 \text{ h})] = 156.25 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.309)$$

$$J_{v,UF \text{ at TMP}=2.75} = [V/(S \times t)] = [100 \text{ L}/(0.64 \text{ m}^2 \times 1.5 \text{ h})] = 104.17 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.310)$$

$$J_{v,UF \text{ at TMP}=2.75} = [V/(S \times t)] = [100 \text{ L}/(0.64 \text{ m}^2 \times 2.0 \text{ h})] = 78.13 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.311)$$



Table 6.42 Removal efficiencies of the main conventional pollutants (TSS, TOC, TDS, COD and sCOD), brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in UF for the raw hospital wastewater at increasing J_v values (78.13, 104.17 and 156.25 L m⁻² h⁻¹), at a constant TMP of 2.75 bar, at a constant pH of 8.00 and at a constant temperature of 25 °C ($n=3$, mean $\pm$ SD)

Conventional Pollutant	Removal efficiency (%)		
	$J_v = 78.13 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 2 h	$J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 1.5 h	$J_v = 156.25 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 1 h
TSS	63.0 $\pm$ 0.5	78.3 $\pm$ 0.5	99.8 $\pm$ 0.5
TOC	38.7 $\pm$ 0.5	54.1 $\pm$ 0.5	74.7 $\pm$ 0.5
TDS	22.2 $\pm$ 0.5	38.5 $\pm$ 0.5	60.4 $\pm$ 0.5
COD	46.9 $\pm$ 0.5	62.8 $\pm$ 0.5	84.0 $\pm$ 0.5
sCOD	41.5 $\pm$ 0.5	56.4 $\pm$ 0.5	79.5 $\pm$ 0.5
Micropollutant	$J_v = 78.13 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 2 h	$J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 1.5 h	$J_v = 156.25 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.64 m ² t = 1 h
α -HBCDD	27.0 $\pm$ 0.5	28.5 $\pm$ 0.5	36.8 $\pm$ 0.5
PBEB	26.8 $\pm$ 0.5	28.0 $\pm$ 0.5	36.4 $\pm$ 0.5
PBT	26.6 $\pm$ 0.5	28.0 $\pm$ 0.5	36.0 $\pm$ 0.5
TBBPA	26.4 $\pm$ 0.5	27.6 $\pm$ 0.5	35.7 $\pm$ 0.5
AHTN	25.6 $\pm$ 0.5	27.3 $\pm$ 0.5	35.2 $\pm$ 0.5
PFOA	25.3 $\pm$ 0.5	27.0 $\pm$ 0.5	34.9 $\pm$ 0.5
PFOS	23.1 $\pm$ 0.5	24.4 $\pm$ 0.5	32.1 $\pm$ 0.5
GFZ	23.6 $\pm$ 0.5	25.6 $\pm$ 0.5	33.6 $\pm$ 0.5
TCS	23.4 $\pm$ 0.5	25.4 $\pm$ 0.5	33.2 $\pm$ 0.5
IBU	22.7 $\pm$ 0.5	23.3 $\pm$ 0.5	30.0 $\pm$ 0.5
CIP	3.5 $\pm$ 0.5	4.8 $\pm$ 0.5	6.2 $\pm$ 0.5
NDMA	3.0 $\pm$ 0.5	4.5 $\pm$ 0.5	5.8 $\pm$ 0.5

The maximum removal efficiencies were obtained at the highest permeate flux (J_v) value of 156.25 L m⁻² h⁻¹ for all the conventional pollutants (TSS, TOC, TDS, COD and sCOD) at the aforementioned experimental conditions in UF (Table 6.42). UF removed approximately 100% TSS at the aforementioned experimental conditions (Table 6.42). TOC, TDS, COD and sCOD were removed with efficiencies of 74.7%, 60.4%, 84.0% and 79.5%, respectively at the aforementioned experimental conditions in UF (Table 6.42). The less removal efficiencies obtained at lower permeate fluxes (78.13 and 104.17 L m⁻² h⁻¹) were due to the reduced hydrodynamic

shear in the vicinity to the valley regions of the ridge-and-valley structures in UF (Tang, Fu, Criddle, & Leckie, 2007). The higher permeate flux ($156.25 \text{ L m}^{-2} \text{ h}^{-1}$) over the valley regions increased the surface area for the attachment of the pollutants might also be responsible for the increased removal efficiencies (Table 6.42) as mentioned by Tang et al (2007).

For this study, the removal of TSS (99.8%), TOC (74.7%), TDS (60.4%), COD (84.0%) and sCOD (79.5%) is thought to be caused by the size exclusion mechanism in UF because of being big molecules and neutral pollutants. The particle sizes of them were measured between $1.2 \text{ }\mu\text{m}$ and 2 nm according to the study of Hocaoglu & Orhon (2013). Size exclusion is based on differences in molecular size (Koyuncu, 2018). The pore size of the UF used in this study were given in a range between 0.01 and $0.1 \text{ }\mu\text{m}$ (provided by the manufacturer). Therefore, the UF used in this study could be removed the conventional pollutants (TSS, TOC, TDS, COD and sCOD) via size exclusion mechanism because the pollutants have larger particle sizes (between $1.2 \text{ }\mu\text{m}$ and 2 nm) than the membrane pores of the UF (between 0.01 and $0.1 \text{ }\mu\text{m}$). Similar results according to this study have been reported by other researchers. Urriaga et al. (2013) found 100% of TSS (10.7 mg L^{-1} initial concentration) removal in UF at an average flowrate of $2.5 \text{ m}^3 \text{ h}^{-1}$ at pH 7.30 for a secondary effluent of a wastewater treatment plant (Urriaga et al., 2013). They explained that size exclusion is the main mechanism for TSS removal due to being a non-charged (neutral) big molecule as an organic pollutant (Urriaga et al., 2013).

All studied micropollutants were removed in a range between 5.8% and 36.8% at the aforementioned experimental conditions in UF (Table 6.42). The removal efficiencies of all studied micropollutants increased with the increase in permeate flux (J_v) at the aforementioned experimental conditions in UF (Table 6.42). Tang et al. (2007) concluded that the higher permeate fluxes over the valley regions of UF increased the surface area for the attachment of the micropollutants (Tang et al., 2007). As a consequence, the removal efficiencies of the all studied micropollutants increased at the aforementioned experimental conditions in UF (Table 6.42).

The brominated (α -HBCDD, PBEB, PBT and TBBPA), fluoro (PFOA and PFOS), aromatic (AHTN) and some phenolic (GFZ, TCS and IBU) micropollutants were accepted as quite hydrophobic micropollutants due to its log K_{OW} values (higher than 3.0). The adsorption of micropollutants over the membrane surface was the function of their hydrophobic value (log K_{OW}) (Khanzada et al., 2019). The aforementioned hydrophobic micropollutants in this study adsorbed over the membrane surface due to their physicochemical properties (high hydrophobicity, log $K_{OW} > 3.0$). Therefore, the removal of hydrophobic micropollutants were mainly due to the adsorption mechanism at the maximum permeate flux (J_v) of $156.25 \text{ L m}^{-2} \text{ h}^{-1}$ at the aforementioned experimental conditions (higher than 30%) (Table 6.42). The adsorbed micropollutant masses and adsorption efficiencies were shown in the next section 6.4.3.1, in Table 6.47. These results supported that the removal mechanism of hydrophobic micropollutants were adsorption at the aforementioned operational conditions in this study. In some recent literatures it was reported that the removal mechanisms of pollutants might be size exclusion and hydrophobic adsorption onto UF surface (Khanzada et al., 2019). In size exclusion mechanism, the molecular weight cut-off (MWCO) is used to describe pore size distribution and retention capabilities of membranes. It is defined as the lowest molecular weight (in Daltons) at which greater than 90% of a solute with a known molecular weight is retained by the membrane (Koyuncu, 2018). However, the removal of micropollutants via size exclusion is often considered negligible owing to the large MWCO value of UF membranes (10–100 kDa), which is generally larger than the molecular weight of most micropollutants ($\approx 1 \text{ kDa}$) (Kim et al., 2018). In this study, UF had a higher MWCO value (10 kDa) than the studied micropollutants ($\approx 1 \text{ kDa}$), therefore, UF was inadequate to remove the micropollutants via size exclusion mechanism. Since UF membranes are not effective to remove micropollutants based on size exclusion mechanism, adsorption is thus considered the main removal mechanism contributing to the elimination of micropollutants by UF membranes (Khanzada et al., 2019). Generally, membranes with larger pore sizes (UF membranes) allow micropollutants to access the membrane's internal porous structure (more adsorption sites) (Khanzada et al., 2019). Hence, the micropollutants adsorbed on to the membrane surface as a function of their physicochemical characteristics (Khanzada et al., 2019).

In this study, CIP and NDMA having high hydrophilic properties ($\log K_{OW} < 2.5$) were insufficient to be adsorbed over the membrane surface and showed lower than 6.2% removal efficiencies at the aforementioned experimental conditions (Table 6.42). Wray, Andrews, & Bérubé, (2014) observed lower than 5% removals for some hydrophilic micropollutants (selected micropollutants have $\log K_{OW}$ values lower than 2.0) having initial concentrations of 1000 ng L^{-1} in UF operating at a permeate flux of $30 \text{ L m}^{-2} \text{ h}^{-1}$ and at a pH of 8.00 for a synthetic wastewater. They concluded that the UF can not removed the micropollutants via size exclusion mechanism and the UF was insufficient to remove the hydrophilic micropollutants via adsorption (Wray et al., 2014).

There was a linear regression between permeate flux (J_v) values and pollutants removals ($R^2 = 0.998$ for conventionals and $R^2 = 0.999$ for all studied micropollutants) in UF. The effect of lower permeate fluxes (J_v) (78.13 and $104.17 \text{ L m}^{-2} \text{ h}^{-1}$) on the pollutants removals were not found to be significant at the aforementioned experimental conditions in UF ($P = 0.130$, $\alpha = 0.05$, $F = 2.85$ for conventionals and $P = 0.073$, $\alpha = 0.05$, $F = 3.63$ for hydrophobic micropollutants). However, the effect of the highest permeate flux ($156.25 \text{ L m}^{-2} \text{ h}^{-1}$) on the pollutants removals was significant at the aforementioned experimental conditions in UF according to the ANOVA (one-way) test statistics results ($P = 0.005$, $\alpha = 0.05$, $F = 8.32$ for conventionals and $P = 1.50 \times 10^{-11}$, $\alpha = 0.05$, $F = 72.12$ for hydrophobic micropollutants).

Snyder et al. (2007) observed only 7% of removal for IBU (39 ng L^{-1} initial IBU concentration) in UF at $35 \text{ gallons feet}^{-2} \text{ day}^{-1}$ flux for a secondary effluent from a municipal wastewater treatment plant at 20°C and at pH 7.00 (Snyder et al., 2007). Urtiaga et al. (2013) found 100% of TSS, 40% of TOC and less than 40% of TDS removals in UF at an average flowrate of $2.5 \text{ m}^3 \text{ h}^{-1}$ at pH 7.30 for a secondary effluent of a wastewater treatment plant (Urtiaga et al., 2013). Tunc et al. (2014) determined approximately 50% COD removal and no change in TDS in a caustic mercerization wastewater for initial COD and TDS concentrations of $448 \pm 28 \text{ mg L}^{-1}$ and $6.69 \pm 0.01 \text{ g L}^{-1}$, respectively with UF at a TMP of 2 bar at $20 \pm 2^\circ \text{C}$ and at

pH 12.65 (Tunc et al., 2014). Pramanik et al. (2017) investigated the efficiency of a PVDF hollow-fiber UF membrane (Asahi Kasei Chemicals, Japan, pore size 0.1 μm) for the removal of PFOS and PFOA from lake water. Their results revealed that the UF membrane had low removal efficiency for both PFOS and PFOA (~ 20 and $\sim 28\%$, respectively) (Pramanik et al., 2017). The results obtained in this study (84.0% COD, 74.7% TOC, 30.0% IBU, 60.4% TDS, 32.1% PFOS and 34.9% PFOA) at the aforementioned experimental conditions were higher than the literature data (Table 6.42).

6.4.1.2 Effects of Different Cross-Flow Velocities (CFV) on the Removals of Conventional Pollutants (TOC, TSS, TDS, COD and sCOD), Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants in UF

The experiments were carried out at increasing cross-flow velocity (CFV) values (0.08, 0.11 and 0.16 m h^{-1}) based on the study given by Varol, Uzal, Dilek, Kitis, & Yetis (2015), at a constant TMP (2.75 bar), at a constant pH (8.00) and at a constant temperature (25 $^{\circ}\text{C}$) in UF (Table 6.43). The experimental conditions of TMP, pH and temperature were obtained from the preliminary study for UF.

The CFVs of UF were changed between 0.08 and 0.16 m h^{-1} at membrane operation times varying between 1.0 and 2.0 h at a constant TMP of 2.75 bar, at a constant raw hospital wastewater volume of 100 L (0.10 m^3), at a constant membrane surface area of 0.64 m^2 , at a constant temperature of 25 $^{\circ}\text{C}$ and at a constant pH of 8.00 (Equation 6.312, 6.313 and 6.314).

$$\text{CFV}_{\text{UF}, \text{TMP}=2.75} = Q/S = [(V/t)/S] = [(0.10/1.0)/0.64] = 0.16 \text{ m h}^{-1} \quad (6.312)$$

$$\text{CFV}_{\text{UF}, \text{TMP}=2.75} = Q/S = [(V/t)/S] = [(0.10/1.5)/0.64] = 0.11 \text{ m h}^{-1} \quad (6.313)$$

$$\text{CFV}_{\text{UF}, \text{TMP}=2.75} = Q/S = [(V/t)/S] = [(0.10/2.0)/0.64] = 0.08 \text{ m h}^{-1} \quad (6.314)$$

Table 6.43 Removal efficiencies of the main conventional pollutants (TSS, TOC, TDS, COD and sCOD), brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in UF for the raw hospital wastewater at increasing CFV values (0.08, 0.11 and 0.16 m h⁻¹), at a constant TMP of 2.75 bar, at a constant pH of 8.00 and at a constant temperature of 25 °C ($n=3$, mean $\pm$ SD)

Conventional Pollutant	Removal efficiency (%)		
	CFV = 0.08 m h ⁻¹ t = 2 h	CFV = 0.11 m h ⁻¹ t = 1.5 h	CFV = 0.16 m h ⁻¹ t = 1 h
TSS	63.0 $\pm$ 0.5	78.3 $\pm$ 0.5	99.8 $\pm$ 0.5
TOC	38.7 $\pm$ 0.5	54.1 $\pm$ 0.5	74.7 $\pm$ 0.5
TDS	22.2 $\pm$ 0.5	38.5 $\pm$ 0.5	60.4 $\pm$ 0.5
COD	46.9 $\pm$ 0.5	62.8 $\pm$ 0.5	84.0 $\pm$ 0.5
sCOD	41.5 $\pm$ 0.5	56.4 $\pm$ 0.5	79.5 $\pm$ 0.5
Micropollutant	CFV = 0.08 m h ⁻¹ t = 2 h	CFV = 0.11 m h ⁻¹ t = 1.5 h	CFV = 0.16 m h ⁻¹ t = 1 h
α -HBCDD	27.0 $\pm$ 0.5	28.5 $\pm$ 0.5	36.8 $\pm$ 0.5
PBEB	26.8 $\pm$ 0.5	28.0 $\pm$ 0.5	36.4 $\pm$ 0.5
PBT	26.6 $\pm$ 0.5	28.0 $\pm$ 0.5	36.0 $\pm$ 0.5
TBBPA	26.4 $\pm$ 0.5	27.6 $\pm$ 0.5	35.7 $\pm$ 0.5
AHTN	25.6 $\pm$ 0.5	27.3 $\pm$ 0.5	35.2 $\pm$ 0.5
PFOA	25.3 $\pm$ 0.5	27.0 $\pm$ 0.5	34.9 $\pm$ 0.5
PFOS	23.1 $\pm$ 0.5	24.4 $\pm$ 0.5	32.1 $\pm$ 0.5
GFZ	23.6 $\pm$ 0.5	25.6 $\pm$ 0.5	33.6 $\pm$ 0.5
TCS	23.4 $\pm$ 0.5	25.4 $\pm$ 0.5	33.2 $\pm$ 0.5
IBU	22.7 $\pm$ 0.5	23.3 $\pm$ 0.5	30.0 $\pm$ 0.5
CIP	3.5 $\pm$ 0.5	4.8 $\pm$ 0.5	6.2 $\pm$ 0.5
NDMA	3.0 $\pm$ 0.5	4.5 $\pm$ 0.5	5.8 $\pm$ 0.5

The maximum removal efficiencies were obtained at the highest CFV (0.16 m h⁻¹) for the conventional pollutants (higher than 60%) at the aforementioned experimental conditions in UF (Table 6.43). In general, an increase in cross-flow velocity (CFV) results in an increased removal performance by affecting the concentration polarization mechanism occurring at the solution-membrane interface (Khanzada et al., 2019). Concentration polarization refers to the reversible accumulation of rejected molecules close to the membrane surface. In membrane processes all components in the feed are transported to the membrane surface by convection, and the rate increases as the permeation increases through the membrane (Koyuncu, 2018).

The conventional pollutants (TSS, TOC, TDS, COD and sCOD) were neutral compounds and removed via size exclusion mechanism (higher than 60%) at the optimum CFV of 0.16 m h^{-1} at the aforementioned experimental conditions in UF because they all have larger particle sizes (between $1.2 \text{ }\mu\text{m}$ and 2 nm) than the membrane pores of the UF (between 0.01 and $0.1 \text{ }\mu\text{m}$) (Table 6.43).

The maximum removal efficiencies of the all studied micropollutants were found at the highest CFV (0.16 m h^{-1}) in the comparison with the other CFVs (0.08 and 0.11 m h^{-1}) at the aforementioned experimental conditions in UF (Table 6.43). The increased cross-flow velocity (CFV) increased the removal performances of the micropollutants by affecting the concentration polarization mechanism occurring at the solution-membrane interface in UF as mentioned by Khanzada et al. (2019).

The size exclusion mechanism could not affected the removals of all studied micropollutants because the MWCO of UF (10 kDa) was higher than the molecular weights of the micropollutants ($\approx 1 \text{ kDa}$) in this study. Therefore, all studied micropollutants were able to pass through the UF surface. The brominated (α -HBCDD, PBEB, PBT and TBBPA), fluoro (PFOA and PFOS), aromatic (AHTN) and some phenolic (GFZ, TCS and IBU) micropollutants were removed via adsorption depending on their hydrophobicity values ($\log K_{OW} > 3.0$). Since the adsorption of them on the membrane surface were mainly derived by their hydrophobicity, adsorption was considered as the key removal mechanism (higher than 30%) for the hydrophobic micropollutants removals in this study (Table 6.43). The adsorbed micropollutant masses and adsorption efficiencies were calculated in the next section 6.4.3.1, in Table 6.47. The UF was inadequate to remove (lower than 6.2%) the hydrophilic micropollutants (CIP and NDMA) due to their physicochemical properties ($\log K_{OW} < 3.0$) at the aforementioned experimental conditions (Table 6.43).

There was a linear regression between CFVs and pollutants removals at the aforementioned experimental conditions in UF ($R^2 = 0.998$ for conventionals and $R^2 = 0.999$ for all studied micropollutants). The effect of lower CFVs (0.08 and 0.11 m

h^{-1}) on the pollutants removals were not significant ($P = 0.130$, $\alpha = 0.05$, $F = 2.85$ for conventionals and $P = 0.073$, $\alpha = 0.05$, $F = 3.63$ for hydrophobic micropollutants), however, the effect of the maximum CFV (0.16 m h^{-1}) on the pollutants removals was significant at the aforementioned experimental conditions in UF according to the ANOVA (one-way) test statistics results ($P = 0.005$, $\alpha = 0.05$, $F = 8.32$ for conventionals and $P = 1.50 \times 10^{-11}$, $\alpha = 0.05$, $F = 72.12$ for hydrophobic micropollutants).

Urtiaga et al. (2013) reported 1.2% removal efficiency for IBU at an initial concentration of $2.5 \mu\text{g L}^{-1}$ in UF having an average pore size of $0.2 \mu\text{m}$ and at an average flowrate of $2.5 \text{ m}^3 \text{ h}^{-1}$ at pH 7.30 for a secondary effluent of a wastewater treatment plant (Urtiaga et al., 2013). Varol et al. (2015) obtained 83.8% COD removal for an initial COD concentration of 8.5 g L^{-1} with UF at a TMP of 4.03 bar at $20 \pm 2 \text{ }^\circ\text{C}$ at pH = 12.3 from a mercerizing wastewater (Varol et al., 2015). The results obtained in this study (30.0% IBU and 84.0% COD) at the aforementioned experimental conditions were higher than the results previously obtained by the other authors (1.2% IBU and 83.8% COD) for UF treatment experiments (Table 6.43).

6.4.2 Effects of Operational Parameters [Permeate Flux (J_v), Cross-Flow Velocity (CFV) and Transmembrane Pressure (TMP)] on the Removals of Pollutants in RO

6.4.2.1 Effects of Different Permeate Fluxes (J_v) on the Removals of Conventional Pollutants (TOC, TSS, TDS, COD and sCOD), Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants in RO

The experiments were carried out at increasing permeate flux (J_v) values (104.17, 114.47 and $125.50 \text{ L m}^{-2} \text{ h}^{-1}$) based on the study tested by Wang et al. (2009), at a constant TMP (2.75 bar) based on the study performed by Yuksel, Kabay, & Yuksel (2013), at a constant pH (8.00) and temperature ($25 \text{ }^\circ\text{C}$) based on the study researched by Jadhao and Dawande (2012) in RO (Table 6.44).

The RO membrane showed permeate fluxes (J_v) up to 52.08 and 104.17 L m⁻² h⁻¹ for membrane operation times changing between 1.0 and 2.0 h at a constant TMP of 2.75 bar, at a constant raw hospital wastewater volume of 100 L, at a constant temperature of 25 °C, at a constant pH of 8.00 for a constant membrane surface area of 0.96 m² (Equation 6.315, 6.316 and 6.317).

$$J_{v, \text{RO at TMP}=2.75} = [V/(S \times t)] = [100/(0.96 \times 1.0)] = 104.17 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.315)$$

$$J_{v, \text{RO at TMP}=2.75} = [V/(S \times t)] = [100/(0.96 \times 1.5)] = 69.44 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.316)$$

$$J_{v, \text{RO at TMP}=2.75} = [V/(S \times t)] = [100/(0.96 \times 2.0)] = 52.08 \text{ L m}^{-2} \text{ h}^{-1} \quad (6.317)$$



Table 6.44 Removal efficiencies of the main conventional pollutants (TSS, TOC, TDS, COD and sCOD), brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in RO for the raw hospital wastewater at increasing J_v values (52.08, 69.44 and 104.17 L m⁻² h⁻¹), at a constant TMP of 2.75 bar, at a constant pH of 8.00 and at a constant temperature of 25 °C ($n=3$, mean $\pm$ SD)

Conventional Pollutant	Removal efficiency (%)		
	$J_v = 52.08 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 2 h	$J_v = 69.44 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 1.5 h	$J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 1 h
TSS	71.2 $\pm$ 0.5	81.1 $\pm$ 0.5	100.0 $\pm$ 0.5
TOC	55.7 $\pm$ 0.5	62.5 $\pm$ 0.5	83.0 $\pm$ 0.5
TDS	59.0 $\pm$ 0.5	70.7 $\pm$ 0.5	90.0 $\pm$ 0.5
COD	57.2 $\pm$ 0.5	65.5 $\pm$ 0.5	85.5 $\pm$ 0.5
sCOD	55.2 $\pm$ 0.5	64.4 $\pm$ 0.5	83.3 $\pm$ 0.5
Micropollutant	$J_v = 52.08 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 2 h	$J_v = 69.44 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 1.5 h	$J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ V = 100 L S = 0.96 m ² t = 1 h
α -HBCDD	51.3 $\pm$ 0.5	55.0 $\pm$ 0.5	86.2 $\pm$ 0.5
PBEB	51.0 $\pm$ 0.5	54.3 $\pm$ 0.5	83.0 $\pm$ 0.5
PBT	51.0 $\pm$ 0.5	54.0 $\pm$ 0.5	83.1 $\pm$ 0.5
TBBPA	50.6 $\pm$ 0.5	53.2 $\pm$ 0.5	82.4 $\pm$ 0.5
AHTN	50.0 $\pm$ 0.5	52.5 $\pm$ 0.5	82.0 $\pm$ 0.5
PFOA	49.7 $\pm$ 0.5	51.4 $\pm$ 0.5	81.0 $\pm$ 0.5
PFOS	47.3 $\pm$ 0.5	50.4 $\pm$ 0.5	79.3 $\pm$ 0.5
GFZ	48.7 $\pm$ 0.5	51.0 $\pm$ 0.5	80.6 $\pm$ 0.5
TCS	48.0 $\pm$ 0.5	50.4 $\pm$ 0.5	80.2 $\pm$ 0.5
IBU	45.0 $\pm$ 0.5	48.0 $\pm$ 0.5	78.1 $\pm$ 0.5
CIP	40.5 $\pm$ 0.5	43.5 $\pm$ 0.5	70.5 $\pm$ 0.5
NDMA	38.7 $\pm$ 0.5	42.4 $\pm$ 0.5	70.0 $\pm$ 0.5

The conventional pollutants (TSS, TOC, TDS, COD and sCOD) were removed higher than 83.0% at the maximum permeate flux (J_v) of 104.17 L m⁻² h⁻¹ at the aforementioned experimental conditions in RO (Table 6.44). The higher permeate flux (104.17 L m⁻² h⁻¹) over the valley regions of the ridge-and-valley structures in RO increased the surface area for the attachment of the pollutants (Tang et al., 2007). Therefore, the removal efficiencies of conventional pollutants increased at the highest permeate flux (104.17 L m⁻² h⁻¹) in RO at the aforementioned experimental conditions (Table 6.44).

It was considered that the removals of conventional pollutants (TSS, TOC, TDS, COD and sCOD) could be due to the size exclusion (or steric hindrance) by the RO surface. The mechanism of size exclusion (or steric hindrance) for uncharged pollutants provided higher removals having larger particle size (between 1.2 μm and 2 nm) than the membrane pores of the RO (between 0.22 and 0.44 nm – provided by the manufacturer).

The all studied micropollutants were removed higher than 70.0% at the maximum permeate flux (J_v) of 104.17 $\text{L m}^{-2} \text{h}^{-1}$ at the aforementioned experimental conditions in RO (Table 6.44). The maximum removal efficiencies were obtained at the maximum permeate flux value (104.17 $\text{L m}^{-2} \text{h}^{-1}$). Therefore, increased permeate flux increased the surface area over the valley regions of the ridge-and-valley structures in RO and micropollutants reached more surface area for the attachment (Tang et al., 2007).

The removals through RO processes are mainly due to size exclusion, electrostatic interaction (or charge repulsion) and hydrophobic adsorption (Narbaitz et al., 2013). It was reported that the size exclusion mechanism made contribution to the removals of neutral micropollutants namely α -HBCDD, TBBPA, PBEB, PBT and TCS ($\text{pK}_a = \text{pH}$) because the MWCO of RO (0.1 kDa – provided by the manufacturer) was lower than the molecular weights of the micropollutants (≈ 1 kDa) at the aforementioned experimental conditions in RO as reported by Khanzada et al. (2019). In RO treatment, the removal of a compound is dependent on many factors such as the chemical structure of the compound, membrane characteristics, water matrix and adsorption interactions between the compound and membrane (Al-Rifai, Gabelish & Schäfer, 2007).

In this study, the pH value of the raw hospital wastewater was kept at 8.00 which its original value. PFOS ($\text{pK}_a < 1.0$), PFOA ($\text{pK}_a = 2.80$), GFZ ($\text{pK}_a = 4.75$), CIP ($\text{pK}_a = 3.6, 5.6, 6.2$), IBU ($\text{pK}_a = 4.91$) and NDMA ($\text{pK}_a = 3.52$) exist in their anionic forms ($\text{pK}_a < \text{pH}$) in the raw hospital wastewater and the negatively charged RO surface at pH 8.00 increased their removals via the electrostatic interaction

mechanism (Table 6.44). Despite being quite hydrophilic micropollutants ($\log K_{OW} < 3.0$), CIP and NDMA were removed 70% in RO, because electrostatic repulsion mechanism was effective for their removals (Table 6.44). Licona et al. (2018) were observed similar behaviours for the anionic hydrophilic micropollutants in RO treatment and explained that the electrostatic repulsion between the hydrophilic micropollutants and the negatively charged RO membrane surface helped to remove the hydrophilic micropollutants more effectively (Licona et al., 2018). Since pKa value of α -HBCDD, TBBPA, PBEB, PBT and TCS is between 7.5 and 8.5, these micropollutants exist in their neutral form at pH 8.00 (Table 6.44). Therefore, the electrostatic repulsion of them from membrane surface did not play any role for their removal mechanism.

The hydrophobic brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN) and phenolic (TCS) micropollutants have $\log K_{OW}$ values greater than 3.0 in this study (for the numerical values see Table 5.2). They adsorbed onto membrane surface and removed mainly by hydrophobic adsorption mechanism at the aforementioned experimental conditions in RO. The adsorbed micropollutant masses and adsorption efficiencies were determined in the next section 6.4.3.2, in Table 6.48. The fluoro (PFOA and PFOS) and some phenolic (GFZ and IBU) micropollutants also have high hydrophobicities ($\log K_{OW} > 3.0$). Therefore, hydrophobic adsorption made contribution to their removals at the aforementioned experimental conditions in RO. The RO used in the experiments was made of polyamide thin-film composite (TFC) material. The polyamide thin film composite (TFC) membranes with a typical three-layer structure are considered as the most successful and commercialized membranes. It is comprised of a thin composite active layer (in the order of 100 nm thickness for RO) attached with a more open intermediate layer (about 40 μ m) and an even more open support layer. The possible reason for micropollutants removals by the membrane might be the strong interaction of organic pollutants with the membrane polymer (Hofs et al., 2013).

Micropollutant separation by the electrostatic interaction mechanism arises when the electrostatic repulsive forces between the charged membrane surface and the ions

of electrolyte micropollutant inhibits the ion form contacting the membrane (Narbaitz et al., 2013). In general, the separation trend of the micropollutants was the hydrophobic adsorption as a function of their log K_{OW} values. Since the adsorption of micropollutants over the membrane surface was the function of their hydrophobic value, it was believed that micropollutants with high hydrophilic properties (less hydrophobic; log $Kow < 3.0$) were improbable to be adsorbed over the membrane surface. However, micropollutants with high hydrophobicity (log $Kow > 3.0$) reflected the opposite behavior (Wray et al., 2014).

For RO, the ANOVA (one-way) test statistics showed that a linear regression between permeate flux (J_v) values and pollutants removals were observed ($R^2 = 0.997$ for conventionals and $R^2 = 0.987$ for micropollutants). The effect of lower permeate fluxes (J_v) (52.08 and 69.44 L m⁻² h⁻¹) on the pollutants removals were not found to be significant at the aforementioned experimental conditions in RO ($P = 0.074$, $\alpha = 0.05$, $F = 4.21$ for conventionals and $P = 0.104$, $\alpha = 0.05$, $F = 2.88$ for micropollutants). However, the effect of the highest permeate flux (104.17 L m⁻² h⁻¹) on the pollutants removals was significant at the aforementioned experimental conditions in RO ($P = 0.00011$, $\alpha = 0.05$, $F = 21.46$ for conventionals and $P = 4.80 \times 10^{-19}$, $\alpha = 0.05$, $F = 196.05$ for micropollutants).

6.4.2.2 Effects of Different Cross-Flow Velocities (CFV) on the Removals of Conventional Pollutants (TOC, TSS, TDS, COD and sCOD), Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants in RO

The experiments were carried out at increasing CFVs (0.05, 0.07 and 0.10 m h⁻¹) based on the study performed by Urtiaga et al. (2013), at a constant TMP (2.75 bar), at a constant pH (8.00) and at a constant temperature (25 °C) in RO (Table 6.45). The experimental conditions of TMP, pH and temperature were obtained from the preliminary study for RO.

The CFVs of RO were calculated between 0.05 and 0.10 m h⁻¹ for the membrane operation times changing between 1.0 and 2.0 h at a constant TMP of 2.75 bar, at a constant raw hospital wastewater volume of 100 L (0.10 m³), at a constant membrane surface area of 0.96 m², at a constant temperature of 25 °C and at a constant pH of 8.00 (Equation 6.318, 6.319 and 6.320).

$$CFV_{RO,TMP=2.75} = Q/S = [(V/t)/S] = [(0.10/1.0)/0.96] = 0.10 \text{ m h}^{-1} \quad (6.318)$$

$$CFV_{RO,TMP=2.75} = Q/S = [(V/t)/S] = [(0.10/1.5)/0.96] = 0.07 \text{ m h}^{-1} \quad (6.319)$$

$$CFV_{RO,TMP=2.75} = Q/S = [(V/t)/S] = [(0.10/2.0)/0.96] = 0.05 \text{ m h}^{-1} \quad (6.320)$$



Table 6.45 Removal efficiencies of the main conventional pollutants (TSS, TOC, TDS, COD and sCOD), brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in RO for the raw hospital wastewater at increasing CFV values (0.05, 0.07 and 0.10 m h⁻¹), at a constant TMP of 2.75 bar, at a constant pH of 8.00 and at a constant temperature of 25 °C ($n=3$, mean $\pm$ SD)

Conventional Pollutant	Removal efficiency (%)		
	CFV = 0.05 m h ⁻¹ t = 2 h	CFV = 0.07 m h ⁻¹ t = 1.5 h	CFV = 0.10 m h ⁻¹ t = 1 h
TSS	71.2 $\pm$ 0.5	81.1 $\pm$ 0.5	100.0 $\pm$ 0.5
TOC	55.7 $\pm$ 0.5	62.5 $\pm$ 0.5	83.0 $\pm$ 0.5
TDS	59.0 $\pm$ 0.5	70.7 $\pm$ 0.5	90.0 $\pm$ 0.5
COD	57.2 $\pm$ 0.5	65.5 $\pm$ 0.5	85.5 $\pm$ 0.5
sCOD	55.2 $\pm$ 0.5	64.4 $\pm$ 0.5	83.3 $\pm$ 0.5
Micropollutant			
	CFV = 0.05 m h ⁻¹ t = 2 h	CFV = 0.07 m h ⁻¹ t = 1.5 h	CFV = 0.10 m h ⁻¹ t = 1 h
α -HBCDD	51.3 $\pm$ 0.5	55.0 $\pm$ 0.5	86.2 $\pm$ 0.5
PBEB	51.0 $\pm$ 0.5	54.3 $\pm$ 0.5	83.0 $\pm$ 0.5
PBT	51.0 $\pm$ 0.5	54.0 $\pm$ 0.5	83.1 $\pm$ 0.5
TBBPA	50.6 $\pm$ 0.5	53.2 $\pm$ 0.5	82.4 $\pm$ 0.5
AHTN	50.0 $\pm$ 0.5	52.5 $\pm$ 0.5	82.0 $\pm$ 0.5
PFOA	49.7 $\pm$ 0.5	51.4 $\pm$ 0.5	81.0 $\pm$ 0.5
PFOS	47.3 $\pm$ 0.5	50.4 $\pm$ 0.5	79.3 $\pm$ 0.5
GFZ	48.7 $\pm$ 0.5	51.0 $\pm$ 0.5	80.6 $\pm$ 0.5
TCS	48.0 $\pm$ 0.5	50.4 $\pm$ 0.5	80.2 $\pm$ 0.5
IBU	45.0 $\pm$ 0.5	48.0 $\pm$ 0.5	78.1 $\pm$ 0.5
CIP	40.5 $\pm$ 0.5	43.5 $\pm$ 0.5	70.5 $\pm$ 0.5
NDMA	38.7 $\pm$ 0.5	42.4 $\pm$ 0.5	70.0 $\pm$ 0.5

The highest removal efficiencies were achieved at the maximum CFV value of 0.10 m h⁻¹ for the conventional pollutants (higher than 83.0% for all) at the aforementioned experimental conditions in RO (Table 6.45). Higher removal efficiencies are expected at higher CFV values due to the concentration polarization mechanism occurring at the solution-membrane interface (Khanzada et al., 2019). Also, the permeate flux (J_v) increases (from 52.08 to 104.17 L m⁻² h⁻¹) by an increase in CFV (from 0.05 to 0.10 m h⁻¹) due to the reducing effect on the cake resistance (Varol et al., 2015). Higher CFV (0.10 m h⁻¹) of the RO membrane were obtained at the highest permeate flux (104.17 L m⁻² h⁻¹) at the aforementioned experimental conditions (Table 6.45).

The conventional pollutants (TSS, TOC, TDS, COD and sCOD) removed via size exclusion due to being larger molecules and existing in their neutral forms at the aforementioned experimental conditions in RO. The size exclusion (or steric hindrance) mechanism provides higher removal efficiencies for neutral and big particle sized molecules as mentioned by Narbaitz et al. (2013).

The maximum micropollutant removal efficiencies were found (higher than 70.0% for all) at the maximum CFV value of 0.10 m h^{-1} at the aforementioned experimental conditions in RO (Table 6.45). Higher removal efficiencies were determined at the maximum CFV value of 0.10 m h^{-1} at the aforementioned experimental conditions due to the concentration polarization mechanism occurring at the solution-membrane interface in RO (Khanzada et al., 2019).

The brominated (α -HBCDD, PBEB, PBT and TBBPA) and phenolic (TCS) micropollutants had nonionic structures and existed in their neutral forms (all pKa values were in a range between 7.5 and 8.5) at the operating pH value (8.00) in RO. Gur-Reznik, Koren-Menashe, Heller-Grossman, Rufel, & Dosoretz (2011) explained that the size exclusion made contribution to the removal of neutral micropollutants in RO because non-ionic micropollutants can not pass through the membrane pores due to their higher molecular weights ($\approx 1 \text{ kDa}$ for our study) than the MWCO value of RO (0.1 kDa for our study) (Gur-Reznik et al., 2011).

All brominated, aromatic (AHTN) and some phenolic (TCS) micropollutants are neutral ($\text{pKa} = \text{pH}$), quite hydrophobic (all $\log K_{\text{OW}}$ values > 3.0) and have high molecular weights ($\approx 1 \text{ kDa}$) than the MWCO value of RO (0.1 kDa) in this study. Therefore, size exclusion and hydrophobic adsorption made contributions to their removals at the aforementioned experimental conditions in RO. The adsorbed micropollutant masses and adsorption efficiencies were presented in the next section 6.4.3.2, in Table 6.48. Despite being anionic micropollutants ($\text{pKa} < \text{pH}$), the fluoro (PFOA and PFOS) and some phenolic (GFZ and IBU) were also hydrophobic compounds ($\log K_{\text{OW}}$ values > 3.0) and hydrophobic adsorption made contribution to their removals.

The fluoro (PFOA and PFOS) and some phenolic (GFZ and IBU) micropollutants existed in their anionic forms ($pK_a < pH$) in the raw hospital wastewater and the negatively charged RO surface at pH 8.00 increased their removals via the electrostatic interaction mechanism. The nitroso (NDMA) and some phenolic (CIP) micropollutants were quite hydrophilic micropollutants with their relatively low $\log K_{OW}$ values (-0.57 for NDMA and 0.28 for CIP). However, NDMA and CIP had pK_a values of 3.52 and 3.6 (or 5.6 and 6.2), respectively and existed in their anionic forms at pH 8.00. Therefore, the electrostatic interaction between the anionic micropollutants and the negatively charged RO surface increased the removal efficiencies of NDMA and CIP at the aforementioned experimental conditions.

According to the ANOVA (one-way) test statistics results, the relationship between CFV and pollutants removals at the optimum CFV of 0.10 m h^{-1} at the aforementioned experimental conditions in RO was found to be significant ($R^2 = 0.997$, $P = 0.00011$, $\alpha = 0.05$, $F = 21.46$ for conventionals and $R^2 = 0.987$, $P = 4.80 \times 10^{-19}$, $\alpha = 0.05$, $F = 196.05$ for micropollutants). The effect of lower CFVs (0.05 and 0.07 m h^{-1}) on the pollutants removals were not significant at the aforementioned experimental conditions in RO ($P = 0.074$, $\alpha = 0.05$, $F = 4.21$ for conventionals and $P = 0.104$, $\alpha = 0.05$, $F = 2.88$ for micropollutants).

Radjenović et al. (2008) obtained GFZ removal in a range of 50-70% with RO at a TMP of $7.3\text{-}8.7 \text{ kg cm}^{-2}$ for an initial GFZ concentration of 10.3 ng L^{-1} in a hospital wastewater at 17°C and at a pH range of 5.6-6.1 (Radjenović et al., 2008). Bunani et al. (2015) found 76.4% removal for TOC ($10.2\text{-}13.7 \text{ mg L}^{-1}$ initial concentration) with RO at 10 bar operating pressure in a pH range of 8.00-8.34 for a secondary treated urban wastewater (Bunani et al., 2015). The removal efficiencies in RO determined in this study (80.6% GFZ and 83.0% TOC at a CFV of 0.10 m h^{-1} at the aforementioned experimental conditions) were higher than the literature (50-70% GFZ and 76.4 TOC) (Table 6.45).

6.4.2.3 Effects of Different Transmembrane Pressures (TMP) on the Removals of Conventional Pollutants (TOC, TSS, TDS, COD and sCOD), Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants in RO

The experiments were carried out at increasing TMPs (2.75, 3.75 and 4.75 bar) based on the study performed by Yuksel et al. (2013), at a constant permeate flux (J_v) ($104.17 \text{ L m}^{-2} \text{ h}^{-1}$), at a constant CFV (0.10 m h^{-1}), at a constant pH (8.00), at a constant temperature (25°C) and at a constant time (1 h) in RO (Table 6.46). The experimental conditions of J_v , CFV, pH, temperature and time were obtained from the preliminary study for RO.

TMP of the RO was calculated by taking the arithmetic average of the operating pressure measured at the inlet (P1) and the outlet (P2), where the permeate side was open to the atmosphere (P3). The outlet (P2) and permeate (P3) pressures were stable as 0.5 bar and 0 bar, respectively in RO. The RO was operated at three different operating pressures (5, 7 and 9 bars) corresponding to three different TMPs as 2.75, 3.75 and 4.75 bar calculated in Equations 6.321 to 6.323, respectively.

$$\text{TMP}_{\text{RO at 5 bar OP}} = [(P1 + P2)/(2-P3)] = [(5 + 0.5)/(2-0)] = 2.75 \text{ bar} \quad (6.321)$$

$$\text{TMP}_{\text{RO at 7 bar OP}} = [(P1 + P2)/(2-P3)] = [(7 + 0.5)/(2-0)] = 3.75 \text{ bar} \quad (6.322)$$

$$\text{TMP}_{\text{RO at 9 bar OP}} = [(P1 + P2)/(2-P3)] = [(9 + 0.5)/(2-0)] = 4.75 \text{ bar} \quad (6.323)$$

Table 6.46 Removal efficiencies of the main conventional pollutants (TSS, TOC, TDS, COD and sCOD), brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in RO for the raw hospital wastewater at increasing TMPs (2.75, 3.75 and 4.75 bar), at a constant permeate flux (J_v) ($104.17 \text{ L m}^{-2} \text{ h}^{-1}$), at a constant CFV (0.10 m h^{-1}), at a constant pH of 8.00 and at a constant temperature of $25 \text{ }^\circ\text{C}$ ($n=3$, mean $\pm$ SD)

Conventional Pollutant	Removal efficiency (%)		
	TMP = 2.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h	TMP = 3.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h	TMP = 4.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h
TSS	100.0 ± 0.5	100.0 ± 0.5	100.0 ± 0.5
TOC	83.0 ± 0.5	87.8 ± 0.5	95.5 ± 0.5
TDS	90.0 ± 0.5	95.3 ± 0.5	99.0 ± 0.5
COD	85.5 ± 0.5	92.1 ± 0.5	98.6 ± 0.5
sCOD	83.3 ± 0.5	88.2 ± 0.5	95.5 ± 0.5
Micropollutant			
	TMP = 2.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h	TMP = 3.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h	TMP = 4.75 bar $J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$ CFV = 0.10 m h^{-1} t = 1 h
α -HBCDD	86.2 ± 0.5	88.0 ± 0.5	99.0 ± 0.5
PBEB	83.0 ± 0.5	86.0 ± 0.5	98.5 ± 0.5
PBT	83.1 ± 0.5	85.8 ± 0.5	98.2 ± 0.5
TBBPA	82.4 ± 0.5	85.6 ± 0.5	98.0 ± 0.5
AHTN	82.0 ± 0.5	85.0 ± 0.5	97.8 ± 0.5
PFOA	81.0 ± 0.5	84.4 ± 0.5	97.7 ± 0.5
PFOS	79.3 ± 0.5	82.3 ± 0.5	96.0 ± 0.5
GFZ	80.6 ± 0.5	84.1 ± 0.5	97.3 ± 0.5
TCS	80.2 ± 0.5	83.8 ± 0.5	97.1 ± 0.5
IBU	78.1 ± 0.5	81.0 ± 0.5	95.8 ± 0.5
CIP	70.5 ± 0.5	77.4 ± 0.5	95.6 ± 0.5
NDMA	70.0 ± 0.5	75.5 ± 0.5	95.3 ± 0.5

The maximum removals were observed at the highest TMP of 4.75 bar for all studied conventional pollutants (above 95% for all) at the aforementioned experimental conditions in RO (Table 6.46). Higher removals are expected at higher TMPs for RO, since increasing the pressure difference affect positively the filtration driving force through the membrane (Varol et al., 2015).

The conventional pollutants (TSS, TOC, TDS, COD and sCOD) removed mainly by size exclusion mechanism due to being larger and neutral molecules at the aforementioned experimental conditions in RO. Koyuncu (2018) explained that if particle size of the pollutant is higher than the particle size of the membrane pores, the pollutant can not pass through the membrane (Koyuncu, 2018). In this study, all pollutants have higher particle sizes (between 1.2 μm and 2 nm) than the particle size of RO pores (between 0.22 and 0.44 nm).

All the studied micropollutants removed with the maximum removal efficiencies (above 95%) at the highest TMP of 4.75 bar at the aforementioned experimental conditions in RO (Table 6.46). Higher removals were obtained due to the increased pressure difference affected positively the filtration driving force through the RO at higher TMPs (Varol et al., 2015). The higher TMP means the more rapidly saturation was achieved for the micropollutants (Causserand, Aymar, Cravedi, & Singlande, 2005).

The size exclusion made contribution to the removals of the neutral brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN) and phenolic (TCS) micropollutants at the aforementioned experimental conditions. The size exclusion mechanism supported their removals owing to their higher molecular weights (≈ 1 kDa) than the MWCO value of the RO (0.1 kDa) as mentioned by Schlautman & Morgan (1993).

The hydrophobic adsorption affected positively the removals of hydrophobic brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS) and some phenolic (GFZ, TCS and IBU) micropollutants having higher $\log K_{OW}$ values than 3.0. The reason for their hydrophobic adsorption is presumably the occurrence of hydrogen bonding between the polyamide RO surface and the micropollutants as mentioned by Nghiem, Manis, Soldenhoff, & Schäfer (2004). The adsorbed micropollutant masses and adsorption efficiencies were detected in the next section 6.4.3.2, in Table 6.48.

The other hydrophobic and anionic fluoro (PFOA and PFOS) and phenolic (GFZ and IBU) micropollutants removed by hydrophobic adsorption and electrostatic interactions. The electrostatic repulsion between the negatively charged RO surface and the anionic micropollutants ($pK_a < pH$) increased the removal efficiencies at the aforementioned experimental conditions in RO. The hydrophilic anionic phenolic (CIP) and nitroso (NDMA) micropollutants removed by electrostatic interactions owing to their lower pK_a values than the operating pH value (8.00) at the aforementioned experimental conditions in RO.

The increased TMP had a positive effect both for the conventional pollutants and micropollutants removals at the aforementioned experimental conditions in RO (Table 6.46). The ANOVA (one-way) test statistics showed that a linear regression between TMPs and pollutants removals ($R^2 = 0.943$ for conventionals and $R^2 = 0.936$ for micropollutants) were observed at a TMP of 4.75 bar at the aforementioned experimental conditions for RO. According to the ANOVA (one-way) test statistics results the effect of TMP on pollutants removals were found to be significant at 4.75 bar TMP at the aforementioned experimental conditions in RO ($P = 0.045$, $\alpha = 0.05$, $F = 4.08$ for conventionals and $P = 2.40 \times 10^{-13}$, $\alpha = 0.05$, $F = 79.48$ for micropollutants). However, there is no significant relationship between lower TMPs (2.75 and 3.75 bar) and pollutants removals at the aforementioned experimental conditions in RO according to the ANOVA (one-way) test statistics results ($P = 0.301$, $\alpha = 0.05$, $F = 1.22$ for conventionals and $P = 0.0567$, $\alpha = 0.05$, $F = 4.05$ for micropollutants).

Snyder et al. (2007) determined higher than 85% of removal efficiencies for GFZ, IBU and TCS having initial concentrations of 234, 302 and 166 $\mu\text{g L}^{-1}$, respectively in RO at 12 gallons $\text{feet}^{-2} \text{day}^{-1}$ flux for a saline groundwater at 25 °C and at pH 7.00-8.00 (Snyder et al., 2007). Steinle-Darling et al. (2007) studied the removal of NDMA by RO at 15.5 bar TMP with 10 cm sec^{-1} CFV at 25 ± 0.5 °C for an initial concentration of 200 $\mu\text{g L}^{-1}$ and obtained 56% removal efficiency for NDMA in deionized water (Steinle-Darling et al., 2007). Xie et al. (2012) confirmed that high TCS removal (>90%) with RO occurred via adsorption having a $\log K_{OW}$ value higher

than 4.0 ($\log K_{OW}$ of TCS = 4.76), steric hindrance having a larger molecular width than the membrane pore size (molecular width of TCS = 0.75 nm and RO pore size = 0.22-0.44 nm) and electrostatic repulsion between negative surface charge of the membrane and negatively charged TCS at pH = 8.50 (pK_a of TCS = 7.9) for 500 $\mu\text{g L}^{-1}$ TCS at an operating pressure of 10 bar and at 25 ± 1 °C in a synthetic wastewater (Xie et al., 2012). IBU and GFZ removed 95% by RO operating at 25 bar pressure through electrostatic repulsion from the negatively charged membrane surface at neutral pH (7.00) for the initial concentrations of 2 $\mu\text{g L}^{-1}$ in a synthetic wastewater (D'Haese et al., 2013). Urtiaga et al. (2013) determined higher than 95% of TDS removal for an initial concentration of 639 mg L^{-1} by RO at a constant flowrate of 2.4 $\text{m}^3 \text{h}^{-1}$ and at 11 bar pressure gradient at pH 6.40 for a secondary effluent of a wastewater treatment plant (Urtiaga et al., 2013). The maximum removal efficiencies determined at the optimum experimental conditions (TMP = 4.75 bar, $J_v = 104.17 \text{ L m}^{-2} \text{h}^{-1}$, CFV = 0.10 m h^{-1} , pH = 8.00, T = 25 °C) for GFZ (95%), IBU (94%), TCS (95%), NDMA (91%) and TDS (99%) in this study were higher than the literature (>85% for GFZ-IBU-TCS, 56% NDMA and 95% TDS) (Table 6.46).

Permeate flux (J_v) of the UF and RO membranes were found as 156.25 $\text{L m}^{-2} \text{h}^{-1}$ and 104.17 $\text{L m}^{-2} \text{h}^{-1}$, respectively at the same TMP of 2.75 bar for the same membrane operation time (1 h) (Section 5.5.4.1.2). The UF gave a higher permeate flux (156.25 $\text{L m}^{-2} \text{h}^{-1}$) than RO (104.17 $\text{L m}^{-2} \text{h}^{-1}$) at a TMP of 2.75 bar because of its larger pore size in the comparison with RO. UF has a pore size range of 0.01-0.1 μm , while RO has a pore size range of 0.22-0.44 nm. Permeate flux (J_v) is highly related with the pore size of the membranes along with the pressure applied during the process (Yuksel et al., 2013).

6.4.3 Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants Removals via Hydrophobic Adsorption in UF and RO

6.4.3.1 Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants Removals via Hydrophobic Adsorption in UF

A mass balance study was prepared to calculate the hydrophobic adsorption of all studied micropollutants in UF at the following experimental conditions: at a constant TMP of 2.75 bar, at a constant permeate flux (J_v) of $156.25 \text{ L m}^{-2} \text{ h}^{-1}$, at a constant CFV of 0.16 m h^{-1} , at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25°C (Table 6.47).

Table 6.47 The adsorption amounts (M_{ads}) and adsorption percentages (Adsorption, %) of all studied micropollutants in UF for the raw hospital wastewater at a constant TMP of 2.75 bar, at a constant permeate flux (J_v) of $156.25 \text{ L m}^{-2} \text{ h}^{-1}$, at a constant CFV of 0.16 m h^{-1} , at a constant pH of 8.00 and at a constant temperature of 25°C ($n=3$, mean $\pm$ SD)

Micropollutant	Feed concentration $C_f (\mu\text{g L}^{-1})$	Permeate concentration $C_p (\mu\text{g L}^{-1})$	M_{ads} ($\mu\text{g m}^{-2}$)	Adsorption (%)	Total Removal Efficiency (%)
α -HBCDD	0.0115 ± 0.001	0.00727 ± 0.001	0.66125 ± 0.001	36.8 ± 0.5	36.8 ± 0.5
PBEB	0.00328 ± 0.001	0.00209 ± 0.001	0.18655 ± 0.001	36.4 ± 0.5	36.4 ± 0.5
PBT	0.00231 ± 0.001	0.00148 ± 0.001	0.12994 ± 0.001	36.0 ± 0.5	36.0 ± 0.5
TBBPA	0.0170 ± 0.001	0.01093 ± 0.001	0.94828 ± 0.001	35.7 ± 0.5	35.7 ± 0.5
AHTN	0.206 ± 0.020	0.13349 ± 0.020	11.3300 ± 0.020	35.2 ± 0.5	35.2 ± 0.5
PFOA	0.1770 ± 0.001	0.11523 ± 0.001	9.65203 ± 0.001	34.9 ± 0.5	34.9 ± 0.5
PFOS	0.018 ± 0.001	0.01222 ± 0.001	0.90281 ± 0.001	32.1 ± 0.5	32.1 ± 0.5
GFZ	53.30 ± 0.05	35.39 ± 0.05	2798.25 ± 0.05	33.6 ± 0.5	33.6 ± 0.5
TCS	361.00 ± 0.05	241.15 ± 0.05	18726.88 ± 0.05	33.2 ± 0.5	33.2 ± 0.5
IBU	42.50 ± 0.05	29.75 ± 0.05	1992.19 ± 0.05	30.0 ± 0.5	30.0 ± 0.5
CIP	522.00 ± 0.05	489.64 ± 0.05	5056.88 ± 0.05	6.2 ± 0.5	6.2 ± 0.5
NDMA	0.165 ± 0.020	0.15543 ± 0.020	1.49531 ± 0.020	5.8 ± 0.5	5.8 ± 0.5

An example calculation was made for the amount of α -HBCDD (M_{feed}) in the influent of UF (Equation 6.324), adsorption amount of α -HBCDD (M_{ads}) in UF (Equation 6.325) and the adsorption percentage of α -HBCDD (Adsorption, %) in UF (Equation 6.326) at the aforementioned experimental conditions (Table 6.47). The concentration of α -HBCDD was measured as 0.0115 and 0.00727 in feed and permeate, respectively (Table 6.47). The UF membrane surface area was 0.64 m^2 while, the volumes were 100.0 L both for feed and permeate at the aforementioned experimental conditions.

$$M_{\text{feed}} = \frac{(C_f \times V_f)}{A} = \frac{(0.0115 \times 100)}{0.64} = 1.797 \text{ } \mu\text{g m}^{-2} \quad (6.324)$$

$$M_{\text{ads}} = \frac{[(C_f V_f) - (C_p V_p)]}{A} = \frac{[(0.0115 \times 100) - (0.00727 \times 100)]}{0.64} = 0.661 \text{ } \mu\text{g m}^{-2} \quad (6.325)$$

$$\text{Adsorption (\%)} = \frac{M_{\text{ads}}}{M_{\text{feed}}} \times 100 = \frac{0.661 \text{ } \mu\text{g m}^{-2}}{1.797 \text{ } \mu\text{g m}^{-2}} \times 100 = 36.80\% \quad (6.326)$$

The brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS) and some phenolic (GFZ, TCS and IBU) are accepted as hydrophobic micropollutants owing to their higher $\log K_{\text{OW}}$ values (> 3.0). They removed with higher adsorption efficiencies (between 30.0% and 36.8%) in the comparison with the hydrophilic micropollutants (CIP and NDMA) (5.8% and 6.2%) at the aforementioned experimental conditions in UF (Table 6.47). There is a strong correlation between the $\log K_{\text{OW}}$ values and adsorption removals of the micropollutants ($R^2 = 0.936$) and this relationship was found to be significant at the aforementioned experimental conditions in UF according to the ANOVA (one-way) test statistics results ($P = 1.60 \times 10^{-7}$, $\alpha = 0.05$, $F = 56.50$). Yoon, Westerhoff, Yoon, & Snyder (2004) also revealed that the hydrophobic adsorption was the main mechanism for the removal of hydrophobic micropollutants and that the adsorption was positively correlated with hydrophobicity ($\log K_{\text{OW}}$ values) in membrane systems (Yoon et al., 2004).

6.4.3.2 Brominated (α -HBCDD, TBBPA, PBT and PBEB), Fluoro (PFOS and PFOA), Phenolic (TCS, GFZ, CIP and IBU), Nitroso (NDMA) and Aromatic (AHTN) Micropollutants Removals via Hydrophobic Adsorption in RO

To quantify hydrophobic adsorption of all studied micropollutants in RO, mass balances were calculated based on the concentration of each compound in feed, permeate and retentate at the following experimental conditions: at increasing TMPs of 2.75, 3.75 and 4.75 bar, at a constant permeate flux (J_v) of $104.17 \text{ L m}^{-2} \text{ h}^{-1}$, at a constant CFV of 0.10 m h^{-1} , at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25°C (Table 6.48).

Table 6.48 The adsorption amounts (M_{ads}) and adsorption percentages (Adsorption, %) of all studied micropollutants in RO for the raw hospital wastewater at increasing TMPs of 2.75, 3.75 and 4.75 bar, at a constant permeate flux (J_v) of $104.17 \text{ L m}^{-2} \text{ h}^{-1}$, at a constant CFV of 0.10 m h^{-1} , at a constant pH of 8.00 and at a constant temperature of 25°C ($n=3$, mean $\pm$ SD)

Micropollutant	TMP (bar)	Feed concentration $C_f (\mu\text{g L}^{-1})$	Permeate concentration $C_p (\mu\text{g L}^{-1})$	Retentate concentration $C_r (\mu\text{g L}^{-1})$	M_{ads} $(\mu\text{g m}^{-2})$	Adsorption (%)	Total Removal Efficiency (%)
α -HBCDD	2.75	0.0115 ± 0.001	0.00159 ± 0.001	0.00476 ± 0.001	0.812 ± 0.001	67.79 ± 0.5	86.2 ± 0.5
	3.75	0.0115 ± 0.001	0.00138 ± 0.001	0.00414 ± 0.001	0.862 ± 0.001	71.99 ± 0.5	88.0 ± 0.5
	4.75	0.0115 ± 0.001	0.00011 ± 0.001	0.00034 ± 0.001	1.170 ± 0.001	97.67 ± 0.5	99.0 ± 0.5
PBEB	2.75	0.00328 ± 0.001	0.00056 ± 0.001	0.00139 ± 0.001	0.225 ± 0.001	65.99 ± 0.5	83.0 ± 0.5
	3.75	0.00328 ± 0.001	0.00046 ± 0.001	0.00115 ± 0.001	0.246 ± 0.001	71.99 ± 0.5	86.0 ± 0.5
	4.75	0.00328 ± 0.001	0.00005 ± 0.001	0.00012 ± 0.001	0.331 ± 0.001	97.00 ± 0.5	98.5 ± 0.5
PBT	2.75	0.00231 ± 0.001	0.00039 ± 0.001	0.00105 ± 0.001	0.154 ± 0.001	63.94 ± 0.5	83.1 ± 0.5
	3.75	0.00231 ± 0.001	0.00033 ± 0.001	0.00089 ± 0.001	0.168 ± 0.001	69.70 ± 0.5	85.8 ± 0.5
	4.75	0.00231 ± 0.001	0.00004 ± 0.001	0.00011 ± 0.001	0.231 ± 0.001	96.16 ± 0.5	98.2 ± 0.5
TBBPA	2.75	0.0170 ± 0.001	0.00299 ± 0.001	0.00808 ± 0.001	1.106 ± 0.001	62.44 ± 0.5	82.4 ± 0.5
	3.75	0.0170 ± 0.001	0.00245 ± 0.001	0.00661 ± 0.001	1.227 ± 0.001	69.27 ± 0.5	85.6 ± 0.5
	4.75	0.0170 ± 0.001	0.00034 ± 0.001	0.00092 ± 0.001	1.695 ± 0.001	95.73 ± 0.5	98.0 ± 0.5
AHTN	2.75	0.206 ± 0.020	0.03708 ± 0.020	0.10012 ± 0.020	13.22 ± 0.020	61.59 ± 0.5	82.0 ± 0.5
	3.75	0.206 ± 0.020	0.03090 ± 0.020	0.08343 ± 0.020	14.59 ± 0.020	67.99 ± 0.5	85.0 ± 0.5
	4.75	0.206 ± 0.020	0.00453 ± 0.020	0.01224 ± 0.020	20.45 ± 0.020	95.31 ± 0.5	97.8 ± 0.5
PFOA	2.75	0.1770 ± 0.001	0.03363 ± 0.001	0.09080 ± 0.001	10.96 ± 0.001	59.46 ± 0.5	81.0 ± 0.5
	3.75	0.1770 ± 0.001	0.02761 ± 0.001	0.07455 ± 0.001	12.30 ± 0.001	66.71 ± 0.5	84.4 ± 0.5
	4.75	0.1770 ± 0.001	0.00407 ± 0.001	0.01099 ± 0.001	17.53 ± 0.001	95.09 ± 0.5	97.7 ± 0.5

Table 6.48 continues

Micropollutant	TMP (bar)	Feed concentration C_f ($\mu\text{g L}^{-1}$)	Permeate concentration C_p ($\mu\text{g L}^{-1}$)	Retentate concentration C_r ($\mu\text{g L}^{-1}$)	M_{ads} ($\mu\text{g m}^{-2}$)	Adsorption (%)	Total Removal Efficiency (%)
PFOS	2.75	0.0180 ± 0.001	0.00373 ± 0.001	0.01006 ± 0.001	1.047 ± 0.001	55.83 ± 0.5	79.3 ± 0.5
	3.75	0.0180 ± 0.001	0.00319 ± 0.001	0.00860 ± 0.001	1.167 ± 0.001	62.23 ± 0.5	82.3 ± 0.5
	4.75	0.0180 ± 0.001	0.00049 ± 0.001	0.00131 ± 0.001	1.767 ± 0.001	94.24 ± 0.5	96.0 ± 0.5
GFZ	2.75	53.30 ± 0.05	10.34 ± 0.05	27.92 ± 0.05	3253.65 ± 0.05	58.60 ± 0.5	80.6 ± 0.5
	3.75	53.30 ± 0.05	8.47 ± 0.05	22.88 ± 0.05	3668.32 ± 0.05	66.07 ± 0.5	84.1 ± 0.5
	4.75	53.30 ± 0.05	1.55 ± 0.05	4.17 ± 0.05	5208.50 ± 0.05	93.81 ± 0.5	97.3 ± 0.5
TCS	2.75	361.00 ± 0.05	71.48 ± 0.05	192.99 ± 0.05	21715.95 ± 0.05	57.75 ± 0.5	80.2 ± 0.5
	3.75	361.00 ± 0.05	58.48 ± 0.05	157.90 ± 0.05	24604.71 ± 0.05	65.43 ± 0.5	83.8 ± 0.5
	4.75	361.00 ± 0.05	14.44 ± 0.05	38.99 ± 0.05	34394.43 ± 0.05	91.46 ± 0.5	97.1 ± 0.5
IBU	2.75	42.50 ± 0.05	9.31 ± 0.05	25.13 ± 0.05	2358.20 ± 0.05	53.27 ± 0.5	78.1 ± 0.5
	3.75	42.50 ± 0.05	8.08 ± 0.05	21.80 ± 0.05	2632.16 ± 0.05	59.46 ± 0.5	81.0 ± 0.5
	4.75	42.50 ± 0.05	1.79 ± 0.05	4.82 ± 0.05	4030.31 ± 0.05	91.04 ± 0.5	95.8 ± 0.5
CIP	2.75	522.00 ± 0.05	153.99 ± 0.05	646.76 ± 0.05	4097.27 ± 0.05	7.54 ± 0.5	70.5 ± 0.5
	3.75	522.00 ± 0.05	117.97 ± 0.05	660.64 ± 0.05	4381.91 ± 0.05	8.06 ± 0.5	77.4 ± 0.5
	4.75	522.00 ± 0.05	22.97 ± 0.05	700.52 ± 0.05	4906.47 ± 0.05	9.02 ± 0.5	95.6 ± 0.5
NDMA	2.75	0.165 ± 0.020	0.04950 ± 0.020	0.20790 ± 0.020	1.026 ± 0.020	5.97 ± 0.5	70.0 ± 0.5
	3.75	0.165 ± 0.020	0.04043 ± 0.020	0.21021 ± 0.020	1.180 ± 0.020	6.87 ± 0.5	75.5 ± 0.5
	4.75	0.165 ± 0.020	0.00776 ± 0.020	0.22490 ± 0.020	1.293 ± 0.020	7.52 ± 0.5	95.3 ± 0.5

An example calculation was made for the amount of α -HBCDD (M_{feed}) in the influent of RO (Equation 6.327), adsorption amount of α -HBCDD (M_{ads}) in RO (Equation 6.328) and the adsorption percentage of α -HBCDD (Adsorption, %) in RO (Equation 6.329) for a TMP of 2.75 bar at the aforementioned experimental conditions (Table 6.48). The concentration of α -HBCDD was measured as 0.0115, 0.00159 and 0.00476 $\mu\text{g L}^{-1}$ in feed, permeate and retentate, respectively (Table 6.48). The RO membrane surface area was 0.96 m^2 while, the volumes were 100.0, 33.3 and 66.7 L for feed, permeate and retentate, respectively at the aforementioned experimental conditions.

$$M_{\text{feed}} = \frac{(C_f \times V_f)}{A} = \frac{(0.0115 \times 100)}{0.96} = 1.198 \mu\text{g m}^{-2} \quad (6.327)$$

$$M_{\text{ads}} = \frac{(C_f V_f) - [(C_p V_p) + (C_r V_r)]}{A} = \frac{(0.0115 \times 100) - [(0.00159 \times 33.3) + (0.00476 \times 66.7)]}{0.96} = 0.812 \mu\text{g m}^{-2} \quad (6.328)$$

$$\text{Adsorption (\%)} = \frac{M_{\text{ads}}}{M_{\text{feed}}} \times 100 = \frac{0.812 \mu\text{g m}^{-2}}{1.198 \mu\text{g m}^{-2}} \times 100 = 67.79\% \quad (6.329)$$

The hydrophobic micropollutants (α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, PFOS, GFZ, TCS and IBU) having higher $\log K_{\text{OW}}$ values (> 3.0) showed higher adsorption removals (between 53% and 98%) in the comparison with the hydrophilic micropollutants (CIP and NDMA) (between 5% and 9%) at the aforementioned experimental conditions in RO (Table 6.48). There is a strong correlation between the $\log K_{\text{OW}}$ values and adsorption removals of the micropollutants at the aforementioned experimental conditions in RO ($R^2 = 0.994$). The ANOVA (one-way) test statistics showed that this relationship was significant at the aforementioned experimental conditions in RO ($P = 0.031$, $\alpha = 0.05$, $F = 3.88$). Secondes, Naddeo, Belgiorio, & Ballesteros (2014) also explained that the removal trend of micropollutants via hydrophobic adsorption were in correlation with their hydrophobic characteristics ($\log K_{\text{OW}}$ values) in membrane treatment (Secondes et al., 2014).

6.5 Kinetic Studies

6.5.1 Determination of Kinetic Constants (Zero-Order, Half-Order, First-Order, Second-Order and Monod) in the Anaerobic/Aerobic Sequential Biological Reactor System

Recent literature studies showed that the kinetic of the anaerobic and aerobic biological reactors treating raw hospital wastewater containing both macro and micropollutants have not been investigated. In this study, the experimental data obtained from the anaerobic and aerobic biological reactor effluents at 5, 30, 45 and 55 days of SRTs were applied to various kinetic models such as; zero-order, half-order, first-order, second-order and Monod to determine the optimum brominated micropollutants (α -HBCDD, TBBPA, PBT and PBEB), fluoro micropollutants (PFOA and PFOS), nitroso micropollutant (NDMA), phenolic micropollutants (TCS, GFZ, CIP and IBU), aromatic micropollutant (AHTN) and macropollutants (COD and sCOD) removal kinetics.

6.5.1.1 Monod Kinetic Model

To determine the value of growth yield coefficient (Y) and endogenous decay coefficient (k_d), the inverse of sludge retention time ($1/\text{SRT}$) was plotted against the specific substrate utilization rate (U) ($(S_i - S_e)/\text{SRT} \times X$). Y was determined from the slope of the line and k_d was determined from the intercept of the y-axis. The half saturation concentration (K_s) and the maximum specific growth rate ($\mu_{\max}$) were determined by plotting the $(\text{SRT}/1 + \text{SRT} \times k_d)$ against the inverse of the effluent substrate concentration ($1/S_e$). K_s was determined from the slope of the line and $\mu_{\max}$ was determined from the intercept of the y-axis.

6.5.1.1.1 Monod Kinetic Model for α -HBCDD. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.051 $\mu\text{g VSS}/\mu\text{g } \alpha\text{-HBCDD}$ and 0.0010 day^{-1} , respectively with a correlation coefficient (R^2) of 0.990 for α -HBCDD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Figure 6.57.a) (Table 6.49). Y and k_d values were calculated as 0.326 $\mu\text{g VSS}/\mu\text{g } \alpha\text{-HBCDD}$ and 0.0108 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for α -HBCDD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Figure 6.57.b) (Table 6.49).

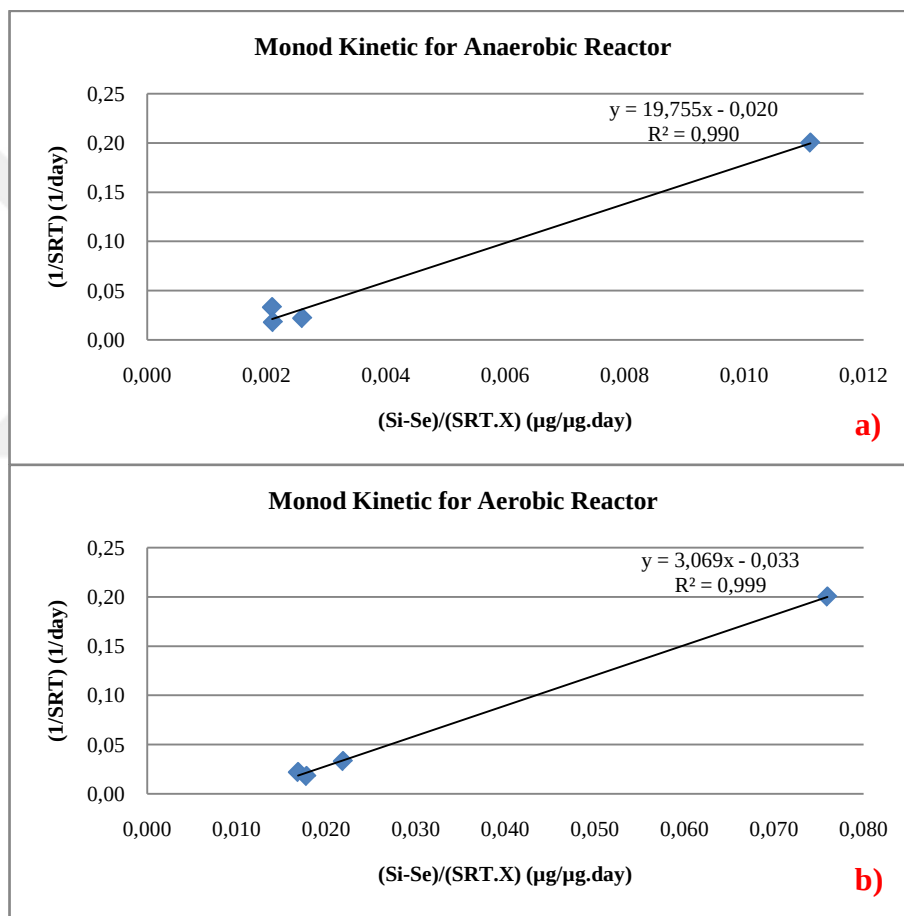


Figure 6.57 Determination of growth yield coefficient (Y) and endogenous decay coefficient (k_d) for α -HBCDD at 5, 30, 45 and 55 days of SRT in the (a) anaerobic reactor and (b) aerobic reactor

Table 6.49 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for α -HBCDD in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	α -HBCDD	0.051	0.990	0.0010	0.990	0.0010	0.967	0.0088	0.967
Aerobic reactor	α -HBCDD	0.326	0.999	0.0108	0.999	0.0030	0.918	0.0057	0.918

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as $0.0088 \mu\text{g L}^{-1}$ and 0.0010 day^{-1} , respectively with a correlation coefficient (R^2) of 0.967 for α -HBCDD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Figure 6.58.a) (Table 6.49). K_s and $\mu_{\max}$ values were calculated as $0.0057 \mu\text{g L}^{-1}$ and 0.0030 day^{-1} , respectively with a correlation coefficient (R^2) of 0.918 for α -HBCDD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Figure 6.58.b) (Table 6.49).

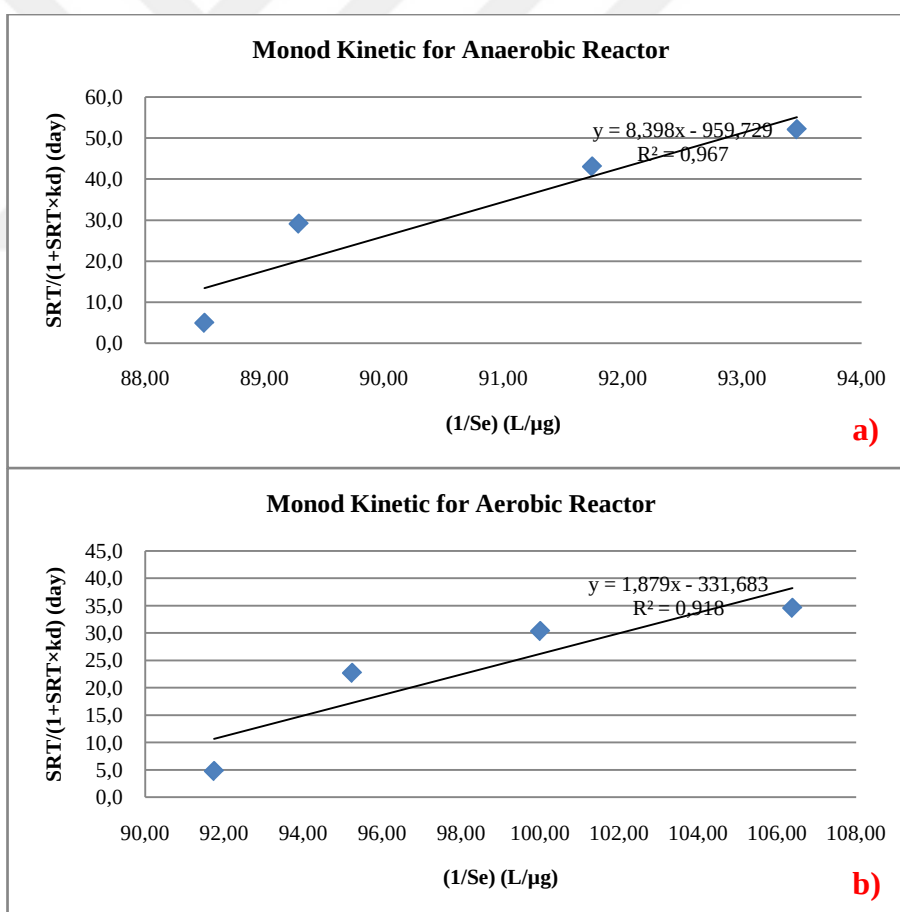


Figure 6.58 Determination of half saturation constant (K_s) and maximum specific growth rate ($\mu_{\max}$) for α -HBCDD at 5, 30, 45 and 55 days of SRT in the (a) anaerobic reactor and (b) aerobic reactor

The growth yield coefficient (Y) increased from 0.051 to 0.326 $\mu\text{g VSS}/\mu\text{g } \alpha\text{-HBCDD}$ in anaerobic and aerobic reactors, respectively showing that the aerobic reactor had higher growth yield ratio for $\alpha\text{-HBCDD}$ (Table 6.49). There was an increase for maximum specific growth rate (μ_{max}) from 0.0010 to 0.0030 day^{-1} in anaerobic and aerobic reactors, respectively for $\alpha\text{-HBCDD}$ (Table 6.49). The half saturation constant (K_s) of $\alpha\text{-HBCDD}$ ($0.0088 \mu\text{g L}^{-1}$) in anaerobic biological reactor was higher than the half saturation constant (K_s) of $\alpha\text{-HBCDD}$ ($0.0057 \mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.49). The lower K_s value in aerobic reactor shows that the aerobic biodegradation of $\alpha\text{-HBCDD}$ was higher than that of the anaerobic biodegradation. The results supported that the aerobic reactor had better removal performance (12.1%) for removing $\alpha\text{-HBCDD}$ than anaerobic reactor (7.0%) at 55 days SRT (Table 6.7). $\alpha\text{-HBCDD}$ was a hydrophobic micropollutant having low water solubility ($2.09 \times 10^{-5} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{\text{OW}} = 7.74$) and low Henry's Law constant ($1.72 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$) and these physicochemical properties makes $\alpha\text{-HBCDD}$ hardly biodegradable in both reactors.

6.5.1.1.2 Monod Kinetic Model for PBEB. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.053 $\mu\text{g VSS}/\mu\text{g PBEB}$ and 0.0005 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PBEB in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 1.a) (Table 6.50). Y and k_d values were calculated as 0.363 $\mu\text{g VSS}/\mu\text{g PBEB}$ and 0.0098 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PBEB in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 1.b) (Table 6.50).

Table 6.50 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for PBEB in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	μ_{max} (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	PBEB	0.053	0.999	0.0005	0.999	0.0010	0.906	0.0029	0.906
Aerobic reactor	PBEB	0.363	0.999	0.0098	0.999	0.0031	0.949	0.0018	0.949

The half saturation concentration (K_s) and maximum specific growth rate (μ_{max}) values were calculated as 0.0029 $\mu\text{g L}^{-1}$ and 0.0010 day^{-1} , respectively with a

correlation coefficient (R^2) of 0.906 for PBEB in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 2.a) (Table 6.50). K_s and $\mu_{\max}$ values were calculated as $0.0018 \mu\text{g L}^{-1}$ and 0.0031 day^{-1} , respectively with a correlation coefficient (R^2) of 0.949 for PBEB in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 2.b) (Table 6.50).

The anaerobic reactor have lower growth yield coefficient (Y) ($0.053 \mu\text{g VSS}/\mu\text{g PBEB}$) and lower maximum specific growth rate ($\mu_{\max}$) (0.0010 day^{-1}) than aerobic reactor for Y ($0.363 \mu\text{g VSS}/\mu\text{g PBEB}$) and $\mu_{\max}$ (0.0031 day^{-1}) values (Table 6.50). The half saturation constant (K_s) of PBEB ($0.0029 \mu\text{g L}^{-1}$) in anaerobic biological reactor was higher than the half saturation constant (K_s) of PBEB ($0.0018 \mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.50). Higher Y and $\mu_{\max}$ values with lower K_s value in aerobic reactor showed that PBEB was consumed as co-substrate more effectively in aerobic reactor than anaerobic reactor. PBEB has low water solubility ($2.90 \times 10^{-7} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{\text{OW}} = 7.48$) and low Henry's Law constant ($7.92 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) values. PBEB was hardly removed by biodegradation in both anaerobic (7.6%) and aerobic (12.4%) reactors because of being a hydrophobic micropollutant due its physicochemical properties (Table 6.9).

6.5.1.1.3 Monod Kinetic Model for PBT. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as $0.055 \mu\text{g VSS}/\mu\text{g PBT}$ and 0.0002 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PBT in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 3.a) (Table 6.51). Y and k_d values were calculated as $0.366 \mu\text{g VSS}/\mu\text{g PBT}$ and 0.0055 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PBT in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 3.b) (Table 6.51).

Table 6.51 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for PBT in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	PBT	0.055	0.999	0.0002	0.999	0.0010	0.921	0.0021	0.921
Aerobic reactor	PBT	0.366	0.999	0.0055	0.999	0.0031	0.961	0.0017	0.961

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as $0.0021 \mu\text{g L}^{-1}$ and 0.0010 day^{-1} , respectively with a correlation coefficient (R^2) of 0.921 for PBT in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 4.a) (Table 6.51). K_s and $\mu_{\max}$ values were calculated as $0.0017 \mu\text{g L}^{-1}$ and 0.0031 day^{-1} , respectively with a correlation coefficient (R^2) of 0.961 for PBT in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 4.b) (Table 6.51).

The aerobic reactor have higher growth yield coefficient (Y) ($0.366 \mu\text{g VSS}/\mu\text{g PBT}$) in comparison with anaerobic reactor's Y ($0.055 \mu\text{g VSS}/\mu\text{g PBT}$) (Table 6.51). The aerobic reactor also showed higher maximum specific growth rate ($\mu_{\max}$) (0.0031 day^{-1}) than anaerobic reactor (0.0010 day^{-1}) indicating better removal performance for removing PBT (Table 6.51). The half saturation constant (K_s) of PBT in aerobic biological reactor ($0.0017 \mu\text{g L}^{-1}$) was lower than the half saturation constant (K_s) of PBT in anaerobic biological reactor ($0.0021 \mu\text{g L}^{-1}$) (Table 6.51). It is important to note that the lower K_s value is an evidence that aerobic reactor (12.7%) was more succesful to biodegrade the PBT than that of the anaerobic reactor (7.9%) (Table 6.11). However, the removal efficiencies of PBT were low in both reactors and this could be attributed to being a hydrophobic micropollutant and hardly removed by biodegradation due to its low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 6.99$) and low Henry's Law constant ($5.97 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$) values.

6.5.1.1.4 Monod Kinetic Model for TBBPA. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as $0.056 \mu\text{g VSS}/\mu\text{g TBBPA}$ and 0.0001 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for TBBPA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs

(Appendice-1, Figure 5.a) (Table 6.52). Y and k_d values were calculated as $0.366 \mu\text{g VSS}/\mu\text{g TBBPA}$ and 0.0040 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for TBBPA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 5.b) (Table 6.52).

Table 6.52 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for TBBPA in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	TBBPA	0.056	0.999	0.0001	0.999	0.0010	0.943	0.0145	0.943
Aerobic reactor	TBBPA	0.366	0.999	0.0040	0.999	0.0032	0.948	0.0112	0.948

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as $0.0145 \mu\text{g L}^{-1}$ and 0.0010 day^{-1} , respectively with a correlation coefficient (R^2) of 0.943 for TBBPA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 6.a) (Table 6.52). K_s and $\mu_{\max}$ values were calculated as $0.0112 \mu\text{g L}^{-1}$ and 0.0032 day^{-1} , respectively with a correlation coefficient (R^2) of 0.948 for TBBPA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 6.b) (Table 6.52).

The growth yield coefficient (Y) increased from 0.056 to $0.366 \mu\text{g VSS}/\mu\text{g TBBPA}$ for TBBPA in anaerobic and aerobic reactors, respectively (Table 6.52). The anaerobic bacteria have lower growth yields compared to aerobic ones. The maximum specific growth rate ($\mu_{\max}$) increased from 0.0010 to 0.0032 day^{-1} in anaerobic and aerobic reactors, respectively due to the high yield ratios of aerobic bacteria than anaerobic bacteria (Table 6.52). The half saturation constant (K_s) of TBBPA ($0.0145 \mu\text{g L}^{-1}$) in anaerobic biological reactor was higher compared to the half saturation constant (K_s) of TBBPA ($0.0112 \mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.52). The lower K_s value indicates the affinity of aerobic microorganisms to TBBPA as co-substrate. Moreover, the aerobic biodegradation removal efficiency of TBBPA was 13.5% while the anaerobic removal efficiency was measured as 8.2% at 55 days SRT (Table 6.13). TBBPA was a hydrophobic micropollutant having low water solubility ($7.65 \times 10^{-6} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{OW} = 5.90$) and low Henry's Law constant ($1.47 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$). These hydrophobic

properties makes TBBPA hardly biodegradable and that's why TBBPA was removed with low biodegradation yields in both reactors.

6.5.1.1.5 Monod Kinetic Model for AHTN. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.070 $\mu\text{g VSS}/\mu\text{g AHTN}$ and 0.0004 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for AHTN in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 7.a) (Table 6.53). Y and k_d values were calculated as 0.368 $\mu\text{g VSS}/\mu\text{g AHTN}$ and 0.0029 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for AHTN in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 7.b) (Table 6.53).

Table 6.53 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for AHTN in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	AHTN	0.070	0.999	0.0004	0.999	0.0012	0.961	0.150	0.961
Aerobic reactor	AHTN	0.368	0.999	0.0029	0.999	0.0035	0.939	0.147	0.939

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as 0.150 $\mu\text{g L}^{-1}$ and 0.0012 day^{-1} , respectively with a correlation coefficient (R^2) of 0.961 for AHTN in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 8.a) (Table 6.53). K_s and $\mu_{\max}$ values were calculated as 0.147 $\mu\text{g L}^{-1}$ and 0.0035 day^{-1} , respectively with a correlation coefficient (R^2) of 0.939 for AHTN in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 8.b) (Table 6.53).

The anerobic bacteria have lower growth yields compared to aerobic ones that the growth yield coefficient (Y) of anaerobic bacteria was 0.070 $\mu\text{g VSS}/\mu\text{g AHTN}$ while the aerobic bacteria had a growth yield coefficient (Y) of 0.368 $\mu\text{g VSS}/\mu\text{g AHTN}$ (Table 6.53). The maximum specific growth rate ($\mu_{\max}$) of AHTN increased from 0.0012 to 0.0035 day^{-1} in anaerobic and aerobic reactors, respectively (Table 6.53). The half saturation constant (K_s) of AHTN (0.150 $\mu\text{g L}^{-1}$) in anaerobic biological reactor was higher compared to the half saturation constant (K_s) of AHTN

(0.147 $\mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.53). It is important to note that the lower K_s value shows the higher biodegradation removals. The aerobic reactor had higher AHTN removal efficiency (15.0%) than the anaerobic reactor (11.1%) at 55 days SRT (Table 6.15). AHTN had lower biodegradation yields both in anaerobic and aerobic reactors because it was a hydrophobic micropollutant and resistant to extensive biodegradation (low water solubility = $1.25 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 5.70$ and low Henry's Law constant = $1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$).

6.5.1.1.6 Monod Kinetic Model for PFOA. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.081 $\mu\text{g VSS}/\mu\text{g PFOA}$ and 0.0002 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PFOA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 9.a) (Table 6.54). Y and k_d values were calculated as 0.371 $\mu\text{g VSS}/\mu\text{g PFOA}$ and 0.0030 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PFOA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 9.b) (Table 6.54).

Table 6.54 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for PFOA in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	PFOA	0.081	0.999	0.0002	0.999	0.0012	0.999	0.1416	0.999
Aerobic reactor	PFOA	0.371	0.999	0.0030	0.999	0.0036	0.972	0.1079	0.972

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as 0.1416 $\mu\text{g L}^{-1}$ and 0.0012 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PFOA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 10.a) (Table 6.54). K_s and $\mu_{\max}$ values were calculated as 0.1079 $\mu\text{g L}^{-1}$ and 0.0036 day^{-1} , respectively with a correlation coefficient (R^2) of 0.972 for PFOA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 10.b) (Table 6.54).

The anaerobic bacteria have lower growth yields (Y) (0.081 $\mu\text{g VSS}/\mu\text{g PFOA}$), lower maximum specific growth rate (μ_{max}) (0.0012 day^{-1}) and higher half saturation constant (K_s) ($0.1416 \mu\text{g L}^{-1}$) of PFOA than aerobic bacteria for $Y = 0.371 \mu\text{g VSS}/\mu\text{g PFOA}$, $\mu_{\text{max}} = 0.0036 \text{ day}^{-1}$ and $K_s = 0.1079 \mu\text{g L}^{-1}$ values, respectively (Table 6.54). The aerobic reactor had better growth yields and also better PFOA removal due to the lower half saturation constant (K_s). Lower K_s value indicates affinity of aerobic bacteria to PFOA as co-substrate. The previous results also supported that aerobic reactor (18.1%) had better PFOA removal efficiency than the anaerobic reactor (12.0%) at 55 days SRT (Table 6.17). PFOA was a hydrophobic micropollutant having low water solubility ($0.481 \times 10^{-3} \text{ g L}^{-1}$), high octanol/water partition coefficient ($\log K_{\text{OW}} = 4.81$) and low Henry's Law constant ($9.08 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$). This is the reason why PFOA had low biodegradation removal efficiencies in both reactors because biodegradation of PFOA was limited due to its physicochemical properties.

6.5.1.1.7 Monod Kinetic Model for PFOS. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as $0.097 \mu\text{g VSS}/\mu\text{g PFOS}$ and 0.0003 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PFOS in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 11.a) (Table 6.55). Y and k_d values were calculated as $0.399 \mu\text{g VSS}/\mu\text{g PFOS}$ and 0.0056 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for PFOS in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 11.b) (Table 6.55).

Table 6.55 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for PFOS in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	μ_{max} (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	PFOS	0.097	0.999	0.0003	0.999	0.0012	0.933	0.0147	0.933
Aerobic reactor	PFOS	0.399	0.999	0.0056	0.999	0.0135	0.977	0.0086	0.977

The half saturation concentration (K_s) and maximum specific growth rate (μ_{max}) values were calculated as $0.0147 \mu\text{g L}^{-1}$ and 0.0012 day^{-1} , respectively with a correlation coefficient (R^2) of 0.933 for PFOS in the anaerobic biological reactor at

5, 30, 45 and 55 days SRTs (Appendice-1, Figure 12.a) (Table 6.55). K_s and $\mu_{\max}$ values were calculated as $0.0086 \mu\text{g L}^{-1}$ and 0.0135 day^{-1} , respectively with a correlation coefficient (R^2) of 0.977 for PFOS in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 12.b) (Table 6.55).

The growth yield coefficient (Y) of PFOS increased from 0.097 to $0.399 \mu\text{g VSS}/\mu\text{g PFOS}$ and also the maximum specific growth rate ($\mu_{\max}$) of PFOS increased from 0.0012 to 0.0135 day^{-1} in anaerobic and aerobic reactors, respectively (Table 6.55). The half saturation concentration (K_s) decreased from 0.0147 to $0.0086 \mu\text{g L}^{-1}$ in anaerobic and aerobic reactors, respectively (Table 6.55). The lower K_s value indicates the affinity of aerobic microorganisms to co-substrate (PFOS). These results were in accordance with the previous results showing that the aerobic reactor had better PFOS removal (37.0%) than anaerobic reactor (16.4%) at 55 days SRT (Table 6.19). The biodegradation removal efficiencies of PFOS were low in both reactors because PFOS was a hydrophobic micropollutant and resistant to extensive biodegradation due to its physicochemical properties (low water solubility = $0.104 \times 10^{-3} \text{ g L}^{-1}$, high $\log K_{OW} = 4.49$ and low Henry's Law constant = $1.10 \times 10^{-2} \text{ atm m}^3 \text{ mol}^{-1}$).

6.5.1.1.8 Monod Kinetic Model for GFZ. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as $0.085 \mu\text{g VSS}/\mu\text{g GFZ}$ and 0.0001 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for GFZ in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 13.a) (Table 6.56). Y and k_d values were calculated as $0.374 \mu\text{g VSS}/\mu\text{g GFZ}$ and 0.0022 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for GFZ in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 13.b) (Table 6.56).

Table 6.56 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for GFZ in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	μ_{max} (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	GFZ	0.085	0.999	0.0001	0.999	0.0012	0.983	42.55	0.983
Aerobic reactor	GFZ	0.374	0.999	0.0022	0.999	0.0037	0.962	32.35	0.962

The half saturation concentration (K_s) and maximum specific growth rate (μ_{max}) values were calculated as $42.55 \mu\text{g L}^{-1}$ and 0.0012 day^{-1} , respectively with a correlation coefficient (R^2) of 0.983 for GFZ in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 14.a) (Table 6.56). K_s and μ_{max} values were calculated as $32.35 \mu\text{g L}^{-1}$ and 0.0037 day^{-1} , respectively with a correlation coefficient (R^2) of 0.962 for GFZ in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 14.b) (Table 6.56).

The growth yield coefficient (Y) increased from 0.085 to $0.374 \mu\text{g VSS}/\mu\text{g GFZ}$ for GFZ in anaerobic and aerobic reactors, respectively (Table 6.56). The anerobic bacteria have lower growth yields compared to aerobic ones. The maximum specific growth rate (μ_{max}) increased from 0.0012 to 0.0037 day^{-1} in anaerobic and aerobic reactors, respectively due to the high yield ratios of aerobic bacteria than anaerobic bacteria based on the production of biomass (Table 6.56). The half saturation constant (K_s) of GFZ ($42.55 \mu\text{g L}^{-1}$) in anaerobic biological reactor was higher compared to the half saturation constant (K_s) of GFZ ($32.35 \mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.56). The lower K_s value indicates the affinity of aerobic microorganisms to GFZ as co-substrate. Besides, the previous results proved that the aerobic reactor (20.1%) had better removal efficiencies than anaerobic reactor (14.5%) for GFZ removals at 55 days SRT (Table 6.21). GFZ was a hydrophobic micropollutants and partly removed by biodegradation both in anaerobic and aerobic reactors because of its hydrophobic structure (low water solubility = $4.964 \times 10^{-3} \text{ g L}^{-1}$ and high $\log K_{\text{OW}} = 4.77$).

6.5.1.1.9 Monod Kinetic Model for TCS. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.091 $\mu\text{g VSS}/\mu\text{g TCS}$ and 0.0002 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for TCS in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 15.a) (Table 6.57). Y and k_d values were calculated as 0.392 $\mu\text{g VSS}/\mu\text{g TCS}$ and 0.0027 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for TCS in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 15.b) (Table 6.57).

Table 6.57 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for TCS in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	μ_{max} (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	TCS	0.091	0.999	0.0002	0.999	0.0012	0.944	306.44	0.944
Aerobic reactor	TCS	0.392	0.999	0.0027	0.999	0.0040	0.952	240.81	0.952

The half saturation concentration (K_s) and maximum specific growth rate (μ_{max}) values were calculated as 306.44 $\mu\text{g L}^{-1}$ and 0.0012 day^{-1} , respectively with a correlation coefficient (R^2) of 0.944 for TCS in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 16.a) (Table 6.57). K_s and μ_{max} values were calculated as 240.81 $\mu\text{g L}^{-1}$ and 0.0040 day^{-1} , respectively with a correlation coefficient (R^2) of 0.952 for TCS in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 16.b) (Table 6.57).

The anaerobic reactor have lower growth yield coefficient (Y) (0.091 $\mu\text{g VSS}/\mu\text{g TCS}$) and lower maximum specific growth rate (μ_{max}) (0.0012 day^{-1}) than aerobic reactor for Y (0.392 $\mu\text{g VSS}/\mu\text{g TCS}$) and μ_{max} (0.0040 day^{-1}) values (Table 6.57). The half saturation constant (K_s) of TCS (306.44 $\mu\text{g L}^{-1}$) in anaerobic biological reactor was higher than the half saturation constant (K_s) of TCS (240.81 $\mu\text{g L}^{-1}$) in aerobic biological reactor (Table 6.57). Higher Y and μ_{max} values with lower K_s value in aerobic reactor showed that TCS was consumed as co-substrate more effectively in aerobic reactor than anaerobic reactor. The aerobic reactor biodegraded TCS with a removal efficiency of 20.4% while the anaerobic reactor removed by 14.3% at 55 days SRT (Table 6.23). The low biodegradation yields in both reactors could be

attributed to the physicochemical properties of TCS because it was resistant to extensive biodegradation (low water solubility = 4.621×10^{-3} g L⁻¹ and high log K_{OW} = 4.76).

6.5.1.1.10 Monod Kinetic Model for IBU. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.116 µg VSS/µg IBU and 0.00005 day⁻¹, respectively with a correlation coefficient (R²) of 0.999 for IBU in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 17.a) (Table 6.58). Y and k_d values were calculated as 0.404 µg VSS/µg IBU and 0.000004 day⁻¹, respectively with a correlation coefficient (R²) of 0.999 for IBU in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 17.b) (Table 6.58).

Table 6.58 Comparison of the kinetic constants and regression coefficients (R²) relevant to Monod for IBU in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y (µg µg ⁻¹)	R ²	k _d (day ⁻¹)	R ²	µ _{max} (day ⁻¹)	R ²	K _s (µg L ⁻¹)	R ²
Anaerobic reactor	IBU	0.116	0.999	0.00005	0.999	0.0077	0.954	18.25	0.954
Aerobic reactor	IBU	0.404	0.999	0.000004	0.999	0.0804	0.995	4.85	0.995

The half saturation concentration (K_s) and maximum specific growth rate (µ_{max}) values were calculated as 18.25 µg L⁻¹ and 0.0077 day⁻¹, respectively with a correlation coefficient (R²) of 0.954 for IBU in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 18.a) (Table 6.58). K_s and µ_{max} values were calculated as 4.85 µg L⁻¹ and 0.0804 day⁻¹, respectively with a correlation coefficient (R²) of 0.995 for IBU in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 18.b) (Table 6.58).

Increased Y (from 0.116 to 0.404 µg VSS/µg IBU) and µ_{max} (from 0.0077 to 0.0804 day⁻¹) values with lower K_s value (from 18.25 to 4.85 µg L⁻¹) in aerobic reactor (Table 6.58) showed that IBU was consumed as co-substrate more effectively in aerobic reactor (77.9% at 55 days SRT) than anaerobic reactor (45.5% at 55 days SRT) supporting the previous results in Table 6.25. IBU has higher Monod kinetic coefficients in comparison with all studied hydrophobic micropollutants (all

brominated, aromatic, fluoro, GFZ and TCS) in this study. IBU was accepted as a moderate hydrophobic micropollutant having low water solubility ($4.105 \times 10^{-4} \text{ g L}^{-1}$) with moderate high octanol/water partition coefficient ($\log K_{OW} = 3.79$) and these physicochemical properties makes IBU more biodegradable than other studied hydrophobic micropollutants.

6.5.1.1.11 Monod Kinetic Model for CIP. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as $0.213 \text{ } \mu\text{g VSS}/\mu\text{g CIP}$ and 0.0001 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for CIP in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 19.a) (Table 6.59). Y and k_d values were calculated as $0.418 \text{ } \mu\text{g VSS}/\mu\text{g CIP}$ and 0.0008 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for CIP in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 19.b) (Table 6.59).

Table 6.59 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for CIP in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y ($\mu\text{g } \mu\text{g}^{-1}$)	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s ($\mu\text{g L}^{-1}$)	R^2
Anaerobic reactor	CIP	0.213	0.999	0.0001	0.999	0.0084	0.988	217.53	0.988
Aerobic reactor	CIP	0.418	0.999	0.0008	0.999	0.0833	0.929	26.01	0.929

The half saturation concentration (K_s) and maximum specific growth rate ($\mu_{\max}$) values were calculated as $217.53 \text{ } \mu\text{g L}^{-1}$ and 0.0084 day^{-1} , respectively with a correlation coefficient (R^2) of 0.988 for CIP in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 20.a) (Table 6.59). K_s and $\mu_{\max}$ values were calculated as $26.01 \text{ } \mu\text{g L}^{-1}$ and 0.0833 day^{-1} , respectively with a correlation coefficient (R^2) of 0.929 for CIP in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 20.b) (Table 6.59).

Higher Y ($0.418 \text{ } \mu\text{g VSS}/\mu\text{g CIP}$) and $\mu_{\max}$ (0.0833 day^{-1}) values with lower K_s value ($26.01 \text{ } \mu\text{g L}^{-1}$) of aerobic reactor in comparison with anaerobic reactor ($Y = 0.213 \text{ } \mu\text{g VSS}/\mu\text{g CIP}$, $\mu_{\max} = 0.0084 \text{ day}^{-1}$ and $K_s = 217.53 \text{ } \mu\text{g L}^{-1}$) (Table 6.59) supported that aerobic bacteria consumed CIP as co-substrate more effectively in

aerobic reactor (86.3% at 55 days SRT) than anaerobic reactor (50.0% at 55 days SRT) in accordance with the previous results in Table 6.27. CIP could be treated with high removal efficiencies in both reactors and has high Monod kinetic coefficients in this study. CIP has a hydrophilic structure, therefore, it was found as an appropriate micropollutant to biodegradation due to its physicochemical properties (quite high water solubility = 1.148×10^4 g L⁻¹ and quite low octanol/water partition coefficient, log K_{OW} = 0.28).

6.5.1.1.12 Monod Kinetic Model for NDMA. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.258 µg VSS/µg NDMA and 0.0005 day⁻¹, respectively with a correlation coefficient (R²) of 0.999 for NDMA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 21.a) (Table 6.60). Y and k_d values were calculated as 0.427 µg VSS/µg NDMA and 0.0009 day⁻¹, respectively with a correlation coefficient (R²) of 0.999 for NDMA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 21.b) (Table 6.60).

Table 6.60 Comparison of the kinetic constants and regression coefficients (R²) relevant to Monod for NDMA in the anaerobic and aerobic reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Y (µg µg ⁻¹)	R ²	k _d (day ⁻¹)	R ²	µ _{max} (day ⁻¹)	R ²	K _s (µg L ⁻¹)	R ²
Anaerobic reactor	NDMA	0.258	0.999	0.0005	0.999	0.0124	0.988	0.048	0.988
Aerobic reactor	NDMA	0.427	0.999	0.0009	0.999	0.0839	0.945	0.004	0.945

The half saturation concentration (K_s) and maximum specific growth rate (µ_{max}) values were calculated as 0.048 µg L⁻¹ and 0.0124 day⁻¹, respectively with a correlation coefficient (R²) of 0.988 for NDMA in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 22.a) (Table 6.60). K_s and µ_{max} values were calculated as 0.004 ng L⁻¹ and 0.0839 day⁻¹, respectively with a correlation coefficient (R²) of 0.945 for NDMA in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 22.b) (Table 6.60).

The aerobic reactor have higher growth yield coefficient (Y) (0.427 µg VSS/µg NDMA) and maximum specific growth rate (µ_{max}) (0.0839 day⁻¹) with lower half

saturation constant (K_s) ($0.004 \mu\text{g L}^{-1}$) than anaerobic reactor ($Y = 0.258 \mu\text{g VSS}/\mu\text{g NDMA}$, $\mu_{\max} = 0.0124 \text{ day}^{-1}$ and $K_s = 0.048 \mu\text{g L}^{-1}$) (Table 6.60). These kinetic coefficients proved that aerobic reactor (89.8% at 55 days SRT) was more successful to biodegrade NDMA than that of the anaerobic reactor (64.8% at 55 days SRT) supporting the previous results obtained in Table 6.29. NDMA could be treated with high removal efficiencies in both reactors and has the highest Monod kinetic coefficients in comparison with all studied micropollutants in this study. Because NDMA was a quite hydrophilic micropollutant having quite high water solubility ($4.104 \times 10^5 \text{ g L}^{-1}$) with quite low octanol/water partition coefficient ($\log K_{OW} = -0.57$) and these physicochemical properties makes NDMA easily biodegradable in both reactors.

6.5.1.1.13 Monod Kinetic Model for COD. Y and k_d values were calculated as $0.290 \text{ mg VSS}/\text{mg COD}$ and 0.0006 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for COD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 23.a) (Table 6.61). Y and k_d values were calculated as $0.454 \text{ mg VSS}/\text{mg COD}$ and 0.0036 day^{-1} , respectively with a correlation coefficient (R^2) of 0.999 for COD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 23.b) (Table 6.61).

Table 6.61 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for COD in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days of SRTs

Reactor type	Substrate	Y (mg mg^{-1})	R^2	k_d (day^{-1})	R^2	$\mu_{\max}$ (day^{-1})	R^2	K_s (mg L^{-1})	R^2
Anaerobic reactor	COD	0.290	0.999	0.0006	0.999	0.0570	0.959	156.25	0.959
Aerobic reactor	COD	0.454	0.999	0.0036	0.999	0.0856	0.918	17.20	0.918

K_s and $\mu_{\max}$ values were calculated as 156.25 mg L^{-1} and 0.0570 day^{-1} , respectively with a correlation coefficient (R^2) of 0.959 for COD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 24.a) (Table 6.61). K_s and $\mu_{\max}$ values were calculated as 17.20 mg L^{-1} and 0.0856 day^{-1} , respectively with a correlation coefficient (R^2) of 0.918 for COD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 24.b) (Table 6.61).

The growth yield coefficient (Y) increased from 0.290 to 0.454 mg VSS/mg COD in anaerobic and aerobic reactors, respectively showing that the aerobic reactor had higher growth yield ratio for COD (Table 6.61). The half saturation constant (K_s) of COD (156.25 mg L⁻¹) in anaerobic biological reactor was higher than the half saturation constant (K_s) of COD (17.20 mg L⁻¹) in aerobic biological reactor (Table 6.61). The lower K_s value in aerobic reactor shows that the aerobic biodegradation of COD was higher than that of the anaerobic biodegradation. The results supported that the aerobic reactor had better removal performance (90.0%) for removing COD than anaerobic reactor (80.6%) at 55 days SRT (Figure 6.2).

6.5.1.1.14 Monod Kinetic Model for sCOD. The value of growth yield coefficient (Y) and endogenous decay coefficient (k_d) values were calculated as 0.298 mg VSS/mg sCOD and 0.0001 day⁻¹, respectively with a correlation coefficient (R^2) of 0.999 for sCOD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 25.a) (Table 6.62). Y and k_d values were calculated as 0.458 mg VSS/mg sCOD and 0.0046 day⁻¹, respectively with a correlation coefficient (R^2) of 0.999 for sCOD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 25.b) (Table 6.62).

Table 6.62 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Monod for sCOD in the anaerobic and aerobic reactors at 5, 30, 45 and 55 days of SRTs

Reactor type	Substrate	Y (mg mg ⁻¹)	R^2	k_d (day ⁻¹)	R^2	μ_{max} (day ⁻¹)	R^2	K_s (mg L ⁻¹)	R^2
Anaerobic reactor	sCOD	0.298	0.999	0.0001	0.999	0.0758	0.944	119.78	0.944
Aerobic reactor	sCOD	0.458	0.999	0.0046	0.999	0.0860	0.957	8.25	0.957

The half saturation concentration (K_s) and maximum specific growth rate (μ_{max}) values were calculated as 119.78 mg L⁻¹ and 0.0758 day⁻¹, respectively with a correlation coefficient (R^2) of 0.944 for sCOD in the anaerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 26.a) (Table 6.62). K_s and μ_{max} values were calculated as 8.25 mg L⁻¹ and 0.0860 day⁻¹, respectively with a correlation coefficient (R^2) of 0.957 for sCOD in the aerobic biological reactor at 5, 30, 45 and 55 days SRTs (Appendice-1, Figure 26.b) (Table 6.62).

The anaerobic reactor have lower growth yield coefficient (Y) (0.298 mg VSS/mg sCOD) and maximum specific growth rate ($\mu_{\max}$) (0.0758 day^{-1}) than aerobic reactor for Y (0.458 mg VSS/mg sCOD) and $\mu_{\max}$ (0.0860 day^{-1}) values (Table 6.62). The half saturation constant (K_s) of sCOD (119.78 mg L^{-1}) in anaerobic biological reactor was higher than the half saturation constant (K_s) of sCOD (8.25 mg L^{-1}) in aerobic biological reactor (Table 6.62). Higher Y and $\mu_{\max}$ values with lower K_s values in aerobic reactor showed that sCOD was consumed as primary substrate more effectively in aerobic reactor than that in anaerobic reactor. These kinetic results of sCOD was also supported the biodegradation results of sCOD in the content of this study. sCOD was more biodegraded in aerobic reactor (92.0%) than in anaerobic reactor (84.3%) at 55 days SRT (Figure 6.3).

6.5.1.2 Zero-Order Removal Models

The zero-order kinetic constant (k_0 , day^{-1}) can be obtained from the slope of the line plotting the (S_e) versus time (t). Where, S_e is effluent COD, sCOD or micropollutant concentrations ($\mu\text{g L}^{-1}$, ng L^{-1} or mg L^{-1}). Time (t) is solids retention time representing SRT (day) through pollutant removal.

6.5.1.2.1 Zero-Order Removal Model for α -HBCDD. Zero-order α -HBCDD removal constants, k_0 values were calculated as 1×10^{-5} and $3 \times 10^{-5} \text{ day}^{-1}$ with correlation coefficients (R^2) of 0.882 and 0.917 for the anaerobic and aerobic biological reactors, respectively (Figure 6.59.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.63).

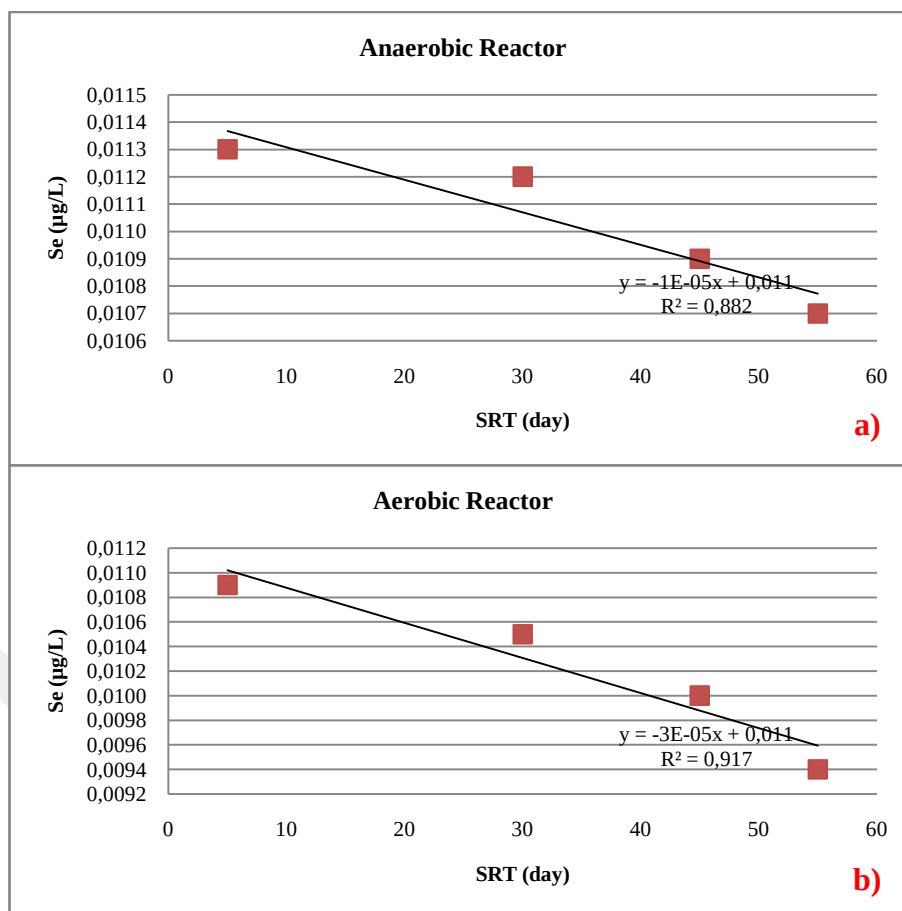


Figure 6.59 Zero-order removal model for α -HBCDD in (a) anaerobic reactor and (b) aerobic reactor

Table 6.63 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Zero-order	
		k_0 (day ⁻¹)	R^2
Anaerobic reactor	α -HBCDD	1×10^{-5}	0.882
Aerobic reactor	α -HBCDD	3×10^{-5}	0.917

6.5.1.2.2 Zero-Order Removal Model for PBEB. Zero-order PBEB removal constants, k_0 values were calculated as 0.003 and 0.007 day⁻¹ with correlation coefficients (R^2) of 0.910 and 0.934 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 1.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.64).

Table 6.64 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	PBEB	0.003	0.910
Aerobic reactor	PBEB	0.007	0.934

6.5.1.2.3 *Zero-Order Removal Model for PBT*. Zero-order PBT removal constants, k_0 values were calculated as 0.002 and 0.004 day⁻¹ with correlation coefficients (R^2) of 0.939 and 0.926 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 2.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.65).

Table 6.65 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	PBT	0.002	0.939
Aerobic reactor	PBT	0.004	0.926

6.5.1.2.4 *Zero-Order Removal Model for TBBPA*. Zero-order TBBPA removal constants, k_0 values were calculated as 1×10^{-5} and 3×10^{-5} day⁻¹ with correlation coefficients (R^2) of 0.948 and 0.901 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 3.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.66).

Table 6.66 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	TBBPA	1×10^{-5}	0.948
Aerobic reactor	TBBPA	3×10^{-5}	0.901

6.5.1.2.5 *Zero-Order Removal Model for AHTN*. Zero-order AHTN removal constants, k_0 values were calculated as 0.233 and 0.451 day⁻¹ with correlation coefficients (R^2) of 0.963 and 0.968 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 4.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.67).

Table 6.67 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Zero-order	
		k_0 (day ⁻¹)	R^2
Anaerobic reactor	AHTN	0.233	0.963
Aerobic reactor	AHTN	0.451	0.968

6.5.1.2.6 *Zero-Order Removal Model for PFOA*. Zero-order PFOA removal constants, k_0 values were calculated as 0.0002 and 0.0004 day⁻¹ with correlation coefficients (R^2) of 0.999 and 0.992 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 5.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.68).

Table 6.68 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Zero-order	
		k_0 (day ⁻¹)	R^2
Anaerobic reactor	PFOA	0.0002	0.999
Aerobic reactor	PFOA	0.0004	0.992

6.5.1.2.7 *Zero-order Removal Model for PFOS*. Zero-order PFOS removal constants, k_0 values were calculated as 0.016 and 0.077 day⁻¹ with correlation coefficients (R^2) of 0.925 and 0.959 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 6.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.69).

Table 6.69 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	PFOS	0.016	0.925
Aerobic reactor	PFOS	0.077	0.959

6.5.1.2.8 *Zero-Order Removal Model for GFZ.* Zero-order GFZ removal constants, k_0 values were calculated as 0.055 and 0.112 day⁻¹ with correlation coefficients (R^2) of 0.983 and 0.975 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 7.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.70).

Table 6.70 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	GFZ	0.055	0.983
Aerobic reactor	GFZ	0.112	0.975

6.5.1.2.9 *Zero-Order Removal Model for TCS.* Zero-order TCS removal constants, k_0 values were calculated as 0.349 and 0.789 day⁻¹ with correlation coefficients (R^2) of 0.945 and 0.969 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 8.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.71).

Table 6.71 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	TCS	0.349	0.945
Aerobic reactor	TCS	0.789	0.969

6.5.1.2.10 *Zero-Order Removal Model for IBU.* Zero-order IBU removal constants, k_0 values were calculated as 0.160 and 0.197 day⁻¹ with correlation coefficients (R^2) of 0.984 and 0.999 for the anaerobic and aerobic biological reactors,

respectively (Appendice-2, Figure 9.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.72).

Table 6.72 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	IBU	0.160	0.984
Aerobic reactor	IBU	0.197	0.999

6.5.1.2.11 Zero-Order Removal Model for CIP. Zero-order CIP removal constants, k_0 values were calculated as 2.094 and 2.260 day⁻¹ with correlation coefficients (R^2) of 0.990 and 0.993 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 10.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.73).

Table 6.73 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	CIP	2.094	0.990
Aerobic reactor	CIP	2.260	0.993

6.5.1.2.12 Zero-Order Removal Model for NDMA. Zero-order NDMA removal constants, k_0 values were calculated as 0.661 and 0.679 day⁻¹ with correlation coefficients (R^2) of 0.974 and 0.979 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 11.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.74).

Table 6.74 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero order			
Reactor type	Co-substrate	k_0 (day ⁻¹)	R^2
Anaerobic reactor	NDMA	0.661	0.974
Aerobic reactor	NDMA	0.679	0.979

6.5.1.2.13 *Zero-Order Removal Model for COD.* Zero-order COD removal constants, k_0 values were calculated as 6.863 and 4.656 day^{-1} with correlation coefficients (R^2) of 0.983 and 0.916 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 12.a and b) (Table 6.75).

Table 6.75 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Substrate	k_0 (day^{-1})	R^2
Anaerobic reactor	COD	6.863	0.983
Aerobic reactor	COD	4.656	0.916

6.5.1.2.14 *Zero-Order Removal Model for sCOD.* Zero-order sCOD removal constants, k_0 values were calculated as 5.746 and 3.354 day^{-1} with correlation coefficients (R^2) of 0.988 and 0.924 for the anaerobic and aerobic biological reactors, respectively (Appendice-2, Figure 13.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.76).

Table 6.76 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Zero-order			
Reactor type	Substrate	k_0 (day^{-1})	R^2
Anaerobic reactor	sCOD	5.746	0.988
Aerobic reactor	sCOD	3.354	0.924

6.5.1.3 Half-Order Removal Models

The half-order kinetic constant ($k_{1/2}$, day^{-1}) can be obtained from the slope of the line plotting the $(1/\sqrt{S_e})$ versus time (t). Where, S_e is effluent COD, sCOD or micropollutant concentrations ($\mu\text{g L}^{-1}$, ng L^{-1} or mg L^{-1}). Time (t) is solids retention time representing SRT (day) through pollutant removal.

6.5.1.3.1 *Half-Order Removal Model for α -HBCDD*. Half-order α -HBCDD removal constants, $k_{1/2}$ values were calculated as 0.005 and 0.013 day⁻¹ with correlation coefficients (R^2) of 0.877 and 0.899 for the anaerobic and aerobic biological reactors, respectively (Figure 6.60.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.77).

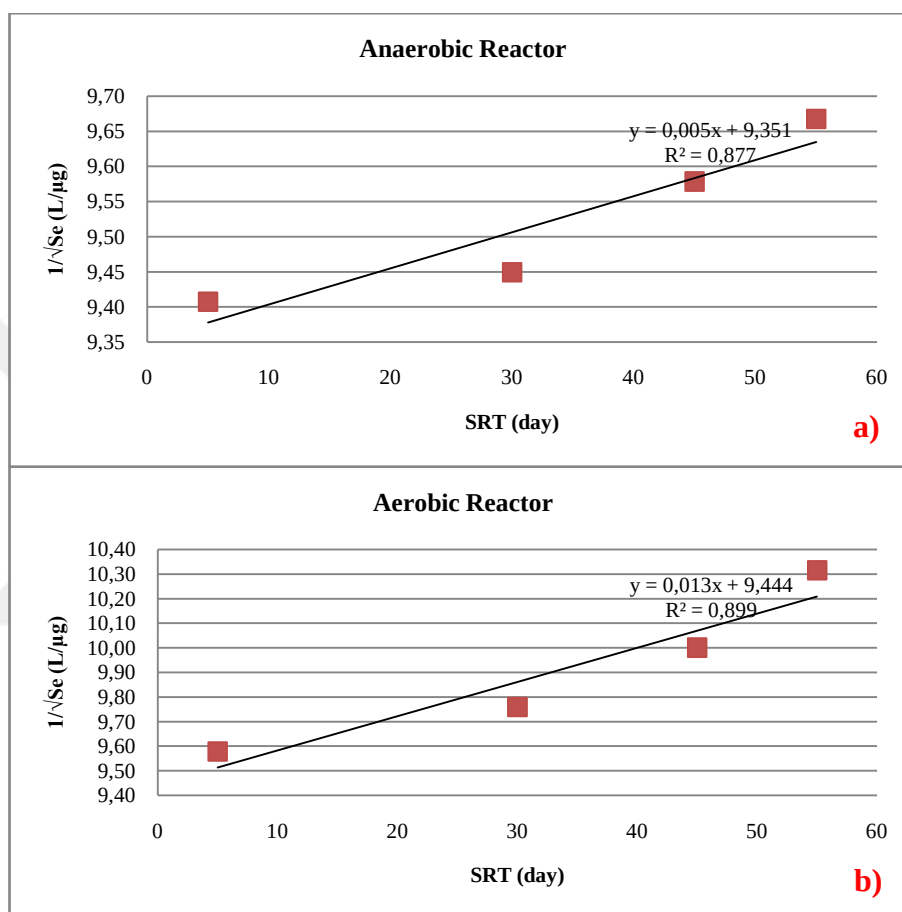


Figure 6.60 Half-order removal model for α -HBCDD in (a) anaerobic reactor and (b) aerobic reactor

Table 6.77 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	α -HBCDD	0.005	0.877
Aerobic reactor	α -HBCDD	0.013	0.899

6.5.1.3.2 *Half-Order Removal Model for PBEB*. Half-order PBEB removal constants, $k_{1/2}$ values were calculated as 0.0003 and 0.0008 day⁻¹ with correlation coefficients (R^2) of 0.905 and 0.920 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 1.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.78).

Table 6.78 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	PBEB	0.0003	0.905
Aerobic reactor	PBEB	0.0008	0.920

6.5.1.3.3 *Half-Order Removal Model for PBT*. Half-order PBT removal constants, $k_{1/2}$ values were calculated as 0.0003 and 0.0009 day⁻¹ with correlation coefficients (R^2) of 0.934 and 0.912 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 2.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.79).

Table 6.79 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	PBT	0.0003	0.934
Aerobic reactor	PBT	0.0009	0.912

6.5.1.3.4 *Half-Order Removal Model for TBBPA*. Half-order TBBPA removal constants, $k_{1/2}$ values were calculated as 0.003 and 0.010 day⁻¹ with correlation coefficients (R^2) of 0.944 and 0.887 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 3.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.80).

Table 6.80 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	TBBPA	0.003	0.944
Aerobic reactor	TBBPA	0.010	0.887

6.5.1.3.5 *Half-Order Removal Model for AHTN*. Half-order AHTN removal constants, $k_{1/2}$ values were calculated as 0.00004 and 0.00010 day⁻¹ with correlation coefficients (R^2) of 0.962 and 0.957 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 4.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.81).

Table 6.81 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	AHTN	0.00004	0.962
Aerobic reactor	AHTN	0.00010	0.957

6.5.1.3.6 *Half-Order Removal Model for PFOA*. Half-order PFOA removal constants, $k_{1/2}$ values were calculated as 0.001 and 0.004 day⁻¹ with correlation coefficients (R^2) of 0.999 and 0.985 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 5.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.82).

Table 6.82 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	PFOA	0.001	0.999
Aerobic reactor	PFOA	0.004	0.985

6.5.1.3.7 Half-Order Removal Model for PFOS. Half-order PFOS removal constants, $k_{1/2}$ values were calculated as 0.0001 and 0.0010 day⁻¹ with correlation coefficients (R^2) of 0.930 and 0.929 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 6.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.83).

Table 6.83 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	PFOS	0.0001	0.930
Aerobic reactor	PFOS	0.0010	0.929

6.5.1.3.8 Half-Order Removal Model for GFZ. Half-order GFZ removal constants, $k_{1/2}$ values were calculated as 0.0001 and 0.0002 day⁻¹ with correlation coefficients (R^2) of 0.983 and 0.970 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 7.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.84).

Table 6.84 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	GFZ	0.0001	0.983
Aerobic reactor	GFZ	0.0002	0.970

6.5.1.3.9 Half-Order Removal Model for TCS. Half-order TCS removal constants, $k_{1/2}$ values were calculated as 0.00003 and 0.00009 day⁻¹ with correlation coefficients (R^2) of 0.944 and 0.962 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 8.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.85).

Table 6.85 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	TCS	0.00003	0.944
Aerobic reactor	TCS	0.00009	0.962

6.5.1.3.10 *Half-Order Removal Model for IBU*. Half-order IBU removal constants, $k_{1/2}$ values were calculated as 0.0006 and 0.0035 day⁻¹ with correlation coefficients (R^2) of 0.963 and 0.938 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 9.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.86).

Table 6.86 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	IBU	0.0006	0.963
Aerobic reactor	IBU	0.0035	0.938

6.5.1.3.11 *Half-Order Removal Model for CIP*. Half-order CIP removal constants, $k_{1/2}$ values were calculated as 0.0002 and 0.0016 day⁻¹ with correlation coefficients (R^2) of 0.991 and 0.908 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 10.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.87).

Table 6.87 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Co-substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	CIP	0.0002	0.991
Aerobic reactor	CIP	0.0016	0.908

6.5.1.3.12 *Half-Order Removal Model for NDMA*. Half-order NDMA removal constants, $k_{1/2}$ values were calculated as 0.0005 and 0.0046 day⁻¹ with correlation coefficients (R^2) of 0.988 and 0.859 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 11.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.88).

Table 6.88 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	NDMA	0.0005	0.988
Aerobic reactor	NDMA	0.0046	0.859

6.5.1.3.13 *Half-Order Removal Model for COD*. Half-order COD removal constants, $k_{1/2}$ values were calculated as 0.0006 and 0.0031 day⁻¹ with correlation coefficients (R^2) of 0.987 and 0.886 for the anaerobic and aerobic reactors, respectively (Appendice-3, Figure 12.a and b) (Table 6.89).

Table 6.89 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Substrate	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	COD	0.0006	0.987
Aerobic reactor	COD	0.0031	0.886

6.5.1.3.14 *Half-Order Removal Model for sCOD*. Half-order sCOD removal constants, $k_{1/2}$ values were calculated as 0.0007 and 0.0041 day⁻¹ with correlation coefficients (R^2) of 0.978 and 0.848 for the anaerobic and aerobic biological reactors, respectively (Appendice-3, Figure 13.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.90).

Table 6.90 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Half-order			
Reactor type	Substrate	$k_{1/2}$ (day ⁻¹)	R^2
Anaerobic reactor	sCOD	0.0007	0.978
Aerobic reactor	sCOD	0.0041	0.848

6.5.1.4 First-Order Removal Models

The first-order kinetic constant (k_1 , day⁻¹) can be obtained from the slope of the line plotting the $\ln(S_e)$ versus time (t). Where, S_e is effluent COD, sCOD or micropollutant concentrations ($\mu\text{g L}^{-1}$, ng L^{-1} or mg L^{-1}). Time (t) is solids retention time representing SRT (day) through pollutant removal.

6.5.1.4.1 First-Order Removal Model for α -HBCDD. First-order α -HBCDD removal constants, k_1 values were calculated as 0.001 and 0.002 day⁻¹ with correlation coefficients (R^2) of 0.879 and 0.905 for the anaerobic and aerobic biological reactors, respectively (Figure 6.61.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.91).

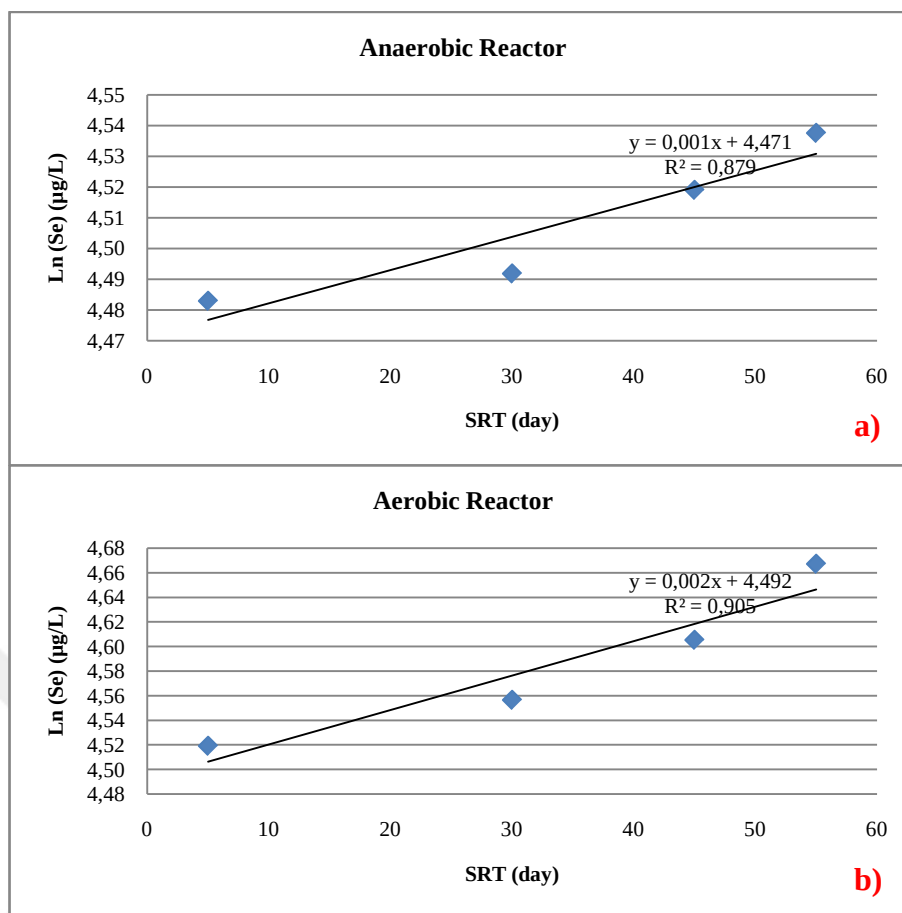


Figure 6.61 First-order removal model for α -HBCDD in (a) anaerobic reactor and (b) aerobic reactor

Table 6.91 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	α -HBCDD	0.001	0.879
Aerobic reactor	α -HBCDD	0.002	0.905

6.5.1.4.2 First-Order Removal Model for PBEB. First-order PBEB removal constants, k_1 values were calculated as 0.001 and 0.002 day⁻¹ with correlation coefficients (R^2) of 0.907 and 0.925 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 1.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.92).

Table 6.92 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	PBEB	0.001	0.907
Aerobic reactor	PBEB	0.002	0.925

6.5.1.4.3 *First-Order Removal Model for PBT*. First-order PBT removal constants, k_1 values were calculated as 0.0009 and 0.0024 day⁻¹ with correlation coefficients (R^2) of 0.936 and 0.917 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 2.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.93).

Table 6.93 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	PBT	0.0009	0.936
Aerobic reactor	PBT	0.0024	0.917

6.5.1.4.4 *First-Order Removal Model for TBBPA*. First-order TBBPA removal constants, k_1 values were calculated as 0.0009 and 0.0024 day⁻¹ with correlation coefficients (R^2) of 0.946 and 0.892 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 3.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.94).

Table 6.94 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	TBBPA	0.0009	0.946
Aerobic reactor	TBBPA	0.0024	0.892

6.5.1.4.5 First-Order Removal Model for AHTN. First-order AHTN removal constants, k_1 values were calculated as 0.001 and 0.002 day⁻¹ with correlation coefficients (R^2) of 0.962 and 0.961 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 4.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.95).

Table 6.95 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	AHTN	0.001	0.962
Aerobic reactor	AHTN	0.002	0.961

6.5.1.4.6 First-Order Removal Model for PFOA. First-order PFOA removal constants, k_1 values were calculated as 0.001 and 0.003 day⁻¹ with correlation coefficients (R^2) of 0.999 and 0.988 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 5.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.96).

Table 6.96 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	PFOA	0.001	0.999
Aerobic reactor	PFOA	0.003	0.988

6.5.1.4.7 First-Order Removal Model for PFOS. First-order PFOS removal constants, k_1 values were calculated as 0.0011 and 0.0067 day⁻¹ with correlation coefficients (R^2) of 0.928 and 0.940 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 6.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.97).

Table 6.97 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	PFOS	0.0011	0.928
Aerobic reactor	PFOS	0.0067	0.940

6.5.1.4.8 *First-Order Removal Model for GFZ*. First-order GFZ removal constants, k_1 values were calculated as 0.001 and 0.002 day⁻¹ with correlation coefficients (R^2) of 0.983 and 0.971 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 7.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.98).

Table 6.98 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	GFZ	0.001	0.983
Aerobic reactor	GFZ	0.002	0.971

6.5.1.4.9 *First-Order Removal Model for TCS*. First-order TCS removal constants, k_1 values were calculated as 0.001 and 0.002 day⁻¹ with correlation coefficients (R^2) of 0.944 and 0.964 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 8.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.99).

Table 6.99 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

First-order			
Reactor type	Co-substrate	k_1 (day ⁻¹)	R^2
Anaerobic reactor	TCS	0.001	0.944
Aerobic reactor	TCS	0.002	0.964

6.5.1.4.10 *First-Order Removal Model for IBU*. First-order IBU removal constants, k_1 values were calculated as 0.005 and 0.020 day⁻¹ with correlation coefficients (R^2) of 0.971 and 0.971 for the anaerobic and aerobic biological reactors,

respectively (Appendice-4, Figure 9.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.100).

Table 6.100 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	IBU	0.005	0.971
Aerobic reactor	IBU	0.020	0.971

6.5.1.4.11 First-Order Removal Model for CIP. First-order CIP removal constants, k_1 values were calculated as 0.006 and 0.027 day⁻¹ with correlation coefficients (R^2) of 0.992 and 0.962 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 10.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.101).

Table 6.101 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	CIP	0.006	0.992
Aerobic reactor	CIP	0.027	0.962

6.5.1.4.12 First-Order Removal Model for NDMA. First-order NDMA removal constants, k_1 values were calculated as 0.008 and 0.035 day⁻¹ with correlation coefficients (R^2) of 0.985 and 0.945 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 11.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.102).

Table 6.102 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	NDMA	0.008	0.985
Aerobic reactor	NDMA	0.035	0.945

6.5.1.4.13 *First-Order Removal Model for COD*. First-order COD removal constants, k_1 values were calculated as 0.020 and 0.049 day⁻¹ with correlation coefficients (R^2) of 0.997 and 0.972 for the anaerobic and aerobic reactors, respectively (Appendice-4, Figure 12.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.103).

Table 6.103 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	COD	0.020	0.997
Aerobic reactor	COD	0.049	0.972

6.5.1.4.14 *First-Order Removal Model for sCOD*. First-order sCOD removal constants, k_1 values were calculated as 0.022 and 0.052 day⁻¹ with correlation coefficients (R^2) of 0.995 and 0.963 for the anaerobic and aerobic biological reactors, respectively (Appendice-4, Figure 13.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.104).

Table 6.104 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Substrate	First-order	
		k_1 (day ⁻¹)	R^2
Anaerobic reactor	sCOD	0.022	0.995
Aerobic reactor	sCOD	0.052	0.963

6.5.1.5 Second-Order Removal Models

The second-order kinetic constant (k_2 , L mg⁻¹ day⁻¹ or L µg⁻¹ day⁻¹) can be obtained from the slope of the line plotting the 1/(S_e) versus time (t). Where, S_e is effluent COD, sCOD or micropollutant concentrations (µg L⁻¹ or mg L⁻¹). Time (t) is solids retention time representing SRT (day) through pollutant removal.

6.5.1.5.1 Second-Order Removal Model for α -HBCDD. Second-order α -HBCDD removal constants, k_2 values were calculated as 0.098 and 0.275 L $\mu\text{g}^{-1} \text{day}^{-1}$ with correlation coefficients (R^2) of 0.876 and 0.893 for the anaerobic and aerobic biological reactors, respectively (Figure 6.62.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.105).

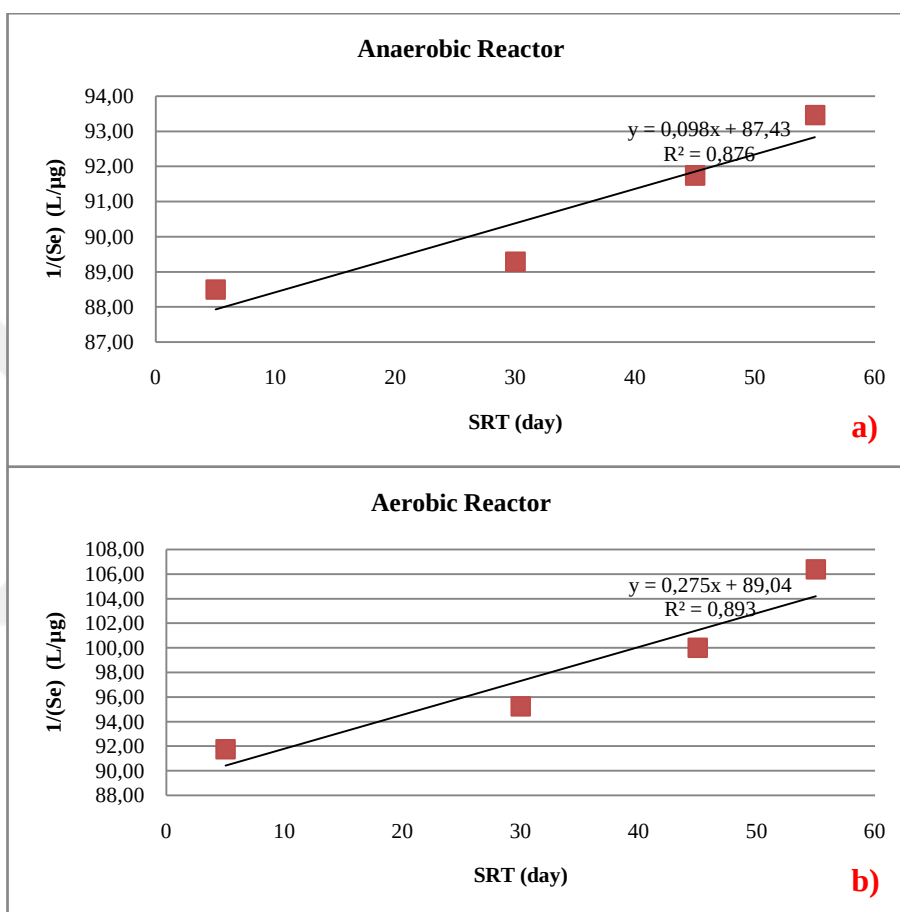


Figure 6.62 Second-order removal model for α -HBCDD in (a) anaerobic reactor and (b) aerobic reactor

Table 6.105 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L $\mu\text{g}^{-1} \text{day}^{-1}$)	R^2
Anaerobic reactor	α -HBCDD	0.098	0.876
Aerobic reactor	α -HBCDD	0.275	0.893

6.5.1.5.2 Second-Order Removal Model for PBEB. Second-order PBEB removal constants, k_2 values were calculated as 3×10^{-7} and 1×10^{-6} L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.903 and 0.915 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 1.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.106).

Table 6.106 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L μg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	PBEB	3×10^{-7}	0.903
Aerobic reactor	PBEB	1×10^{-6}	0.915

6.5.1.5.3 Second-Order Removal Model for PBT. Second-order PBT removal constants, k_2 values were calculated as 4×10^{-7} and 1.20×10^{-6} L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.933 and 0.907 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 2.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.107).

Table 6.107 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L μg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	PBT	4×10^{-7}	0.933
Aerobic reactor	PBT	1.20×10^{-6}	0.907

6.5.1.5.4 Second-Order Removal Model for TBBPA. Second-order TBBPA removal constants, k_2 values were calculated as 0.054 and 0.166 L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.943 and 0.882 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 3.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.108).

Table 6.108 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	TBBPA	0.054	0.943
Aerobic reactor	TBBPA	0.166	0.882

6.5.1.5.5 *Second-Order Removal Model for AHTN*. Second-order AHTN removal constants, k_2 values were calculated as 1×10^{-8} and $2 \times 10^{-8} L \mu g^{-1} day^{-1}$ with correlation coefficients (R^2) of 0.961 and 0.952 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 4.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.109).

Table 6.109 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	AHTN	1×10^{-8}	0.961
Aerobic reactor	AHTN	2×10^{-8}	0.952

6.5.1.5.6 *Second-Order Removal Model for PFOA*. Second-order PFOA removal constants, k_2 values were calculated as 0.007 and 0.021 $L \mu g^{-1} day^{-1}$ with correlation coefficients (R^2) of 0.999 and 0.982 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 5.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.110).

Table 6.110 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	PFOA	0.007	0.999
Aerobic reactor	PFOA	0.021	0.982

6.5.1.5.7 Second-Order Removal Model for PFOS. Second-order PFOS removal constants, k_2 values were calculated as 7×10^{-8} and 6×10^{-7} L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.930 and 0.917 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 6.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.111).

Table 6.111 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L μg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	PFOS	7×10^{-8}	0.930
Aerobic reactor	PFOS	6×10^{-7}	0.917

6.5.1.5.8 Second-Order Removal Model for GFZ. Second-order GFZ removal constants, k_2 values were calculated as 0.00002 and 0.00007 L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.983 and 0.967 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 7.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.112).

Table 6.112 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L μg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	GFZ	0.00002	0.983
Aerobic reactor	GFZ	0.00007	0.967

6.5.1.5.9 Second-Order Removal Model for TCS. Second-order TCS removal constants, k_2 values were calculated as 3×10^{-6} and 1×10^{-5} L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.943 and 0.958 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 8.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.113).

Table 6.113 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	TCS	3×10^{-6}	0.943
Aerobic reactor	TCS	1×10^{-5}	0.958

6.5.1.5.10 *Second-Order Removal Model for IBU*. Second-order IBU removal constants, k_2 values were calculated as 0.0002 and $0.0024 L \mu g^{-1} day^{-1}$ with correlation coefficients (R^2) of 0.954 and 0.895 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 9.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.114).

Table 6.114 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	IBU	0.0002	0.954
Aerobic reactor	IBU	0.0024	0.895

6.5.1.5.11 *Second-Order Removal Model for CIP*. Second-order CIP removal constants, k_2 values were calculated as 2×10^{-5} and $0.0004 L \mu g^{-1} day^{-1}$ with correlation coefficients (R^2) of 0.988 and 0.837 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 10.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.115).

Table 6.115 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Co-substrate	k_2 ($L \mu g^{-1} day^{-1}$)	R^2
Anaerobic reactor	CIP	2×10^{-5}	0.988
Aerobic reactor	CIP	0.0004	0.837

6.5.1.5.12 *Second-Order Removal Model for NDMA*. Second-order NDMA removal constants, k_2 values were calculated as 1×10^{-7} and 2.5×10^{-6} L μg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.988 and 0.753 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 11.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.116).

Table 6.116 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Co-substrate	Second-order	
		k_2 (L μg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	NDMA	1×10^{-7}	0.988
Aerobic reactor	NDMA	2.50×10^{-6}	0.753

6.5.1.5.13 *Second-Order Removal Model for COD*. Second-order COD removal constants, k_2 values were calculated as 7×10^{-5} and 0.0009 L mg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.962 and 0.752 for the anaerobic and aerobic reactors biological, respectively (Appendice-5, Figure 12.a and b) (Table 6.117).

Table 6.117 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Substrate	Second-order	
		k_2 (L mg^{-1} day $^{-1}$)	R^2
Anaerobic reactor	COD	7×10^{-5}	0.962
Aerobic reactor	COD	0.0009	0.752

6.5.1.5.14 *Second-Order Removal Model for sCOD*. Second-order sCOD removal constants, k_2 values were calculated as 1×10^{-4} and 0.0015 L mg^{-1} day $^{-1}$ with correlation coefficients (R^2) of 0.945 and 0.701 for the anaerobic and aerobic biological reactors, respectively (Appendice-5, Figure 13.a and b) at 5, 30, 45 and 55 days of SRTs (Table 6.118).

Table 6.118 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Second-order			
Reactor type	Substrate	k_2 (L mg ⁻¹ day ⁻¹)	R^2
Anaerobic reactor	sCOD	1×10^{-4}	0.945
Aerobic reactor	sCOD	0.0015	0.701

6.5.1.6 Evaluation of Kinetic Constants (Zero-Order, Half-Order, First-Order, Second-Order and Monod) in the Anaerobic/Aerobic Sequential Biological Reactor System

Increased growth yield coefficients (Y) with maximum specific growth rates ($\mu_{\max}$) and decreased half saturation concentrations (K_s) in the aerobic reactor showed that the Monod substrate removal kinetic model was more appropriate for all studied micropollutants (α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, PFOS, GFZ, TCS, IBU, CIP and NDMA) and macropollutants (COD and sCOD) (Table 6.119). Monod could be used for predicting the biodegradation performance of the laboratory scale anaerobic UASB/aerobic CSTR sequential biological reactor system treating these micropollutants as co-substrate and macropollutants as primary substrates. Increased growth yield coefficients (Y) with maximum specific growth rates ($\mu_{\max}$) can be explained with the high yield ratios of aerobic bacteria than anaerobic bacteria based on the production of biomass. The anaerobic bacteria have lower growth yields compared to aerobic ones (Table 6.119). On the other hand, the unoxigenated conditions in the anaerobic reactor and the electron donors like CO_2 and H_2 is completely different from the oxygenated conditions which the electron donors were O_2 in the aerobic reactor. These operational parameters affect the solubility, the adsorption and the octanol/water partition coefficients of the micropollutants based on the removals in the reactors. The lower K_s value indicates the affinity of aerobic microorganisms to the primary substrates (COD and sCOD). The aerobic microorganisms consumed co-substrates (micropollutants) with the primary substrates in co-metabolic pathways. Therefore, it can be said that the aerobic reactor was more successful to remove all studied micropollutants (α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, PFOS, GFZ, TCS, IBU, CIP and

NDMA) and macropollutants (COD and sCOD) than the anaerobic reactor (Table 6.119). Isik & Sponza (2005) determined the Monod kinetics of Y , k_d , $\mu_{\max}$ and K_S values as 0.125 g VSS/g COD, 0.0065 d⁻¹, 0.105 d⁻¹ and 4 g COD L⁻¹, respectively in an UASB reactor treating textile wastewater for 4214 mg L⁻¹ influent COD concentration at 100 h HRT and 736 day SRT (Isik & Sponza, 2005). Bhunia & Ghangrekar (2008) found 0.083 g VSS/g COD, 0.006 d⁻¹, 0.058 d⁻¹ and 0.226 g COD L⁻¹ for Y , k_d , $\mu_{\max}$ and K_S values, respectively in an UASB reactor treating synthetic wastewater including sucrose for an influent COD concentration of 778.25 mg L⁻¹ at 8 h HRT and at 150.86 d SRT (Bhunia & Ghangrekar, 2008). In a kinetic study from the literature; Y , k_d , $\mu_{\max}$ and K_S values were calculated 0.608 g VSS/g COD, 0.164 d⁻¹, 0.008 d⁻¹ and 0.189 g COD L⁻¹, respectively in an UASB reactor treating weak industrial wastewater having an initial COD concentration of 54.33 mg L⁻¹ at a HRT of 0.9 day and at an OLR of 0.85 kg COD m⁻³ d⁻¹ (Abtahi, Amin, Nateghi, Vosoogh & Dooranmahalleh, 2013). Another study from the literature evaluated the Y and k_d values as 0.63 g VSS/g COD and 0.0387 d⁻¹, respectively, while $\mu_{\max}$ and K_S values were obtained as 0.366 d⁻¹ and 13.8 mg sCOD L⁻¹, respectively in a pilot-scale activated sludge process treating municipal wastewater for 575 mg L⁻¹ influent COD concentration at 4.55 h HRT and 5 d SRT (Mardani, Mirbagheri, Amin, & Ghasemian, 2011). The obtained aerobic ($Y = 0.290$ mg VSS/mg COD, $k_d = 0.0006$ d⁻¹ and $\mu_{\max} = 0.0570$ d⁻¹) and anaerobic ($Y = 0.454$ mg VSS/mg COD, $k_d = 0.0036$ d⁻¹ and $\mu_{\max} = 0.0856$ d⁻¹) kinetic coefficients for COD in this study were in line with the results taken from the literature (Table 6.119). The slight differences in kinetic coefficients compared to other studies is due to the reactor characteristics and the type of substrate or influent wastewater as mentioned by Isik & Sponza (2005). In this study, aerobic reactor had higher $\mu_{\max}$ values than the anaerobic reactor (Table 6.119) and it was stated that the aerobic culture used for the treatment of raw hospital wastewater adapted more rapidly to wastewater and more quickly consumed the carbon sources than anaerobic culture.

Table 6.119 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order, half-order, first-order, second-order and Monod for COD, sCOD, brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Reactor type	Substrate or co-substrate	Log K_{ow} (unitless)	Y^*	R^2	k_d (day ⁻¹)	Monod				
						R^2	μ_{max} (day ⁻¹)	R^2	K_s^{**}	R^2
Anaerobic reactor	α -HBCDD	7.74	0.051	0.990	0.0010	0.990	0.0010	0.967	0.0088	0.967
	PBEB	7.48	0.053	0.999	0.0005	0.999	0.0010	0.906	0.0029	0.906
	PBT	6.99	0.055	0.999	0.0002	0.999	0.0010	0.921	0.0021	0.921
	TBBPA	5.90	0.056	0.999	0.0001	0.999	0.0010	0.943	0.0145	0.943
	AHTN	5.70	0.070	0.999	0.0004	0.999	0.0012	0.961	0.150	0.961
	PFOA	4.81	0.081	0.999	0.0002	0.999	0.0012	0.999	0.1416	0.999
	PFOS	4.49	0.097	0.999	0.0003	0.999	0.0012	0.933	0.0147	0.933
	GFZ	4.77	0.085	0.999	0.0001	0.999	0.0012	0.983	42.55	0.983
	TCS	4.76	0.091	0.999	0.0002	0.999	0.0012	0.944	306.44	0.944
	IBU	3.79	0.116	0.999	0.00005	0.999	0.0077	0.954	18.25	0.954
	CIP	0.28	0.213	0.999	0.0001	0.999	0.0084	0.988	217.53	0.988
	NDMA	-0.57	0.258	0.999	0.0005	0.999	0.0124	0.988	0.048	0.988
	COD	--	0.290	0.999	0.0006	0.999	0.0570	0.959	156.25	0.959
	sCOD	--	0.298	0.999	0.0001	0.999	0.0758	0.944	119.78	0.944

*: (mg VSS/mg) for COD and sCOD and the others in ($\mu\text{g VSS}/\mu\text{g}$)

** : (mg L⁻¹) for COD and sCOD and the others in ($\mu\text{g L}^{-1}$)

Table 6.119 continues

Reactor type	Substrate or co-substrate	Log K _{ow} (unitless)	Y*	R ²	k _d (day ⁻¹)	Monod				
						R ²	μ _{max} (day ⁻¹)	R ²	K _s **	R ²
Aerobic reactor	α-HBCDD	7.74	0.326	0.999	0.0108	0.999	0.0030	0.918	0.0057	0.918
	PBEB	7.48	0.363	0.999	0.0098	0.999	0.0031	0.949	0.0018	0.949
	PBT	6.99	0.366	0.999	0.0055	0.999	0.0031	0.961	0.0017	0.961
	TBBPA	5.90	0.366	0.999	0.0040	0.999	0.0032	0.948	0.0112	0.948
	AHTN	5.70	0.368	0.999	0.0029	0.999	0.0035	0.939	0.147	0.939
	PFOA	4.81	0.371	0.999	0.0030	0.999	0.0036	0.972	0.1079	0.972
	PFOS	4.49	0.399	0.999	0.0056	0.999	0.0135	0.977	0.0086	0.977
	GFZ	4.77	0.374	0.999	0.0022	0.999	0.0037	0.962	32.35	0.962
	TCS	4.76	0.392	0.999	0.0027	0.999	0.0040	0.952	240.81	0.952
	IBU	3.79	0.404	0.999	0.000004	0.999	0.0804	0.995	4.85	0.995
	CIP	0.28	0.418	0.999	0.0008	0.999	0.0833	0.929	26.01	0.929
	NDMA	-0.57	0.427	0.999	0.0009	0.999	0.0839	0.945	0.004	0.945
	COD	--	0.454	0.999	0.0036	0.999	0.0856	0.918	17.20	0.918
	sCOD	--	0.458	0.999	0.0046	0.999	0.0860	0.957	8.25	0.957

*: (mg VSS/mg) for COD and sCOD and the others in (μg VSS/μg)

**.: (mg L⁻¹) for COD and sCOD and the others in (μg L⁻¹)

Table 6.119 continues

Reactor type	Substrate or co-substrate	Zero-order		Half-order		First-order		Second-order	
		k_0 (day ⁻¹)	R ²	$k_{1/2}$ (day ⁻¹)	R ²	k_1 (day ⁻¹)	R ²	k_2^{***}	R ²
Anaerobic reactor	α -HBCDD	1×10^{-5}	0.882	0.005	0.877	0.001	0.879	0.098	0.876
	PBEB	0.003	0.910	0.0003	0.905	0.001	0.907	3×10^{-7}	0.903
	PBT	0.002	0.939	0.0003	0.934	0.0009	0.936	4×10^{-7}	0.933
	TBBPA	1×10^{-5}	0.948	0.003	0.944	0.0009	0.946	0.054	0.943
	AHTN	0.233	0.963	0.00004	0.962	0.001	0.962	1×10^{-8}	0.961
	PFOA	0.0002	0.999	0.001	0.999	0.001	0.999	0.007	0.999
	PFOS	0.016	0.925	0.0001	0.930	0.0011	0.928	7×10^{-8}	0.930
	GFZ	0.055	0.983	0.0001	0.983	0.001	0.983	0.00002	0.983
	TCS	0.349	0.945	0.00003	0.944	0.001	0.944	3×10^{-6}	0.943
	IBU	0.160	0.984	0.0006	0.963	0.005	0.971	0.0002	0.954
	CIP	2.094	0.990	0.0002	0.991	0.006	0.992	2×10^{-5}	0.988
	NDMA	0.661	0.974	0.0005	0.988	0.008	0.985	1×10^{-7}	0.988
	COD	6.863	0.983	0.0006	0.987	0.020	0.997	7×10^{-5}	0.962
	sCOD	5.746	0.988	0.0007	0.978	0.022	0.995	1×10^{-4}	0.945

***: (L mg⁻¹ day⁻¹) for COD and sCOD and the others in (L μ g⁻¹ day⁻¹)

Table 6.119 continues

Reactor type	Substrate or co-substrate	Zero-order		Half-order		First-order		Second-order	
		k_0 (day ⁻¹)	R ²	$k_{1/2}$ (day ⁻¹)	R ²	k_1 (day ⁻¹)	R ²	k_2^{***}	R ²
Aerobic reactor	α -HBCDD	3×10^{-5}	0.917	0.013	0.899	0.002	0.905	0.275	0.893
	PBEB	0.007	0.934	0.0008	0.920	0.002	0.925	1×10^{-6}	0.915
	PBT	0.004	0.926	0.0009	0.912	0.0024	0.917	1.20×10^{-6}	0.907
	TBBPA	3×10^{-5}	0.901	0.010	0.887	0.0024	0.892	0.166	0.882
	AHTN	0.451	0.968	0.00010	0.957	0.002	0.961	2×10^{-8}	0.952
	PFOA	0.0004	0.992	0.004	0.985	0.003	0.988	0.021	0.982
	PFOS	0.077	0.959	0.0010	0.929	0.0067	0.940	6×10^{-7}	0.917
	GFZ	0.112	0.975	0.0002	0.970	0.002	0.971	0.00007	0.967
	TCS	0.789	0.969	0.00009	0.962	0.002	0.964	1×10^{-5}	0.958
	IBU	0.197	0.999	0.0035	0.938	0.020	0.971	0.0024	0.895
	CIP	2.260	0.993	0.0016	0.908	0.027	0.962	0.0004	0.837
	NDMA	0.679	0.979	0.0046	0.859	0.035	0.945	2.50×10^{-6}	0.753
	COD	4.656	0.916	0.0031	0.886	0.049	0.972	0.0009	0.752
	sCOD	3.354	0.924	0.0041	0.848	0.052	0.963	0.0015	0.701

***: (L mg⁻¹ day⁻¹) for COD and sCOD and the others in (L μ g⁻¹ day⁻¹)

6.5.2 Determination of Adsorption Isotherms in the Anaerobic/Aerobic Sequential Biological Reactor System

In this study, Langmuir and Freundlich isotherms were used to calculate the relationship between brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOA and PFOS), nitroso (NDMA), phenolic (TCS, GFZ, CIP and IBU), aromatic (AHTN) micropollutants and macropollutants (COD and sCOD) as adsorbate and anaerobic – aerobic biological sludges as adsorbent during 5, 30, 45 and 55 days of SRTs.

6.5.2.1 Freundlich Isotherm

In Freundlich isotherm, constants of $1/n$ and K_F were determined by plotting the $\ln$ value of effluent adsorbate concentration ($\ln C_e$) against the $\ln$ value of concentration of adsorbate on adsorbent ($\ln q_e$). The value of K_F can then be calculated from intercept of the straight line while $1/n$ can be obtained from the slope of the line.

6.5.2.1.1 Freundlich Isotherm for α -HBCDD. n , K_F and R^2 values were calculated as 25.64 unitless, $134.42 \text{ L } \mu\text{g}^{-1}$ and 0.973, respectively for adsorption of α -HBCDD on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 8.00 unitless, $322.79 \text{ L } \mu\text{g}^{-1}$ and 0.940, respectively for adsorption of α -HBCDD on aerobic biological sludge (Figure 6.63.a and b) (Table 6.120).

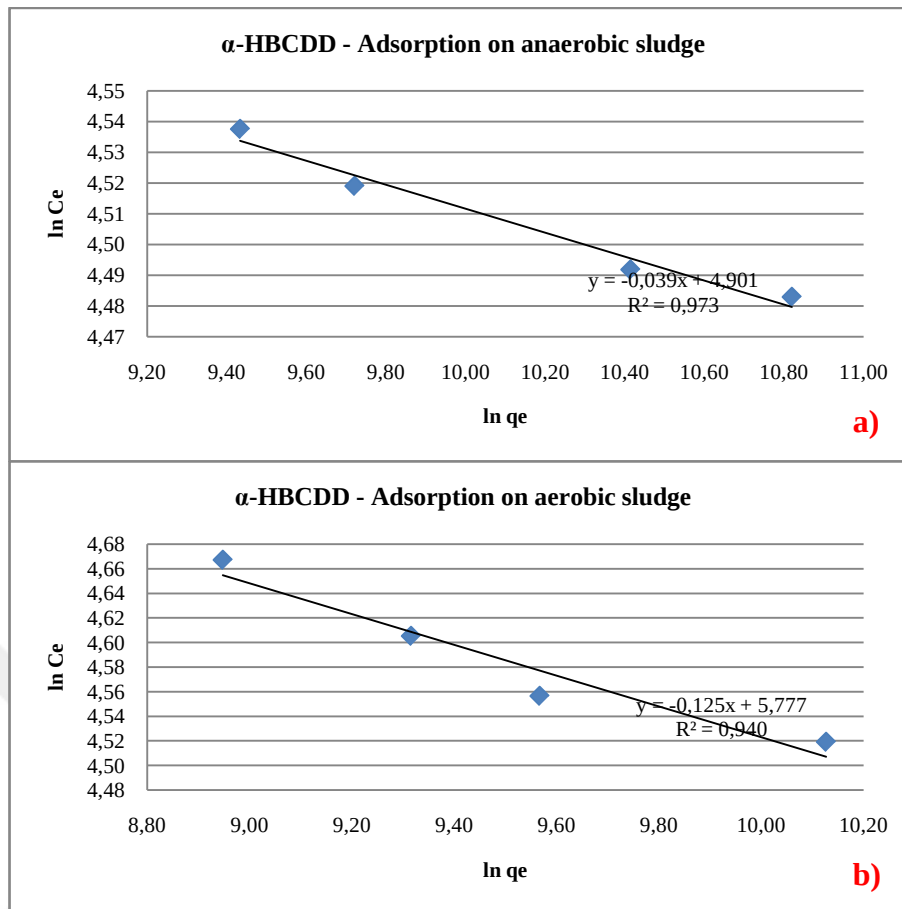


Figure 6.63 Freundlich isotherm for α -HBCDD in (a) anaerobic reactor and (b) aerobic reactor

Table 6.120 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($L \mu g^{-1}$)	R^2
Anaerobic sludge	α -HBCDD	25.64	134.42	0.973
Aerobic sludge	α -HBCDD	8.00	322.79	0.940

α -HBCDD has the highest $\log K_{OW}$ value (7.74) between the other micropollutants and showed the highest resistance to biodegradation due to its physicochemical properties such as low water solubility ($2.09 \times 10^{-5} g L^{-1}$) and low Henry's Law constant ($1.72 \times 10^{-6} atm m^3 mol^{-1}$). The main removal mechanism was found as adsorption onto anaerobic (86.09%) and aerobic (79.91%) biological sludges for α -HBCDD at the optimum SRT of 55 days (Table 6.8). The anaerobic reactor had higher adsorption intensity, n value (25.64) than the aerobic reactor (8.00) (Table 6.120) because α -HBCDD removal via adsorption was higher in the

anaerobic reactor than the aerobic reactor at all SRTs (Table 6.8). It can be concluded that the description of adsorption process with Freundlich isotherm is an appropriate modelling for α -HBCDD adsorption on anaerobic and aerobic biological sludges.

6.5.2.1.2 Freundlich Isotherm for PBEB. n , K_F and R^2 values were calculated as 20.00 unitless, 555.57 L μg^{-1} and 0.979, respectively for adsorption of PBEB on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 10.10 unitless, 989.30 L μg^{-1} and 0.955, respectively for adsorption of PBEB on aerobic biological sludge (Appendice-6, Figure 1.a and b) (Table 6.121).

Table 6.121 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
Anaerobic sludge	PBEB	20.00	555.57	0.979
Aerobic sludge	PBEB	10.10	989.30	0.955

PBEB has high kinetic constants due to its physicochemical properties such as high octanol/water partition coefficient ($\log K_{OW} = 7.48$), low water solubility (2.90×10^{-7} g L $^{-1}$) and low Henry's Law constant (7.92×10^{-5} atm m ^{3} mol $^{-1}$). The anaerobic reactor had higher n value (20.00) than the aerobic reactor (10.10) (Table 6.121) because adsorption mechanism was more dominant in the anaerobic reactor (85.56%) than the aerobic reactor (79.16%) at the optimum SRT of 55 days (Table 6.10). Having higher adsorption intensity (n) values than 1.00 for PBEB in the anaerobic (20.00) and aerobic (10.10) reactors (Table 6.121) make the adsorption process acceptable for PBEB on anaerobic and aerobic biological sludges with Freundlich isotherm.

6.5.2.1.3 Freundlich Isotherm for PBT. n , K_F and R^2 values were calculated as 17.54 unitless, 868.70 L μg^{-1} and 0.984, respectively for adsorption of PBT on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 6.41

unitless, 2768.33 L μg^{-1} and 0.986, respectively for adsorption of PBT on aerobic biological sludge (Appendice-6, Figure 2.a and b) (Table 6.122).

Table 6.122 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
Anaerobic sludge	PBT	17.54	868.70	0.984
Aerobic sludge	PBT	6.41	2768.33	0.986

PBT has high Freundlich isotherm constants with its high adsorption capacity because PBT has high octanol/water partition coefficient ($\log K_{OW} = 6.99$), low water solubility ($9.35 \times 10^{-7} \text{ g L}^{-1}$) and low Henry's Law constant ($5.97 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$). The anaerobic reactor had higher n value (17.54) than aerobic reactor (6.41) (Table 6.122). Because of the adsorption intensity value (n) was higher than 1.00 for anaerobic (17.54) and aerobic (6.41) reactors, it can be concluded that Freundlich isotherm was suitable for PBT both in anaerobic and aerobic reactors (Table 6.122).

6.5.2.1.4 Freundlich Isotherm for TBBPA. n, K_F and R^2 values were calculated as 15.87 unitless, 111.94 L μg^{-1} and 0.990, respectively for adsorption of TBBPA on anaerobic biological sludge while, n, K_F and R^2 values were calculated as 5.92 unitless, 309.51 L μg^{-1} and 0.998, respectively for adsorption of TBBPA on aerobic biological sludge (Appendice-6, Figure 3.a and b) (Table 6.123).

Table 6.123 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
Anaerobic sludge	TBBPA	15.87	111.94	0.990
Aerobic sludge	TBBPA	5.92	309.51	0.998

The adsorption intensity, n value of anaerobic reactor (15.87) was higher than aerobic reactor (5.92) for TBBPA (Table 6.123) because adsorption was higher in the anaerobic reactor (84.71%) than the aerobic reactor (77.24%) at the optimum SRT of

55 days (Table 6.14). TBBPA was adsorbed onto anaerobic and aerobic biological sludges according to the Freundlich isotherm because the adsorption intensity (n) was higher than 1.00 for the anaerobic (15.87) and aerobic (5.92) reactors (Table 6.123). TBBPA is a hydrophobic micropollutant and can be easily adsorbed onto biological sludges due to its physicochemical properties like high octanol/water partition coefficient ($\log K_{OW} = 5.90$), low water solubility ($7.65 \times 10^{-6} \text{ g L}^{-1}$) and low Henry's Law constant ($1.47 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$).

6.5.2.1.5 Freundlich Isotherm for AHTN. n , K_F and R^2 values were calculated as 12.35 unitless, $8.89 \text{ L } \mu\text{g}^{-1}$ and 0.984, respectively for adsorption of AHTN on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 4.59 unitless, $20.17 \text{ L } \mu\text{g}^{-1}$ and 0.984, respectively for adsorption of AHTN on aerobic biological sludge (Appendice-6, Figure 4.a and b) (Table 6.124).

Table 6.124 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	AHTN	12.35	8.89	0.984
Aerobic sludge	AHTN	4.59	20.17	0.984

AHTN adsorbed onto anaerobic and aerobic biological sludges according to Freundlich isotherm due to its physicochemical properties like high octanol/water partition coefficient ($\log K_{OW} = 5.70$), low water solubility ($1.25 \times 10^{-3} \text{ g L}^{-1}$) and low Henry's Law constant ($1.40 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$). The n value of anaerobic reactor (12.35) was higher than aerobic reactor (4.59) for AHTN (Table 6.124) because adsorption mechanism was more dominant in anaerobic reactor (80.90%) than aerobic reactor (74.73%) at the optimum SRT of 55 days (Table 6.16). It can be concluded that the description of adsorption process with Freundlich isotherm is an appropriate modelling for AHTN adsorption on anaerobic and aerobic biological sludges.

6.5.2.1.6 *Freundlich Isotherm for PFOA*. n , K_F and R^2 values were calculated as 10.10 unitless, 11.75 L μg^{-1} and 0.992, respectively for adsorption of PFOA on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 3.44 unitless, 43.08 L μg^{-1} and 0.999, respectively for adsorption of PFOA on aerobic biological sludge (Appendice-6, Figure 5.a and b) (Table 6.125).

Table 6.125 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
Anaerobic sludge	PFOA	10.10	11.75	0.992
Aerobic sludge	PFOA	3.44	43.08	0.999

Having appropriate physicochemical properties such as high octanol/water partition coefficient ($\log K_{OW} = 4.81$), low water solubility (0.481×10^{-3} g L $^{-1}$) and low Henry's Law constant (9.08×10^{-2} atm m ^{3} mol $^{-1}$) makes PFOA hardly biodegradable but easiliy adsorbed onto anaerobic and aerobic biological sludges in the anaerobic/aerobic sequential biological treatment system. The n value of the anaerobic reactor (10.10) was higher than the aerobic reactor (3.44) for PFOA (Table 6.125) because removal via adsorption was higher in the anaerobic reactor (78.64%) than the aerobic reactor (70.00%) at the optimum SRT of 55 days (Table 6.18). Freundlich isotherm was found to be suitable for PFOA removal both in the anaerobic (10.10) and aerobic (3.44) reactors because the adsorption intensity (n) value was higher than 1.00 for the anaerobic and aerobic reactors (Table 6.125).

6.5.2.1.7 *Freundlich Isotherm for PFOS*. n , K_F and R^2 values were calculated as 6.25 unitless, 243.96 L μg^{-1} and 0.999, respectively for adsorption of PFOS on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 2.39 unitless, 2387.50 L μg^{-1} and 0.994, respectively for adsorption of PFOS on aerobic biological sludge (Appendice-6, Figure 6.a and b) (Table 6.126).

Table 6.126 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($L \mu g^{-1}$)	R^2
Anaerobic sludge	PFOS	6.25	243.96	0.999
Aerobic sludge	PFOS	2.39	2387.50	0.994

The physicochemical properties of PFOS such as high octanol/water partition coefficient ($\log K_{OW} = 4.49$), low water solubility ($0.104 \times 10^{-3} g L^{-1}$) and low Henry's Law constant ($1.10 \times 10^{-2} atm m^3 mol^{-1}$) made the adsorption process possible for PFOS in anaerobic and aerobic reactors. The anaerobic reactor had higher n value (6.25) than aerobic reactor (2.39) (Table 6.126) because adsorption mechanism was more dominant in anaerobic reactor (58.11%) than aerobic reactor (52.26%) at the optimum SRT of 55 days (Table 6.20). The adsorption intensity (n) value was higher than 1.00 for anaerobic (6.25) and aerobic (2.39) reactors (Table 6.126), so Freundlich isotherm was suitable for PFOS both in anaerobic and aerobic reactors.

6.5.2.1.8 Freundlich Isotherm for GFZ. n, K_F and R^2 values were calculated as 7.69 unitless, $44.17 L \mu g^{-1}$ and 0.994, respectively for adsorption of GFZ on anaerobic biological sludge while, n, K_F and R^2 values were calculated as 2.72 unitless, $35.37 L \mu g^{-1}$ and 0.996, respectively for adsorption of GFZ on aerobic biological sludge (Appendice-6, Figure 7.a and b) (Table 6.127).

Table 6.127 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($L \mu g^{-1}$)	R^2
Anaerobic sludge	GFZ	7.69	44.17	0.994
Aerobic sludge	GFZ	2.72	35.37	0.996

The anaerobic reactor had higher n value (7.69) than the aerobic reactor (2.72) in Freundlich isotherm (Table 6.127). The adsorption intensity (n) value was higher than 1.00 for anaerobic (7.69) and aerobic (2.72) reactors (Table 6.127), therefore, it can be concluded that the Freundlich isotherm was suitable for GFZ removal both in

the anaerobic and aerobic reactors. GFZ was adsorbed onto the anaerobic and aerobic biological sludges according to the Langmuir isotherm because its physicochemical properties were appropriate for the adsorption process like high octanol/water partition coefficient ($\log K_{OW} = 4.77$), low water solubility ($4.964 \times 10^{-3} \text{ g L}^{-1}$) and low Henry's Law constant ($1.19 \times 10^{-8} \text{ atm m}^3 \text{ mol}^{-1}$).

6.5.2.1.9 *Freundlich Isotherm for TCS*. n , K_F and R^2 values were calculated as 7.87 unitless, $382.22 \text{ L } \mu\text{g}^{-1}$ and 0.993, respectively for adsorption of TCS on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 2.96 unitless, $462.20 \text{ L } \mu\text{g}^{-1}$ and 0.992, respectively for adsorption of TCS on aerobic biological sludge (Appendice-6, Figure 8.a and b) (Table 6.128).

Table 6.128 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	TCS	7.87	382.22	0.993
Aerobic sludge	TCS	2.96	462.20	0.992

The n value of the anaerobic reactor (7.87) was higher than the aerobic reactor (2.96) for TCS (Table 6.128) because adsorption was higher in the anaerobic reactor (74.87%) than aerobic reactor (66.95%) at the optimum SRT of 55 days (Table 6.24). TCS was an appropriate micropollutant to be adsorbed on biological sludges process due to its hydrophobic properties like high octanol/water partition coefficient ($\log K_{OW} = 4.76$), low water solubility ($4.621 \times 10^{-3} \text{ g L}^{-1}$) and low Henry's Law constant ($4.99 \times 10^{-9} \text{ atm m}^3 \text{ mol}^{-1}$). TCS was adsorbed onto the anaerobic and aerobic biological sludges according to the Freundlich isotherm because the adsorption intensity (n) of TCS were higher than 1.00 both for anaerobic (7.87) and aerobic (2.96) reactors (Table 6.128). Therefore, the description of adsorption process with Freundlich isotherm is an appropriate modelling for TCS adsorption on anaerobic and aerobic biological sludges.

6.5.2.1.10 *Freundlich Isotherm for IBU*. n , K_F and R^2 values were calculated as 1.85 unitless, 33.65 L μg^{-1} and 0.984, respectively for adsorption of IBU on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 0.14 unitless, 529.54 L μg^{-1} and 0.666, respectively for adsorption of IBU on aerobic biological sludge (Appendice-6, Figure 9.a and b) (Table 6.129).

Table 6.129 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
Anaerobic sludge	IBU	1.85	33.65	0.984
Aerobic sludge	IBU	0.14	529.54	0.666

IBU has a moderate octanol/water partition coefficient ($\log K_{OW} = 3.79$) between the other studied micropollutants. Although having low water solubility (4.105×10^{-4} g L $^{-1}$) and low Henry's Law constant (1.52×10^{-7} atm m ^{3} mol $^{-1}$) values, the main removal mechanism was found as biodegradation both in the anaerobic (45.51%) and aerobic (77.89%) reactors at the optimum SRT of 55 days (Table 6.26). This is the reason why IBU showed lower adsorption intensity values in the comparison with the other hydrophobic micropollutants (α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, PFOS, GFZ and TCS). The anaerobic reactor had higher n value (1.85) than the aerobic reactor (0.14) (Table 6.129) because adsorption was higher in the anaerobic reactor (15.29%) than the aerobic reactor (10.23%) at 55 days SRT (Table 6.26). Freundlich isotherm was only found suitable in the anaerobic reactor for IBU removal because the adsorption intensity (n) value was higher than 1.00 for the anaerobic (1.85) reactor (Table 6.129).

6.5.2.1.11 *Freundlich Isotherm for CIP*. n , K_F and R^2 values were calculated as 1.58 unitless, 2083.91 L μg^{-1} and 0.985, respectively for adsorption of CIP on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 0.03 unitless, 3.97×10^{47} L μg^{-1} and 0.875, respectively for adsorption of CIP on aerobic biological sludge (Appendice-6, Figure 10.a and b) (Table 6.130).

Table 6.130 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($L \mu g^{-1}$)	R^2
Anaerobic sludge	CIP	1.58	2083.91	0.985
Aerobic sludge	CIP	0.03	3.97×10^{47}	0.875

CIP is a hydrophilic micropollutant and can be easily biodegrade due to its physicochemical properties like low log K_{OW} value (0.28), high water solubility ($1.148 \times 10^4 \text{ g L}^{-1}$) and low Henry's Law constant ($5.09 \times 10^{-19} \text{ atm m}^3 \text{ mol}^{-1}$). The main removal mechanism was found as biodegradation both in the anaerobic (50.00%) and aerobic (86.32%) reactors at the optimum SRT of 55 days (Table 6.28). Consequently, adsorption intensity values of anaerobic and aerobic reactors were lower than the other aforementioned hydrophobic micropollutants. The anaerobic reactor had higher n value (1.58) than the aerobic reactor (0.03) (Table 6.130) because adsorption was higher in the anaerobic reactor (8.20%) than the aerobic reactor (4.29%) at the optimum SRT of 55 days (Table 6.28). Although CIP was suitable for biodegradation, the adsorbed CIP amounts onto the anaerobic biological sludge could be described with Freundlich isotherm because the adsorption intensity (n) value was higher than 1.00 for the anaerobic (1.58) reactor (Table 6.130).

6.5.2.1.12 Freundlich Isotherm for NDMA. n, K_F and R^2 values were calculated as 0.85 unitless, $3401.60 \text{ L } \mu g^{-1}$ and 0.988, respectively for adsorption of NDMA on anaerobic biological sludge while, n and R^2 values were calculated as 0.01 unitless and 0.869, respectively for adsorption of NDMA on aerobic biological sludge (Appendice-6, Figure 11.a and b) (Table 6.131).

Table 6.131 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F ($L \mu g^{-1}$)	R^2
Anaerobic sludge	NDMA	0.85	3401.60	0.988
Aerobic sludge	NDMA	0.01	--	0.869

NDMA showed the highest biodegradation removal efficiency both in anaerobic (64.84%) and aerobic (89.83%) reactors between the other studied micropollutants at 55 days SRT due to its hydrophilic structure such as quite low octanol/water partition coefficient ($\log K_{OW} = -0.57$), high water solubility ($4.104 \times 10^5 \text{ g L}^{-1}$) and low Henry's Law constant ($2.06 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$) (Table 6.30). As a result, the lowest adsorption intensity (n) values were determined for NDMA from the all studied micropollutants. The anaerobic reactor had higher n value (0.85) than the aerobic reactor (0.01) (Table 6.131) because adsorption was higher in the anaerobic reactor (4.65%) than the aerobic reactor (3.32%) at the optimum SRT of 55 days (Table 6.30). The adsorbed NDMA amounts onto the anaerobic and aerobic biological sludges could not be described with Freundlich isotherm. Because the adsorption intensity (n) value must be higher than 1.00, however, the calculated n values were found lower than 1.00 both for the anaerobic (0.85) and aerobic (0.01) reactors (Table 6.131).

6.5.2.1.13 Freundlich Isotherm for COD. n, K_F and R^2 values were calculated as 0.60 unitless, $272938.02 \text{ L mg}^{-1}$ and 0.954, respectively for adsorption of COD on anaerobic biological sludge (Appendice-6, Figure 12.a) (Table 6.132) while, n, K_F and R^2 values were calculated as 0.22 unitless, $17396.08 \text{ L mg}^{-1}$ and 0.908, respectively for adsorption of COD on aerobic biological sludge (Appendice-6, Figure 12.b) (Table 6.132).

Table 6.132 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L mg^{-1})	R^2
Anaerobic sludge	COD	0.60	272938.02	0.954
Aerobic sludge	COD	0.22	17396.08	0.908

The adsorption intensity (n) values of COD were found low due to its physicochemical properties like easiliy biodegradable in anaerobic and aerobic biological reactors. If the main removal mechanism of COD was found as adsorption rather than biodegradation, the kinetic constants would be expected to rise higher.

The anaerobic reactor had higher n value (0.60) than aerobic reactor (0.22) (Table 6.132) because adsorption mechanism was more dominant in anaerobic reactor than aerobic reactor for all SRTs (Table 6.2). The adsorption intensity (n) of COD were lower than 1.00 both for anaerobic (0.60) and aerobic (0.22) reactors (Table 6.132) in Freundlich isotherm. Therefore, the description of adsorption process with Freundlich isotherm was not an appropriate modelling for COD adsorption on anaerobic and aerobic biological sludges.

6.5.2.1.14 Freundlich Isotherm for sCOD. n , K_F and R^2 values were calculated as 0.47 unitless, 1246686.76 L mg⁻¹ and 0.950, respectively for adsorption of sCOD on anaerobic biological sludge while, n , K_F and R^2 values were calculated as 0.26 unitless, 1211.97 L mg⁻¹ and 0.949, respectively for adsorption of sCOD on aerobic biological sludge (Appendice-6, Figure 13.a and b) (Table 6.133).

Table 6.133 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	n (unitless)	K_F (L µg ⁻¹)	R^2
Anaerobic sludge	sCOD	0.47	1246686.76	0.950
Aerobic sludge	sCOD	0.26	1211.97	0.949

sCOD was the most biodegradable compound from all the studied macro and micropollutants and had lower adsorption intensity (n) values due to its physicochemical properties both in anaerobic and aerobic reactors. The anaerobic reactor had higher n value (0.47) than aerobic reactor (0.26) (Table 6.133) because adsorption mechanism was more dominant in anaerobic reactor than aerobic reactor for all SRTs (Table 6.3). The adsorption intensity (n) of sCOD were lower than 1.00 both for anaerobic (0.47) and aerobic (0.26) reactors (Table 6.133) in Freundlich isotherm. As a consequence, the description of adsorption process with Freundlich isotherm was not an appropriate modelling for sCOD adsorption both for anaerobic and aerobic reactors.

6.5.2.2 Langmuir Isotherm

To determine the Langmuir isotherm constant (K_L) and maximum capacity of the adsorbent (q_m), the inverse of capacity of the adsorbent ($1/q_e$) was plotted against the inverse of effluent adsorbate concentration ($1/C_e$). q_m was determined from the slope of the line and K_L was determined from the intercept of the y-axis.

6.5.2.2.1 Langmuir Isotherm for α -HBCDD. q_m , K_L and R^2 values were calculated as $0.0001 \mu\text{g g}^{-1}$, $0.000001 \text{ L } \mu\text{g}^{-1}$ and 0.894 , respectively for α -HBCDD adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.0009 \mu\text{g g}^{-1}$, $0.00001 \text{ L } \mu\text{g}^{-1}$ and 0.821 , respectively for α -HBCDD adsorption on aerobic biological sludge (Figure 6.64.a and b) (Table 6.134).

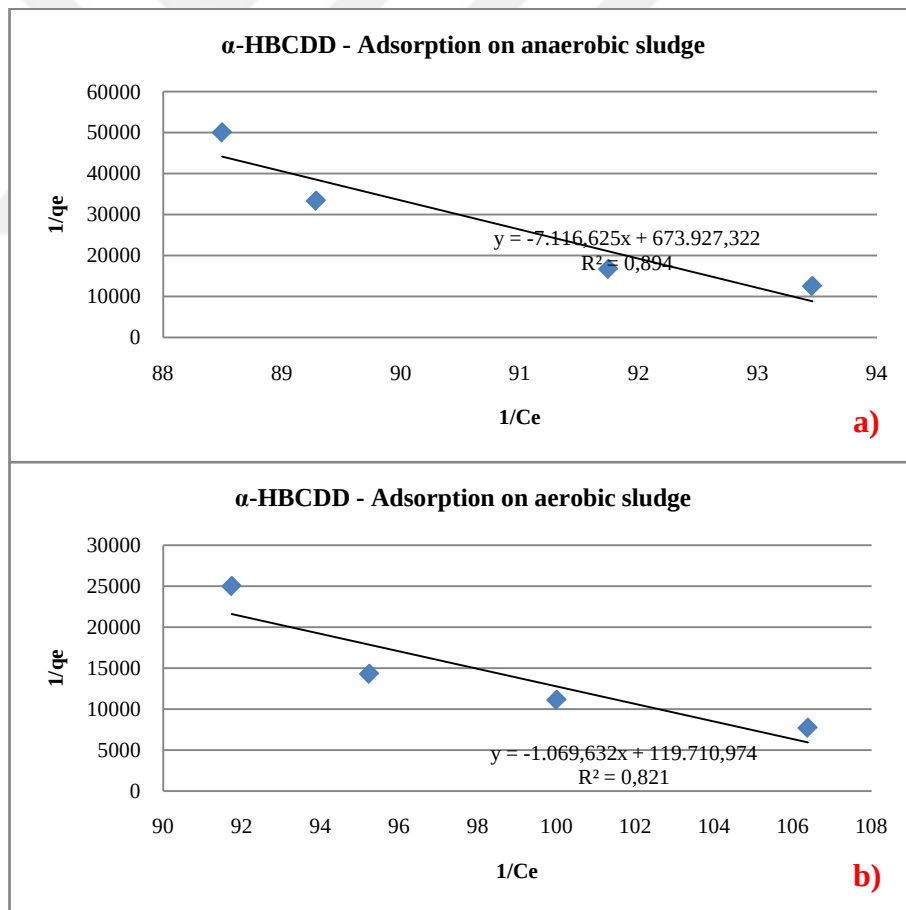


Figure 6.64 Langmuir isotherm for adsorption of α -HBCDD during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

Table 6.134 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for α -HBCDD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	α -HBCDD	0.0001	0.000001	0.894
Aerobic sludge	α -HBCDD	0.0009	0.00001	0.821

6.5.2.2.2 *Langmuir Isotherm for PBEB.* q_m , K_L and R^2 values were calculated as $0.0002 \mu\text{g g}^{-1}$, $7.03 \times 10^{-7} \text{ L } \mu\text{g}^{-1}$ and 0.918, respectively for PBEB adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.0009 \mu\text{g g}^{-1}$, $0.000002 \text{ L } \mu\text{g}^{-1}$ and 0.836, respectively for PBEB adsorption on aerobic biological sludge (Appendice-7, Figure 1.a and b) (Table 6.135).

Table 6.135 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PBEB in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	PBEB	0.0002	7.03×10^{-7}	0.918
Aerobic sludge	PBEB	0.0009	0.000002	0.836

6.5.2.2.3 *Langmuir Isotherm for PBT.* q_m , K_L and R^2 values were calculated as $0.0003 \mu\text{g g}^{-1}$, $6.47 \times 10^{-3} \text{ L } \mu\text{g}^{-1}$ and 0.938, respectively for PBT adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.0014 \mu\text{g g}^{-1}$, $0.000002 \text{ L } \mu\text{g}^{-1}$ and 0.936, respectively for PBT adsorption on aerobic biological sludge (Appendice-7, Figure 2.a and b) (Table 6.136).

Table 6.136 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PBT in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	PBT	0.0003	6.47×10^{-3}	0.938
Aerobic sludge	PBT	0.0014	0.000002	0.936

6.5.2.2.4 *Langmuir Isotherm for TBBPA.* q_m , K_L and R^2 values were calculated as $0.0004 \mu\text{g g}^{-1}$, $5.87 \times 10^{-6} \text{ L } \mu\text{g}^{-1}$ and 0.962, respectively for TBBPA adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.0017 \mu\text{g g}^{-1}$, $5.87 \times 10^{-6} \text{ L } \mu\text{g}^{-1}$ and 0.962, respectively for TBBPA adsorption on aerobic biological sludge (Appendice-7, Figure 3.a and b) (Table 6.137).

g^{-1} , $0.00002 \text{ L } \mu\text{g}^{-1}$ and 0.973 , respectively for TBBPA adsorption on aerobic biological sludge (Appendice-7, Figure 3.a and b) (Table 6.137).

Table 6.137 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for TBBPA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	TBBPA	0.0004	5.87×10^{-6}	0.962
Aerobic sludge	TBBPA	0.0017	0.00002	0.973

6.5.2.2.5 *Langmuir Isotherm for AHTN*. q_m , K_L and R^2 values were calculated as $0.0006 \mu\text{g g}^{-1}$, $0.0001 \text{ L } \mu\text{g}^{-1}$ and 0.945 , respectively for AHTN adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.0048 \mu\text{g g}^{-1}$, $0.001 \text{ L } \mu\text{g}^{-1}$ and 0.940 , respectively for AHTN adsorption on aerobic biological sludge (Appendice-7, Figure 4.a and b) (Table 6.138).

Table 6.138 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for AHTN in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	AHTN	0.0006	0.0001	0.945
Aerobic sludge	AHTN	0.0048	0.001	0.940

6.5.2.2.6 *Langmuir Isotherm for PFOA*. q_m , K_L and R^2 values were calculated as $0.001 \mu\text{g g}^{-1}$, $0.0001 \text{ L } \mu\text{g}^{-1}$ and 0.970 , respectively for PFOA adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.892 \mu\text{g g}^{-1}$, $0.002 \text{ L } \mu\text{g}^{-1}$ and 0.751 , respectively for PFOA adsorption on aerobic biological sludge (Appendice-7, Figure 5.a and b) (Table 6.139).

Table 6.139 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PFOA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	PFOA	0.001	0.0001	0.970
Aerobic sludge	PFOA	0.892	0.002	0.751

6.5.2.2.7 *Langmuir Isotherm for PFOS*. q_m , K_L and R^2 values were calculated as $0.0025 \mu\text{g g}^{-1}$, $3.40 \times 10^{-5} \text{ L } \mu\text{g}^{-1}$ and 0.996, respectively for PFOS adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.014 \mu\text{g g}^{-1}$, $0.0001 \text{ L } \mu\text{g}^{-1}$ and 0.962, respectively for PFOS adsorption on aerobic biological sludge (Appendice-7, Figure 6.a and b) (Table 6.140).

Table 6.140 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PFOS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	PFOS	0.0025	3.40×10^{-5}	0.996
Aerobic sludge	PFOS	0.014	0.0001	0.962

6.5.2.2.8 *Langmuir Isotherm for GFZ*. q_m , K_L and R^2 values were calculated as $0.0017 \mu\text{g g}^{-1}$, $0.070 \text{ L } \mu\text{g}^{-1}$ and 0.977, respectively for GFZ adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.007 \mu\text{g g}^{-1}$, $0.199 \text{ L } \mu\text{g}^{-1}$ and 0.979, respectively for GFZ adsorption on aerobic biological sludge (Appendice-7, Figure 7.a and b) (Table 6.141).

Table 6.141 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for GFZ in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	GFZ	0.0017	0.070	0.977
Aerobic sludge	GFZ	0.007	0.199	0.979

6.5.2.2.9 *Langmuir Isotherm for TCS*. q_m , K_L and R^2 values were calculated as $0.0016 \mu\text{g g}^{-1}$, $0.458 \text{ L } \mu\text{g}^{-1}$ and 0.975, respectively for TCS adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $0.006 \mu\text{g g}^{-1}$, $1.267 \text{ L } \mu\text{g}^{-1}$ and 0.971, respectively for TCS adsorption on aerobic biological sludge (Appendice-7, Figure 8.a and b) (Table 6.142).

Table 6.142 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for TCS in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	TCS	0.0016	0.458	0.975
Aerobic sludge	TCS	0.006	1.267	0.971

6.5.2.2.10 *Langmuir Isotherm for IBU*. q_m , K_L and R^2 values were calculated as $0.030 \mu\text{g g}^{-1}$, $0.521 \text{ L } \mu\text{g}^{-1}$ and 0.938, respectively for IBU adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $2.57 \mu\text{g g}^{-1}$, $1.62 \text{ L } \mu\text{g}^{-1}$ and 0.511, respectively for IBU adsorption on aerobic biological sludge (Appendice-7, Figure 9.a and b) (Table 6.143).

Table 6.143 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for IBU in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	IBU	0.030	0.521	0.938
Aerobic sludge	IBU	2.57	1.62	0.511

6.5.2.2.11 *Langmuir Isotherm for CIP*. q_m , K_L and R^2 values were calculated as $0.041 \mu\text{g g}^{-1}$, $7.75 \text{ L } \mu\text{g}^{-1}$ and 0.943, respectively for CIP adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $14.29 \mu\text{g g}^{-1}$, $21.74 \text{ L } \mu\text{g}^{-1}$ and 0.716, respectively for CIP adsorption on aerobic biological sludge (Appendice-7, Figure 10.a and b) (Table 6.144).

Table 6.144 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for CIP in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
Anaerobic sludge	CIP	0.041	7.75	0.943
Aerobic sludge	CIP	14.29	21.74	0.716

6.5.2.2.12 *Langmuir Isotherm for NDMA*. q_m , K_L and R^2 values were calculated as $0.143 \mu\text{g g}^{-1}$, $0.005 \text{ L } \mu\text{g}^{-1}$ and 0.952, respectively for NDMA adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined $40.00 \mu\text{g g}^{-1}$

¹, 0.005 L μg^{-1} and 0.885, respectively for NDMA adsorption on aerobic biological sludge (Appendice-7, Figure 11.a and b) (Table 6.145).

Table 6.145 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for NDMA in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L (L μg^{-1})	R^2
Anaerobic sludge	NDMA	0.143	0.005	0.952
Aerobic sludge	NDMA	40.00	0.005	0.885

6.5.2.2.13 *Langmuir Isotherm for COD*. In Langmuir isotherm, q_m , K_L and R^2 values were calculated as 0.34 mg g^{-1} , 37.04 L mg^{-1} and 0.821, respectively for COD adsorption on anaerobic biological sludge (Appendice-7, Figure 12.a) (Table 6.146) while, q_m , K_L and R^2 values were determined 2.12 mg g^{-1} , 27.78 L mg^{-1} and 0.891, respectively for COD adsorption on aerobic biological sludge (Appendice-7, Figure 12.b) (Table 6.146).

Table 6.146 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for COD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
Anaerobic sludge	COD	0.34	37.04	0.821
Aerobic sludge	COD	2.12	27.78	0.891

6.5.2.2.14 *Langmuir Isotherm for sCOD*. q_m , K_L and R^2 values were calculated as 0.97 mg g^{-1} , 66.67 L mg^{-1} and 0.111, respectively for sCOD adsorption on anaerobic biological sludge while, q_m , K_L and R^2 values were determined 2.35 mg g^{-1} , 22.73 L mg^{-1} and 0.868, respectively for sCOD adsorption on aerobic biological sludge (Appendice-7, Figure 13.a and b) (Table 6.147).

Table 6.147 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for sCOD in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Adsorbent	Adsorbate	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
Anaerobic sludge	sCOD	0.97	66.67	0.111
Aerobic sludge	sCOD	2.35	22.73	0.868

6.5.2.3 Evaluation of Freundlich and Langmuir Isotherms in the Anaerobic/Aerobic Sequential Biological Reactor System

The kinetic data showed that the kinetic constants were not found to be meaningful for Langmuir isotherm in the comparison with Freundlich isotherm. The adsorption of hydrophobic micropollutants ($\log K_{OW} > 4.00$) on anaerobic biological sludge followed the Freundlich isotherm and the kinetic constants (n and K_F) were found to be meaningful (Table 6.148). In Freundlich isotherm, the adsorption intensity (n) must be higher than 1.00 to provide physical adsorption process (Orbak, 2009). The adsorption intensity (n value) of all hydrophobic micropollutants were higher than 1.00 in the anaerobic reactor (Table 6.148). However, the hydrophilic micropollutants ($\log K_{OW} < 2.50$) and macropollutants (COD and sCOD) did not follow the Freundlich isotherm in the anaerobic reactor (Table 6.148). The kinetic constants (K_F) were not meaningful and/or the adsorption intensities (n value) were lower than 1.00 in the anaerobic reactor (Table 6.148). The adsorption of hydrophobic micropollutants ($\log K_{OW} > 4.00$) on aerobic biological sludge followed the Freundlich isotherm and the kinetic constants were found to be meaningful except for IBU (Table 6.148). IBU did not follow the Freundlich isotherm in aerobic reactor due to its lower n value (0.14) than 1.00 because it was found that the main removal mechanism was biodegradation in the aerobic reactor (Table 6.148). Also, the hydrophilic micropollutants ($\log K_{OW} < 2.50$) and macropollutants (COD and sCOD) did not follow the Freundlich isotherm in the aerobic reactor (Table 6.148). They all had lower adsorption intensities (n value) than 1.00 in the aerobic reactor (Table 6.148). Moreover, the kinetic constants (K_F) of hydrophilic micropollutants (CIP and NDMA) and macropollutants (COD and sCOD) were not meaningful in the aerobic reactor (Table 6.148). The more hydrophobic micropollutants ($\log K_{OW} > 4.00$) had higher adsorption intensity (n) values than the other hydrophobic micropollutants (Table 6.148). Therefore, the description of adsorption process with Freundlich isotherm was suitable for brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS) and some phenolic (GFZ, TCS and IBU) micropollutants in the anaerobic/aerobic sequential biological reactor system (Table 6.148).

Table 6.148 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm in the anaerobic and aerobic biological reactors at 5, 30 45 and 55 days of SRTs

Micropollutant	Log K_{OW} (unitless)	Freundlich Isotherm					
		Anaerobic Reactor			Aerobic Reactor		
		n (unitless)	K_F (L μg^{-1})	R^2	n (unitless)	K_F (L μg^{-1})	R^2
α -HBCDD	7.74	25.64	134.42	0.973	8.00	322.79	0.940
PBEB	7.48	20.00	555.57	0.979	10.10	989.30	0.955
PBT	6.99	17.54	868.70	0.984	6.41	2768.33	0.986
TBBPA	5.90	15.87	111.94	0.990	5.92	309.51	0.998
AHTN	5.70	12.35	8.89	0.984	4.59	20.17	0.984
PFOA	4.81	10.10	11.75	0.992	3.44	43.08	0.999
GFZ	4.77	7.69	44.17	0.994	2.72	35.37	0.996
TCS	4.76	7.87	382.22	0.993	2.96	462.20	0.992
PFOS	4.49	6.25	243.96	0.999	2.39	2387.50	0.994
IBU	3.79	1.85	33.65	0.984	0.14	529.54	0.666
CIP	0.28	1.58	2083.91	0.985	0.03	3.97×10^{47}	0.875
NDMA	-0.57	0.85	3401.60	0.988	0.01	--	0.869
COD	--	0.60	272938.02	0.954	0.22	17396.08	0.908
sCOD	--	0.47	1246686.76	0.950	0.26	1211.97	0.949

6.5.3 Photocatalytic Treatment Kinetics

The experimental results obtained from the photocatalytic treatment were applied to Langmuir and Freundlich isotherm models to determine the optimum brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOA and PFOS), nitroso (NDMA), phenolic (TCS, GFZ, CIP and IBU) and aromatic (AHTN) micropollutant removal kinetics with nano-TiO₂ and nano-CeO₂. The kinetic studies of photocatalytic treatment were investigated using nano-TiO₂ and nano-CeO₂ (0.25, 0.50, 1.00 and 1.50 g L⁻¹) at the following experimental conditions: 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00.

6.5.3.1 Langmuir Isotherms

The maximum capacity of the adsorbent (q_m , $\mu\text{g g}^{-1}$) and Langmuir isotherm constant (K_L , L μg^{-1}) can be obtained from the slope and intercept of the line, respectively plotting the ($1/q_e$) versus ($1/C_e$). q_e and C_e represent capacity of the adsorbent ($\mu\text{g g}^{-1}$) and effluent micropollutant concentration ($\mu\text{g L}^{-1}$), respectively.

6.5.3.1.1 Langmuir Isotherm for α -HBCDD. In Langmuir isotherm, the R^2 value of the linear line was 0.955, while q_m and K_L values were calculated as 71.43 $\mu\text{g g}^{-1}$ and 0.077 L μg^{-1} , respectively with nano-TiO₂ for α -HBCDD (Figure 6.65.a) (Table 6.149). The R^2 value of the linear line was 0.853, while q_m and K_L values were calculated as 76.92 $\mu\text{g g}^{-1}$ and 0.109 L μg^{-1} , respectively with nano-CeO₂ for α -HBCDD (Figure 6.65.b) (Table 6.149).

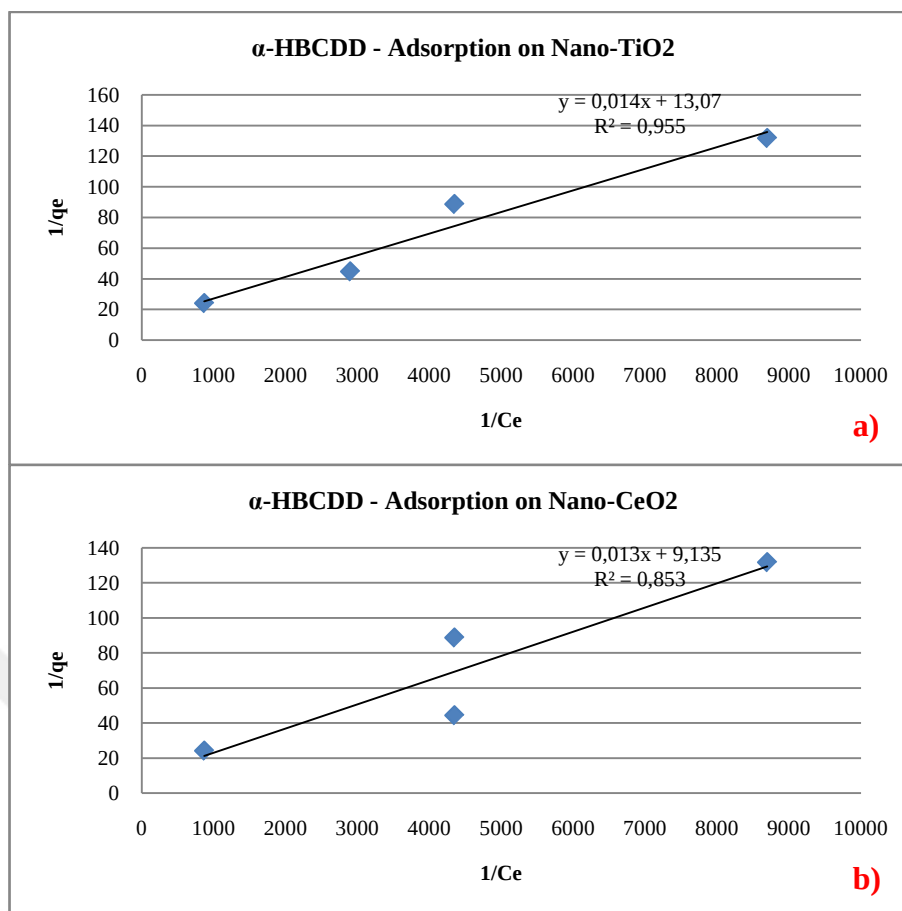


Figure 6.65 Langmuir isotherm for α -HBCDD adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

Table 6.149 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for α -HBCDD with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	α -HBCDD	71.43	0.077	0.955
nano-CeO ₂	α -HBCDD	76.92	0.109	0.853

6.5.3.1.2 Langmuir Isotherm for PBEB. The R^2 value of the linear line was 0.937, while q_m and K_L values were calculated as $66.67 \mu\text{g g}^{-1}$ and $0.076 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PBEB (Appendice-8, Figure 1.a) (Table 6.150). The R^2 value of the linear line was 0.935, while q_m and K_L values were calculated as $66.67 \mu\text{g g}^{-1}$ and $0.084 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PBEB (Appendice-8, Figure 1.b) (Table 6.150).

Table 6.150 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PBEB with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	PBEB	66.67	0.076	0.937
nano-CeO ₂	PBEB	66.67	0.084	0.935

6.5.3.1.3 *Langmuir Isotherm for PBT*. The R^2 value of the linear line was 0.932, while q_m and K_L values were calculated as $66.67 \mu\text{g g}^{-1}$ and $0.076 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PBT (Appendice-8, Figure 2.a) (Table 6.151). The R^2 value of the linear line was 0.931, while q_m and K_L values were calculated as $66.67 \mu\text{g g}^{-1}$ and $0.082 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PBT (Appendice-8, Figure 2.b) (Table 6.151).

Table 6.151 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PBT with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	PBT	66.67	0.076	0.932
nano-CeO ₂	PBT	66.67	0.082	0.931

6.5.3.1.4 *Langmuir Isotherm for TBBPA*. The R^2 value of the linear line was 0.972, while q_m and K_L values were calculated as $28.57 \mu\text{g g}^{-1}$ and $0.071 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for TBBPA (Appendice-8, Figure 3.a) (Table 6.152). The R^2 value of the linear line was 0.817, while q_m and K_L values were calculated as $30.30 \mu\text{g g}^{-1}$ and $0.075 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for TBBPA (Appendice-8, Figure 3.b) (Table 6.152).

Table 6.152 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for TBBPA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	TBBPA	28.57	0.071	0.972
nano-CeO ₂	TBBPA	30.30	0.075	0.817

6.5.3.1.5 *Langmuir Isotherm for AHTN*. The R^2 value of the linear line was 0.922, while q_m and K_L values were calculated as $1.03 \mu\text{g g}^{-1}$ and $0.071 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for AHTN (Appendice-8, Figure 4.a) (Table 6.153). The R^2 value of the linear line was 0.803, while q_m and K_L values were calculated as $1.08 \mu\text{g g}^{-1}$ and $0.072 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for AHTN (Appendice-8, Figure 4.b) (Table 6.153).

Table 6.153 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for AHTN with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	AHTN	1.03	0.071	0.922
nano-CeO ₂	AHTN	1.08	0.072	0.803

6.5.3.1.6 *Langmuir Isotherm for PFOA*. The R^2 value of the linear line was 0.930, while q_m and K_L values were calculated as $1.00 \mu\text{g g}^{-1}$ and $0.063 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PFOA (Appendice-8, Figure 5.a) (Table 6.154). The R^2 value of the linear line was 0.870, while q_m and K_L values were calculated as $1.08 \mu\text{g g}^{-1}$ and $0.066 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PFOA (Appendice-8, Figure 5.b) (Table 6.154).

Table 6.154 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PFOA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	PFOA	1.00	0.063	0.930
nano-CeO ₂	PFOA	1.08	0.066	0.870

6.5.3.1.7 *Langmuir Isotherm for PFOS*. The R^2 value of the linear line was 0.954, while q_m and K_L values were calculated as $0.91 \mu\text{g g}^{-1}$ and $0.006 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PFOS (Appendice-8, Figure 6.a) (Table 6.155). The R^2 value of the linear line was 0.999, while q_m and K_L values were calculated as $1.03 \mu\text{g g}^{-1}$ and $0.006 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PFOS (Appendice-8, Figure 6.b) (Table 6.155).

Table 6.155 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for PFOS with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	PFOS	0.91	0.006	0.954
nano-CeO ₂	PFOS	1.03	0.006	0.999

6.5.3.1.8 *Langmuir Isotherm for GFZ*. The R^2 value of the linear line was 0.807, while q_m and K_L values were calculated as $0.91 \mu\text{g g}^{-1}$ and $0.026 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for GFZ (Appendice-8, Figure 7.a) (Table 6.156). The R^2 value of the linear line was 0.903, while q_m and K_L values were calculated as $1.07 \mu\text{g g}^{-1}$ and $0.027 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for GFZ (Appendice-8, Figure 7.b) (Table 6.156).

Table 6.156 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for GFZ with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	GFZ	0.91	0.026	0.807
nano-CeO ₂	GFZ	1.07	0.027	0.903

6.5.3.1.9 *Langmuir Isotherm for TCS*. The R^2 value of the linear line was 0.873, while q_m and K_L values were calculated as $0.91 \mu\text{g g}^{-1}$ and $0.015 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for TCS (Appendice-8, Figure 8.a) (Table 6.157). The R^2 value of the linear line was 0.904, while q_m and K_L values were calculated as $1.04 \mu\text{g g}^{-1}$ and $0.015 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for TCS (Appendice-8, Figure 8.b) (Table 6.157).

Table 6.157 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for TCS with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	TCS	0.91	0.015	0.873
nano-CeO ₂	TCS	1.04	0.015	0.904

6.5.3.1.10 *Langmuir Isotherm for IBU*. The R^2 value of the linear line was 0.923, while q_m and K_L values were calculated as $0.35 \mu\text{g g}^{-1}$ and $0.006 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for IBU (Appendice-8, Figure 9.a) (Table 6.158). The R^2 value of the linear line was 0.964, while q_m and K_L values were calculated as $0.41 \mu\text{g g}^{-1}$ and $0.006 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for IBU (Appendice-8, Figure 9.b) (Table 6.158).

Table 6.158 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for IBU with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	IBU	0.35	0.006	0.923
nano-CeO ₂	IBU	0.41	0.006	0.964

6.5.3.1.11 *Langmuir Isotherm for CIP*. The R^2 value of the linear line was 0.988, while q_m and K_L values were calculated as $0.23 \mu\text{g g}^{-1}$ and $0.0004 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for CIP (Appendice-8, Figure 10.a) (Table 6.159). The R^2 value of the linear line was 0.989, while q_m and K_L values were calculated as $0.37 \mu\text{g g}^{-1}$ and $0.0005 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for CIP (Appendice-8, Figure 10.b) (Table 6.159).

Table 6.159 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for CIP with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	CIP	0.23	0.0004	0.988
nano-CeO ₂	CIP	0.37	0.0005	0.989

6.5.3.1.12 *Langmuir Isotherm for NDMA*. The R^2 value of the linear line was 0.988, while q_m and K_L values were calculated as $0.23 \mu\text{g g}^{-1}$ and $0.0001 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for NDMA (Appendice-8, Figure 11.a) (Table 6.160). The R^2 value of the linear line was 0.998, while q_m and K_L values were calculated as $0.32 \mu\text{g g}^{-1}$ and $0.0001 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for NDMA (Appendice-8, Figure 11.b) (Table 6.160).

Table 6.160 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Langmuir isotherm for NDMA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	NDMA	0.23	0.0001	0.988
nano-CeO ₂	NDMA	0.32	0.0001	0.998

6.5.3.2 Freundlich Isotherms

Freundlich isotherm constants; adsorption intensity, n (unitless) and Freundlich constant, K_F ($\text{L } \mu\text{g}^{-1}$) can be obtained from the slope and intercept of the line, respectively by plotting the $(\ln C_e)$ versus $(\ln q_e)$. q_e and C_e represent capacity of the adsorbent ($\mu\text{g g}^{-1}$) and effluent micropollutant concentration ($\mu\text{g L}^{-1}$), respectively.

6.5.3.2.1 Freundlich Isotherm for α -HBCDD. The R^2 value of the linear line was 0.953, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 0.79 unitless and $3.53 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for α -HBCDD (Figure 6.66.a) (Table 6.161). The R^2 , n and K_F values were calculated as 0.828, 0.84 unitless and $4.21 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for α -HBCDD (Figure 6.66.b) (Table 6.161).

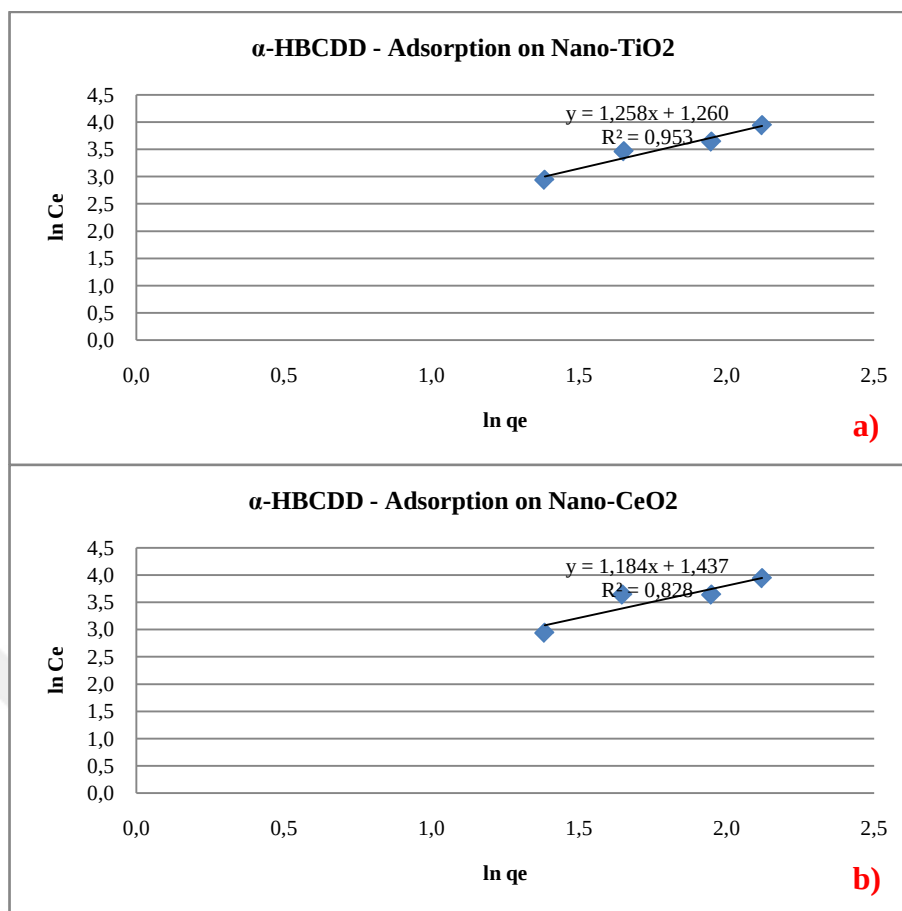


Figure 6.66 Freundlich isotherm for α -HBCDD adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

Table 6.161 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for α -HBCDD with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
nano-TiO ₂	α -HBCDD	0.79	3.53	0.953
nano-CeO ₂	α -HBCDD	0.84	4.21	0.828

6.5.3.2.2 Freundlich Isotherm for PBEB. The R^2 value of the linear line was 0.949, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 1.18 unitless and 8.60 L μg^{-1} , respectively with nano-TiO₂ for PBEB (Appendice-9, Figure 1.a) (Table 6.162). The R^2 , n and K_F , values were calculated as 0.946, 1.19 unitless and 8.85 L μg^{-1} , respectively with nano-CeO₂ for PBEB (Appendice-9, Figure 1.b) (Table 6.162).

Table 6.162 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PBEB with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	PBEB	1.18	8.60	0.949
nano-CeO ₂	PBEB	1.19	8.85	0.946

6.5.3.2.3 *Freundlich Isotherm for PBT*. The R^2 value of the linear line was 0.938, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 1.23 unitless and 9.67 L µg⁻¹, respectively with nano-TiO₂ for PBT (Appendice-9, Figure 2.a) (Table 6.163). The R^2 , n and K_F values were calculated as 0.936, 1.24 unitless and 9.83 L µg⁻¹, respectively with nano-CeO₂ for PBT (Appendice-9, Figure 2.b) (Table 6.163).

Table 6.163 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PBT with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	PBT	1.23	9.67	0.938
nano-CeO ₂	PBT	1.24	9.83	0.936

6.5.3.2.4 *Freundlich Isotherm for TBBPA*. The R^2 value of the linear line was 0.972, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 1.37 unitless and 7.58 L µg⁻¹, respectively with nano-TiO₂ for TBBPA (Appendice-9, Figure 3.a) (Table 6.164). The R^2 , n and K_F values were calculated as 0.833, 1.42 unitless and 8.14 L µg⁻¹, respectively with nano-CeO₂ for TBBPA (Appendice-9, Figure 3.b) (Table 6.164).

Table 6.164 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for TBBPA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	TBBPA	1.37	7.58	0.972
nano-CeO ₂	TBBPA	1.42	8.14	0.833

6.5.3.2.5 *Freundlich Isotherm for AHTN*. The R^2 value of the linear line was 0.905, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 4.67 unitless and $3.18 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for AHTN (Appendice-9, Figure 4.a) (Table 6.165). The R^2 , n and K_F values were calculated as 0.911, 4.59 unitless and $3.21 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for AHTN (Appendice-9, Figure 4.b) (Table 6.165).

Table 6.165 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for AHTN with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	AHTN	4.67	3.18	0.905
nano-CeO ₂	AHTN	4.59	3.21	0.911

6.5.3.2.6 *Freundlich Isotherm for PFOA*. The R^2 value of the linear line was 0.982, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 4.20 unitless and $3.22 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PFOA (Appendice-9, Figure 5.a) (Table 6.166). The R^2 , n and K_F values were calculated as 0.932, 4.20 unitless and $3.28 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PFOA (Appendice-9, Figure 5.b) (Table 6.166).

Table 6.166 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PFOA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	PFOA	4.20	3.22	0.982
nano-CeO ₂	PFOA	4.20	3.28	0.932

6.5.3.2.7 *Freundlich Isotherm for PFOS*. The R^2 value of the linear line was 0.943, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 4.61 unitless and $6.99 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for PFOS (Appendice-9, Figure 6.a) (Table 6.167). The R^2 , n and K_F values were calculated as 0.998, 4.72 unitless and $7.60 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for PFOS (Appendice-9, Figure 6.b) (Table 6.167).

Table 6.167 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for PFOS with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	PFOS	4.61	6.99	0.943
nano-CeO ₂	PFOS	4.72	7.60	0.998

6.5.3.2.8 *Freundlich Isotherm for GFZ*. The R^2 value of the linear line was 0.902, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 3.17 unitless and 3.78 L µg⁻¹, respectively with nano-TiO₂ for GFZ (Appendice-9, Figure 7.a) (Table 6.168). The R^2 , n and K_F values were calculated as 0.876, 3.68 unitless and 4.26 L µg⁻¹, respectively with nano-CeO₂ for GFZ (Appendice-9, Figure 7.b) (Table 6.168).

Table 6.168 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for GFZ with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	GFZ	3.17	3.78	0.902
nano-CeO ₂	GFZ	3.68	4.26	0.876

6.5.3.2.9 *Freundlich Isotherm for TCS*. The R^2 value of the linear line was 0.961, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 3.66 unitless and 4.78 L µg⁻¹, respectively with nano-TiO₂ for TCS (Appendice-9, Figure 8.a) (Table 6.169). The R^2 , n and K_F values were calculated as 0.979, 3.75 unitless and 5.10 L µg⁻¹, respectively with nano-CeO₂ for TCS (Appendice-9, Figure 8.b) (Table 6.169).

Table 6.169 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for TCS with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K _F (L µg ⁻¹)	R ²
nano-TiO ₂	TCS	3.66	4.78	0.961
nano-CeO ₂	TCS	3.75	5.10	0.979

6.5.3.2.10 *Freundlich Isotherm for IBU*. The R^2 value of the linear line was 0.813, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 10.10 unitless and $5.61 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for IBU (Appendice-9, Figure 9.a) (Table 6.170). The R^2 , n and K_F values were calculated as 0.868, 9.17 unitless and $5.70 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for IBU (Appendice-9, Figure 9.b) (Table 6.170).

Table 6.170 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for IBU with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	IBU	10.10	5.61	0.813
nano-CeO ₂	IBU	9.17	5.70	0.868

6.5.3.2.11 *Freundlich Isotherm for CIP*. The R^2 value of the linear line was 0.982, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 16.67 unitless and $15.00 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for CIP (Appendice-9, Figure 10.a) (Table 6.171). The R^2 , n and K_F values were calculated as 0.981, 13.70 unitless and $15.91 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for CIP (Appendice-9, Figure 10.b) (Table 6.171).

Table 6.171 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for CIP with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F ($\text{L } \mu\text{g}^{-1}$)	R^2
nano-TiO ₂	CIP	16.67	15.00	0.982
nano-CeO ₂	CIP	13.70	15.91	0.981

6.5.3.2.12 *Freundlich Isotherm for NDMA*. The R^2 value of the linear line was 0.982, while the adsorption intensity (n) and Freundlich constant (K_F) values were calculated as 16.67 unitless and $24.00 \text{ L } \mu\text{g}^{-1}$, respectively with nano-TiO₂ for NDMA (Appendice-9, Figure 11.a) (Table 6.172). The R^2 , n and K_F values were calculated as 0.936, 16.13 unitless and $26.15 \text{ L } \mu\text{g}^{-1}$, respectively with nano-CeO₂ for NDMA (Appendice-9, Figure 11.b) (Table 6.172).

Table 6.172 Comparison of the kinetic constants and regression coefficients (R^2) relevant to Freundlich isotherm for NDMA with nano-TiO₂ and nano-CeO₂

Adsorbent	Adsorbate	n (unitless)	K_F (L μg^{-1})	R^2
nano-TiO ₂	NDMA	16.67	24.00	0.982
nano-CeO ₂	NDMA	16.13	26.15	0.936

6.5.3.3 Evaluation of Adsorption Isotherms in the Photocatalytic Treatment Process

In Freundlich isotherm the adsorption intensity (n) must be higher than 1 to provide physical adsorption process (Olakitan, Mi-Hwa, & Dong-Su, 2009). In this study, the n value of α -HBCDD was lower than 1 both for the experiments with nano-TiO₂ and nano-CeO₂ (Table 6.173). The kinetic data showed that the kinetic constants were meaningful for Langmuir isotherm in the comparison with Freundlich isotherm. The kinetic constants of Langmuir isotherm were found to be high for hydrophobic (brominated, aromatic, fluoro and phenolic) micropollutants ($\log K_{OW} > 4.0$) in the comparison with hydrophilic (CIP and NDMA) micropollutants ($\log K_{OW} < 2.5$) for 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00 (Table 6.173). The highest Langmuir isotherm constants; q_m and K_L were found between 28.57 – 76.92 $\mu\text{g g}^{-1}$ and 0.071 – 0.109 L μg^{-1} , respectively for the brominated micropollutants at the aforementioned experimental conditions (Table 6.173). Moreover, the lowest Langmuir isotherm constants; q_m and K_L were calculated between 0.23 – 0.37 $\mu\text{g g}^{-1}$ and 0.0001 – 0.0005 L μg^{-1} , respectively for the hydrophilic (CIP and NDMA) micropollutants at the aforementioned experimental conditions (Table 6.173). As a result of this study, the description of adsorption process with Langmuir isotherm is an appropriate modelling rather than Freundlich isotherm both for the experiments with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions.

Table 6.173 Langmuir isotherm constants (q_m , K_L and R^2) for all studied micropollutants with nano-TiO₂ and nano-CeO₂

Micropollutant	Langmuir isotherm with nano-TiO ₂			Langmuir isotherm with nano-CeO ₂		
	q_m ($\mu\text{g g}^{-1}$)	K_L (L μg^{-1})	R^2	q_m ($\mu\text{g g}^{-1}$)	K_L (L μg^{-1})	R^2
α-HBCDD	71.43	0.077	0.955	76.92	0.109	0.853
PBEB	66.67	0.076	0.937	66.67	0.084	0.935
PBT	66.67	0.076	0.932	66.67	0.082	0.931
TBBPA	28.57	0.071	0.972	30.30	0.075	0.817
AHTN	1.03	0.071	0.922	1.08	0.072	0.803
PFOA	1.00	0.063	0.930	1.08	0.066	0.870
PFOS	0.91	0.006	0.954	1.03	0.006	0.954
GFZ	0.91	0.026	0.807	1.07	0.027	0.903
TCS	0.91	0.015	0.873	1.04	0.015	0.904
IBU	0.35	0.006	0.923	0.41	0.006	0.964
CIP	0.23	0.0004	0.988	0.37	0.0005	0.989
NDMA	0.23	0.0001	0.988	0.32	0.0001	0.998

6.5.4 Ultrasound Treatment Kinetics

Recent literature studies showed that the kinetics of the ultrasound treatment process treating raw hospital wastewater containing micropollutants have not been investigated. In this study, the experimental results obtained from the ultrasound treatment were applied to various kinetic models such as, zero, half, first and second-order to determine the optimum brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOA and PFOS), nitroso (NDMA), phenolic (TCS, GFZ, CIP and IBU) and aromatic (AHTN) micropollutant removal kinetics with nano-TiO₂ and nano-CeO₂. The kinetic studies of ultrasound treatment were carried out with nano-TiO₂ and nano-CeO₂ (0.20, 0.40, 0.60 and 0.80 g L⁻¹) at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C and constant sonicator frequency of 132 kHz.

6.5.4.1 Zero-Order Removal Models

The zero-order kinetic constant (k_0 , day⁻¹) can be obtained from the slope of the line plotting the (S_e) versus time (t). (S_e) shows effluent micropollutant concentration ($\mu\text{g L}^{-1}$). (t) is time representing experimental duration (min) through micropollutant removal.

6.5.4.1.1 Zero-Order Removal Model for α -HBCDD. Zero-order α -HBCDD removal constant, k_0 value was calculated as $3 \times 10^{-5} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.994 for α -HBCDD in the ultrasound treatment experiments with nano-TiO₂ (Figure 6.67.a). For the experiments carried out with nano-CeO₂, zero-order α -HBCDD removal constant, k_0 value was calculated as $3 \times 10^{-5} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.987 for α -HBCDD in the ultrasound treatment experiments with nano-CeO₂ (Figure 6.67.b).

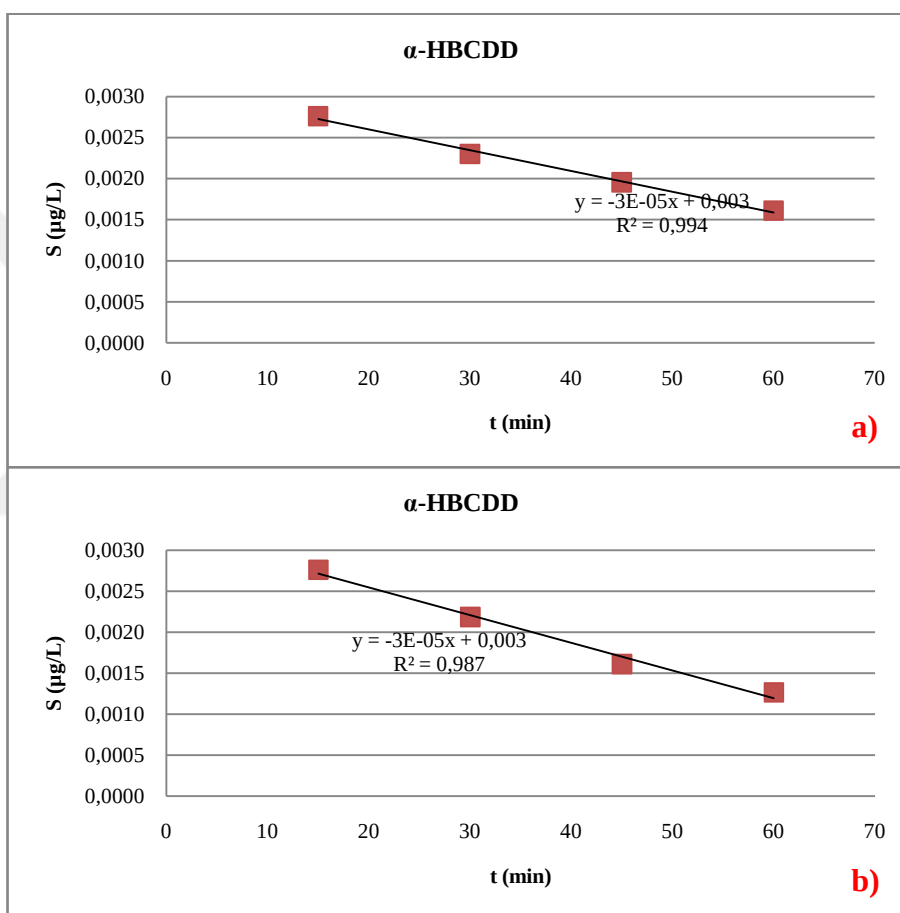


Figure 6.67 Zero-order α -HBCDD removal with (a) nano-TiO₂ (b) nano-CeO₂

Table 6.174 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for α -HBCDD with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day ⁻¹)	R^2
nano-TiO ₂	α -HBCDD	3×10^{-5}	0.994
nano-CeO ₂	α -HBCDD	3×10^{-5}	0.987

6.5.4.1.2 *Zero-Order Removal Model for PBEB.* Zero-order PBEB removal constant, k_0 value was calculated as $7 \times 10^{-6} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.994 for PBEB in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 1.a) (Table 6.175). For the experiments with nano-CeO₂, zero-order PBEB removal constant, k_0 value was calculated as $9 \times 10^{-6} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.975 for PBEB (Appendice-10, Figure 1.b) (Table 6.175).

Table 6.175 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PBEB with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day^{-1})	R^2
nano-TiO ₂	PBEB	7×10^{-6}	0.994
nano-CeO ₂	PBEB	9×10^{-6}	0.975

6.5.4.1.3 *Zero-Order Removal Model for PBT.* Zero-order PBT removal constant, k_0 value was calculated as $5 \times 10^{-6} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.996 for PBT in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 2.a) (Table 6.176). For the experiments with nano-CeO₂, zero-order PBT removal constant, k_0 value was calculated as $6 \times 10^{-6} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.965 for PBT (Appendice-10, Figure 2.b) (Table 6.176).

Table 6.176 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PBT with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day^{-1})	R^2
nano-TiO ₂	PBT	5×10^{-6}	0.996
nano-CeO ₂	PBT	6×10^{-6}	0.965

6.5.4.1.4 *Zero-Order Removal Model for TBBPA.* Zero-order TBBPA removal constant, k_0 value was calculated as $3 \times 10^{-5} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.994 for TBBPA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 3.a) (Table 6.177). For the experiments with nano-CeO₂, zero-order TBBPA removal constant, k_0 value was calculated as $4 \times 10^{-5} \text{ day}^{-1}$ with a

correlation coefficient (R^2) of 0.962 for TBBPA (Appendice-10, Figure 3.b) (Table 6.177).

Table 6.177 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for TBBPA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day ⁻¹)	R^2
nano-TiO ₂	TBBPA	3×10^{-5}	0.994
nano-CeO ₂	TBBPA	4×10^{-5}	0.962

6.5.4.1.5 Zero-Order Removal Model for AHTN. Zero-order AHTN removal constant, k_0 value was calculated as 0.453 day⁻¹ with a correlation coefficient (R^2) of 0.994 for AHTN in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 4.a) (Table 6.178). For the experiments with nano-CeO₂, zero-order AHTN removal constant, k_0 value was calculated as 0.687 day⁻¹ with a correlation coefficient (R^2) of 1.000 for AHTN (Appendice-10, Figure 4.b) (Table 6.178).

Table 6.178 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for AHTN with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day ⁻¹)	R^2
nano-TiO ₂	AHTN	0.453	0.994
nano-CeO ₂	AHTN	0.687	1.000

6.5.4.1.6 Zero-Order Removal Model for PFOA. Zero-order PFOA removal constant, k_0 value was calculated as 0.0004 day⁻¹ with a correlation coefficient (R^2) of 0.995 for PFOA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 5.a) (Table 6.179). For the experiments with nano-CeO₂, zero-order PFOA removal constant, k_0 value was calculated as 0.001 day⁻¹ with a correlation coefficient (R^2) of 0.995 for PFOA (Appendice-10, Figure 5.b) (Table 6.179).

Table 6.179 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PFOA with nano-TiO₂ and nano-CeO₂

Zero-order			
Nanoparticle	Micropollutant	k_0 (day ⁻¹)	R^2
nano-TiO ₂	PFOA	0.0004	0.995
nano-CeO ₂	PFOA	0.001	0.995

6.5.4.1.7 Zero-Order Removal Model for PFOS. Zero-order PFOS removal constant, k_0 value was calculated as 5×10^{-5} day⁻¹ with a correlation coefficient (R^2) of 0.980 for PFOS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 6.a) (Table 6.180). For the experiments with nano-CeO₂, zero-order PFOS removal constant, k_0 value was calculated as 7×10^{-5} day⁻¹ with a correlation coefficient (R^2) of 0.996 for PFOS (Appendice-10, Figure 6.b) (Table 6.180).

Table 6.180 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for PFOS with nano-TiO₂ and nano-CeO₂

Zero-order			
Nanoparticle	Micropollutant	k_0 (day ⁻¹)	R^2
nano-TiO ₂	PFOS	5×10^{-5}	0.980
nano-CeO ₂	PFOS	7×10^{-5}	0.996

6.5.4.1.8 Zero-Order Removal Model for GFZ. Zero-order GFZ removal constant, k_0 value was calculated as 0.081 day⁻¹ with a correlation coefficient (R^2) of 0.988 for GFZ in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 7.a) (Table 6.181). For the experiments with nano-CeO₂, zero-order GFZ removal constant, k_0 value was calculated as 0.092 day⁻¹ with a correlation coefficient (R^2) of 0.965 for GFZ (Appendice-10, Figure 7.b) (Table 6.181).

Table 6.181 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for GFZ with nano-TiO₂ and nano-CeO₂

Zero-order			
Nanoparticle	Micropollutant	k_0 (day ⁻¹)	R^2
nano-TiO ₂	GFZ	0.081	0.988
nano-CeO ₂	GFZ	0.092	0.965

6.5.4.1.9 Zero-Order Removal Model for TCS. Zero-order TCS removal constant, k_0 value was calculated as 0.553 day^{-1} with a correlation coefficient (R^2) of 0.988 for TCS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 8.a) (Table 6.182). For the experiments with nano-CeO₂, zero-order TCS removal constant, k_0 value was calculated as 0.770 day^{-1} with a correlation coefficient (R^2) of 0.966 for TCS (Appendice-10, Figure 8.b) (Table 6.182).

Table 6.182 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for TCS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day^{-1})	R^2
nano-TiO ₂	TCS	0.553	0.988
nano-CeO ₂	TCS	0.770	0.966

6.5.4.1.10 Zero-Order Removal Model for IBU. Zero-order IBU removal constant, k_0 value was calculated as 0.073 day^{-1} with a correlation coefficient (R^2) of 0.965 for IBU in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 9.a) (Table 6.183). For the experiments with nano-CeO₂, zero-order IBU removal constant, k_0 value was calculated as 0.116 day^{-1} with a correlation coefficient (R^2) of 0.968 for IBU (Appendice-10, Figure 9.b) (Table 6.183).

Table 6.183 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for IBU with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Zero-order	
		k_0 (day^{-1})	R^2
nano-TiO ₂	IBU	0.073	0.965
nano-CeO ₂	IBU	0.116	0.968

6.5.4.1.11 Zero-Order Removal Model for CIP. Zero-order CIP removal constant, k_0 value was calculated as 1.148 day^{-1} with a correlation coefficient (R^2) of 0.994 for CIP in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 10.a) (Table 6.184). For the experiments with nano-CeO₂, zero-order CIP removal constant, k_0 value was calculated as 1.183 day^{-1} with a correlation coefficient (R^2) of 0.996 for CIP (Appendice-10, Figure 10.b) (Table 6.184).

Table 6.184 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for CIP with nano-TiO₂ and nano-CeO₂

Zero-order			
Nanoparticle	Micropollutant	k_0 (day ⁻¹)	R^2
nano-TiO ₂	CIP	1.148	0.994
nano-CeO ₂	CIP	1.183	0.996

6.5.4.1.12 *Zero-Order Removal Model for NDMA*. Zero-order NDMA removal constant, k_0 value was calculated as 0.429 day⁻¹ with a correlation coefficient (R^2) of 0.965 for NDMA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-10, Figure 11.a) (Table 6.185). For the experiments with nano-CeO₂, zero-order NDMA removal constant, k_0 value was calculated as 0.627 day⁻¹ with a correlation coefficient (R^2) of 0.974 for NDMA (Appendice-10, Figure 11.b) (Table 6.185).

Table 6.185 Comparison of the kinetic constants and regression coefficients (R^2) relevant to zero-order for NDMA with nano-TiO₂ and nano-CeO₂

Zero-order			
Nanoparticle	Micropollutant	k_0 (day ⁻¹)	R^2
nano-TiO ₂	NDMA	0.429	0.965
nano-CeO ₂	NDMA	0.627	0.974

6.5.4.2 Half-Order Removal Models

The half-order kinetic constant ($k_{1/2}$, day⁻¹) can be obtained from the slope of the line plotting the $(1/\sqrt{S_e})$ versus time (t). S_e shows effluent micropollutant concentration ($\mu\text{g L}^{-1}$). (t) is time representing experimental duration (min) through micropollutant removal.

6.5.4.2.1 *Half-Order Removal Model for α -HBCDD*. Half-order α -HBCDD removal constant, $k_{1/2}$ value was calculated as 0.129 day⁻¹ with a correlation coefficient (R^2) of 0.995 for α -HBCDD in the ultrasound treatment experiments with nano-TiO₂ (Figure 6.68.a) (Table 6.186). For the experiments carried out with nano-CeO₂, half-order α -HBCDD removal constant, $k_{1/2}$ value was calculated as 0.205 day⁻¹.

¹ with a correlation coefficient (R^2) of 0.994 for α -HBCDD in the ultrasound treatment experiments with nano-CeO₂ (Figure 6.68.b) (Table 6.186).

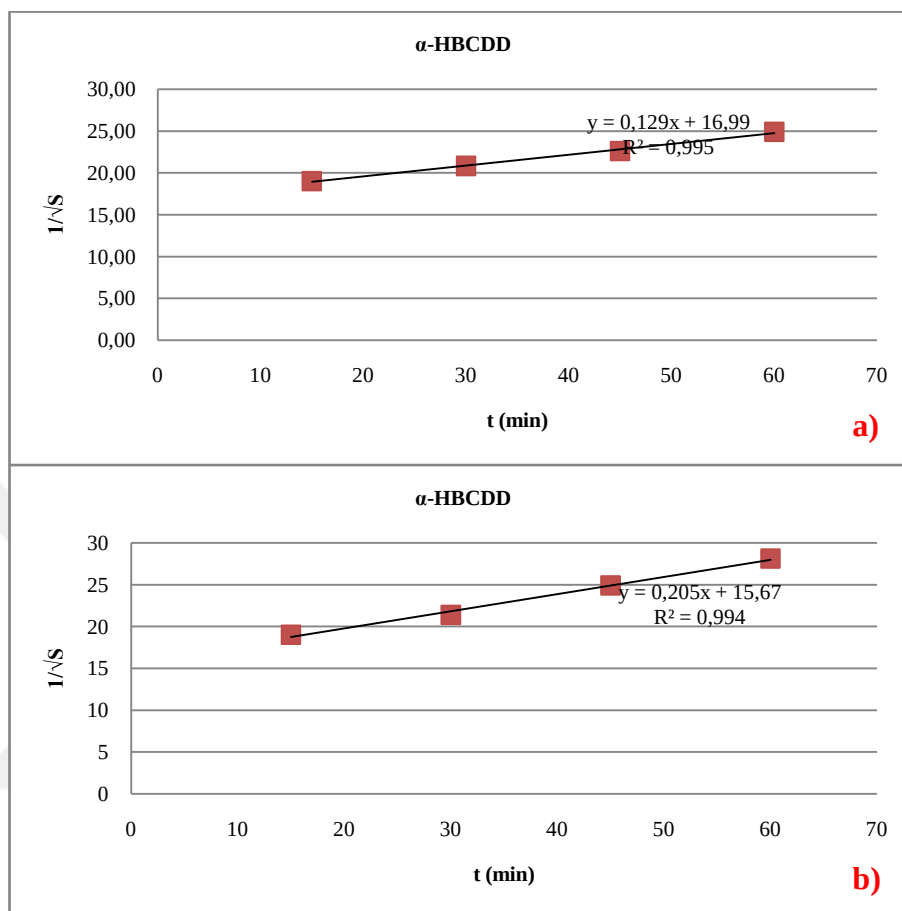


Figure 6.68 Half-order α -HBCDD removal with (a) nano-TiO₂ (b) nano-CeO₂

Table 6.186 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for α -HBCDD with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	α -HBCDD	0.129	0.995
nano-CeO ₂	α -HBCDD	0.205	0.994

6.5.4.2.2 Half-Order Removal Model for PBEB. Half-order PBEB removal constant, $k_{1/2}$ value was calculated as 0.179 day⁻¹ with a correlation coefficient (R^2) of 0.998 for PBEB in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 1.a) (Table 6.187). For the experiments with nano-CeO₂, half-order PBEB removal constant, $k_{1/2}$ value was calculated as 0.314 day⁻¹ with a

correlation coefficient (R^2) of 0.999 for PBEB (Appendice-11, Figure 1.b) (Table 6.187).

Table 6.187 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PBEB with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	PBEB	0.179	0.998
nano-CeO ₂	PBEB	0.314	0.999

6.5.4.2.3 Half-Order Removal Model for PBT. Half-order PBT removal constant, $k_{1/2}$ value was calculated as 0.253 day⁻¹ with a correlation coefficient (R^2) of 0.987 for PBT in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 2.a) (Table 6.188). For the experiments with nano-CeO₂, half-order PBT removal constant, $k_{1/2}$ value was calculated as 0.428 day⁻¹ with a correlation coefficient (R^2) of 0.953 for PBT (Appendice-11, Figure 2.b) (Table 6.188).

Table 6.188 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PBT with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	PBT	0.253	0.987
nano-CeO ₂	PBT	0.428	0.953

6.5.4.2.4 Half-Order Removal Model for TBBPA. Half-order TBBPA removal constant, $k_{1/2}$ value was calculated as 0.133 day⁻¹ with a correlation coefficient (R^2) of 0.973 for TBBPA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 3.a) (Table 6.189). For the experiments with nano-CeO₂, half-order TBBPA removal constant, $k_{1/2}$ value was calculated as 0.237 day⁻¹ with a correlation coefficient (R^2) of 0.863 for TBBPA (Appendice-11, Figure 3.b) (Table 6.189).

Table 6.189 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for TBBPA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	TBBPA	0.133	0.973
nano-CeO ₂	TBBPA	0.237	0.863

6.5.4.2.5 *Half-Order Removal Model for AHTN*. Half-order AHTN removal constant, $k_{1/2}$ value was calculated as 0.0006 day⁻¹ with a correlation coefficient (R^2) of 0.999 for AHTN in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 4.a) (Table 6.190). For the experiments with nano-CeO₂, half-order AHTN removal constant, $k_{1/2}$ value was calculated as 0.001 day⁻¹ with a correlation coefficient (R^2) of 0.977 for AHTN (Appendice-11, Figure 4.b) (Table 6.190).

Table 6.190 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for AHTN with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	AHTN	0.0006	0.999
nano-CeO ₂	AHTN	0.001	0.977

6.5.4.2.6 *Half-Order Removal Model for PFOA*. Half-order PFOA removal constant, $k_{1/2}$ value was calculated as 0.010 day⁻¹ with a correlation coefficient (R^2) of 0.999 for PFOA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 5.a) (Table 6.191). For the experiments with nano-CeO₂, half-order PFOA removal constant, $k_{1/2}$ value was calculated as 0.018 day⁻¹ with a correlation coefficient (R^2) of 0.982 for PFOA (Appendice-11, Figure 5.b) (Table 6.191).

Table 6.191 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PFOA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	PFOA	0.010	0.999
nano-CeO ₂	PFOA	0.018	0.982

6.5.4.2.7 *Half-Order Removal Model for PFOS*. Half-order PFOS removal constant, $k_{1/2}$ value was calculated as 0.043 day⁻¹ with a correlation coefficient (R^2) of 0.991 for PFOS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 6.a) (Table 6.192). For the experiments with nano-CeO₂, half-order PFOS removal constant, $k_{1/2}$ value was calculated as 0.067 day⁻¹ with a correlation coefficient (R^2) of 0.973 for PFOS (Appendice-11, Figure 6.b) (Table 6.192).

Table 6.192 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for PFOS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	PFOS	0.043	0.991
nano-CeO ₂	PFOS	0.067	0.973

6.5.4.2.8 *Half-Order Removal Model for GFZ*. Half-order GFZ removal constant, $k_{1/2}$ value was calculated as 0.006 day⁻¹ with a correlation coefficient (R^2) of 0.979 for GFZ in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 7.a) (Table 6.193). For the experiments with nano-CeO₂, half-order GFZ removal constant, $k_{1/2}$ value was calculated as 0.006 day⁻¹ with a correlation coefficient (R^2) of 0.988 for GFZ (Appendice-11, Figure 7.b) (Table 6.193).

Table 6.193 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for GFZ with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	GFZ	0.006	0.979
nano-CeO ₂	GFZ	0.006	0.988

6.5.4.2.9 Half-Order Removal Model for TCS. Half-order TCS removal constant, $k_{1/2}$ value was calculated as 0.001 day^{-1} with a correlation coefficient (R^2) of 0.996 for TCS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 8.a) (Table 6.194). For the experiments with nano-CeO₂, half-order TCS removal constant, $k_{1/2}$ value was calculated as 0.002 day^{-1} with a correlation coefficient (R^2) of 0.957 for TCS (Appendice-11, Figure 8.b) (Table 6.194).

Table 6.194 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for TCS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day^{-1})	R^2
nano-TiO ₂	TCS	0.001	0.996
nano-CeO ₂	TCS	0.002	0.957

6.5.4.2.10 Half-Order Removal Model for IBU. Half-order IBU removal constant, $k_{1/2}$ value was calculated as 0.003 day^{-1} with a correlation coefficient (R^2) of 0.907 for IBU in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 9.a) (Table 6.195). For the experiments with nano-CeO₂, half-order IBU removal constant, $k_{1/2}$ value was calculated as 0.004 day^{-1} with a correlation coefficient (R^2) of 0.990 for IBU (Appendice-11, Figure 9.b) (Table 6.195).

Table 6.195 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for IBU with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day^{-1})	R^2
nano-TiO ₂	IBU	0.003	0.907
nano-CeO ₂	IBU	0.004	0.990

6.5.4.2.11 Half-Order Removal Model for CIP. Half-order CIP removal constant, $k_{1/2}$ value was calculated as 0.001 day^{-1} with a correlation coefficient (R^2) of 0.996 for CIP in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 10.a) (Table 6.196). For the experiments with nano-CeO₂, half-order CIP removal constant, $k_{1/2}$ value was calculated as 0.001 day^{-1} with a correlation coefficient (R^2) of 0.976 for CIP (Appendice-11, Figure 10.b) (Table 6.196).

Table 6.196 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for CIP with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	CIP	0.001	0.996
nano-CeO ₂	CIP	0.001	0.976

6.5.4.2.12 *Half-Order Removal Model for NDMA*. Half-order NDMA removal constant, $k_{1/2}$ value was calculated as 0.0005 day⁻¹ with a correlation coefficient (R^2) of 0.987 for NDMA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-11, Figure 11.a) (Table 6.197). For the experiments with nano-CeO₂, half-order NDMA removal constant, $k_{1/2}$ value was calculated as 0.001 day⁻¹ with a correlation coefficient (R^2) of 0.944 for NDMA (Appendice-11, Figure 11.b) (Table 6.197).

Table 6.197 Comparison of the kinetic constants and regression coefficients (R^2) relevant to half-order for NDMA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Half-order	
		$k_{1/2}$ (day ⁻¹)	R^2
nano-TiO ₂	NDMA	0.0005	0.987
nano-CeO ₂	NDMA	0.001	0.944

6.5.4.3 First-Order Removal Models

The first-order kinetic constant (k_1 , day⁻¹) can be obtained from the slope of the line plotting the Ln (S_e) versus time (t). S_e shows effluent micropollutant concentration ($\mu\text{g L}^{-1}$). (t) is time representing experimental duration (min) through micropollutant removal.

6.5.4.3.1 *First-Order Removal Model for α -HBCDD*. First-order α -HBCDD removal constant, k_1 value was calculated as 0.012 day⁻¹ with a correlation coefficient (R^2) of 0.999 for α -HBCDD in the ultrasound treatment experiments with nano-TiO₂ (Figure 6.69.a) (Table 6.198). For the experiments carried out with nano-CeO₂, first-order α -HBCDD removal constant, k_1 value was calculated as 0.018 day⁻¹

with a correlation coefficient (R^2) of 0.997 for α -HBCDD in the ultrasound treatment experiments with nano-CeO₂ (Figure 6.69.b) (Table 6.198).

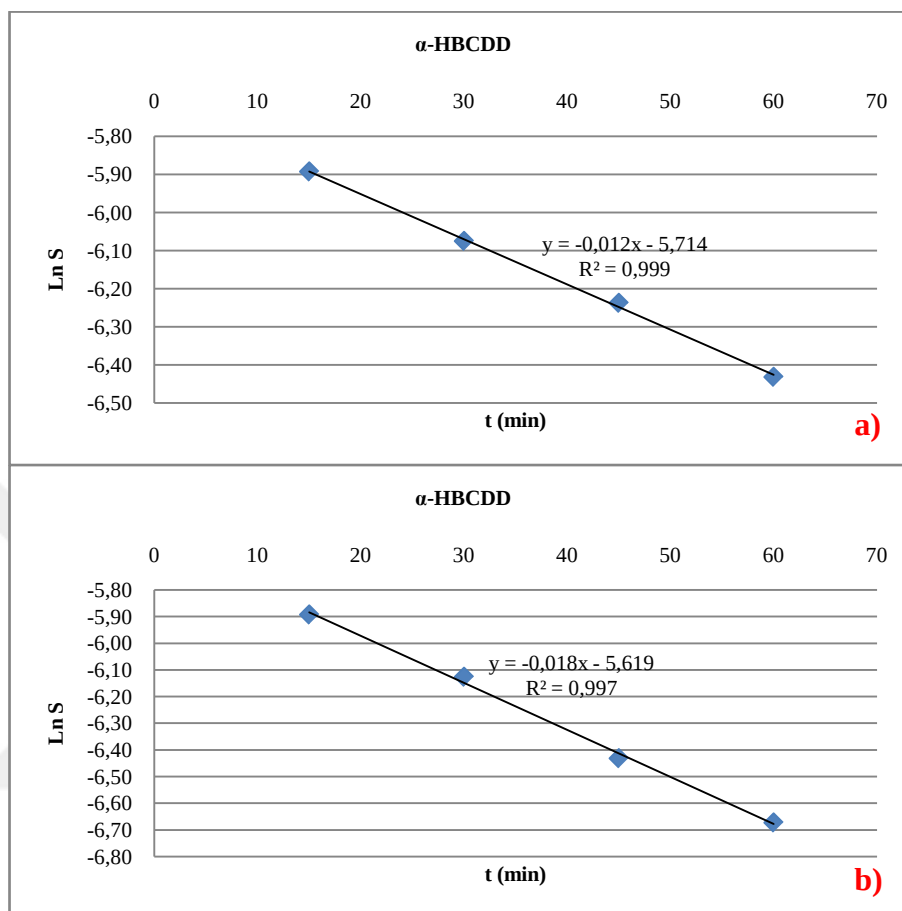


Figure 6.69 First-order α -HBCDD removal with (a) nano-TiO₂ (b) nano-CeO₂

Table 6.198 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for α -HBCDD with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	α -HBCDD	0.012	0.999
nano-CeO ₂	α -HBCDD	0.018	0.997

6.5.4.3.2 First-Order Removal Model for PBEB. First-order PBEB removal constant, k_1 value was calculated as 0.010 day⁻¹ with a correlation coefficient (R^2) of 0.999 for PBEB in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 1.a) (Table 6.199). For the experiments with nano-CeO₂, first-order PBEB removal constant, k_1 value was calculated as 0.015 day⁻¹ with a

correlation coefficient (R^2) of 0.997 for PBEB (Appendice-12, Figure 1.b) (Table 6.199).

Table 6.199 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PBEB with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	PBEB	0.010	0.999
nano-CeO ₂	PBEB	0.015	0.997

6.5.4.3.3 First-Order Removal Model for PBT. First-order PBT removal constant, k_1 value was calculated as 0.011 day⁻¹ with a correlation coefficient (R^2) of 0.993 for PBT in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 2.a) (Table 6.200). For the experiments with nano-CeO₂, first-order PBT removal constant, k_1 value was calculated as 0.016 day⁻¹ with a correlation coefficient (R^2) of 0.960 for PBT (Appendice-12, Figure 2.b) (Table 6.200).

Table 6.200 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PBT with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	PBT	0.011	0.993
nano-CeO ₂	PBT	0.016	0.960

6.5.4.3.4 First-Order Removal Model for TBBPA. First-order TBBPA removal constant, k_1 value was calculated as 0.013 day⁻¹ with a correlation coefficient (R^2) of 0.985 for TBBPA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 3.a) (Table 6.201). For the experiments with nano-CeO₂, first-order TBBPA removal constant, k_1 value was calculated as 0.021 day⁻¹ with a correlation coefficient (R^2) of 0.903 for TBBPA (Appendice-12, Figure 3.b) (Table 6.201).

Table 6.201 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for TBBPA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	TBBPA	0.013	0.985
nano-CeO ₂	TBBPA	0.021	0.903

6.5.4.3.5 *First-Order Removal Model for AHTN*. First-order AHTN removal constant, k_1 value was calculated as 0.009 day⁻¹ with a correlation coefficient (R^2) of 0.999 for AHTN in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 4.a) (Table 6.202). For the experiments with nano-CeO₂, first-order AHTN removal constant, k_1 value was calculated as 0.015 day⁻¹ with a correlation coefficient (R^2) of 0.990 for AHTN (Appendice-12, Figure 4.b) (Table 6.202).

Table 6.202 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for AHTN with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	AHTN	0.009	0.999
nano-CeO ₂	AHTN	0.015	0.990

6.5.4.3.6 *First-Order Removal Model for PFOA*. First-order PFOA removal constant, k_1 value was calculated as 0.006 day⁻¹ with a correlation coefficient (R^2) of 0.998 for PFOA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 5.a) (Table 6.203). For the experiments with nano-CeO₂, first-order PFOA removal constant, k_1 value was calculated as 0.009 day⁻¹ with a correlation coefficient (R^2) of 0.988 for PFOA (Appendice-12, Figure 5.b) (Table 6.203).

Table 6.203 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PFOA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	PFOA	0.006	0.998
nano-CeO ₂	PFOA	0.009	0.988

6.5.4.3.7 First-Order Removal Model for PFOS. First-order PFOS removal constant, k_1 value was calculated as 0.007 day⁻¹ with a correlation coefficient (R^2) of 0.989 for PFOS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 6.a) (Table 6.204). For the experiments with nano-CeO₂, first-order PFOS removal constant, k_1 value was calculated as 0.011 day⁻¹ with a correlation coefficient (R^2) of 0.984 for PFOS (Appendice-12, Figure 6.b) (Table 6.204).

Table 6.204 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for PFOS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	PFOS	0.007	0.989
nano-CeO ₂	PFOS	0.011	0.984

6.5.4.3.8 First-Order Removal Model for GFZ. First-order GFZ removal constant, k_1 value was calculated as 0.022 day⁻¹ with a correlation coefficient (R^2) of 0.995 for GFZ in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 7.a) (Table 6.205). For the experiments with nano-CeO₂, first-order GFZ removal constant, k_1 value was calculated as 0.024 day⁻¹ with a correlation coefficient (R^2) of 0.996 for GFZ (Appendice-12, Figure 7.b) (Table 6.205).

Table 6.205 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for GFZ with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	GFZ	0.022	0.995
nano-CeO ₂	GFZ	0.024	0.996

6.5.4.3.9 First-Order Removal Model for TCS. First-order TCS removal constant, k_1 value was calculated as 0.014 day^{-1} with a correlation coefficient (R^2) of 0.998 for TCS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 8.a) (Table 6.206). For the experiments with nano-CeO₂, first-order TCS removal constant, k_1 value was calculated as 0.022 day^{-1} with a correlation coefficient (R^2) of 0.963 for TCS (Appendice-12, Figure 8.b) (Table 6.206).

Table 6.206 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for TCS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day^{-1})	R^2
nano-TiO ₂	TCS	0.014	0.998
nano-CeO ₂	TCS	0.022	0.963

6.5.4.3.10 First-Order Removal Model for IBU. First-order IBU removal constant, k_1 value was calculated as 0.013 day^{-1} with a correlation coefficient (R^2) of 0.929 for IBU in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 9.a) (Table 6.207). For the experiments with nano-CeO₂, first-order IBU removal constant, k_1 value was calculated as 0.018 day^{-1} with a correlation coefficient (R^2) of 0.987 for IBU (Appendice-12, Figure 9.b) (Table 6.207).

Table 6.207 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for IBU with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day^{-1})	R^2
nano-TiO ₂	IBU	0.013	0.929
nano-CeO ₂	IBU	0.018	0.987

6.5.4.3.11 First-Order Removal Model for CIP. First-order CIP removal constant, k_1 value was calculated as 0.012 day^{-1} with a correlation coefficient (R^2) of 0.999 for CIP in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 10.a) (Table 6.208). For the experiments with nano-CeO₂, first-order CIP removal constant, k_1 value was calculated as 0.017 day^{-1} with a correlation coefficient (R^2) of 0.988 for CIP (Appendice-12, Figure 10.b) (Table 6.208).

Table 6.208 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for CIP with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	CIP	0.012	0.999
nano-CeO ₂	CIP	0.017	0.988

6.5.4.3.12 *First-Order Removal Model for NDMA*. First-order NDMA removal constant, k_1 value was calculated as 0.007 day⁻¹ with a correlation coefficient (R^2) of 0.981 for NDMA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-12, Figure 11.a) (Table 6.209). For the experiments with nano-CeO₂, first-order NDMA removal constant, k_1 value was calculated as 0.011 day⁻¹ with a correlation coefficient (R^2) of 0.958 for NDMA (Appendice-12, Figure 11.b) (Table 6.209).

Table 6.209 Comparison of the kinetic constants and regression coefficients (R^2) relevant to first-order for NDMA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	First-order	
		k_1 (day ⁻¹)	R^2
nano-TiO ₂	NDMA	0.007	0.981
nano-CeO ₂	NDMA	0.011	0.958

6.5.4.4 Second-Order Removal Models

The second-order kinetic constant (k_2 , L μg^{-1} day⁻¹) can be obtained from the slope of the line plotting the $1/(S_e)$ versus time (t). S_e shows effluent micropollutant concentration ($\mu\text{g L}^{-1}$). (t) is time representing experimental duration (min) through micropollutant removal.

6.5.4.4.1 *Second-Order Removal Model for α -HBCDD*. Second-order α -HBCDD removal constant, k_2 value was calculated as 5.687 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.989 for α -HBCDD in the ultrasound treatment experiments with nano-TiO₂ (Figure 6.70.a) (Table 6.210). For the experiments carried out with nano-CeO₂, second-order α -HBCDD removal constant, k_2 value was calculated as 9.653 L

$\mu\text{g}^{-1} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.985 for α -HBCDD in the ultrasound treatment experiments with nano-CeO₂ (Figure 6.70.b) (Table 6.210).

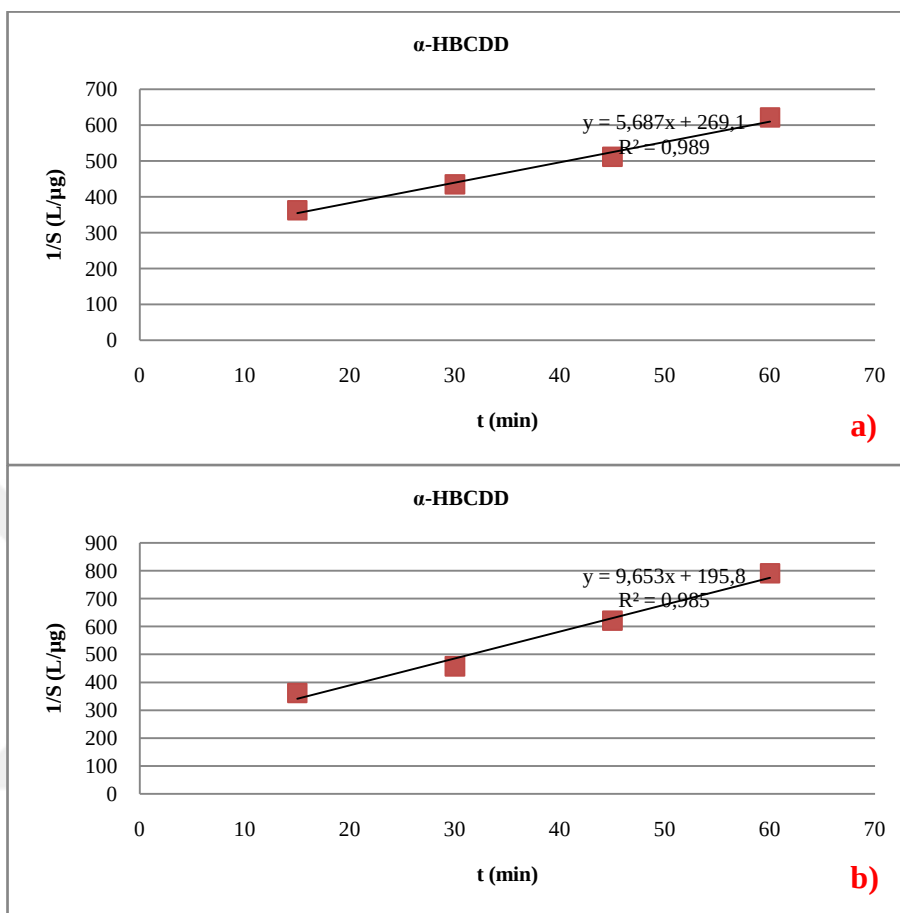


Figure 6.70 Second-order α -HBCDD removal with (a) nano-TiO₂ (b) nano-CeO₂

Table 6.210 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for α -HBCDD with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 ($\text{L } \mu\text{g}^{-1} \text{ day}^{-1}$)	R^2
nano-TiO ₂	α -HBCDD	5.687	0.989
nano-CeO ₂	α -HBCDD	9.653	0.985

6.5.4.4.2 Second-Order Removal Model for PBEB. Second-order PBEB removal constant, k_2 value was calculated as $13.30 \text{ L } \mu\text{g}^{-1} \text{ day}^{-1}$ with a correlation coefficient (R^2) of 0.994 for PBEB in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 1.a) (Table 6.211). For the experiments with nano-CeO₂, second-order PBEB removal constant, k_2 value was calculated as $25.99 \text{ L } \mu\text{g}^{-1} \text{ day}^{-1}$

with a correlation coefficient (R^2) of 0.997 for PBEB (Appendice-13, Figure 1.b) (Table 6.211).

Table 6.211 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PBEB with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	PBEB	13.30	0.994
nano-CeO ₂	PBEB	25.99	0.997

6.5.4.4.3 Second-Order Removal Model for PBT. Second-order PBT removal constant, k_2 value was calculated as 23.45 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.980 for PBT in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 2.a) (Table 6.212). For the experiments with nano-CeO₂, second-order PBT removal constant, k_2 value was calculated as 45.53 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.944 for PBT (Appendice-13, Figure 2.b) (Table 6.212).

Table 6.212 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PBT with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	PBT	23.45	0.980
nano-CeO ₂	PBT	45.53	0.944

6.5.4.4.4 Second-Order Removal Model for TBBPA. Second-order TBBPA removal constant, k_2 value was calculated as 5.631 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.958 for TBBPA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 3.a) (Table 6.213). For the experiments with nano-CeO₂, second-order TBBPA removal constant, k_2 value was calculated as 11.01 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.822 for TBBPA (Appendice-13, Figure 3.b) (Table 6.213).

Table 6.213 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for TBBPA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	TBBPA	5.631	0.958
nano-CeO ₂	TBBPA	11.01	0.822

6.5.4.4.5 *Second-Order Removal Model for AHTN*. Second-order AHTN removal constant, k_2 value was calculated as 0.0002 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.996 for AHTN in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 4.a) (Table 6.214). For the experiments with nano-CeO₂, second-order AHTN removal constant, k_2 value was calculated as 0.0004 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.960 for AHTN (Appendice-13, Figure 4.b) (Table 6.214).

Table 6.214 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for AHTN with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	AHTN	0.0002	0.996
nano-CeO ₂	AHTN	0.0004	0.960

6.5.4.4.6 *Second-Order Removal Model for PFOA*. Second-order PFOA removal constant, k_2 value was calculated as 0.079 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.999 for PFOA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 5.a) (Table 6.215). For the experiments with nano-CeO₂, second-order PFOA removal constant, k_2 value was calculated as 0.141 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.975 for PFOA (Appendice-13, Figure 5.b) (Table 6.215).

Table 6.215 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PFOA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	PFOA	0.079	0.999
nano-CeO ₂	PFOA	0.141	0.975

6.5.4.4.7 *Second-Order Removal Model for PFOS*. Second-order PFOS removal constant, k_2 value was calculated as 1.027 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.992 for PFOS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 6.a) (Table 6.216). For the experiments with nano-CeO₂, second-order PFOS removal constant, k_2 value was calculated as 1.685 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.960 for PFOS (Appendice-13, Figure 6.b) (Table 6.216).

Table 6.216 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for PFOS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	PFOS	1.027	0.992
nano-CeO ₂	PFOS	1.685	0.960

6.5.4.4.8 *Second-Order Removal Model for GFZ*. Second-order GFZ removal constant, k_2 value was calculated as 0.006 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.953 for GFZ in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 7.a) (Table 6.217). For the experiments with nano-CeO₂, second-order GFZ removal constant, k_2 value was calculated as 0.006 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.965 for GFZ (Appendice-13, Figure 7.b) (Table 6.217).

Table 6.217 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for GFZ with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	GFZ	0.006	0.953
nano-CeO ₂	GFZ	0.006	0.965

6.5.4.4.9 *Second-Order Removal Model for TCS*. Second-order TCS removal constant, k_2 value was calculated as 0.0004 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.989 for TCS in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 8.a) (Table 6.218). For the experiments with nano-CeO₂, second-order TCS removal constant, k_2 value was calculated as 0.001 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.946 for TCS (Appendice-13, Figure 8.b) (Table 6.218).

Table 6.218 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for TCS with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	TCS	0.0004	0.989
nano-CeO ₂	TCS	0.001	0.946

6.5.4.4.10 *Second-Order Removal Model for IBU*. Second-order IBU removal constant, k_2 value was calculated as 0.002 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.884 for IBU in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 9.a) (Table 6.219). For the experiments with nano-CeO₂, second-order IBU removal constant, k_2 value was calculated as 0.003 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.988 for IBU (Appendice-13, Figure 9.b) (Table 6.219).

Table 6.219 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for IBU with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	IBU	0.002	0.884
nano-CeO ₂	IBU	0.003	0.988

6.5.4.4.11 *Second-Order Removal Model for CIP*. Second-order CIP removal constant, k_2 value was calculated as 0.0001 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.990 for CIP in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 10.a) (Table 6.220). For the experiments with nano-CeO₂, second-order CIP removal constant, k_2 value was calculated as 0.0003 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.960 for CIP (Appendice-13, Figure 10.b) (Table 6.220).

Table 6.220 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for CIP with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	CIP	0.0001	0.990
nano-CeO ₂	CIP	0.0003	0.960

6.5.4.4.12 *Second-Order Removal Model for NDMA*. Second-order NDMA removal constant, k_2 value was calculated as 0.0001 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.992 for NDMA in the ultrasound treatment experiments with nano-TiO₂ (Appendice-13, Figure 11.a) (Table 6.221). For the experiments with nano-CeO₂, second-order NDMA removal constant, k_2 value was calculated as 0.0002 L μg^{-1} day⁻¹ with a correlation coefficient (R^2) of 0.927 for NDMA (Appendice-13, Figure 11.b) (Table 6.221).

Table 6.221 Comparison of the kinetic constants and regression coefficients (R^2) relevant to second-order for NDMA with nano-TiO₂ and nano-CeO₂

Nanoparticle	Micropollutant	Second-order	
		k_2 (L μg^{-1} day ⁻¹)	R^2
nano-TiO ₂	NDMA	0.0001	0.992
nano-CeO ₂	NDMA	0.0002	0.927

6.5.4.5 Evaluation of Kinetic Models in the Ultrasound Treatment Process

The kinetic data showed that the first-order removal model was a more appropriate model compared to the zero, half and second-order kinetic models for predicting the ultrasonic-degradation performance of the lab. scale ultrasound treatment system treating the brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants with 0.40 g L⁻¹ nanoparticle concentration (both for nano-TiO₂ and nano-CeO₂) at 120 W sonicator power at a pH of 4.00 at 40 °C throughout 60 min sonication time and at a constant sonicator frequency of 132 kHz (Table 6.222).

Table 6.222 Comparison of first-order kinetic constants and R^2 values for brominated (α -HBCDD, PBEB, PBT and TBBPA), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP), nitroso (NDMA) and aromatic (AHTN) micropollutants for the experiments with nano-TiO₂ and nano-CeO₂

Group	Micropollutant	First-order with nano-TiO ₂		Total removal efficiency (%)	First-order with nano-CeO ₂		Total removal efficiency (%)
		k_1 (day ⁻¹)	R^2		k_1 (day ⁻¹)	R^2	
Brominated	TBBPA	0.0127	0.985	90	0.0209	0.903	93
	α -HBCDD	0.0119	0.999	86	0.0176	0.997	89
	PBT	0.0110	0.993	84	0.0162	0.960	89
	PBEB	0.0097	0.999	82	0.0154	0.997	87
Fluoro	PFOS	0.0072	0.989	67	0.0108	0.984	72
	PFOA	0.0055	0.998	65	0.0092	0.988	70
Phenolic	GFZ	0.0221	0.995	96	0.0239	0.996	96
	TCS	0.0138	0.998	92	0.0216	0.964	94
	IBU	0.0126	0.929	90	0.0181	0.987	90
	CIP	0.0119	0.999	86	0.0169	0.988	91
Nitroso	NDMA	0.0073	0.981	70	0.0114	0.958	75
Aromatic	AHTN	0.0089	0.992	80	0.0154	0.990	85

All studied micropollutants followed first-order removal model with the meaningful highest kinetic constants and R^2 values between zero, half and second-order kinetic models both for the experiments with nano-TiO₂ and nano-CeO₂ (Table 6.222). The first-order kinetic constant, k_1 values were found between 0.0127 - 0.0097 day⁻¹ and 0.0209 - 0.0154 day⁻¹ for the brominated (α -HBCDD, PBEB, PBT and TBBPA) micropollutants with nano-TiO₂ and nano-CeO₂, respectively (Table 6.222). k_1 values were found between 0.0072 - 0.0055 day⁻¹ and 0.0108 - 0.0092 day⁻¹ for the fluoro (PFOA and PFOS) micropollutants with nano-TiO₂ and nano-CeO₂, respectively (Table 6.222). k_1 values were found between 0.0221 - 0.0119 day⁻¹ and 0.0239 - 0.0169 day⁻¹ for the phenolic (GFZ, TCS, IBU and CIP) micropollutants with nano-TiO₂ and nano-CeO₂, respectively (Table 6.222). k_1 value was found as 0.0089 and 0.0154 day⁻¹ for the aromatic (AHTN) micropollutant with nano-TiO₂ and nano-CeO₂, respectively (Table 6.222). k_1 value was found as 0.0073 and 0.0114 day⁻¹ for the nitroso (NDMA) micropollutant with nano-TiO₂ and nano-CeO₂, respectively (Table 6.222).

Maximum ultrasound removal efficiency was achieved for GFZ with nano-TiO₂ (96%) and nano-CeO₂ (96%) at the aforementioned experimental conditions (Table 6.222). Therefore, GFZ showed maximum kinetic constants with nano-TiO₂ (0.0221 day⁻¹) and nano-CeO₂ (0.0239 day⁻¹) at the aforementioned experimental conditions (Table 6.222). Furthermore, minimum ultrasound removal efficiency was calculated for PFOA with nano-TiO₂ (65%) and nano-CeO₂ (70%) at the aforementioned experimental conditions (Table 6.222). As a result, PFOA showed minimum kinetic constants with nano-TiO₂ (0.0055 day⁻¹) and nano-CeO₂ (0.0092 day⁻¹) at the aforementioned experimental conditions (Table 6.222).

In the literature, there are no calculated kinetic coefficients for ultrasound treatments of micropollutants from raw hospital wastewater. A kinetic study from the literature determined that some polycyclic aromatic hydrocarbons (PAHs) in petrochemical, olive mill and textile industry real wastewaters were sonodegraded according to the pseudo first order reaction kinetic both with only sonication and

with 20.00 mg L⁻¹ nano-TiO₂ addition after 150 min at 60 °C at 640 W at 35 kHz and at 90.54 W cm⁻² sonication intensity (Oztekin, 2011).

6.6 Cost Analysis

6.6.1 Cost Analysis for Biological Treatment Process

The calculations for a cost analysis was made for the biological treatment of all studied micropollutants from 1 m³ raw hospital wastewater at 55 days of SRT, at a pH of 7.50 and at 37 °C with an anaerobic/aerobic sequential biological reactor system (Table 6.223). The price of NaHCO₃ for alkalinity adjustment, investment cost, electricity consumption, biogas income, total cost and unit cost were considered in this study (Table 6.223). 0.25 € year⁻¹ was found for alkalinity adjustment and 6.65 € year⁻¹ was calculated as the investment cost, while the electricity consumption was determined as 0.41 € year⁻¹ (Table 6.223). Electric energy was obtained from the CH₄ gas produced from the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system used in this study. The CH₄ gas produced from the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system at a SRT of 55 days was equal to 2.84×10⁻⁴ m³ day⁻¹ (Table 6.5). The electricity energy produced from 1 m³ CH₄ is equal to 4.70 kWh (Gümüüşçü & Uyanık, 2010). Therefore, the electricity energy production from the CH₄ was equal to 1.33×10⁻³ kWh day⁻¹ corresponding to 0.49 kWh year⁻¹ in the anaerobic reactor (Equation 6.330).

$$(2.84 \times 10^{-4} \text{ m}^3 \text{ CH}_4 \text{ day}^{-1}) \times (4.70 \text{ kWh/m}^3 \text{ CH}_4) \times (365 \text{ d/year}) = 0.49 \text{ kWh year}^{-1} \quad (6.330)$$

The cost of 1 kWh electricity energy was accepted as 0.04 € (0.04 € kWh⁻¹). Therefore, the total biogas cost was calculated by multiplying the electricity production (kWh year⁻¹) with specific energy cost (€ kWh⁻¹) in Equation 6.331.

$$(0.49 \text{ kWh year}^{-1}) \times (0.04 \text{ € kWh}^{-1}) = 0.02 \text{ € year}^{-1} \quad (6.331)$$

The electricity energy obtained from the CH₄ gas in the anaerobic reactor was calculated as 0.02 € year⁻¹ while the electricity energy consumption was found as 0.41 € year⁻¹. Therefore, it can be concluded that approximately 5% of the total electricity energy expenses could be received from the CH₄ gas production (Equation 6.332).

$$(0.02 \text{ € year}^{-1})/(0.41 \text{ € year}^{-1}) \times 100 \approx 5.0\% \quad (6.332)$$

The price of NaHCO₃ for alkalinity adjustment, investment cost, electricity consumption and biogas income (0.41 – 0.02 € year⁻¹) were added and as a consequence, the total cost was found as 7.29 € year⁻¹ at the aforementioned experimental conditions (Table 6.223). The total cost of the biological treatment of all studied micropollutants from 1 m³ raw hospital wastewater was determined as 3.14 € m⁻³ by dividing the total cost to flowrate in the anaerobic/aerobic sequential biological reactor system at the aforementioned experimental conditions as is shown in Equation 6.333 (Table 6.223).

$$(7.29 \text{ € year}^{-1})/(2.32 \text{ m}^3 \text{ year}^{-1}) = 3.14 \text{ € m}^{-3} \quad (6.333)$$

Table 6.223 Cost analysis for the biological treatment of all studied micropollutants for 1 m³ raw hospital wastewater with anaerobic/aerobic sequential biological reactor system at the following experimental conditions: at 55 days of SRT, at a pH of 7.50 and at 37 °C

Cost analysis	Biological treatment of all studied micropollutants from raw hospital wastewater with an anaerobic/aerobic sequential biological reactor system
Chemical for alkalinity adjustment	NaHCO_3 (0.1 N requires 8.40 g NaHCO_3/L): 2.50 €/1 kg 0.1 N used for 30 days: $(8.40 \text{ g}/30 \text{ day}) \times (1 \text{ kg}/1000 \text{ g}) = 2.80 \times 10^{-4} \text{ kg/day}$ $(2.80 \times 10^{-4} \text{ kg/day}) \times (2.50 \text{ €/1 kg}) \times (365 \text{ days/year}) = 0.25 \text{ €/year}$
Investment cost (Anaerobic UASB, aerobic CSTR, feeding tank, air pump, peristaltic pumps, heater)	1 anaerobic UASB (2.5 L): 25.00 € Lifetime of 1 anaerobic UASB: 10 years (accepted) 1 anaerobic UASB: $(25.00 \text{ €}) / (10 \text{ years}) = 2.50 \text{ €/year}$ 1 aerobic CSTR (2.0 L): 6.50 € Lifetime of 1 aerobic CSTR: 10 years (accepted) 1 aerobic CSTR: $(6.50 \text{ €}) / (10 \text{ years}) = 0.65 \text{ €/year}$ feeding tank, air pump, 2 peristaltic pumps, heater and montage: 35.00 € Lifetime of feeding tank, air pump, 2 peristaltic pumps, heater and montage: 10 years (accepted) Feeding tank, air pump, peristaltic pumps, heater and montage: $(35.00 \text{ €}) / (10 \text{ years}) = 3.50 \text{ €/year}$
Electricity consumption	air pump: 0.01 kWh/day, 2 peristaltic pumps: 0.004 kWh/day, heater 0.01 kWh/day 1 kWh electricity: 0.04 € $(0.028 \text{ kWh/day}) \times (0.04 \text{ €/1 kWh}) \times (365 \text{ days/year}) = 0.41 \text{ €/year}$
Biogas income	$(2.84 \times 10^{-4} \text{ m}^3 \text{ day}^{-1}) \times (4.70 \text{ kWh/m}^3) \times (365 \text{ day/year}) \times (0.04 \text{ €/kWh}) = 0.02 \text{ €/year}$
Total cost	$(0.25 \text{ €/year}) + (2.50 \text{ €/year} + 0.65 \text{ €/year} + 3.50 \text{ €/year}) + (0.41 \text{ €/year} - 0.02 \text{ €/year}) = 7.29 \text{ €/year}$
Unit cost (Total cost/flowrate)	$(7.29 \text{ €/year}) / (2.32 \text{ m}^3/\text{year}) = 3.14 \text{ €/m}^3$

Note: The cost of the chemicals are calculated according to the market prices. Electricity consumption is considered according to the residential customer. Recent Euro exchange rate was used to convert the Euro currency to Turkish Liras (1 € = 6.50 TL, June 2019).

6.6.2 Cost Analysis for Photocatalytic Treatment Process

A cost analysis was carried out for the photocatalytic treatment of all studied micropollutants from 1 m³ raw hospital wastewater for 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00 with nano-TiO₂ and nano-CeO₂ (Table 6.224). The required UV power was provided using 7 UV lamps (Table 6.224). The price of the UV lamps, investment cost, electricity consumption, purchase price of the nanoparticles and regeneration cost of the nanoparticles were considered in this study (Table 6.224). 9.84×10⁻³ € was spent on 7 UV lamps and 3.21×10⁻³ € was determined as the investment cost, while the electricity consumption was found as 6.30×10⁻³ € (Table 6.224). 0.50 g nano-TiO₂ and nano-CeO₂ required to treat 1 L raw hospital wastewater but the nanoparticles can be recovered from the photocatalytic treatment for five sequential treatment steps (0.50 g nanoparticle was used for 5 cycles/L= 0.10 g/L). Therefore, 100 g nano-TiO₂ and nano-CeO₂ required to treat 1 m³ raw hospital wastewater (Table 6.224). The purchase prices were calculated as 2.00 € and 1.20 € for TiO₂ and CeO₂ nanoparticles, respectively (Table 6.224). The regeneration cost of the TiO₂ and CeO₂ nanoparticles were found as 4.17 € (Table 6.224). The cost analysis showed that the photocatalytic treatment with nano-CeO₂ (5.39 €) was a cheaper option in the comparison with the nano-TiO₂ (6.19 €) (Table 6.224). In addition to this, the photocatalytic treatment with nano-CeO₂ (higher than 66% for all studied micropollutants) gave higher removal efficiencies than the nano-TiO₂ (higher than 60% for all studied micropollutants) at the aforementioned experimental conditions (Figure 6.43 for nano-TiO₂ and Figure 6.44 for nano-CeO₂).

No recent literature was found concerning the photocatalytic cost of the micropollutants studied. However, some costs were compared with our data: Zhang et al. (2011) calculated that 99 € was needed to treat 500 m³ of wastewater containing 34 mg L⁻¹ methyl orange dye using only 1.9 g L⁻¹ TiO₂ (Zhang et al., 2011). Fenoll, Flores, Hellín, Martínez, & Navarro, 2012 and Wandre et al. (2016) found that the cost of photodegrading 1 m³ of wastewater containing 12 mg L⁻¹ TCS

and 20 mg L⁻¹ methyl orange was 102 € and 127 €, respectively in the presence of 2 g L⁻¹ nano-TiO₂ and CeO₂ (Fenoll et al., 2012 and Wandre et al., 2016). These data are higher than our cost of treating the raw hospital wastewater containing the twelve micropollutants.



Table 6.224 Cost analysis for the photocatalytic treatment of all studied micropollutants for 1 m³ raw hospital wastewater with nano-TiO₂ and nano-CeO₂ at the following experimental conditions: 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00

Cost analysis	Photocatalytic treatment of all studied micropollutants from raw hospital wastewater with nano-TiO ₂	Photocatalytic treatment of all studied micropollutants from raw hospital wastewater with nano-CeO ₂
UV lamps	1 UV lamp: 15 €	1 UV lamp: 15 €
	Lifetime of 1 UV lamp: 8000 h	Lifetime of 1 UV lamp: 8000 h
	7 UV lamp: $7 \times (1.875 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 9.84 \times 10^{-3} \text{ €}$	7 UV lamp: $7 \times (1.875 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 9.84 \times 10^{-3} \text{ €}$
Investment cost (Photocatalytic reactor, isolated cabin and magnetic stirrer)	1 photocatalytic reactor: 10 €	1 photocatalytic reactor: 10 €
	Lifetime of 1 photocatalytic reactor: 8760 h (accepted)	Lifetime of 1 photocatalytic reactor: 8760 h (accepted)
	$(1.14 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 8.56 \times 10^{-4} \text{ €}$	$(1.14 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 8.56 \times 10^{-4} \text{ €}$
	1 isolated cabin: 46 €	1 isolated cabin: 46 €
	Lifetime of 1 isolated cabin: 87600 h (accepted)	Lifetime of 1 isolated cabin: 87600 h (accepted)
	$(5.25 \times 10^{-4} \text{ €/h}) \times (0.75 \text{ h}) = 3.94 \times 10^{-4} \text{ €}$	$(5.25 \times 10^{-4} \text{ €/h}) \times (0.75 \text{ h}) = 3.94 \times 10^{-4} \text{ €}$
Electricity consumption	1 magnetic stirrer: 230 €	1 magnetic stirrer: 230 €
	Lifetime of 1 magnetic stirrer: 87600 h (accepted)	Lifetime of 1 magnetic stirrer: 87600 h (accepted)
	$(2.62 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 1.96 \times 10^{-3} \text{ €}$	$(2.62 \times 10^{-3} \text{ €/h}) \times (0.75 \text{ h}) = 1.96 \times 10^{-3} \text{ €}$
	1 UV lamp: 30 W power and 1 kW = 1000 W	1 UV lamp: 30 W power and 1 kW = 1000 W
	45 min = 0.75 h and 1 kWh electricity: 0.04 €	45 min = 0.75 h and 1 kWh electricity: 0.04 €
	$(30 \text{ W/lamp}) \times (7 \text{ lamps}) \times (1 \text{ kW}/1000 \text{ W}) \times (0.75 \text{ h}) \times (0.04 \text{ €/1 kWh}) = 6.30 \times 10^{-3} \text{ €}$	$(30 \text{ W/lamp}) \times (7 \text{ lamps}) \times (1 \text{ kW}/1000 \text{ W}) \times (0.75 \text{ h}) \times (0.04 \text{ €/1 kWh}) = 6.30 \times 10^{-3} \text{ €}$
Nanoparticles	Titanium (IV) oxide (TiO ₂) nanopowder (25 kg): 500 €	Cerium (IV) oxide (CeO ₂) nanopowder (10 kg): 120 €
	0.50 g nanoparticle was used for 5 cycles/L: 0.10 g/L = 100 g/m ³	0.50 g nanoparticle was used for 5 cycles/L: 0.10 g/L = 100 g/m ³
	100 g nano-TiO ₂ for 1 m ³ = 2.00 €	100 g nano-CeO ₂ for 1 m ³ = 1.20 €
Regeneration of nanoparticles	0.10 M HCl in ethanol = 83 mL HCl + 917 mL ethanol	0.10 M HCl in ethanol = 83 mL HCl + 917 mL ethanol
	$(83 \text{ mL HCl}) \times (3 \text{ €/1000 mL}) \times (2 \text{ times/year}) \times (1 \text{ year}) = 0.50 \text{ €}$	$(83 \text{ mL HCl}) \times (3 \text{ €/1000 mL}) \times (2 \text{ times/year}) \times (1 \text{ year}) = 0.50 \text{ €}$
	$(917 \text{ mL ethanol}) \times (2 \text{ €/1000 mL}) \times (2 \text{ times/year}) \times (1 \text{ year}) = 3.67 \text{ €}$	$(917 \text{ mL ethanol}) \times (2 \text{ €/1000 mL}) \times (2 \text{ times/year}) \times (1 \text{ year}) = 3.67 \text{ €}$
Total cost	$(9.84 \times 10^{-3} \text{ €}) + (8.56 \times 10^{-4} \text{ €} + 3.94 \times 10^{-4} \text{ €} + 1.96 \times 10^{-3} \text{ €})$	$(9.84 \times 10^{-3} \text{ €}) + (8.56 \times 10^{-4} \text{ €} + 3.94 \times 10^{-4} \text{ €} + 1.96 \times 10^{-3} \text{ €})$
	$+ (6.30 \times 10^{-3} \text{ €}) + (2.00 \text{ €}) + (0.50 \text{ €} + 3.67 \text{ €}) = 6.19 \text{ €}$	$+ (6.30 \times 10^{-3} \text{ €}) + (1.20 \text{ €}) + (0.50 \text{ €} + 3.67 \text{ €}) = 5.39 \text{ €}$

Note: The cost of the chemicals are calculated according to the market prices. Electricity consumption is considered according to the residential customer. Recent Euro exchange rate was used to convert the Euro currency to Turkish Liras (1 € = 6.50 TL, June 2019).

6.6.3 Cost Analysis for Ultrasound Treatment Process

The calculations for a cost analysis was made for the ultrasound treatment of all studied micropollutants from 1 m³ raw hospital wastewater at 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz with nano-TiO₂ and nano-CeO₂ (Table 6.225). The price of the chemical for pH adjustment, investment cost, electricity consumption, purchase price of the nanoparticles and regeneration cost of the nanoparticles were determined in Table 6.225. 0.022 € was spent on pH adjustment and 0.011 € was determined as the investment cost, while the electricity consumption was calculated as 0.0048 € (Table 6.225). 0.40 g nano-TiO₂ and nano-CeO₂ required to treat 1 L raw hospital wastewater but the nanoparticles can be recovered from the ultrasound treatment for five sequential treatment steps (0.40 g nanoparticle was used for 5 cycles/L= 0.08 g/L). Therefore, 80 g nano-TiO₂ and nano-CeO₂ required to treat 1 m³ raw hospital wastewater (Table 6.225). The purchase prices were 1.60 € and 1.28 € for TiO₂ and CeO₂ nanoparticles, respectively (Table 6.225). The regeneration cost of the TiO₂ and CeO₂ nanoparticles were found as 4.17 € (Table 6.225). The cost analysis for the ultrasound treatment of all studied micropollutants from raw hospital wastewater showed that the ultrasound treatment with nano-CeO₂ (5.49 €) was cheaper compared to nano-TiO₂ (5.81 €) at the aforementioned experimental conditions (Table 6.225). Also, the ultrasound treatment with nano-CeO₂ (higher than 70% for all studied micropollutants) gave higher removal efficiencies than the nano-TiO₂ (higher than 65% for all studied micropollutants) at the aforementioned experimental conditions (Figure 6.55 for nano-TiO₂ and Figure 6.56 for nano-CeO₂).

Table 6.225 Cost analysis for the ultrasound treatment of all studied micropollutants for 1 m³ raw hospital wastewater with nano-TiO₂ and nano-CeO₂ at the following experimental conditions: 120 W constant sonicator power, 60 min constant sonication time, constant pH of 4.00, constant temperature of 40 °C, constant nanoparticle concentration of 0.40 g L⁻¹ and constant sonicator frequency of 132 kHz

Cost analysis	Ultrasound treatment of all studied micropollutants from raw hospital wastewater with nano-TiO ₂	Ultrasound treatment of all studied micropollutants from raw hospital wastewater with nano-CeO ₂
Chemical for pH adjustment	HCl (0.1 N requires 3.65 mL HCl/L): 3 €/1000 mL (3.65 mL) × (3 €/1000 mL) × (2 times/year) × (1 year) = 0.022 €	HCl (0.1 N requires 3.65 mL HCl/L): 3 €/1000 mL (3.65 mL) × (3 €/1000 mL) × (2 times/year) × (1 year) = 0.022 €
Investment cost (Sonicator at 132 kHz, 120 W, 5.40 L)	1 sonicator: 1000 € Lifetime of 1 sonicator: 87600 h (accepted) (1000 €) / (87600 h) = 0.011 €/h (0.011 €/h) × (1 h) = 0.011 €	1 sonicator: 1000 € Lifetime of 1 sonicator: 87600 h (accepted) (1000 €) / (87600 h) = 0.011 €/h (0.011 €/h) × (1 h) = 0.011 €
Electricity consumption	1 sonicator: 120 W power and 1 kW = 1000 W 60 min = 1 h and 1 kWh electricity: 0.04 € (120 W/sonicator) × (1 kW/1000 W) × (1 h) × (0.04 €/1 kWh) = 0.0048 €	1 sonicator: 120 W power and 1 kW = 1000 W 60 min = 1 h and 1 kWh electricity: 0.04 € (120 W/sonicator) × (1 kW/1000 W) × (1 h) × (0.04 €/1 kWh) = 0.0048 €
Nanoparticles	Titanium (IV) oxide (TiO ₂) nanopowder (25 kg): 500 € 0.40 g nanoparticle was used for 5 cycles/L: 0.08 g/L=80 g/m ³ 80 g nano-TiO ₂ for 1 m ³ = 1.60 €	Cerium (IV) oxide (CeO ₂) nanopowder (10 kg): 120 € 0.40 g nanoparticle was used for 5 cycles/L: 0.08 g/L=80 g/m ³ 80 g nano-CeO ₂ for 1 m ³ = 1.28 €
Regeneration of nanoparticles	0.10 M HCl in ethanol = 83 mL HCl + 917 mL ethanol (83 mL HCl) × (3 €/1000 mL) × (2 times/year) × (1 year) = 0.50 € (917 mL ethanol) × (2 €/1000 mL) × (2 times/year) × (1 year) = 3.67€	0.10 M HCl in ethanol = 83 mL HCl + 917 mL ethanol (83 mL HCl) × (3 €/1000 mL) × (2 times/year) × (1 year) = 0.50 € (917 mL ethanol) × (2 €/1000 mL) × (2 times/year) × (1 year) = 3.67€
Total cost	(0.022 €) + (0.011 €) + (0.0048 €) + (1.60 €) + (0.50 € + 3.67 €) = 5.81 €	(0.022 €) + (0.011 €) + (0.0048 €) + (1.28 €) + (0.50 € + 3.67 €) = 5.49 €

Note: The cost of the chemicals are calculated according to the market prices. Electricity consumption is considered according to the residential customer. Recent Euro exchange rate was used to convert the Euro currency to Turkish Liras (1 € = 6.50 TL, June 2019).

6.6.4 Cost Analysis for Membrane Treatment Process

A cost analysis study was performed for the membrane treatment of all studied micropollutants from 1 m³ raw hospital wastewater with UF [at a constant TMP of 2.75 bar, at a constant permeate flux (J_v) of 156.25 L m⁻² h⁻¹, at a constant CFV of 0.16 m h⁻¹, at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C] and RO [at a constant TMP of 4.75 bar, at a constant permeate flux (J_v) of 104.17 L m⁻² h⁻¹, at a constant CFV of 0.10 m h⁻¹, at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C] (Table 6.226). The investment cost, electricity consumption and purchase price of the chemicals used for membrane cleaning were taken into consideration in this study (Table 6.226). The investment cost involves the prices of membrane, feeding tank, pump, store equipments and montage (Table 6.226). It was thought that UF and RO membranes should be renewed after two years (Table 6.226). UF and RO were costed 0.0086 € and 0.0217 €, respectively in two years period (Table 6.226). Lifetime of feeding tank, pump, store equipments and montage accepted as ten years both for UF and RO and were costed 0.0017 € totally for ten years lifetime (Table 6.226). The electricity consumption was calculated as 0.01 € both for UF and RO (Table 6.226). The purchase prices were 0.396 € and 0.24 € for HNO₃ and NaOH, respectively to clean UF and RO membranes (Table 6.226). There were no difference between the cost values for UF (0.66 €) and RO (0.67 €) at the aforementioned experimental conditions (Table 6.226). Furthermore, the membrane treatment with RO (higher than 95% for all studied micropollutants) gave higher removal efficiencies than the UF (between 5.8% and 36.8% for all studied micropollutants) at the aforementioned experimental conditions (Table 6.43 for UF and Table 6.46 for RO).

Table 6.226 Cost analysis for the membrane treatment of all studied micropollutants for 1 m³ raw hospital wastewater with UF [at a constant TMP of 2.75 bar, at a constant permeate flux (J_v) of 156.25 L m⁻² h⁻¹, at a constant CFV of 0.16 m h⁻¹, at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C] and RO [at a constant TMP of 4.75 bar, at a constant permeate flux (J_v) of 104.17 L m⁻² h⁻¹, at a constant CFV of 0.10 m h⁻¹, at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C]

Cost analysis	UF	RO
	TMP = 2.75 bar, J_v = 156.25 L m ⁻² h ⁻¹ CFV = 0.16 m h ⁻¹ , time = 1 h, pH = 8.00, temp = 25 °C	TMP = 4.75 bar, J_v = 104.17 L m ⁻² h ⁻¹ CFV = 0.10 m h ⁻¹ , time = 1 h, pH = 8.00, temp = 25 °C
Investment cost (membrane, feeding tank, pump, store equipments and montage)	UF membrane: 150 €	RO membrane: 380 €
	Lifetime of UF: 2 years = 17520 h (accepted) (0.009 €/h) × (1 h) = 0.0086 €	Lifetime of RO: 2 years = 17520 h (accepted) (0.022 €/h) × (1 h) = 0.0217 €
	feeding tank, pump, store equipments and montage: 150 €	feeding tank, pump, store equipments and montage: 150 €
	Lifetime of feeding tank, pump, store equipments and montage: 10 years = 87600 h (accepted) (0.0017 €/h) × (1 h) = 0.0017 €	Lifetime of feeding tank, pump, store equipments and montage: 10 years = 87600 h (accepted) (0.0017 €/h) × (1 h) = 0.0017 €
Electricity consumption	pump: 0.25 kW power 1 kWh electricity: 0.04 € (0.25 kW) × (1 h) × (0.04 €/1 kWh) = 0.01 €	pump: 0.25 kW power 1 kWh electricity: 0.04 € (0.25 kW) × (1 h) × (0.04 €/1 kWh) = 0.01 €
Cleaning of membranes (once a month)	HNO ₃ (0.1 N requires 6 mL HNO ₃ /L): 2.75 €/1000 mL (6 mL) × (2.75 €/1000 mL) × (12 times/year) × (2 years) = 0.396 €	HNO ₃ (0.1 N requires 6 mL HNO ₃ /L): 2.75 €/1000 mL (6 mL) × (2.75 €/1000 mL) × (12 times/year) × (2 years) = 0.396 €
	NaOH (0.1 N requires 4 g NaOH/L): 2.5 €/1000 g (4 g) × (2.5 €/1000 g) × (12 times/year) × (2 years) = 0.24 €	NaOH (0.1 N requires 4 g NaOH/L): 2.5 €/1000 g (4 g) × (2.5 €/1000 g) × (12 times/year) × (2 years) = 0.24 €
Total cost	(0.0086 €) + (0.0017 €) + (0.01 €) + (0.396 € + 0.24 €) = 0.66 €	(0.0217 €) + (0.0017 €) + (0.01 €) + (0.396 € + 0.24 €) = 0.67 €

Note: The cost of the chemicals are calculated according to the market prices. Electricity consumption is considered according to the residential customer. Recent Euro exchange rate was used to convert the Euro currency to Turkish Liras (1 € = 6.50 TL, June 2019).

There is no available data about treatability cost of micropollutants in UF or RO membranes in the literature. Nevertheless some researchers reported some cost analysis results related to RO membranes. Atikol & Aybar (2005) determined 0.86 \$ m⁻³ cost for a pilot-scale RO plant treating sea water into fresh water at a flowrate of 1000 m³ day⁻¹ (Atikol & Aybar, 2005). Total cost of 0.88 € m⁻³ was calculated for a pilot-scale RO plant treating produced water originated from oil and gas production wells with a flowrate capacity of 300 m³ day⁻¹ (Ersahin et al., 2018). These data are higher than our cost value treating the raw hospital wastewater using RO membrane (0.67 € m⁻³).

In order to evaluate whether the treated hospital wastewater with RO can be reused as irrigation water in the hospital area, the effluent concentrations of RO at 4.75 bar TMP at the aforementioned experimental conditions were analyzed according to Wastewater Treatment Plant Technical Methods, Table E7.2 – E.7.7 (2010) and Su Kirliliği Kontrolü Yönetmeliği Teknik Usuller Tebliği, Table 4 (1991). The results were shown in Table 6.227.

Table 6.227 RO effluent concentrations at a TMP of 4.75 bar at the aforementioned experimental conditions and the classification of the effluent water according to the regulations of Wastewater Treatment Plant Technical Methods - Table E7.2 and E7.7 (2010) and Su Kirliliği Kontrolü Yönetmeliği Teknik Usuller Tebliği - Table 4 (1991)

Parameters	RO effluent (TMP=4.75 bar)	Wastewater Treatment Plant Technical Methods - Table E7.2 (2010)	Su Kirliliği Kontrolü Yönetmeliği Teknik Usuller Tebliği - Table 4 (1991)
EC (dS/m)	0.04	EC (dS/m) < 0.25: excellent	
TDS (mg/L)	2.50	TDS (mg/L) < 200: good	
Na ⁺ (mg/L)	5.52	Na ⁺ (mg/L) < 100: degree of restriction on use is none	
Na ⁺ (meq/L)	0.24	Na ⁺ (meq/L) < 3.0: degree of restriction on use is none	
Ca ⁺² (mg/L)	6.20		
Ca ⁺² (meq/L)	0.31		
Mg ⁺² (mg/L)	3.12		
Mg ⁺² (meq/L)	0.26		
Cl ⁻ (meq/L)	0.00	Cl ⁻ (meq/L) < 2.0: safe for irrigation	0 < Cl ⁻ (meq/L) < 4: First class water (very good)
SAR (meq/L)	$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{+2}] + [Mg^{+2}]}{2}}} = 0.45$	EC (dS/m) < 0.25 and SAR < 10: degree of restriction is low and satisfactory for all crops	SAR < 10: First class water (very good)
pH	8.00	6.5 < pH < 8.4: normal range	6.5 < pH < 8.5: First class water (very good)
RSC (meq/L)	0.00	RSC (meq/L) < 1.25: safe for irrigation	RSC (meq/L) < 1.25: First class water (very good)
HCO ₃ ⁻ (mg/L)	1.20		
HCO ₃ ⁻ (meq/L)	0.02	HCO ₃ ⁻ (meq/L) < 1.5: degree of restriction on use is none	
SO ₄ ²⁻ (mg/L)	2.40		0 < SO ₄ ²⁻ (mg/L) < 142: First class water (very good)
SO ₄ ²⁻ (meq/L)	0.05		0 < SO ₄ ²⁻ (meq/L) < 4: First class water (very good)
Boron (B) (mg/L)	0.01		0 < B (mg/L) < 0.5: First class water (very good)
NH ₄ ⁺ (mg/L)	0.01		0 < NH ₄ ⁺ (mg/L) < 5: First class water (very good)
Fecal coliform (1/100 ml)	0.00		0 < Fecal coliform (1/100 ml) < 2: First class water (very good)
BOD ₅ (mg/L)	24.80		0 < BOD ₅ (mg/L) < 25: First class water (very good)
TSS (mg/L)	0.00		≤ 20: First class water (very good)
Temperature (°C)	15.0		≤ 30: First class water (very good)

Table 6.227 continues

Elements	Maximum total conc. to the unit area (kg/ha)	Maximum allowed concentrations in Wastewater Treatment Plant Technical Methods - Table E7.7 (2010)		RO effluent (TMP=4.75 bar)	Comparison of RO effluent with the limit values for irrigation (mg/l)
		Limit values for irrigation (mg/l)	In the areas containing aluminum with pH values between 6,0 and 8,5 when the irrigation duration is low than 24 years (mg/l)		
Aluminum (Al)	4600	5.0	20.0	0.0000	0.0000 < 5.0
Arsenic (As)	90	0.1	2.0	0.0004	0.0004 < 0.1
Beryllium (Be)	90	0.1	0.5	0.0000	0.0000 < 0.1
Boron (B)	680	1000	2.0	0.0122	0.0122 < 1000
Cadmium (Cd)	9	0.01	0.05	0.0001	0.0001 < 0.1
Chrome (Cr)	90	0.1	1.0	0.0000	0.0000 < 0.1
Cobalt (Co)	45	0.05	5.0	0.0000	0.0000 < 0.05
Copper (Cu)	190	0.2	5.0	0.0205	0.0205 < 0.2
Fluorine (F)	920	1.0	15.0	0.0000	0.0000 < 1.0
Iron (Fe)	4600	5.0	20.0	0.0105	0.0105 < 5.0
Lead (Pb)	4600	5.0	10.0	0.0024	0.0024 < 5.0
Lithium (Li)	-	2.5	2.5	0.0000	0.0000 < 2.5
Manganese (Mn)	920	0.2	10.0	0.0025	0.0025 < 0.2
Molybdenum (Mo)	9	0.01	0.05 ²	0.0000	0.0000 < 0.01
Nickel (Ni)	920	0.2	2.0	0.0000	0.0000 < 0.2
Selenium (Se)	16	0.02	0.02	0.0002	0.0002 < 0.02
Vanadium (V)	-	0.1	1.0	0.0000	0.0000 < 0.1
Zinc (Zn)	1840	2.0	10.0	0.0537	0.0537 < 2.0

RO effluent at 4.75 bar TMP was found to be first class irrigation water at the aforementioned experimental conditions (Table 6.227). Therefore, a cost analysis was performed if the hospital management used the RO effluent as irrigation water in the hospital area. Treatment cost of RO at a TMP of 4.75 bar for the raw hospital wastewater was calculated as 0.67 € m⁻³ (Table 6.226). It is assumed that irrigation water consumption of Dokuz Eylul University Hospital was 100 m³ day⁻¹. The drinking and usage water of 100 m³ taken from the network system was calculated as 132.48 € according to the Equation 6.334.

$$(13 \text{ m}^3 \times 4.33 \text{ TL/m}^3) + (7 \text{ m}^3 \times 4.69 \text{ TL/m}^3) + (80 \text{ m}^3 \times 9.65 \text{ TL/m}^3) = 861.12 \text{ TL} \quad (6.334)$$

Recent Euro exchange rate was used to convert the Euro currency to Turkish Liras (1 € = 6.50 TL, June 2019). Therefore, the cost was calculated as 132.48 € according to the Equation 6.335.

$$(861.12 \text{ TL}) / (6.50 \text{ €/TL}) = 132.48 \text{ €} \quad (6.335)$$

The treatment cost of RO (TMP=4.75 bar) was found as 0.67 € m⁻³ (67 €/100 m³) at the aforementioned experimental conditions (Table 6.226). 65.48 € was calculated as the daily benefit for RO treatment (Equation 6.336). Approximately a benefit of 24000 € year⁻¹ can be obtained from the irrigation water cost with RO treatment of the raw hospital wastewater according to the Equation 6.337.

$$(132.48 \text{ € day}^{-1}) - (67 \text{ € day}^{-1}) = 65.48 \text{ € day}^{-1} \quad (6.336)$$

$$(65.48 \text{ € day}^{-1}) \times (365 \text{ day year}^{-1}) = 23900.20 \text{ € year}^{-1} \quad (6.337)$$

CHAPTER SEVEN

CONCLUSIONS

This Ph.D thesis was performed to investigate the treatability of the raw hospital wastewater containing some brominated (α -HBCDD, PBEB, PBT and TBBPA), fluoro (PFOA and PFOS), nitroso (NDMA), phenolic (GFZ, TCS, IBU and CIP) and aromatic (AHTN) micropollutants in an anaerobic/aerobic sequential biological reactor system, in a photocatalytic reactor system, in an ultrasound treatment system, in an ultrafiltration (UF) membrane treatment system and in a reverse osmosis (RO) membrane treatment system. The results from these treatment processes are summarized below:

7.1 The Performance of Anaerobic UASB/Aerobic CSTR Sequential Biological Reactor System Treating Raw Hospital Wastewater

The anaerobic UASB/aerobic CSTR sequential biological reactor system was operated at 5, 30, 45 and 55 days SRTs and the highest removal efficiencies were obtained at the highest SRT operation of 55 days for all studied micropollutants and macropollutants (COD and sCOD) under mesophilic conditions (37 ± 2 °C) and at a pH of 7.50 (Table 7.1). In order to detect the main removal mechanisms of all studied micropollutants and macropollutants (COD and sCOD); biodegradation, adsorption, sorption and volatilization tests were performed during 5, 30, 45 and 55 days of SRTs. The main removal mechanisms were found adsorption for all brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), and some phenolic (GFZ and TCS) micropollutants in the anaerobic (between 58% and 86%) (Table 6.31), in the aerobic (between 52% and 79%) (Table 6.31) and in the anaerobic/aerobic sequential biological reactor system (between 51% and 80%) (Table 7.1) at 55 days SRT. The main removal mechanisms were found biodegradation for some phenolic (IBU and CIP) and nitroso (NDMA) micropollutants and macropollutants (COD and sCOD) in the anaerobic (between 45% and 90%) (Table 6.31), in the aerobic (between 77% and 94%) (Table 6.31) and in the anaerobic/aerobic sequential biological reactor system (between 87% and

98%) (Table 7.1) at 55 days SRT. For the micropollutants with log K_{OW} values greater than 4.0 (all brominated, aromatic, fluoro, GFZ and TCS), which are less susceptible to biodegradation, removal via adsorption onto anaerobic and aerobic biological sludges were likely to be the major removal mechanism because of their high adsorption potentials. The moderate hydrophobic phenolic micropollutant (IBU, log K_{OW} = 3.97), hydrophilic micropollutants with a log K_{OW} of less than 2.5 (CIP and NDMA) and macropollutants (COD and sCOD), exhibited minimum adsorption potential onto anaerobic and aerobic biological sludges and the major removal mechanisms were found to be biodegradation in all reactors at all SRTs. The biodegradation was the major removal mechanism for COD and sCOD because they served as primary substrates for the growth of anaerobic and aerobic bacteria using carbon and energy source.

Table 7.1 The anaerobic UASB/aerobic CSTR sequential biological reactor system

Pollutant	Influent conc. ($\mu\text{g L}^{-1}$)	$\log K_{ow}$ (unitless)	Removal Efficiency (%)				Removal Kinetic	Adsorption Isotherm
			Biodegradation (%)	Adsorption (%)	Sorption (%)	Volatilization (%)		
α -HBCDD	0.0115	7.74	18.26 $\pm$ 0.5	80.87 $\pm$ 0.5	0.97 $\pm$ 0.1	0.00009 $\pm$ 0.00005	Monod	Freundlich
PBEB	0.00328	7.48	19.05 $\pm$ 0.5	80.05 $\pm$ 0.5	0.89 $\pm$ 0.1	0.00000 $\pm$ 0.00005	Monod	Freundlich
PBT	0.00231	6.99	19.57 $\pm$ 0.5	79.56 $\pm$ 0.5	0.91 $\pm$ 0.1	0.00000 $\pm$ 0.00005	Monod	Freundlich
TBBPA	0.0170	5.90	20.59 $\pm$ 0.5	78.56 $\pm$ 0.5	0.92 $\pm$ 0.1	0.00010 $\pm$ 0.00005	Monod	Freundlich
AHTN	0.206	5.70	24.40 $\pm$ 0.5	74.48 $\pm$ 0.5	1.12 $\pm$ 0.1	0.00022 $\pm$ 0.00005	Monod	Freundlich
PFOA	0.1770	4.81	27.96 $\pm$ 0.5	71.06 $\pm$ 0.5	1.04 $\pm$ 0.1	0.00030 $\pm$ 0.00005	Monod	Freundlich
PFOS	0.0180	4.49	47.33 $\pm$ 0.5	51.70 $\pm$ 0.5	1.00 $\pm$ 0.1	0.00026 $\pm$ 0.00005	Monod	Freundlich
GFZ	53.30	4.77	31.69 $\pm$ 0.5	67.17 $\pm$ 0.5	1.14 $\pm$ 0.1	0.00007 $\pm$ 0.00005	Monod	Freundlich
TCS	361.00	4.76	31.77 $\pm$ 0.5	67.11 $\pm$ 0.5	1.13 $\pm$ 0.1	0.00005 $\pm$ 0.00005	Monod	Freundlich
IBU	42.50	3.79	87.95 $\pm$ 0.5	10.98 $\pm$ 0.5	0.85 $\pm$ 0.1	0.00007 $\pm$ 0.00005	Monod	--
CIP	522.00	0.28	93.16 $\pm$ 0.5	5.51 $\pm$ 0.5	0.66 $\pm$ 0.1	0.00000 $\pm$ 0.00005	Monod	--
NDMA	0.165	-0.57	96.42 $\pm$ 0.5	3.10 $\pm$ 0.5	0.47 $\pm$ 0.1	0.00007 $\pm$ 0.00005	Monod	--
COD	950.00*	--	98.05 $\pm$ 0.5	1.10 $\pm$ 0.5	0.38 $\pm$ 0.1	0.00000 $\pm$ 0.00005	Monod	--
sCOD	850.00*	--	98.75 $\pm$ 0.5	0.95 $\pm$ 0.5	0.33 $\pm$ 0.1	0.00000 $\pm$ 0.00005	Monod	--
Biological treatment of all studied micropollutants and macropollutants from raw hospital wastewater with an anaerobic/aerobic sequential biological reactor system: 3.14 €/m ³								

*: concentration in mg L⁻¹

The experimental data obtained from the anaerobic and aerobic biological reactor effluents at 5, 30, 45 and 55 days of SRTs were applied to various kinetic models such as, zero-order, half-order, first-order, second-order and Monod to determine the optimum micropollutants and macropollutants (COD and sCOD) removals for predicting the biodegradation performance of the lab scale anaerobic UASB/aerobic CSTR sequential biological reactor system. The kinetic data showed that the Monod substrate removal kinetic model was a more appropriate model for all studied brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS), phenolic (GFZ, TCS, IBU and CIP) and nitroso (NDMA) micropollutants as co-substrate and macropollutants (COD and sCOD) as primary substrates both in the anaerobic and aerobic reactors (Table 7.1). The aerobic reactor had higher growth yield coefficient (Y) and maximum specific growth rate ($\mu_{\max}$) values than anaerobic reactor for all studied micropollutants and macropollutants (Table 6.119). Furthermore, the half saturation concentration (K_s) values decreased in aerobic reactor in comparison with the anaerobic reactor (Table 6.119). Higher Y and $\mu_{\max}$ values with lower K_s values in aerobic reactor showed that micropollutants as co-substrates and macropollutants as primary substrates consumed more effectively in aerobic reactor than anaerobic reactor. The highest growth yield coefficient (Y) and maximum specific growth rate ($\mu_{\max}$) values were obtained for macropollutants (COD and sCOD) due to being primary substrates and easily biodegradable carbon sources (Table 6.119). The growth yield coefficient (Y) values were calculated as 0.290 mg VSS/mg COD and 0.298 mg VSS/mg sCOD for COD and sCOD, respectively in anaerobic reactor, while, they were found as 0.454 mg VSS/mg COD and 0.458 mg VSS/mg sCOD for COD and sCOD, respectively in aerobic reactor (Table 6.119). The maximum specific growth rate ($\mu_{\max}$) values were determined as 0.0570 day⁻¹ and 0.0758 day⁻¹ for COD and sCOD, respectively in anaerobic reactor, while, they were obtained as 0.0856 day⁻¹ and 0.0860 day⁻¹ for COD and sCOD, respectively in aerobic reactor (Table 6.119). In the Monod kinetics, hydrophilic micropollutants (CIP and NDMA) and macropollutants (COD and sCOD) were removed with high removal efficiencies and high Monod kinetic coefficients (Table 6.119). Half saturation concentrations (K_s) of hydrophilic micropollutants and macropollutants were found low with high R^2 (0.999) values

(Table 6.119). The growth yield coefficients (Y) and maximum specific growth rates ($\mu_{\max}$) of hydrophilic micropollutants and macropollutants were higher than hydrophobic micropollutants (α -HBCDD, PBEB, PBT, TBBPA, AHTN, PFOA, PFOS, GFZ, TCS and IBU), while endogenous decay coefficient (k_d) values of hydrophilic micropollutants were lower than hydrophobic micropollutants (Table 6.119). Higher Y and $\mu_{\max}$ values with lower K_s and k_d values in Monod kinetics showed that hydrophilic micropollutants were consumed as co-substrate more effectively than hydrophobic micropollutants due to their physicochemical properties (high water solubility and low octanol/water partition coefficients). In the Monod kinetics, hydrophobic micropollutants were removed with low removal efficiencies and their K_s values were high with high R^2 (0.999) values (Table 6.119). Other calculated Monod kinetic coefficients were also found meaningful for all hydrophobic micropollutants. The R^2 values of zero, half, first and second-order kinetics were found low in the comparison with Monod kinetics (Table 6.119). Considering the difference of the removal mechanisms of hydrophobic (adsorption mechanism) and hydrophilic (biodegradation mechanism) micropollutants, the calculated zero, half, first and second-order kinetic coefficients (k_0 , $k_{1/2}$, k_1 and k_2) were not found meaningful related to their physicochemical properties and it was demonstrated that micropollutants could not be eliminated according to these kinetics. There is no study in the literature comparing Monod kinetics with other zero, half, first and second-order kinetics for removing micropollutants in both anaerobic and aerobic biological processes. Some studies have revealed that α -HBCDD was eliminated in accordance with first-order kinetics. Peng et al. (2015) operated a continuous anaerobic reactor having a total volume of 100 mL which contained 60 mL mixed liquor and they obtained the first-order kinetic coefficient as 0.1286 day^{-1} with a R^2 value of 0.9437 for $533.8 \text{ } \mu\text{g L}^{-1}$ initial α -HBCDD concentration at $30 \text{ }^\circ\text{C}$, at a pH of 7.00 and at 300 days HRT in synthetic wastewater (Peng et al., 2015). The time-dependent degradation behavior of α -HBCDD was investigated in the presence of Fe_3O_4 micro/nanomaterial at $200 \text{ }^\circ\text{C}$ by Wu et al. (2019). It was found that first-order degradation constant was detected as 0.04 min^{-1} with a R^2 value of 0.86 within 1 h (Wu et al. 2019). Davis et al. (2006) suggested that the biodegradation kinetics of α -HBCDD are significantly impacted by the

concentration of the micropollutant from the first order to zero order in anaerobic digester sludge and in activated (aerobic) sludge prepared under anaerobic and aerobic conditions for 4.2 mg L^{-1} and 3.6 mg L^{-1} , respectively (Davis et al., 2006). The differences in operating parameters, reactor configurations and environmental conditions are thought to affect the kinetic results in this study in the comparison with the aforementioned literature studies.

Langmuir and Freundlich isotherms were used to calculate the relationship between pollutants (all studied micropollutants, COD and sCOD) and biological sludge (anaerobic and aerobic) at 5, 30, 45 and 55 days of SRTs. The description of adsorption process with Freundlich isotherm was an appropriate modelling for the hydrophobic micropollutants (all brominated, aromatic, fluoro, GFZ and TCS) on anaerobic and aerobic biological sludges (Table 7.1). The hydrophobic micropollutants were removed by the adsorption mechanism with high adsorption coefficients (Freundlich Isotherm) in the anaerobic/aerobic sequential reactor system (Table 6.148). The highest Freundlich isotherm constants were found for the most hydrophobic micropollutant namely α -HBCDD ($\log K_{OW} = 7.74$) in the anaerobic and aerobic reactors (Table 6.120). The adsorption intensities (n value) and Freundlich isotherm constants (K_F) were calculated as 25.64 unitless and $134.42 \text{ L } \mu\text{g}^{-1}$, respectively in the anaerobic reactor, while they were found as 8.00 and $322.79 \text{ } \mu\text{g}^{-1}$, respectively in the aerobic reactor (Table 6.120). The moderate hydrophobic micropollutant (IBU), hydrophilic micropollutants (CIP and NDMA) and macropollutants (COD and sCOD) could not be represented with Freundlich isotherm because they all showed tendency for biodegradation in all reactors at all SRTs (Table 7.1). IBU, CIP, NDMA, COD and sCOD were removed mainly by the biodegradation mechanism, therefore, their adsorption coefficients in Freundlich Isotherm were found low in comparison with the hydrophobic micropollutants in the anaerobic/aerobic sequential reactor system (Table 6.148).

The calculations for a cost analysis was made for the biological treatment of all studied micropollutants from 1 m^3 raw hospital wastewater at 55 days of SRT, at a pH of 7.50 and at 37°C with an anaerobic/aerobic sequential biological reactor

system. Electric energy was obtained from the CH₄ gas produced from the anaerobic reactor of the anaerobic/aerobic sequential biological reactor system used in this study. The CH₄ gas production was decreased the cost of electricity consumption. The total cost of the biological treatment of all studied micropollutants from 1 m³ raw hospital wastewater was determined as 3.14 € m⁻³ in the anaerobic/aerobic sequential biological reactor system at the aforementioned experimental conditions (Table 7.1).

7.2 The Performance of Photocatalytic Reactor System Treating Raw Hospital Wastewater

In the preliminary studies of the photocatalytic treatment process, the effects of different nanoparticles [silicon dioxide, zinc oxide, graphene, titanium (IV) oxide (nano-TiO₂) and cerium (IV) oxide (nano-CeO₂)] were researched at increasing nanoparticle concentrations (0.25, 0.50 and 1.50 g L⁻¹), at increasing irradiation times (45, 60 and 90 min), at increasing UV light powers (120, 210 and 300 W), at increasing temperatures (25, 35 and 45 °C) and at increasing pHs (4.00, 7.00 and 8.50) on the photocatalytic removals of the selected micropollutants [PBT (representing brominated group), CIP (representing phenolic group), NDMA (nitroso group), PFOA (representing fluoro group) and AHTN (aromatic group)] for 100 µg L⁻¹ initial PBT, CIP, NDMA, PFOA and AHTN concentrations. After the preliminary studies, it was decided to use nano-TiO₂ and nano-CeO₂ for the photocatalytic experiments. The effects of adsorption (0.50 g L⁻¹ nano-TiO₂ and nano-CeO₂ concentrations, 60 min stirring time, 25 °C and a pH of 7.00) and photolysis (60 min irradiation time, 210 W UV light power, 25 °C and a pH of 7.00) were tested on the photocatalytic removals of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants from the raw hospital wastewater. It can be concluded that the removals of all studied micropollutants occurred mainly by photocatalytic processes at the optimum experimental conditions. In the second step of the photocatalytic treatment process; the effects of increasing nanoparticle concentrations (0.25, 0.50, 1.00 and 1.50 g L⁻¹), irradiation times (15, 30, 45, 60 and

90 min), light powers (80, 120, 210 and 300 W), temperatures (25, 35, 45 and 60 °C) and pHs (4.00, 7.00 and 8.50) were determined on the photocatalytic removals of brominated (α -HBCDD, TBBPA, PBT and PBEB), fluoro (PFOS and PFOA), phenolic (TCS, GFZ, CIP and IBU), nitroso (NDMA) and aromatic (AHTN) micropollutants from the raw hospital wastewater. The results obtained from the second step of this study showed that the optimum experimental conditions were 0.50 g L⁻¹ nano-TiO₂ and nano-CeO₂ concentrations, 45 min irradiation time, 210 W UV light power, 60 °C hospital wastewater temperature and a pH of 7.00 for the maximum photocatalytic removals of all studied micropollutants from the raw hospital wastewater (Table 7.2).

[illegible]Photocatalytic treatment of all studied micropollutants from raw hospital wastewater with nano-CeO₂: 5.39 €/m³

In order to decrease the catalyst cost, reusability of nano-TiO₂ and nano-CeO₂ were researched throughout six sequential treatment steps in this study. The TiO₂ and CeO₂ nanoparticles were reused at the following experimental conditions: 0.50 g L⁻¹ constant nanoparticle concentration, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00. The experimental results showed that nano-TiO₂ and nano-CeO₂ can be reused effectively during five sequential times for the photocatalytic treatment of all studied micropollutants from the raw hospital wastewater in order to decrease the cost of treatment at the aforementioned experimental conditions.

The experimental results obtained from the photocatalytic treatment were applied to Langmuir and Freundlich isotherm models to determine the optimum brominated micropollutant removal kinetics with nano-TiO₂ and nano-CeO₂. The kinetic data showed that the kinetic constants were meaningful for Langmuir isotherm in the comparison with Freundlich isotherm. The kinetic constants of Langmuir isotherm were found to be high for hydrophobic (brominated, aromatic, fluoro and phenolic) micropollutants ($\log K_{OW} > 4.0$) in the comparison with hydrophilic (CIP and NDMA) micropollutants ($\log K_{OW} < 2.5$) for 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00 (Table 7.2). The highest Langmuir isotherm constants; q_m and K_L were found between 28.57 – 76.92 $\mu\text{g g}^{-1}$ and 0.071 – 0.109 L μg^{-1} , respectively for the brominated micropollutants at the aforementioned experimental conditions (Table 7.2). Moreover, the lowest Langmuir isotherm constants; q_m and K_L were calculated between 0.23 – 0.37 $\mu\text{g g}^{-1}$ and 0.0001 – 0.0005 L μg^{-1} , respectively for the hydrophilic (CIP and NDMA) micropollutants at the aforementioned experimental conditions (Table 7.2).

A cost analysis was carried out for the photocatalytic treatment of all studied micropollutants from 1 m³ raw hospital wastewater for 0.50 g L⁻¹ constant nano-TiO₂ and nano-CeO₂ concentrations, 45 min constant irradiation time, 210 W constant UV light power, a constant temperature of 60 °C and a constant pH of 7.00 with (Table 7.2). The cost analysis showed that the photocatalytic treatment with nano-CeO₂

(5.39 €) was a cheaper option in the comparison with the nano-TiO₂ (6.19 €) (Table 7.2). In addition to this, the photocatalytic treatment with nano-CeO₂ (higher than 66% for all studied micropollutants) gave higher removal efficiencies than the nano-TiO₂ (higher than 60% for all studied micropollutants) at the aforementioned experimental conditions (Table 7.2).

7.3 The Performance of Ultrasound Treatment System Treating Raw Hospital Wastewater

In this study, effects of sonicator power (20, 70 and 120 W), sonication time (15, 30, 45, 60 and 90 min), pHs (4.00, 7.00 and 8.50), temperatures (25, 40, 50, 65 and 80 °C), nano-TiO₂ and nano-CeO₂ concentrations (0.00, 0.20, 0.40, 0.60 and 0.80 g L⁻¹) were investigated on the ultrasound removals of all studied micropollutants from the raw hospital wastewater at a constant sonicator frequency of 132 kHz. The maximum ultrasound removal efficiencies were achieved at 120 W sonicator power for 60 min sonication time at a pH of 4.00 at 40 °C with 0.40 g L⁻¹ nano-TiO₂ and nano-CeO₂ concentrations and at a constant sonicator frequency of 132 kHz for all studied micropollutants from the raw hospital wastewater (Table 7.3).

Table 7.3 The ultrasound treatment system with 0.40 g L⁻¹ nano-TiO₂ and nano-CeO₂ concentrations, 60 min sonication time, 120 W sonicator power, 40 °C hospital wastewater temperature and a pH of 4.00

[illegible]

In order to decrease the catalyst cost, reusability of nano-TiO₂ and nano-CeO₂ were researched at the aforementioned experimental conditions. Six sequential treatment steps were investigated in order to determine the possible reusability of the TiO₂ and CeO₂ nanoparticles. The results showed that nano-TiO₂ and nano-CeO₂ can be used effectively five sequential treatment steps for the sonocatalytic treatment of all studied micropollutants from raw hospital wastewater in order to decrease the cost of treatment with 0.40 g L⁻¹ constant nanoparticle (both for nano-TiO₂ and nano-CeO₂) concentration at the aforementioned optimum experimental conditions.

The experimental results obtained from the ultrasound treatment were applied to various kinetic models such as, zero, half, first and second-order to determine the optimum micropollutant removal kinetics with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions. All studied micropollutants followed first-order removal model with the meaningful highest kinetic constants and R² values between zero, half and second-order kinetic models both for the experiments with nano-TiO₂ and nano-CeO₂ at the aforementioned experimental conditions (Table 7.3). The highest first-order kinetic constant, k₁ value was found as 0.0221 and 0.0239 day⁻¹ with nano-TiO₂ and nano-CeO₂, respectively for GFZ (Table 7.3). Because GFZ had the maximum removal efficiency as 96% both for the experiments with nano-TiO₂ and nano-CeO₂ (Table 7.3). The lowest first-order kinetic constant, k₁ value was found as 0.0055 and 0.0092 day⁻¹ with nano-TiO₂ and nano-CeO₂, respectively for PFOA owing to that PFOA had the minimum removal efficiency as 65% and 70% for nano-TiO₂ and nano-CeO₂, respectively (Table 7.3).

The calculations for a cost analysis was made for the ultrasound treatment of all studied micropollutants from 1 m³ raw hospital wastewater at the aforementioned optimum experimental conditions with nano-TiO₂ and nano-CeO₂ (Table 7.3). The cost analysis showed that the ultrasound treatment with nano-CeO₂ (5.49 €) was cheaper compared to nano-TiO₂ (5.81 €) at the aforementioned experimental conditions (Table 7.3). Also, the ultrasound treatment with nano-CeO₂ (higher than 70% for all studied micropollutants) gave higher removal efficiencies than the nano-

TiO₂ (higher than 65% for all studied micropollutants) at the aforementioned experimental conditions (Table 7.3).

7.4 The Performance of UF and RO Membrane Treatment System Treating Raw Hospital Wastewater

The UF membrane used separately and fed with the raw hospital wastewater in this study. The effects of operational parameters [permeate flux, J_v (78.13, 104.17 and 156.25 L m⁻² h⁻¹) and cross-flow velocity, CFV (0.08, 0.11 and 0.16 m h⁻¹)] on the removals of conventional pollutants (TSS, TOC, TDS, COD and sCOD) and micropollutants (brominated, aromatic, fluoro, phenolic and nitroso) were investigated at constant TMP (2.75 bar), pH (8.00) and temperature (25 °C). The maximum removal efficiencies (higher than 60% for conventional pollutants and higher than 5% for micropollutants) were obtained at the highest permeate flux (J_v) value of 156.25 L m⁻² h⁻¹ and at the highest CFV (0.16 m h⁻¹) at a pH of 8.00 and at 25 °C in UF (Table 7.4).

Table 7.4 The UF and RO membrane treatment systems

Pollutant	Influent conc. ($\mu\text{g L}^{-1}$)	log K_{ow} (unitless)	UF	RO
			$J_v = 156.25 \text{ L m}^{-2} \text{ h}^{-1}$, CFV = 0.16 m h^{-1} TMP = 2.75 bar pH = 8.00, T = 25 °C V = 100 L, S = 0.64 m^2 , t = 1 h	$J_v = 104.17 \text{ L m}^{-2} \text{ h}^{-1}$, CFV = 0.10 m h^{-1} TMP = 4.75 bar pH = 8.00, T = 25 °C V = 100 L, S = 0.96 m^2 , t = 1 h
α -HBCDD	0.0115	7.74	36.8±0.5	99.0±0.5
PBEB	0.00328	7.48	36.4±0.5	98.5±0.5
PBT	0.00231	6.99	36.0±0.5	98.2±0.5
TBBPA	0.0170	5.90	35.7±0.5	98.0±0.5
AHTN	0.206	5.70	35.2±0.5	97.8±0.5
PFOA	0.1770	4.81	34.9±0.5	97.7±0.5
PFOS	0.0180	4.49	32.1±0.5	96.0±0.5
GFZ	53.30	4.77	33.6±0.5	97.3±0.5
TCS	361.00	4.76	33.2±0.5	97.1±0.5
IBU	42.50	3.79	30.0±0.5	95.8±0.5
CIP	522.00	0.28	6.2±0.5	95.6±0.5
NDMA	0.165	-0.57	5.8±0.5	95.3±0.5
TSS	130.00*	--	99.8±0.5	100.0±0.5
TOC	325.00*	--	74.7±0.5	95.5±0.5
TDS	250.00*	--	60.4±0.5	99.0±0.5
COD	950.00*	--	84.0±0.5	98.6±0.5
sCOD	850.00*	--	79.5±0.5	95.5±0.5
UF treatment of all studied micropollutants and macropollutants from raw hospital wastewater: 0.66 €/m^3				
RO treatment of all studied micropollutants and macropollutants from raw hospital wastewater: 0.67 €/m^3				

*: concentration in mg L^{-1}

The RO membrane also used separately and fed with the raw hospital wastewater. The effects of operational parameters [transmembrane pressure, TMP (2.75, 3.75 and 4.75 bar), permeate flux, J_v (52.08, 69.44 and 104.17 L m⁻² h⁻¹) and cross-flow velocity, CFV (0.05, 0.07 and 0.10 m h⁻¹)] on the removals of conventional pollutants (TSS, TOC, TDS, COD and sCOD) and micropollutants (brominated, aromatic, fluoro, phenolic and nitroso) were investigated at a constant pH (8.00) and temperature (25 °C). The maximum removal efficiencies (higher than 95% both for conventional pollutants and micropollutants) were obtained at the highest TMP of 4.75 bar at the highest permeate flux (J_v) value of 104.17 L m⁻² h⁻¹ and at the highest CFV (0.10 m h⁻¹) for 1 h at a pH of 8.00 and at 25 °C in RO (Table 7.4).

RO gave higher removal efficiencies than UF both for conventional pollutants and micropollutants from the raw hospital wastewater at the aforementioned experimental conditions (Table 7.4). The conventional pollutants (TSS, TOC, TDS, COD and sCOD) removed mainly by size exclusion mechanism due to being larger and neutral molecules at the aforementioned experimental conditions in RO. The size exclusion mechanism made contribution to the removals of the neutral brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN) and phenolic (TCS) micropollutants at the aforementioned experimental conditions. The hydrophobic adsorption mechanism affected positively the removals of hydrophobic brominated (α -HBCDD, PBEB, PBT and TBBPA), aromatic (AHTN), fluoro (PFOA and PFOS) and some phenolic (GFZ, TCS and IBU) micropollutants having higher log K_{ow} values than 3.0. The other hydrophobic and anionic fluoro (PFOA and PFOS) and phenolic (GFZ and IBU) micropollutants removed by hydrophobic adsorption mechanism and electrostatic interactions.

A cost analysis study was performed for the membrane treatment of all studied micropollutants from 1 m³ raw hospital wastewater with UF [at a constant TMP of 2.75 bar, at a constant permeate flux (J_v) of 156.25 L m⁻² h⁻¹, at a constant CFV of 0.16 m h⁻¹, at a constant operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C] and RO [at a constant TMP of 4.75 bar, at a constant permeate flux (J_v) of 104.17 L m⁻² h⁻¹, at a constant CFV of 0.10 m h⁻¹, at a constant

operation time of 1 h, at a constant pH of 8.00 and at a constant temperature of 25 °C] (Table 7.4). There were no difference between the cost values for UF (0.66 €) and RO (0.67 €) at the aforementioned experimental conditions (Table 7.4). Furthermore, the membrane treatment with RO (higher than 95% for all studied micropollutants) gave higher removal efficiencies than the UF (between 5.8% and 36.8% for all studied micropollutants) at the aforementioned experimental conditions (Table 7.4).

In order to evaluate whether the treated hospital wastewater with RO can be reused as irrigation water in the hospital area, the effluent concentrations of RO at 4.75 bar TMP at the aforementioned experimental conditions were analyzed according to Wastewater Treatment Plant Technical Methods, Table E7.2 – E.7.7 (2010) and Su Kirliliği Kontrolü Yönetmeliği Teknik Usuller Tebliği, Table 4 (1991). RO effluent at 4.75 bar TMP was found to be first class irrigation water according to the aforementioned regulations at the aforementioned experimental conditions (Table 6.227). Therefore, a cost analysis was performed if the hospital management used the RO effluent as irrigation water in the hospital area. Approximately a benefit of 24000 € year⁻¹ can be obtained from the irrigation water if the raw hospital wastewater was treated with RO and the permeate was used as irrigation water in the hospital area (Equation 6.337).

7.5 Recommendations

RO membrane system is a suitable choice for the raw hospital wastewater treatment since it can be removed both macropollutants (TSS, TOC, TDS, COD and sCOD) and all studied micropollutants that are presented at quite high concentrations in this type of wastewater. RO also provides the cheapest treatment option through the other treatment options (biological, photocatalytic and ultrasound) with the total cost of 0.67 € to treat 1 m³ raw hospital wastewater (Table 7.5). RO effluent at the optimum experimental conditions found to be first class irrigation water in this study. Therefore, if the hospital management used the RO effluent as irrigation water in the hospital area, it is possible to provide a benefit of 24000 € year⁻¹ from the irrigation

water. Several offers were collected from the market for a real-scale RO facility installation in the hospital area. The offer of the company which offers the best price was given in Appendix-14. An initial investment cost of 11800 € is required to benefit 24000 € per year from irrigation water cost. If the RO system is installed and operated, the system will be able to amortize itself in a period of approximately 6 months. Considering the high removal efficiencies, low treatment costs, use of permeate as irrigation water and the system's ability to amortize itself, it is a feasible option to treat the raw hospital wastewater with the RO membrane system.



Table 7.5 Summary of the results for all studied micropollutants with biological, photocatalytic, ultrasound and membrane treatment systems

Micropollutant	Influent conc. ($\mu\text{g L}^{-1}$)	log K_{ow} (unitless)	Anaerobic/Aerobic Sequential Biological Reactor System				Photocatalytic treatment with nano-CeO ₂	Ultrasound treatment with nano-CeO ₂	RO membrane
			Bio-degradation (%)	Adsorption (%)	Sorption (%)	Volatilization (%)	Total Removal (%)	Total Removal (%)	Total Removal (%)
α -HBCDD	0.0115	7.74	18.26±0.5	80.87±0.5	0.97±0.1	0.00009±0.00005	98±0.5	89±0.5	99.0±0.5
PBEB	0.00328	7.48	19.05±0.5	80.05±0.5	0.89±0.1	0.00000±0.00005	96±0.5	87±0.5	98.5±0.5
PBT	0.00231	6.99	19.57±0.5	79.56±0.5	0.91±0.1	0.00000±0.00005	97±0.5	89±0.5	98.2±0.5
TBBPA	0.0170	5.90	20.59±0.5	78.56±0.5	0.92±0.1	0.00010±0.00005	97±0.5	93±0.5	98.0±0.5
AHTN	0.206	5.70	24.40±0.5	74.48±0.5	1.12±0.1	0.00022±0.00005	97±0.5	85±0.5	97.8±0.5
PFOA	0.1770	4.81	27.96±0.5	71.06±0.5	1.04±0.1	0.00030±0.00005	75±0.5	70±0.5	97.7±0.5
PFOS	0.0180	4.49	47.33±0.5	51.70±0.5	1.00±0.1	0.00026±0.00005	76±0.5	72±0.5	96.0±0.5
GFZ	53.30	4.77	31.69±0.5	67.17±0.5	1.14±0.1	0.00007±0.00005	95±0.5	96±0.5	97.3±0.5
TCS	361.00	4.76	31.77±0.5	67.11±0.5	1.13±0.1	0.00005±0.00005	97±0.5	94±0.5	97.1±0.5
IBU	42.50	3.79	87.95±0.5	10.98±0.5	0.85±0.1	0.00007±0.00005	95±0.5	90±0.5	95.8±0.5
CIP	522.00	0.28	93.16±0.5	5.51±0.5	0.66±0.1	0.00000±0.00005	98±0.5	91±0.5	95.6±0.5
NDMA	0.165	-0.57	96.42±0.5	3.10±0.5	0.47±0.1	0.00007±0.00005	66±0.5	75±0.5	95.3±0.5
Cost to treat 1 m ³ raw hospital wastewater			3.14 €				5.39 €	5.49 €	0.67 €

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APPENDICES

Appendix-1: Monod Kinetic Model for Biological Treatment

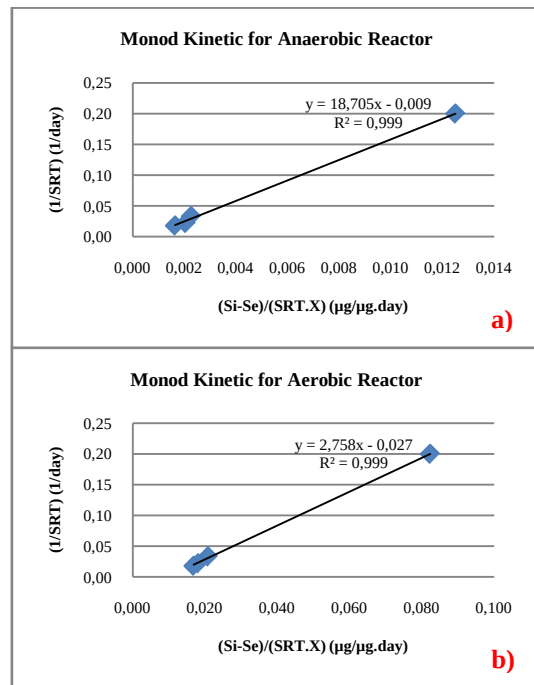


Figure 1 Determination of Y and k_d for PBEB in the (a) anaerobic and (b) aerobic reactor

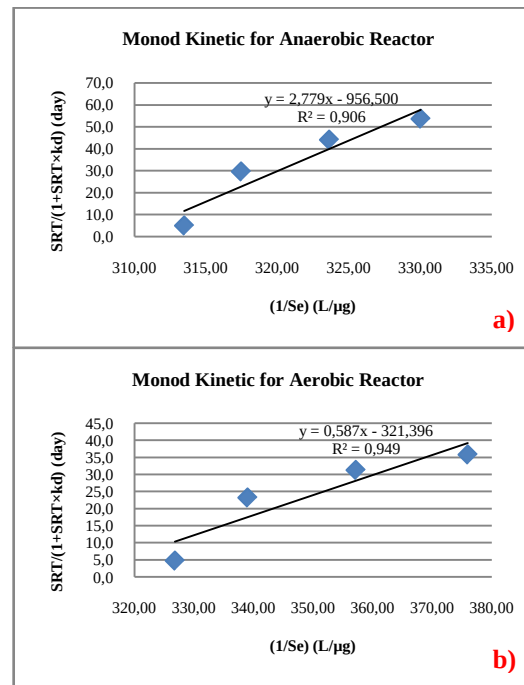


Figure 2 Determination of K_s and μ_{max} for PBEB in the (a) anaerobic and (b) aerobic reactor

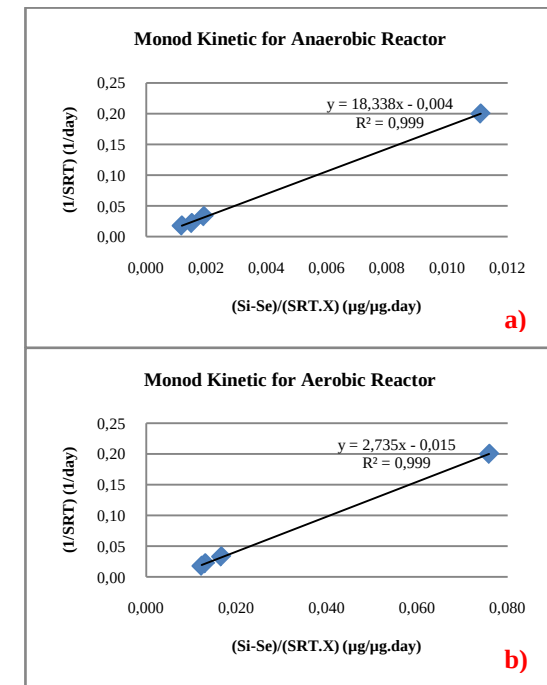


Figure 3 Determination of Y and k_d for PBT in the (a) anaerobic and (b) aerobic reactor

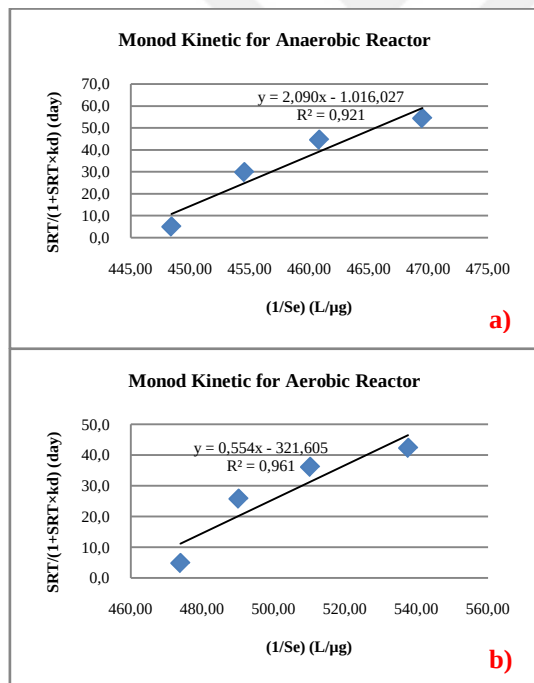


Figure 4 Determination of K_s and μ_{max} for PBT in the (a) anaerobic and (b) aerobic reactor

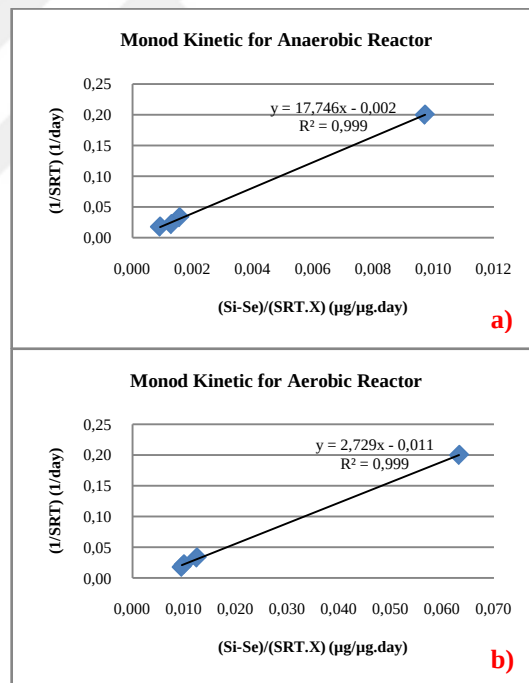


Figure 5 Determination of Y and k_d for TBBPA in the (a) anaerobic and (b) aerobic reactor

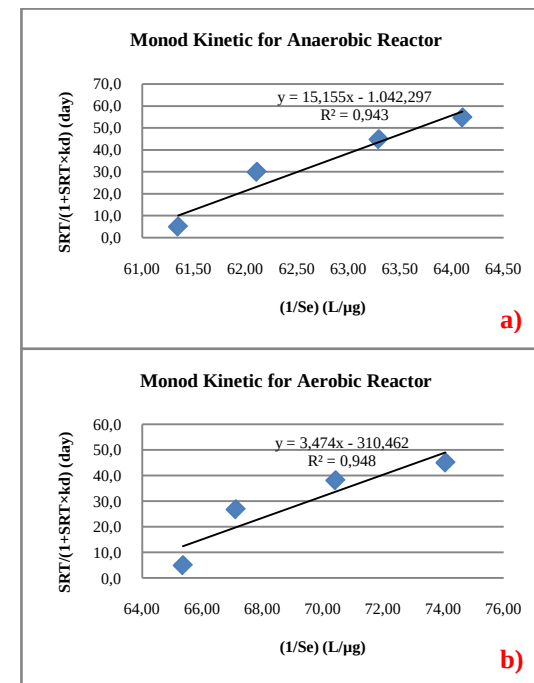


Figure 6 Determination of K_s and μ_{max} for TBBPA in (a) anaerobic and (b) aerobic reactor

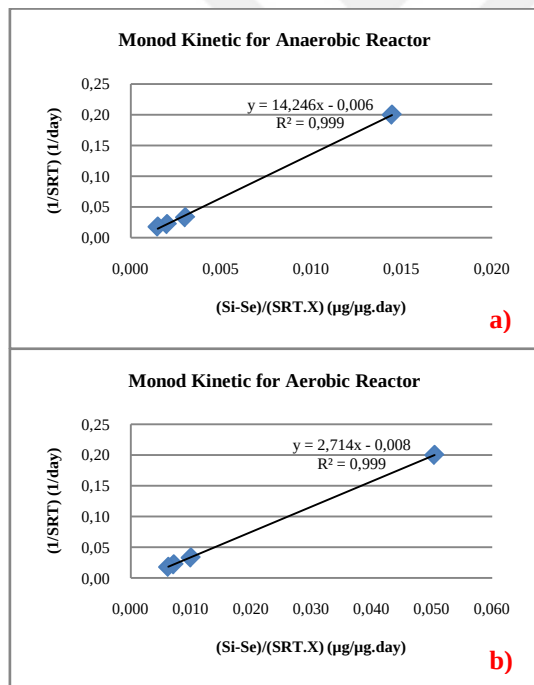


Figure 7 Determination of Y and k_d for AHTN in the (a) anaerobic and (b) aerobic reactor

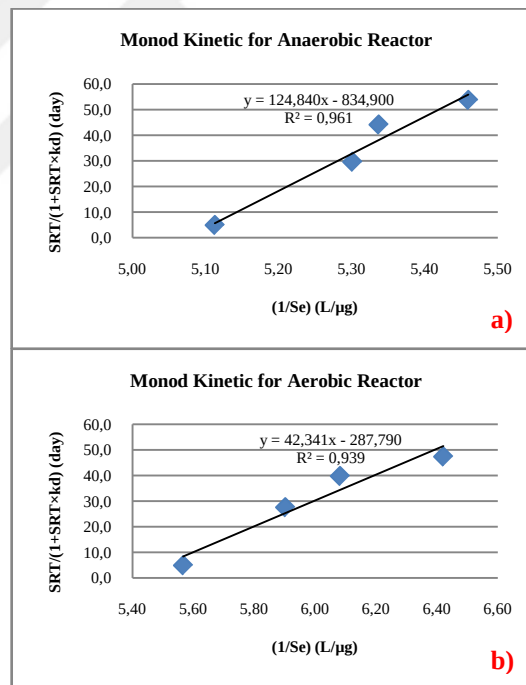


Figure 8 Determination of K_s and μ_{max} for AHTN in the (a) anaerobic and (b) aerobic reactor

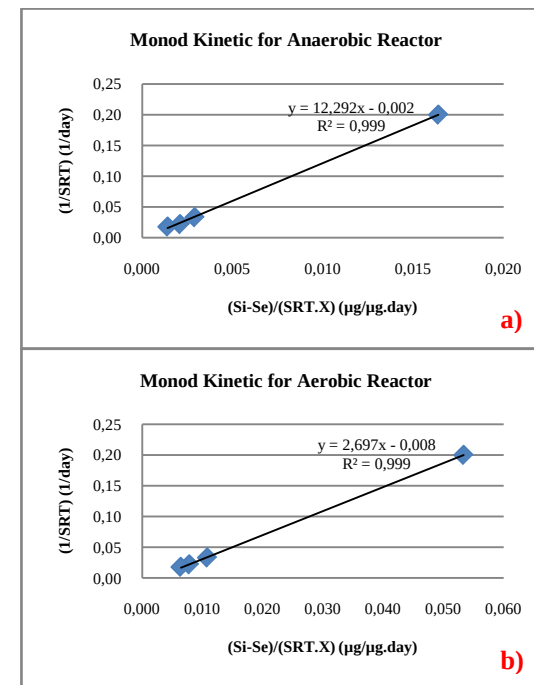


Figure 9 Determination of Y and k_d for PFOA in the (a) anaerobic and (b) aerobic reactor

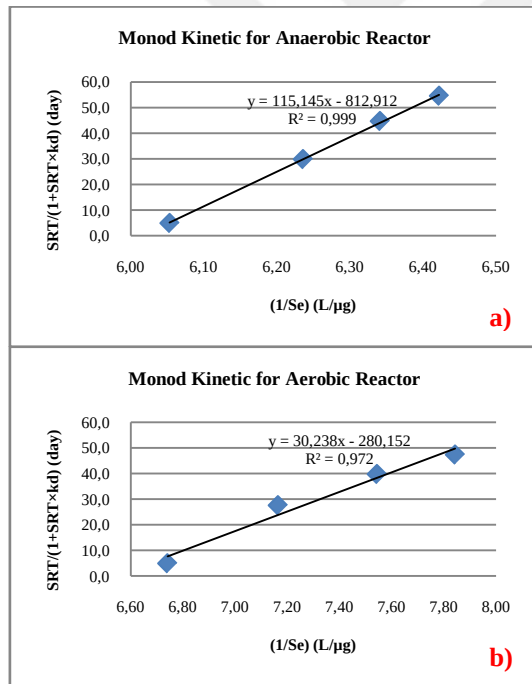


Figure 10 Determination of K_s and μ_{max} for PFOA in the (a) anaerobic and (b) aerobic reactor

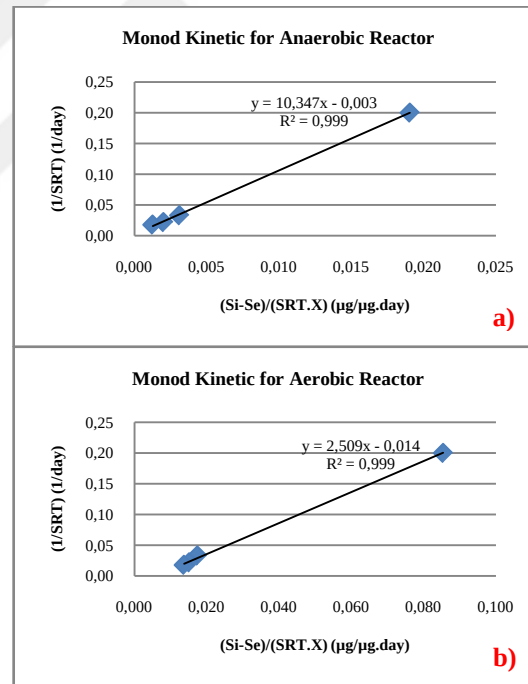


Figure 11 Determination of Y and k_d for PFOS in the (a) anaerobic and (b) aerobic reactor

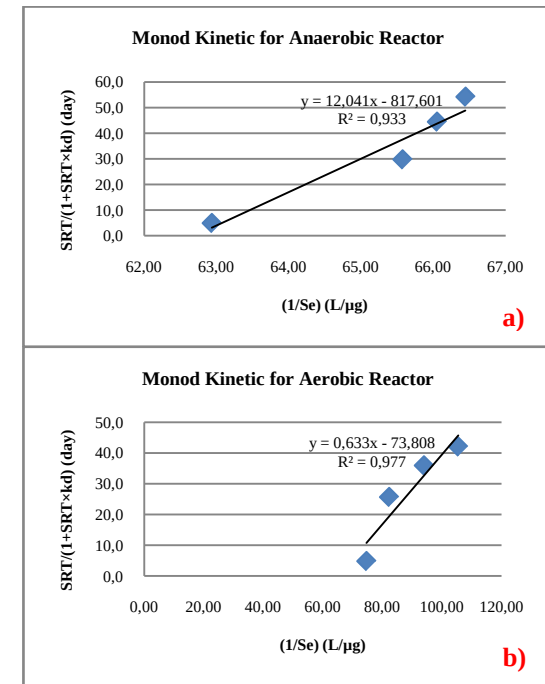


Figure 12 Determination of K_s and μ_{max} for PFOS in the (a) anaerobic and (b) aerobic reactor

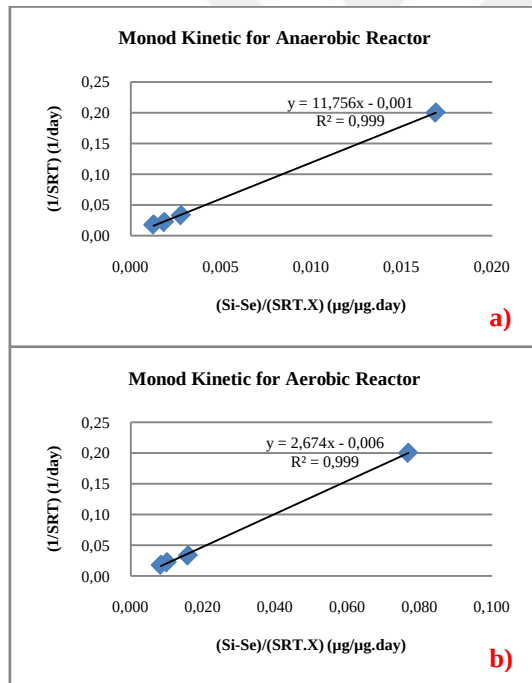


Figure 13 Determination of Y and k_d for GFZ in the (a) anaerobic and (b) aerobic reactor

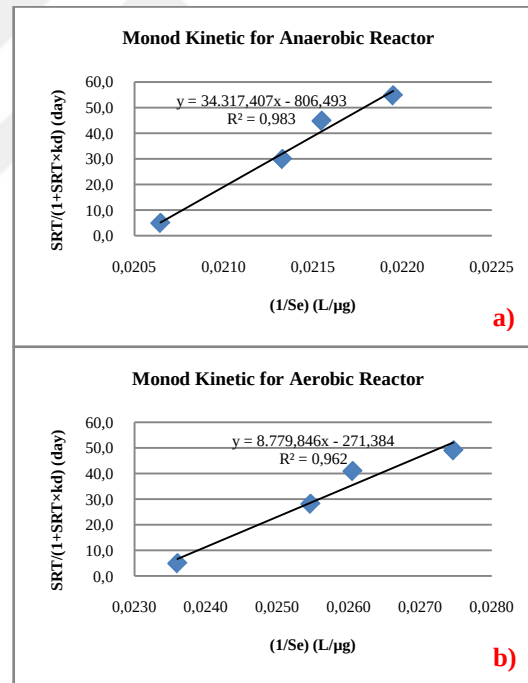


Figure 14 Determination of K_s and μ_{max} for GFZ in the (a) anaerobic and (b) aerobic reactor

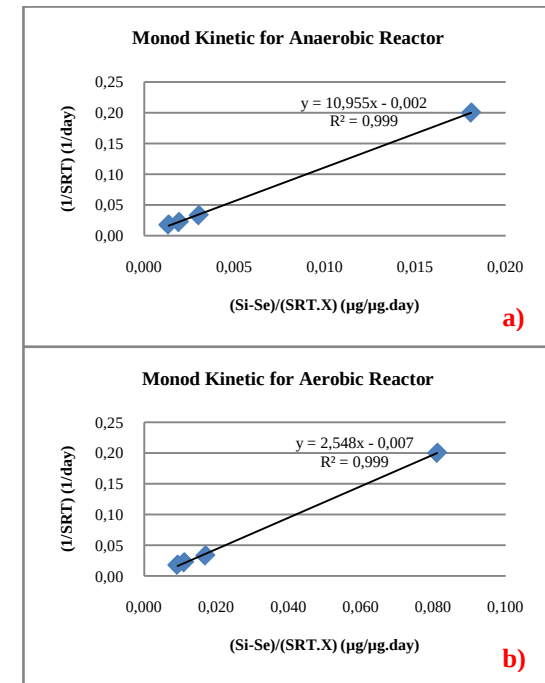


Figure 15 Determination of Y and k_d for TCS in the (a) anaerobic and (b) aerobic reactor

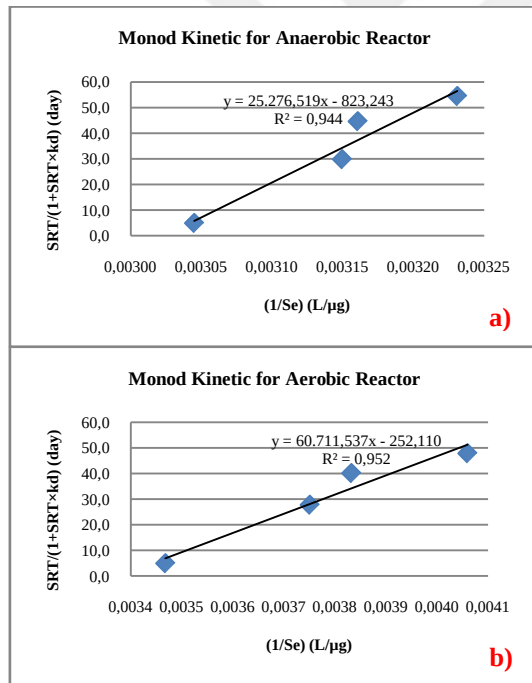


Figure 16 Determination of K_s and μ_{max} for TCS in the (a) anaerobic and (b) aerobic reactor

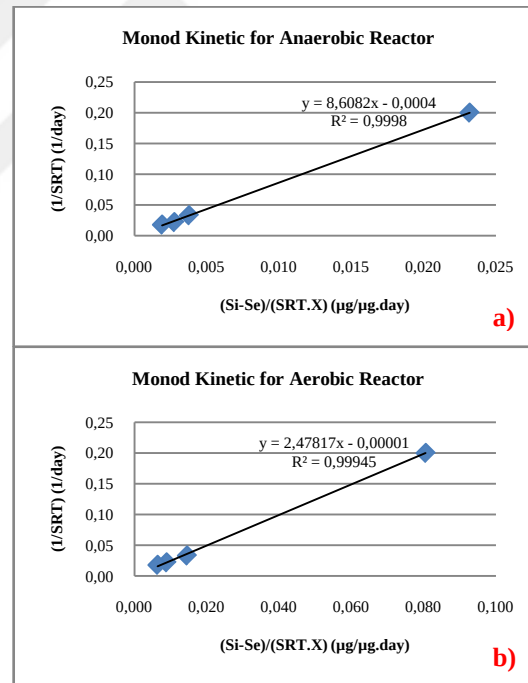


Figure 17 Determination of Y and k_d for IBU in the (a) anaerobic and (b) aerobic reactor

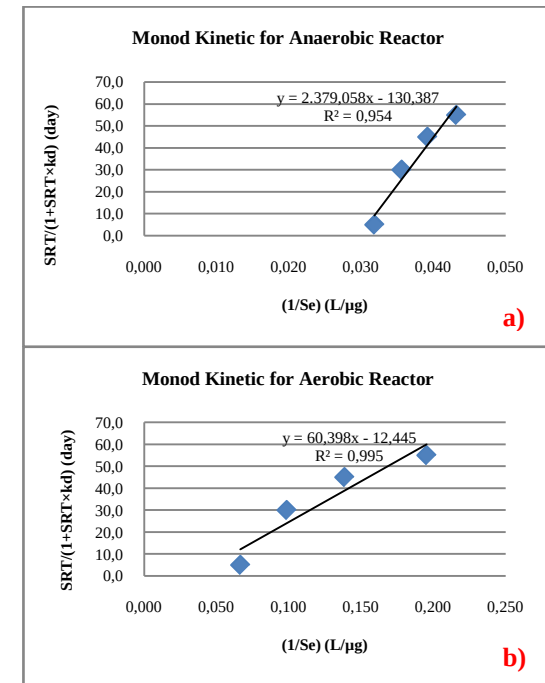


Figure 18 Determination of K_s and μ_{max} for IBU in the (a) anaerobic and (b) aerobic reactor

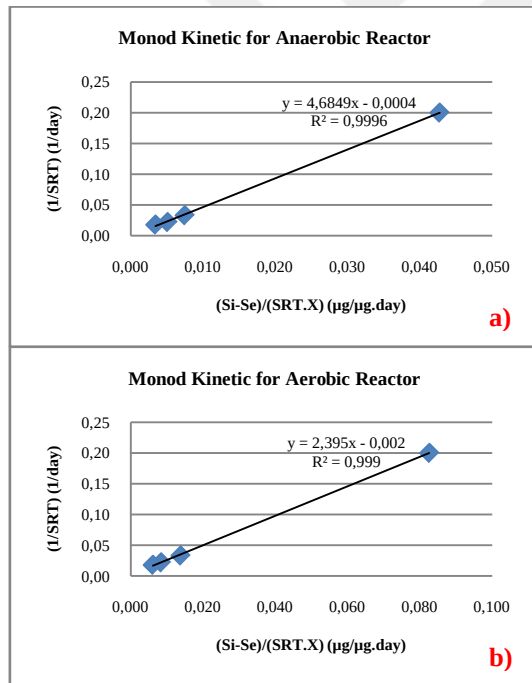


Figure 19 Determination of Y and k_d for CIP in the (a) anaerobic and (b) aerobic reactor

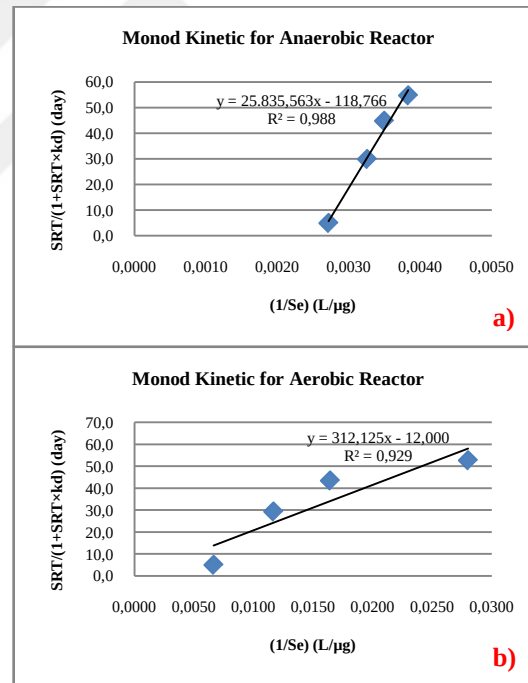


Figure 20 Determination of K_s and μ_{max} for CIP in the (a) anaerobic and (b) aerobic reactor

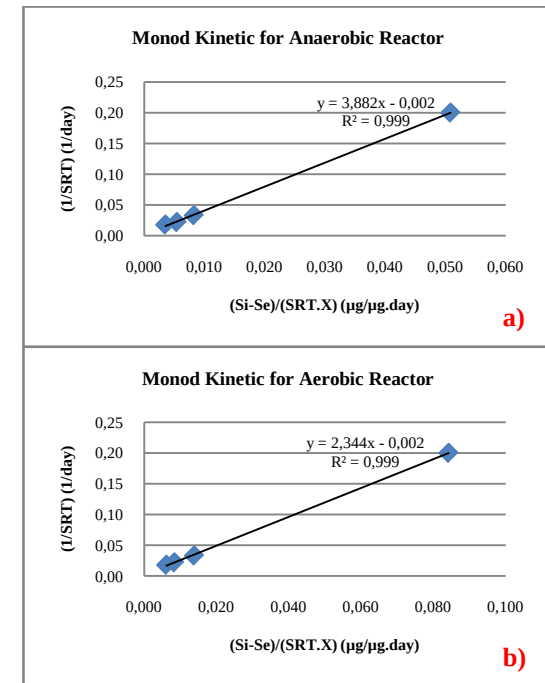


Figure 21 Determination of Y and k_d for NDMA in the (a) anaerobic and (b) aerobic reactor

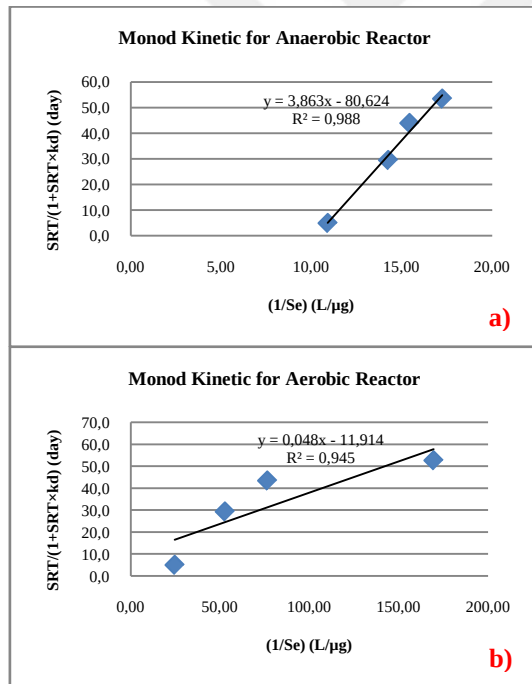


Figure 22 Determination of K_s and μ_{max} for NDMA in (a) anaerobic and (b) aerobic reactor

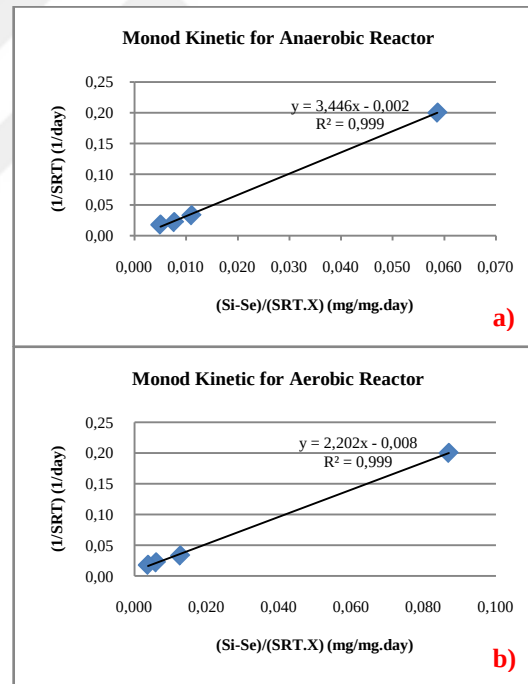


Figure 23 Determination of Y and k_d for COD in the (a) anaerobic and (b) aerobic reactor

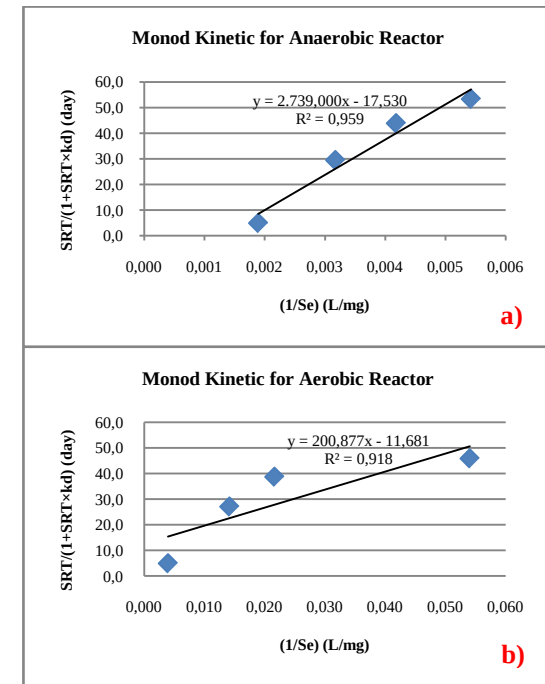


Figure 24 Determination of K_s and μ_{max} for COD in (a) anaerobic and (b) aerobic reactor

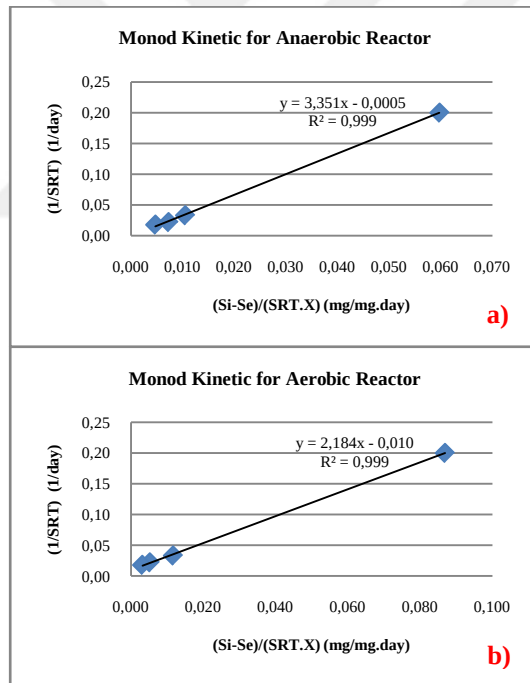


Figure 25 Determination of Y and k_d for sCOD in the (a) anaerobic and (b) aerobic reactor

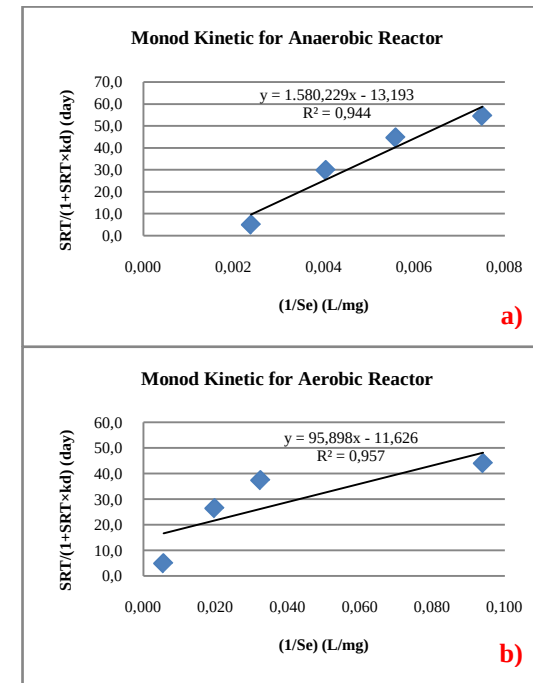


Figure 26 Determination K_s and μ_{max} for sCOD in the (a) anaerobic and (b) aerobic reactor

Appendix-2: Zero-Order Removal Model for Biological Treatment

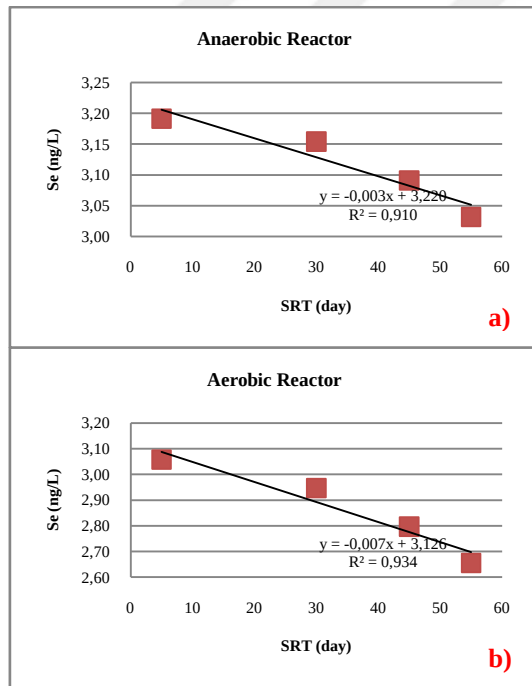


Figure 1 Zero-order PBEB removal model in (a) anaerobic and (b) aerobic reactor

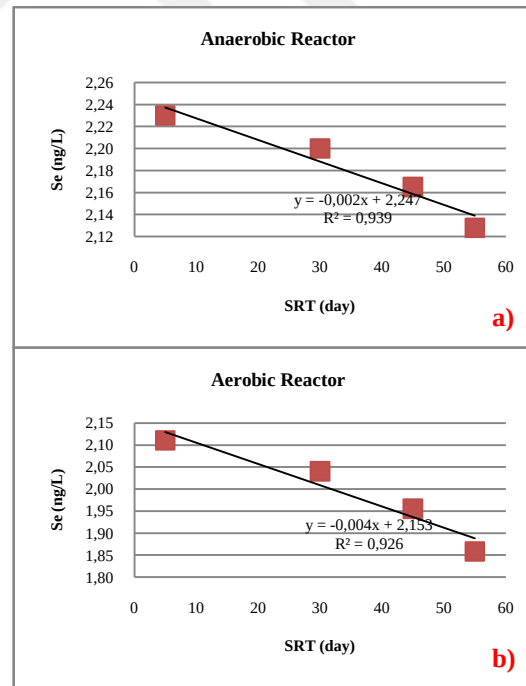


Figure 2 Zero-order PBT removal model in (a) anaerobic and (b) aerobic reactor

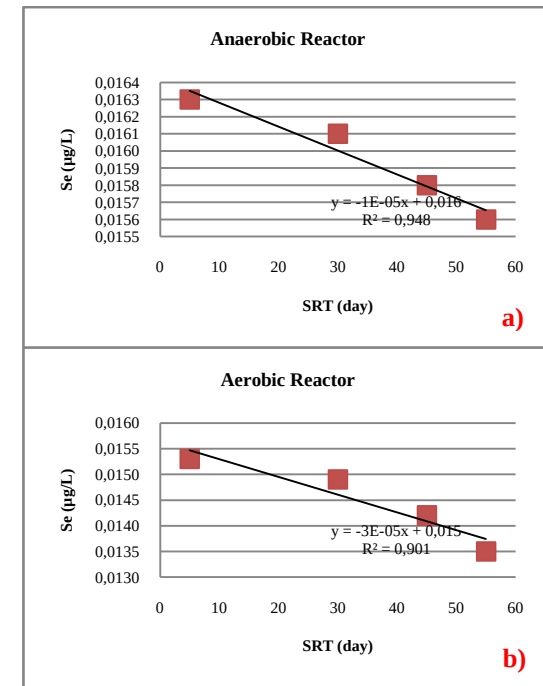


Figure 3 Zero-order TBBPA removal model in (a) anaerobic and (b) aerobic reactor

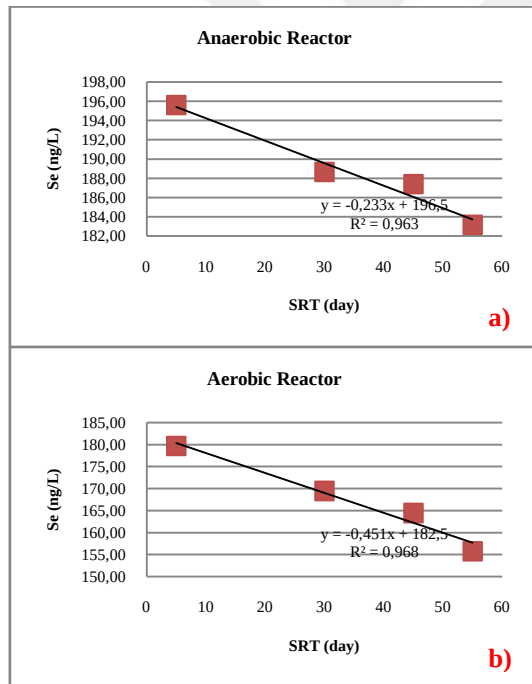


Figure 4 Zero-order AHTN removal model in (a) anaerobic and (b) aerobic reactor

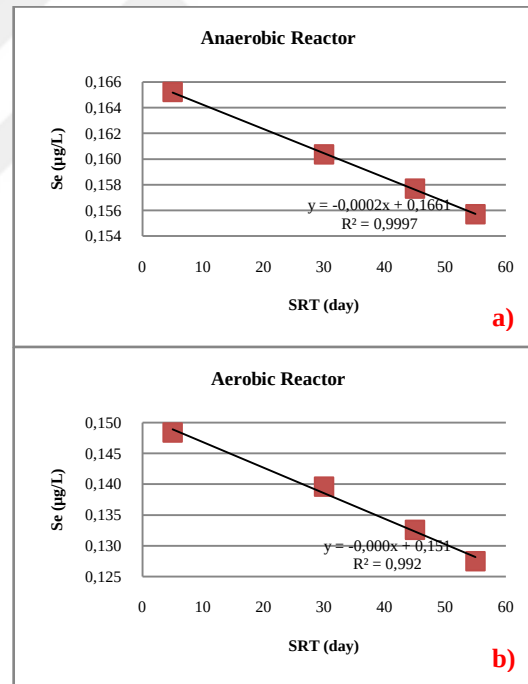


Figure 5 Zero-order PFOA removal model in (a) anaerobic and (b) aerobic reactor

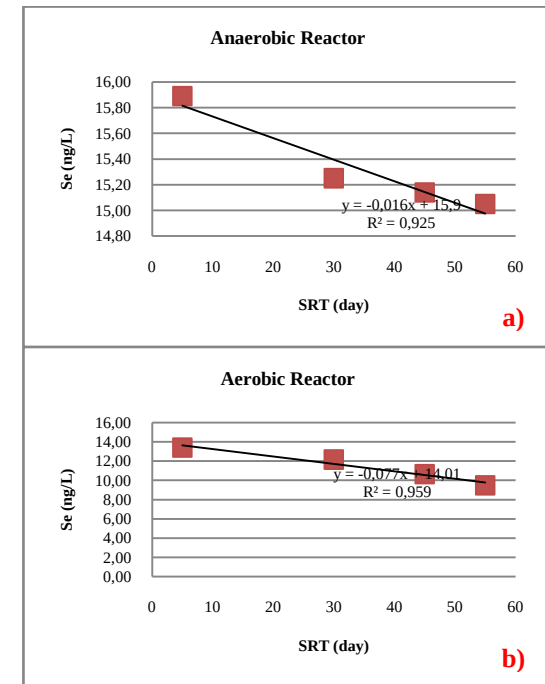


Figure 6 Zero-order PFOS removal model in (a) anaerobic and (b) aerobic reactor

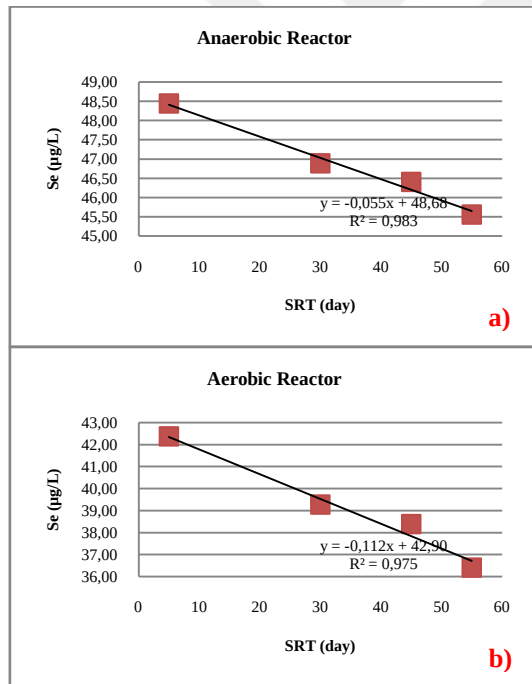


Figure 7 Zero-order GFZ removal model in (a) anaerobic and (b) aerobic reactor

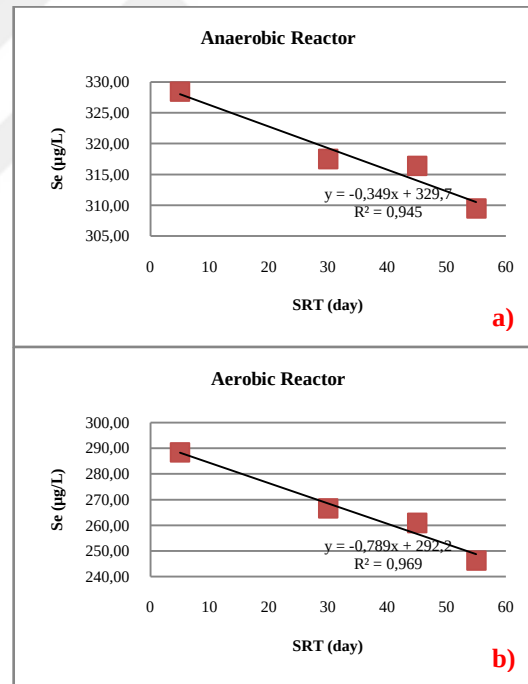


Figure 8 Zero-order TCS removal model in (a) anaerobic and (b) aerobic reactor

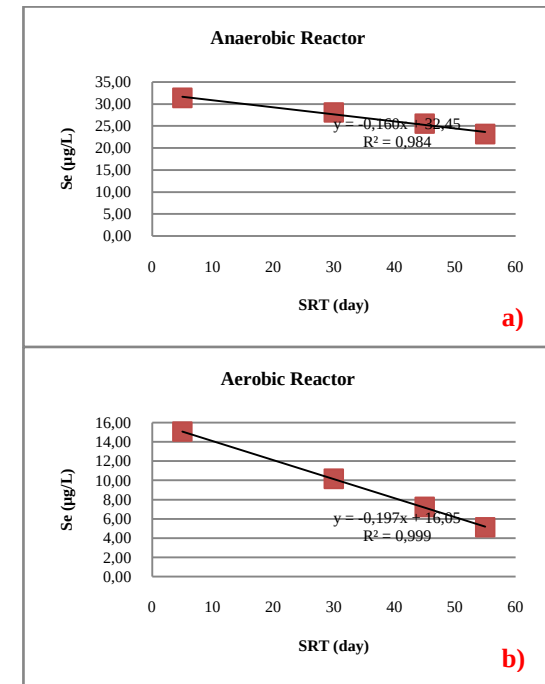


Figure 9 Zero-order IBU removal model in (a) anaerobic and (b) aerobic reactor

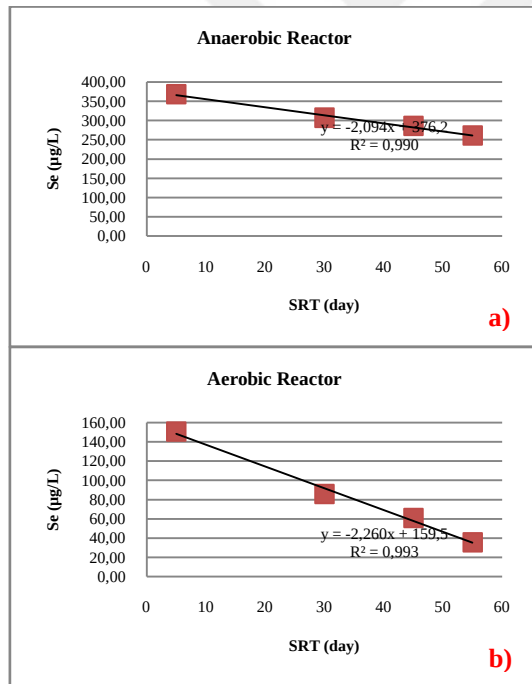


Figure 10 Zero-order CIP removal model in (a) anaerobic and (b) aerobic reactor

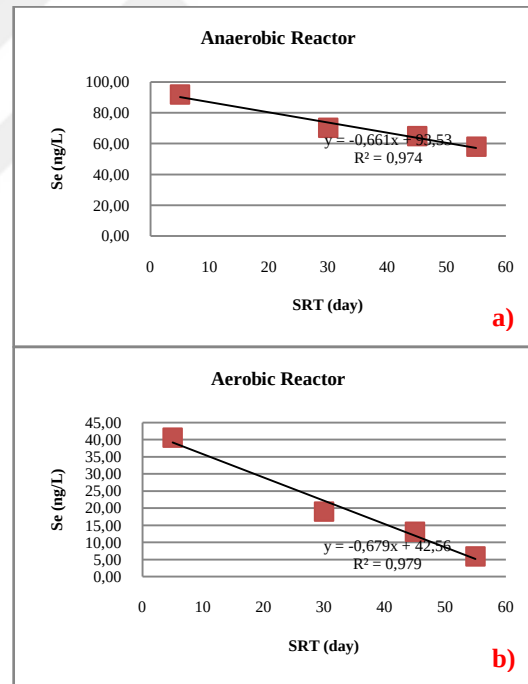


Figure 11 Zero-order NDMA removal model in (a) anaerobic and (b) aerobic reactor

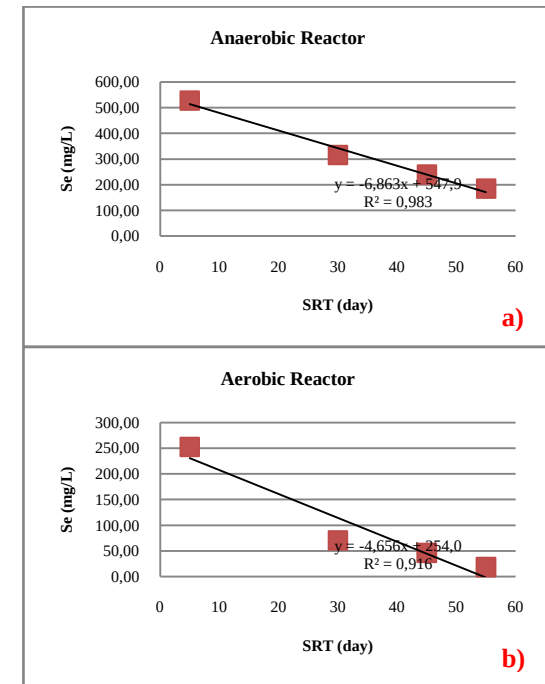


Figure 12 Zero-order COD removal model in (a) anaerobic and (b) aerobic reactor

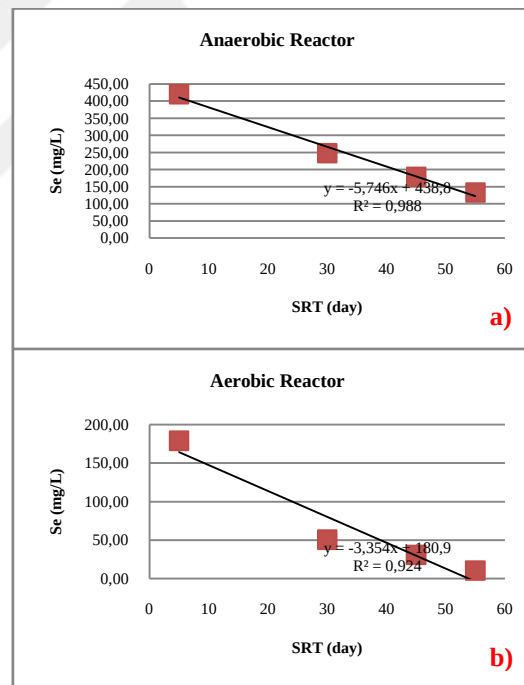


Figure 13 Zero-order sCOD removal model in (a) anaerobic and (b) aerobic reactor

Appendix-3: Half-Order Removal Model for Biological Treatment

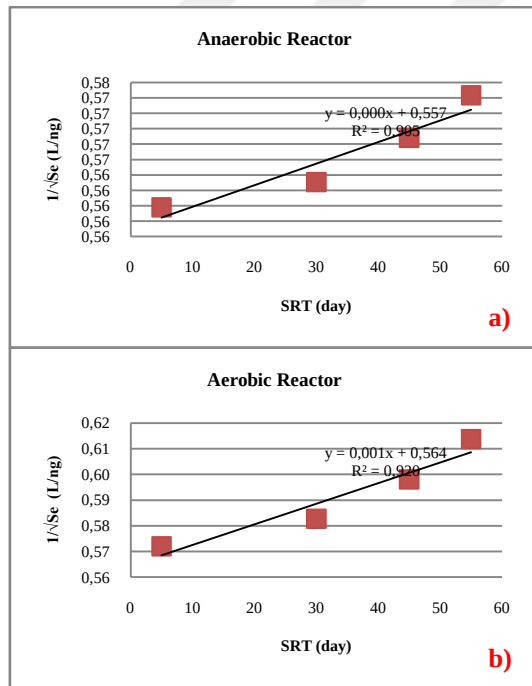


Figure 1 Half-order PBEB removal model in (a) anaerobic reactor and (b) aerobic reactor

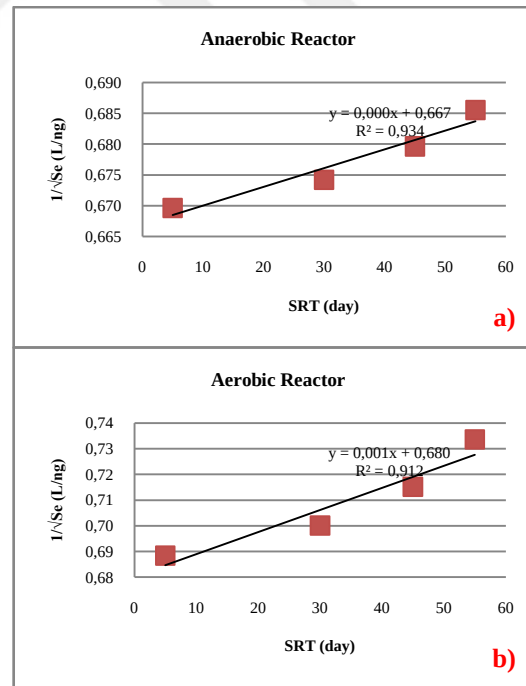


Figure 2 Half-order PBT removal model in (a) anaerobic reactor and (b) aerobic reactor

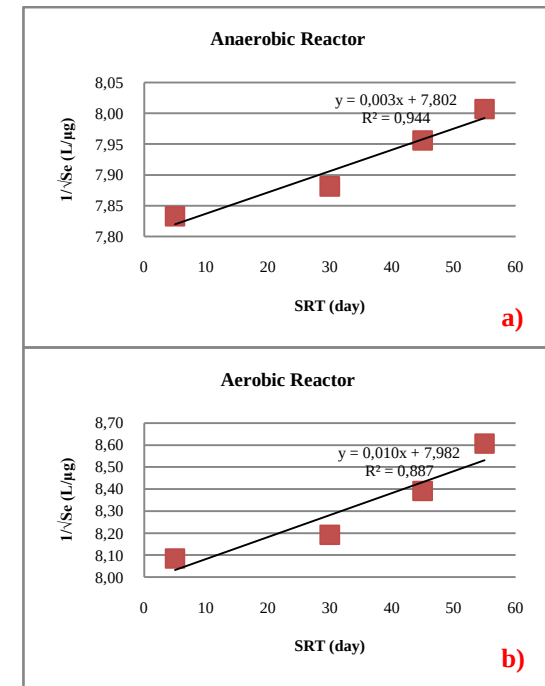


Figure 3 Half-order TBBPA removal model in (a) anaerobic reactor and (b) aerobic reactor

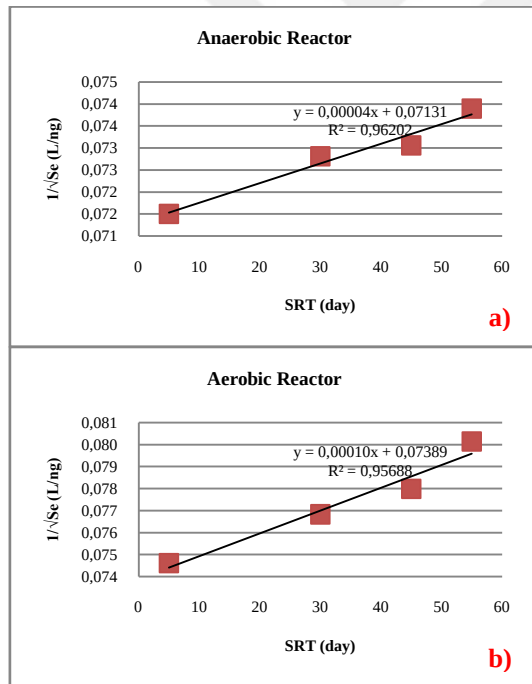


Figure 4 Half-order AHTN removal model in (a) anaerobic reactor and (b) aerobic reactor

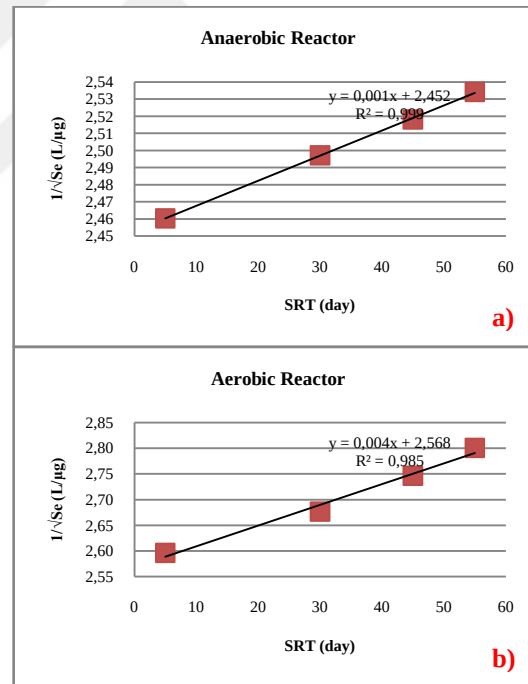


Figure 5 Half-order PFOA removal model in (a) anaerobic reactor and (b) aerobic reactor

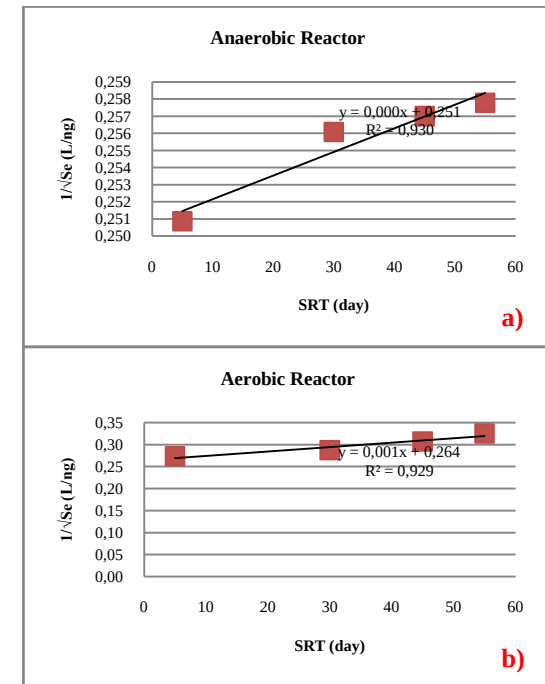


Figure 6 Half-order PFOS removal model in (a) anaerobic reactor and (b) aerobic reactor

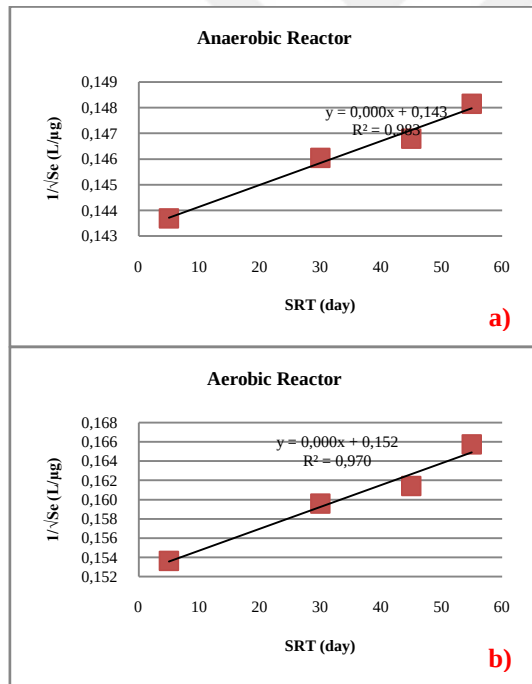


Figure 7 Half-order GFZ removal model in (a) anaerobic reactor and (b) aerobic reactor

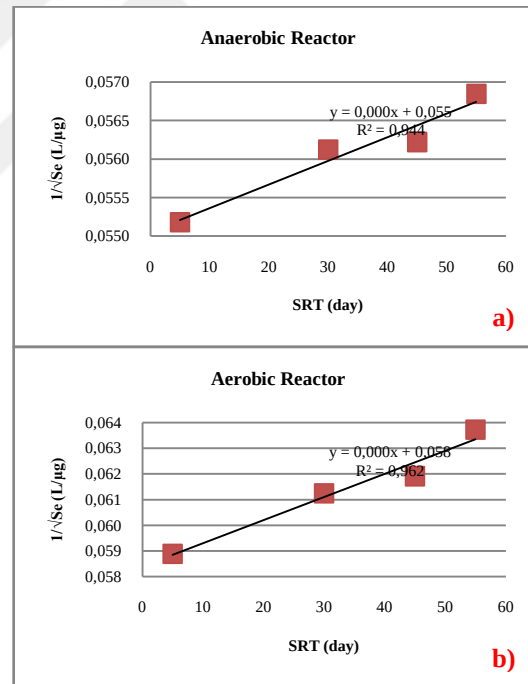


Figure 8 Half-order TCS removal model in (a) anaerobic reactor and (b) aerobic reactor

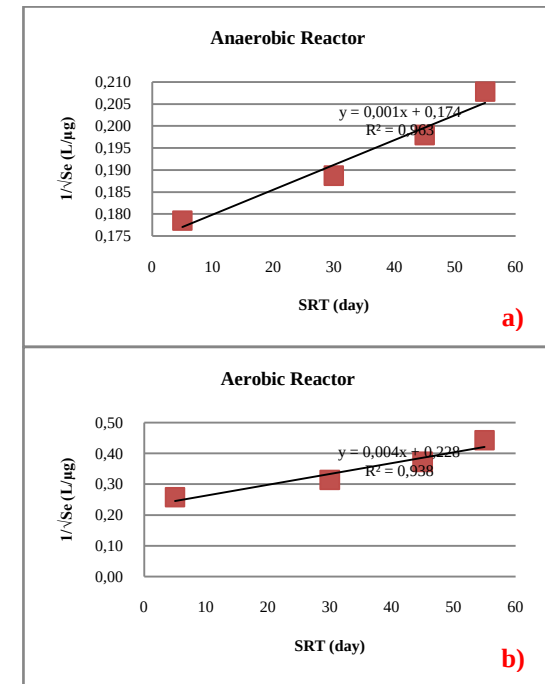


Figure 9 Half-order IBU removal model in (a) anaerobic reactor and (b) aerobic reactor

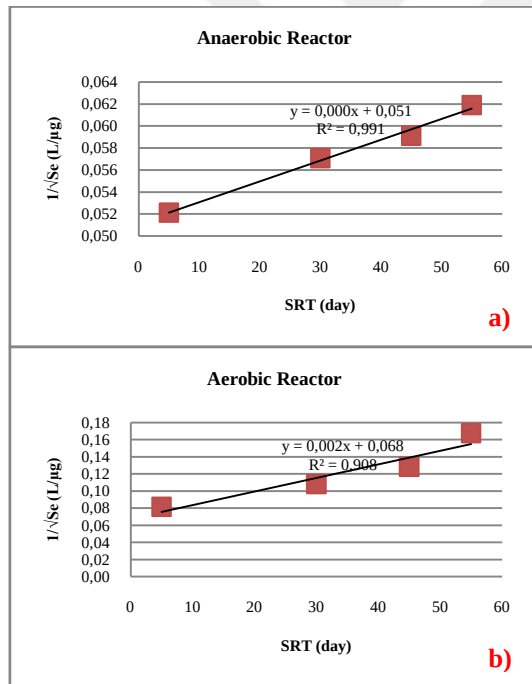


Figure 10 Half-order CIP removal model in (a) anaerobic reactor and (b) aerobic reactor

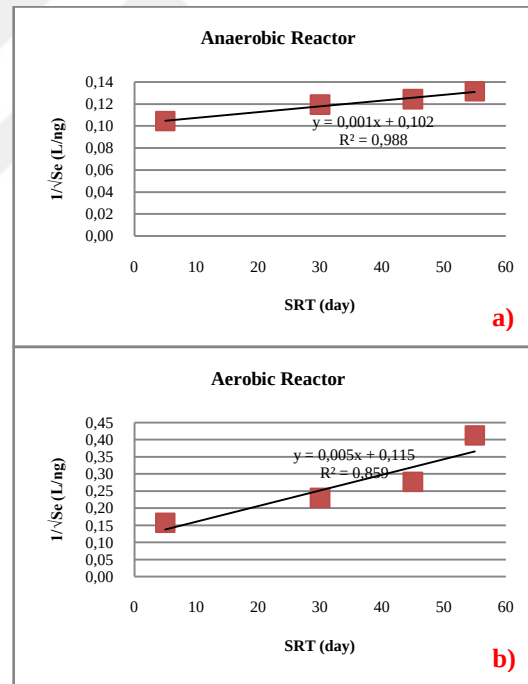


Figure 11 Half-order NDMA removal model in (a) anaerobic reactor and (b) aerobic reactor

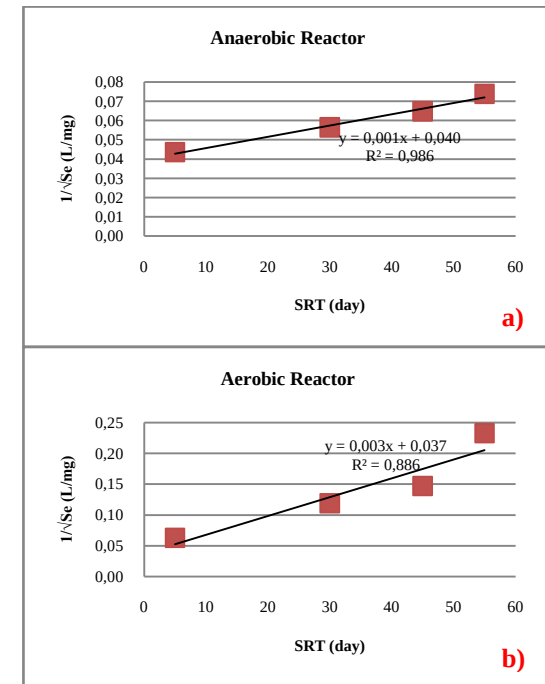


Figure 12 Half-order COD removal model in (a) anaerobic reactor and (b) aerobic reactor

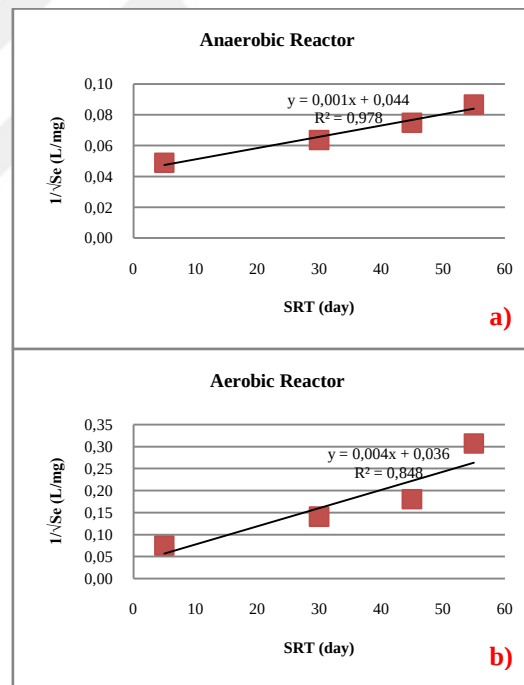


Figure 13 Half-order sCOD removal model in (a) anaerobic reactor and (b) aerobic reactor

Appendix-4: First-Order Removal Model for Biological Treatment

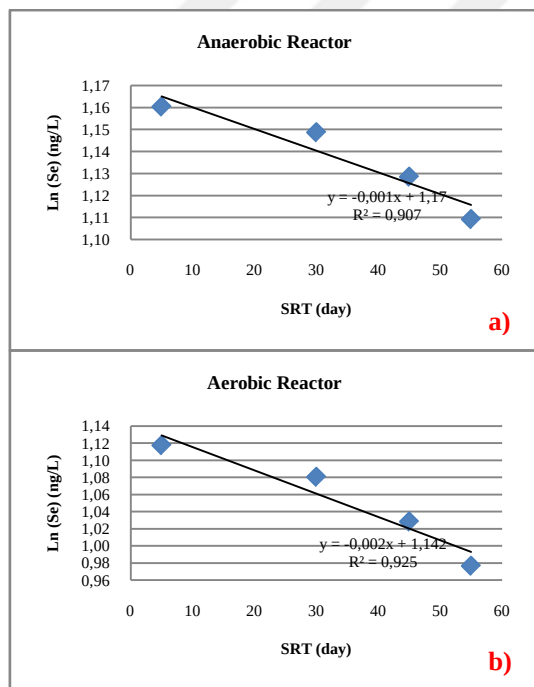


Figure 1 First-order PBEB removal model in (a) anaerobic reactor and (b) aerobic reactor

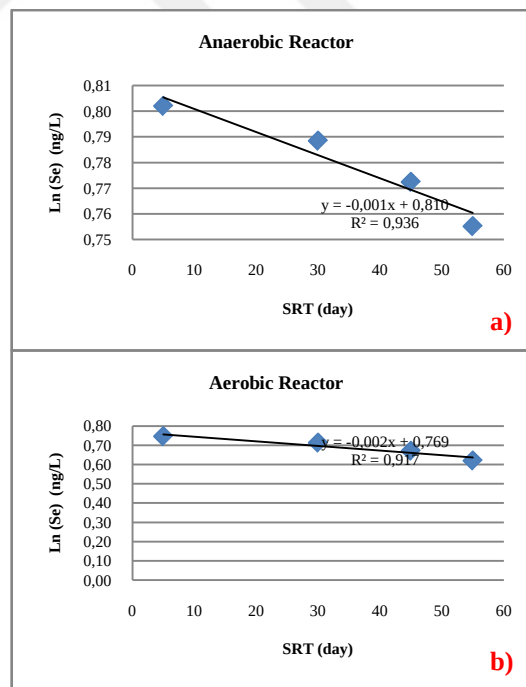


Figure 2 First-order PBT removal model in (a) anaerobic reactor and (b) aerobic reactor

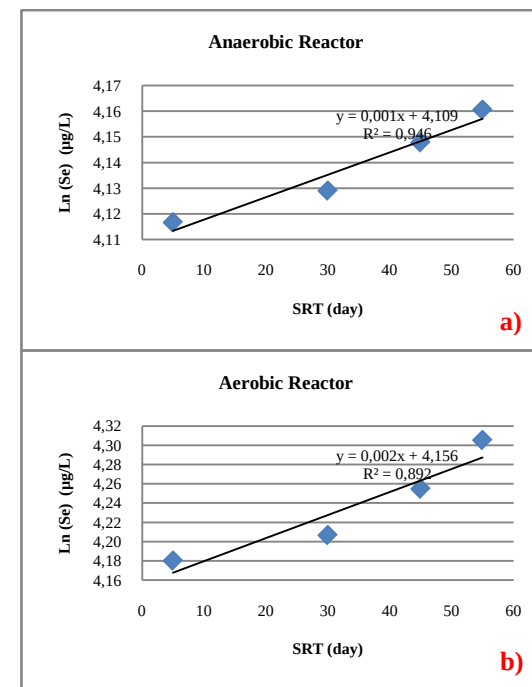


Figure 3 First-order TBBPA removal model in (a) anaerobic reactor and (b) aerobic reactor

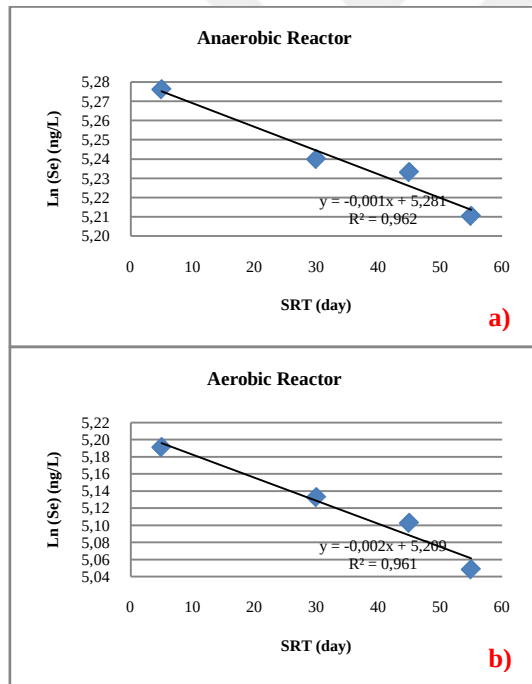


Figure 4 First-order AHTN removal model in (a) anaerobic reactor and (b) aerobic reactor

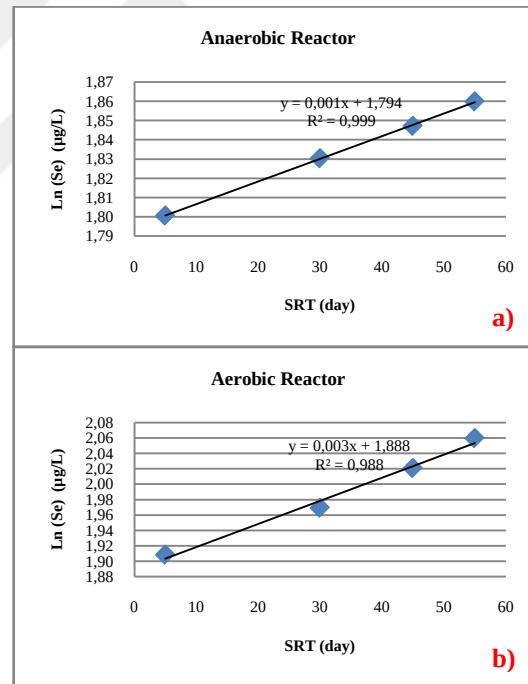


Figure 5 First-order PFOA removal model in (a) anaerobic reactor and (b) aerobic reactor

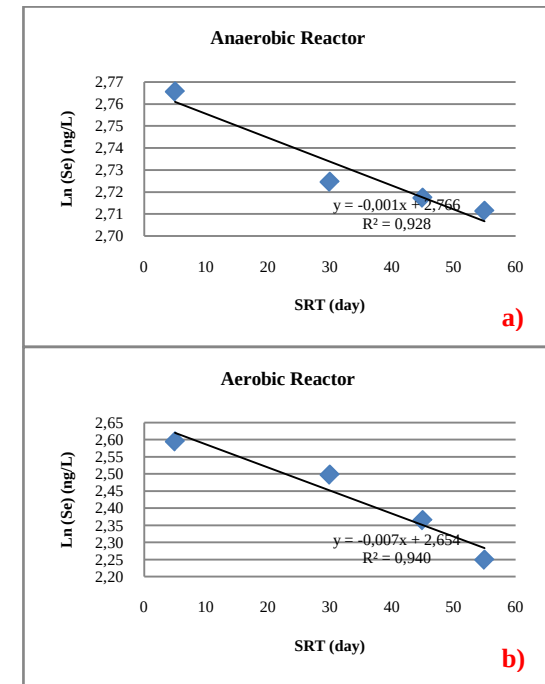


Figure 6 First-order PFOS removal model in (a) anaerobic reactor and (b) aerobic reactor

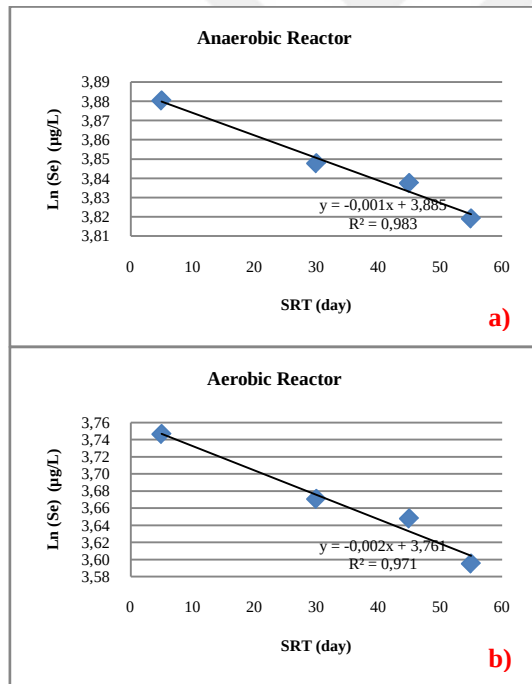


Figure 7 First-order GFZ removal model in (a) anaerobic reactor and (b) aerobic reactor

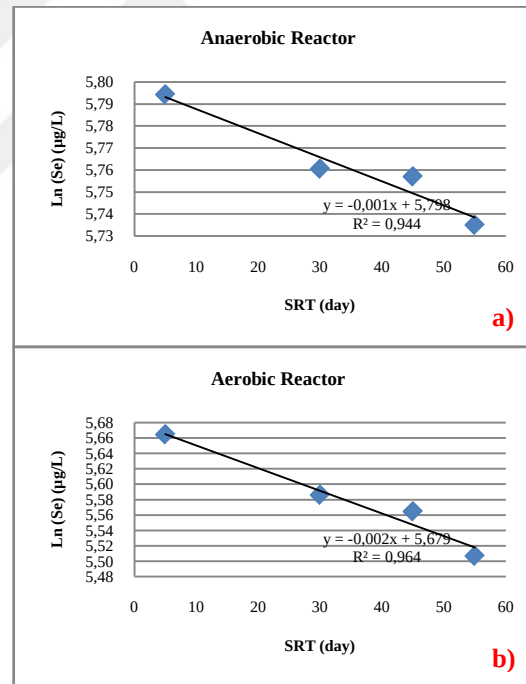


Figure 8 First-order TCS removal model in (a) anaerobic reactor and (b) aerobic reactor

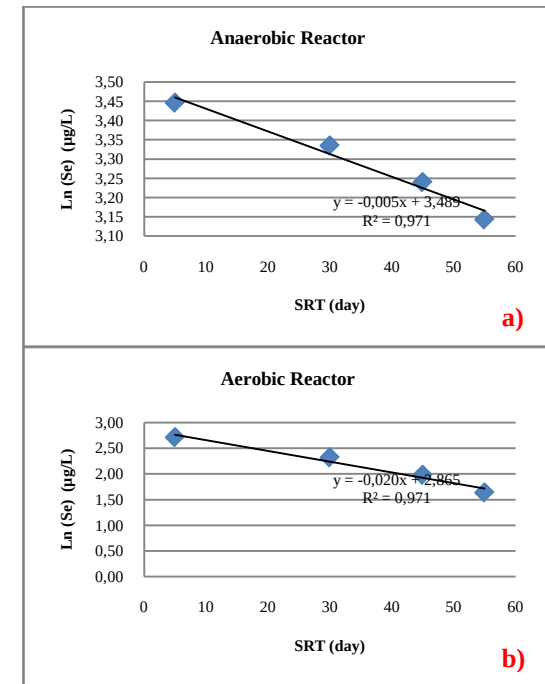


Figure 9 First-order IBU removal model in (a) anaerobic reactor and (b) aerobic reactor

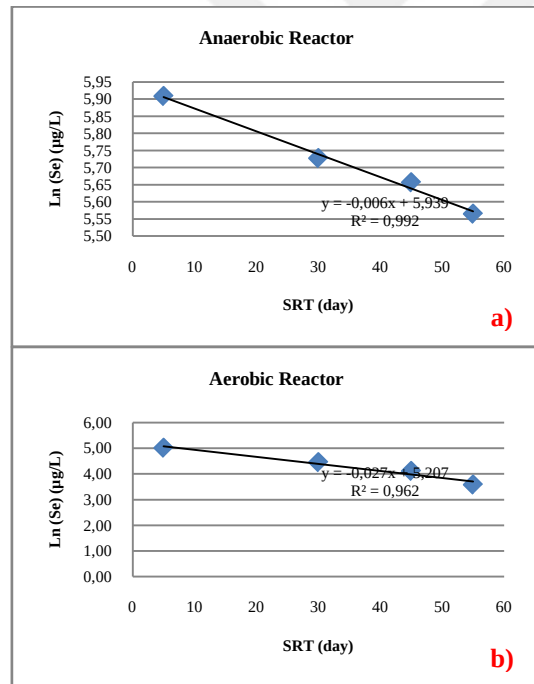


Figure 10 First-order CIP removal model in (a) anaerobic reactor and (b) aerobic reactor

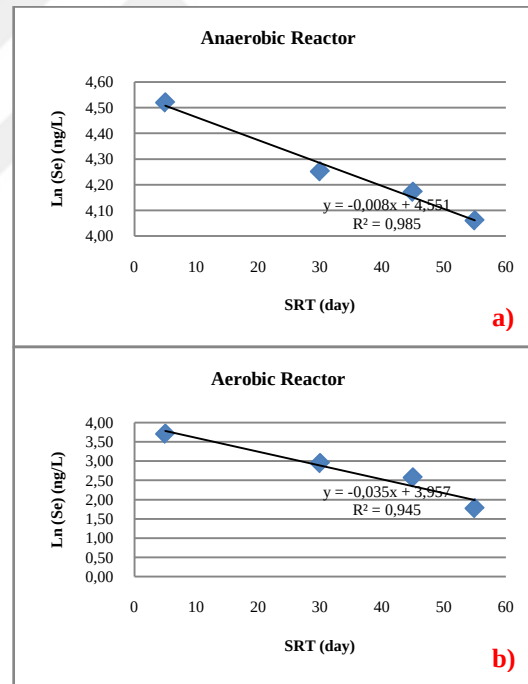


Figure 11 First-order NDMA removal model in (a) anaerobic reactor and (b) aerobic reactor

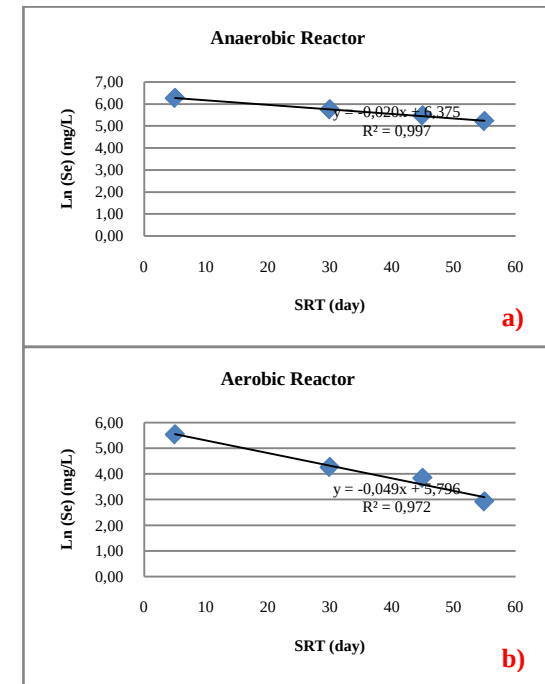


Figure 12 First-order COD removal model in (a) anaerobic reactor and (b) aerobic reactor

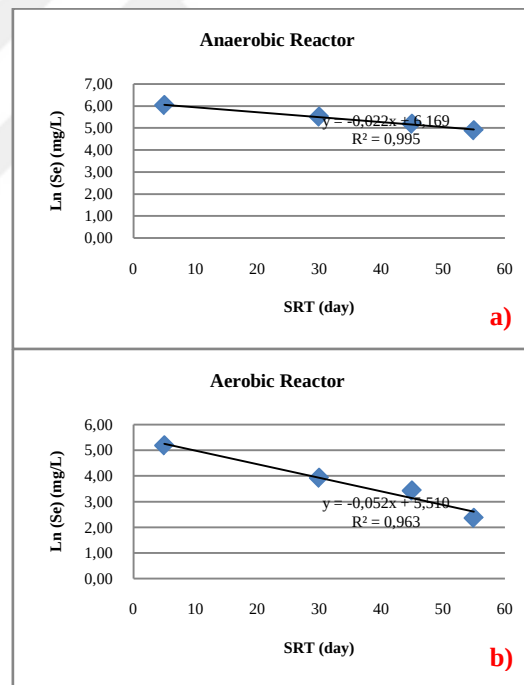


Figure 13 First-order sCOD removal model in (a) anaerobic reactor and (b) aerobic reactor

Appendix-5: Second-Order Removal Model for Biological Treatment

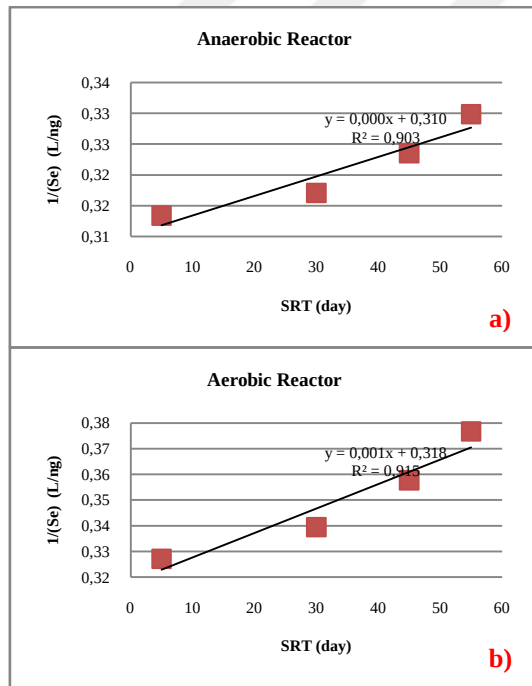


Figure 1 Second-order PBEB removal model in (a) anaerobic reactor and (b) aerobic reactor

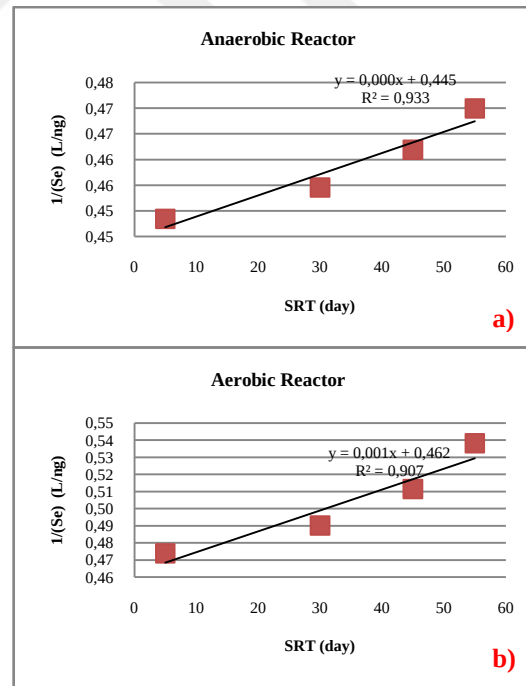


Figure 2 Second-order PBT removal model in (a) anaerobic reactor and (b) aerobic reactor

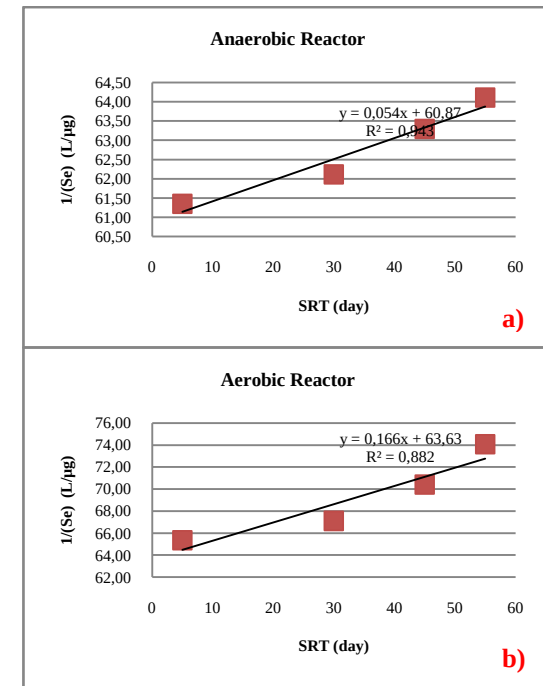


Figure 3 Second-order TBBPA removal model in (a) anaerobic reactor and (b) aerobic reactor

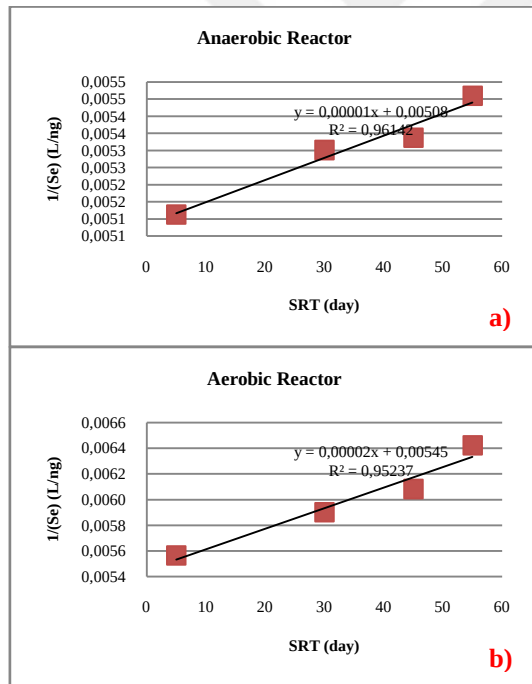


Figure 4 Second-order AHTN removal model in (a) anaerobic reactor and (b) aerobic reactor

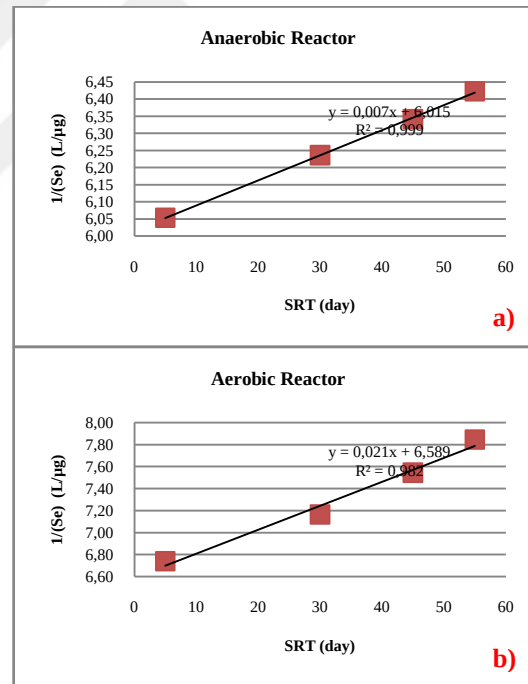


Figure 5 Second-order PFOA removal model in (a) anaerobic reactor and (b) aerobic reactor

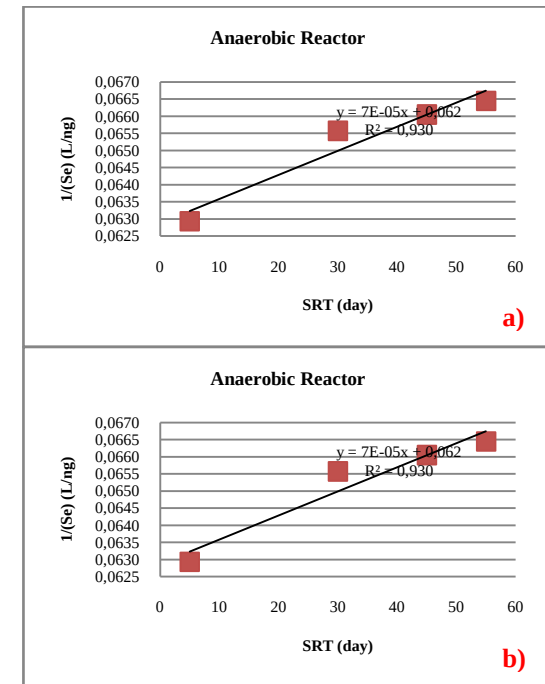


Figure 6 Second-order PFOS removal model in (a) anaerobic reactor and (b) aerobic reactor

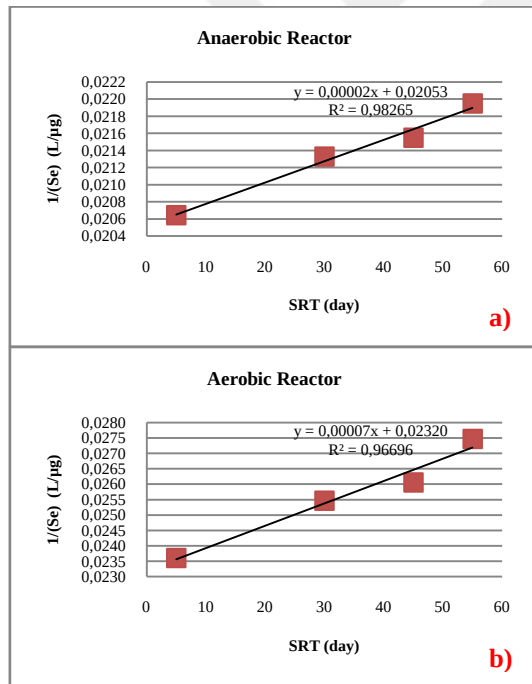


Figure 7 Second-order GFZ removal model in (a) anaerobic reactor and (b) aerobic reactor

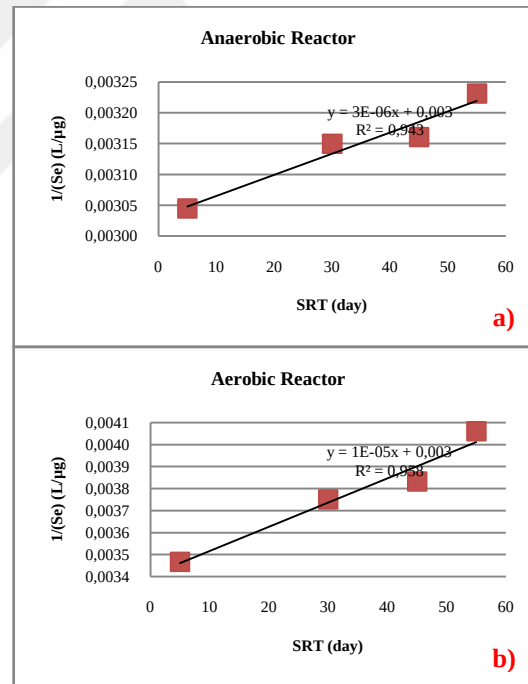


Figure 8 Second-order TCS removal model in (a) anaerobic reactor and (b) aerobic reactor

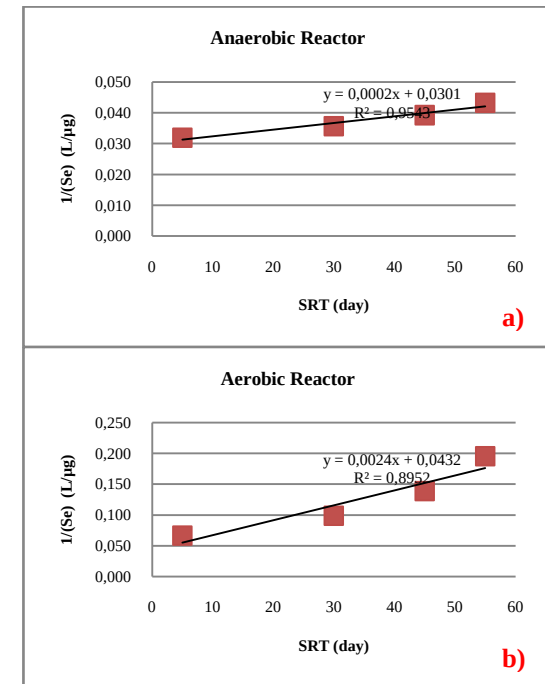


Figure 9 Second-order IBU removal model in (a) anaerobic reactor and (b) aerobic reactor

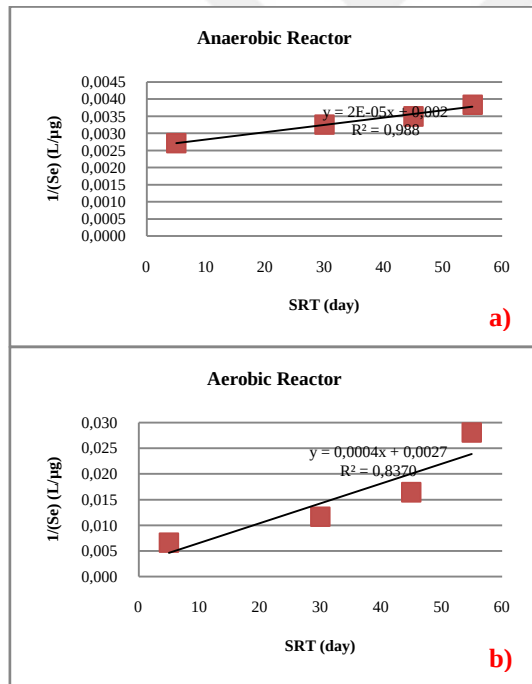


Figure 10 Second-order CIP removal model in (a) anaerobic reactor and (b) aerobic reactor

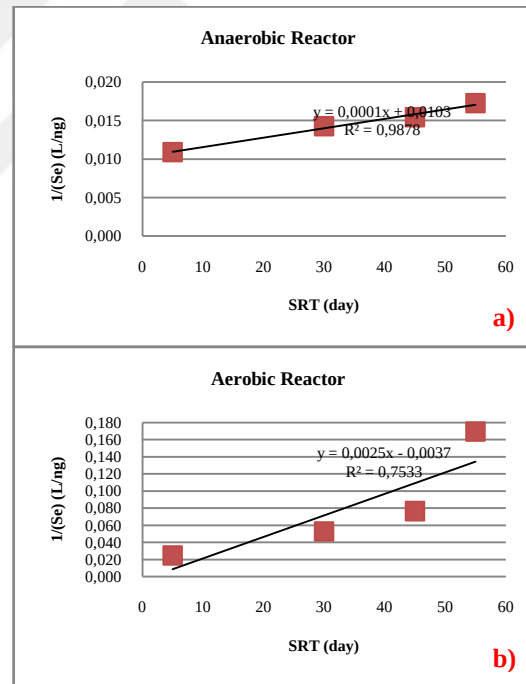


Figure 11 Second-order NDMA removal model in (a) anaerobic reactor and (b) aerobic reactor

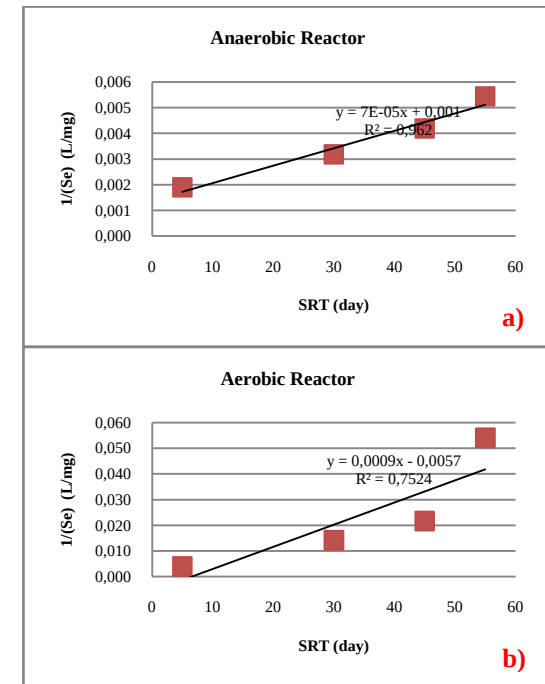


Figure 12 Second-order COD removal model in (a) anaerobic reactor and (b) aerobic reactor

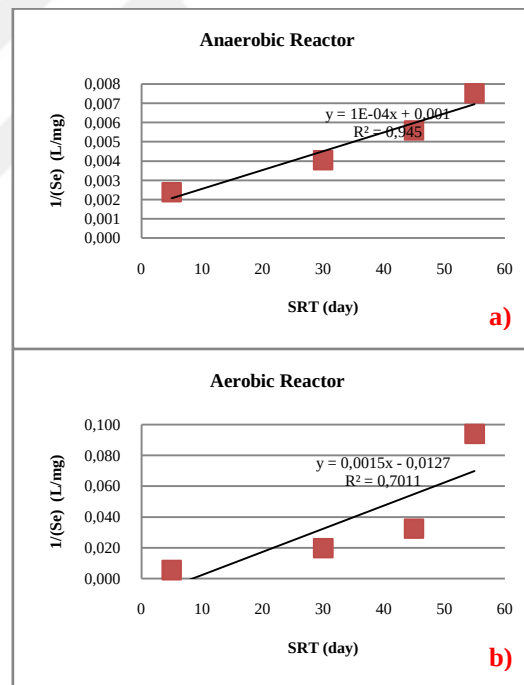


Figure 13 Second-order sCOD removal model in (a) anaerobic reactor and (b) aerobic reactor

Appendix-6: Freundlich Isotherm for Biological Treatment

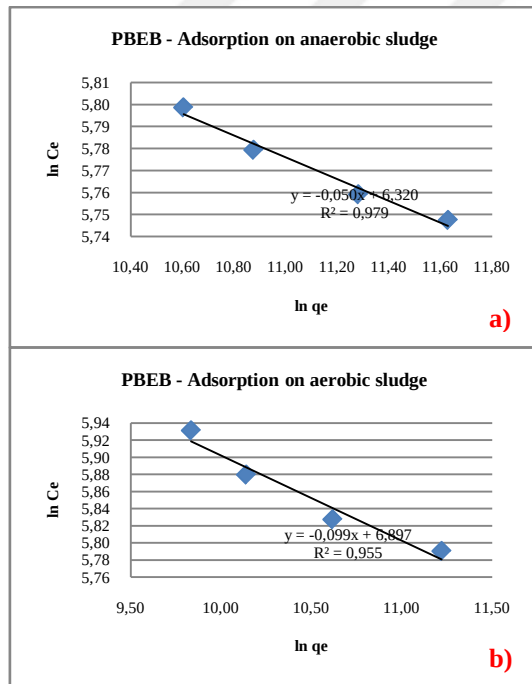


Figure 1 Freundlich isotherm for adsorption of PBEB during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

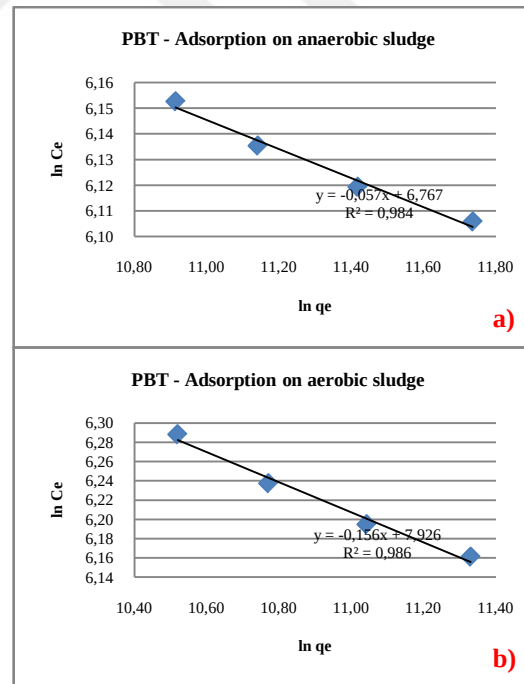


Figure 2 Freundlich isotherm for adsorption of PBT during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

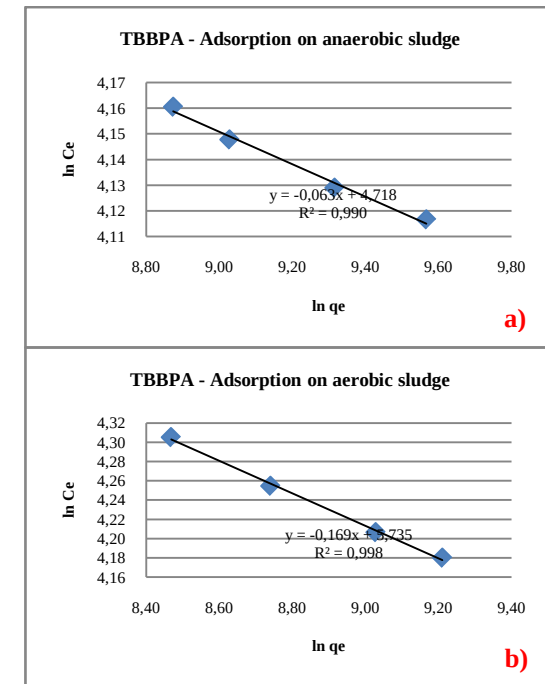


Figure 3 Freundlich isotherm for adsorption of TBBPA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

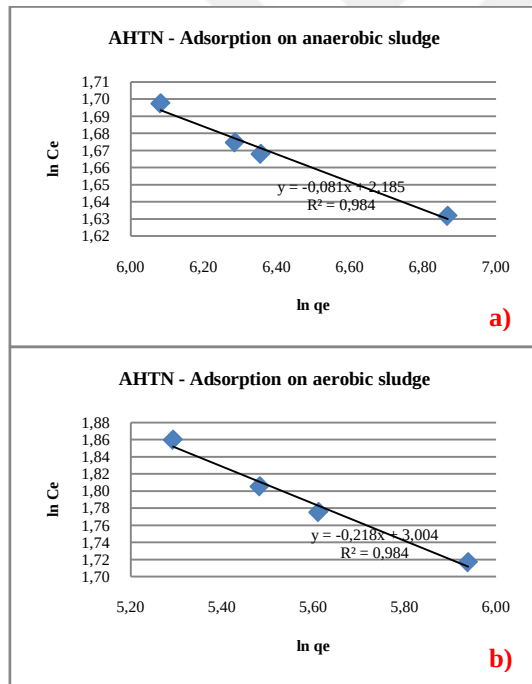


Figure 4 Freundlich isotherm for adsorption of AHTN during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

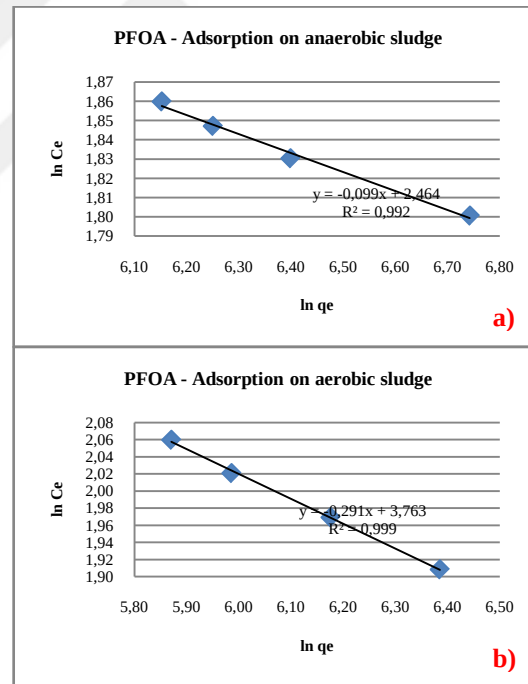


Figure 5 Freundlich isotherm for adsorption of PFOA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

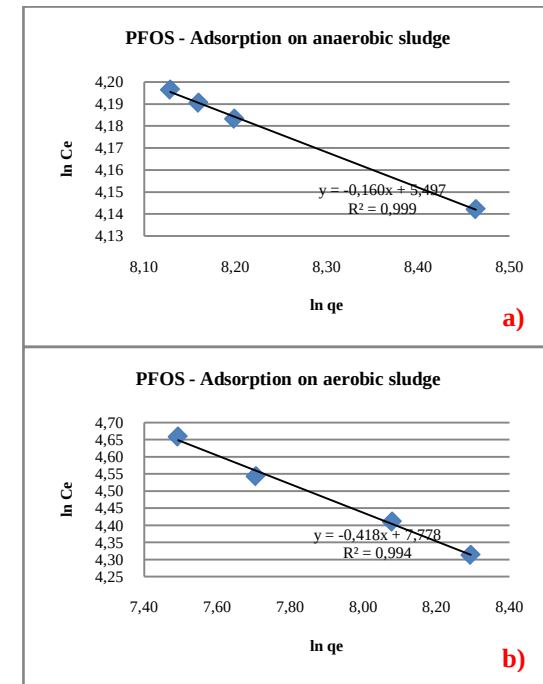


Figure 6 Freundlich isotherm for adsorption of PFOS during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

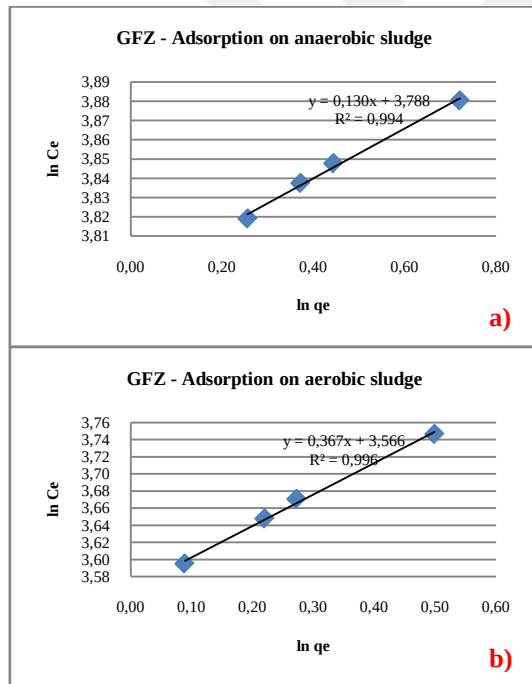


Figure 7 Freundlich isotherm for adsorption of GFZ during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

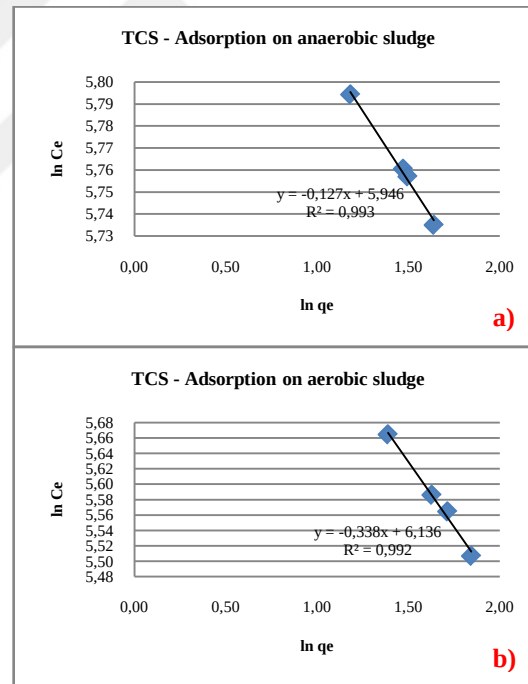


Figure 8 Freundlich isotherm for adsorption of TCS during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

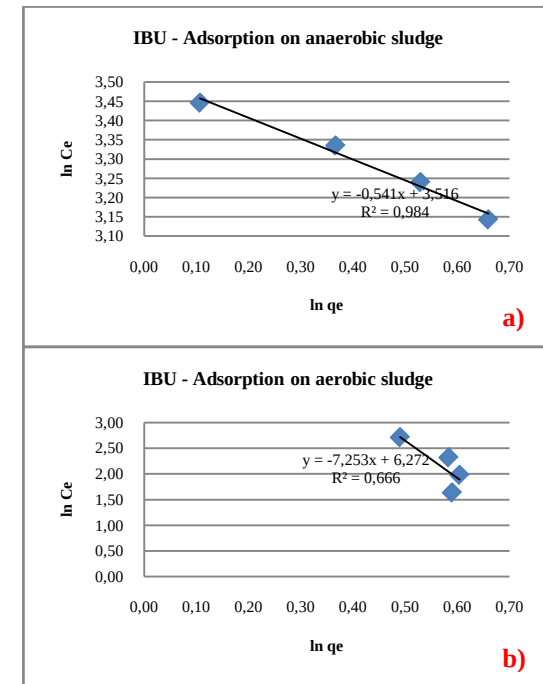


Figure 9 Freundlich isotherm for adsorption of IBU during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

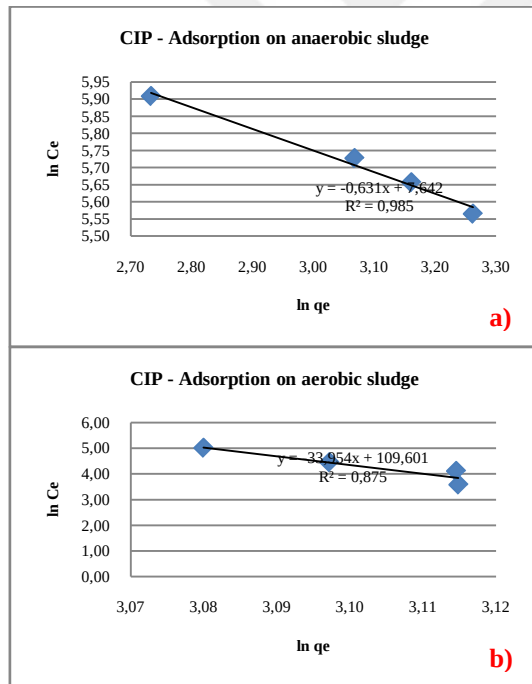


Figure 10 Freundlich isotherm for adsorption of CIP during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

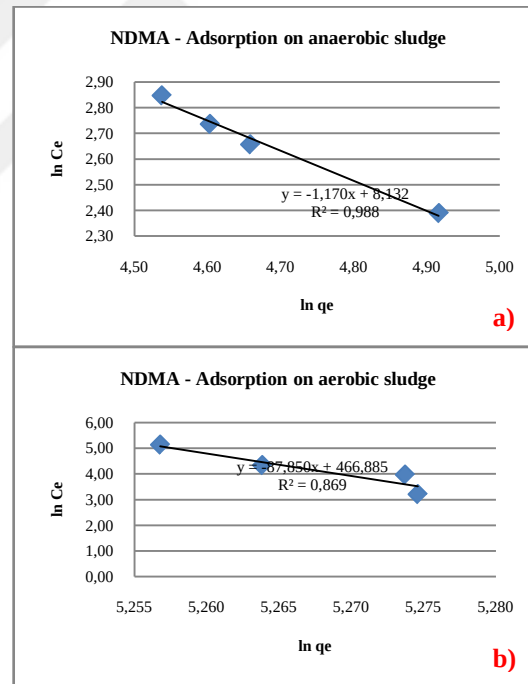


Figure 11 Freundlich isotherm for adsorption of NDMA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

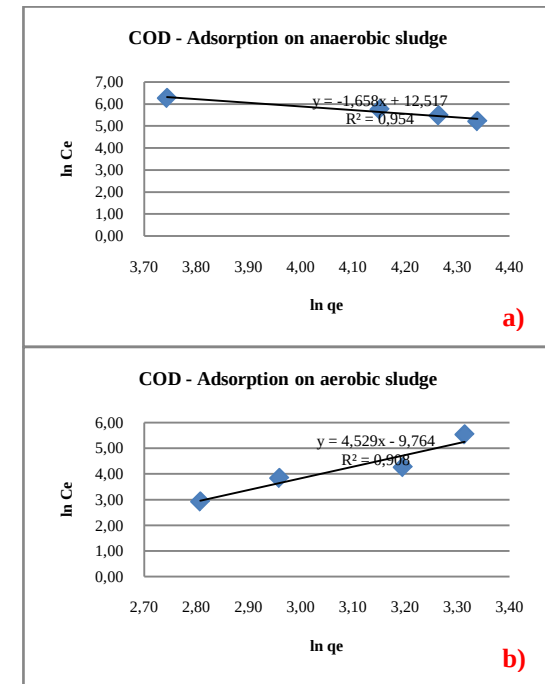


Figure 12 Freundlich isotherm for adsorption of COD during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

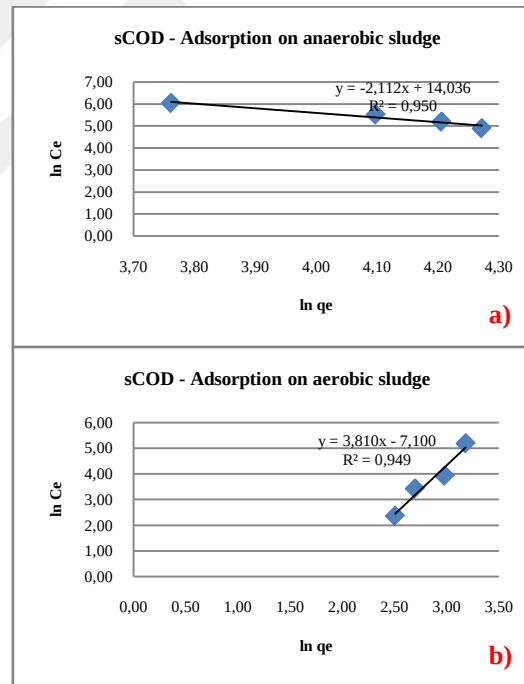


Figure 13 Freundlich isotherm for adsorption of sCOD during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

Appendix-7: Langmuir Isotherm for Biological Treatment

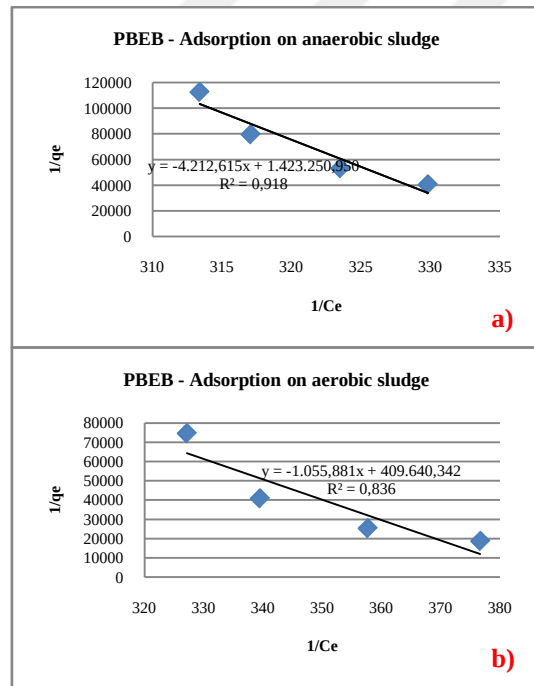


Figure 1 Langmuir isotherm for adsorption of PBEB during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

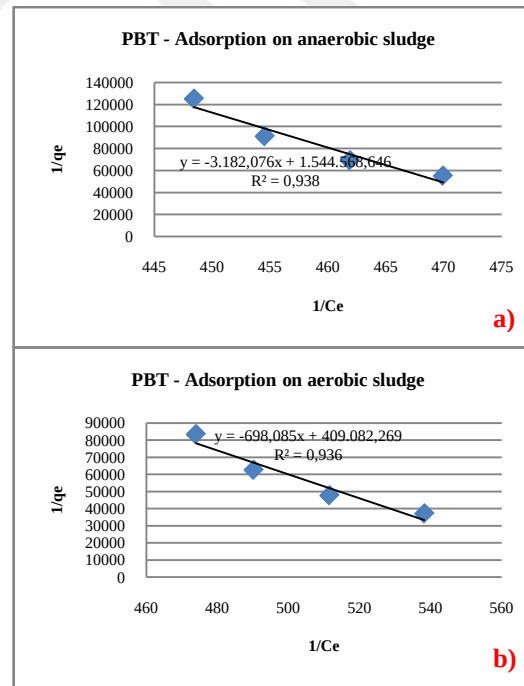


Figure 2 Langmuir isotherm for adsorption of PBT during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

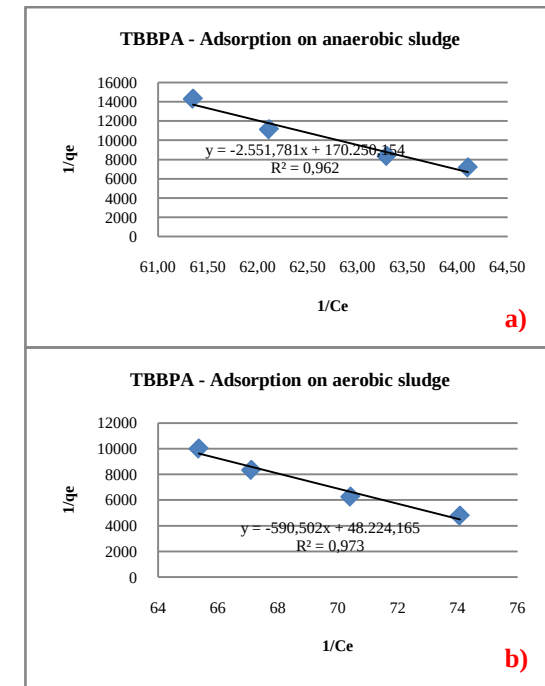


Figure 3 Langmuir isotherm for adsorption of TBBPA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

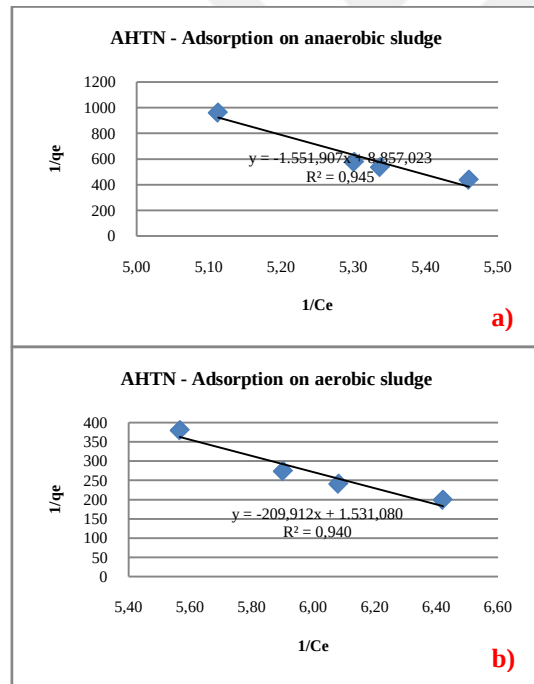


Figure 4 Langmuir isotherm for adsorption of AHTN during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

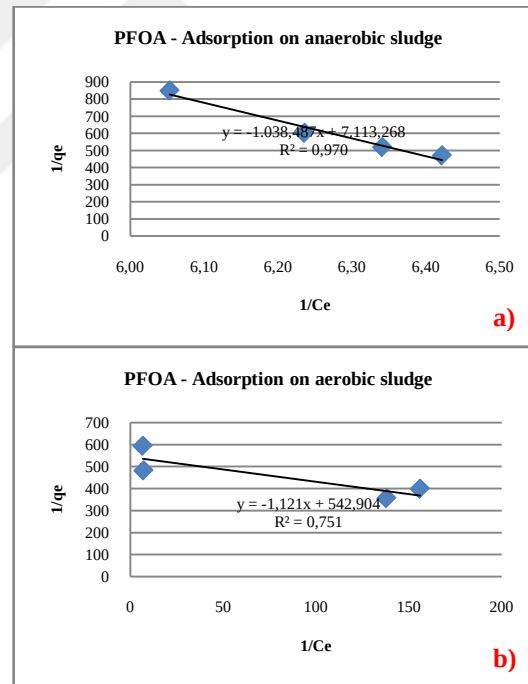


Figure 5 Langmuir isotherm for adsorption of PFOA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

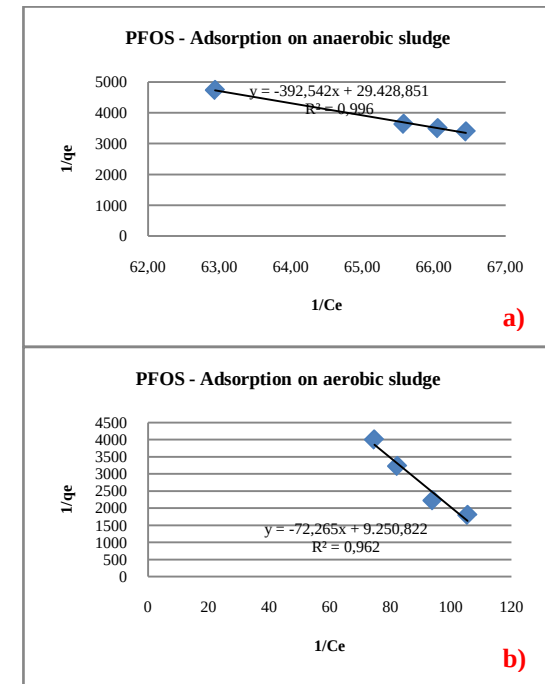


Figure 6 Langmuir isotherm for adsorption of PFOS during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

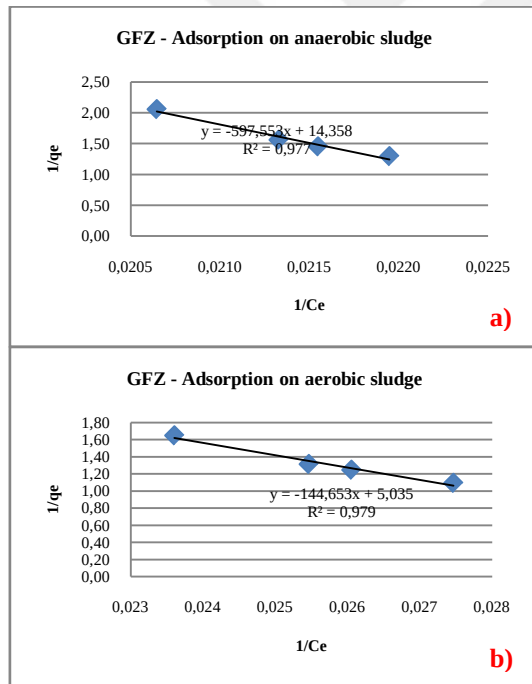


Figure 7 Langmuir isotherm for adsorption of GFZ during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

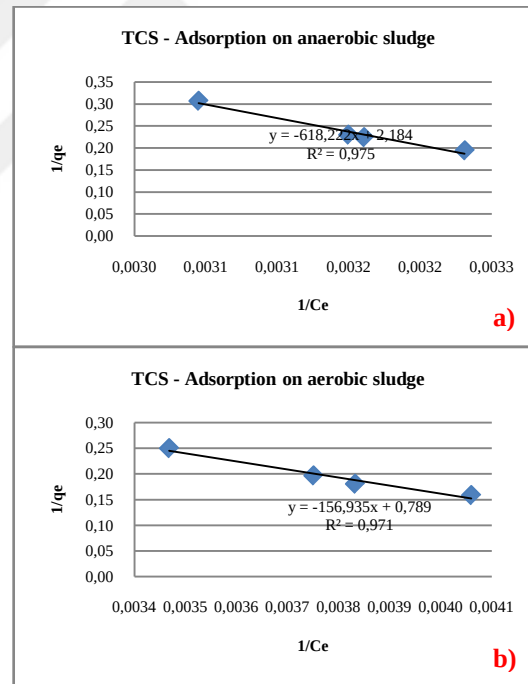


Figure 8 Langmuir isotherm for adsorption of TCS during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

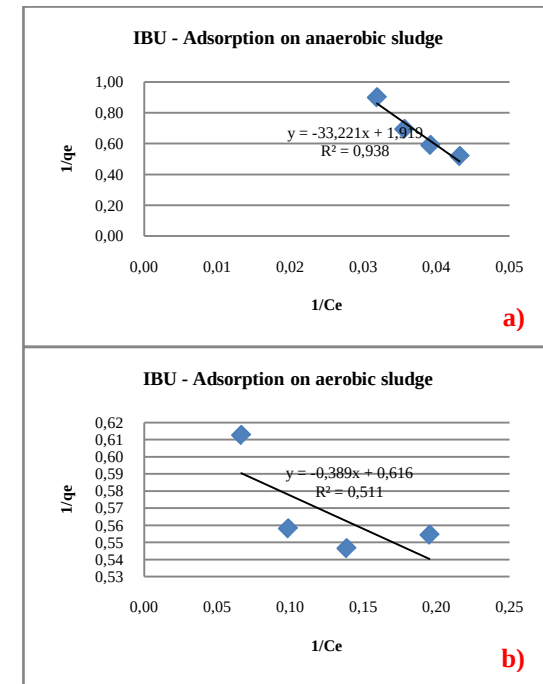


Figure 9 Langmuir isotherm for adsorption of IBU during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

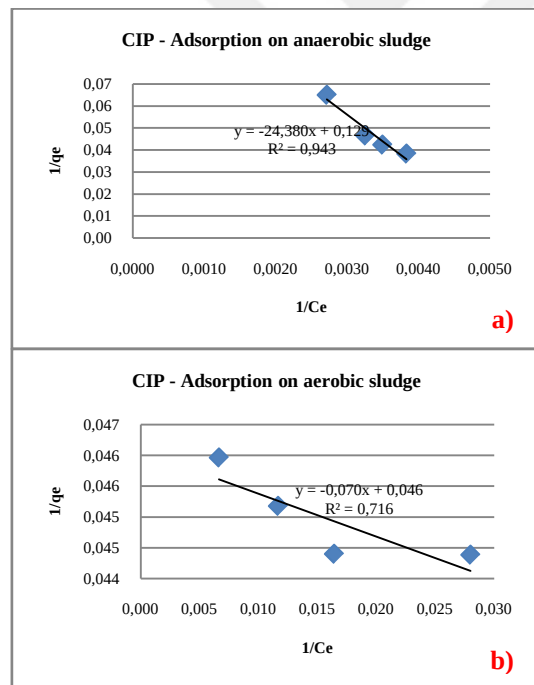


Figure 10 Langmuir isotherm for adsorption of CIP during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

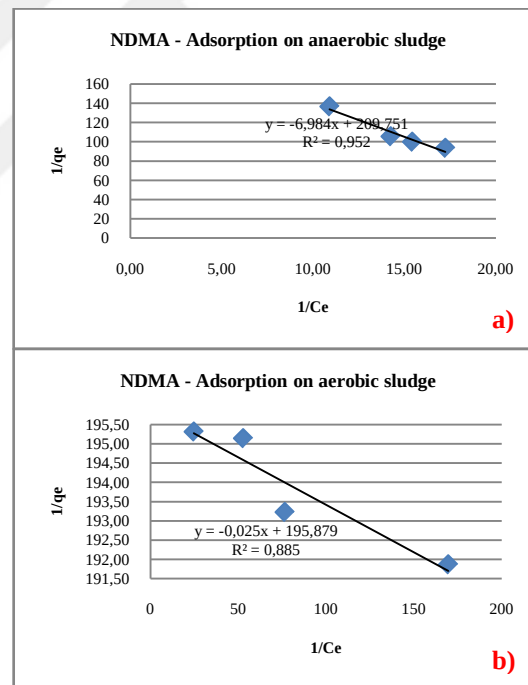


Figure 11 Langmuir isotherm for adsorption of NDMA during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

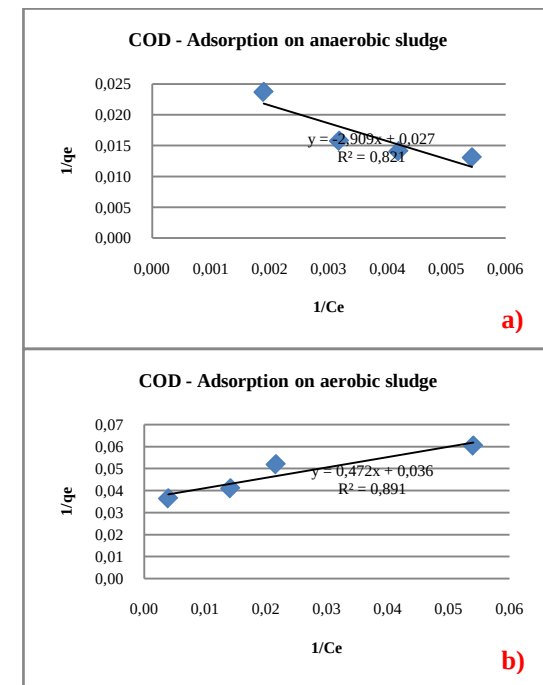


Figure 12 Langmuir isotherm for adsorption of COD during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

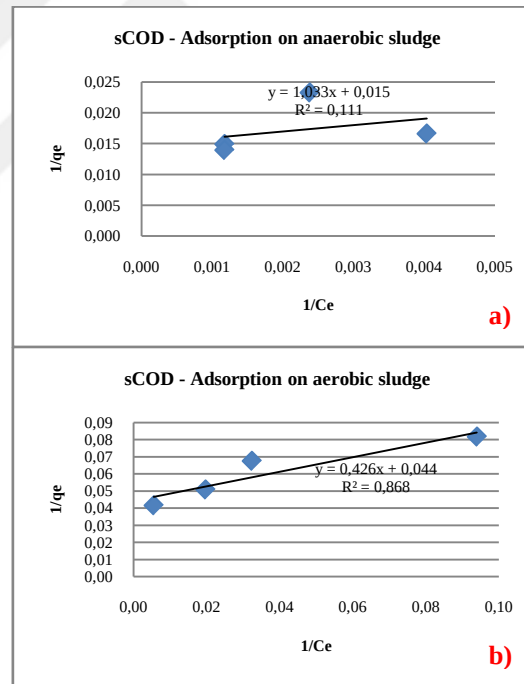


Figure 13 Langmuir isotherm for adsorption of sCOD during 5, 30, 45 and 55 days of SRTs on (a) anaerobic biological sludge and (b) aerobic biological sludge

Appendix-8: Langmuir Isotherm for Photocatalytic Treatment

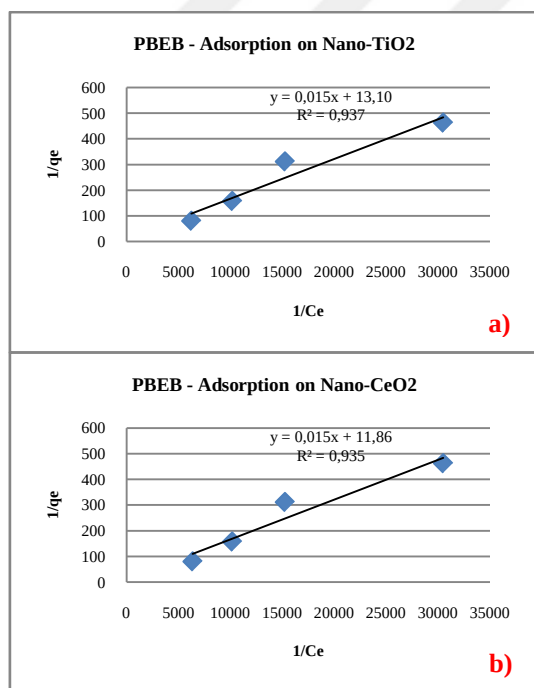


Figure 1 Langmuir isotherm for PBEB adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

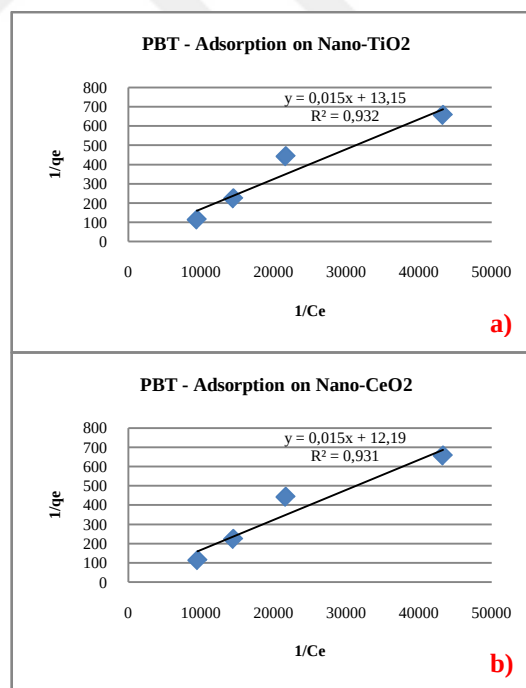


Figure 2 Langmuir isotherm for PBT adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

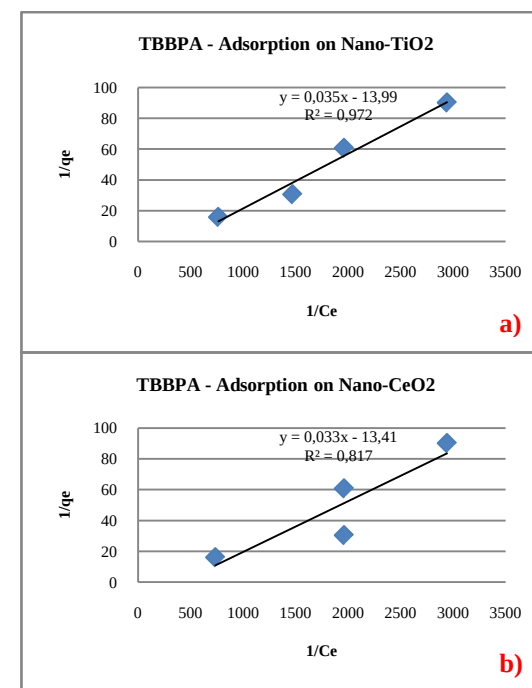


Figure 3 Langmuir isotherm for TBBPA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

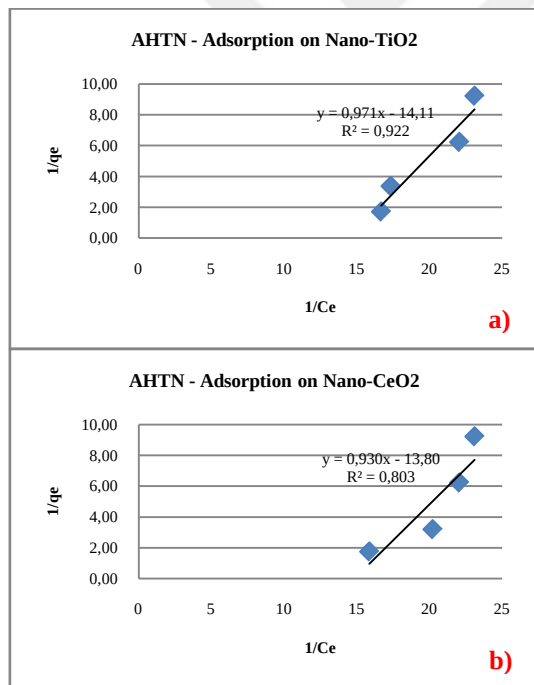


Figure 4 Langmuir isotherm for AHTN adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

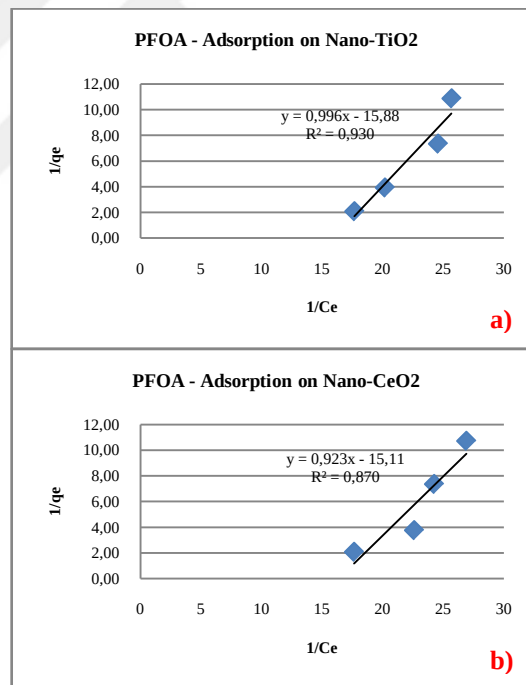


Figure 5 Langmuir isotherm for PFOA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

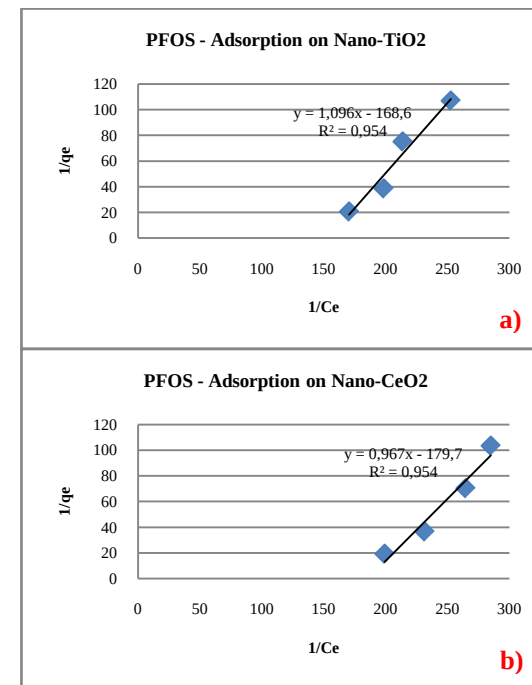


Figure 6 Langmuir isotherm for PFOS adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

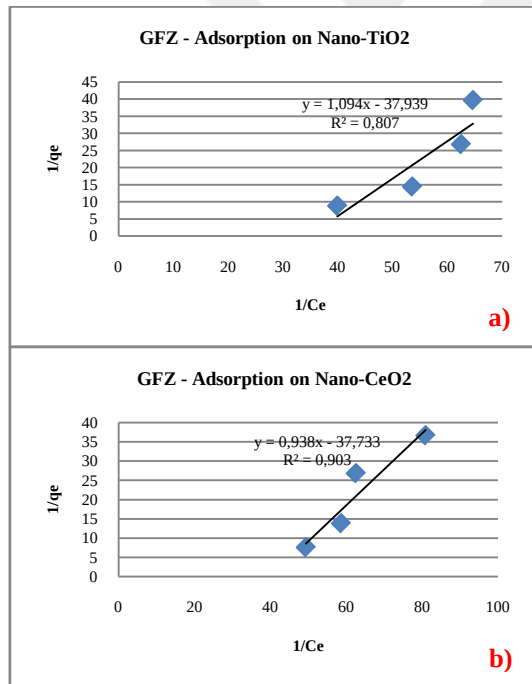


Figure 7 Langmuir isotherm for GFZ adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

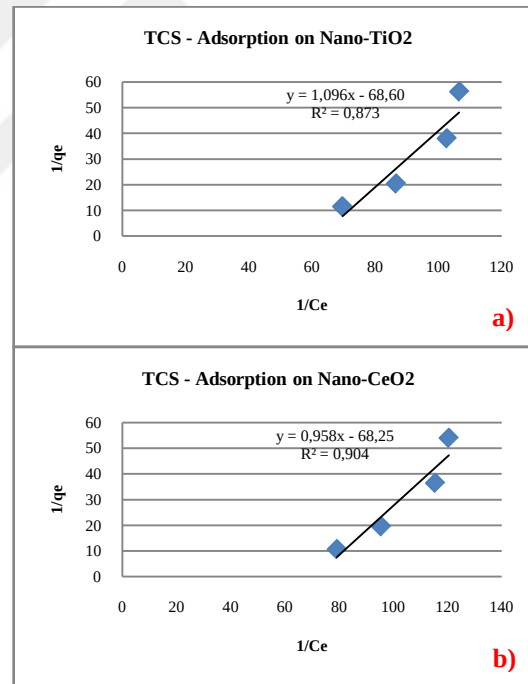


Figure 8 Langmuir isotherm for TCS adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

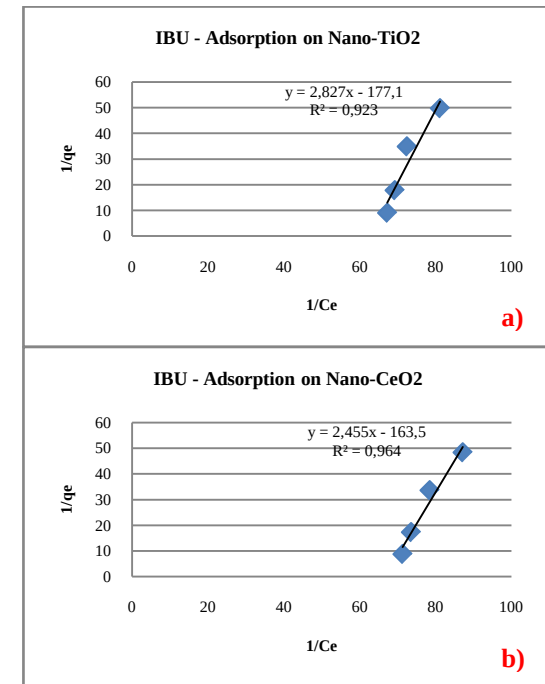


Figure 9 Langmuir isotherm for IBU adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

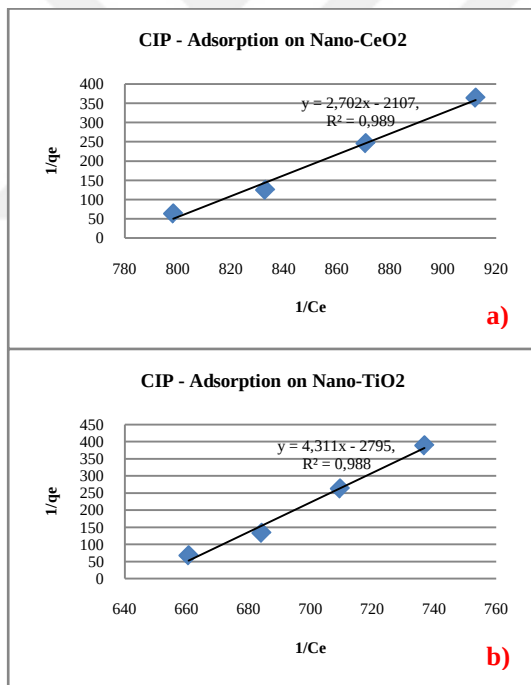


Figure 10 Langmuir isotherm for CIP adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

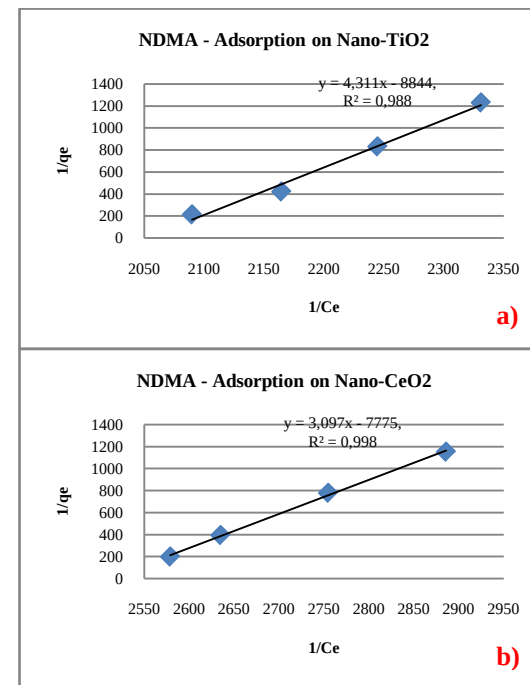


Figure 11 Langmuir isotherm for NDMA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

Appendix-9: Freundlich Isotherm for Photocatalytic Treatment

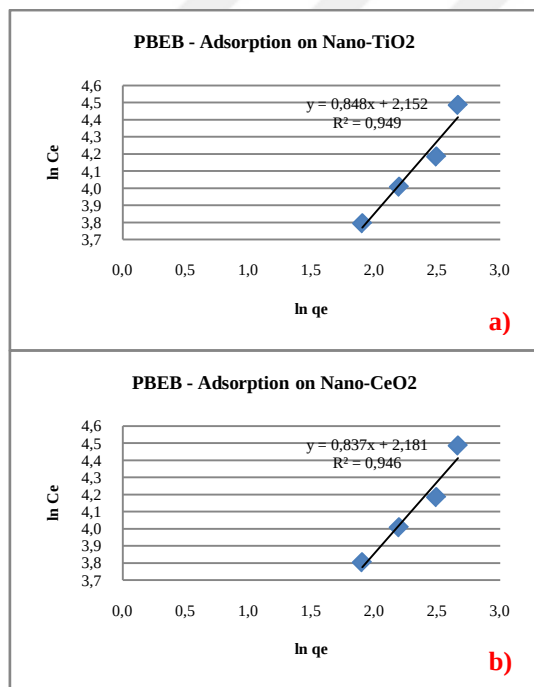


Figure 1 Freundlich isotherm for PBEB adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

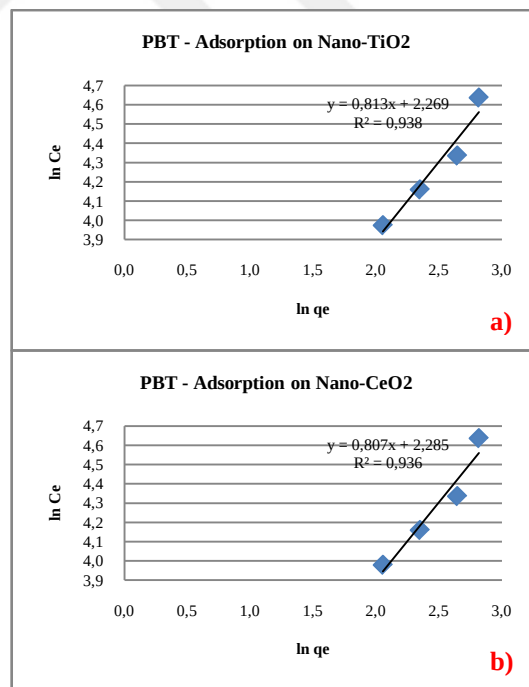


Figure 2 Freundlich isotherm for PBT adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

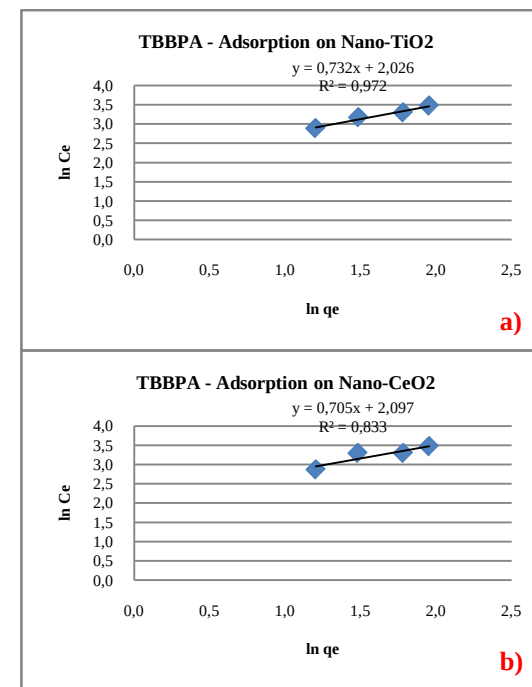


Figure 3 Freundlich isotherm for TBBPA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

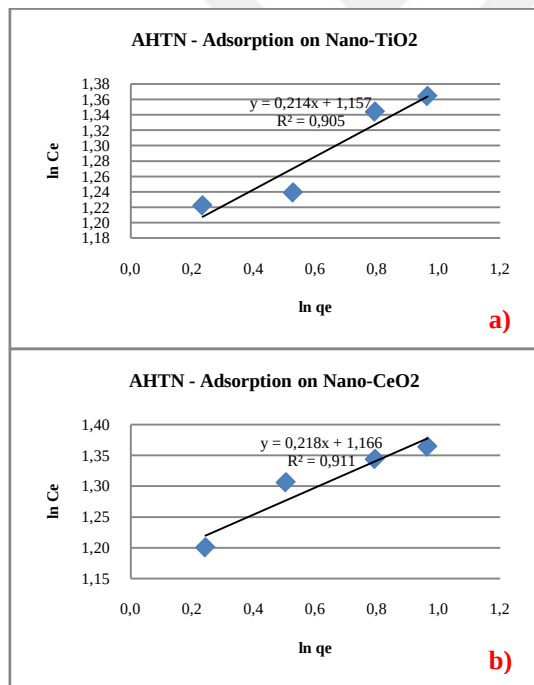


Figure 4 Freundlich isotherm for AHTN adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

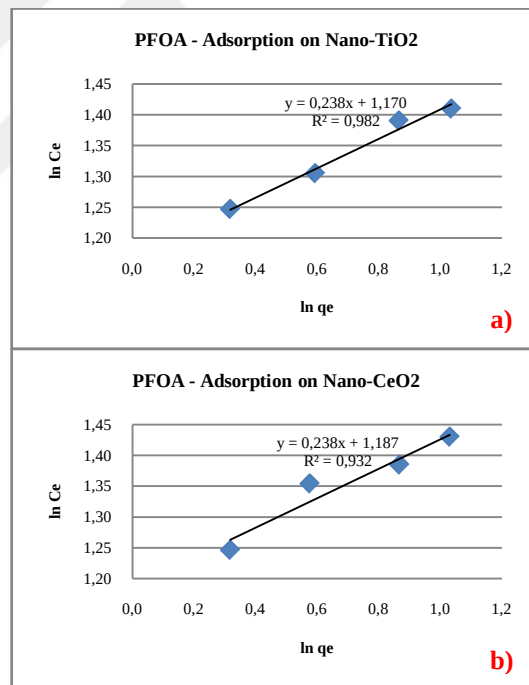


Figure 5 Freundlich isotherm for PFOA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

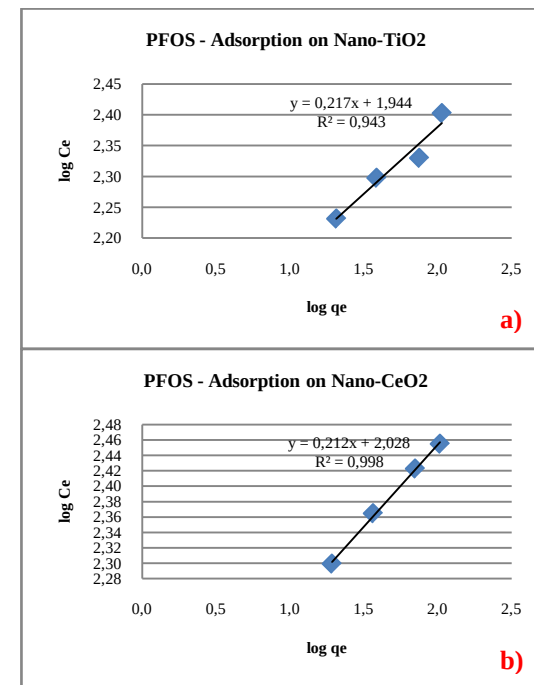


Figure 6 Freundlich isotherm for PFOS adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

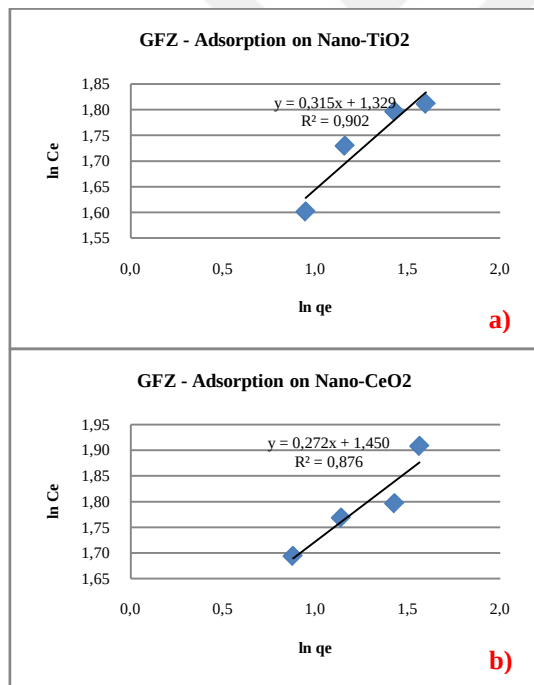


Figure 7 Freundlich isotherm for GFZ adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

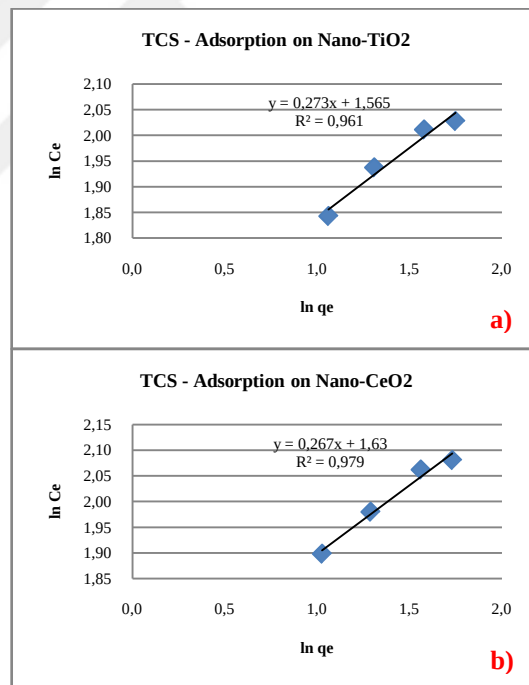


Figure 8 Freundlich isotherm for TCS adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

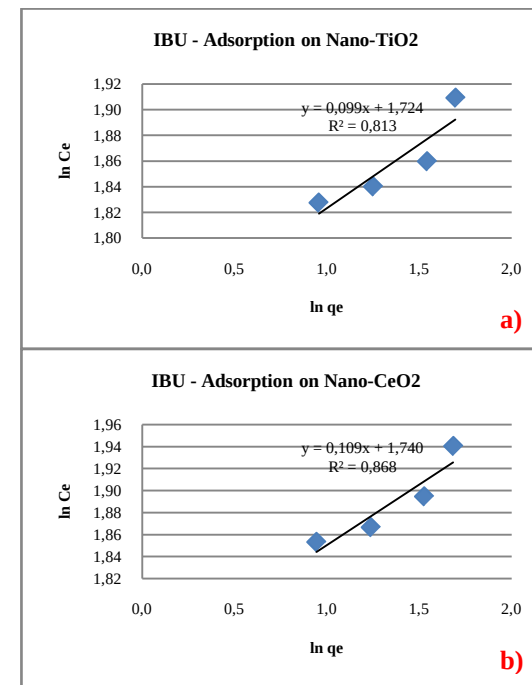


Figure 9 Freundlich isotherm for IBU adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

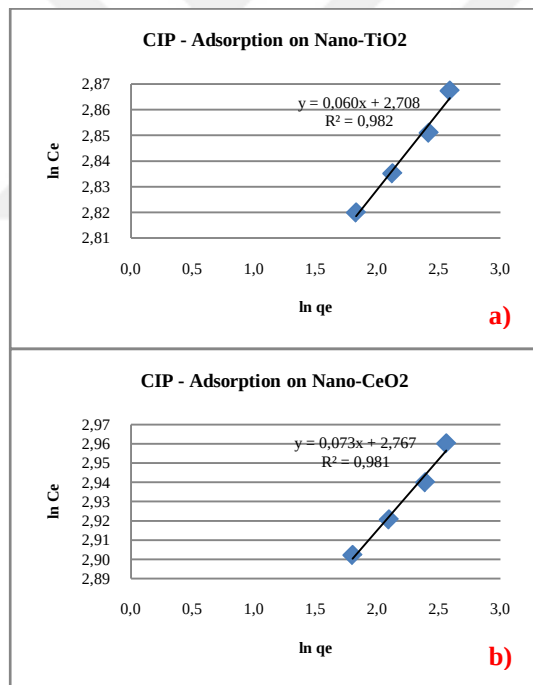


Figure 10 Freundlich isotherm for CIP adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

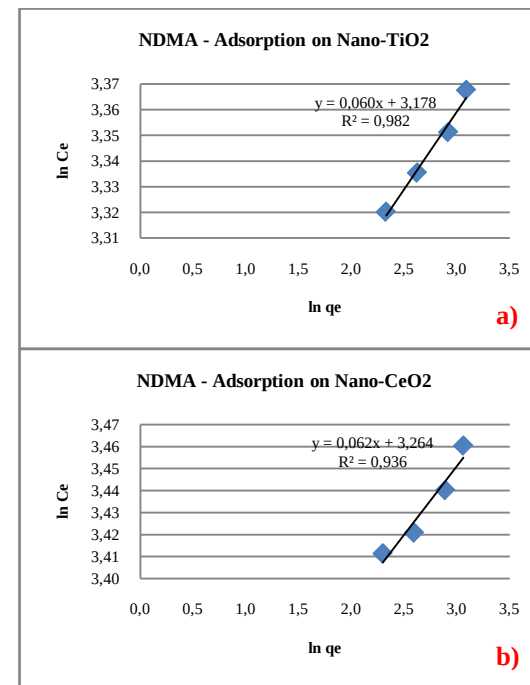


Figure 11 Freundlich isotherm for NDMA adsorption on (a) nano-TiO₂ and (b) nano-CeO₂

Appendix-10: Zero-Order Removal Model for Ultrasound Treatment

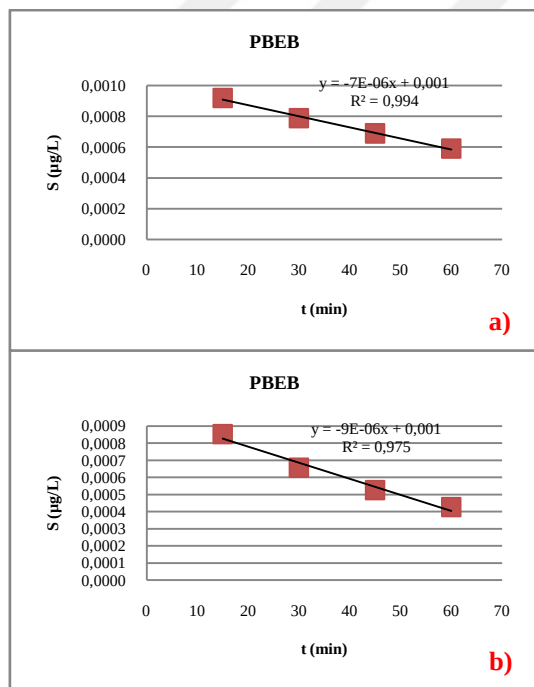


Figure 1 Zero-order PBEb removal with (a) nano-TiO₂ (b) nano-CeO₂

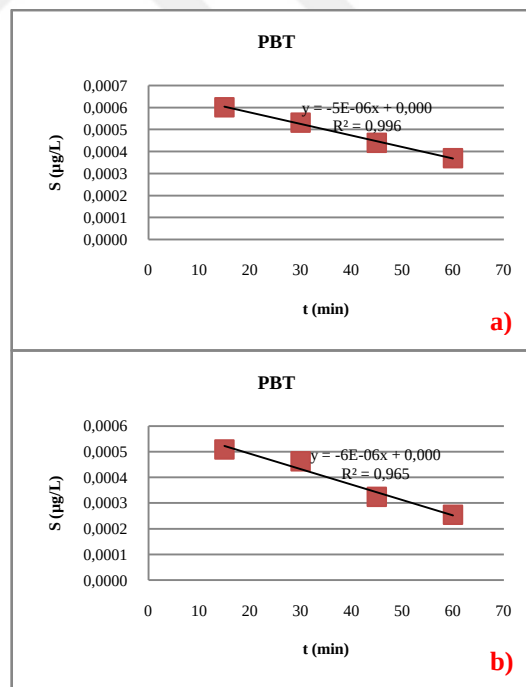


Figure 2 Zero-order PBT removal with (a) nano-TiO₂ (b) nano-CeO₂

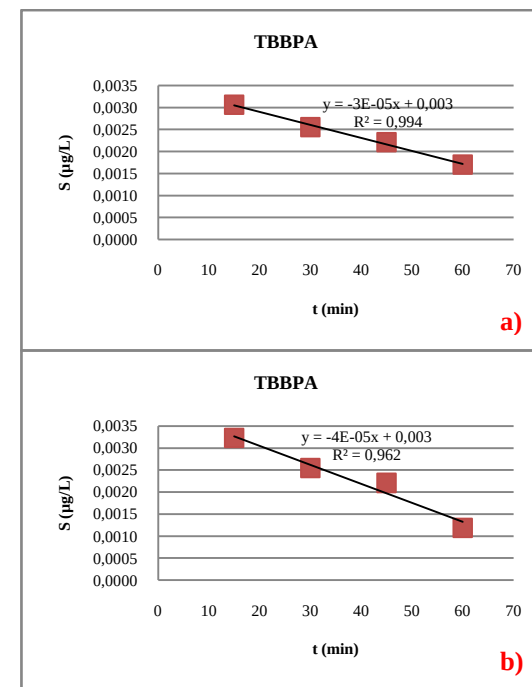


Figure 3 Zero-order TBBPA removal with (a) nano-TiO₂ (b) nano-CeO₂

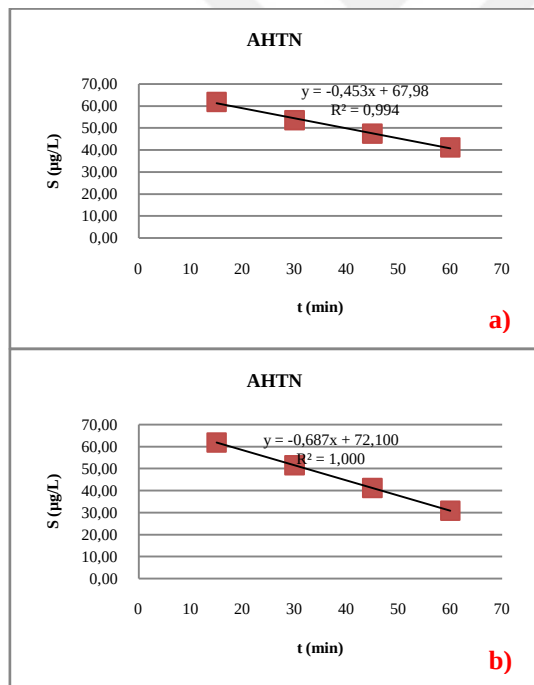


Figure 4 Zero-order AHTN removal with (a) nano-TiO₂ (b) nano-CeO₂

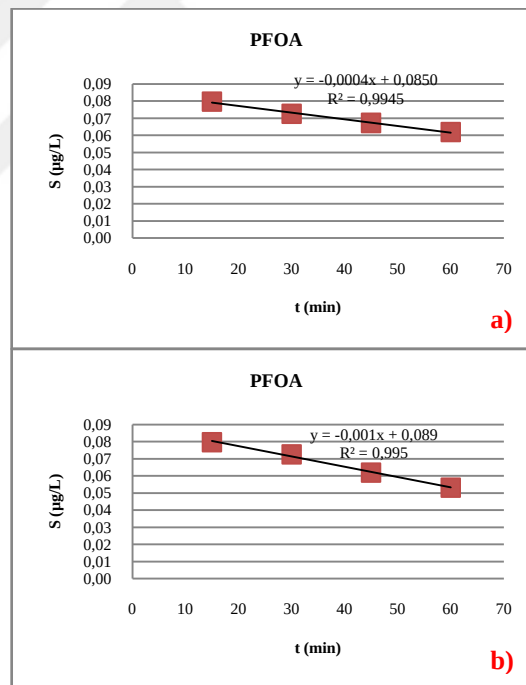


Figure 5 Zero-order PFOA removal with (a) nano-TiO₂ (b) nano-CeO₂

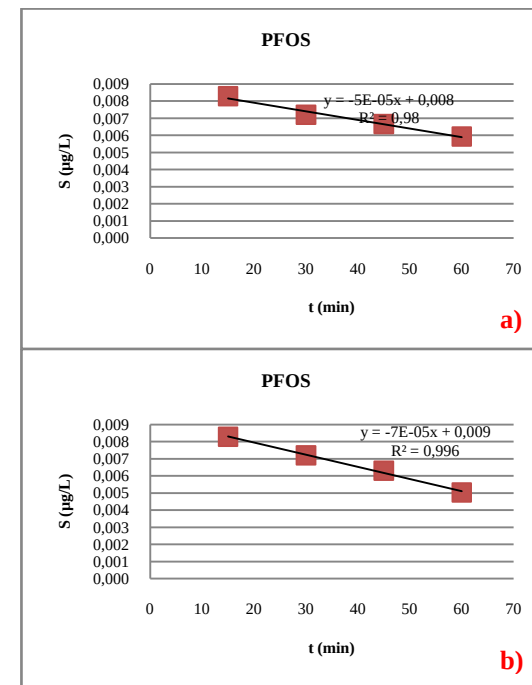


Figure 6 Zero-order PFOS removal with (a) nano-TiO₂ (b) nano-CeO₂

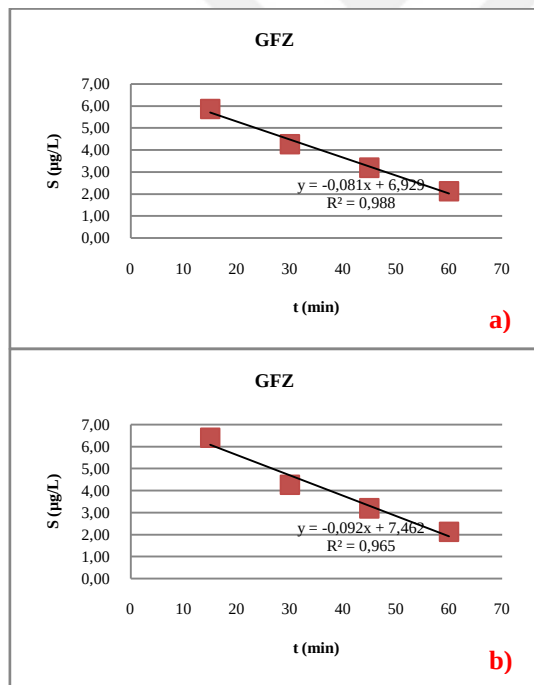


Figure 7 Zero-order GFZ removal with (a) nano-TiO₂ (b) nano-CeO₂

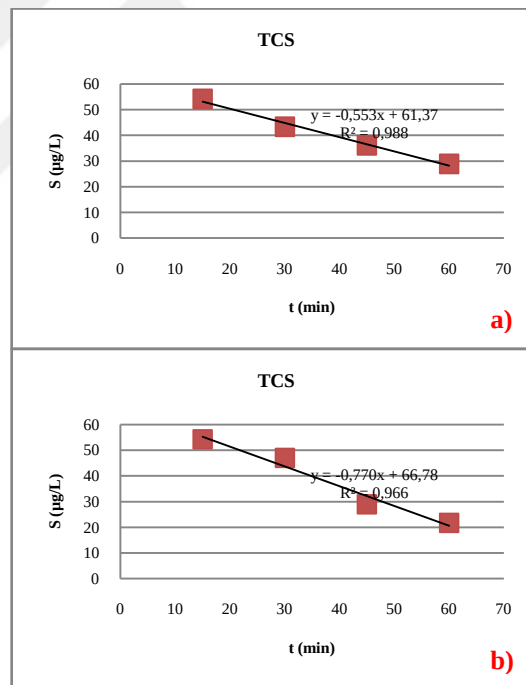


Figure 8 Zero-order TCS removal with (a) nano-TiO₂ (b) nano-CeO₂

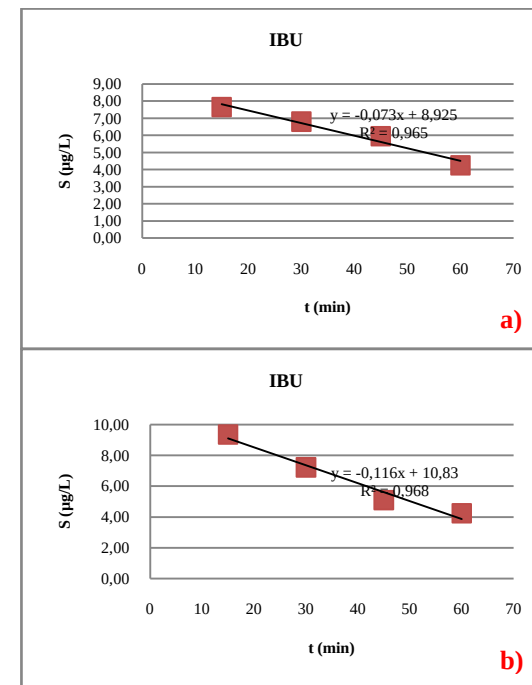


Figure 9 Zero-order IBU removal with (a) nano-TiO₂ (b) nano-CeO₂

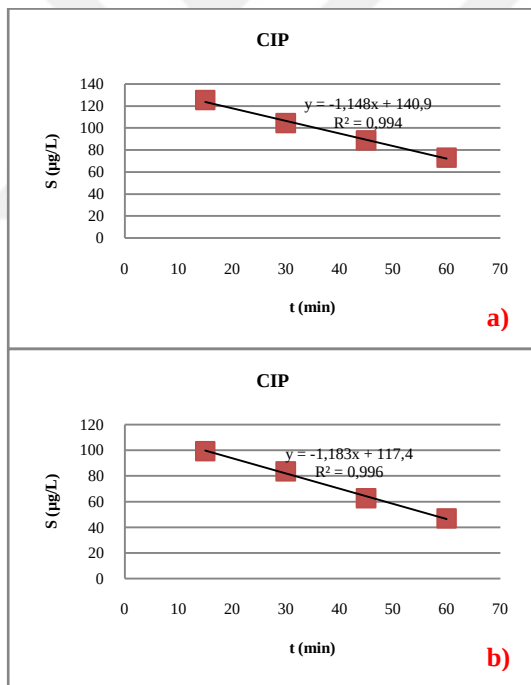


Figure 10 Zero-order CIP removal with (a) nano-TiO₂ (b) nano-CeO₂

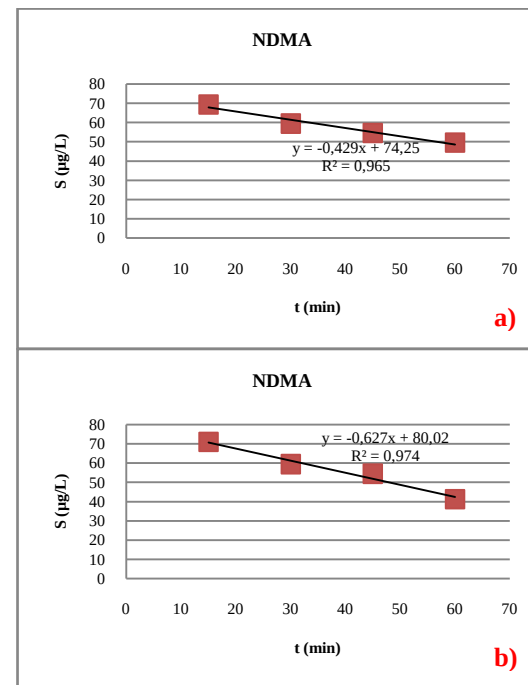


Figure 11 Zero-order NDMA removal with (a) nano-TiO₂ (b) nano-CeO₂

Appendix-11: Half-Order Removal Model for Ultrasound Treatment

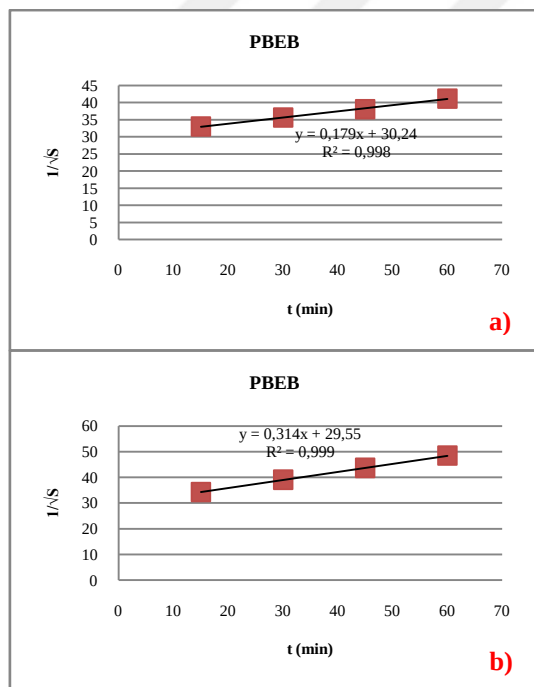


Figure 1 Half-order PBEB removal with (a) nano-TiO₂ (b) nano-CeO₂

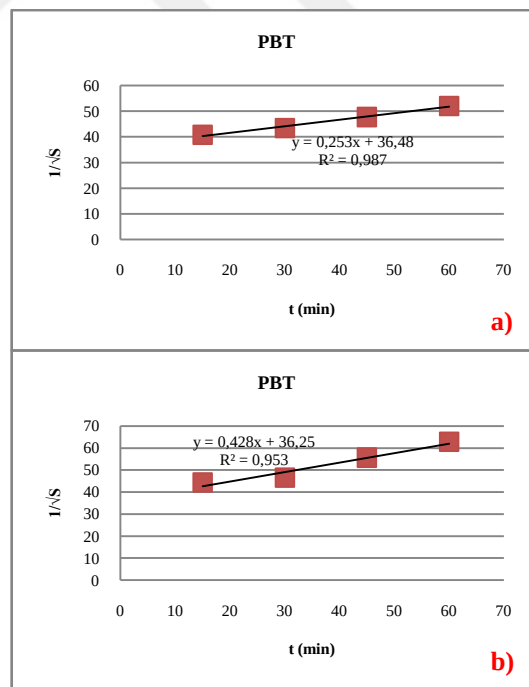


Figure 2 Half-order PBT removal with (a) nano-TiO₂ (b) nano-CeO₂

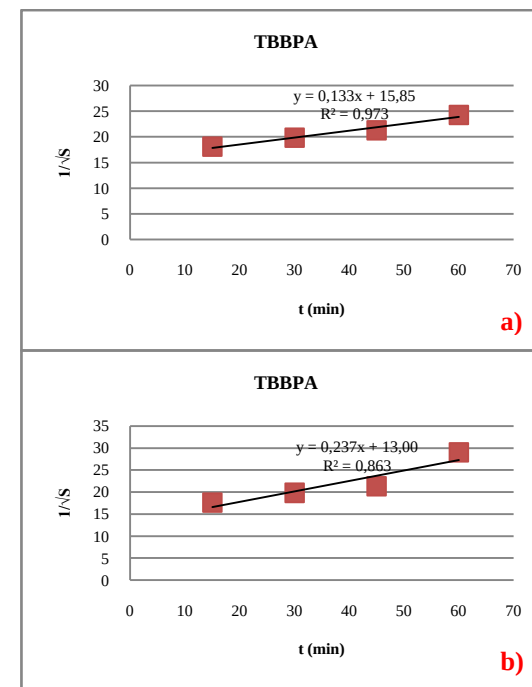


Figure 3 Half-order TBBPA removal with (a) nano-TiO₂ (b) nano-CeO₂

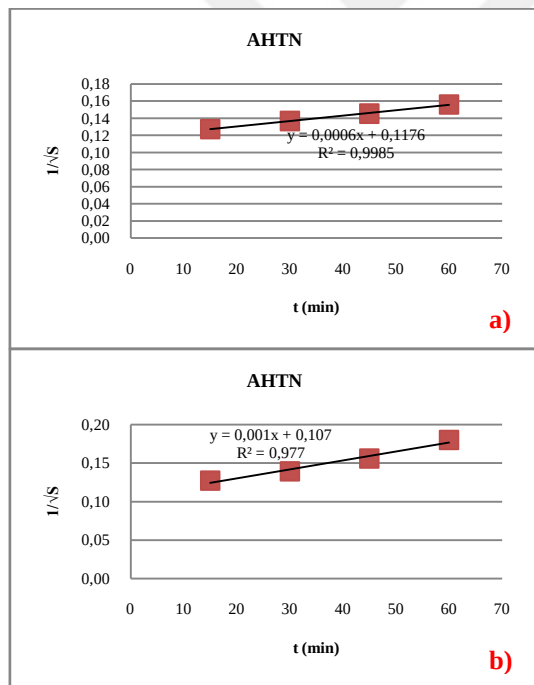


Figure 4 Half-order AHTN removal with (a) nano-TiO₂ (b) nano-CeO₂

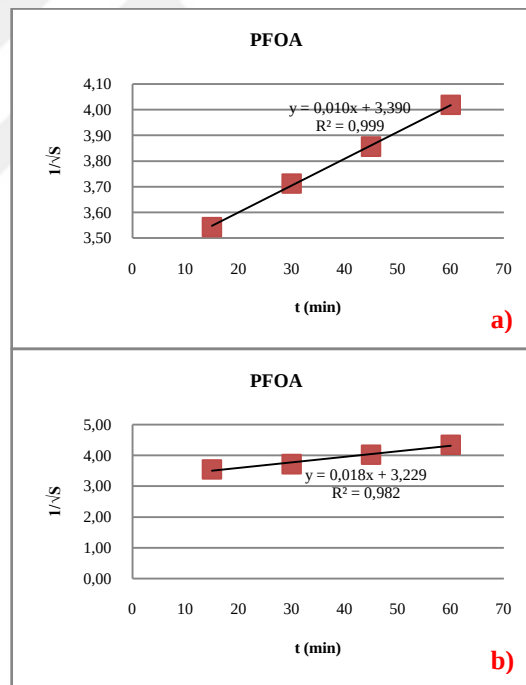


Figure 5 Half-order PFOA removal with (a) nano-TiO₂ (b) nano-CeO₂

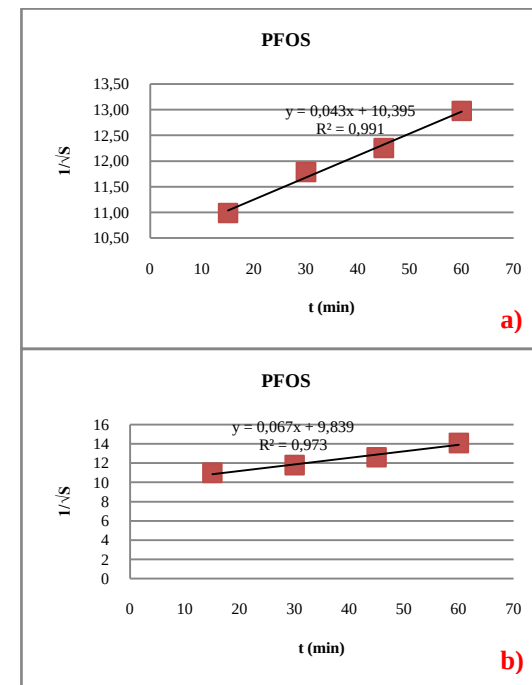


Figure 6 Half-order PFOS removal with (a) nano-TiO₂ (b) nano-CeO₂

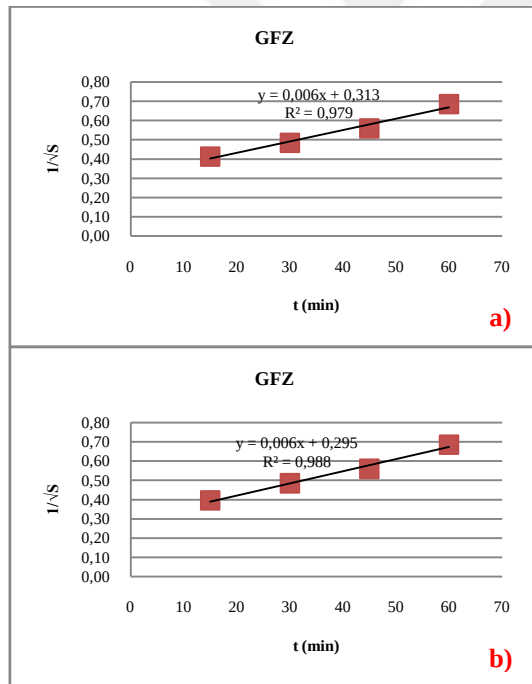


Figure 7 Half-order GFZ removal with (a) nano-TiO₂ (b) nano-CeO₂

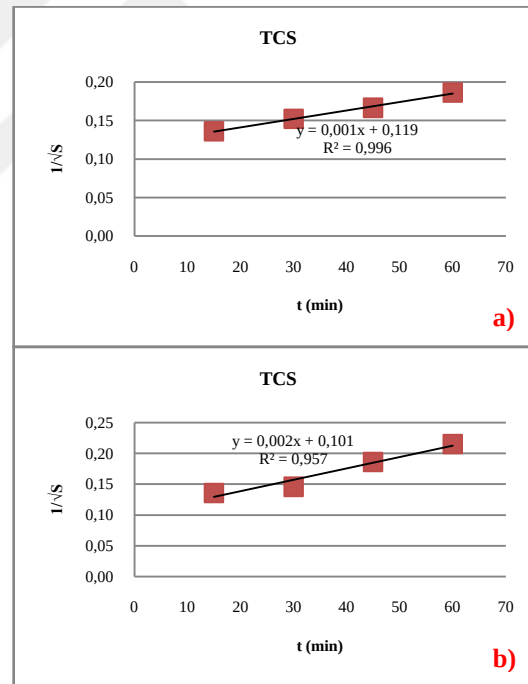


Figure 8 Half-order TCS removal with (a) nano-TiO₂ (b) nano-CeO₂

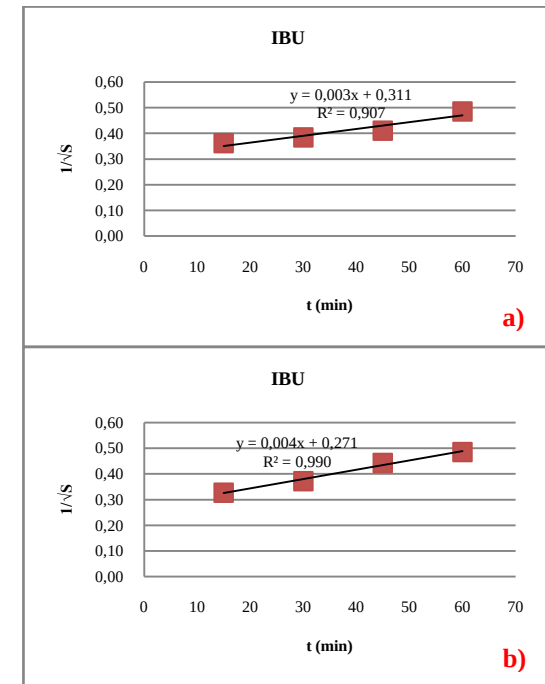


Figure 9 Half-order IBU removal with (a) nano-TiO₂ (b) nano-CeO₂

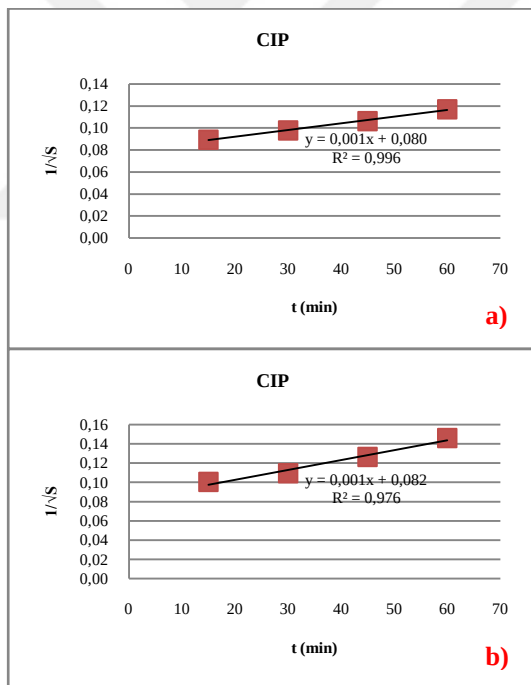


Figure 10 Half-order CIP removal with (a) nano-TiO₂ (b) nano-CeO₂

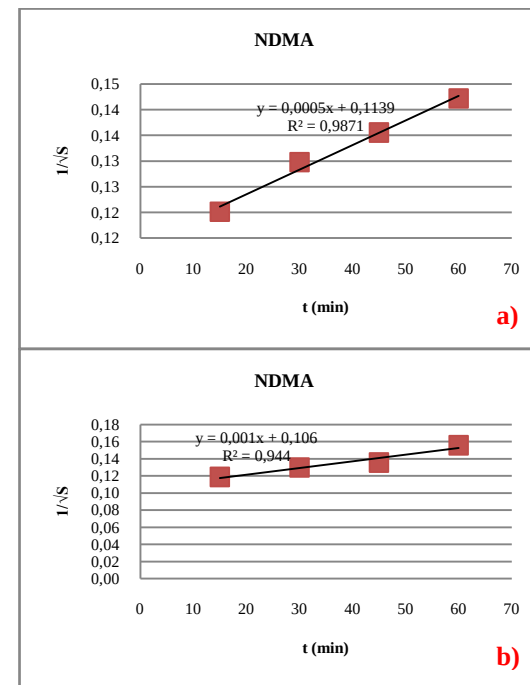


Figure 11 Half-order NDMA removal with (a) nano-TiO₂ (b) nano-CeO₂

Appendix-12: First-Order Removal Model for Ultrasound Treatment

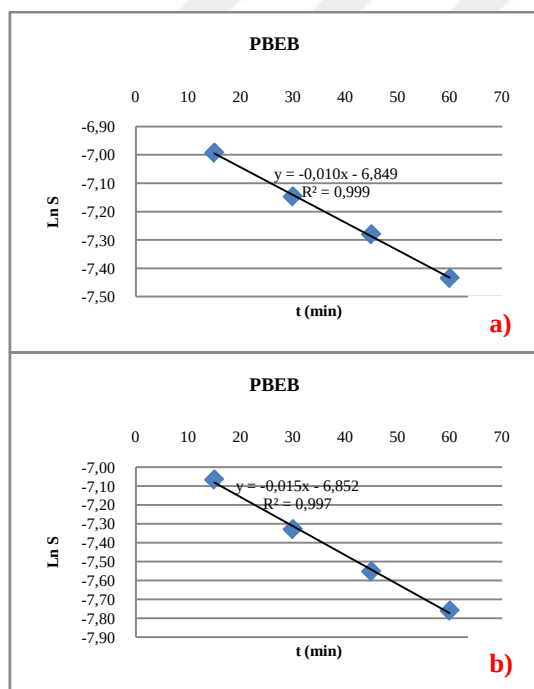


Figure 1 First-order PBEB removal with (a) nano-TiO₂ (b) nano-CeO₂

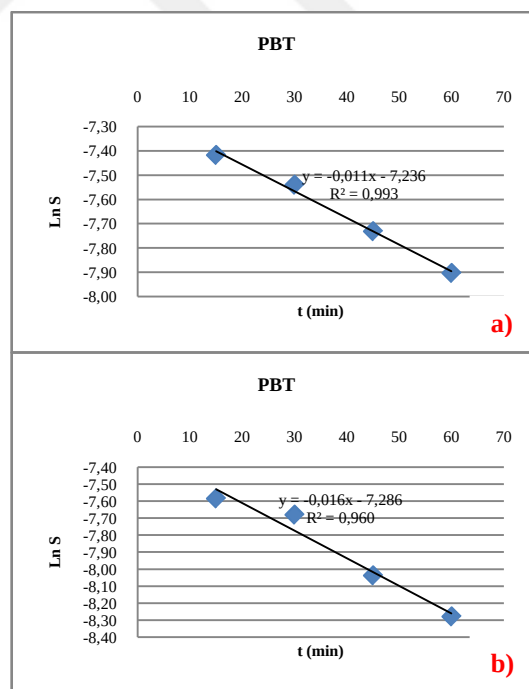


Figure 2 First-order PBT removal with (a) nano-TiO₂ (b) nano-CeO₂

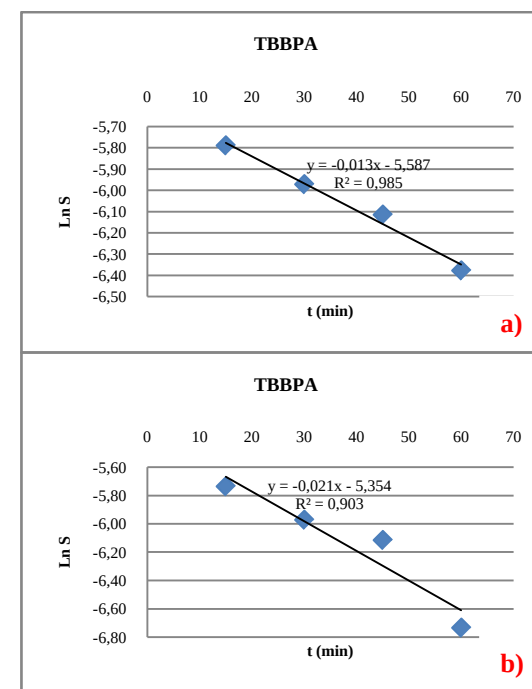


Figure 3 First-order TBBPA removal with (a) nano-TiO₂ (b) nano-CeO₂

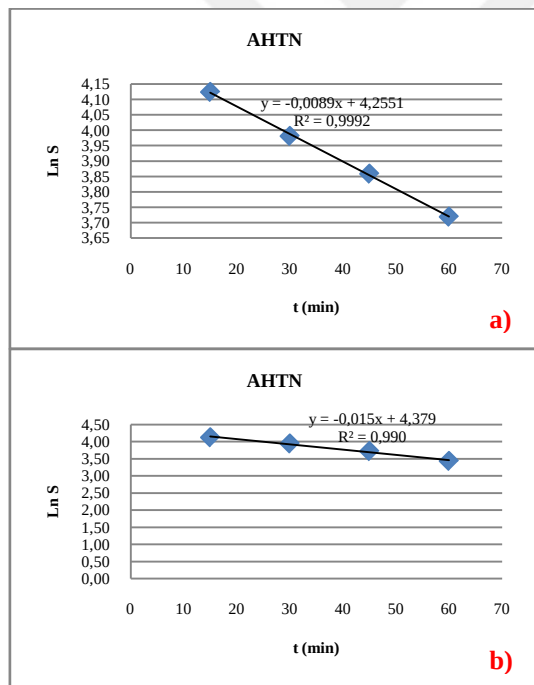


Figure 4 First-order AHTN removal with (a) nano-TiO₂ (b) nano-CeO₂

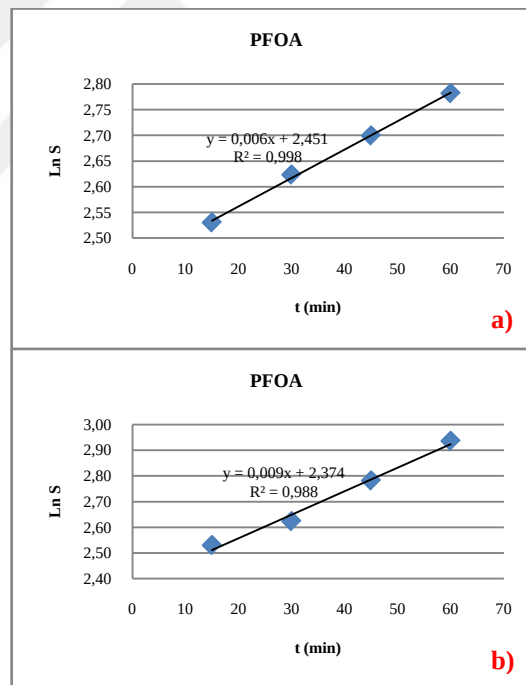


Figure 5 First-order PFOA removal with (a) nano-TiO₂ (b) nano-CeO₂

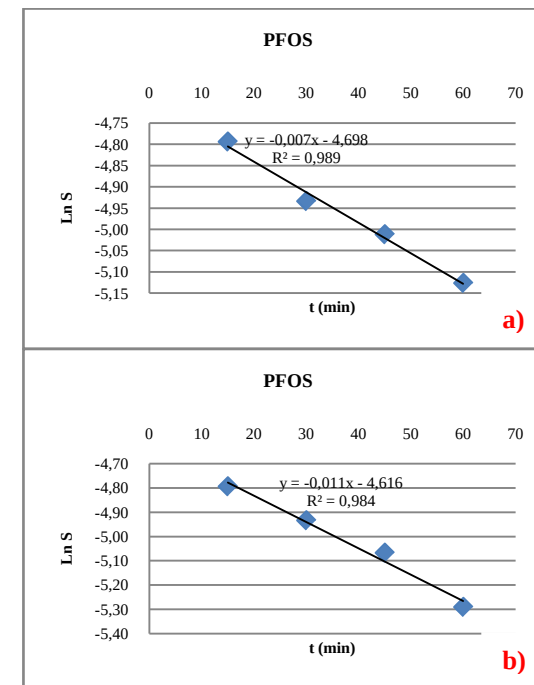


Figure 6 First-order PFOS removal with (a) nano-TiO₂ (b) nano-CeO₂

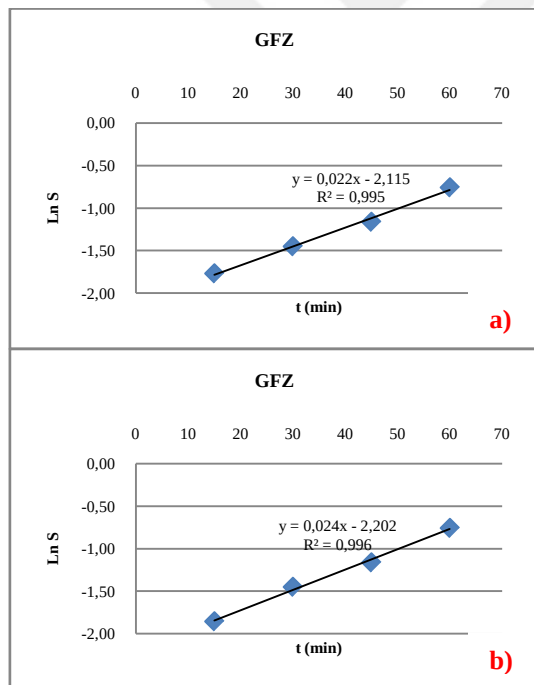


Figure 7 First-order GFZ removal with (a) nano-TiO₂ (b) nano-CeO₂

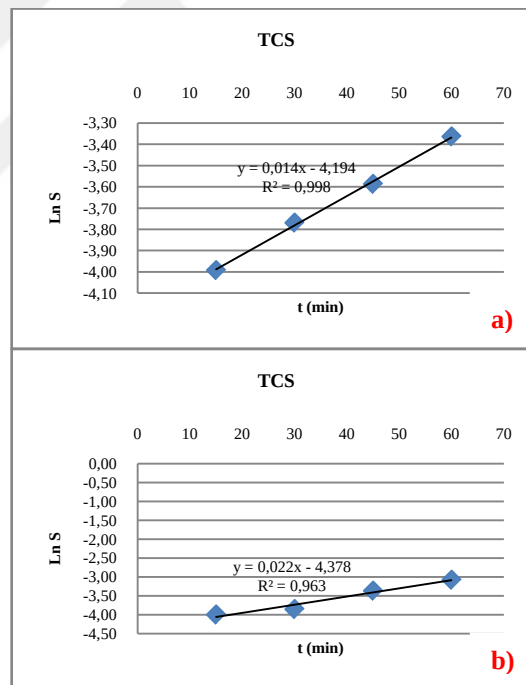


Figure 8 First-order TCS removal with (a) nano-TiO₂ (b) nano-CeO₂

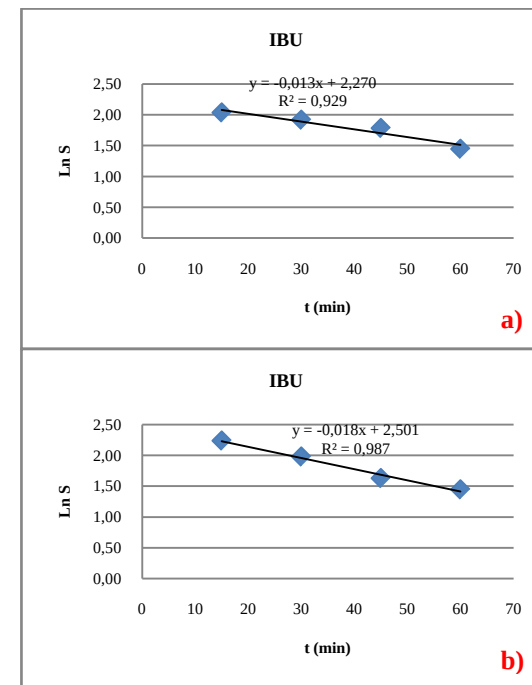


Figure 9 First-order IBU removal with (a) nano-TiO₂ (b) nano-CeO₂

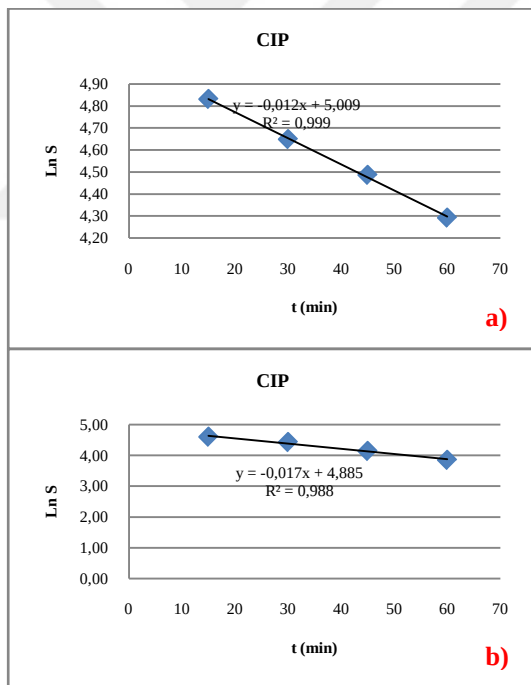


Figure 10 First-order CIP removal with (a) nano-TiO₂ (b) nano-CeO₂

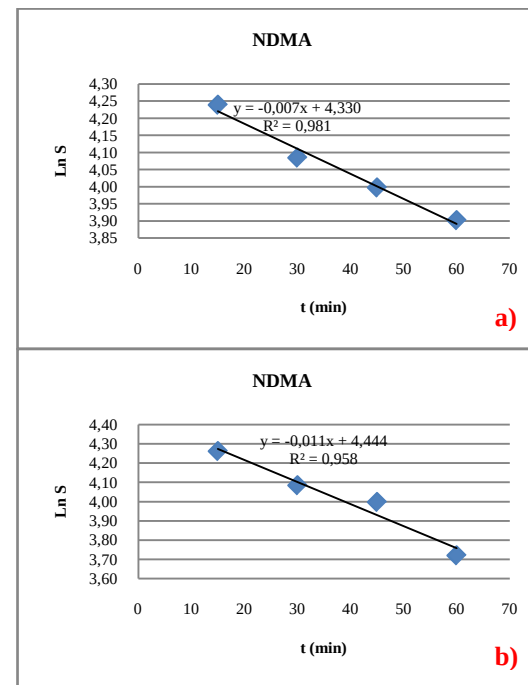


Figure 11 First-order NDMA removal with (a) nano-TiO₂ (b) nano-CeO₂

Appendix-13: Second-Order Removal Model for Ultrasound Treatment

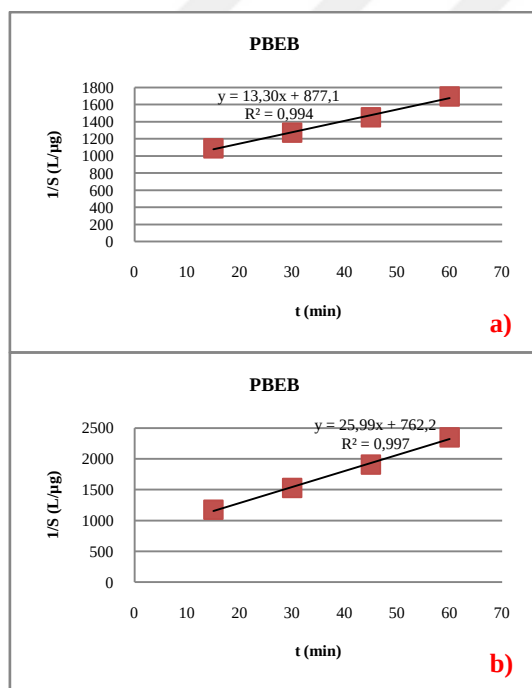


Figure 1 Second-order PBEB removal with (a) nano-TiO₂ (b) nano-CeO₂

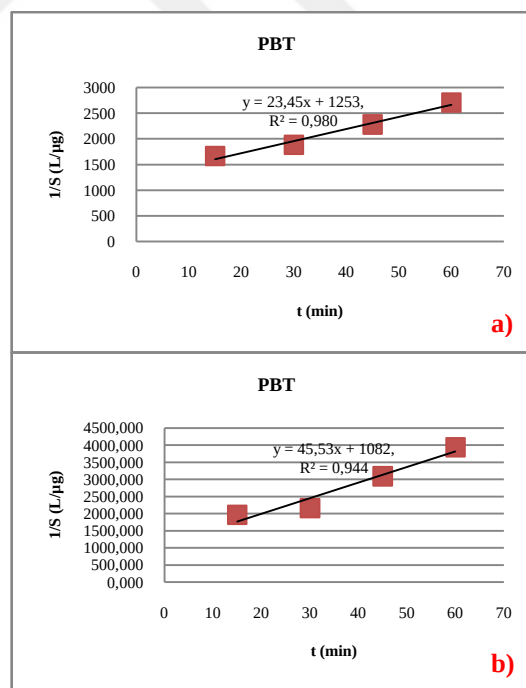


Figure 2 Second-order PBT removal with (a) nano-TiO₂ (b) nano-CeO₂

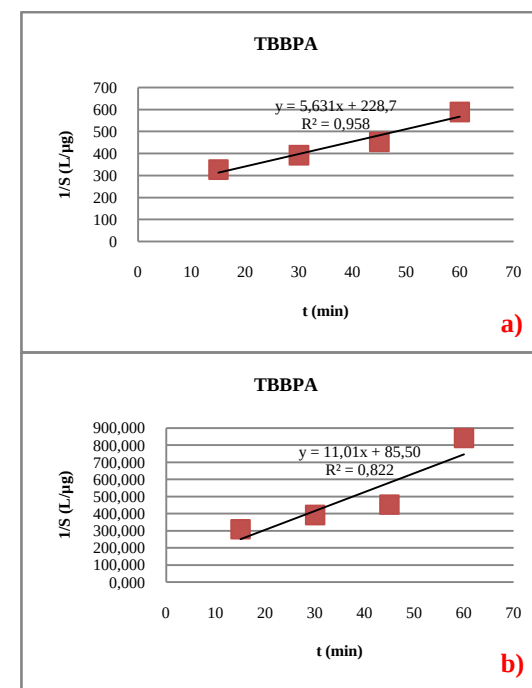


Figure 3 Second-order TBBPA removal with (a) nano-TiO₂ (b) nano-CeO₂

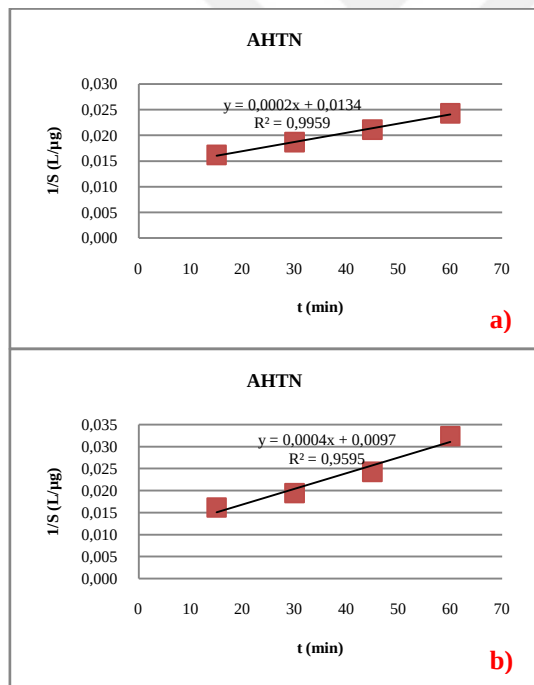


Figure 4 Second-order AHTN removal with (a) nano-TiO₂ (b) nano-CeO₂

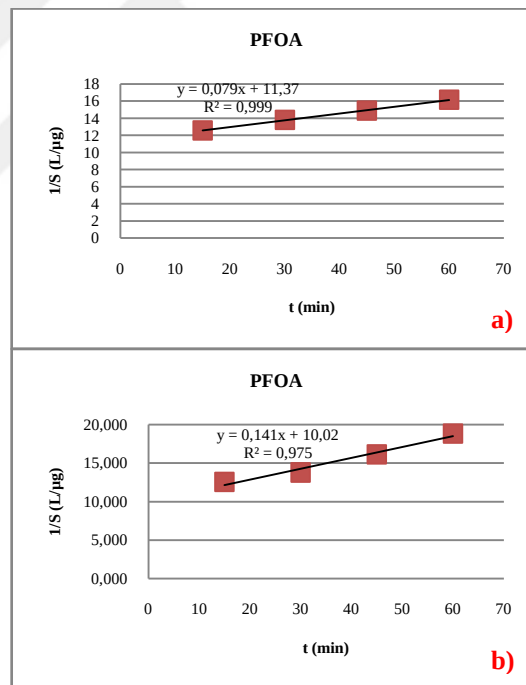


Figure 5 Second-order PFOA removal with (a) nano-TiO₂ (b) nano-CeO₂

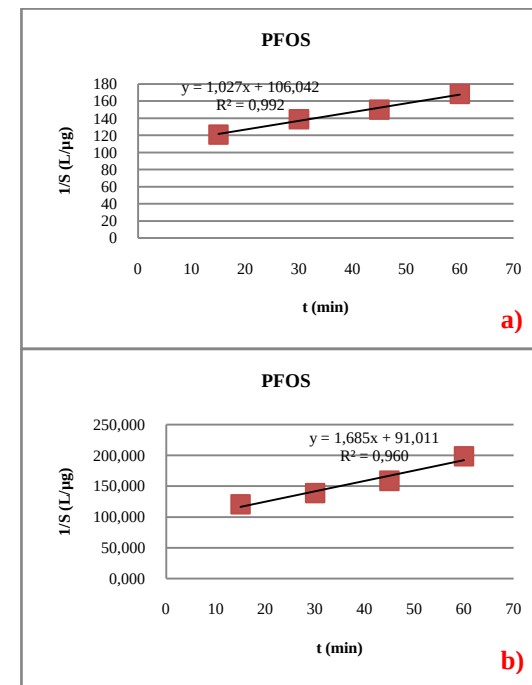


Figure 6 Second-order PFOS removal with (a) nano-TiO₂ (b) nano-CeO₂

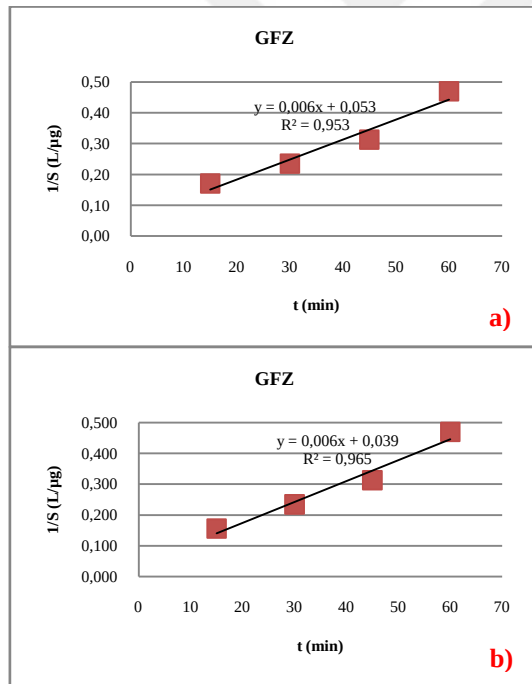


Figure 7 Second-order GFZ removal with (a) nano-TiO₂ (b) nano-CeO₂

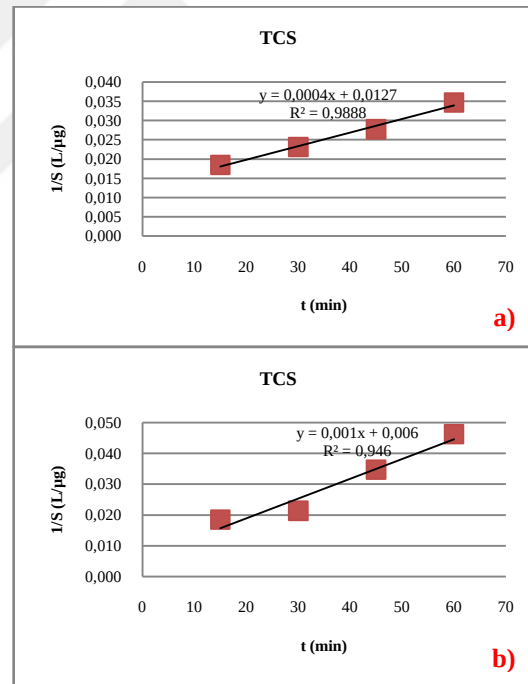


Figure 8 Second-order TCS removal with (a) nano-TiO₂ (b) nano-CeO₂

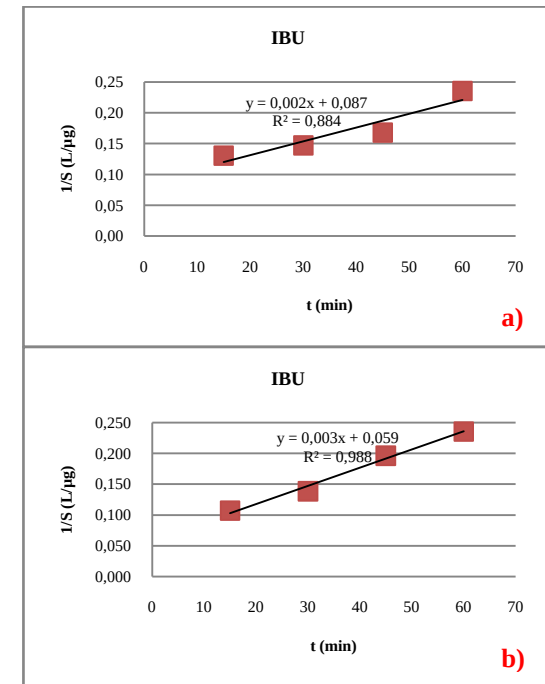
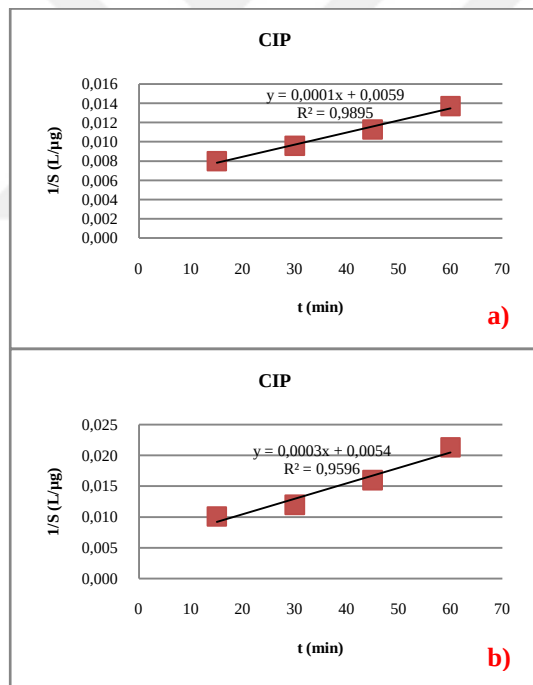
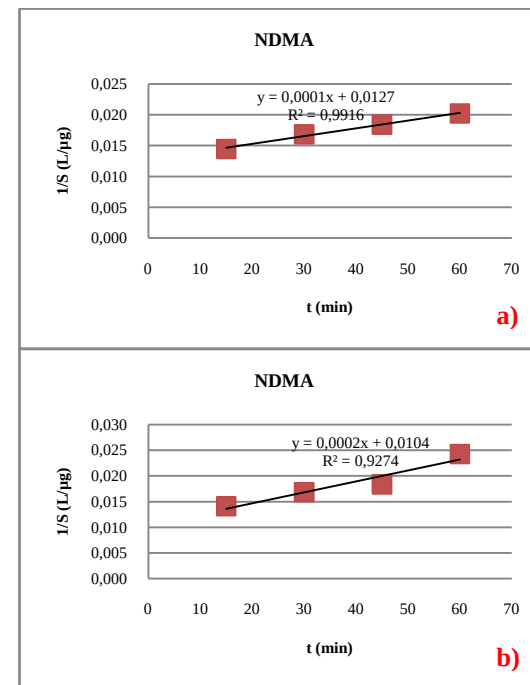


Figure 9 Second-order IBU removal with (a) nano-TiO₂ (b) nano-CeO₂

Figure 10 Second-order CIP removal with (a) nano-TiO₂ (b) nano-CeO₂Figure 11 Second-order NDMA removal with (a) nano-TiO₂ (b) nano-CeO₂

Appendix-14: Price Offer for a Real-Scale RO Facility



04.06.2019

DOKUZ EYLÜL UNIVERSITY
To the attention of the person concerned

No	Name of the material	Quantity	Unit price	Cost
1	Reverse Osmosis Treatment System for 100 m ³ /day capacity	1	unit 10.000,00 EUR	10.000,00 EUR

Total : 10.000,00 EUR

KDV* : 1.800,00 EUR

General total : 11.800,00 EUR

KDV* (VALUE-ADDED TAX) IS EXCLUDED.
DELIVERY TAKES 4-6 WEEKS.

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