REPUBLIC OF TURKEY
ADANA ALPARSLAN TÜRKEŞ SCIENCE AND TECHNOLOGY UNIVERSITY

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FOOD INDUSTRY WASTEWATER TREATMENT BY CERAMIC MICRO- AND ULTRAFILTRATION MEMBRANES

DEMET CAVLAK GÖÇER

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ASST. PROF. DR. ALİ EMRAH ÇETİN

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Submitted by **Demet CAVLAK GÖÇER** in partial fulfillment of the requirements for the degree of **Master of Science in Department of Nanotechnology and Engineering Sciences, Adana Alparslan Türkeş Science and Technology University** by,

Assoc. Prof. Dr. Gözde Baydemir PEŞİNT
Graduate School Director

Asst. Dr. Hatice İmge OKTAY BAŞEĞMEZ
Department Chair

Asst. Prof. Dr. Ali Emrah ÇETİN
Supervisor

Prof. Dr. Muhsin ÇIFTÇİOĞLU
Co-Supervisor

Thesis Committee

Assist. Prof. Dr. Ali Emrah ÇETİN
Adana Alparslan Türkeş Science and Technology University

Asst. Prof. Dr. Hüsnü Arda YURTSEVER
Adana Alparslan Türkeş Science and Technology University

Asst. Prof. Dr. Fatma Burcu ALP
Süleyman Demirel Üniversitesi

Thesis Defense Date

20/06/2019

I hereby declare that all information in this thesis has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all information that is not original to this work.

Demet CAVLAK GÖÇER

ABSTRACT

FOOD INDUSTRY WASTEWATER TREATMENT BY CERAMIC MICRO-, AND ULTRAFILTRATION MEMBRANES

Demet CAVLAK GÖÇER

Department of Nanotechnology and Engineering Sciences

Supervisor: Asst. Prof. Dr. Ali Emrah ÇETİN

Co-Supervisor: Prof. Dr. Muhsin ÇİFTÇİOĞLU

Ağustos 2019, 86 pages

Water scarcity is one of the global problems threatening all living species on Earth. Several solutions have been suggested for resolving the water scarcity. One of these solutions is the treatment of domestic and industrial wastewaters. Treatment and reuse of domestic and industrial wastewaters will significantly contribute to the prevention of the water scarcity. Membrane technology has been used for the treatment of wastewaters and water desalination. Membranes used are generally polymeric membranes. Studies however have been conducted to evaluate the performances of ceramic membranes in wastewater treatment.

The goal of this thesis was to prepare tubular ceramic membranes for the treatment of food industry wastewaters. Tubular Al_2O_3 supports, MF and UF layer coated supports were prepared and used for the treatment of oil containing wastewaters obtained from the different stages in the wastewater treatment facility of the food processing plant. Total suspended solid content (TSS), chemical oxygen demand (COD), color, turbidity and oil content of the wastewaters were determined before and after filtration experiments. Permeate fluxes, TSS, turbidity and color of the permeate samples taken in certain time intervals were also monitored.

Permeate fluxes much lower than clean water fluxes of the membrane were observed during the filtration of oily wastewater. In general, increasing cross flow velocity increased the permeate flux while the increase in transmembrane pressure decreased the flux. The lower

initial permeate fluxes indicated the rapid membrane fouling by oil and lipids present in the wastewater. Decrease in the fluxes in the course of filtration also pointed out the formation of a fouling layer. Filtration experiments performed using tubular ceramic supports and MF membranes resulted in 97-99 %, 91-98 %, 78-99 % and 63-99 % reductions in TSS, COD, turbidity and color values of the oily wastewater, respectively. No oil could be detected in the permeate samples collected and oil removal efficiencies were found to be 100 % in all experiments.

Keywords: ceramic membrane, food industry wastewaters, oil content, filtration, permeate

ÖZET

SERAMİK MİKRO- VE ULTRAFİLTRASYON MEMBRANLARI İLE GIDA ENDÜSTRİSİ ATIKSULARININ ARITILMASI

Demet CAVLAK GÖÇER
Nanoteknoloji ve Mühendislik Bilimleri Anabilim Dalı
Danışman: Dr. Öğretim Üyesi Ali Emrah ÇETİN
İkinci Danışman: Prof. Dr. Muhsin ÇİFTÇİOĞLU
Ağustos 2019, 86 sayfa

Su kıtlığı, dünyadaki tüm canlı türlerini tehdit eden küresel sorunlardan biridir. Su kıtlığının giderilmesi için çeşitli çözümler önerilmiştir. Bu çözümlerden biri evsel ve endüstriyel atık suların arıtılmasıdır. Evsel ve endüstriyel atık suların arıtılması ve yeniden kullanılması, su kıtlığının azaltılmasına önemli katkı sağlayacaktır. Atık suların arıtılması ve tuzlu sudan su eldesi için membran teknolojisi kullanılmaktadır. Bu amaçla genellikle polimerik membranlar kullanılmaktadır. Bununla birlikte, atık su arıtımındaki seramik membranların performansını değerlendirmek için çalışmalar yapılmaktadır.

Bu tezin amacı, gıda endüstrisi atıksularının arıtılması için tübüler seramik membranların hazırlanmasıdır. Çalışmada tübüler Al_2O_3 destekleri, MF ve UF tabakası kaplı Al_2O_3 destekleri hazırlanmış ve bir gıda işlemesinin atık su arıtma tesisinin farklı aşamalarından elde edilen yağlı atık suların arıtılmasında kullanılmıştır. Atıksuların toplam askıda katı madde içeriği (AKM), kimyasal oksijen ihtiyacı (KOİ), renk, bulanıklık değerleri ve yağ içerikleri filtrasyon işlemlerinden önce ve sonra belirlenmiştir. Ayrıca filtrasyon işlemleri süresince belirli zaman aralıklarında alınan süzüntü örneklerinin, akı, AKM, bulanıklık ve renk değerleri de izlenmiştir.

Filtrasyon deneyleri sırasında membranların temiz su akılarına kıyasla çok daha düşük süzüntü akıları gözlenmiştir. Genel olarak membrane geçiş basıncı arttığında süzüntü akısında azalma gözlenirken çapraz akış hızı arttığında süzüntü akısının arttığı gözlenmiştir. Düşük

başlangıç süzüntü akıları membranların atık suda yağ ve lipidler tarafından hızlı bir şekilde tıkandığını göstermiştir. Filtrasyon işlemleri sırasında süzüntü akılarındaki azalma da tıkayıcı bir tabakanın oluşumuna işaret etmiştir. Genel olarak, tübüler seramik destekler ve MF membranları kullanılarak yapılan filtrasyon işleminde yağlı atık suyun TSS, COD, bulanıklık ve renk değerlerinde sırasıyla % 97-99, % 91-98, % 78-99 ve % 63-99 azalma gözlenmiştir. Tüm filtrasyon deneylerinde, toplanan süzüntü numunelerinde yağ tespit edilememiş ve atıksulardan yağın % 100 verimle uzaklaştırıldığı bulunmuştur.

Anahtar Kelimeler: seramik membran, gıda endüstrisi atık suları, yağ içeriği, filtrasyon, süzüntü

to my family

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NOMENCLATURE

CFV	: Cross flow velocity
COD	: Chemical oxygen demand
D_i	: Inner diameter of the tubular support/membrane
Flux	: Permeate flux
L	: Length
MF	: Microfiltration
MWCO	: Molecular weight-cut-off
NTU	: Turbidity
T	: Time
TMP	: Transmembrane pressure
TSS	: Total suspended solid content
UF	: Ultrafiltration
UNESCO	: United Nations Educational, Scientific and Cultural Organization
UNICEF	: United Nations Children's Fund
V	: Volume of water or wastewater collected at the tank entrance for a time
V_p	: Volume of permeate
WHO	: World Health Organization

1. INTRODUCTION

Water crisis, a decrease in the available quantity and quality of fresh water to a significant level where the human health and/or economy are adversely affected, has been classified as one of the top five global risks in terms of its impact since 2012 (World Economic Forum, 2019). The water use has increased with a rate more than twice the rate of the population growth for the 21th century ("Water Scarcity", 2019). A changing climate, growing population, increasing agricultural and industrial activities, overuse and wasting of water and pollution of fresh water resources all contribute to global water crisis.

All living species on Earth have to consume water for their survival since cellular reactions take place in an aqueous environment. Although water is crucial for life and civilization, its resources are limited. Total water reserves on Earth contain approximately 1.39 x 10^9 km^3 water and only 2.53 % of this is fresh water reserves (Shiklomanov, 1993). Since fresh water includes fresh surface and ground water as well as water in icecaps and glaciers, the main sources of water available for human consumption, fresh water lakes and rivers, correspond to approximately 0.0067 % of total water on Earth (Shiklomanov, 1993).

Human beings not only drink water but also use it for cooking, washing, cleaning and bathing. Sustainable supply of clean water is therefore essential for ensuring proper nutrition, hygiene and sanitation in a healthy life. More than 3.4 million people die each year because of the issues related to water, hygiene and sanitation according to World Health Organization (WHO) statistics (WHO, 2004). The number of death related to the unsafe water and unsanitary conditions today is reported to be 2.6 million (Acquistapace, 2018). Approximately 2.3 billion people lived without a basic sanitation service while 600 million people used common sanitation facilities in 2015 according to "Progress on Sanitation and Drinking Water-2017 Update" report prepared by WHO and the United Nations Children's Fund (UNICEF) (WHO and UNICEF, 2017). Although 71 % of the global population used a safely managed drinking water system, 844 million people still needed a basic drinking water system in 2015 (WHO and UNICEF, 2017).

When the water available in a country is below 4600 liters/day for a person, that country experience water stress ("Water Scarcity," 2019). The further decrese in the water available

for a person to 2700 and 1400 liters/day are defined as water scarcity and absolute water scarcity, respectively ("Water Scarcity," 2019). Fresh water resources are inequally distributed on Earth. There are now countries already experiencing water stress, water scarcity or absolute water scarcity. United Nations World Water Development Report (UNESCO, 2019) stated that the current number of people living in the water scarce areas estimated as 3.6 billion at the moment would rise to 4.7-5.8 billion by 2050. According to predicted percentages of available fresh water supplies that would be withdrawn for agricultural, industrial and municipal uses in 2040, 35 countries will be withdrawing more than 80 % of their available fresh water supplies (Barbier, 2019). Thirty one countries including our country, Turkey, will experience high level of water shortage by discharging 40-80 % of available fresh water supplies (Barbier, 2019).

Water crisis is not only the physical shortage of water but also scarcity due to the inability to provide regular water supply or the absence of adequate infrastructure ("Water Scarcity," 2019). Inequity among people to have regular fresh water supply and the use of the significant fraction of available fresh water supply indicate that water crisis is a multi-dimensional water management problem. Construction of adequate infrastuructures for fresh water supply for all, the protection of water resources, the prevention of climate change, avoiding water overuse and wastage, collection of precipitation, ground water recharging and recycling of wastewaters are the major actions which can be taken to cope with the global water scarcity. The countries already experiencing or the countries having higher potential to face water scarcity in future should immediately take certain precautions to resolve water scarcity. Recycling of industrial and municipal wastewaters seems to be the most effective solution among the others in this regard. It will help recover the significant amount of fresh water used and decrease the amount discharged. According to Turkish Statistics Institute (TUIK, 2010), industry in Turkey withdrew 1.637 billion m^3 water/year from water supply lines, springs, seas, lakes, rivers, wells, water trucks, industrial zones and other sources and used 1.631 billion m^3 water/year in 2010. The discharged amount was 1.256 billion m^3 water/year (TUIK, 2010). 164 million m^3 of this was discharged after treatment however 1.092 billion m^3 was discharged without treatment.

Minimization of wastewater generated in industries which use larger quantities of water such as food, textile and ceramic and recovery of water from these wastewaters has become a

current issue because of the global warming and water scarcity and environmental regulations (Casani, Rouhany and Knøchel, 2005; Fähnrich, Mavrov and Chmiel, 1998; Sarkar, Chakrabarti, Vijaykumar and Kale, 2006; Simate, Cluett, Iyuke, Musapatika, Ndlovu, Walubita and Alvarez, 2011; Tang and Chen, 2002; Kurt, Koseoglu-Imer, Dizge, Chellam and Koyuncu, 2012; Debik, Kaykioglu, Coban and Koyuncu, 2010; Allégre, Moulin, Maisseu, Charbit, 2006; Fersi and Dhahbi, 2008).

Food industry uses larger quantity of water per ton of a product (Casani et al., 2005). The amounts of water used by food industry in Canada in 1991, Germany in 1995 and Netherlands in 1996 were reported to be 347.2, 455 and 247 million m^3/year, respectively. When various food processing sectors were considered, wastewaters generated per ton of a product in meat processing, fruit juice, vegetable processing (including olive milling), patato starch, beer and dairy industries were reported to be 2.7, 1.7, 30, 2.2, 4.2 and 91.5 m^3, respectively (Muro et al., 2012). This signifies that food industry wastewaters are potential sources for the water recovery. Unfourtanetely, information on the amount of water used and wastewater discharged by the food industry in our country is limited.

Membranes are semi-permeable barriers enabling the separation of molecules and particles from fluid streams. They separate two phases by avoiding their contact. The separation of molecules is preformed by various mechanisms; size exclusion, differences in electrical charges, solubilities and diffusion coefficients and etc. Micro-, ultra-, nanofiltration, reverse osmosis and pervaporation are pressure driven membrane processes. While dialysis, membrane extraction and separations using liquid membranes employ concentration difference as a driving force, electrofiltration and electrodialysis uses the differences in electrical potentials. Two different types of membranes, polymeric and ceramic are generally employed in membrane separation processes. While the first commercial application of polymeric membranes was reverse osmosis in sea water desalination (Baker, 2012), large scale applications of ceramic membranes started upon the need for the uranium isotope enrichment for nuclear plants (Gillot, 1991). Membranes are now widely used in chemical, pharmaceutical and food industries, biotechnology and medical applications, water purification and desalination and wastewater treatment. Although polymeric membranes are generally used in these applications, ceramic membranes offer several advantages over polymeric membranes due to their thermal, chemical and mechanical stabilities as well as

their service life. Ceramic membranes therefore hold a potential to provide cost-effective solutions for water treatment and water recycling by wastewater treatment.

This thesis is one of the series of thesis prepared under the context of the research project entitled with “The Micro/nanodesign of Ceramic Tubular MF-UF-NF Membrane Modules and the Investigation of Their Utilization in Industrial Wastewater Management” supported by The Scientific and Technological Research Council of Turkey (TUBITAK) 1003 - Primary Subjects R&D Funding Program. This project was based on the preparation of single channel alumina supports by extrusion, coating of selective micro-, ultra- and nanofiltration layers on the supports and evaluation of their water recovery potential by pilot scale textile, ceramic and food industry wastewater treatment experiments.

The goals of this thesis were therefore

1) to prepare single channel tubular supports, micro- and ultrafiltration membranes and

2) to determine their performances in the treatment of oil containing wastewaters obtained from food industry.

2. LITERATURE REVIEW

2.1. Membranes and Membrane Separation Processes

Membrane is a semi-permeable barrier which selectively allows the passage of certain molecules while restricting others in fluid streams. It separates two phases and prevents their intimate contact. Semi-permeable nature of the membrane is described by the term permselectivity. The permselectivity is the restriction of the movement of molecules through the membrane in a special way. Size exclusion, differences in diffusion coefficients, electrical charge, solubility, adsorption and/or reactivity on the surfaces are the mechanisms contributing to the permselectivity (Burggraaf and Keizer, 1991). Membranes can be solid, liquid and gas depending on the nature of the separation process applied. Membranes can be used for the separation of molecules or mixtures and manipulations of chemical reactions (shifting of equilibrium or increasing conversion or selectivity) (Burggraaf and Keizer, 1991).

Membrane separation processes and driving forces applied in the separation of molecules are given in Table 2.1. Reverse osmosis (hyperfiltration), nanofiltration, ultrafiltration, microfiltration, membrane gas and vapor separations and pervaporation are the membrane processes in which the pressure difference is the driving force. While porous membranes are used in micro-, ultra- and nano- filtration and reverse osmosis, dense membranes besides porous membranes are employed in membrane gas and vapor separation and pervaporation. Temperature differences hence the differences in partial/vapor pressures of gases/vapors make it possible to separate them by membrane distillation process. Concentration gradient is the major driving force in dialysis, membrane extraction and liquid membrane applications. Separation using electrodialysis and electrofiltration is achieved by the differences in electrical potentials.

Micro-, ultra-, and nanofiltration are the processes in which the separation of molecules is performed by sieving while the solution diffusion is separation mechanism in reverse osmosis (Cheremisinoff, 2002). Pore size and structure of the membrane are the major factors important in the selective separation of molecules. Pore sizes of the membranes used in membrane separation processes are given in Figure 2.1.

Table 2.1. Membrane Separation Processes (Matsuura, 1994; Scott, 1998)

Driving Force	Membrane Processes
Pressure	Reverse Osmosis/Hyperfiltration
	Nanofiltration
	Ultrafiltration
	Microfiltration
	Membrane gas and vapor separation
	Pervaporation
Temperature	Membrane Distillation
Concentration	Dialysis
	Membrane Extraction
	Liquid Membranes
Electrical Potential	Electrodialysis
	Electrofiltration

Pore sizes of the microfiltration membranes range between 0.1 μm and several micrometers. Ultrafiltration membranes have pores in the size range of several nanometers to several hundred nanometers. Lower and upper limits for the pore sizes of nanofiltration membranes are around 1 and 10 nm, respectively. Membranes with pores smaller than 1 nm are used in reverse osmosis. Applications of micro-, ultra-, nanofiltration and reverse osmosis membranes are summarized in Table 2.2. Microfiltration is generally used to remove small particles and bacteria (Scott, 1998) while ultrafiltration is employed for the separation of colloidal particles and macromolecules from solutions (Cheremisinoff, 2002). Nanofiltration is used where the separation capability between ultrafiltration and reverse osmosis required such as the separation of di- and multivalent ions from solutions and the separation of small organic compounds (Cheremisinoff, 2002).

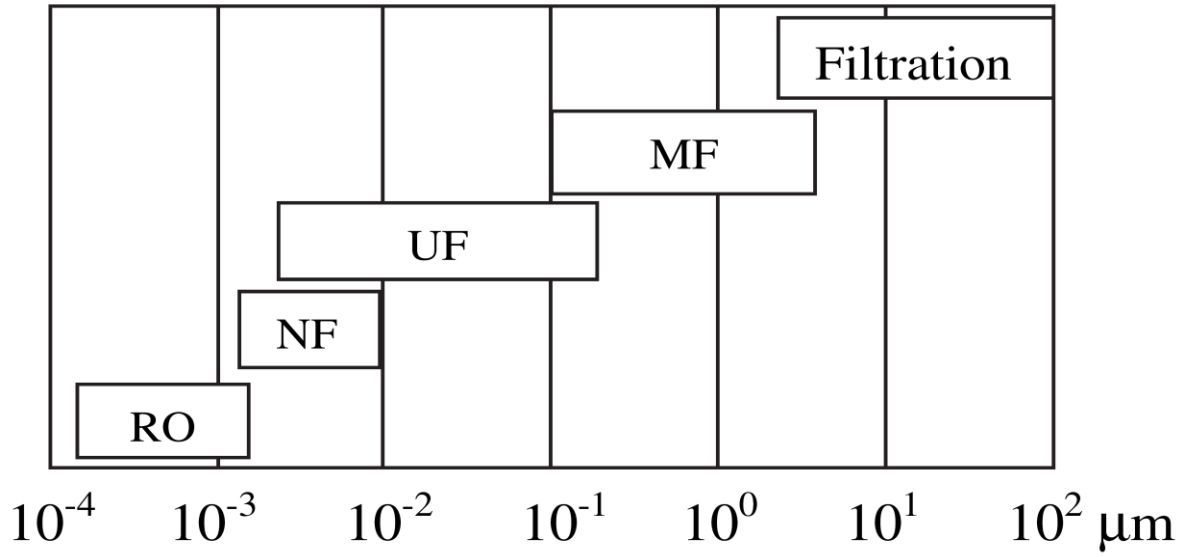

Figure 2.1. Pore sizes of the membranes used in membrane processes (Li, 2007)

Table 2.2. Membrane properties, membrane processes and applications (Scott, 1998, Cheremisinoff, 2002, Rijn, 2004)

Filtration	Pore Size	Membrane Type	Pressure (atm)	Applications
Microfiltration	50 nm - 5 μm	Symmetric, Asymmetric	1-5	Clarification, sterile filtration, Prefiltration in water treatment, dye industry, beverage clarification, screening of bacteria
Ultrafiltration	5 – 100 nm	Asymmetric	2-10	Separation of macromolecular solutions, dairy industry, beverage industry, pharmaceutical industry, separation of water from crude oil, separation of fruit and vegetable extracts, wastewater treatment
Nanofiltration	1 -10 nm	Asymmetric	5-50	Separation of small organic compounds and selected salts from solutions, purification of sugars from acids, salts from dyes, water treatment
Reverse Osmosis	< 1 nm	Asymmetric, composite with homogeneous skin	10-100	Separation of micro-solutes and salts from solutions

Sizes of the several molecules, particles and microorganisms and pore sizes of the membranes used in membrane separation processes (Peter-Varbanets, Zurbrügg, Swartz and Pronk, 2009) are given in Figure 2.2 for comparison. As it is shown in Figure 2.2, microfiltration enables the separation of solutes and particles in microparticle size range such as bacteria, clay particles and several viruses. Ultrafiltration is used to separate molecules in high molecular size to microparticle sizes such as macromolecules and proteins. Nanofiltration is generally used for the separation of solutes or particles in low molecular size range. Reverse osmosis however is employed for the separation of salts and molecules in sizes close to atomic or ionic size range.

Filtration can be operated in two different modes; dead-end and cross flow filtration. The difference in these modes is the direction of the feed flow. Feed is directed perpendicular to the membrane surface in the dead-end mode (Figure 2.3a). Feed flow perpendicular to the membrane surface results in the accumulation of particles and solutes on the membrane surface hence in the membrane fouling and the formation of filtration cake. This in turn causes the significant reduction in permeate flux.

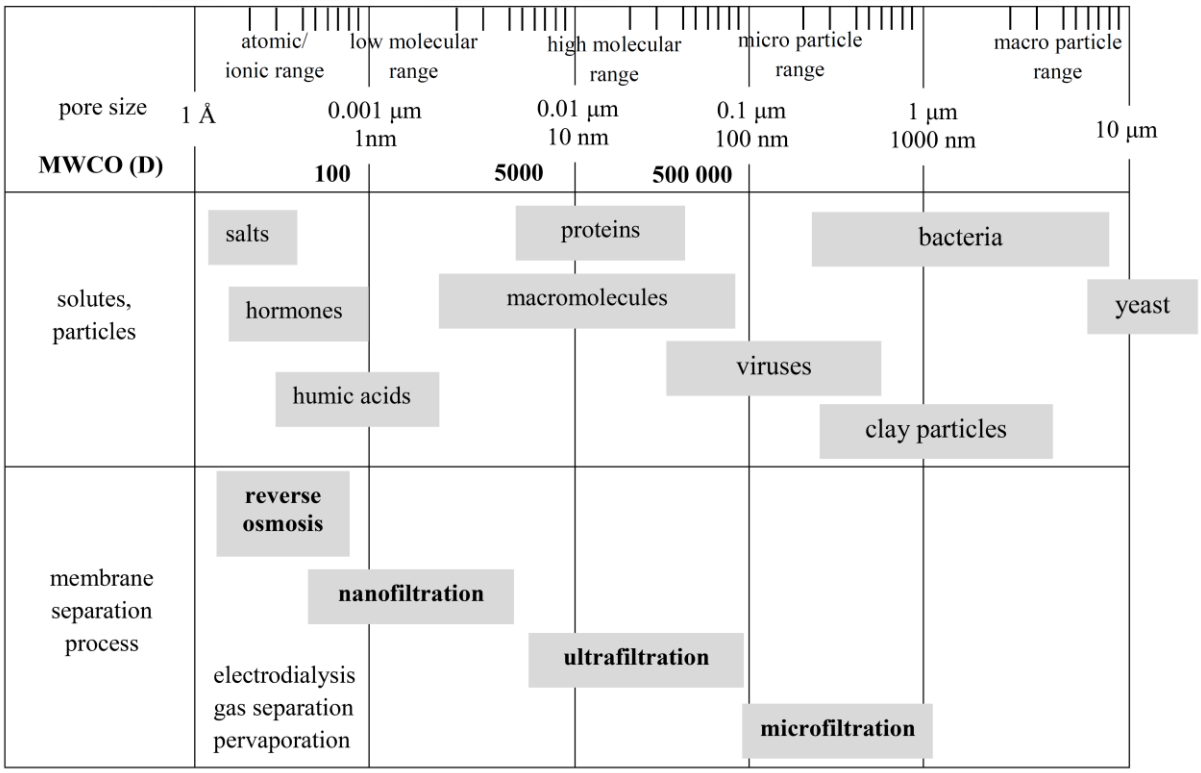

Figure 2.2. Membrane processes, pore sizes, molecular weight-cut-off (MWCO) and sizes of several solutes and particles (Peter-Varbanets et al., 2009)

Cross flow filtration (tangential flow filtration) is the filtration mode where the feed flows parallel/tangential to the surface of the membrane (Figure 2.3.b). The shear forces exerted on the membrane surface due to the feed flow removes the particles and solutes accumulated on the membrane surface. This therefore reduces the degree of membrane fouling and the reduction in the permeate flux. Adjusting the velocity of the feed stream help improve the permeate flux decline in the filtration.

Membranes can be prepared from organic materials (polymeric (synthetic/modified natural)) or inorganic materials. Inorganic membrane materials include ceramics and metals. Materials used in the preparation of membranes are summarized in Table 2.3. These materials are used in the preparation of both porous and dense membranes. Dense membranes are generally prepared from metals as solid layer for H_2 and O_2 separation (Burggraaf, 1996). Porous membranes however can be prepared from all material classes.

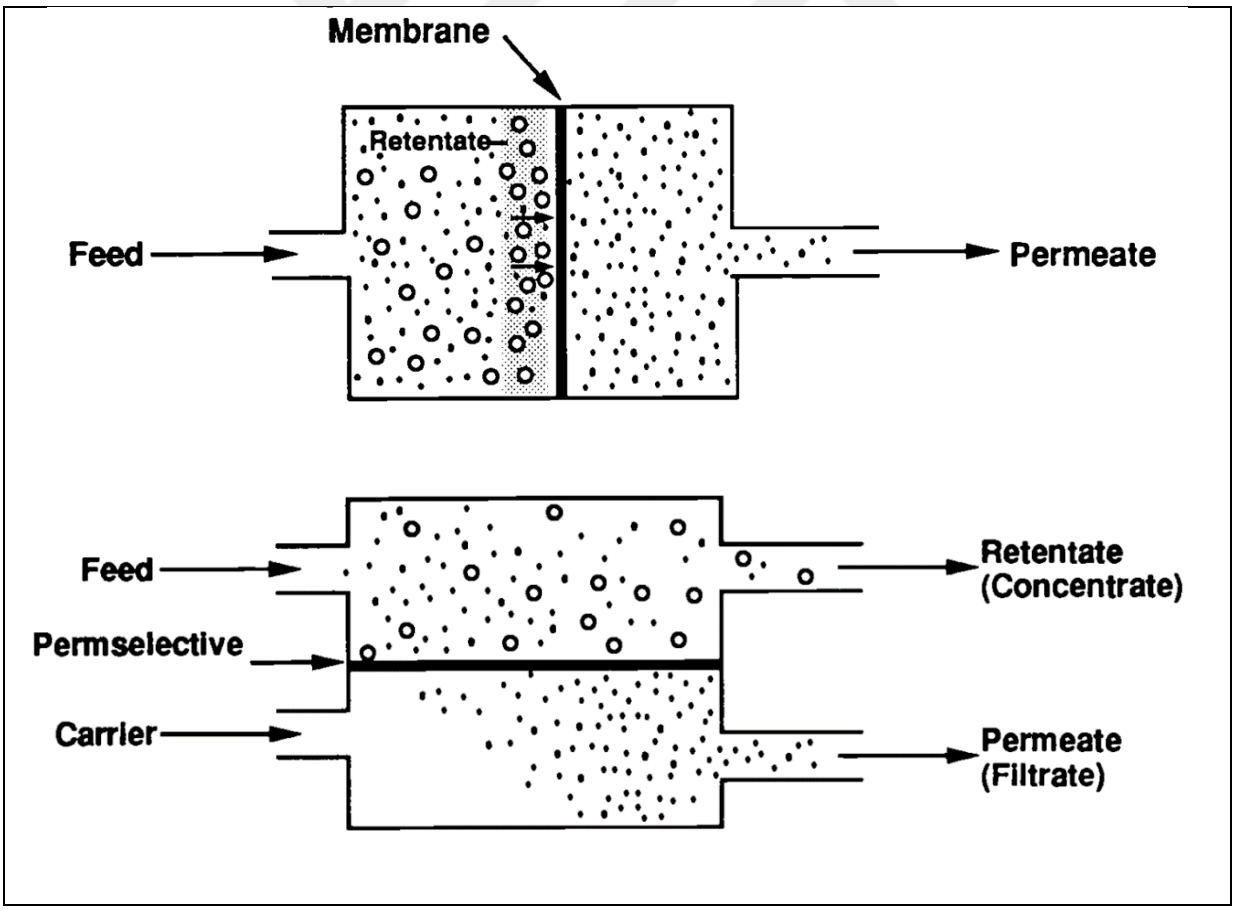

Figure 2.3. Dead-end filtration (a) and cross flow filtration (b) (Hsieh, 1996a)

Table 2.3. Membrane Materials (Burggraaf and Keizer, 1991; Cheremisinoff, 2002; Hsieh, 1996a; Rijn, 2004; Scott, 1998)

Material Class	Membrane Material
Polymeric	Cellulose esters, polyamide, polysulfone, polyacrilonitrile, polyimide, silicon rubber, divinyl benzene, polytetrafluoro ethylene, polyethylene, polypropylene, polycarbonate, polyester, nylon, polyvinyl chloride, styrene/vinylpyridene, poly(ether)imide, polyolefine
Ceramic	α-Al_2O_3, γ- Al_2O_3, ZrO_2, TiO_2, SiO_2, mullite, cordierite, $Zr(OH)_4$, bismuth oxides, V_2O_5, C, SiC, glass, zeolites
Metalllic	Silver and alloys, palladium and alloys, stainless steel (316)

Membranes used in micro-, ultra-, nanofiltration and reverse osmosis are generally polymeric membranes. Polymeric membranes can be prepared from synthetic polymers or modified natural polymers (Scott, 1998). Commonly used polymeric materials used to prepare membranes for microfiltration, ultrafiltratation and reverse osmosis and their properties are given in Table 2.4. As it can be observed from Table 2.4, type of polymeric material to be used to prepare membranes varies according to the application, maximum working temperature and pH stability range.

The important characteristics which membrane material should bear are as follows (Scott and Hughes, 1996):

1. Chemical resistance to both feed solutions and cleaning chemicals
2. Mechanical stability
3. Thermal stability
4. High permeation fluxes
5. High selectivity
6. Stable operation

Table 2.4. Polymeric membrane materials and properties (Hsieh, 1996a)

Material	Application	Maximum Working Temperature (°C)	pH Range
Cellulose acetates	MF, UF, RO	≈ 50	3-7
Aromatic polyimides	UF, RO	≈ 60-80	3-11
Fluorocarbon polymers	MF, UF, RO	≈ 130-150	1-14
Polyimides	UF, RO	≈ 40	2-8
Polysulfone	MF, UF	≈ 80-100	1-13
Nylons	MF, UF	≈ 150-180	
Polycarbonate	MF, UF	≈ 60-70	
Polyvinyl chloride		≈ 120-140	
Polyvinylidene fluoride	UF	≈ 130-150	1-13
Polyphoshazene		≈ 175-200	

The selection of the membrane depends on the properties of feed solution, filtration and membrane cleaning conditions. Mechanical, physical and chemical properties of the membrane determine its suitability for the filtration experiment. Chemical composition, temperature and pH of the feed solution as well as the size range of molecules and particles to be separated are important feed properties affecting membrane material selection. Membrane must be mechanically resistant to pressures applied in the filtration applications. It must be chemically, mechanically, structurally stable so that it preserves its functional integrity both during the filtration and cleaning the membrane. There must be a proper match between pore size and structure of the membrane and the size of the molecules/particles to be separated.

2.2. Ceramic Membranes

Although the engineering of the pore size and structure of the polymeric membranes is somewhat relatively easy compared to ceramic membranes, their chemical and mechanical susceptibility restricts their use in harsh environment, at high temperatures and pressures. Membrane cleaning procedures generally require the use of various chemical solutions. Degradation in these solutions causes the loose of membrane functionality. Irreversible

fouling of the polymeric membranes and membrane susceptibility to cleaning chemicals shortens their service life.

Ceramic membranes therefore offer preferable advantages over polymeric membranes in regards to their thermal, chemical and mechanical, stability, uniform pore size, longer service life and resistance to chemical agents used in membrane cleaning (Tsuru, 2001; Ciora and Liu, 2003; Erdem, 2009). Ceramic membrane materials and their properties are given in Table 2.5. Alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), silica (SiO_2), zeolites, mullite, cordierite, hafnia, silicon carbide and glass are the ceramic materials used in the preparation of ceramic membranes (Biron, Santos and Zeni, 2018). Commercially available ceramic membranes are listed in Table 2.6. As it is seen in Table 2.6, commercial ceramics are generally designed by coating Al_2O_3, ZrO_2, TiO_2, SiO_2 membrane layers on Al_2O_3 supports.

Table 2.5. Ceramic membrane materials and properties (Hsieh, 1996a)

Material	Application	Maximum Working Temperature (°C)	pH Range
γ- Al_2O_3	UF	≈ 300	5-8
α-Al_2O_3	MF	> 900	0-14
ZrO_2	MF, UF	≈ 400	1-14
ZrO_2 (hydrous)	UF, RO	≈ 80-90	4-11
Glass	UF, RO	700	1-9

Ceramic membranes are in porous form. Two types of ceramic membranes can be prepared; symmetrical and asymmetrical (Figure 2.4). Symmetrical (isotropic) membranes have uniform porosity and structure. They are plates, disks or tubes prepared from single or mixtures of ceramic powders. Asymmetric (anisotropic) membranes are however manufactured by coating a thick porous support with a thin membrane layer.

Table 2.6. Commercially available ceramic membranes (Hsieh, 1996b; Keizer, Uhlhorn and Burggraaf, 1995)

Membrane Material	Support Material	Pore Diameter	Element Geometry	Manufacturer
ZrO_2	C	4 nm	tube	SFEC
ZrO_2	C	4-14 nm	tube	UC
$Zr(OH)_4$	Stainless steel	200-500 nm	tube	Carre (Du Pont)
ZrO_2	Al_2O_3	10 nm	tube	TDK
Al_2O_3	Al_2O_3	4-5000 nm	monolith/tube	Alcoa/SCT
Al_2O_3	Al_2O_3	200-1000 nm	tube	Norton/Millipore
Al_2O_3	Al_2O_3	200-5000 nm	tube	NGK
Al_2O_3	Al_2O_3	200 nm	tube	Hoogovens
Al_2O_3	Al_2O_3	25-200 nm	disk	Anotec/Alcan
Al_2O_3	Al_2O_3	200 nm, 800 nm	monolith and tube	
Al_2O_3	Al_2O_3	100-500 nm	tube	Holland Industrial Ceramics
Al_2O_3	Al_2O_3	100-10000 nm	tube	
SiC	SiC	150-8000 nm	tube	Ceram Filters
SiO_2 (glass)		4-120 nm	tube capillary	Asahi,Fuji,Schot
ZrO2	Inconel	100 nm	plate	Ceramesh
Cordierite, Al_2O_3, TiO_2, mullite	-	35-35000 nm	monolith	Corning
Glass	-	4-20 nm	tube and plate	Corning
Glass	-	8-10000 nm	tube and plate	Asahi
Ceramics	SiC	100-10000 nm	monolith	Ceram-Filtre
Ceramic oxides	Ceramic oxides	5-500 nm	monolith and tube	Ceramem
Metal alloys, C, Al_2O_3, ZrO_2, WC	-	> 5000 nm	plate	Astro Met
Ni, Cu, Mg, stainless steel, Al_2O_3	-	> 5000 nm	monolith	DMK TEK
Al_2O_3, mullite, cordierite	-	60-1000 nm	tube	Du Pont
Ceramics	Ceramics	1000-10000 nm	tube and plate	Fairey
C	C	10-10000 nm	tube	Le Carbone (Pechiney)
TiO_2	Al_2O_3	5-50 nm	monolith	NGK
Al_2O_3	Al_2O_3	400-8000 nm	tube and disk	Nihon Cement
Al_2O_3	Al_2O_3	400-12000 nm	tube	NOK
Ceramics	Ceramics	100-25000 nm	tube and plate	Osmonics
Ceramics	-	100-12000 nm	plate	Poretics
ZrO_2/TiO_2	$A1_2O_3/TiO_2$	4-450 nm	monolith	TDK
ZrO_2/TiO_2	C	4-140 nm	tube	TDK
Al_2O_3	Al_2O_3	200-400 nm	Monolith, tube and disk	TOTO
ZrO_2	Al_2O_3	10-60 nm	Monolith, tube and disk	TOTO
Al_2O_3	-	20-200 nm	Plate	Whatman
Al_2O_3	Al_2O_3	4-5000 nm	Monolith and tube	US Filter
ZrO_2	Al_2O_3	20-100 nm	Monolith and tube	US Filter

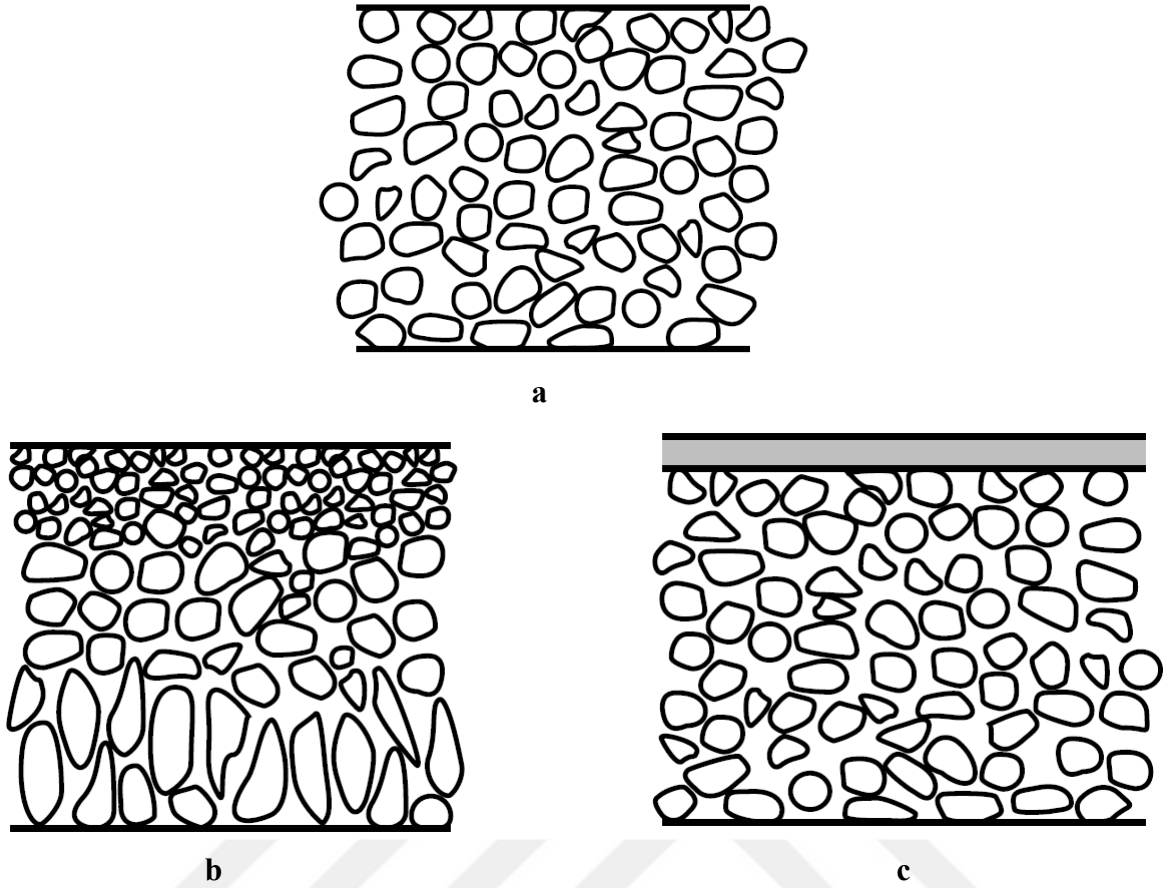

Figure 2.4. Structure of the symmetric membranes (a), asymmetric membranes (b and c) (Baker, 2012)

Ceramic membranes are used in a wide range of applications in chemical, petrochemical, textile, paper and pulp, pharmaceutical, mechanical, automative, metal and food industries. Table 2.7 summarizes liquid phase separations using ceramic membranes in these industries. As it is inferred from Table 2.7, ceramic membranes are generally used in the separation, fractionation, clarification, purification and concentration of products, recovery of by-products, chemicals and solutions, removal of microorganism and production of high purity water.

Table 2.7 Liquid phase separations using ceramic membranes in various industries (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a)

Industry	Applications
Chemical and Petrochemical Industry	Product separation and cleaning
	Concentration of polymer suspensions, latex, and metal hydroxide solutions
	Catalysts recovery
	Deasphalting of petroleum residues
	Brine recycling
	Recovery of dyes and pigments
	Desalination of products
	Cleaning, recovery and recycling of organic solvents
	Fuel oil and ethanol processing, separation of ethanol-water mixtures
	Purification of waste lubricating oil
	Treatment of aqueous streams containing heavy metals, oils and solids at petrochemical plants
	Removal of precipitated heavy metal solids
	Removal of 1,2 dichloroethane emulsions in vinyl chloride monomer production
	Removal of aromatic and paraffinic oils, solids and dirt from wastewater from a linear alkyl benzene plant
	Particle and gel removal from photosists in integrated circuit manufacture
Textiles, Pulp and Paper Industry	Lignosulfonate fractionation
	COD reduction of bleach plant effluents
	Whitewater recovery from paper machines
	Dye or chemical removal from finishing or dyeing waste streams
	Recovery of polyvynil alcohol from textile industry waste streams
	Paper coating recovery
	Recovery of rinse water from primary and secondary wool scouring effluent
	Color removal
	Hot, high quality water recovery for recycling
	Dye bath recovery and reuse
	Spin bath finish and size recovery
	Water jet loom motive water recovery
Pharmaceutical, Cosmetic, and Biotechnology	Concentration, fractionation, isolation of pharmaceutical active agents (antibiotics, enzymes, proteins, amino acids, vitamins, peptides, biopolymers and organic acids), and plant extracts, sterilization
	Separation, concentration, and dewatering of biomass and algae
	Blood fractionation, blood plasma filtering
	Vaccine production
	Processing of alginates and other excipients
	Disposal of fat emulsions
	Desalination
	Fermentation broth clarification, separation of yeast, concentration of bacterial suspensions
	Recovery of polysaccharide from fermentation broth
	Endotoxin removal
	Aqueous stream by-product recovery
	Cleaned-in place (CIP)
	High purity process water (pyrogen and bacteria free)

Table 2.7 Liquid phase separations using ceramic membranes in various industries (Luque, Gómez and Álvarez, 2008; Hsieh, 1996a) (continued)

Industry	Applications
Food, Dairy and Beverages	Clarification and stabilization of wine, beer, cider, soy sauce and vinegar
	Clarification of apple, cranberry, pears, pineapples, peaches, carrots, beets, strawberryand kiwi juices
	Micro- and ultrafiltration of lees or crude wines
	Removal of microorganisms
	Concentration of juices
	Removal or microorganisms from milk and whey
	Separation and fractionation of milk and whey ingredients
	Concentration of whey proteins
	Desalination of whey
	Milk protein standardization
	Concentration of raw or pasteurized whole milk
	Desalting and delactosing dairy products
	Concentration of pasteurized skimmed milk
	Concentration of acidified milk
	Purification of spirits
	Separation of soybean protein
	Protein recovery in fish processing
	Concentration of several animal and plant products
	Caramel color concentration and purification
	Dewatering of products
	Clarification and purification of drinking water
	Sugars and starches processing
	Recovery of product from beer and cider tank bottoms
	Recovery of yeast from beer tank bottoms
	C.I.P. solution renovation
	Microfiltration of vegetable oil-containing sample from a soybean oil refinery
	Recovery of water from waste streams
Automotive, Mechanical, Mineral, Metal Industry, Surface Engineering	Recycling and disposal of degreasing and rinsing bathes
	Treatment of oil/water emulsions
	Removal of oil and grease and suspended solids from aqueous alkaline cleaners
	Recovery of heavy metals
	Cleaning of wastewater from grinding processes
	Treatment of wastewater form glass and glass fiber production
	Pretreatment cleaner
	Washing machine tanks
	Oily wastewater treatment

Mechanical, thermal and chemical properties of ceramic membranes enable their use in the wastewater treatment. Mechanical and thermal stability of the membrane determine operational conditions. Ceramic membranes preserve their integrities in filtration operations performed at higher pressures such as ultra-, and nanofiltrations. Since they are thermally very stable, they can easily be used in the treatment of hot fluid streams or in the filtrations at higher temperatures. Because of their chemical resistance to solvents, acids, bases, oxidative agents, streams containing a wide range of chemicals with pH values of 1 – 14 can be treated using ceramic membranes. Membrane cleaning procedures are selected according to the properties of the membrane materials in the filtrations using polymeric membranes. Type of membrane materials hence its chemical stability determines the chemicals to be used in the cleaning. This restriction results in inefficient cleaning and the performance or service life of the polymeric membranes decreases. Since many solvents, acids, bases and surfactants can be used in the cleaning of ceramic membranes, their service life is longer than that of polymeric membranes. Wastewaters from various industries contain different chemicals and exhibit varying pollution characteristics. Ceramic membranes can be used in the treatment of these wastewaters due to their above stated stabilities. Table 2.8 shows examples of wastewater treatments using ceramic membranes. They are used in the oily wastewater treatment, heavy metal, pharmaceutical, dye, pesticide, microorganism and solid removal, COD and BOD reductions and water recovery.

Table 2.8. Applications of ceramic membranes in wastewater treatment (Luque et al., 2008; Hsieh, 1996a)

Ceramic Membranes in Wastewater Treatment
• Reverse osmosis pretreatment
• Wastewaters and potable water treatment
• Removal of suspended solids
• Emulsified oil removal, edible oils, waste oil treatment
• Removal of pharmaceuticals and pesticides
• Removal of microorganisms
• Removal of heavy metals
• Gray water treatment
• Recycling of water form swimming pools
• Purification of the drain of sewage plants
• Sewer overflow treatment
• Methane digester water recovery
• Upgrading vacuum residual oil
• Landfill leachate processing
• Radioactive wastewater treatment
• Effluent recycling in zero-waste plant
• COD, BOD, and suspended solids reduction
• Turbidity removal from green water, a liquid waste from olive oil processing
• Clarification of wastewater from washing operations in dairy industry
• Treatment of produced water from oil wells
• Treatment of textile industry wastewaters
• Radiactive waste treatment
• Treatment of aqueous streams containing heavy metals, oils and solids at petrochemical plants
• Removal of precipitated heavy metal solids
• COD reduction of bleach plant effluents
• Dye or chemical removal from finishing or dyeing waste streams
• Recovery of polyvynil alcohol from textile industry waste streams
• Color removal
• Disposal of fat emulsions
• Recycling and disposal of degreasing and rinsing bathes
• Oily wastewater treatment
• Recovery of water from waste streams

2.2.1. Oily Wastewater Treatment by Ceramic Membranes

Food processing is an industrial activity where high amounts of water are used per ton of a product (Casani et al., 2005). Water is used not only in the formulation of food products but also in washing, rinsing, peeling, boiling, blanching, heating, steam generation,

pasteurization, sterilization, cooling, transportation of food materials to the processes, general cleaning, sanitation and disinfection. Total water consumptions of food industry alone in Canada in 1991, in Germany in 1995 and in Netherlands in 1996 were 347 million, 455 million and 247 million m^3, respectively (Casani et al., 2005). Unfortunately, statistical data on the amounts of food industry wastewaters in our country is scarce. When different food processing sectors are considered, volume of wastewater generated per one ton of product is reported as 2.7, 1.7, 30, 2.2, 4.2, and 91.5 m^3 for meat processing, fruit juice production, vegetable processing (including oil pressing), potato starch, beer and dairy industries, respectively (Muro, Riera and Diaz, 2012).

According to FAO statistics, globally 173 million tonnes of crops (coconut, cottonseed, groundnut, linseed, maize, olive (virgin), palm, palm kernel, rapeseed, safflower, sesame, soybean and sunflower) were processed into oil in 2014 (FAOSTAT, 2019a). The amount of of oil crops processed in Turkey was 1.3 million tonnes at the same year (FAOSTAT, 2019b). Oil crops are processed into oil either by pressing or solvent extraction after seed preparation. Crude oil then undergoes refining process. Conventional oil refining process where the oil is extracted with solvent is shown in Figure 2.5. Refining includes degumming, neutralization, bleaching, dewaxing and deodorization stages. Phospholipids, mucilaginous substances and some part of heavy metals present in crude oil are removed by degumming performed either by water or acid degumming (Lahde and Kumar, 2010). The next stage in the vegetable oil refining is the neutralization/deacidification where free fatty acids are removed from the oil. The free fatty acids are generally removed by treating oil with alkali solution and removing resulting free fatty acid salts by centrifugation. Color contributing compounds such as chlorophylls and carotenoids are removed using activated clay or carbon in bleaching. Dewaxing (winterization) is applied to remove waxes by crystallization at temperatures below 10°C and filtering (Lahde and Kumar, 2010). Finally odor contributing compounds are removed by steam distillation in a vacuum at higher temperatures (deodorization) (Kalat, 2011). Hydrogenation is applied to refined oil to saturate the unsaturated fatty acids and produce fat in margarine production.

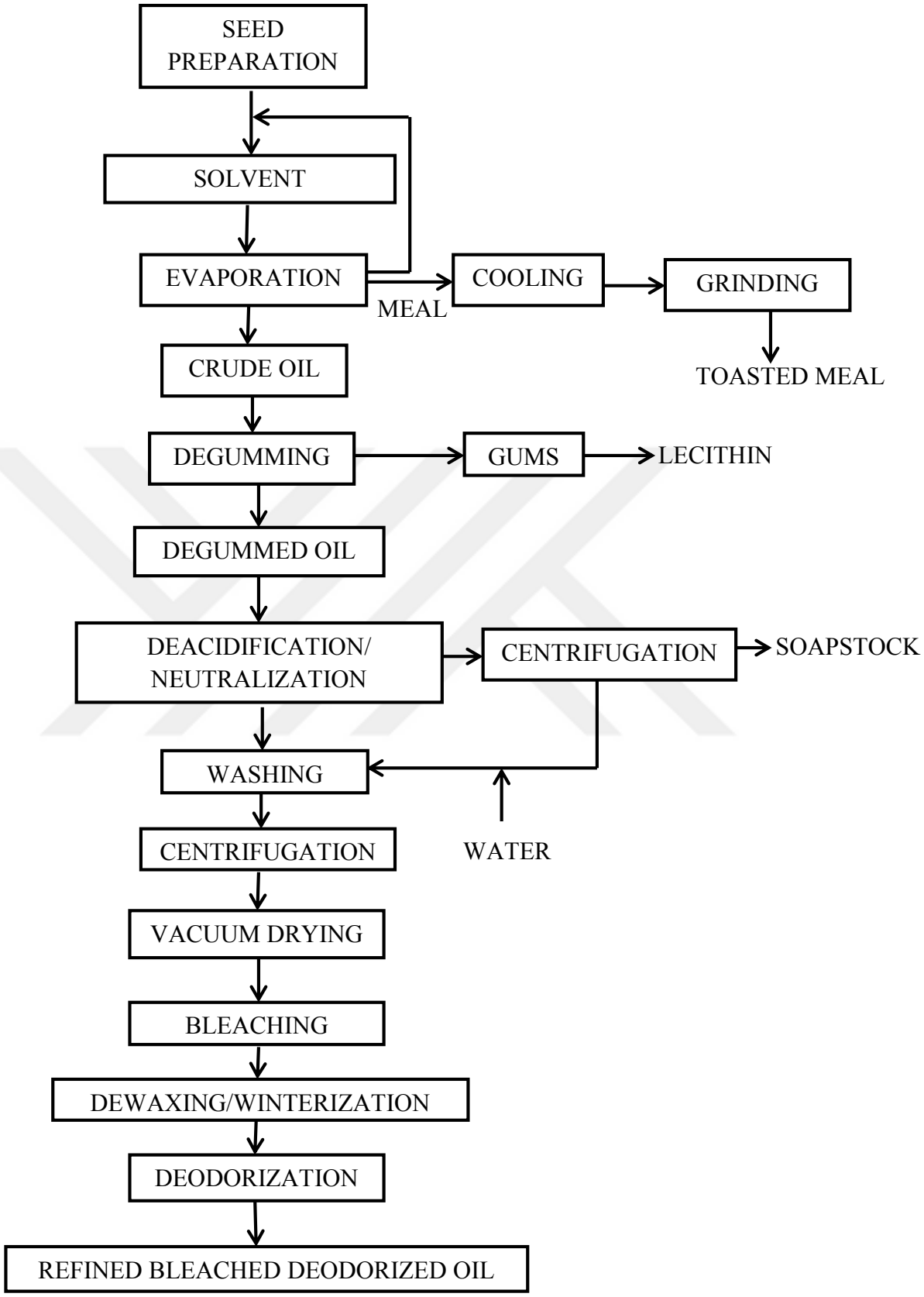

Figure 2.5. Conventional vegetable oil refining process (Lahde and Kumar, 2010)

Vegetable oil refining produces significant amounts of wastewater containing higher concentrations of oil and acids (Decloux, Lameloise, Brocard, Bisson, Parmentier and Spiraers, 2007). Wastewaters in vegetable oil refining industry mainly come from degumming, neutralization and deodorization steps (Gill and Ielase, 1976; Willey, 2001; Pandey, Sanyal, Chattopadhyay and Kaul, 2003; Kalat, 2011; Sharma, Sharma, Verma and Dodiya, 2014). The amount of wastewater generated in degumming is relatively low. For example, 2 % water is added to oil to remove phospholipids in soybean oil refining (Gill and Ielase, 1976). Gums are then separated from water by centrifugation. Phosphoric acid is generally used in acid degumming (Rajkumar, Muthukumar and Sivakumar, 2010). Wastewater generated therefore contains phosphoric acid, residual amounts of gums, and ions. Deacidification/neutralization is the conversion of free fatty acids found in oil into water soluble soaps by NaOH solution and removal by centrifugation. The soapstock and wash water separated from oil is acidified using H_2SO_4 and acidic oil and acidic water are generated. This acidic wastewater is neutralized using NaOH and discharged to wastewater treatment plant (Rajkumar et al., 2010). Oil droplets and volatiles such as free fatty acids, aldehites and ketones carried from deodorizer to live steam are the compounds contributing to wastewater pollution in deodorization (Willey, 2001). Fat scrubbers in batch deodorizers or vapor scrubbers in continuous/semi-continuous deodorizers causes less free fatty acids to escape to the barometric condenser (Willey, 2001). Barometric condenser water is the wastewater generated in higher amounts in vegetable oil refining process. Other sources of wastewater are cleaning of filter pres and floor washing (Kalat, 2011). Activated clay and carbon used in the bleaching is separated from oil using filter press. Water used to clean filtation equipments is drained as wastewater. The amount of wastewater generated and their pollution characteristics change depending on the production capacity of the oil refining plant and the type of oil processed.

Global warming, water scarcity and environmental regulations have signified the minimization of wastewater generated in food industry and the water recovery (Casani et al., 2005; Fahnrich et al., 1998; Sarkar et al., 2006; Simate et al., 2011). Oil is a hazardous compound for environment and aquatic life. Legal regulations limit the oil and grease content of wastewaters from vegetable oil processing at the maximum level of 60 mg/L (Turkish Water Pollution Control Regulation, 2004). Maximum allowable COD is determined as 200 mg/L in these wastewaters while pH should be within the range of 6 – 9. Wastewaters from

vegetable oil processing are classically treated by physico-chemical methods gravity separation, air flotation, skimming of oil, flocculation and coagulation followed by biological treatment (anaerobic or aerobic) (Willey, 2001; Rajkumar et al., 2010). Wastewater minimization, meeting legal discharge limits, inefficiency of conventional methods in the treatment of wastewaters containing stable emulsions in which oil droplets are smaller than 20 μm, high cost of conventional methods and recontamination problems (Kiss, Kocsis, Keszthelyi-Szabó, Hodúr and László, 2014) have led researchers to study alternative methods. Electrocoagulation (Un, Koparal and Ogutveren, 2009), advanced oxidation processes (Tahir, Kareim and Ibrahim, 2016) coagulation and flocculation using bio-flocculant (Dkhissi, Hakmaoui, Souabi, Chatoui, Jada and Akssira, 2018), coalescence (Li, Li and Zhang, 2015) and coagulation by chitosan, aluminum sulphate and polyaluminum chloride (Ahmad, Sumathi and Hameed, 2006) have been used to treat oily wastewaters.

Membrane technology provides several advantages over traditional wastewater treatment methods (Cheryan and Rajagopalan, 1998; Decloux et al., 2007):

- Applicability to broad range of industries
- No chemicals required
- Automated and simply controlled
- Oily wastewaters (generally contains 0.1 – 1 % oil) can be concentrated to 40 – 70 %. Hence, initial volume of wastewaters decreses 40 – 200 folds
- Uniform quality of treated water. Although variations in wastewater properties may result in flux decrease, the quality of water treated water generally stays uniform.
- Lower energy costs compared to thermal treatments
- Small amounts of solid wastes generated
- Compact installation
- Reduced maintanenece requirements

Polymeric membranes (Mohammadi and Esmaeelifar, 2004; Ahmad, Ismail and Bhatia, 2005; Akdemir and Ozer, 2008; Vatai, Krstić, Koris, Gáspár and Tekić, 2009; Masoudnia, Raisi, Aroujalian and Fathizadeh, 2014) and polymeric membranes combined with other treatments (Kiss et al., 2014; Masoudnia et al., 2014) have been used for the treatment of oily wastewaters. Mechanical, thermal and chemical stabilities of ceramic membranes have

directed a scientific interest on the use of ceramic membranes for the treatment of oily wastewater.

Microfiltration experiments were performed using polymeric membranes (0.45 μm hydrophilic PVDF, 0.1 μm polysulfone) and 0.1 μm hydrophilic ZrO_2 coated on a nickel alloy mesh composite membrane (Ceramesh) in the treatment of oil water emulsion in a droplet size of 0.75 μm prepared by mixing dodecane with water (Koltuniewicz, Field and Arnot, 1995). Although polymeric membranes had higher permeability values than ceramic membrane, flux decline was much greater than permeate flux decline observed while using the ceramic membrane. The reduction in fluxes were also found to be rapid than that observed using ceramic membrane. This signified the importance of the membrane material, pore size and structure. Comparison of various cross velocities applied at two different transmembrane pressures showed that permeate flux was independent of cross flow velocity at lower transmembrane pressures. The observation of higher flux decline at higher transmembrane pressure was attributed to the conversion of hydrophilic nature of the surface into oleophilic by the introduction of oil into the membrane pores. The formation of a layer of oil droplets after initial pore blocking and development of cake filtration were proposed. According to the experiments performed at different cross velocities at dead end and cross flow modes showed that the cross flow velocities over 0.8 m/s (corresponding to turbulent flow) increased the permeate flux, it was suggested that the hydrodynamic conditions over membrane surface therefore determines the cake layer thickness and filtration performance.

Mueller, Cen and Davis (1997) used two α-Al_2O_3 (pore sizes of 0.2 and 0.8 μm and a surface modified polyacrylonitrile membrane (pore size of 0.1 μm) for the cross flow microfiltration of oil in water emulsions containing 1-10 μm droplets with oil concentrations varying between 250 and 1000 mg/kg. They reported significant fouling and permeate flux decline for all membranes used during the treatment of emulsions. Ceramic membrane with a greater pore size was reported to be the membrane having the highest initial flux yet quickly fouling. According to similar permeate concentrations and final flux values, they concluded that fouling layer on/in the membranes was formed and controlled the filtration. Internal fouling followed by external fouling was also proposed for the ceramic membranes. They also found that external oil layer was resistant to hydrodynamic conditions and cleaning procedures.

Yang, Zhang, Xu and Shi (1998) used ceramic membranes for the seperation of oil from the steel industry oil/water emulsions containing 2-10 % vegetable/mineral oil, emulsifier and water. Membranes used were γ-Al_2O_3 coated α-Al_2O_3 (pore size: 10 nm), α-Al_2O_3 coated α-Al_2O_3 (pore size: 20 nm), α-Al_2O_3 coated α-Al_2O_3 (pore size: 1 μm), and ZrO_2 coated α-Al_2O_3 (pore size: 0.2 μm). They found that alumina membranes exhibited greater flux decline than ZrO_2 membrane did. This was attributed to the higher hydrocarbon and oil adsorption capacity of alumina surface hence to the surface properties of alumina. According to oil removal efficiencies of 99.8, 99.9, 94.3 and 99.8 % of γ-Al_2O_3 coated α-Al_2O_3 (pore size: 10 nm), α-Al_2O_3 coated α-Al_2O_3 (pore size: 20 nm), α-Al_2O_3 coated α-Al_2O_3 (pore size: 1 μm), and ZrO_2 coated α-Al_2O_3 (pore size: 0.2 μm) membranes, respectively, all but α-Al_2O_3 coated α-Al_2O_3 (pore size: 1 μm) membrane produced wastewaters conforming to discharge limits in terms of oil content.

Microfiltration using ZrO_2 membrane (0.2 μm) with or without flocculation as a pretreatment was used for the treatment of petrochemical industry wastewater coaining 6 g/L oil, water and sludge (COD of 3 g/L, solid content of 5 wt. %) (Zhong, Sun and Wang, 2003). Application of flocculation was found to reduce membrane fouling and to increase the permeate flux. The effects of transmembrane pressure and cross flow velocity on the wastewater characteristic were also determined. Increase in the transembrane pressure increased the oil content of permeate but COD remained unchanged. Cross low velocity however decreased both COD and oil content. Authors suggested the use of cross flow velocities corresponding to turbulent flow for the remediation of this wastewater. Microfiltration using ZrO_2 membrane coupled with flocculation was found to reduce the properties of wastewater below the discharge limits.

Commercial ceramic (MWCO 10 kDa) and polymeric (polyvinylidene diflorid, MWCO 200 kDa) ultrafiltration membranes were used in the treatment of wastewater from palm oil production (Ahmad et al., 2005). Coagulation, flocculation and adsorption on activated carbon were applied prior to filtration, and the effects of TMP and cross flow velocity on the performances of the membranes were determined. Preliminary processes resulted in 99.9 %, 95 %, 86.3 % and 85 % in suspended solid and oil contents, biological oxygen demand (BOD) and chemical oxygen demand (COD) values. It was reported that over 97 % reduction in suspended solid was obtained using both membranes and reduction in suspended solid did not depend on TMP and cross flow velocity. Ultrafiltration using ceramic membrane however

was found to be effective in the reduction of COD and BOD values. Reductions in COD and BOD ranged between 10 and 60 % while the use of polymeric membrane caused 10 to 20 % reduction. The use of additional processes was suggested for ensuring required wastewater standards.

Fontes, Queiroz, Longo, Antunes, (2005) performed microfiltration of water/soybean oil or water/sunflower oil emulsions and macromolecular polysaccharide solutions containing xanthan and guar gums in varying ratios using tubular microporous mullite membrane. Total organic carbon content was decreased below 10 mg/L by microfiltration using mullite membrane. This was almost close to the total organic carbon content of tap water.

Lobo, Cambiella, Benito, Pazos and Coca (2006) determined the effects of cross flow velocity and pH on the ultrafiltration of a model solution simulating metalworking oil in water emulsions. Two different commercial ZrO_2/TiO_2 membrane layer supported on carbon with 50 and 300 kDa molecular weight cut off (MWCO) values were used in their study. The oil in water emulsion contained 1 % vegetable oil, anionic and non-ionic surfactant and water. Ultrafiltration experiments performed at three different cross flow velocities showed that the increase in transmembrane pressure increased the permeate flux at cross flow velocities of 3.4 and 4.2 m/s. The lowest cross flow velocity, 2.5 m/s however resulted in constant flux values at higher transmembrane pressures. This behavior was attributed to the concentration polarization, accumulation of oil near the membrane surface and to the decrease of the flux due to the concentration gradient. The effects of pH on the permeate flux and COD reduction were also evaluated and basic pH values were found to enhance the permeate flux and COD removal efficiency whereas acidic pH decreased the permeate flux and COD removal efficiency. This was related to the membrane surface charge and to the adsorption of surfactants on the membrane surface. COD removal efficiency was found to be over 92 % and independent of operating conditions or pore size. Oil droplets were successfully removed by both membranes.

Hua, Wang, Tsang, Chan, Sin and Chua (2007) used 19 channel- α-Al_2O_3 (pore size: 0.05 μm) ceramic membrane for the microfiltration of homogenized vegetable oil, water and surfactant mixture. They determined the effects of transmembrane pressure, cross flow velocity, oil concentration, pH and salt concentration (ionic strength) on the permeate flux.

Permeate flux was found to increase in TMP but degree of increase was decreased pressures over 0.2 MPa. Permeate flux was found to be independent from oil content but it was significantly affected by the pH of the emulsions. Similar to the findings of Lobo and colleagues (2006), Hua and colleagues (2007) reported that higher pH yielded higher steady flux. Lower permeate fluxes were observed at higher salt concentrations. Total organic carbon removal was found to be greater than 92.4 % in all filtrations.

Decloux, Lameloise, Brocard, Bisson, Parmentier and Spiraers (2007) used three different commercial ceramic membranes (19 channels, 0.2 μm; 37 channels, 0.5 μm; 37 channels 1.14 μm) after treatment with 2 (v/v) % nitric acid at very low transmembrane pressures in order to avoid pore blocking by oil droplets and hydrophobic surface conversion for the treatment of acidic wastewater collected from crude sunflower refining plant. Acidic wastewater contained 7-12 g/L and suspended solids, 2-4 g/L fats with COD value of 10–30 g O_2/L and pH of 1-1.5. They reported that microfiltration using commercial 37 channel-ceramic membranes with pores in 0.5 μm size reduced the suspended solids, oil and COD in 91, 96 and 60 %, respectively.

Performances of polymeric and ceramic ultrafiltration membranes in the treatment of oil in water emulsions were compared by Vatai, Krstić, Koris, Gáspár and Tekić (2009). Single channel tubular ZrO_2 membrane with a pore size of 20 nm and polyaryletherketone membrane with a MWCO 100 kDa were used in the treatment of 5 (w/w) % cutting oil. They found that polymeric membrane exhibited better oil rejection capacity than ceramic membrane. This was attributed to the surface layer formation on the polymeric membrane. They also observed the oil penetration through zirconia membrane at low crossflow velocities and higher trans-membrane pressures. This was related to the hydrophobic nature and bigger pore size of the ceramic membrane.

Nandi, Moparthi, Uppaluri and Purkait (2010) prepared ceramic circular mebranes from kaolin, quartz, feldspar, sodium carbonate, boric acid and sodium metasilicate. Synthetic oil emulsions with concentrations 125 mg/L and 250 mg/L (average particle sizes of 0.78 and 0.92 μm) were treated by ceramic microfiltration membranes in dead-end filtration mode at four different transmembrane pressures (68.95, 137.90, 206.84 and 275.79 kPa). Rapid flux decline in 10-15 minutes of filtration were observed in all filtration experiments and attributed

to the pore blocking and concentration polarization over the membrane surface. Different pore blocking models (cake filtration, intermediate pore blocking, standard pore blocking and complete pore blocking) and artificial nueral network model were used for the representation of membrane fouling. Cake filtration model was suggested to be the best model describing membrane fouling among the pore blocking models. The model based on artificial neural network however reported to be giving better predictions when compared to cake filtration model.

Zhou, Chang, Wang and Meng (2010) used hydrophilic nano-sized zirconia membrane coated on Al_2O_3 support for oil separation from grease, surfactant and water containing emulsion. Zirconia membrane was able to remove 97.8 % oil in the feed solution.

Abadi, Sebzari, Hemati, Rekabdar and Mohammadi (2011) used 19 channel α-Al_2O_3 microfiltration membrane (0.2 μm) for the treatment of oily wastewater containing 92 mg/L total suspended solid, 26 mg/L oil and grease, 141 mg/L total organic carbon and 21 mg/L turbidity. Microfiltration using ceramic membrane resulted in 85, 100 and 98.6 % reductions in oil and grease, total suspended solids and turbidity, respectively. Total organic carbon removal was found to be over 95 %. They determined the effects of backwashing on the recovery of original flux and found that over 95 % of the original flux could be recovered by backwashing. They however pointed out the necessity of membrane cleaning since the backwashing was ineffective to recover reversible fouling in the experiments with very long filtration times. The comparison of permeate properties showed that microfiltration using ceramic membrane resulted in lower oil and grease, total suspended solid, total oraganic carbon and turbidity values than those obtained by biological treatment. They therefore suggested that microfiltration using ceramic membranes could be replaced with conventional biological treatment used for this wastewater.

Abbasi, Sebzari, Salahi and Mirza (2012) prepared mullite microfiltration membranes with an average pore size of 0.476 μm from kaolin clay to characterize gel/cake layer resistance and to model mebrane fouling and flux decline during the cross flow filtration of oil in water emulsions. They reported that the increase of gel layer resistance with increase pressure was reversible. Higher compresibility coefficient of the gel layer was attributed to the presence of high quantities of oil droplets in the emulsion and the formation of incompressible gel layer.

Experimental results were fitted to cake filtration, intermediate pore blocking, standard pore blocking and complete pore blocking models. They suggested that the the best-fitted model was the cake filtration model followed by intermediate pore blocking model.

The effects of membrane surface roughness were studied in the filtration of vegetable oil/water/surfactant homogenate (Zhong, Xing and Zhang, 2013). Three symmetral Al_2O_3 membranes with three different degrees of surface roughness were prepared. All membranes exhibited oil removal in percentages ≥ 99 %. Surface roughness was not found to be effective on the oil retention. The use of smooth membranes was suggested for preventing the membrane fouling.

Kumar, Ghoshal and Pugazhenthi (2015) studied the microfiltration of synthetic oil in water emulsion containing 50, 75, 100, 150 and 250 mg/kg oil using a tubular membrane prepared from clay mixtures. They determined the effects of transmembrane pressure, cross flow velocity and oil content on the permeate flux. They found that the flux increased non-linearly with the increase in the pressure. Flux decline rate was found to be higher when the transmembrane pressure was higher. This was attributed to the faster deposition of oil layer on the surface of the membrane at higher pressures. Increasing cross flow velocity was found to decrease the rate of flux decline. They suggested that higher cross flow velocities reduced the concentration polarization and restricted the cake layer formation. Oil concentration was also found to be effective in the flux decline. Higher oil concentrations resulted in larger flux decline.

Eom, Yeom, Kim and Song (2015) prepared low cost silicate clay membranes (porse size of 0.2 - 0.67 μm) and tested for the treatment of synthetic emulsion prepared by mixing kerosene (600 mg/kg), surfactant (Tween 80) and distilled water in dead end filtration mode. Membranes used were subjected to heat treatment at 600°C in air for the cleaning and recovery of membrane performance. They observed a decrease in membrane fouling from 63.5-78.2 % to 27.1 - 73.1 %, an increase in steady permeate flux from 2.3×10^{-5} - 2.8×10^{-5} $m^3/m^2 \cdot s$ to 4.3×10^{-5} - 5.4×10^{-5} $m^3/m^2 \cdot s$ and increase in oil rejection capacity from 84.1-86.1 % to 88.0-92.9 % after thermal treatment at 600°C in air.

Šereš, Maravić, Takaći, Nikolić, Šoronja-Simović, Jokić and Hodur (2016) evaluated the use of alumina ceramic membrane (pore size of 200 nm) in the treatment of wastewater from oil processing plant after filtration through filter cloth. Trensmembrane pressure values, feed flow rate and temperature of the operation were 1-3 bar, 100-300 L/h and 40-60°C. Feed flow rate was found to be the most important parameter affecting the permeate flux. The permeate flux was not affected by the increase in transmembrane pressure and temperature. The highest permeate flux was obtained during experiments performed at intermediate transmembrane pressures and higher cross flow velocities. The highest reduction in COD (>76 %) was obtained in the microfiltration performed at 60°C. Microfiltration using alumina membrane was suggested as the secondary treatment for the wastewaters from oil processing industry.

Microfiltration using ZrO_2 membrane was also combined with reverse osmosis for the treatment of oily wastewater containing 5 g/L oil with total organic carbon content of 9438 mg/L (Yu, Zhong and Xing, 2010). Permeate obtained after microfiltration using ceramic membrane had 14.2 mg/L oil and 26.8 mg/L total organic carbon content with turbidity and conductivity values of 2.2 NTU, 246 µS/cm, respectively. Reverse osmosis following microfiltration produced permeate with oil content, total organic carbon, turbidity and conductivity values of $\leq$ 0.1 mg/L, $\leq$ 0.6 mg/L, $\leq$ 0.1 NTU and 5 µS/cm, respectively. Permeate with properties comparable to tap water was therefore obtained by combined microfiltration-reverse osmosis.

3. MATERIALS AND METHODS

3.1. Materials

Bare and microfiltration layer coated and ultrafiltration layer coated tubular Al_2O_3 supports were prepared and used in the treatment of food industry wastewaters. The materials used in the preparation of ceramic membranes and characterization of wastewaters and their properties are tabulated in Table 3.1.

Wastewaters used in this study were kindly provided by Sunar Mısır Inc., Adana. They were collected from the different stages of the wastewater treatment facility of the plant.

Table 3.1. Materials used in the experiments and their properties.

Materials	Property
0.18 μm alumina	99.8 % purity, AKP-50, Sumitomo
0.5 μm alumina	99.8 % purity, CT 3000 SG, Almatis
1.3 μm alumina	99.8 % purity, CT 1200 SG, Almatis
5.2 μm alumina	99.8 % purity, CL 4400 FG, Almatis
Boehmite (AlO(OH))	99.8 % purity, Disperal and P2, Sasol
Hydroxypropyl methycellulose (HPMC)	Methocel F4M, The Dow Chemical Company
Glycerin (C_3H8O_3)	99.5 % purity, Merck
Polyvinyl alcohol (PVA)	80 % hydrolyzed, MW= 9000-100000 g/mol, Aldrich
Dolapix CE 64	Eurokimya
Defoamer	Dağlar Kimya
Nitric Acid, HNO_3	65 %, MW=63.01 g/mol, d=1.39 g/cm^3, Merck
Sodium sulfate (Na_2SO_4)	Merck 106649
Sulfurik asit	Merck 112080
n-hexan	Merck 104374
COD Cell Test	Spectroquant® 500 - 10000 mg/L, Merck 114555
COD Cell Test	Spectroquant® 25 - 1500 mg/L, Merck 114541
Dolapix	

3.2. Methods

Preparation of bare, microfiltration layer and ultrafiltration layer coated tubular Al_2O_3 supports were performed under the supervision of Prof. Dr. Muhsin Çiftçioğlu at the Department of Chemical Engineering in Izmir Institute of Technology.

Tubular Al_2O_3 supports were first prepared and microfiltration layers were then coated on the internal surfaces of supports in order to obtain microfiltration membranes. Similarly, ultrafiltration layer was coated on microfiltration layer coated tubes. Supports, microfiltration ultrafiltration membranes were used in the treatment of food industry wastewaters.

3.2.1. Preparation of Tubular Ceramic Supports

Tubular Al_2O_3 supports were prepared by following the procedure stated in Yaltrık (2017) and Cetin (2018). Three different α-alumina (α- Al_2O_3) powders (average particle sizes of 0.5, 1.3 and 5.2 μm), inorganic binder (boehmite, AlO(OH)), organic binder (hydroxypropyl methycellulose) and glycerin were used in the preparation of the supports. The schematic representation of the support preparation is shown in Figure 3.1.

Three different α-alumina powders with average particle sizes of 0.5, 1.3 and 5.2 μm were selected in order to optimize pore structure and mechanical properties of the resultant supports. Al_2O_3 powders and boehmite powder were mixed in a ball mill for 2 h. Water and glycerin was then added while the mixture was being kneaded by hand. Homogenous paste was obtained by further kneading using screw extruder. The resultant paste was fed into a piston extruder to form tubular supports (D_i = 16 mm, D_o = 25 mm and L = 200 mm). Two-step drying procedure was applied to the extruded ceramic tubular supports; initial drying at room temperature for a day on a roller and further drying at in an oven at 90 ºC overnight. Heat treatment at 250-300 °C was applied to the tubular supports in order to remove organic compounds and to decompose inorganic binder. Transformation of boehmite to γ-alumina takes place during this debinding process. The supports were finally heat treated at 1525ºC for 2 hours (Yılmaz, 2016).

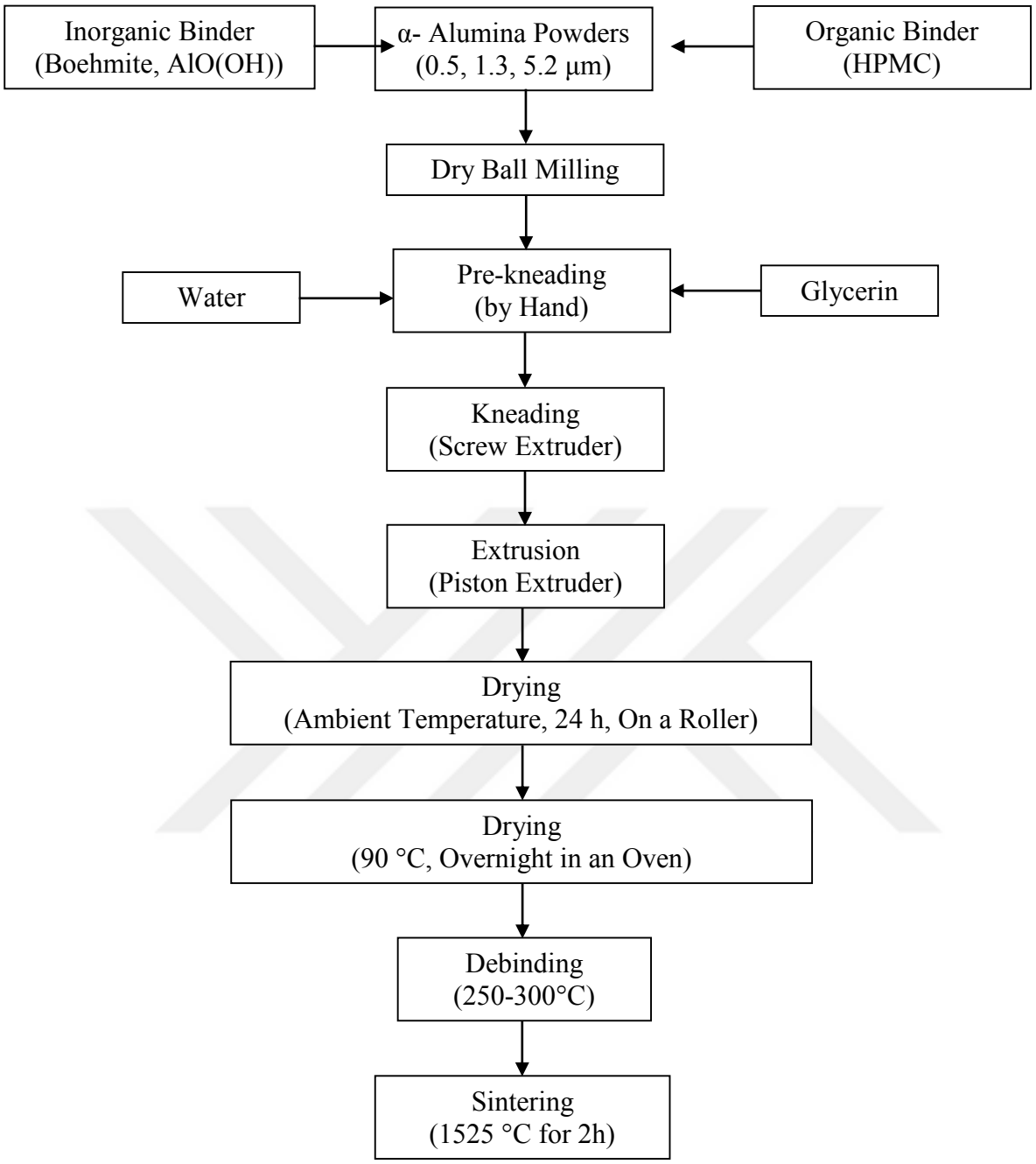

Figure 3.1. Preparation of α-Al_2O_3 tubular supports

3.2.2. Preparation of Microfiltration Layers

Two different types of microfiltration membranes were prepared by coating tubular supports with α- alumina and AKP-50 colloidal sols. The preparation route was followed according to the procedure stated in Yaltrık (2017) and Cetin (2018) and shown in Figure 3.2.

Polyvinyl alcohol was dissolved in water at 70 °C. PVA solution was cooled down to room temperature. 7 wt % alumina solution was prepared by adding α-alumina powder (0.5 μm) to the solution under constant stirring. Dispersant (Dolapix) and defoamer were added slowly during stirring. The resultant solution was subjected to 2 hours ultrasonication in order to disperse agglomerated particles and to obtain a stable, well-dispersed colloidal sol. The resultant sol was left overnight at room temperature for the settlement of large particles at the bottom. Suspension collected from the upper side of the bottle was further used in the coating of tubular supports.

The bottom of the tubular support was sealed using silicone rubber. The stable suspension was then filled into the support and the support was dip coated for 10 minutes. Excess suspension was removed slowly by drilling a small hole in the silicone rubber while creating a smooth surface in the inner walls of the support. Microfiltration layer coated alumina tubes were dried vertically at room temperatures. These tubular ceramic microfiltration membranes were finally subjected to heat treatment in a muffle furnace (Carbolite CWF 1300) according to the following program:

Heating to 110 °C with a rate of 2 °C/min
Heating from 110 °C to 1000 °C at 2.7 °C/min
Heating from 1000 °C to 1200 °C at 2 °C/min
Holding for 60 min at 1200 °C
Cooling to room temperature

AKP-50 MF layer was prepared in a similar way yet using 0.18 μm alumina powder and heat treatment at 1000°C was applied instead of 1200°C.

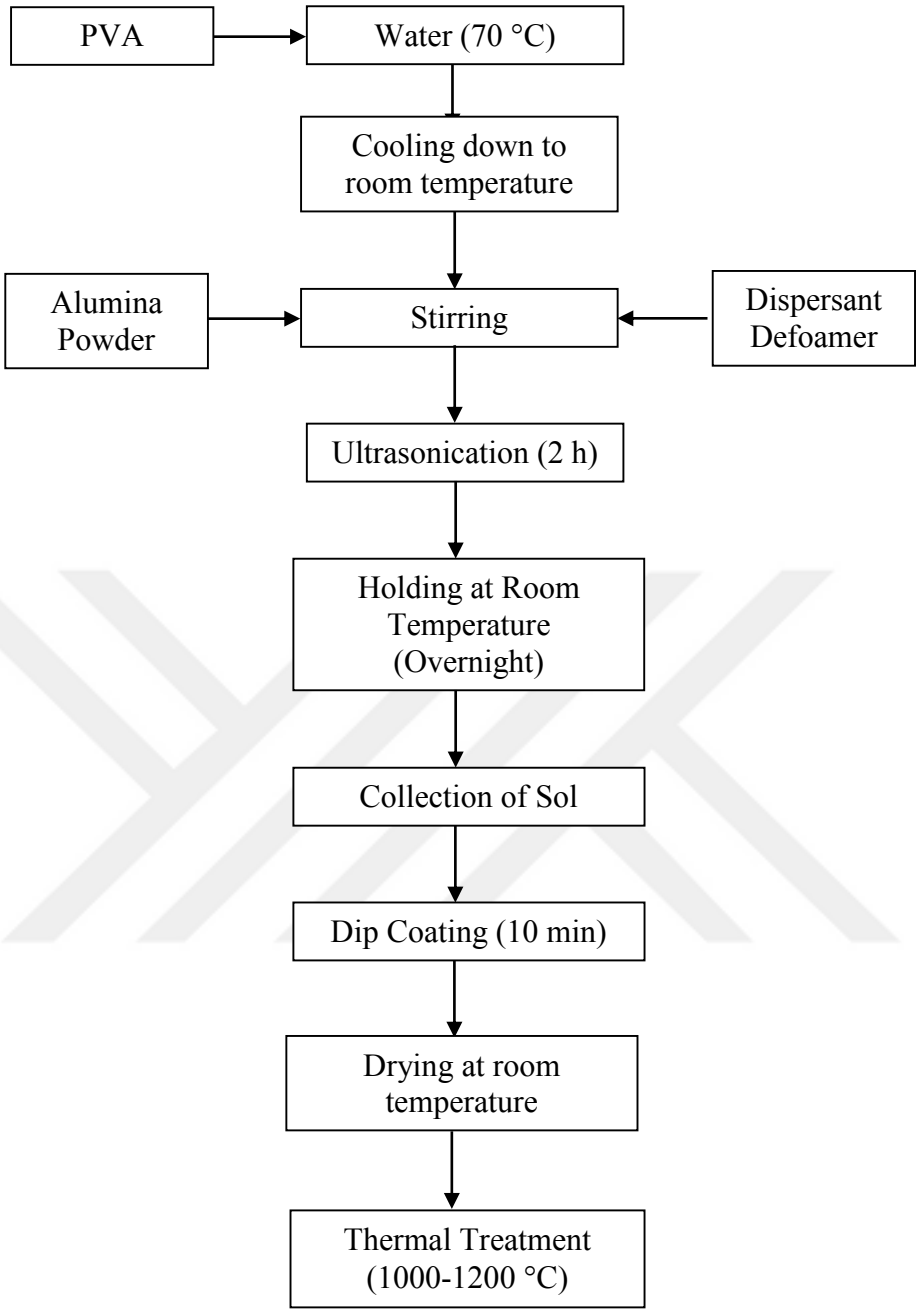

Figure 3.2. Preparation of microfiltration layers

3.2.3. Preparation of Ultrafiltration Layer

Ultrafiltration layer coating on the MF layer-coated tubes was performed in a similar way to that stated in Kırkbas (2016) and Cetin (2018). 3 wt. % boehmite sol was used for the coating. PVA was first dissolved in water at 70°C. After cooling down to room temperature, boehmite powder was added into PVA solution. This solution was then peptized by the drop-wise

addition of 1 M HNO_3 during stirring at room temperature. Ultrasonication was then applied in order to obtain a well-dispersed sol. The tubes were dip coated with the boehmite sol for 10-20 seconds. UF layer coated tubes were dried at ambient temperature for 24 hours in a vertical position. The tubes were finally heated treated at 600°C in a high temperature furnace (Carbolite CWF 1300).

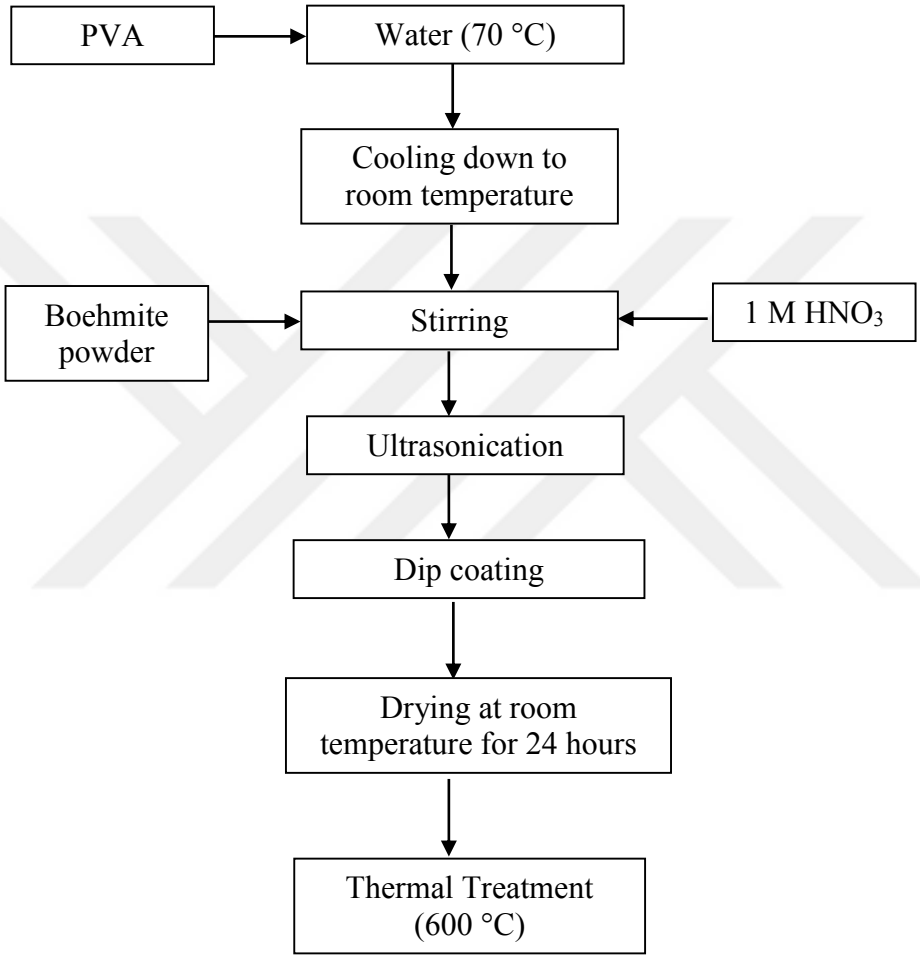

Figure 3.3. Preparation of ultrafiltration layer

3.2.4. Filtration Experiments

Measurement of water fluxes of the tubular ceramic supports and membranes and filtration of food industry wastewater were performed in the system shown in Figure 3.4.

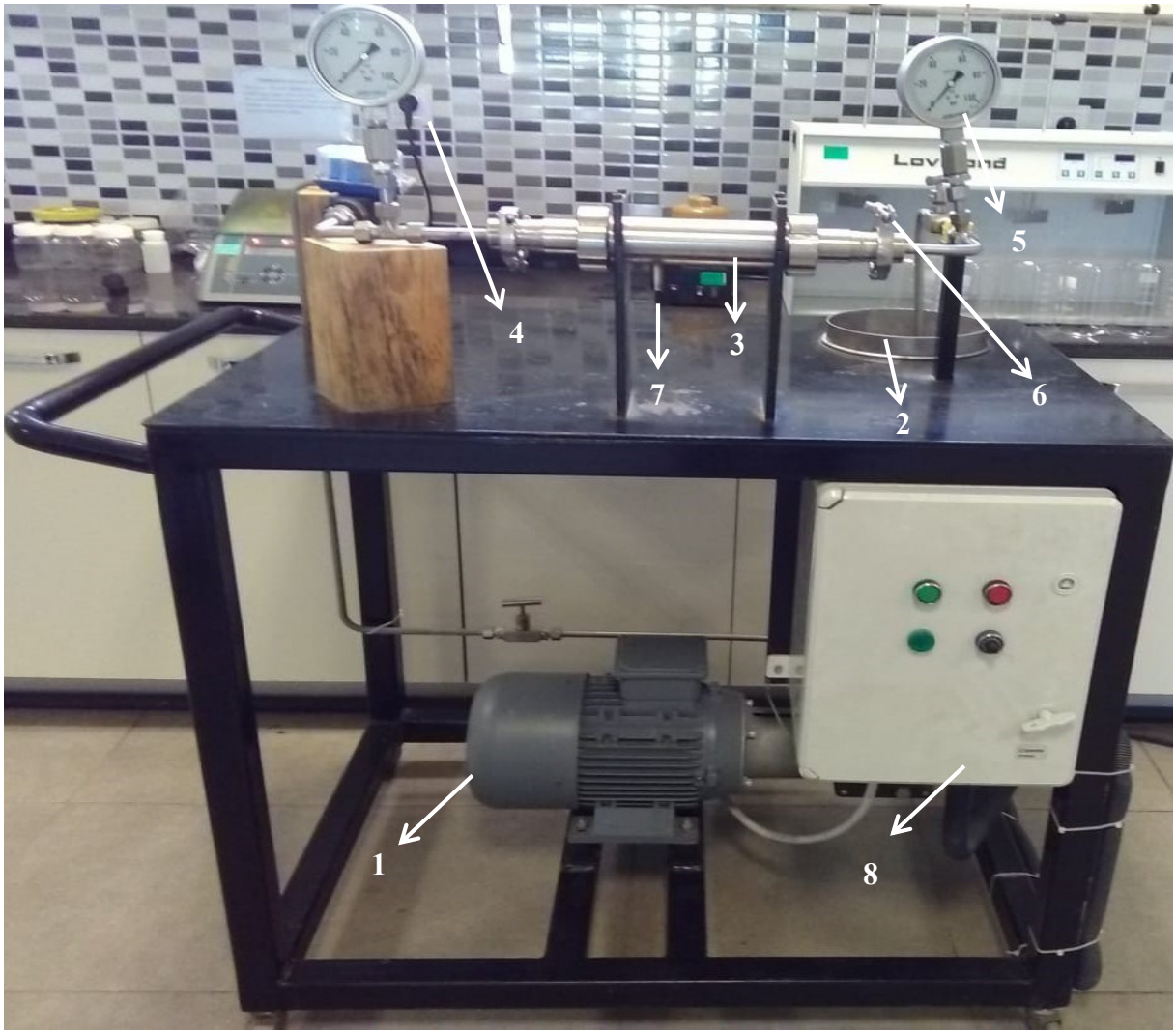

Figure 3.4. Filtration equipment used in this thesis 1. Feed pump, 2. Feed tank, 3. Membrane module, 4. Pressure gauge (membrane inlet), 5. Pressure gauge (membrane outlet), 6. Needle valve, 7. Permeate outlet, 8. Pump controller

3.2.4.1. Measurement of Membrane Water Permeability

Clean water fluxes of the supports and membranes were determined at different cross flow velocities (0.06 m/s, 0.16 m/s and 0.25 m/s) and transmembrane pressures (1, 2, 3, 4, 5, 6, 7 and 8 bar). Ceramic tubular support or membrane was placed inside the stainless steel membrane module shown in Figure 3.4.

Approximately 3 liters of water were added into the feed tank in the system. Pump speed was adjusted to 1.8, 5.4 and 8.4 from control panel so that the cross flow velocities of 0.06 m/s, 0.16 m/s and 0.25 m/s were obtained. System was operated at each crossflow velocities for a

certain period of time. Transmembrane pressure is adjusted by a needle valve and calculated using gauge pressure readings. Volume of water collected at the tank entrance for a defined period time was measured and volumetric flow rate was then calculated. Cross flow velocity however was calculated by dividing volumetric flow rate to inner cross sectional area of the membrane. Permeate flux was calculated in a similar manner. Volume of permeate collected in a definite time interval was used to calculate volumetric flow rate. Water permeability flux was calculated by dividing volumetric flux to the membrane internal surface area.

$$CFV = \frac{\frac{V}{t}}{\pi \frac{D_i^2}{4}} \tag{1}$$

CFV: Cross flow velocity, (*m*/*s*)

V : Volume of water or wastewater collected at the tank entrance for a time, (m^3)

t : Time, (*s)*

D_i : Inner diameter of the tubular support/membrane, (*m*)

$$Flux = = \frac{\frac{V_p}{t}}{\pi D_i L} \tag{2}$$

F*lux*: Permeate flux, (L/m^2s)

V_p : Volume of permeate, (*L*)

t : Time, (*s*)

D_i : Inner diameter of the tubular support/membrane, (*m*)

L : Length, (*m*)

3.2.4.2. Filtration of Food Industry Wastewaters

Wastewaters were filtered through general purpose filter paper before filtration experiments. Approximately 3 liters wastewater was added into the feed tank. Pump speed was adjusted to level greater than desired value and wastewater was circulated in the system. Pump speed was then adjusted to desired value. Wastewater again circulated in the system for a while. Transmembrane pressure is adjusted to the desired value using a needle valve. Cross flow velocity was calculated as it is explained above. Wastewater permeation flux at certain time intervals during the filtration was calculated by measuring the volume of permeates collected in a definite time period. These permeate samples were characterized in terms of total suspended solid content, turbidity and color. Total permeate collected along the filtration process was however analyzed for pH, electrical conductivity, turbidity, color, total suspended solid, chemical oxygen demand and oil content.

3.2.5. Characterization of Wastewaters and Permeates

Wastewaters and total permeates collected during filtration were characterized in terms of pH, electrical conductivity, turbidity, color, total suspended solid, chemical oxygen demand and oil content. Permeates sampled at certain time intervals were subjected to total suspended solid content, turbidity and color measurements.

3.2.5.1. pH and Electrical Conductivity

pH and electrical conductivity of the samples were measured according to TS EN ISO 10523 and TS 9748 EN 27888 methods using pH and electrical conductivity probes, respectively.

3.2.5.2. Turbidity

Turbidity (NTU) values of wastewaters, permeates collected at certain time intervals and total permeates were performed according to TS 5091 EN ISO 7027 Water Quality-Turbidity measurement using Merck Pharo 300 UV-Vis spectrophotometer.

3.2.5.3. Color

Colors of wastewaters and total permeates collected were measured at single wavelength according to a method (SM 2120 C) described in Standard Methods for the Examination of Water and Wastewater (Clescerl, Greenberg and Eaton, 1999). Samples were thoroughly mixed and filtered through a syringe filters and the colors of the samples were measured by Pt-Co analysis using Merck Pharo 300 UV-Vis spectrophotometer.

Colors of permeates collected in timely manner during filtrations however were measured without filtering through the syringe filters since the volumes of the samples were low.

3.2.5.4. Total Suspended Solid Content

Total suspended solid contents of the wastewaters were measured according to TS EN 872 Water Quality – Determination of Suspended Solids. Glass fiber filter and watch glass were dried at 105°C and cooled down to room temperature until constant weight. The weight of glass fiber filter and watch glass was recorded. Sample was first homogenized by through mixing and 25 milliliter sample was filtered through glass fiber filter using vacuum filtration equipment. Filter is then dried on watch glass for 2 hours at 105°C. After holding in desiccator for 2 hours, weight of the filter and glass watch was measured again. Total suspended solid was finally calculated according to following formula:

$$TSS\ (\text{mg/L}) = \frac{m_2 - m_1}{25\ mL} \text{ x } 1000 \qquad (3)$$

TSS = Total suspended solid content (mg/L)
m_1 = Weight of the filter and watch glass
m_2 = Weight of the filter and watch glass after filtration, drying at 105°C and cooling down to room temperature

Total suspended solid contents of the permeates sampled during filtration and total permeates were however analyzed spectrophotometrically using Merck Pharo 300 UV-Vis spectrophotometer.

3.2.5.5. Chemical Oxygen Demand

Chemical oxygen demand of wastewaters and total permeates was measured using Merck Spectroquant 114555 (500-10000 mg/L), 114541 (25-1500 mg/L) or 101797 (5000-90000 mg/L) COD cell tests. Chemical oxygen demand of wastewaters and total permeates was measured according to (Kit Method) ISO 15705. Required volume of homogeneously mixed sample is transferred to reaction cell. The cell was vigorously mixed and then heated for 2 h at 148°C in a previously heated thermoreactor. The cell was removed from the thermoreactor and placed in a tube-rack. It was swirled after 10 minutes and left for complete cooling to room temperature for at least 30 minutes cooling time. COD was measured by reading absorbance at 605 nm in Merck Pharo 300 UV-Vis spectrophotometer.

3.2.5.6. Oil Content

Oil contents of wastewaters and total permeates were determined according to Partition-Gravimetric Method (5520 B) reported in Standard Methods for the Examination of Water and Wastewater with slight modifications (Clescerl et al., 1999). Since the maximum amount of permeates collected was almost 2 liters, volume of samples taken for oil analysis were kept at 150-250 mL.

Sample was first mixed thoroughly and 150-250 mL of sample was taken into borosilicate glass bottles using graduated cylinder. In order to adjust the pH of the samples to 2 or below, 1 mL 1:1 (v/v) H_2SO_4 was added to the samples. pH value of the sample was measured after the addition of sulfuric acid. If the pH was greater than 2, sulfuric acid addition was further continued until pH became 2 or dropped below 2. Sample was then transferred into a separatory funnel. Thirty milliliters of n-hexan was added to the bottle. Bottle was rinsed and hexan was transferred to the separatory funnel. The sample and n-hexan was shaken thoroughly for at least 2 minutes. The funnel was left to stand for the separation of hexan and aqueous phase. If the presence of third phase (emulsion phase with bubbles), 10 seconds ultrasonication was applied for the removal of bubbles and emulsion phase. The funnel is then left to stand for the separation of phases again. The aqueous phase at the bottom of the funnel was taken back to the sample bottle. Certain amount of organic phase was also allowed to pass into the bottle. The oil containing organic phase is filtered through filter paper containing

10 grams of Na_2SO_4 into a clean dark-colored glass bottle. The aqueous phase taken into bottle was subjected to this process twice yet passing of organic phase into the bottle was restricted at the final extraction. Oil containing hexane samples were stored at 4°C until analyses.

Samples were taken into soxhelet beakers which had previously dried until constant weight at 105°C and hexan was evaporated in automated soxhelet extraction equipment (Gerhardt, Germany). Residual n-hexan was removed in an oven at 60°C at least for 2 h. Beakers were weighed after cooling to room temperature. Oil contents of the samples were calculated according to following formula:

$$\text{Oil Content (g/L)} = \frac{m_{y2} - m_{y1}}{V} \text{ x } 1000 \quad (4)$$

m_{y2} = Weight of oil plus extraction beaker

m_{y1} = Weight of extraction beaker

V = Sample volume (mL)

4. RESULTS AND DISCUSSIONS

4.1. Characterization of Food Industry Wastewaters

Wastewaters used in this study were oil-containing wastewaters obtained from different stages of wastewater treatment facility of the plant (Figure 4.1). Wastewaters were collected before fat-trap, after H_2SO_4, and $Al_2(SO_4)_3$ additions and from equilibration.

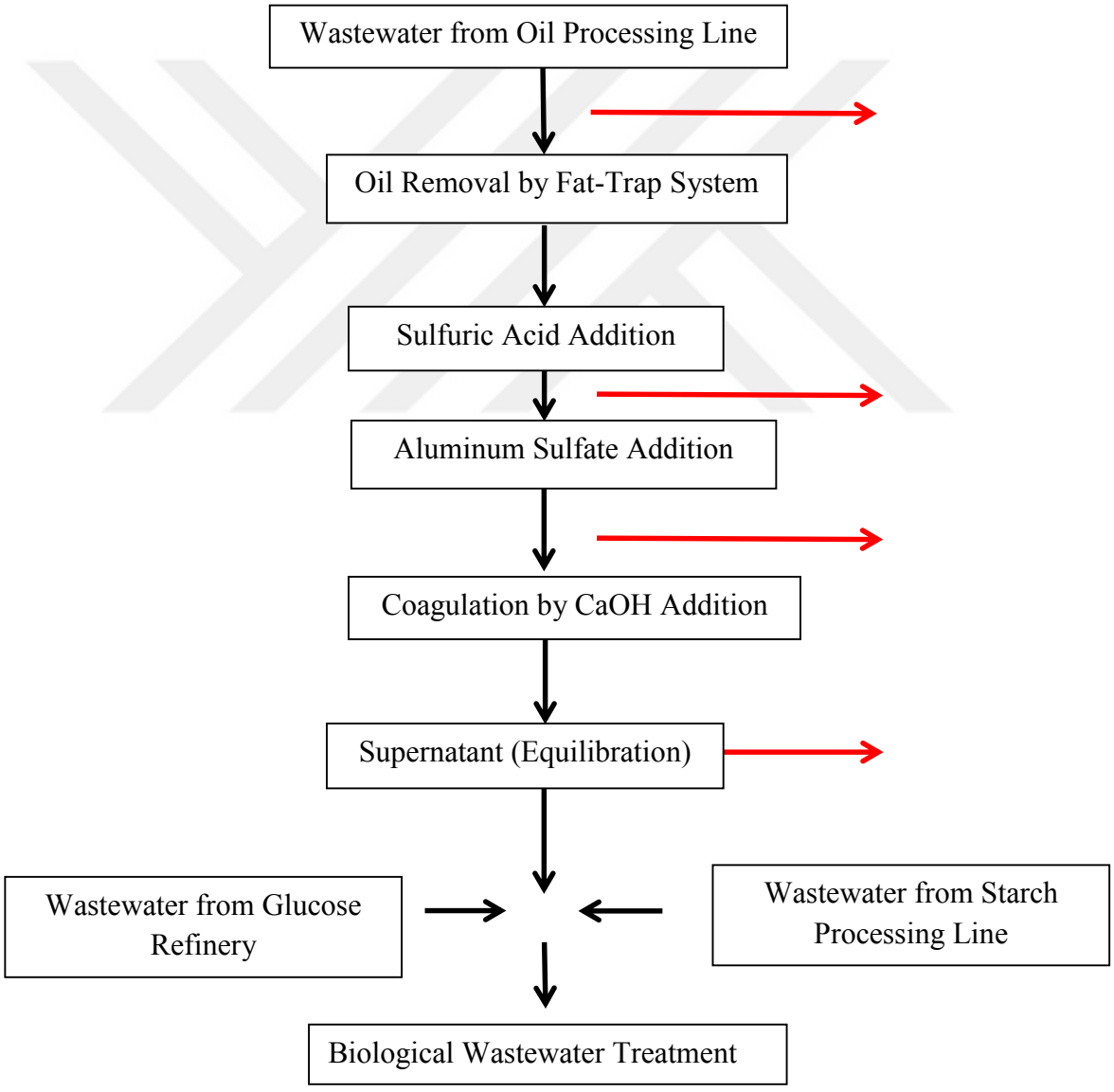

Figure 4.1. Food industry wastewater used in this study

As it is inferred from Figure 4.2, wastewater sampled before oil removal by fat-trap system had the highest amount of oil. When compared to other wastewaters, the lowest amount of oil and total suspended solid and the lowest turbidity values were observed in the wastewater from equilibration stage.

All wastewater were characterized in terms of pH, electrical conductivity, chemical oxygen demand (COD), total suspended solids (TSS), turbidity and color (Table 4.1). When the parameters indicative of pollution were determined, wastewater taken before oil removal by fat-tap system had the highest total suspended solids content, chemical oxygen demand and color values. COD values of this wastewater ranged between 11658 mg/L and 62000 mg/L while TSS content changed between 7881 mg/L and 8393 mg/L. Turbidity and color values were greater than 1000 for this wastewater. When wastewaters sampled after H_2SO_4 and $Al_2(SO_4)_3$ additions were compared to wastewater taken before oil removal by fat –trap system, former wastewaters had lower TSS content, COD, turbidity and color values. The wastewater sample from equilibration stage had the lowest TSS content (141 mg/L) and COD (475 mg/L), turbidity (16.37 NTU) and color (85 Pt-Co) values.

Figure 4.2. Wastewaters a. before fat trap, b. after H_2SO_4 addition, c. after $Al_2(SO_4)_3$ addition, and d. from equilibration.

Table 4.1. Characteristics of Food Industry Wastewater

Wastewater	pH	Electrical Conductivity (µS/cm)	COD (mg/L)	TSS (mg/L)	Turbidity (NTU)	Color (Pt-Co)	Oil (g/L)
Before Fat Trap	6.45-8.79	495 - 2250	11658 - 62000	8137±256	>1000	>1000	8.1 - 24.8
After H_2SO_4 Addition	2.17	9.7	1610	339±10	256.00±9.85	169 ± 16	1.82
After $Al_2(SO_4)_3$ addition	2.05	10.02	1415	339±26	281.00±7.00	210 ± 7	2.9
Equilibration	12.14	15.66	475	141±12	16.37±1.59	85 ± 6	-

Since the filtration experiments performed using oily-wastewater obtained before oil-removal by fat-trap system resulted in the clogging in the system, all wastewaters but wastewater from equilibration were subjected to filtration through general purpose filter paper using vacuum filtration unit (Figure 4.3). As it is inferred from Table 4.2, COD, TSS and oil contents of wastewater obtained before oil removal by fat-trap system has reduced after filtration through filter paper yet it was still the wastewater which had highest levels of pollution parameters. Oil content of this wastewater was reduced to 4.3-15.6 g/L from 8.1-24.8 g/L.

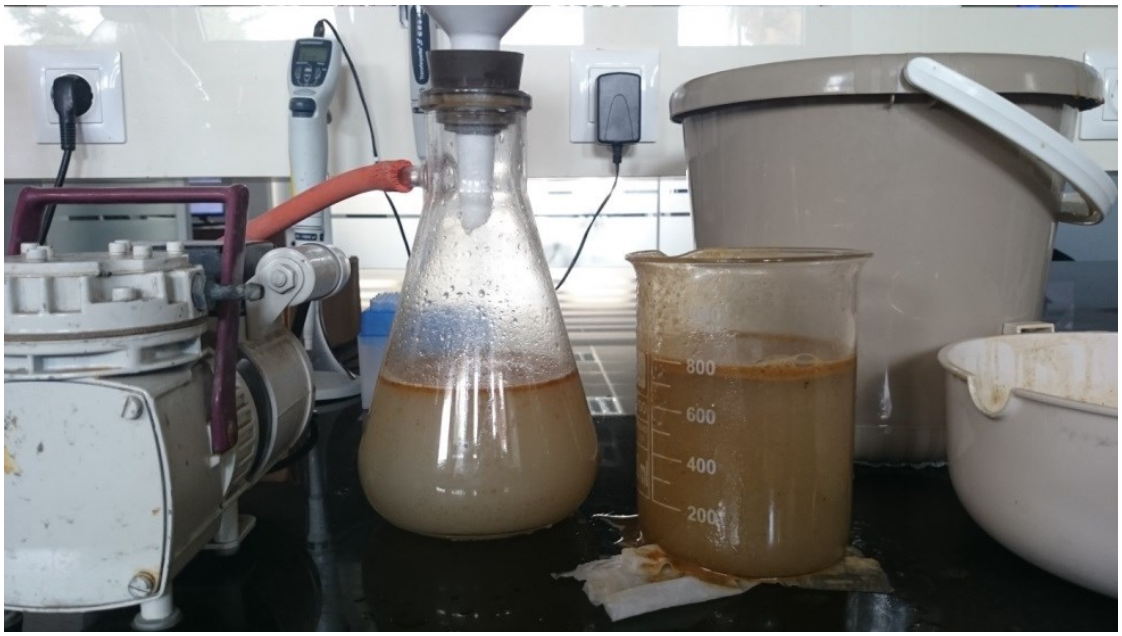

Figure 4.3. Wastewater obtained before oil removal by fat-trap system before (right) and after (left) filtration through general purpose filter paper

Table 4.2. Characteristics of Food Industry Wastewater after Filtration through General Purpose Filter Paper

	Before Fat Trap	Before Fat Trap (After General Purpose Filter)	After H_2SO_4 Addition	After H_2SO_4 Addition (After General Purpose Filter)	After $Al_2(SO_4)_3$ Addition	After $Al_2(SO_4)_3$ Addition (After General Purpose Filter)
pH	6.45 – 8.79	6.44 - 7.13	2.29	2.23	1.71	1.62
Electrical Conductivity (µS/cm)	495 - 2250	562-2300	-	-	8.86	8.22
TSS (mg/L)	8137 - 26656	3128 – 11564	2533	2171	3637	3432
Color (Pt/Co)	> 1000	895 - >1000	83	71	376	381
Turbidity (NTU)	>1000	140 - > 1000	>100	>100	645	434
COD (mg/L)	11658 - 62000	8083 – 44670	6947	6478	18720	14687
Oil (g/L)	8.1 - 24.8	4.3 - 15.6	1.82	1.9	2.9	3.3

4.2. Food Industry Wastewater Treatment Using Ceramic Tubular Membranes

The properties of wastewaters were observed to show variations according to sampling time. Evaluation of each filtration performance was performed by comparing the properties of permeates with the initial properties of the wastewater used at each filtration experiment. All experiments were performed using wastewater filtered through general purpose filter paper.

4.2.1. Treatment of Wastewater Sampled from Equilibration Using Ceramic Tubular Membranes

Preliminary filtration experiments in this study were performed using the wastewater which had the lowest levels of TSS, COD, turbidity, color and oil (Figure 4.2d and Table 4.1). Since the levels of wastewater characteristics were lower microfiltration and ultrafiltration membranes were selected for the treatment of this wastewater.

4.2.1.1. Microfiltration

Clean water fluxes through microfiltration membrane were first calculated by measuring flow rate of the water flowing in the system. Figure 4.4 shows the variation of water fluxes with transmembrane pressure for approximately cross flow velocity of 0.34 m/s. Water flux was found as 151.5 $L/m^2 \cdot h$ when the transmembrane pressure was adjusted to 1. The increase in TMP resulted in the increase in water flux. When TMP was increased to 5 bar, the flux became 1100.8 $L/m^2 \cdot h$. Changing TMP from 5 bar to 6 bar however did not change water flux.

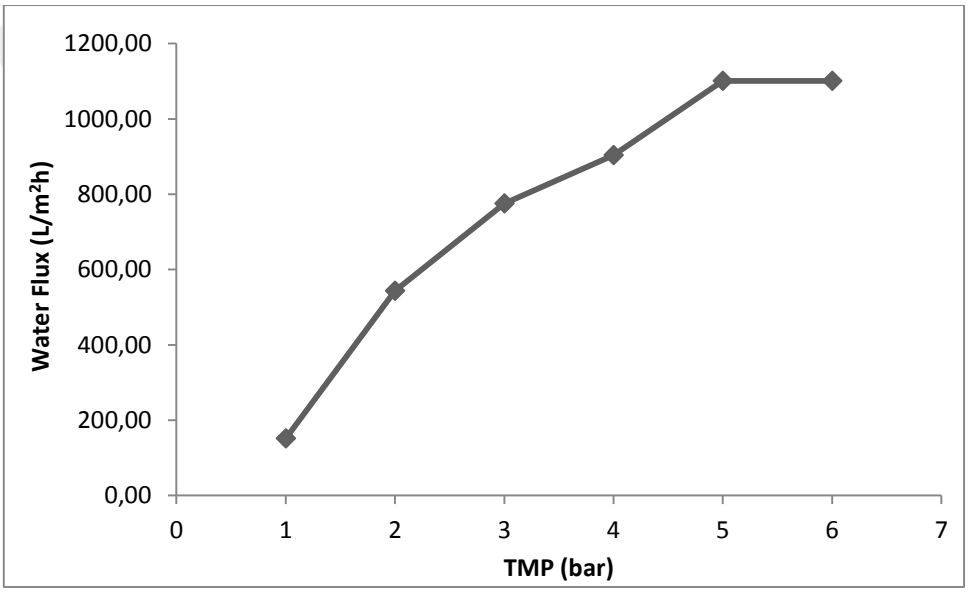

Figure 4.4. Water permeation fluxes through MF membrane vs. TMP for cross flow velocity of 0.34 m/s.

Wastewater fluxes during the microfiltration experiment are show in Figure 4.5. Wastewater fluxes were found to be 1100-1200 $L/m^2 \cdot h$ and stayed constant throughout the filtration. Microfiltration of 5 liters wastewater sampled from equilibration took 33 minutes. Time dependent changes in COD, TSS and turbidity were measured by permeate samples taken at 2^{nd}, 10^{th} and 20^{th} minutes during the microfiltration experiment. The results show (Figure 4.6) that percent reductions in COD, TSS and turbidity values were 10-14 %, 50 % and 90 %, respectively. Total permeate samples collected at the end of 33 min-MF experiment were subjected to COD, TSS, turbidity and color analyses (Table 4.3). Percent reductions of COD, TSS, turbidity and color values of the wastewater after the microfiltration were found as 5.5, 52.5, 93.1 and 9.5 %, respectively.

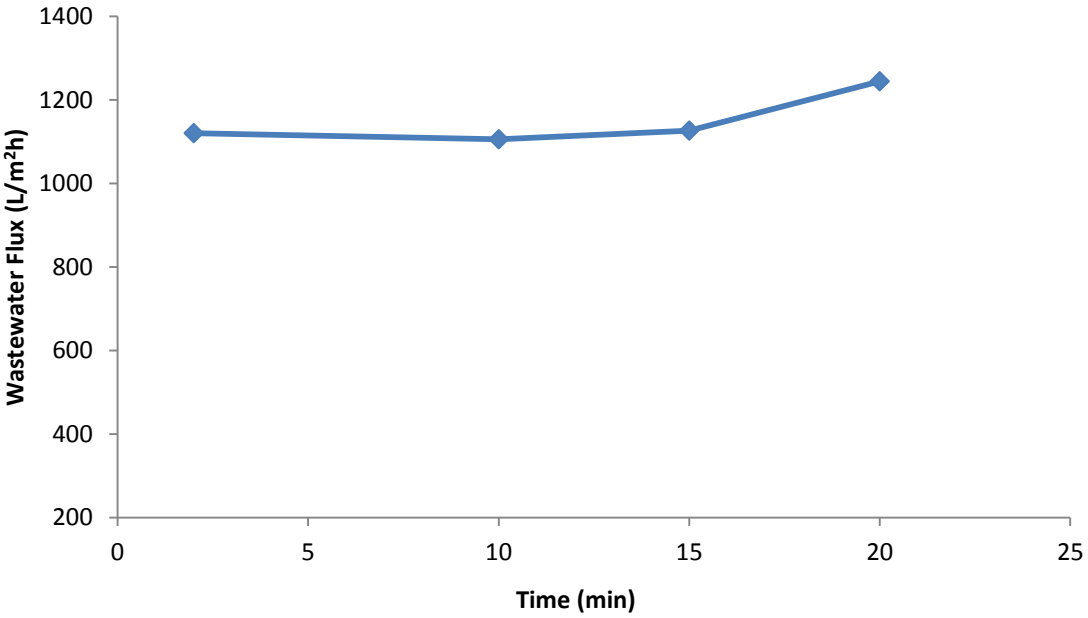

Figure 4.5. Wastewater flux through MF membrane for cross flow velocity of 0.34 m/s and TMP of 4 bar.

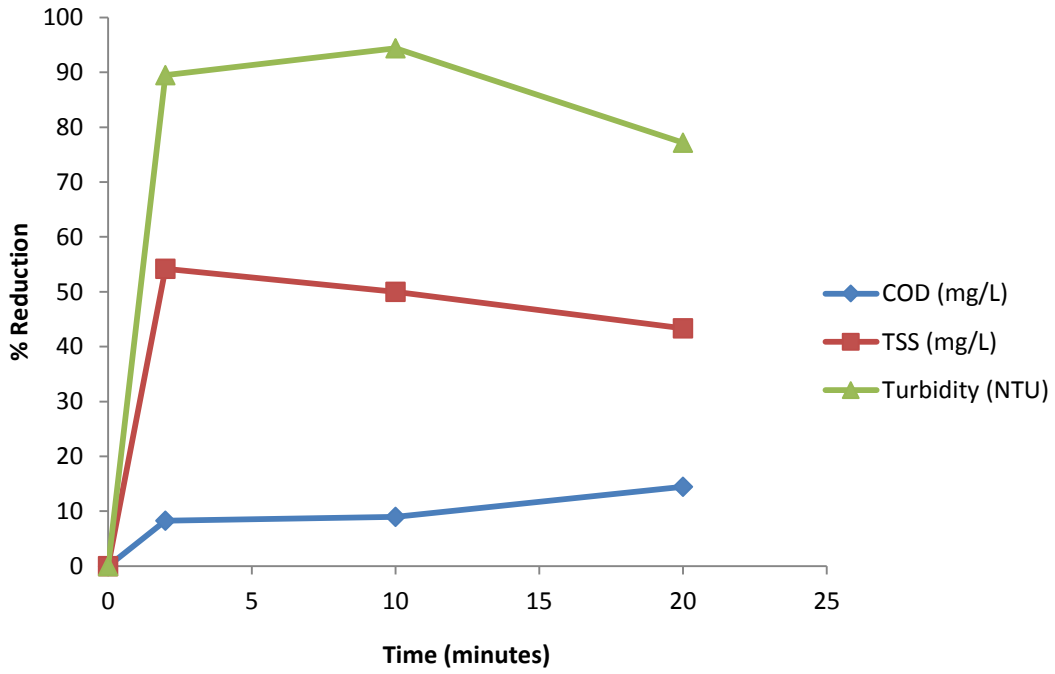

Figure 4.6. Changes in TSS content, COD and turbidity values during the filtration of wastewater sample taken from equilibration stage using ceramic MF membrane TMP: 4 bar, Cross flow velocity: 0.34 m/s.

Table 4.3. Evaluation of the performance of ceramic MF membrane in the filtration of wastewater taken from equilibration stage.

	COD (mg/L)	TSS (mg/L)	Turbidity (NTU)	Color (Pt-Co)
Wastewater	725	600	38.2	42
MF Filtrate	685	285	2.63	38
% Reduction	5.5	52.5	93.1	9.5

The visual appearances of the wastewater sample taken from equilibration stage and filtrate sample collected in microfiltration experiment are given in Figure 4.7. Visual appearances were in good agreement with chemical analysis results. As it is inferred from the figure, color of the wastewater stayed almost constant yet turbidity removal resulted in clear filtrate.

Figure 4.7. Wastewater sample taken from equilibration tank (left), filtrate obtained by the microfiltration of the wastewater using tubular ceramic MF membrane

4.2.1.2. Ultrafiltration

Clean water fluxes measured at various TMPs for ultrafiltration membrane are shown in Figure 4.8. Water flux which were 69.73 L/m^2·h at 1 bar increased with the increase in TMP and reached to the value of 254.98 L/m^2·h at 6 bar. Wastewater flux however 120.96 L/m^2·h at 2nd minutes of filtration continually increased to 206.98 L/m^2·h (30th minutes of filtration). Flux was then gradually decreased to 51.67 L/m^2·h. Ultrafiltration ended after 3 hours. The

increase of wastewater flux was directly related to the instability in TMP. The pressure gauges read 4-5 bar at the beginning of the filtration, it was stabilized at 8 bar at the 30th minutes of the ultrafiltration.

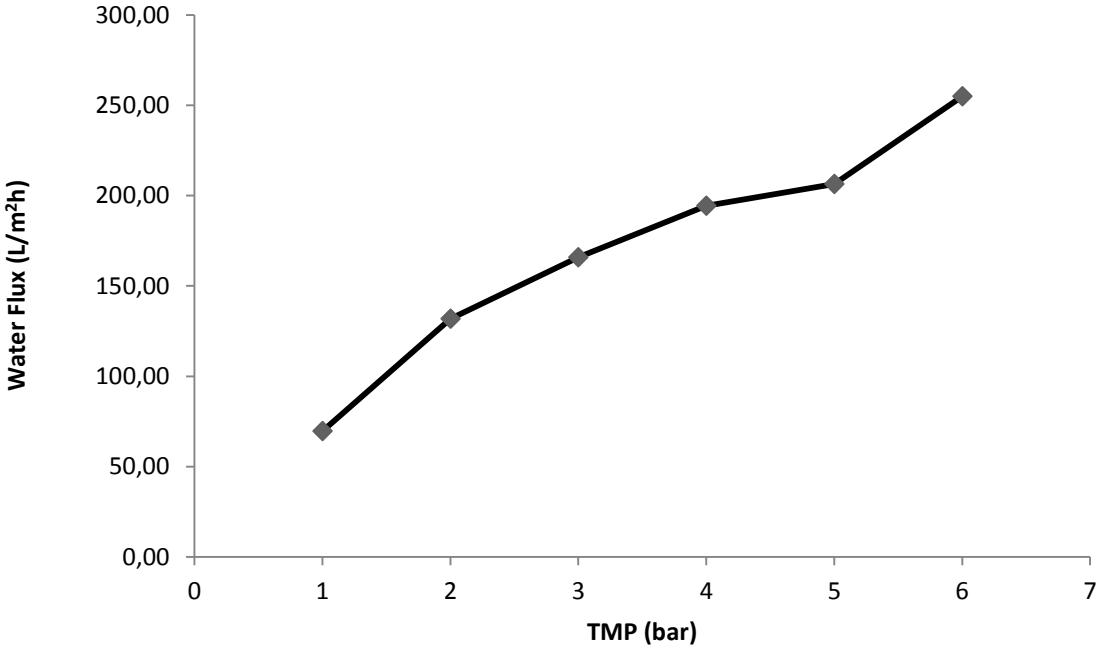

Figure 4.8. Clean water flux through UF membrane at TMP of 8 bar.

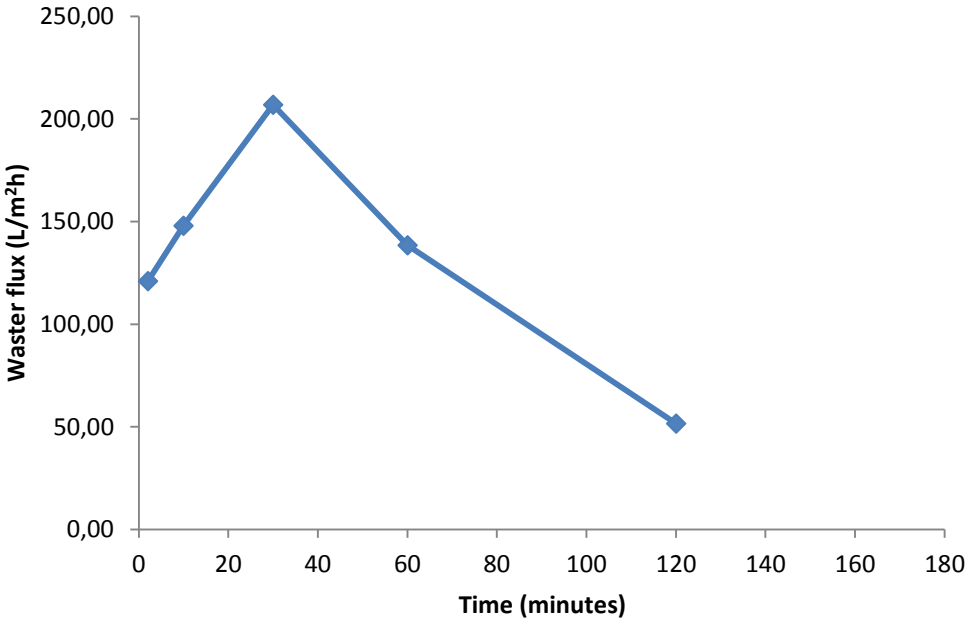

Figure 4.9. Wastewater flux through UF membrane at TMP of 8 bar.

COD, TSS and turbidity of the wastewater decreased during the ultrafiltration process. Color values measured in time showed no significant change during filtration. Percent reductions in COD, TSS and turbidity monitored during ultrafiltration (Figure 4.10) showed that COD removal efficiency was 10-19 % while reduction in TSS ranged from 46 to 59 %. Turbidity reduction (83-99 %) however was greater than those found for COD and TSS.

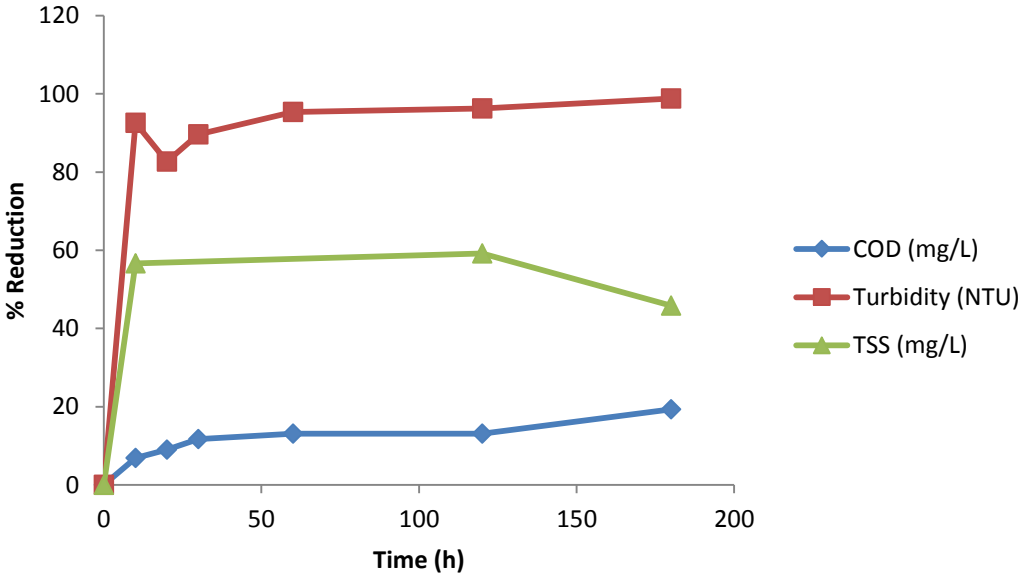

Figure 4.10. Changes in TSS content, COD and turbidity values during the filtration of wastewater sample taken from equilibration stage using ceramic UF membrane TMP: 8 bar, Cross flow velocity: 0.34 m/s.

When the overall ultrafiltration performance was evaluated (Table 4.4), ultrafiltration resulted in 21 % reduction in COD, 13 % reduction in TSS, 96 % reduction in turbidity and 27 % reduction in color. The photographs of UF permeate collected after 10 minutes ultrafiltration is given in Figure 4.11 for comparison with the wastewater.

Table 4.4. Evaluation of the performance of ceramic UF membrane in the filtration of wastewater taken from equilibration stage.

	COD (mg/L)	**TSS (mg/L)**	**Turbidity (NTU)**	**Color (Pt-Co)**
Wastewater	725	600	38.2	42
UF Filtrate	575	525	1.46	14
% Reduction	21	13	96	67

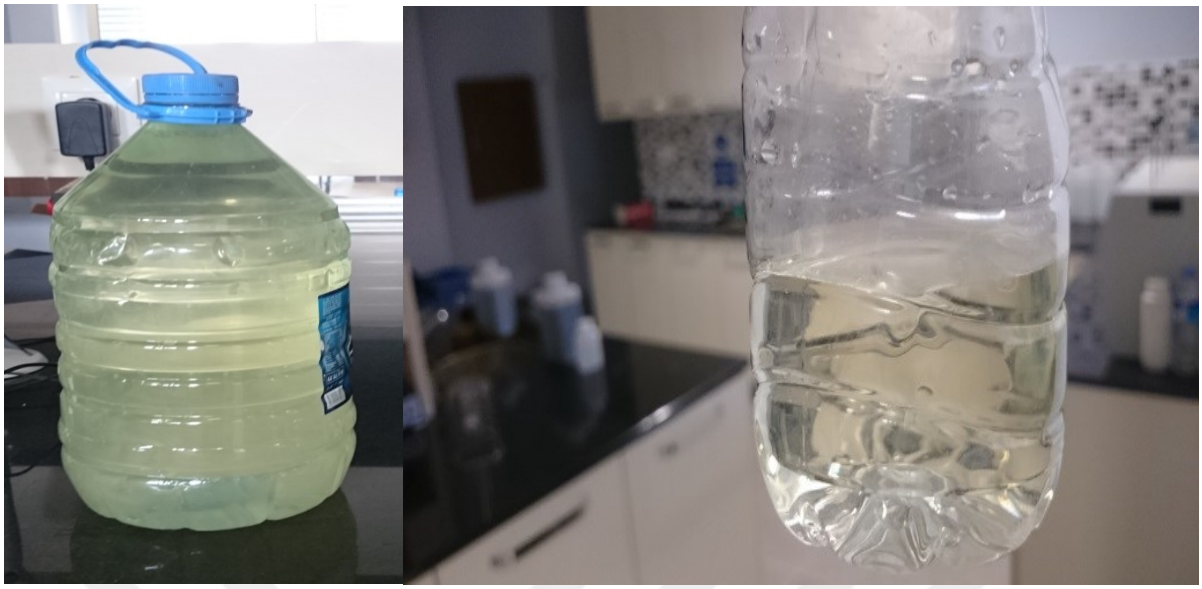

Figure 4.11. The photographs of wastewater taken from equilibration stage (left) and UF filtrate obtained at 10th minute of the filtration.

4.2.2. Treatment of Wastewater Sampled before Oil Removal by Fat Trap System Using Ceramic Tubular Membranes

4.2.2.1. Filtration Using Supports

Water permeation fluxes of a ceramic alumina support were measured prior the filtration of oily wastewater samples taken before oil removal by fat-trap. Changes in the water fluxes of the support with respect to changes in TMP values for cross flow velocity values of 0.06, 0.16, 0.25 and 0.44 m/s are shown in Figure 4.12. Water flux was observed to increase with the increase in transmembrane pressure for all cross flow velocities. The water permeation fluxes measured for the lowest cross flow velocity at all TMP values were higher than those obtained for other cross velocities. Similar permeation fluxes were obtained for all the other cross flow velocities at each TMP. Water permeability flux through the support changed in the range of 100 and 3000 L/m^2·h.

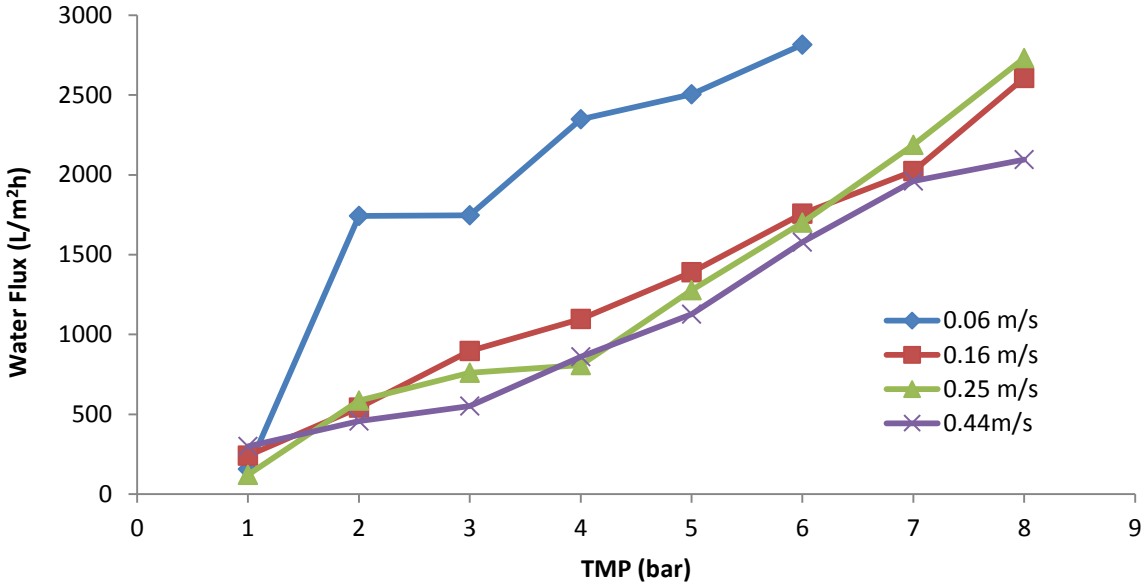

Figure 4.12. Water permeation fluxes through the support vs. TMP for cross flow velocities of 0.06, 0.16, 0.25 and 0.44 m/s.

Filtration of oily-wastewater obtained before the oil removal by fat-trap system was performed at constant TMP of 4 bar for three different cross flow velocities (0.25, 0.35 ve 0.44 m/s). Time dependent changes in the wastewater fluxes through the tubular supports during the filtration of this oily wastewater are shown in Figure 4.13. Initially wastewater fluxes were found to be in the range of 7-11 $L/m^2 \cdot h$. They were decreased to 1-3 $L/m^2 \cdot h$ in time. When the wastewater fluxes were compared to the clean water fluxes, the wastewater fluxes were found to be much lower than the clean water fluxes. Mueller and colleagues (1997) reported a severe and rapid flux decline after early few minutes microfiltration of oily wastewater by 0.8 µm Al_2O_3 membrane which exhibited higher clean water fluxes. This was attributed to the formation of fouling layer by oil on the membrane surface. They suggested that this fouling layer rather than membrane governed the filtration. The initial fluxes in our study were measured at 30th minutes of filtration and found to be very lower when compared to clean water fluxes. This indicated that ceramic membranes quickly fouled in the early stages of filtration experiments by the oil and lipids present in the wastewater. Permeate fluxes measured for three different cross flow velocities at 4 bar were almost similar to each other. This showed that the permeate flux was almost independent of cross flow velocity within cross flow velocity range employed. This was possibly due to the rapid fouling of the membranes and the shear resistant nature of the fouling (oil) layer (Mueller, Cen and Davis, 1997).

The performance of the filtration of the wastewater by tubular Al_2O_3 supports was determined by measuring TSS, turbidity and color of permeate samples taken at certain time intervals (0.5, 1, 1.5, 2, 2.5, 3, 6, 9, 12, 15, 18, 21, 24 ve 27. hours). Figure 4.14, 4.15 and 4.16 show the percent removal of TSS content, turbidity and color values throughout the filtration. Filtration using ceramic supports resulted in 99.6 % or greater reduction in total suspended solid contents. Selected cross flow velocities did not significantly affect the percent reduction in TSS content of the wastewater.

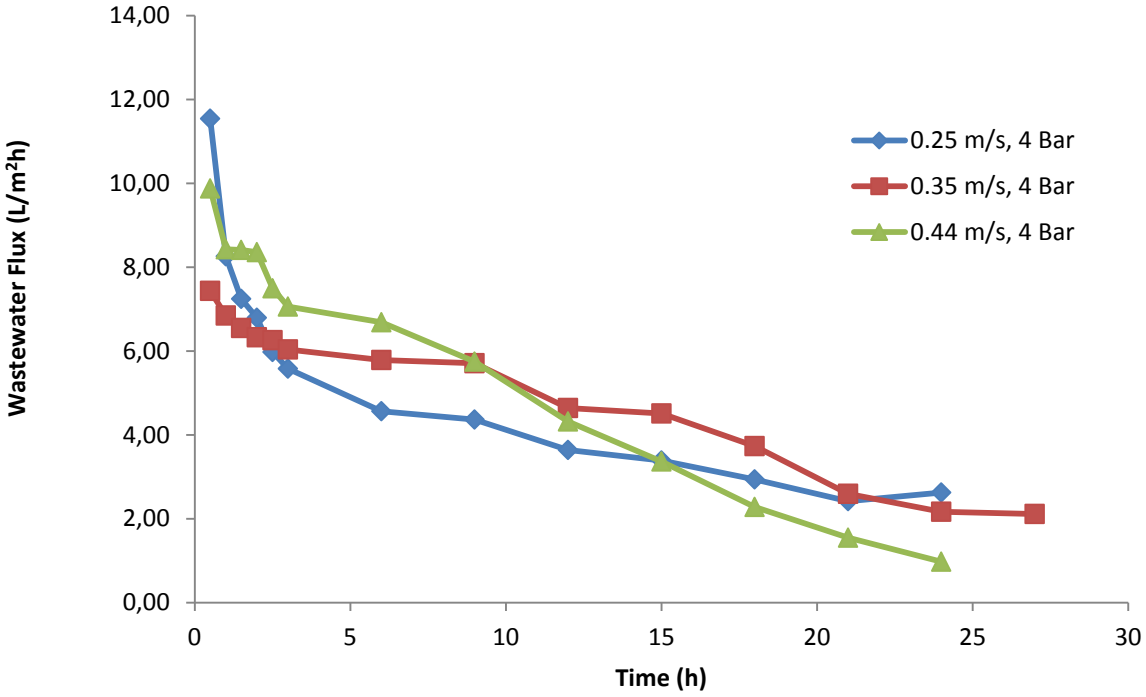

Figure 4.13. Time dependent changes in the wastewater fluxes during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic supports TMP: 4 bar, Cross flow velocity: 0.25, 0.35 and 0.44 m/s.

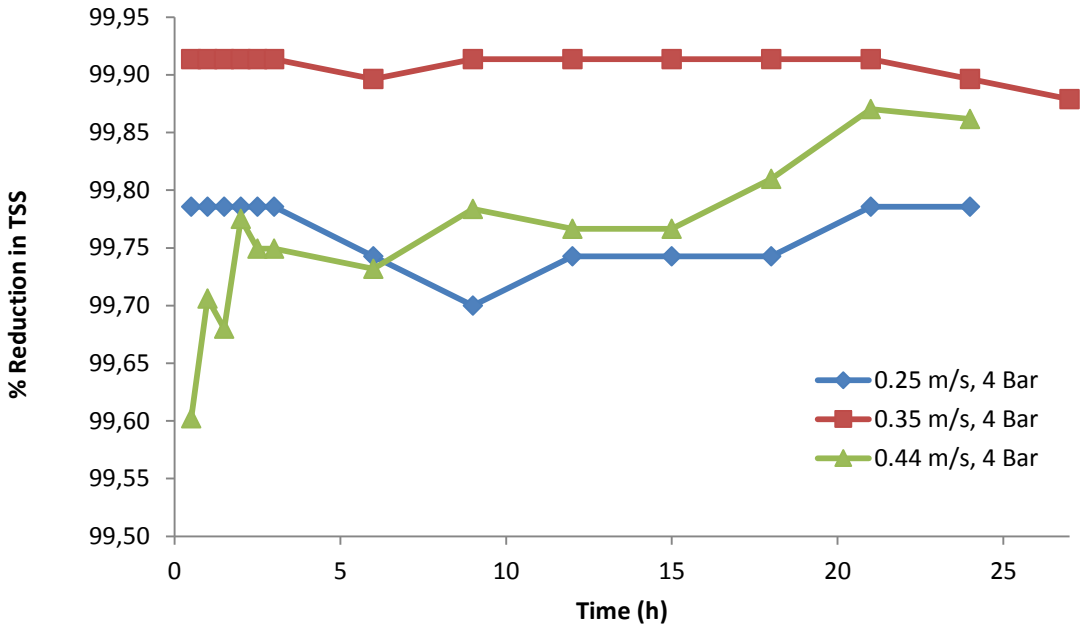

Figure 4.14. Changes in TSS content of oily-wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic supports TMP: 4 bar, Cross flow velocity: 0.25, 0.35 and 0.44 m/s.

Turbidity values of the permeate samples collected during filtration through the supports showed that 99.2-99.8 % reduction was observed when the cross velocity of the wastewater was 0.25 m/s at transmembrane pressure of 4 bar (Figure 4.15). The reduction in turbidity was found to be 94.6-96.4 % for 0.35 m/s while it was in the range of 86.7-97.6 % for 0.44 m/s. Percent reduction in turbidity slightly reduced with the increase in cross flow velocity at constant transmembrane pressure. Evaluation of the time dependent changes in the color of permeate samples during the filtration showed that adjusting the cross flow velocity to 0.25 m/s at 4 bar transmembrane pressure could reduce the color in 96.3 % or over (Figure 4.16). Color removal was almost 90 % and found to be similar for 0.35 and 0.44 m/s during the first 15 hours of the filtration. Color removal percentage stayed constant for 24 hours filtration time for the cross flow velocity of 0.35 m/s. Color removal efficiency however started to decrease after 15 hours of filtration and reached to 71 % at the end of 24 hours when the cross flow velocity was 0.44 m/s.

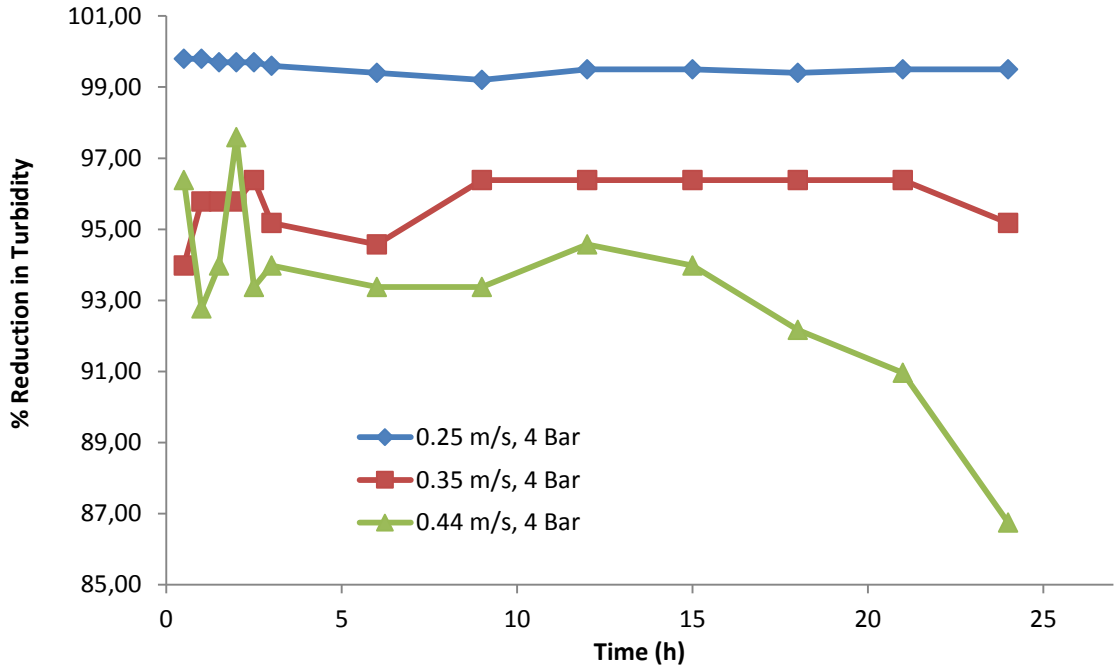

Figure 4.15. Changes in turbidity values of oily-wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic supports TMP: 4 bar, Cross flow velocity: 0.25, 0.35 and 0.44 m/s.

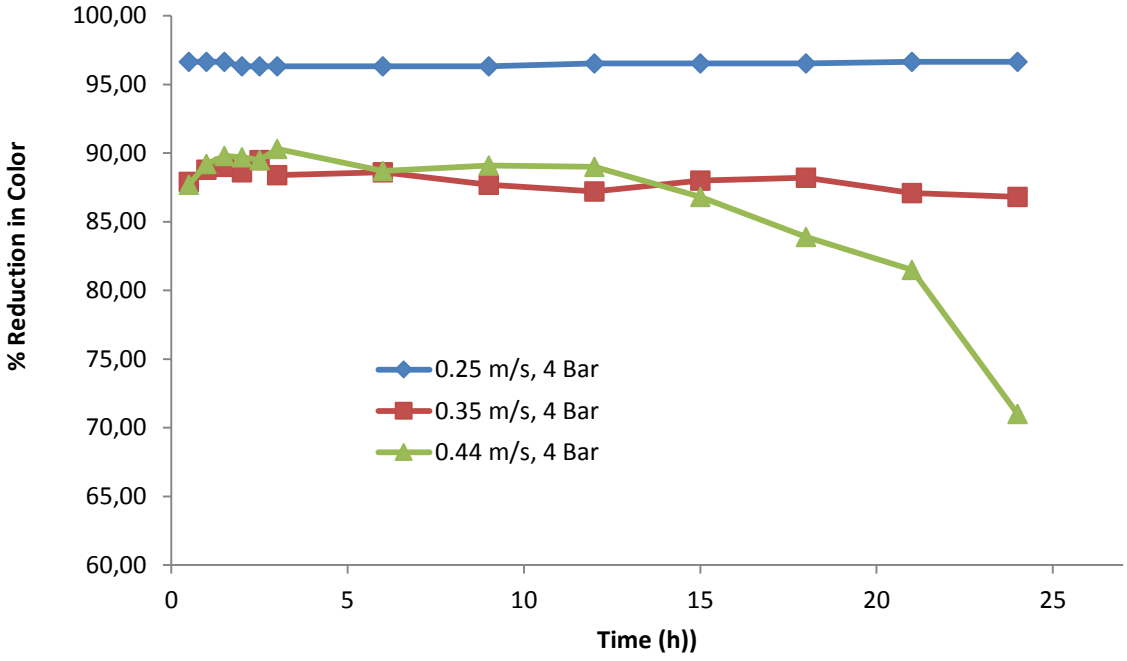

Figure 4.16. Changes in color of oily-wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic supports TMP: 4 bar, Cross flow velocity: 0.25, 0.35 and 0.44 m/s.

Overall performance of the filtration of wastewater using tubular ceramic supports was evaluated by comparing initial parameters of wastewater with total permeates collected during filtration experiments. Changes in TSS and oil content, COD, turbidity and color values after filtration using support for all cross flow velocities at 4 bar transmembrane pressure are shown in Table 4.5. When the removal efficiency of substances contributing to TSS, turbidity and color values were considered, cross flow velocity of 0.25 m/s yielded percent reductions over 96 %. Reduction in suspended solids content was higher than 99 % for all cross flow velocities. Color removal percentages however were found to be 88.6 and 84.4 % for the filtration experiments where cross flow velocities were 0.35 and 0.44 m/s, respectively. Turbidity removal percentages for cross flow velocities of 0.35 and 0.44 m/s were found as 91.6 and 87.4 %, respectively. In contrast to TSS, turbidity and color removal, COD removal percentage for the cross flow velocity of 0.25 m/s (90.1 %) was lower than those found for 0.35 m/s and 0.44 m/s (98.1 % for both). No oil was detected in the permeate samples collected at the end of the filtration experiments. Oil reduction in the filtration of the wastewater for all cross flow velocity values was therefore calculated as 100 %.

Table 4.5. Evaluation of the performances of ceramic tubular supports in the filtration of oily-wastewater taken before fat-trap system.

Cross Flow Velocity		TSS (mg/L)	COD (mg/L)	Color (Pt/Co)	Turbidity (NTU)	Oil (g/L)
0.25 m/s	**Initial**	4665	9891	951	>1000	4.3
	After Filtration	21	978	31	15	ND*
	% Reduction	**99.5**	**90.1**	**96.7**	**98.5**	**100**
0.35 m/s	**Initial**	11564	44670	>1000	166	15.6
	After Filtration	7	862	114	14	ND*
	% Reduction	**99.9**	**98.1**	**88.6**	**91.6**	**100**
0.44 m/s	**Initial**	11564	44670	>1000	166	15.6
	After Filtration	24	859	156	21	ND*
	% Reduction	**99.8**	**98.1**	**84.4**	**87.4**	**100**

*ND: Not detected

4.2.2.2. Microfiltration

Clean water permeation fluxes through the microfiltration membranes at TMP values of 1, 2, 3, 4, 5, 6, 7 and 8 bar for the cross flow velocities of 0.06, 0.16 and 0.25 m/s were determined (Figure 4.17). Clean water fluxes generally decreased with the increase in cross flow velocity at all TMP levels. Increase in TMP led to the increase in the permeation flux until 4 bar. When TMP was further increased, fluxes increased slightly for the cross flow velocities of 0.16 and 0.25 m/s and decreased for 0.06 m/s. Clean water fluxes were generally found in the range of 100 and 600 L/m^2·h.

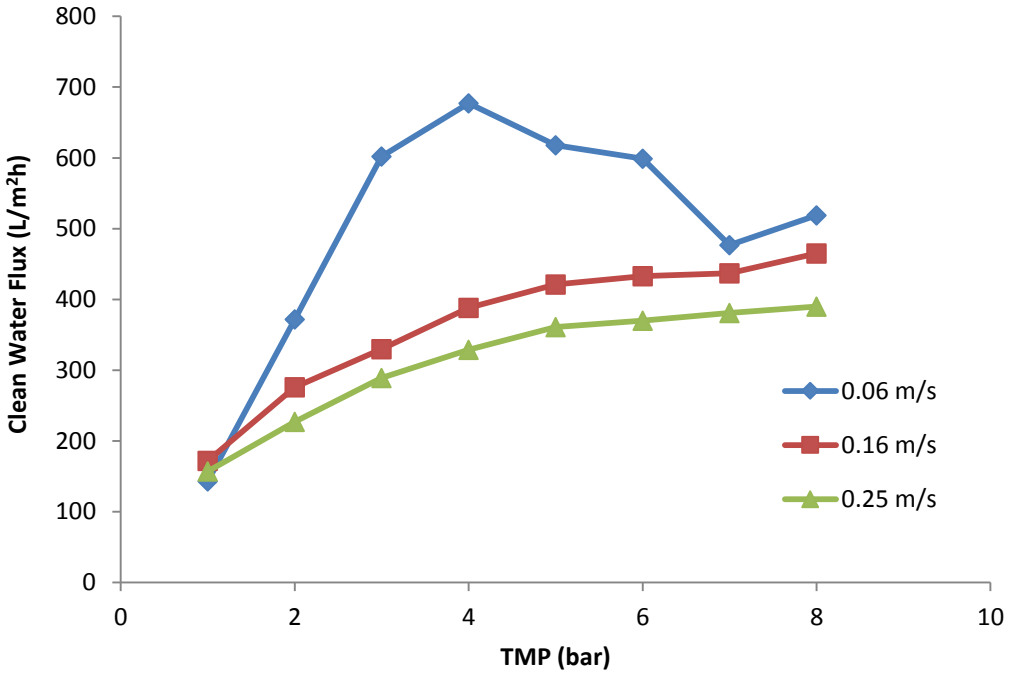

Figure 4.17. Water permeation fluxes through the ceramic tubular microfiltration membrane vs. TMP for cross flow velocities of 0.06, 0.16, 0.25 and 0.44 m/s.

Microfiltration of oily wastewater was performed at two different cross flow velocities (0.16 m/s) and (0.25 m/s) and two different TMP values for each cross flow velocity (2 and 8 bar for 0.16 m/s and 4 and 8 bar for 0.25 m/s). Changes in the wastewater permeation fluxes in these four different microfiltration experiments are shown in Figure 4.18. Wastewater fluxes were found to be much lower than clean water fluxes. Time dependent fouling of the microfiltration membranes caused the wastewater fluxes nearly 1-2 L/m^2·h levels. The maximum initial wastewater flux (7.73 L/m^2·h) was observed for 0.16 m/s at 2 bar while the

lowest initial wastewater flux (3.07 L/m^2·h) was determined for 0.16 m/s at 8 bar. Koltuniewicz, Field and Arnot (1995) observed that the increase in transmembrane pressure resulted in a higher decrease in permeate flux. They concluded that oil was introduced into the pore of membrane at high transmembrane pressures. Abbasi and colleagues (2012) found that the cake layer formed over membrane surface exhibited increasing resistance with increase in pressure in the microfiltration of oily wastewater. The presence of oil in high concentrations in the feed solution was suggested to be responsible for the formation of incompressible cake layer. They also reported a decrease in the porosity of the cake layer with increase in pressure. The higher wastewater fluxes observed at 2 bar than those at 8 bar for cross flow velocity of 0.16 m/s in our study indicated that either oil droples migh have been introduced into the membrane pores or a cake layer with a lower porosity might have been formed over the membrane surface at higher transmembrane pressure. Microfiltration experiments performed at 8 bar for 0.16 m/s and 0.25 m/s cross flow velocities showed that incearing cross flow velocity from 0.16 to 0.25 m/s slightly enhanced the permeate flux. The slight improvement in fluxes was possibly due to the slight increase in cross flow velocity. Although the fluxes obtained for 0.25 m/s were higher than fluxes obtained for 0.16 m/s but they almost reached similar values at the end of filtration.

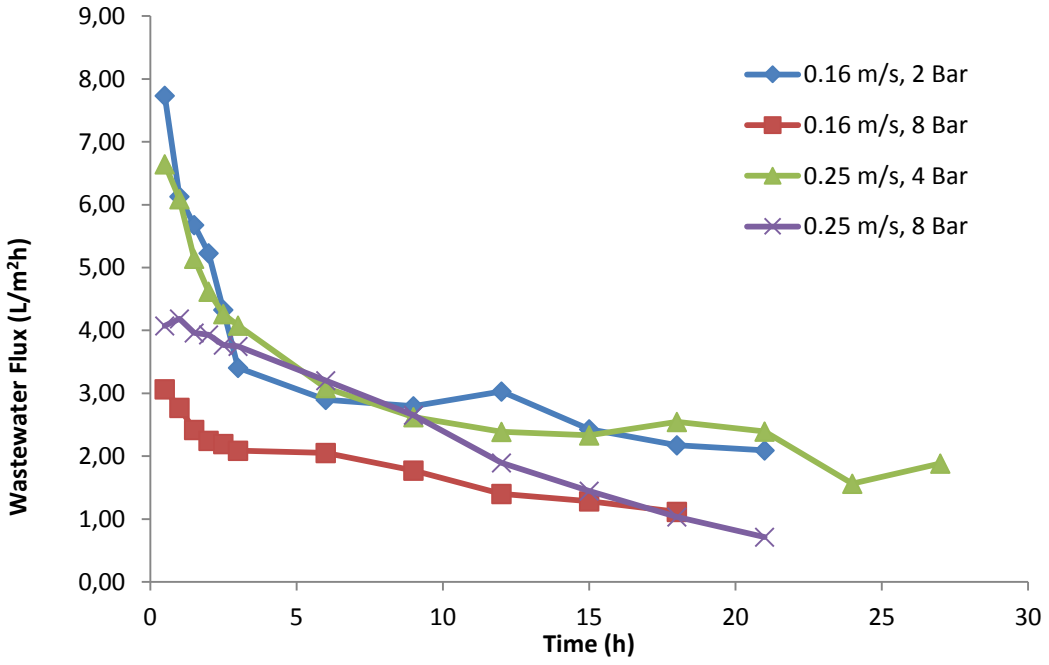

Figure 4.18. Time dependent changes in the wastewater fluxes during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic MF membranes TMP: 2, 4, 8 and CFV: 0.16 and 0.25 m/s.

Microfiltration of oily wastewater using tubular ceramic membranes were evaluated by measuring TSS content, turbidity and color of permeates collected at certain time intervals. Figure 4.19 shows the percent reduction in TSS during microfiltration experiments. All microfiltration experiments performed yielded 99.3 % or greater reduction in TSS content of the wastewater. Reduction in the turbidity (Figure 4.20) was in the range of 99.2 and 99.8 % when the cross flow velocity and TMP were 0.25 m/s and 4 bars. Approximately 98-99 % decrease in the turbidity was observed for cross flow velocity of 0.16 m/s at 2 bars TMP. When the cross flow velocity was kept constant at 0.16 m/s but TMP was increased to 8 bars, 97 % reduction in the turbidity was observed for the first 2 hours of filtration. Turbidity removal efficiency was then started to decrease and reached to 86 % at the 15th hour of filtration. When TMP was held at 8 bar, increasing cross flow velocity resulted in the decrease in turbidity removal efficiency. Percent turbidity removal was found to be 58 % for the permeate sample collected 30 min after start of filtration. It reached to 80-84 % at 1 hour and thereafter.

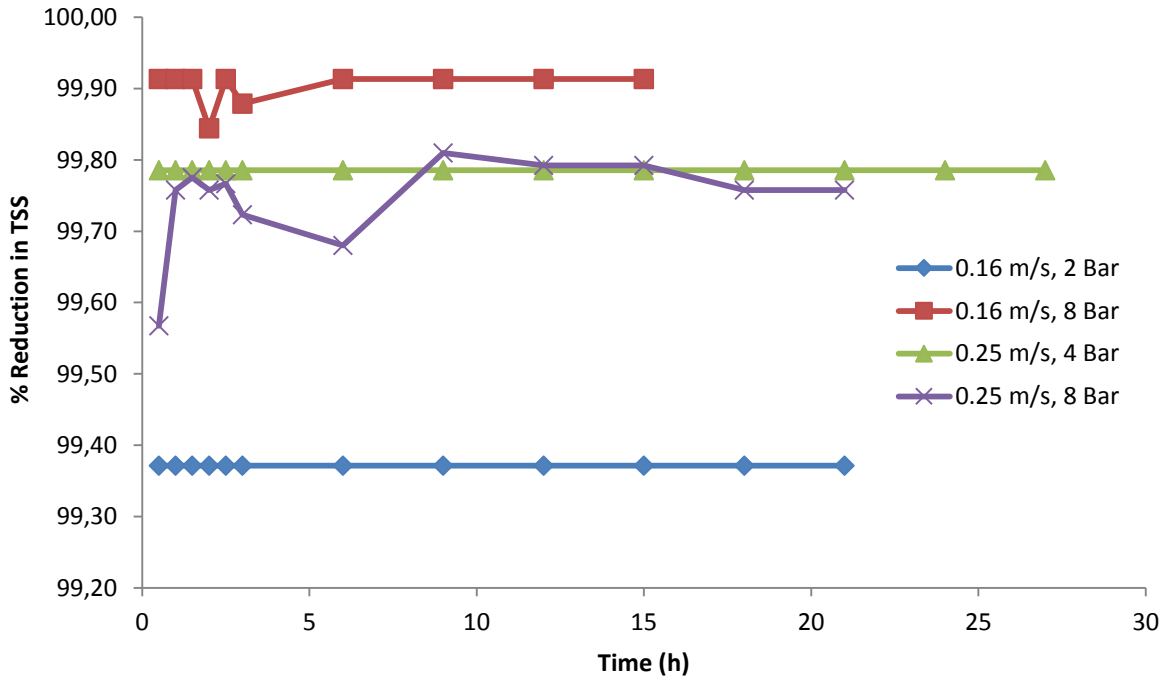

Figure 4.19. Changes in TSS content of oily-wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic MF membrane.

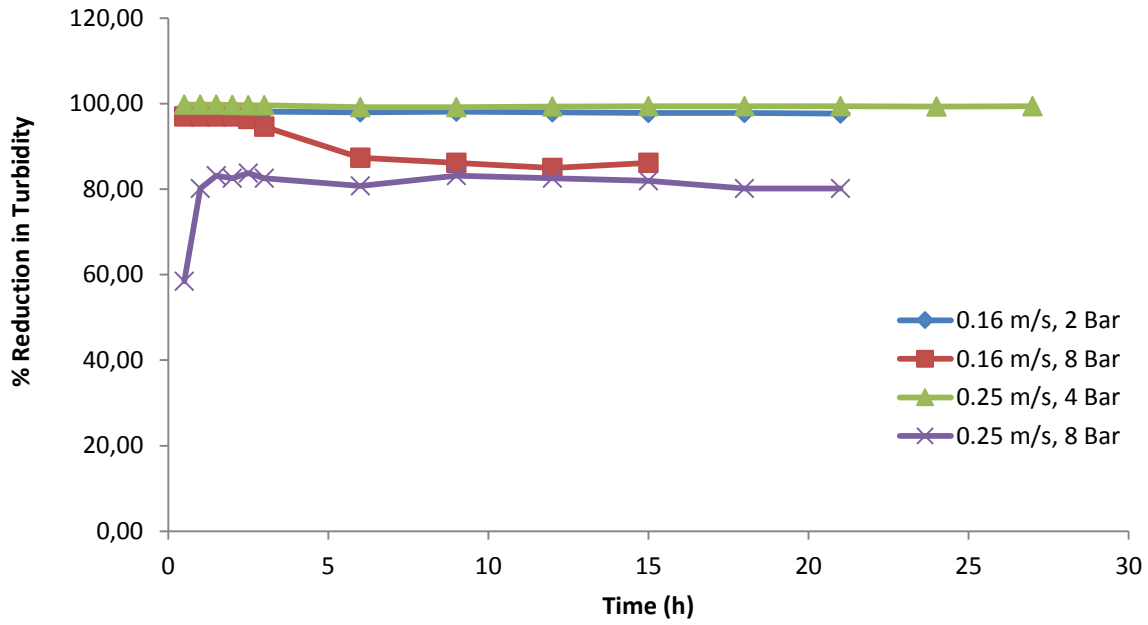

Figure 4.20. Changes in the turbidity of oily wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic MF membrane.

Figure 4.21 shows the color removal efficiency of the MF membranes. Microfiltrations at 8 bar with the cross flow velocity of 0.16 m/s and at 4 bar with the cross flow velocity of 0.25 m/s both reduced the color over 95 %. Color reduction percentage however decreased to 66 and 86 % for 0.16 m/s and 0.25 m/s, respectively at 8 bar.

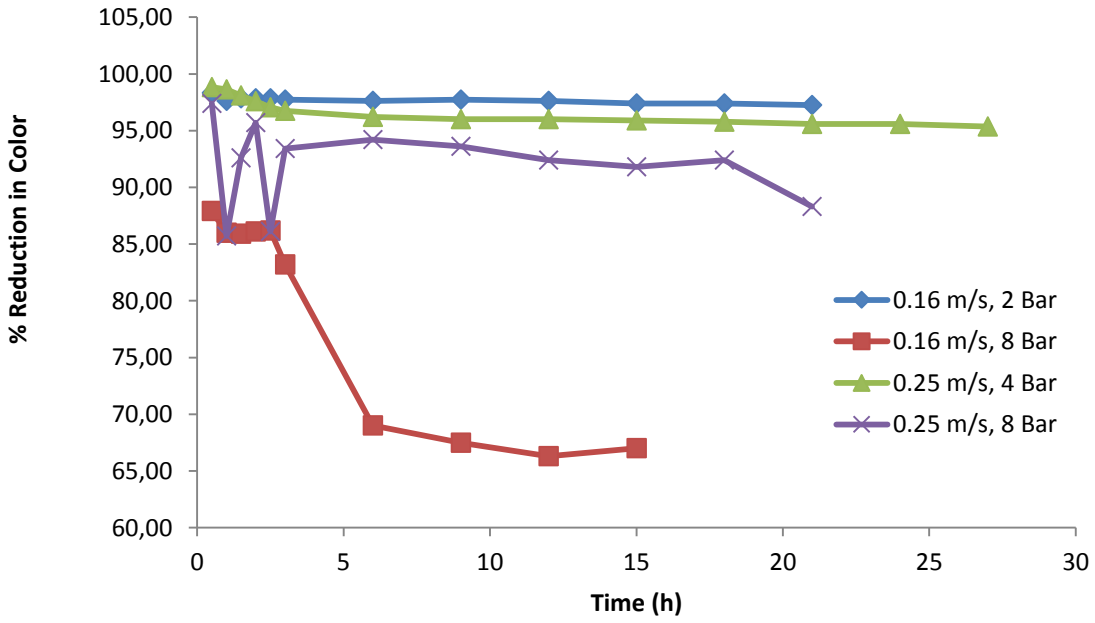

Figure 4.21. Changes in the color of oily-wastewater during the filtration of oily wastewater sample taken before oil removal by fat-trap system using ceramic MF membrane.

Wastewaters used in each filtration experiment were characterized in terms of TSS and oil contents, COD, turbidity and color values. Permeate samples were collected and analyzed for their above stated characteristics. Comparison of the characteristics of the permeate samples with those of the wastewaters made it possible to evaluate efficiency of the microfiltration experiments. The results are given in Table 4.6. No oil was detected in the permeates obtained in all microfiltration experiments. This showed that microfiltration like filtration using supports could be successfully used to remove oil from wastewaters. In general, microfiltration resulted in 99.7, 92.4, 88.9 and 78.4 % reductions in TSS content, COD, color and turbidity values of the wastewaters used. Microfiltration with 0.16 m/s cross flow velocity at 2 bar and microfiltration for CFV of 0.25 m/s at 4 bar were found to be more efficient when the reductions in all the parameters analyzed were taken into consideration. Figure 4.22 shows the wastewater and the permeate sample collected during microfiltration where the cross flow velocity and TMP were 0.16 m/s and 2 bars, respectively for visual comparison.

Table 4.6. Evaluation of the performances of ceramic MF membrane in the filtration of oily-wastewater taken before fat-trap system

Filtration Parameters (CFV) (TMP)		**TSS (mg/L)**	**COD (mg/L)**	**Color (Pt/Co)**	**Turbidity (NTU)**	**Oil (g/L)**
0.16 m/s 2 Bar	**Initial**	1658	7871	839	>1000	4.3
	After Filtration	5	465	21	7	ND*
	% Reduction	**99.7**	**94.1**	**97.5**	**99.3**	**100**
0.16 m/s 8 Bar	**Initial**	11564	44670	>1000	166	15.6
	After Filtration	29	615	111	36	ND*
	% Reduction	**99.7**	**98.6**	**88.9**	**78.4**	**100**
0.25 m/s 4 Bar	**Initial**	4665	9891	951	>1000	4.3
	After Filtration	3	748	29	32	ND*
	% Reduction	**99.9**	**92.4**	**96.9**	**96.8**	**100**
0.25 m/s 8 Bar	**Initial**	11564	44670	>1000	166	15.6
	After Filtration	35	580	66	35	ND*
	% Reduction	**99.7**	**98.7**	**93.4**	**78.9**	**100**

ND*: Not detected

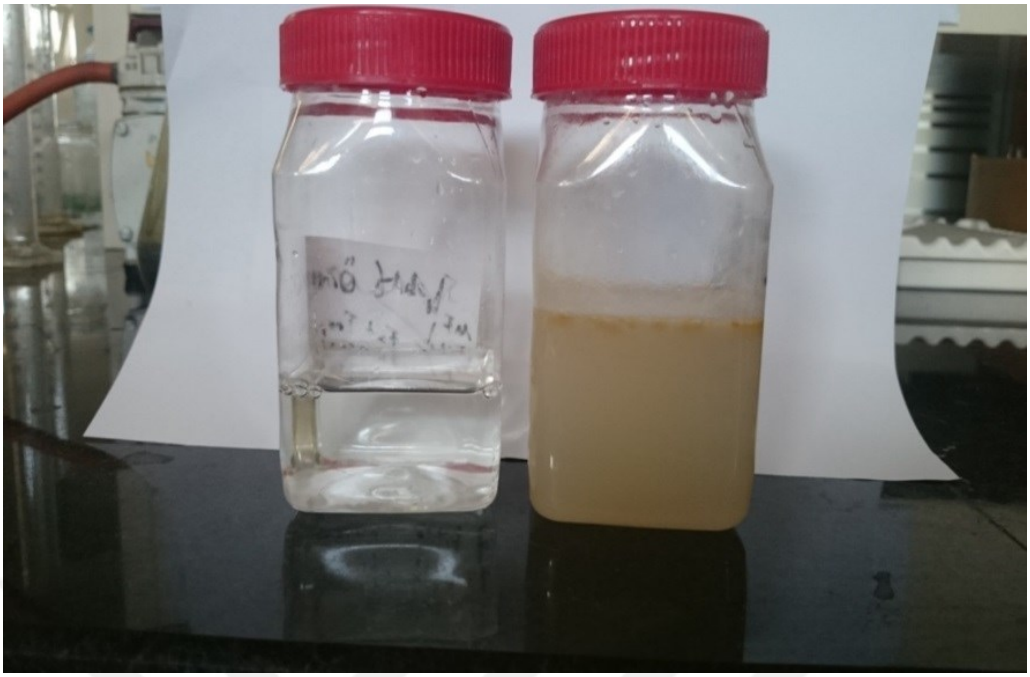

Figure 4.22. Permeate sample collected during microfiltration where the cross flow velocity and TMP were 0.16 m/s and 2 bars and oily-wastewater.

4.2.3. Treatment of Wastewater Sample Taken After Sulfuric Acid Addition Using Ceramic Tubular Membranes

Oil is separated from the wastewater by using fat-trap oil removal system in the wastewater treatment facility of the plant. Sulfuric acid addition is the next step. Since the addition of sulfuric acid converts the fatty acids salts into free fatty acids, wastewater samples were rather obtained after sulfuric acid addition. Ceramic tubular supports and microfiltration membranes were used in the treatment of the wastewater after sulfuric acid addition. Prior the filtration experiments using ceramic membranes, wastewater samples were subjected to vacuum filtration through general purpose filter paper.

4.2.3.1. Filtration Using Supports

Filtration experiments using tubular ceramic supports were performed at TMP values of 4 and 6 bars. Two different cross flow velocities (0.25 and 0.44 m/s) were used at 4 bar TMP. Only one cross flow velocity (0.44 m/s) was selected at 6 bar. Wastewater fluxes over the course of filtration were measured and are shown in Figure 4.23.

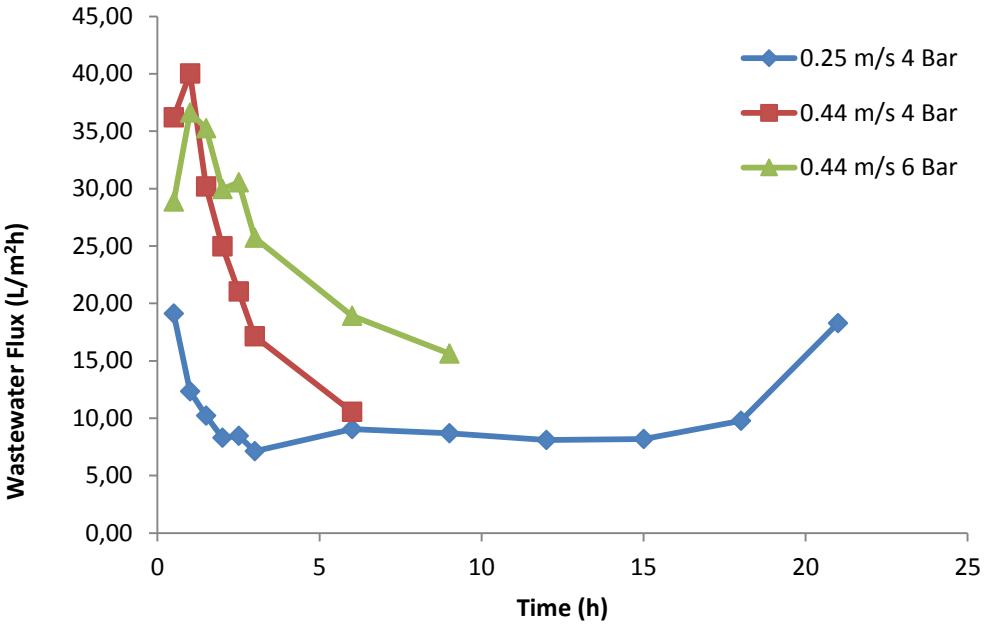

Figure 4.23. Wastewater permeation fluxes during the filtration of wastewater samples obtained after H_2SO_4 addition using tubular ceramic supports.

The highest wastewater fluxes were observed for filtration experiments performed when the cross flow velocity of the wastewater samples was 0.44 m/s. Fluxes which initially ranged between 30-40 L/m^2·h at the beginning of the filtration tend to reduce throughout the filtration experiments. When the cross flow velocity of the wastewater samples was 0.44 m/s, the decrease in the wastewater flux was greater in the filtration experiment where TMP was 4 bar as compared to the experiment performed at 6 bar. The lowest wastewater fluxes were observed in the filtration experiment performed at 4 bar adjusting the cross velocity to 0.25 m/s. The wastewater permeation flux was measured to be around 20 L/m^2·h in the early stages of the filtration and decreased to 7 L/m^2·h onward of filtration. The longer filtration time (21 h) was indicative of low wastewater fluxes. Overall filtration times were 6 and 9 hours for the filtration experiments performed with cross flow velocities of 0.44 m/s at 4 and 6 bars, respectively. Initial flux observed at 4 bar was higher than that observed at 6 bar at constant cross flow velocity (0.44 m/s). As it is inferred from Figure 4.23, increase of TMP from 4 to 6 bar however resulted in higher fluxes after 1 hour of filtration. This was controversial to the results found in the microfiltration experiments using wastewater samples taken before oil removal and after H_2SO_4 addition. The larger pores of the supports compared to microfiltration membranes and the lower oil and TSS content of wastewater samples taken after H_2SO_4 might be the reason for this behavior. Increase in the cross flow velocity from

0.25 to 0.44 m/s at 4 bar however showed that cross flow velocity has a profound effect on the permeate fluxes. Fluxes measured during the filtration of wastewater samples obtained after H_2SO_4 using supports were generally higher than those obtained in the filtration of wastewater samples taken before oil removal. The lower pollution characteristics of the wastewater samples obtained after sulfuric acid addition possibly resulted in the lower degree of fouling.

Changes in TSS content, and turbidity values of the wastewater samples taken after H_2SO_4 addition was measured over the course of filtration experiments. Figure 4.24 and 4.25 show the percent reductions in TSS content and turbidity during the filtration experiments performed using tubular ceramic supports, respectively. TSS reduction during all filtration experiments was around 99.3- 99.5 %. Time dependent reduction in turbidity was found to be ≥ 94 % in the filtration experiments where cross flow velocity and TMP were 0.25 m/s and 4 bar, respectively. Turbidity reductions in the experiments performed at 4 and 6 bar for 0.44 m/s CFV were equal or greater than 97 and 93 %, respectively.

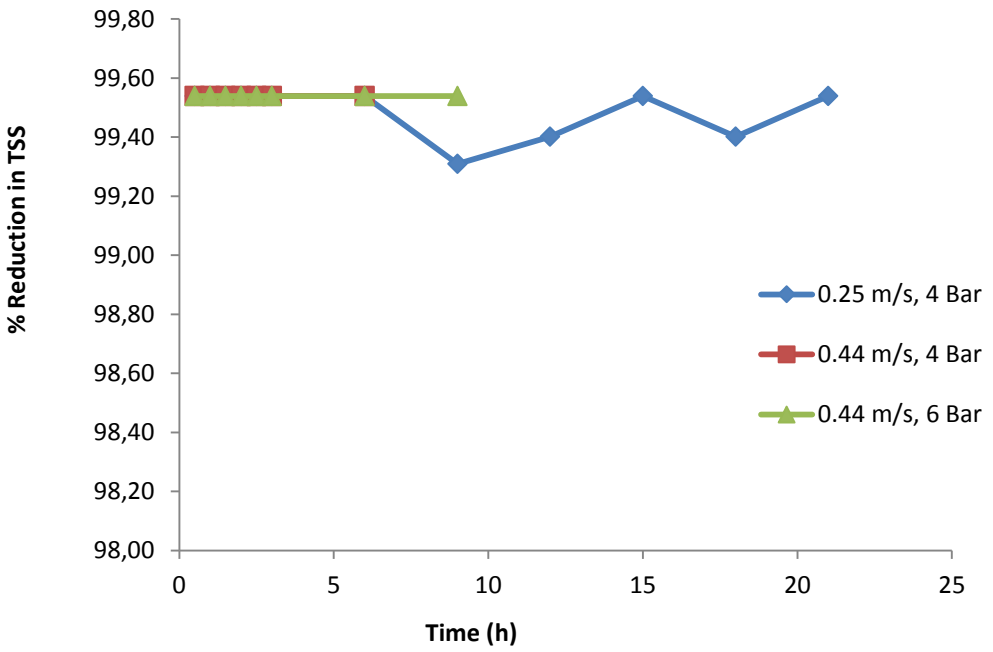

Figure 4.24. Changes in TSS content of wastewater samples obtained after H_2SO_4 addition during the filtration using tubular ceramic support.

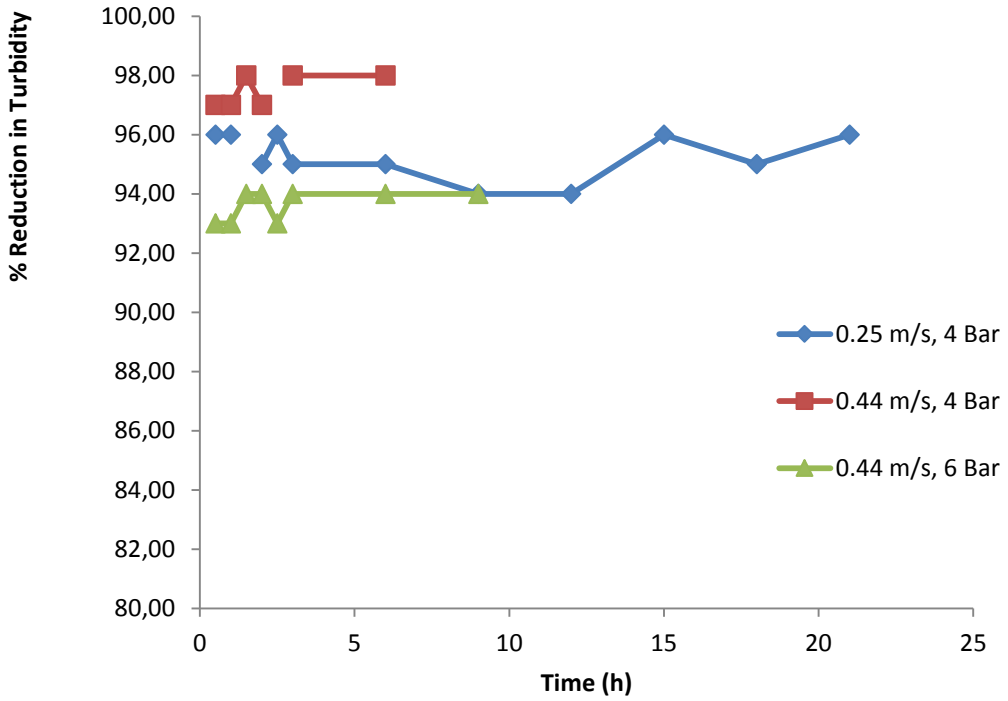

Figure 4.25. Changes in turbidity of wastewater samples obtained after H_2SO_4 addition during the filtration using tubular ceramic support.

When the changes in TSS and oil contents, COD, color and turbidity values of the wastewater samples were determined (Table 4.7), reductions in all parameters except color were found to be similar. In all filtration experiments, oil removal percentages were found as 100 % since no oil was detected in the permeates using oil analysis employed in this study. No color or lower color removal by filtration using tubular ceramic supports suggested that compounds contributing to color of the wastewaters still pass though the supports.

Table 4.7. Evaluation of the performances of ceramic tubular supports in the filtration of wastewater taken after sulfuric acid addition.

Filtration Parameters (CFV) (TMP)		TSS (mg/L)	COD (mg/L)	Color (Pt/Co)	Turbidity (NTU)	Oil (g/L)
0.25 m/s 4 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	<10	500	76	5	ND*
	% Reduction	**99.5**	**92.3**	**-**	**95**	**100**
0.44 m/s 4 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	<10	461	58	3	ND*
	% Reduction	**99.5**	**92.9**	**18.3**	**97**	**100**
0.44 m/s 6 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	12	598	73	6	ND*
	% Reduction	**99.4**	**90.8**	**0**	**94**	**100**

ND*: Not detected

4.2.3.2. Microfiltration

Microfiltration experiments performed using the wastewater samples taken after H_2SO_4 were performed at 4 and 6 bars. Wastewater flow rate in the system was adjusted so that the cross flow velocities of the wastewater samples were 0.16, 0.44 and 0.63 m/s. Wastewater fluxes measured during filtration experiments are shown in Figure 4.26. At 4 bar and the lowest cross flow velocity (0.16 m/s), initial wastewater flux was 8 $L/m^2 \cdot h$ and it reduced to approximately 1.7 $L/m^2 \cdot h$ during the microfiltration. For other cross flow velocities at 4 bar and all cross velocities at 6 bars, wastewater fluxes were found in the range of 1 and 32 $L/m^2 \cdot h$. Microfiltration at 4 bar and for the cross velocity of 0.16 m/s lasted in 27 hours. Other microfiltration experiments however were completed in 6 or 12 hours.

Filtration experiments using both ceramic supports and microfiltration membranes for the treatment of oily wastewater obtained after H_2SO_4 addition showed that cross flow velocity significantly improves permeate flux. Similar effect of cross flow velocity was suggested in the previous studies (Koltuniewicz et al., 1995; Zhong et al., 2003; Ahmad et al., 2005; Hua, Wang, Tsang, Chan, Sin and Chua, 2007). Koltuniewicz and colleagues (1995) stated that

higher cross flow velocities reduces the cake layer thickness at the membrane surface hence the resistance. Increasing transmembrane pressure decreased the permeate flux as it was observed in the microfiltration of wastewater samples taken before oil removal.

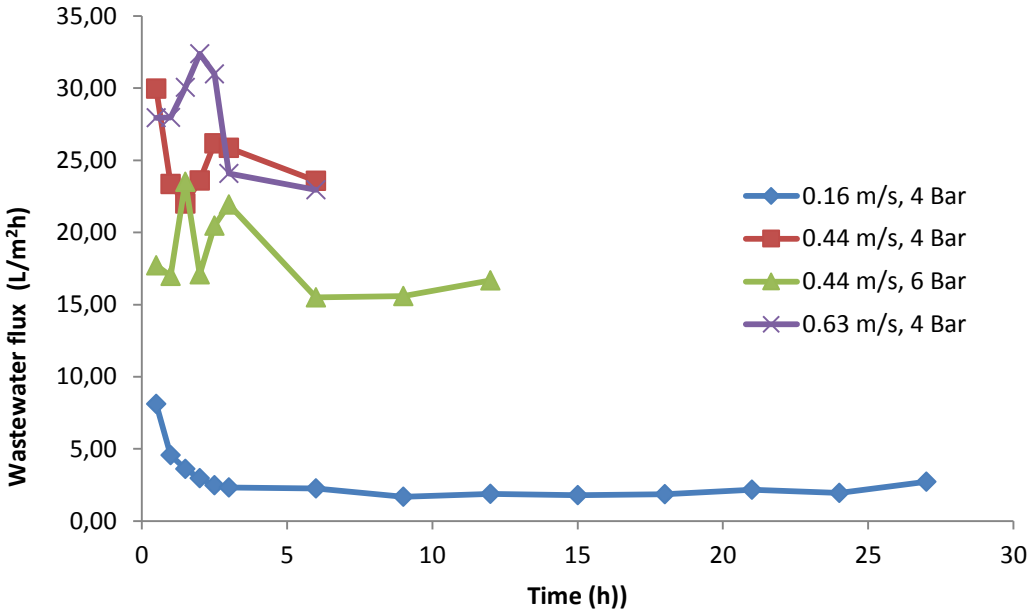

Figure 4.26. Wastewater permeation fluxes during the filtration of wastewater samples obtained after H_2SO_4 addition using ceramic MF membranes.

Percent reductions in TSS content and turbidity values during microfiltration experiments are shown in Figure 4.27 and 4.28, respectively. When the wastewater velocities in the system were 0.44 and 0.68 m/s, reduction in TSS was 99.5 %. However, TSS reduction was decreased to 98 % when cross flow velocity was 0.16 m/s at 4 bar. TSS removal efficiency greater than 98 % showed that the microfiltration membranes can be effectively used to remove suspended solids from aqueous streams.

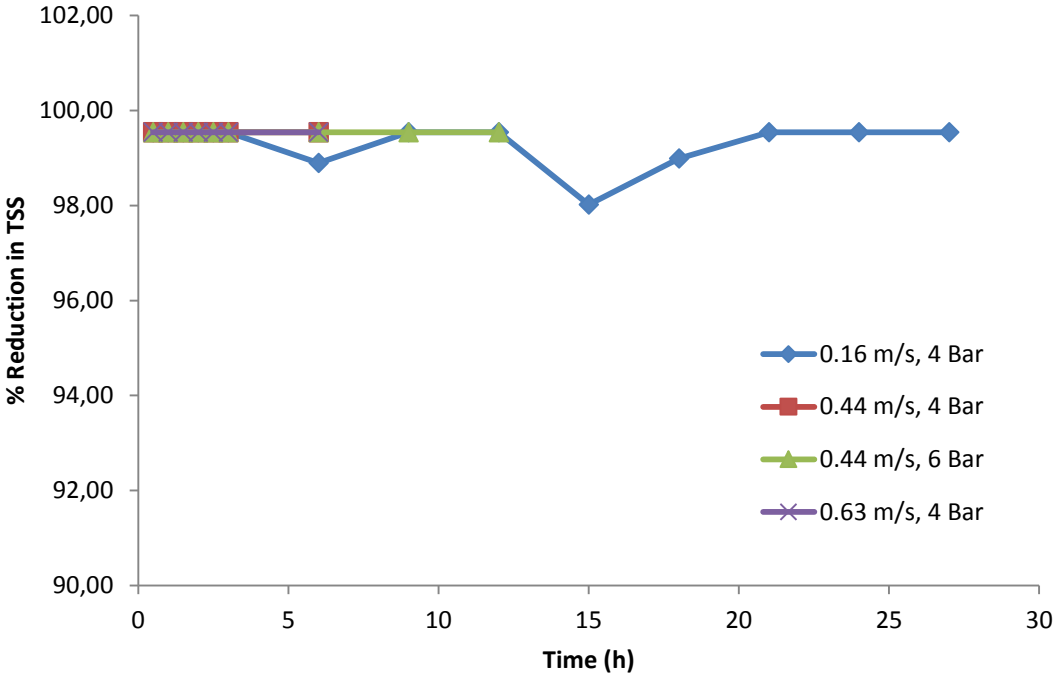

Figure 4.27. Changes in TSS content of wastewater samples obtained after H_2SO_4 addition during the filtration using tubular ceramic MF membranes.

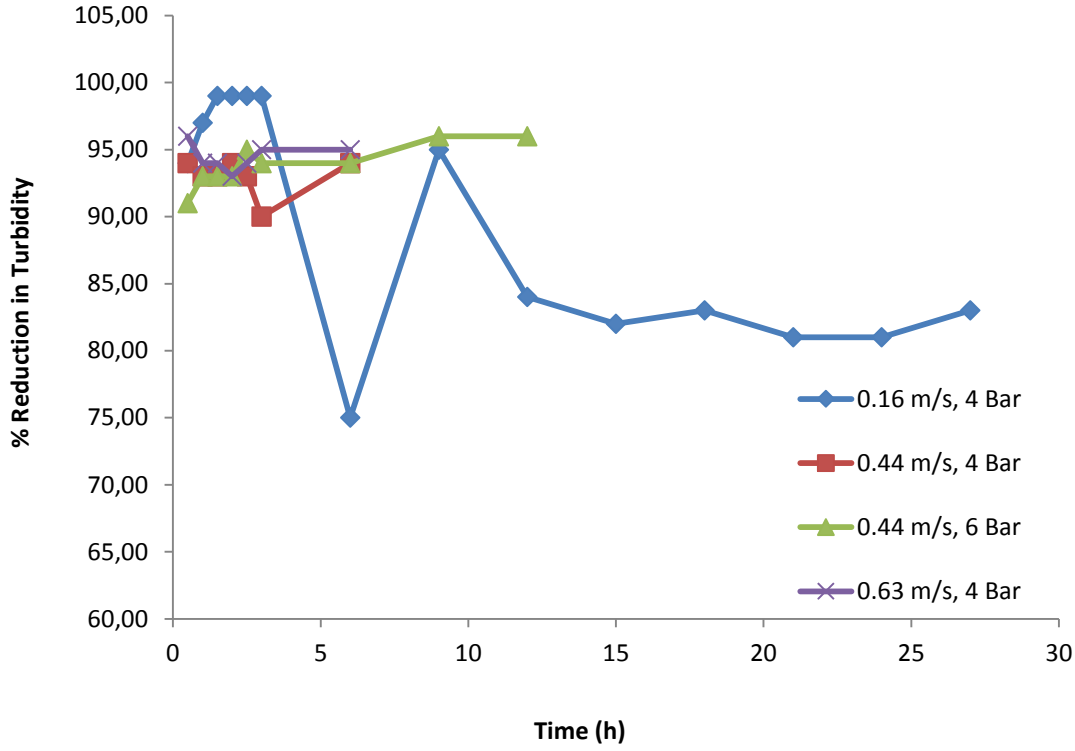

Figure 4.28. Changes in turbidity of wastewater samples obtained after H_2SO_4 addition during the filtration using tubular ceramic MF membranes.

When the time dependent reductions in the turbidity values were determined, the lowest percent reductions were 93 % (CFV: 0.63 m/s, TMP: 4 bar), 91 % (CFV: 0.44 m/s, TMP: 6 bar) and 90 % (CFV: 0.44 m/s, 4 bar). When the cross flow velocity of the wastewater was 0.16 m/s and TMP was adjusted to 4 bars, reduction in turbidity was calculated to be around 75 - 80 %.

Performances of tubular ceramic MF membranes on the treatment of wastewater samples taken after sulfuric acid addition were determined by comparing the parameters of the permeate samples collected after filtration with the initial parameters of wastewater samples (Table 4.8). TSS content which was initially 2171 mg/L was reduced to below 10 mg/L in all microfiltration experiments. Percent reductions were calculated by taking TSS content as 10 mg/L and it was found as 99.5 %. Microfiltration experiments reduced the COD from 6478 mg/L to 438-614 mg/L. The color of the wastewater did not change during the MF experiments. Turbidity value of the wastewater wasgreater than 100 NTU and reduced to the values ranging between 1 and 21 NTU. Oil in the wastewater was removed in all microfiltration experiments performed at different CFV and TMP values.

Table 4.8. Evaluation of the performances of ceramic tubular MF membranes in the filtration of wastewater taken after sulfuric acid addition.

Filtration Parameters (CFV) (TMP)		**TSS (mg/L)**	**COD (mg/L)**	**Color (Pt/Co)**	**Turbidity (NTU)**	**Oil (g/L)**
0.16 m/s 4 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	< 10	614	117	112	ND*
	% Reduction	**99.5**	**90.5**	**-**	**-**	**100**
0.44 m/s 4 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	< 10	438	65	1	ND*
	% Reduction	**99.5**	**93.2**	**8.5**	**99**	**100**
0.44 m/s 6 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	<10	497	71	6	ND*
	% Reduction	**99.5**	**92**	**0**	**94**	**100**
0.63 m/s 4 Bar	**Initial**	2171	6478	71	> 100	1.9
	After Filtration	<10	475	78	21	ND*
	% Reduction	**99.5**	**93**	**-**	**79**	**100**

ND*: Not detected

4.2.4. Treatment of Wastewater Samples Taken After Aluminum Sulfate Addition Using Ceramic Tubular Membranes

Treatment of wastewater samples obtained after $Al_2(SO_4)$ addition was only performed by ceramic tubular supports. Filtration experiments were conducted at 4 and 6 bar transmembrane pressures. Wastewater volumetric flow rate was adjusted so that cross flow velocities of 0.40 and 0.44 m/s at 6 bar and 0.44 m/s at 4 bar were obtained. Initial values of the wastewater fluxes were similar for the same cross flow velocity (0.44 m/s) both at TMP of 4 and 6 bars. The effect of TMP on the wastewater flux was significant after 0.5 hours of filtration and flux started to decrease. This was possibly due to the formation of thicker and/or more compressed cake layer on the membrane surface at higher transmembrane pressure. The wastewater fluxes measured for 0.44 m/s reached to the fluxes measured for cross flow velocity of 0.40 m/s at 6 bar at 10^{th} hour of filtration (Figure 4.29). The highest wastewater fluxes were observed when the cross flow velocity and TMP were 0.44 m/s and 4 bar, respectively. Total filtration times were 12 and 15 hours for 4 and 6 bars for 0.44 m/s cross flow velocity, respectively. Filtration however took 21 hours where cross flow velocity was 0.40 m/s and TMP was 6 bar.

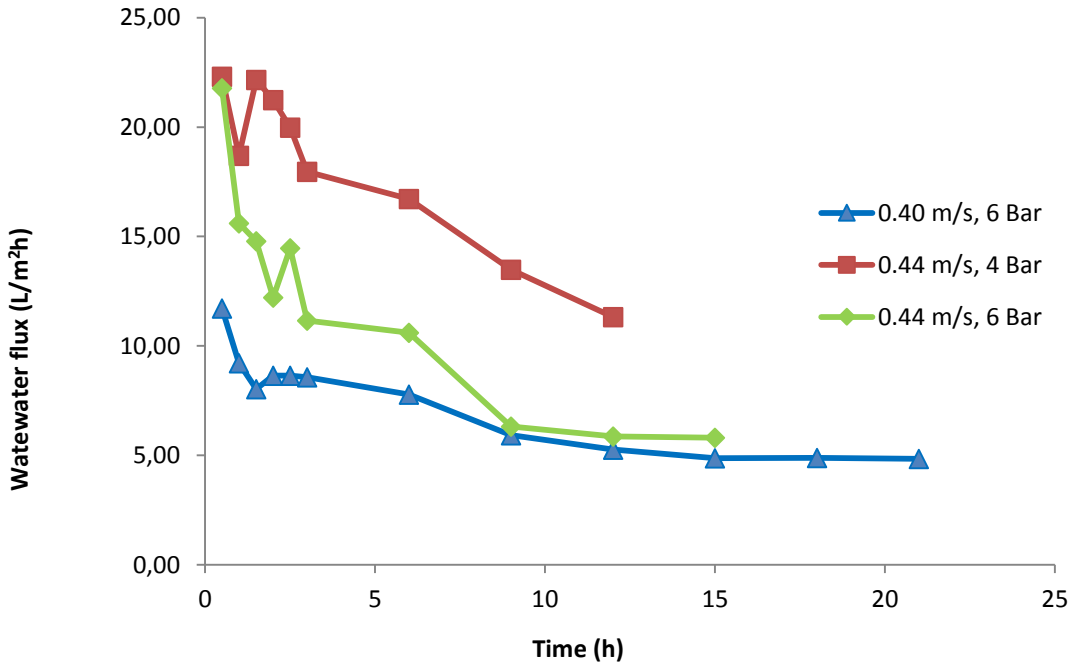

Figure 4.29. Wastewater permeation fluxes during the filtration of wastewater samples obtained after $Al_2(SO_4)_3$ addition using tubular ceramic supports.

Total suspended solid contents of the permeate samples were measured in order to determine the performance of the filtration of wastewater samples obtained after $Al_2(SO_4)$ addition using tubular ceramic supports. In all filtration experiments, TSS removal efficiency was 99 % or greater (Figure 4.30).

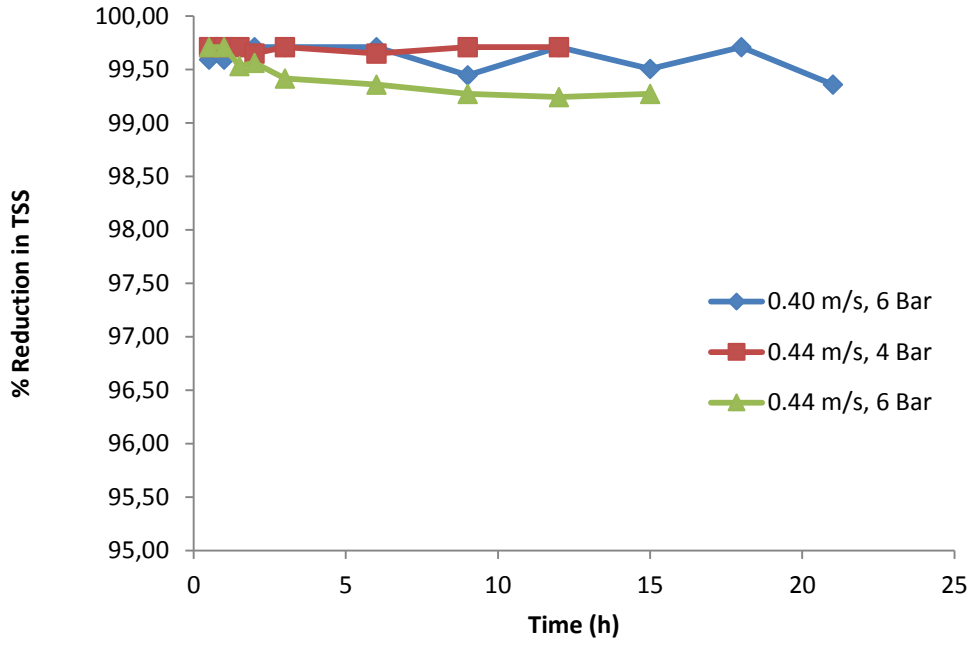

Figure 4.30. Changes in TSS content of wastewater samples obtained after $Al_2(SO_4)_3$ addition during the filtration using tubular ceramic supports.

Turbidity removal efficiency during the filtration of the wastewater was found to be around 98-99 % for the filtration where TMP values were 4 and 6 bars and the cross velocity was adjusted to 0.44 m/s (Figure 4.31). Filtration at 6 bar for the cross flow velocity of 0.40 m/s exhibited similar turbidity reduction percentages. However, the percentage turbidity reduction fell to the values of 92-94 % during the filtration.

Overall evaluation of the filtration of wastewater sample taken after after $Al_2(SO_4)_3$ addition using ceramic tubular supports showed that TSS removal percentages were 99.6 and 99.3% for cross flow velocity of 0.44 m/s at 4 and 6 bars of TMP, respectively (Table 4.9). Filtration at 6 bar but for cross flow velocity of 0.40 m/s gave 97.1 % reduction in TSS. Reductions in COD and turbidity were found to be similar in all filtration experiments. Color removal percentages were around 63-64 % for both cross flow velocities employed at 6 bar. It was

found as 71 % at 4 bar. Any oil could not be detected in all filtrate samples collected during all filtration experiments. Oil removal efficiency is therefore considered as 100 %.

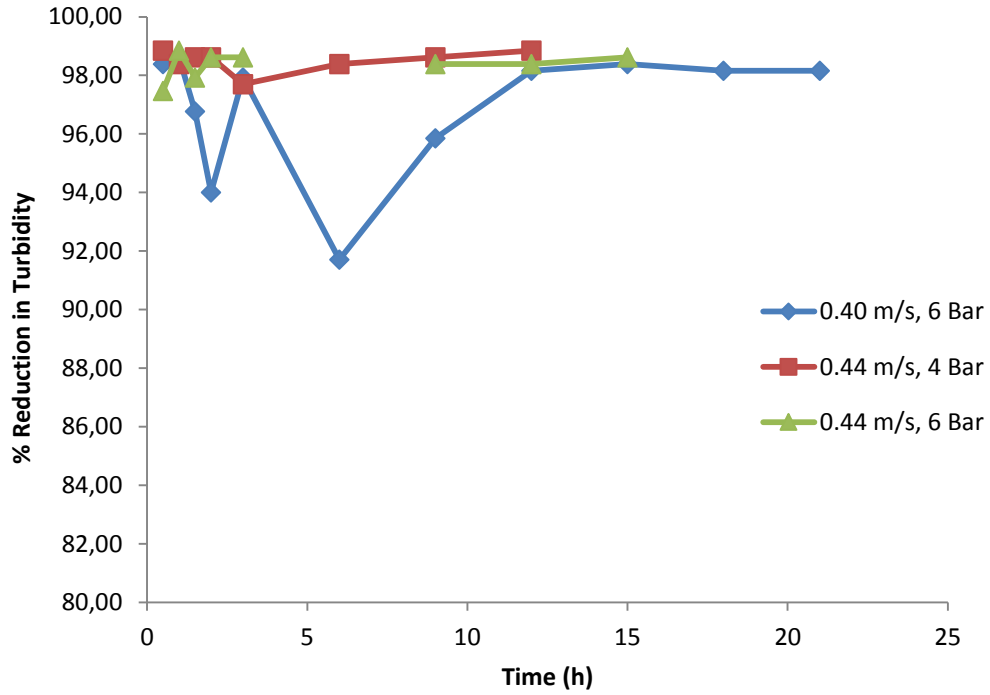

Figure 4.31. Changes in turbidity content of wastewater samples obtained after $Al_2(SO_4)_3$ addition during the filtration using tubular ceramic supports.

Table 4.9. Evaluation of the performances of ceramic tubular supports in the filtration of wastewater taken after after $Al_2(SO_4)_3$ addition.

Filtration Parameters (CFV) (TMP)		**TSS (mg/L)**	**COD (mg/l)**	**Color (Pt/Co)**	**Turbidity (NTU)**	**Oil (g/L)**
0.40 m/s 6 Bar	**Initial**	3432	14687	381	434	3.3
	After Filtration	99.7	767	143	8	**ND***
	% Reduction	**97.1**	**94.8**	**62.5**	**98.2**	**100**
0.44 m/s 4 Bar	**Initial**	3432	14687	381	434	3.3
	After Filtration	14	778	110	8	ND*
	% Reduction	**99.6**	**94.7**	**71.1**	**98.2**	**100**
0.44 m/s 6 Bar	**Initial**	3432	14687	381	434	3.3
	After Filtration	23.0	812	138	8	**ND***
	% Reduction	**99.3**	**94.5**	**63.8**	**98.2**	**100**

ND*: Not detected

The lower wastewater fluxes observed in all filtration experiments compared to clean water fluxes of membranes showed that severe fouling and significant flux decline occurred during filtration of oily wastewater. Fouling resistances in ceramic membrane filtration of oily wastewater were studied in several studies. Cake filtration (Koltuniewicz et al., 1995; Lobo, Cambiella, Benito, Pazos and Coca, 2006; Nandi, Moparthi, Uppaluri and Purkait, 2010; Abbasi, Sebzari, Salahi and Mirza, 2012; Kumar, Ghoshal and Pugazhenthi, 2015) or internal fouling followed by external fouling (thin oil layer) (Mueller et al., 1997) were proposed as a resistance model describing fouling and flux decline. When the effects of cross velocity and transmembrane pressure on the permeate flux in all filtration experiments performed in this sttudy were compared, It can be concluded that in general cross flow velocity increases but transmembrane pressure decreases permeate flux.

Filtration of oily wastewaters obtained from food industry using tubular ceramic supports and MF membranes resulted in significant reductions in the pollution characteristics of the wastewaters. Percent reductions in TSS, COD, turbidity, color values and oil content of the wastewater samples were found to be 97-99 %, 91-98 %, 78-99 %, 63-99 % and 100 %, respectively.

5. CONCLUSIONS

Bare, MF and UF layer coated tubular supports were prepared in this thesis. Bare supports were prepared by extrusion of paste prepared from α-Al_2SO_4 powder. Microfiltration layers were prepared by dip coating of the heat –treated supports using α-Al_2SO_4 sol and thermal treatment at 1200°C. Ultrafiltration layer coating however was performed by dip coating boehmite sol on MF layers and thermal treatment at 600°C.

Food industry wastewaters were obtained from the different stages in the wastewater treatment facility of food processing plant. Wastewater samples were oil-containing wastewaters. They were sampled before oil removal by fat-trap system, after sulfuric acid addition, after aluminum sulfate addition and from equilibration. They were characterized in terms of pH, TSS, COD, turbidity, color and oil contents. Tubular ceramic supports, MF and UF membranes were evaluated for their effectiveness in the treatment of the wastewater samples. Preliminary experiments were performed using the wastewater samples obtained from equilibration. Since the wastewater had the lowest TSS, COD, turbidity and color values, tubular ceramic MF and UF membranes were used in the filtration of this wastewater. Comparison of clean water and wastewater permeation fluxes showed that flux decline due to fouling was not observed in the MF filtration. COD, TSS, turbidity and color reductions were found to be 5.5, 52.5, 93.1 and 9.5 %, respectively. The wastewater flux decline was significant in the treatment of this wastewater. Ultrafiltration resulted in higher percentages in the reduction of COD, turbidity and color as it was expected.

The highest levels of TSS, COD, turbidity, color and oil were observed for the wastewater sample taken before oil removal by fat-trap system. Tubular ceramic supports and MF membranes were therefore selected for the filtration of this wastewater. The filtration experiments ceramic supports were performed at 4 bar. Wastewater volumetric flow rates were adjusted so that three different cross velocities of the wastewater were obtained (0.25, 0.35 and 0.4 m/s). Initial wastewater permeation fluxes ranged between 7-11.5 $L/m^2 \cdot h$ and reduced to 1-2.6 L/m2·h. This showed that the fouling of the supports was severe in this case. Microfiltration at 4 bar with the cross velocity of 0.25 m/s showed significant reductions in TSS, turbidity and color. In contrast COD reduction was lower (90.1 %) than those observed for cross velocities of 0.35 and 0.44 m/s (98.1 %). Microfiltration experiments were

performed at 2 and 8 bar for cross flow velocity of 0.16 m/s and 4 and 8 bar for 0.25 m/s. Flux decline was greater in microfiltration when compared to the filtration using supports. Initial fluxes ranging between 3 and 7 $L/m^2 \cdot h$ were reduced to 0.7 – 2.1 $L/m^2 \cdot h$ at the end of filtrations. When the filtration experiments for constant cross flow velocities at different pressures showed that increase in TMP was found to increase COD reduction percentage but decrease color and turbidity removal percentages. When the reductions in the color were considered, increase in cross flow velocity resulted in the increase in color removal percentage. When the filtration using tubular ceramic support and microfiltration at 4 bar and for cross flow velocity of 0.25 m/s were compared, the reductions in the TSS, COD, color, turbidity and oil were similar. This suggests that the oil and lipids present in the wastewater samples cause fouling of the supports and microfiltration membranes and fouling contributes to the filtration performances at the expense of reductions in the permeate fluxes.

During the filtration of wastewater samples obtained after removal oil and sulfuric acid addition using supports, wastewater fluxes reduced to 11-18 $L/m^2 \cdot h$. Flux decline in the filtration of this wastewater was not as severe as it was observed in the filtration of oily wastewater samples obtained before oil removal. This suggests that the main cause of the fouling of membranes is the oil and similar compounds in the wastewater. Two cross flow velocities selected (0.25 and 0.44 m/s) at 4 bar gave almost similar reductions in TSS, COD and color. Increasing TMP to 6 bar for 0.44 m/s cross flow velocity decreased the COD removal efficiency slightly. Wastewater fluxes obtained during microfiltration showed that increase in cross flow velocity increases permeate flux while increase in TMP reduces the flux. Permeate flux recorded at the end of MF experiments was greater than that measured at the end of filtration using supports. This is possibly related to the smaller pore size of the microfiltration membrane which reduces the fouling of the membrane pores. All MF experiments resulted in 90 or greater percentage reductions in TSS and COD. Turbidity reduction decreased with the increase in cross flow velocity to 0.63 m/s at 4 bar.

The last wastewater used was the wastewater taken after $Al_2(SO_4)_3$ addition. Filtration experiments performed using supports yielded wastewater fluxes 5 to 11 $L/m^2 \cdot h$. Reductions in TSS, COD, turbidity (94.7-99.6 %) and color (62.5-71.1 %) were similar in filtration experiments performed.

In conclusion, filtration using ceramic tubular supports and microfiltration membranes can be effectively remove suspended solids and compounds contributing to COD, color and turbidity depending on the nature of the wastewater. Permeate flux reduction actually fouling however is a serious concern for the treatment of wastewaters which have higher oil and suspended solid materials. Careful determination of wastewater characteristics and selection of ceramic membrane according to the wastewater characteristics and operational parameters should be made. Several preliminary processes such as oil removal and flocculation can be performed prior the filtration using ceramic supports, MF and UF membranes in order to retain higher permeate fluxes.

6. RECOMMENDATIONS

The recommendations on the studies to be performed on the treatment of oily wastewater samples from food industry are listed below:

1.Wastewater characteristics show variations depending on the processing capacity of the plant. These variations should be considered when the evaluation of the performance of the filtration experiments.

2. The permeate flux decline is severe for the wastewater which has higher amounts of oil and materials contributing to TSS and turbidity. The preliminary processes such as oil removal and flocculation will help increase the permeate flux.
Ceramic UF or nanofiltration membranes should be used for the wastewater samples having lower values of TSS, COD, turbidity, color and oil such as the wastewater samples obtained from equilibration stage.

3. Oily wastewater from food industry contains oil and phospholipids such as lecithin. These can be adsorbed on the internal surfaces the membranes or clog the membrane pores. Making the membrane surfaces more hydrophilic will probably reduce the flux decline and decrease the membrane fouling.

4. Cross flow velocities used in this thesis were in the range 0.16 to 0.44 m/s. These are relatively lower cross velocities. Filtration experiments using tubular supports, MF and UF membranes at the various transmembrane pressures by setting the cross flow velocity of the wastewaters at higher levels are suggested. Performances of the ceramic membranes for higher cross flow velocities should be evaluated.

5. The treatment of oily wastewater from food industry using ceramic membranes can also be determined by sequential filtration, filtration through support, MF and UF depending on the wastewater characteristics.

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CURRICULUM VITAE

DEMET CAVLAK GÖÇER

Address	**:** Pınar Mah. 74225 Sok. Saklıkent Sitesi B Blok Kat:12 No:24 Seyhan/ADANA
E-mail	**:** demetcavlak@gmail.com
Birth date/place	**:** 28-02-1985 / Adana
Marital Status	**:** Married
Driving License	**:** B Class (2004)

EDUCATION:

2015 – 2019	Adana Alparslan Türkeş Science and Technology University-Institute of Natural and Applied Sciences, Department of Nanotechnology and Engineering Sciences, MSc Thesis
2011 – 2015	Anadolu University Faculty of Business Administration, Department of Business Administration
2003 – 2008	Hacettepe University Faculty of Engineering, Department of Chemical Engineering (English)

WORK EXPERIENCE:

- (March 2018 -) **KOÇAK ENVIRONMENTAL CO., Adana Hacı Sabancı Industrial Zone Domestic and Industrial Wastewater Treatment Plant Operation, ADANA**
  Wastewater Treatment Plant Operating Manager
- (March 2011- March 2018) **PRESIDENCY OF ADANA HACI SABANCI INDUSTRIAL ZONE, Directorate of Treatment Plants, ADANA**
  Director of Treatment Plants
- (November 2008- March 2011) **KADOOĞLU OIL CO., GAZIANTEP**
  Quality Control Chief

LANGUAGE SKILLS:

- **English** **:** Advanced
- **German** **:** Elementary

COMPUTER SKILLS:

- **Programming Languages** **:** JAVA, Matlab, ChemCAD
- **Application Programs** **:** MS Office Programs