

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

(MSc THESIS)

**AZO DYE DEGRADATION BY ADVANCED
OXIDATION METHODS USING METAL
IMPREGNATED ORGANIC WASTE CATALYST AND
COMPARATIVELY BIOLOGICAL OXIDATION**

Burcu PALAS

Supervisor : Prof. Dr. Süheyda ATALAY

Chemical Engineering Department

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Burcu PALAS tarafından yüksek lisans tezi olarak sunulan “Azo boyar maddelerin organik atık üzerinde metal emdirilmiş bir katalizör kullanılarak ileri oksidasyon yöntemleriyle ve karşılaştırmalı olarak biyolojik oksidasyon ile giderimi-Azo dye degradation by advanced oxidation methods using metal impregnated organic waste catalyst and comparatively biological oxidation” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 27.08.15 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

Jüri Üyeleri:

İmza

Jüri Başkanı : Prof. Dr. Süheyda ATALAY

.....

Raportör Üye : Prof. Dr. Ferhan ATALAY

.....

Üye : Prof Dr. Murat ELİBOL

.....

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İmza

Burcu PALAS

ÖZET**AZO BOYAR MADDELERİN ORGANİK ATIK ÜZERİNDE METAL
EMDİRİLMİŞ BİR KATALİZÖR KULLANILARAK İLERİ
OKSİDASYON YÖNTEMLERİYLE VE KARŞILAŞTIRMALI OLARAK
BİYOLOJİK OKSİDASYON İLE GİDERİMİ**

PALAS, Burcu

Yüksek Lisans Tezi, Kimya Mühendisliği Anabilim Dalı

Tez Danışmanı: Prof. Dr. Süheyda ATALAY

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Bu çalışmada Procion Red MX-5B azo boyar maddesinin çeşitli ileri oksidasyon yöntemleri ve biyolojik oksidasyon ile giderimi karşılaştırmalı olarak incelenmiştir. İleri oksidasyon yöntemleri kapsamında ceviz kabuğundan elde edilen aktif karbon üzerine demir emdirilmiş katalizör kullanılarak Fenton benzeri oksidasyon, fotokatalitik oksidasyon, foto-Fenton benzeri oksidasyon ve katalitik ıslak hava oksidasyon uygulanmıştır. Biyolojik oksidasyonda ise ceviz kabukları; boya giderimi için gerekli enzimleri salgılayacak olan *Phanerochaete chrysosporium* ve *Trametes versicolor* mantar türleri için besin ve tutunma yüzeyi olarak kullanılmıştır.

İleri oksidasyonda katalizör destek malzemesi olarak kullanılan aktif karbon, ceviz kabuklarından, fiziksel aktivasyon ve potasyum hidroksit (KOH), nitrik asit (HNO₃) ve çinko klorür (ZnCl₂) aktivasyonu olmak üzere üç farklı kimyasal aktivasyon yöntemi ayrı ayrı uygulanarak hazırlanmıştır. Hazırlanan her bir aktif karbon üzerine demir emdirilerek Fe/Aktif Karbon ve Fe-TiO₂ emdirilerek Fe-TiO₂/Aktif Karbon katalizörler elde edilmiştir. Fe/Katalizör ve Fe-TiO₂/Katalizör oranları kütlece 1:10 olarak belirlenmiştir. Fe/TiO₂ oranı ise kütlece 1:100'dür. Fe/TiO₂ oranı kütlece 1:100'dür. Fe/Aktif Karbon katalizörlerin performansları çalışma kapsamındaki tüm ileri oksidasyon yöntemlerinde test edilirken Fe-TiO₂/Aktif Karbon katalizörler sadece fotokatalitik oksidasyonda kullanılmıştır. Hazırlanan katalizörler Taramalı Elektron Mikroskopu, X-Işını Difraktometresi ve Brauner Emmett Teller yöntemi

ile analiz edilmiştir. Fenton benzeri ve foto-Fenton benzeri oksidasyonunda en yüksek giderim, KOH aktivasyonu ile hazırlanan katalizörün kullanımında gözlenirken, katalitik ıslak hava oksidasyonunda ise en yüksek giderim $ZnCl_2$ aktivasyonu ile hazırlanan katalizörün kullanımında elde edilmiştir. Katalizör seçimi deneylerinin ardından her bir ileri oksidasyon yönteminde en yüksek performansı gösteren katalizör varlığında optimum reaksiyon koşullarının belirlendiği parametrik çalışmalar yürütülmüştür. Optimum koşullar altında Fenton benzeri, foto-Fenton benzeri, ve katalitik ıslak hava oksidasyonunda sırasıyla %51.6, %50 ve %27.1 boya giderimi, %91.6, %88 ve %13.9 renk giderimi gözlenmiştir. En yüksek boya giderimi değerlerinin sağlandığı Fenton benzeri oksidasyonu için toksisite analizi ve kinetik çalışma yapılmıştır. *Lepidium sativum* tohumları ile gerçekleştirilen toksisite analizinde kök uzamasındaki inhibisyon %1.1 olarak hesaplanmıştır. Renk giderimi verilerinin 30-60°C reaksiyon sıcaklığı aralığında yalancı birinci mertebe, 70°C’de ise yalancı ikinci mertebe reaksiyon kinetiğine uyduğu saptanmış, aktivasyon enerjisi 47.36 kJ/mol bulunmuştur.

Ceviz kabuklarına *Phanerochaete chrysosporium* ve *Trametes versicolor* immobilize edilmesiyle gerçekleştirilen biyolojik oksidasyon kapsamında mikroorganizma seçimi deneylerinde *Trametes versicolor* ile daha yüksek boya giderimi sağlandığı belirlenmiştir. Optimum reaksiyon koşulları altında %52.7 renk giderimi ve %5.1 boya bozunumu elde edilmiştir. Biyolojik oksidasyon ve ileri oksidasyon yöntemleri karşılaştırıldığında Fenton benzeri ve foto-Fenton benzeri yöntemlerinin boya gideriminde biyolojik arıtmaya göre çok daha etkin oldukları tespit edilmiştir.

Anahtar kelimeler: Aktif karbon, Azo boyar madde, Biyolojik oksidasyon, Ceviz kabuğu, İleri oksitlenme süreçleri.

ABSTRACT**AZO DYE DEGRADATION BY ADVANCED OXIDATION METHODS
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PALAS, Burcu

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In this study, the removal of Procion Red MX-5B azo dye was investigated using several advanced oxidation methods in the presence of walnut shell based catalysts and comparatively biological oxidation in which the walnut shells were used as immobilizing agent for the microorganisms. The advanced oxidation methods comprising Fenton like oxidation, photocatalytic oxidation, photo-Fenton like oxidation and catalytic wet air oxidation (CWAO) were applied in the presence of iron on activated carbon catalysts (Fe/AC) containing 10% iron by weight. In addition to Fe/AC, Fe-TiO₂ loaded on activated carbon catalysts (Fe-TiO₂/AC) were used in photocatalytic oxidation. (Fe-TiO₂)/Catalyst:1/10 by wt. and Fe/TiO₂:1/100 by wt. in the photocatalyst. In the biological oxidation, due to the oxidizing enzymes they secreted, the white rot fungi *Phanerochaete chrysosporium* and *Trametes versicolor* were selected to remove Procion Red MX-5B.

The activated carbon, which was used as catalyst support, were prepared using physical activation and three chemical activation methods, using HNO₃, ZnCl₂ and KOH agents. The catalysts were characterized by Scanning electron Microscopy, X-Ray Diffractometry and Brauner Emmett Teller analyses. The performances of the catalysts were compared in the catalyst screening experiments. The highest removal efficiencies in the Fenton like, photo-Fenton like processes were obtained in presence of KOH activated catalyst whereas ZnCl₂ activated catalyst was the most efficient one in the CWAO.

Parametric studies were carried to determine of the optimum conditions for each of the advanced oxidation method in the presence of the most suitable catalyst. Under the optimum reaction conditions, the degradation efficiencies are calculated as 51.6%, 50%, 27.1% and the decolorization efficiencies were evaluated as 91.6%, 88% and 13.9% in the Fenton like, photo-Fenton like, and CWAO processes, respectively. Toxicity tests and kinetic study were performed for Fenton like oxidation which was determined to be the most efficient one among the advanced oxidation methods tested in this study. The toxicity tests with *Lepidium sativum* showed that the growth inhibition was 1.1% after the treatment. It was found that the decolorization kinetics of Procion Red MX-5B followed pseudo-first order reaction kinetics in the temperature range of 30-60°C and pseudo-second order reaction kinetics at 70 °C. The activation energy was determined by 47.36 kJ/mol.

In the biological oxidation *Phanerochaete chrysosporium* and *Trametes versicolor* were immobilized on walnut shells to treat solutions of Procion Red MX-5B. *Trametes versicolor* was determined to be more effective in decolorization in comparison with *Phanerochaete chrysosporium* and 52.7% decolorization and 5.1% degradation were observed under optimum reaction conditions in the presence of this fungus.

When the efficiencies of the biological and advanced oxidation methods are compared Fenton like and photo-Fenton like oxidation methods were determined to be much more effective than the biological oxidation method.

Keyword: Activated carbon, Advanced oxidation, Azo dyestuffs, Biological oxidation, Walnut shells.

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1. INTRODUCTION

Textile dyes are one of the most common hazardous organic compounds constituting threat to the environmental health. Up to 20% of the dyes released in the industrial effluents during the dying processes (Akpan et al., 2009). More than 60% of the dyestuffs are consumed in textile industry and a remarkable amount of these dyes are discharged into water bodies (Pachhade et al., 2009). The textile effluents are deeply colored and affect aquatic life by blocking sunlight penetration, which significantly decreases the amount of dissolved oxygen (Yoon et al., 2012). Azo dyes contain one or more azo bonds ($-N=N-$), and they are widely used in the textile, paint, plastic, foodstuff and cosmetic industries. Some azo dyes are toxic and mutagenic to organisms and known to have potential carcinogens which may result in destruction of aquatic communities. Therefore treatment of textile effluents containing dyes prior to their discharge into water bodies is crucial (Yoon et al., 2012).

Conventional treatment methods for such effluents include adsorption, membrane filtration, coagulation and flocculation and activated sludge. Most of the conventional methods generate great amounts of sludge and solid waste which cannot satisfy the discharge limitations and need further treatment before disposal. These methods generally transfer the pollutants from one phase to another phase rather than degrading them (Abo-Farha, 2010). Recently, advanced oxidation processes (AOPs) are used to remove toxic and persistent pollutants (Su et al., 2011). AOPs are considered as the most efficient alternative methods for textile waste-water treatment since highly reactive radicals are generated during these processes (Ling et al., 2010). Common AOPs involve Fenton, Fenton-like, photo-Fenton, ozonation, photo chemical and electrochemical oxidation, sonolysis, wet oxidation, super critical water oxidation and so on.

A particularly promising AOP is Fenton process which has many advantages such as high performance in decolorization, simplicity and inexpensiveness (Mesquita et al., 2012). In the Fenton process, the hydroxyl radicals are produced by hydrogen peroxide and the iron catalyst (Su et al., 2011). This method destroys organic compounds while most of the conventional methods fail due to the high toxicity or complex chemical structure of the pollutants. In

addition, Fenton and Fenton like oxidations are carried out under mild operating conditions (atmospheric pressure and low temperatures) and don't require complicated equipment. The oxidant, hydrogen peroxide is an environmentally friendly reagent which decomposed into harmless products (H_2O and O_2) (Duarte et al., 2011). In addition to these, high reactions yields with a low cost treatment can be accomplished by the application of Fenton oxidation (Torrades and Montano, 2014). The photo degradation which is one of the most common and efficient AOPs, occurs with the attack of organic pollutants by the activated oxygen species like the superoxide and hydroxyl radicals, formed on the catalyst surface by the oxidation of surface hydroxyl or reduction of dissolved oxygen in solution. The major advantage of advanced oxidation processes over the conventional methods of waste treatment is complete mineralization of the organic compounds (Mahadwad et al., 2011). Wet air oxidation (WAO) is known as one of the most efficient advanced oxidation methods to eliminate highly toxic and concentrated organic pollutants under high pressure and temperature using oxygen as the oxidant without the emissions of dioxins, furans, NO_x , SO_2 , HCl . However, the severe operating conditions increase the cost of the treatment and limit application of this method. In catalytic wet air oxidation (CWAO), a catalyst is added into the system of traditional WAO, thus it reduces the harsh reaction conditions, increases the oxidation capacity of oxidants and shortens reaction time and thereby it reduces the investment in operating costs (Jing et al., 2012).

Although using the homogenous catalysts, such as metal salts, are very effective in advanced oxidation processes, an additional metal separation or recovery step are required to remove the metal ions from the treated solution. So, development of active heterogeneous catalysts is necessary (Kequ et al., 2010, Kim and Ihm 2011). Activated carbon is one of the most common support materials since it exhibits several significant advantages such as high stability and porous structure leading to high surface areas. There are two main steps in preparation of activated carbon including the carbonization of raw material, and chemical or physical activation step. In carbonization step, the raw material is pyrolyzed under an inert atmosphere so in order to remove volatile matter is removed (Aworn et al., 2008). In the activation step, physical or chemical activation is applied. In the physical activation, the carbonizate is subjected to

steam, CO₂, or other oxidizing gases at high temperatures (Yang and Lua, 2003). In the chemical activation, a chemical agent is used to develop the porous structure, to retard the formation of tars and to increase the carbon yield during the carbonization process. In the chemical activation various agents such as zinc chloride, potassium hydroxide and alkaline metals are used (Joseph et al., 2008).

Another remarkable alternative wastewater treatment method is innovative biological oxidation methods. Among them treatment of the dye containing wastewater by white rot fungi which secrete highly oxidative peroxidase and laccase enzyme is one of the most environmentally friendly and efficient one.

When the azo dye oxidation studies reviewed in literature it is concluded that usage of organic waste activated carbons as adsorbent has been investigated extensively. However, many of these studies focused on only the comparison of surface area and adsorption capacities of the activated carbons. Though a few studies on usage of organic waste based activated carbon in catalytic process are reported, in neither of these studies activated carbon support is derived from walnut shells. Also, using an organic waste as catalyst support in chemical oxidation and as immobilizing agent in biological oxidation processes is an innovative approach that has never been studied so far.

In this frame, the main objective of this study is to replace the conventional wastewater treatment methods, which have already been applied in industry, with the innovative advanced oxidation and biological oxidation methods using organic waste based catalyst or microorganism carriers. In this context, the degradation and the decolorization of Procion Red MX-5B was investigated using several advanced oxidation methods comprising Fenton like oxidation, photocatalytic oxidation, photo-Fenton like oxidation and catalytic wet air oxidation in the presence of walnut shell based catalyst supports. In the biological oxidation section *Phanerochaete chrysosporium* and *Trametes versicolor* immobilized on walnut shell powder were used to treat Procion Red MX-5B solutions. Procion Red MX-5B was selected as model pollutant because of its complex chemical structure and high water solubility. In the advanced oxidation processes walnut shells used to prepare activated carbon catalyst support on which iron or Fe-TiO₂ was impregnated. The activated carbons were prepared by several physical and

chemical activation methods using HNO_3 , ZnCl_2 and KOH as activation agents. After the catalyst screening experiments were performed, the optimum reaction conditions were determined in the presence of the most suitable catalyst determined for each of the advanced oxidation method. In the biological treatment, the white rot fungi *Trametes versicolor* and *Phanerochaete chrysosporium* were immobilized on walnut shell powder. The optimum reaction conditions were determined after the microorganism selection experiments.

2. THEORETICAL BACKGROUND

2.1. Industrial Wastewaters

Water is an essential natural resource for the living beings and is a significant factor in industrial activities of various consumer goods (Rosa et al., 2012). Water sources are polluted due to the many reasons such as climate change, growing population, problematic urbanization. The pollution of water bodies is, nowadays, a serious threat to environment, influencing human health and ecosystems.

The effluents, discharged from most of the industries pose a threat to the human health. Wastewater is produced in almost all industries which use water such as pulp and paper, textile, dyes, painting, cement, iron-steel, fertilizers, glass, food, nuclear industries, organic chemical companies, petroleum refines, power plants, aircraft plating, mines etc., thus causing severe pollution. Among them, textile industry is regarded as one of the most polluting industry (Berberidou et al., 2007, Coleman et al., 2000). The World Bank accounts that 17-20% of industrial water pollution arise from textile industry (Baseri et al., 2012).

2.1.1. Textile wastewater and dyes

Textile industry is considered as one of the largest industries in the world and receives attention because of the pollution of water caused by dyestuff (Kumar et al., 2008). The quantity of wastewater coming from textile industry is reported to be between of 2–180 L of wastewater per kg of textile products (Ong et al., 2014).

The textile wastewaters contain a wide variety of dyes and chemical additions, and, damage the environmental health due not only its chemical compositions but also quantity of liquid waste. Main pollution in textile wastewaters is generated in dyeing and finishing processes (Akpan et al., 2009). Significant pollutants in textile wastewater are especially toxic compounds, inhibitor, acids, heavy metals, pesticides, pigments, dyes and salts which results in high chemical oxygen demand (COD), biological oxygen demand (BOD), pH, and solid materials in textile effluents. The characteristics of a typical textile industry wastewater are presented in Table 2.1 (Singh et al., 2010).

Table 2.1.Textile industry waste water characteristics

Parameters	Values
pH	7.0 - 9.0
Biochemical Oxygen Demand (mg/L)	80 - 6,000
Chemical Oxygen Demand (mg/L)	150 - 12,000
Total Suspended Solids (mg/L)	15 - 8,000
Total Dissolved Solids (mg/L)	2,900 -3,100
Chloride (mg/L)	1000 - 1600
Total Kjeldahl Nitrogen (mg/L)	70 - 80
Colour (Pt-Co)	50-2500

The effluents of textile and dyeing industries are generally strongly colored, and the release of the wastewater into receiving water bodies without treatment destroys human health as well as the aquatic life (Daud et al., 2010).

Pollutants in textile wastewater accumulate in water ecosystem and decrease the light permeability besides disrupting the aesthetic of the water. Reduction of the light permeability and the amount of dissolved oxygen result in the extinction of aquatic livings and limits the reuse of the water, inhibits the photosynthesis, and, therefore, growth of aquatic biota (Rodriguez-Couto, 2009). Also, the environmental pollution arise from the textile wastewater significantly affects the health of peoples consuming marine foods. The pollutants are absorbed by the marine and fresh water biota directly or are contaminated the ground water. Polluted ground water and the marine foods which are extensively used lead to the diseases such as tumor, cancer, sexual diseases, psychiatric diseases, and, brain diseases, etc. The impact of the pollutants may not immediately be quite evident, however, their indistinct influences are fatal with the passing of time (Imtiazuddin et al., 2012).

Dyes are widely used in broad industrial sectors such as textile manufacturing, leather tanning, cosmetics, paper, food processing, and pharmaceutical industries. The annual production of synthetic dyes and dyeing stuffs are generally exceeding 700,000 tones (Rahmani et al., 2010).

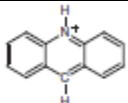
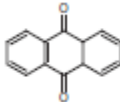
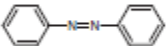
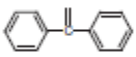
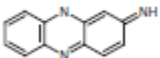
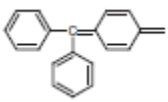
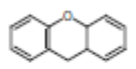
Synthetic dyes have been extensively produced in the last century and have unique properties like brilliant shades, simple synthesis methods and relative low cost. They can be categorized according to their application areas, namely reactive, direct, acid, basic, disperse, mordant, metal complex, vat, and sulfur dyes (Blanco et al., 2014). Classification of the dyes according to their usage areas is summarized in Table 2.2 (<http://textInfo.wordpress.com/2011/12/04/classification-of-dyes>, 2014).

Table 2.2. Synthetic dyes and their application

Group	Application
Direct	Cotton, cellulosic and blends
Vat dyes	Cotton, cellulosic and blends
Sulphur	Cotton, cellulosic fibers
Organic pigments	Cotton, cellulosic, blended fabrics, paper
Reactive	Cellulosic fibers and fabric
Dispersed dyes	Synthetic fibers
Acid Dyes	Wool, Silk, Synthetic fibers, leather
Azoic dyes	Printing inks and pigments
Basic Dyes	Silk, wool, cotton
Oxidation dyes	Hair
Developed Dyes	Cellulosic fibers and Fabric
Mordant dyes	Cellulosic fibers and Fabric, Silk, Wool
Optical/Fluorescent Brighteners	Synthetic fibers, leather, cotton, sports goods
Solvent dyes	Wood Staining, solvent inks, waxes, coloring oils

As well as classifying according to the application areas, dyes can also be classified depending on their chromophores and chemical structures. This classification comprises the azo dyes, anthraquinone dyes, acridine dyes, quinineamine dyes, nitro dyes, xanthenes dyes, arylmethane dyes, etc. Table 2.3 summarizes the structures of various classes of dyes (Rauf et al., 2011).

Table 2.3. Classification of dyes according to their chemical structures

Class	Chemical Structure
Acridine	
Anthraquinone	
Azo	
Diarylmethane	
Quinone-imine	
Nitro	
Triarylmethane	
Xanthene	

▪ Reactive dyes

Reactive dyes are used in the textile industry as the largest group of dyeing materials for cellulose and cotton fibers. These are characterized by high water solubility, non-biodegradability and low adsorption ability onto the biomass (Nabil et al., 2014). Though the fiber-reactive dyes were designed for cellulose fibers primarily, there are also used commercially for protein and polyamide fibers. When a reactive group in the dye applied to a fiber in a weakly alkaline dye bath, it forms a chemical bond with the fiber. Reactive dyes can also be used to dye nylon and wool; in this case these dyes are applied under weakly acidic conditions. Reactive dyes are the most permanent of all dye types. Unlike other dyes the reactive dyes bind to the textile fibers chemically which significantly improve the color of the product, and stability (<http://www.dyescolours.com/reactive-dyes.html>, 2014). However, the application of these dyes has a significant disadvantage in terms of environmental impact.

The reactive dyes react with ionized hydroxyl groups on the cellulose substrate. Nevertheless, hydroxyl ions in the dye bath compete with the cellulose substrate due to alkaline dyeing conditions, resulting in a percentage of hydrolysed dyes cannot react with the fiber. Therefore, 10–50% (corresponding to a degree of fixation in the range of 50–90%) of the initial dye load remain in the dye bath effluent giving rise to a highly colored effluent (Al-Degs et al., 2000).

▪ **Azo Dyes**

Azo dyes are characterized by the presence of azo groups bounding to aromatic rings (naphthalene or rings benzene). They are the most common and significant class of synthetic organic dyes as well as being the largest class of dyes used in the textile industry. It is reported that more than 50% of all dyes in industrial use are azo dyes due to their versatility and chemical stability (Daud et al. 2010).

Azo bonds and their associated auxochromes and chromophores determine the color of the azo dye. The most active parts of the azo dye molecule is the azo bonds and can be oxidized by hydroxyl radical, positive hole or can be reduced by electron in the conduction band. The cleavage of azo bonds results in the decolorization of azo dyes (Rauf et al., 2011).

Azo dyes can be categorized as monoazo (e.g. Methyl red, Acid orange 7, etc.), diazo (e.g. Naphthol Blue Black, Reactive Black 5, etc.), triazo (e.g. Direct Blue 71, Reactive red 120, , etc.) and triazine containing azo dyes (e.g. Procion red MX-5B).

It is well known that precursors and degradation products of the azo dyes (e.g. aromatic amines) are identified as highly carcinogenic (Elmorsi et. al., 2010). Due to the persistence and toxicity of azo dyes, removal of the azo dyes from the wastewater has become a significant issue of interest in recent years (Sun et al., 2007).

In this study, the degradation and decolorization of Procion Red MX-5B which is an azo dye (according to the chemical structure) and a reactive dye (according to the application area) was studied in presence of iron on activated carbon catalysts.

□ Procion Red MX-5B

Procion is a brand of fiber reactive dyes. They are dichlorotriazine dyes and their production was originally launched by Imperial Chemical Industries (ICI). The range of Procion dyes was superior to direct and vat dyes, having excellent wash fastness and a wide range of brilliant colors. Procion dyes can be applied in both batch and continuous processes. Procion MX is a trade name used for fiber reactive cold water dye. This type of dyes is commonly sold as a dry powder (<http://archive.today/D5Vz>, 2014).

In this study, Procion Red MX-5B is selected as a model for azo dyes because of its high molecular weight, high solubility, complex chemical structure, and persistence in water. This anionic monoazo dye is highly water-soluble and can be used for dyeing wool, silk, nylon, and, cellulose. The physical properties of the Procion Red MX-5B are tabulated in Table 2.4 and the molecular structure and properties of MX-5B are given in Figure 2.1 (Lin et al., 2010, Pachhade et al., 2009, Binupriya et al., 2010, <http://www.sigmaaldrich.com/catalog/product/sial/404365?lang=en®ion=TR>, 2014).

Table 2.4. Chemical and Physical properties of Procion red MX-5B

Formula	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$
Synonym	Reactive red 2
Physical state	Solid
Appearance	Powder
Composition	Dye content, 40%
Molecular weight(g/mol)	615
pH	3.9
λ_{max} (nm)	538
COD (mg Γ^{-1})	150
TOC (mg Γ^{-1})	32
Density(g/cm³)	1.88
Solubility	Soluble in water (partly)
Reactive index	n_D^{20} 1.80 (Predicted)
Melting Point ($^{\circ}C$)	>300

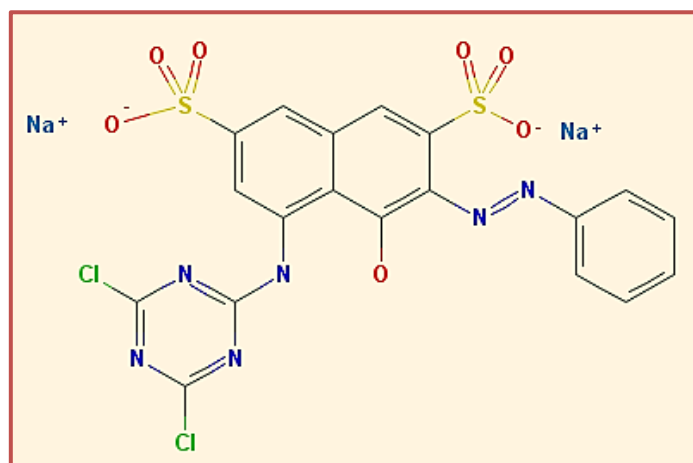


Figure 2.1. Procion Red MX-5B

2.2. Textile Wastewater Treatment

The effluents of the textile mills create an important pollution problem due to the dyes they contained in the textile wastewaters. Dyes are recalcitrant organic compounds which cause intense color in the textile effluents. They contribute to toxicity and organic load of the textile wastewater. The colored wastewaters coming from dying industries are harmful to the aquatic ecosystem in the rivers and lakes because of the presence of metal complex dyes which are highly toxic (Mishra and Bajpai, 2005).

Most of the dyes are stable to chemical degradation and biodegradation. Therefore, many industrial wastewater treatment methods have been developed and applied for the treatment of the textile wastewater prior to discharge into the natural water sources. The wastewater treatment methods can be investigated in two main sections including the conventional methods and the innovative advanced oxidation methods.

2.2.1. Conventional wastewater treatment methods

Physical, chemical, and biological methods have been applied conventionally for the treatment of wastewater discharged from various industries. The conventional treatment techniques comprise physical methods (e.g. screening filtration, sedimentation, aeration, flotation and skimming, degasification, equalization), chemical methods (e.g. chlorination, neutralization, coagulation, adsorption, ion exchange) and biological process (e.g. activated sludge, aerobic and anaerobic digestion, trickling filtration, oxidation ponds, lagoons, septic

tanks) (Gaehr et al., 2008). Some of the most common conventional treatment methods are briefly introduced below:

- **Filtration**

Filtration methods such as ultrafiltration, nanofiltration and reverse osmosis have been used for wastewater treatment, chemical recovery and water reuse. In the textile industry, filtration methods can be applied for recycling of pigment rich wastewaters in addition to mercerizing and bleaching wastewaters. The specific temperature and chemical composition of the wastewaters determine the type and porosity of the filter to be used (Verma et al., 2012).

- **Sedimentation**

Sedimentation process is particularly applied when the wastewater contains of high percentage of settleable solids or when the waste is subjected to combined treatment including sewage. The sedimentation tanks are designed to settle the small and light particles under gravity. The most common sedimentation equipment includes horizontal flow tanks and centre-feed circular clarifiers. The settled sludge is discharged from the sedimentation tanks by mechanical scrapping into hoppers and pumping it out subsequently (<http://www.fibre2fashion.com/industry-article/pdffiles/TextileEffluentTreatment.pdf>, 2014).

- **Membrane technology**

In literature it is reported that the utilization of membrane technology for dye removal from textile wastewater is effective. Nevertheless, membrane filtration processes suffers from several significant problems such as fouling and subsequent clogging of membrane surfaces, which resulted in reduction of wastewater flows, shorter membrane life leading to increase the cost of the treatment. In a typical membrane process is difficult to achieve complete color removal, since the chromophoric dissolved organic compounds have a low range of molecular weight. For these reasons, membrane filtration processes may not be suitable to treat the wastewaters especially having a high-strength of organic matters (Yoon et al, 2013).

▪ **Coagulation–flocculation**

In the coagulation-flocculation processes suspended solids agglomerate together into bigger bodies so that an easier physical filtration processes can be applied to remove them. These processes are usually followed by gravity separation (sedimentation or flotation) and filtration. A chemical coagulant, such as polymers or iron and aluminum salts, is added to wastewater to facilitate bonding among particulates. Coagulants create a chemical reaction and eliminate the negative charges which cause particles to repel each other (<http://www.drinking-water.org/html/en/Treatment/Coagulation-Flocculation-technologies.html>, 2014). Coagulation of the dyes has limitations because some highly soluble low molecular weight cationic dyes might not be removed effectively and the main disadvantage of this process is need for the disposal of the sludge produced inherently (Rodrigues et al., 2013).

▪ **Ion exchange**

In ion exchange processes, ions interchange reversibly between the solid and liquid phases, where a resin (an insoluble substance) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent quantity without any change in the structure of the resin (Kurniawan et al., 2006). The main negative drawback of the ion exchange method is the cost of the refreshing the resins.

▪ **Activated sludge proses**

In the activated sludge process, air and a biological floc composed of bacteria and protozoa were used to treat the wastewater. Even though it is an economical process, due to the high amount of hydrophobic compounds present in the textile component, the biological stage of the plant often suffers from sludge bulking and foaming problems. Also, a tertiary treatment stage is required to remove refractory compounds and color (Lotito et al., 2014).

▪ **Adsorption**

Mainly, adsorption is a mass transfer phenomenon by which a substance is transferred from the liquid or gas phase to the surface of a solid, and bounds by

physical or chemical interactions. Different types waste materials such as, saw dust, alum sludge, mud, nut shells and hulls, and other waste materials can be used as adsorbents. Because of its large surface area and high adsorption capacity, adsorption using activated carbon can remove pollutants effectively. (Chiban et al, 2012). However, adsorption is ineffective against some types of dyes, the regeneration of the adsorbent is expensive and results in loss of the adsorbent, non-destructive process (Crini, 2006).

The conventional treatment methods applied in the dye containing wastewater treatment are unsatisfactory due to the complicated molecular structure of the dyes. For this reason, it is necessary to find innovative and effective treatment technologies such as advance oxidation that leads to complete degradation and decolorization (Lucas and Peres 2006, Ersöz, et al. 2014).

2.2.2. Advanced oxidation processes

Advanced oxidation methods are the innovative technologies for wastewater treatment and are extremely useful for the elimination of substances resistant to conventional methods. They accomplish complete color removal, detoxification and mineralization in the effluents of textile dyeing mills. Highly reactive radicals are generated (e.g. hydroxyl radical, superoxide radical) that are very effective in decomposing organic pollutants due to their strong oxidant power and non-selective species. These radicals can reduce organic compounds to harmless end products such as CO₂ and H₂O (Kumar and Bansal, 2013).

The main advantages and the disadvantages of the advanced oxidation processes are summarized below (Freitas et al, 2012):

Advantages;

- Full mineralization of pollutants with harmless end-products,
- Able to degrade wide variety of organic molecules,
- Employed in the degradation of refractory compounds resistant to conventional methods,
- Used in treatment of highly toxic wastewater that can cause difficulty in biodegradation,
- Can be integrated with another process as pre- or post-treatment,

- Allow in situ treatment,
- Improve organoleptic properties of treated water;
- High oxidizing reaction rates.

Disadvantages;

- High treatment costs due to high energy consumption
- Some processes are not available at appropriate scale;
- Some types cannot be applied to wastewaters with high organic capability, turbidity or color.

Common AOPs comprise Fenton processes, ozonation, electrochemical oxidation, sonolysis, photocatalysis, super critical water oxidation, catalytic wet oxidation, and various combinations of advanced oxidation constituents like H_2O_2 , O_2 , O_3 and light sources. Some of the most common advanced oxidation methods including those of applied in this study (Fenton like oxidation, photo-Fenton like oxidation, photocatalytic degradation and catalytic wet air oxidation) are introduced below.

▪ **Ozone and ozone-based oxidation**

Ozonation has been reported as a powerful technology capable of degrading variety of organic pollutants. Especially transition metals catalyzed ozonation improve the oxidizing power of ozone, leading to a quicker removal of organic pollutants and markedly reducing the ozone dose and thereby the economic cost. Even though single ozonation has been proven to be effective for color removal; it has insignificant effect on dye mineralization (Zhang et al., 2013).

▪ **Sonochemical degradation:**

Sonolysis usually includes the influence of ultrasound that rise when a sound wave is passed through an aqueous media. Generally, the formation of highly reactive radical species like $\text{H}\cdot$ and $\cdot\text{OH}$ occur as a consequence of the homolytic cleavage of water in the cavitation bubbles. After these reactive radicals are formed, they attack any organic pollutants present in the water phase non-selectively and convert them into a various end products. Nenertheless, this method often fails to accomplish complete mineralization in short irradiation

times because of several reasons, such as the generation of hydrophilic intermediate products and volatility of the target pollutants (Madhavan et al., 2010).

- **Supercritical water oxidation (SCWO)**

This technology has a significant potential for eliminating a large variety of industrial pollutants. It is an appealing alternative to the conventional treatment methods due to the unique reaction features of supercritical water. Water has low viscosity and low dielectric constant, high diffusion coefficient in the supercritical region (374°C and 22.1 MPa) generating a homogeneous and high temperature environment, which simplifies a fast oxidation rate in supercritical water. So, even recalcitrant refractory pollutants can be easily converted into H₂O, CO₂ and N₂ as end products by supercritical water oxidation method. However, high operating costs, corrosion and salt deposition problems are of importance which restricts the application of super critical water oxidation (Wei et al., 2008).

- **Electrochemical oxidation**

Electrochemical Advanced Oxidation Processes (EAOPs) have been gaining attention for wastewater treatment. EAOPs which have been developed for water remediation offer some advantages such as versatility, high energy efficiency, safety. These methods are based on the in situ generation of hydroxyl radicals, reacting with most of the organic substances and mineralize them into CO₂, H₂O and inorganic ions due to its high standard redox potential. The most powerful In EAOP H₂O₂ is generated from the two-electron reduction of injected O₂. However, some of the electrochemical methods can only partially remove organic pollutants and forms undesirable by products. In addition, they require specially trained operators, which would likely increase labor cost (Pipi et al., 2014).

- **The Fenton and Fenton like oxidation**

Fenton oxidation is one of the oldest and most common advanced oxidation methods. It is cheap and easy to handle. Fenton process is superior to most of the treatment methods because of high performance in decolorization, simplicity in the oxidation of a wide range of persistent contaminants and being inexpensive (Mesquita et al., 2012).

The Fenton and Fenton like system use ferrous ions (Fe^{2+}) and ferric ion (Fe^{3+}) catalysts that react with H_2O_2 , producing hydroxyl radicals with powerful oxidizing ability for the destruction of organic pollutants as shown in the following equations (Wang, 2008):



Ferric (Fe^{3+}) ions can be reacted to produce ferrous ions (Fe^{2+}). The reaction of H_2O_2 , with ferric ions is referred to Fenton-like reaction:



Advantages of Fenton and Fenton like process over other oxidizing treatment methods are numerous. Fenton oxidation degrades the highly toxic organic substances or refractory pollutants which most of the conventional processes fails. Additionally, Fenton oxidation is performed under mild operating conditions and the process does not require specific reactor systems. Also, the end products of the Fenton like oxidation are usually harmless and non-toxic (Duarte et al., 2011, Torrades and Montano, 2014).

Although the homogeneous Fenton or Fenton like oxidation is known for its simplicity, efficiency and low investment cost; it has some significant disadvantages like the generation of a high concentration of anions in the treated wastewater and high concentration of iron ion sludge (Umar et al., 2010). Homogeneous Fenton reactions require up to 80 ppm of Fe ions in solution, which is extremely above the European Union limitations allowing 2 ppm of iron ions in treated water to be discharged directly into the environment. Furthermore, the

removal of the iron containing sludge at the end of the wastewater treatment is expensive and requires large amount of chemicals and manpower (Ramirez et al., 2007).

In order to overcome these problems, the metal phase can be supported on a solid porous matrix-such as activated carbon, clay, zeolite, etc. the which is as called heterogeneous Fenton process (Duarte et al., 2013).

▪ **Photo-Fenton like oxidation**

The advanced oxidation of textile dyes and dye house effluent with Fenton and photo-Fenton processes ($\text{H}_2\text{O}_2/\text{UV}/\text{Fe}^{2+}$) have recently received great attention because of their high efficiency in oxidizing a great variety of organic contaminants, ease of operation and relatively low operating costs (Arslan-Alaton et al., 2009).

The main target pollutants of Fenton and photo-Fenton process are water soluble and aromatic substances. Fenton processes are based on hydroxyl radicals formation via decomposition of hydrogen peroxide reacting with iron ions (Fe^{2+} and/or Fe^{3+}) acting as catalyst at acidic conditions.

The irradiation of Fenton oxidation systems using UV or Visible light sources severely accelerates the degradation rate of a large variety of pollutants. Under typical photo-Fenton reaction conditions, Fenton and photo-Fenton reactions occur simultaneously in the reaction mixture. Light is often the limiting reagent in photochemical reactions and photo-Fenton reactions are usually conducted in photoreactors in which the solution is well mixed or circulated through the reactor (Machulek et al., 2012).

In photo-Fenton oxidation, in addition to the Fenton reactions the formation of hydroxyl radical also occurs by the reactions given below:



The organic pollutant degradation rate can be increased by irradiation of UV light (photo-Fenton process). UV light leads to the generation of additional $\bullet\text{OH}$

radicals and recycling of ferrous catalyst by reduction of ferric ions. Therefore, the concentration of ferrous ions is enhanced and the overall reaction is accelerated. Among the advanced oxidation methods, the Fenton or Fenton like oxidation and photo-Fenton oxidation are proven to be promising treatment methods for an efficient decolorization and degradation of dyes (Malik and Saha, 2003).

In the photo-Fenton oxidation, H_2O_2 photolysis degrades many industrial pollutants including azo dyes. There are three types UV lamps which are UV-A (400-315 nm), UV-B (315-280 nm) and UV-C (280-100 nm) lamps which have been used in photocatalytic processes (Yoon et al., 2012). Because UV absorption by H_2O_2 is negligible above 280 nm, the process requires UV-C irradiation. The absorption of H_2O_2 is greatest near 220 nm, and for 254 nm irradiation, which is appropriately provided by low pressure mercury lamps. Usually, dye-decolorization rates enhance with increasing H_2O_2 concentration, but reach a limit when all the UV is absorbed. In this regard, a UV-C was used in the photo-Fenton and the phototocatalytic degradation sections of this study (Egerton and Purnama, 2014).

The homogeneous photo-Fenton like processes suffers from the same major drawback of formation of sludge and high iron leaching as in the Fenton like process. These drawbacks in the homogeneous photo-Fenton like oxidation can be overcome by using catalyst supports that fix the iron ions and prevent them to be dissolved in the reaction medium.

▪ **Photocatalytic Oxidation**

Among many advanced oxidation method, photocatalysis has received great attention as it is one of the most viable and environmentally friendly technologies; yet its cost competitiveness is still lower than conventional wastewater treatment methods and some of the advanced oxidation process (Park et al., 2013). The main steps of heterogeneous photocatalysis comprises transferring of the reactants in the liquid phase onto the catalyst surface, adsorption of the reactant on the catalyst surface, reaction in the adsorbed phase, desorption of the reaction products and removal of the final products in the liquid phase. In detailed, when the photocatalyst absorb UV light electrons are promoted from the valence band

to the conduction band and electron–hole pairs (h_{vb}^+ and e_{cb}^-) are generated. Mostly, h_{vb}^+ react with surface bound H_2O to produce hydroxyl radicals whereas, e_{cb}^- react with O_2 to produce superoxide radical anion $\bullet O_2^-$. These radicals react with the dyes to mineralize them. The photocatalytic reactions can be summarized in the following equations (Rauf et al., 2011, Khataee et al., 2009):



The mechanism of the photocatalytic degradation is given in Figure 2.2 (Chong et al., 2010).

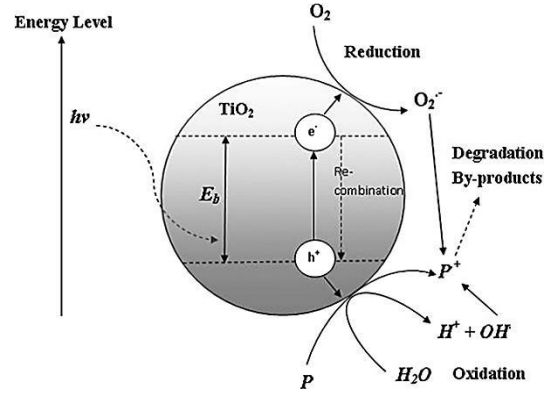


Figure 2.2. The mechanism of the photocatalytic degradation

Titania (TiO_2) is the most widely used photocatalyst due to its high efficiency, low cost, and chemical stability (Le et al., 2012). TiO_2 has three polymorphic forms which are anatase, rutile, and brookite. Anatase is reported to show the highest photocatalytic activity under illumination of UV light (Tada et al., 2011). However, the main disadvantage of using pure TiO_2 anatase phase is that the bandgap (E_g) is about 3.2 eV, which needs excitation wavelengths of $\lambda < 376$ nm. This means the TiO_2 anatase phase shows low

photocatalytic activity under visible light. In addition, high recombination rate of photoinduced electron-hole pairs leads to decrease in efficiency of photocatalytic reactions (Wang et al., 2011).

In order to overcome these problems, several methods were developed. Among them, doping transition metals onto TiO_2 is the most common one. Ferric ion is one of the most appropriate and effective dopant to improve the photocatalytic activity of titania due to its suitable band gap and similar size to that of Ti^{4+} . Fe^{3+} ions form shallow traps in the TiO_2 lattice and increase the surface oxygen deficient sites where peroxide and superoxide species are generated and electron-hole recombination is reduced (Yalçın et al., 2010, Bajamundi et al., 2011).

Recently, TiO_2 has been immobilized on different supports like glass beds, silica, activated carbon, biodegradable polymer and zeolites in order to recover the catalyst more easily and utilize the adsorption capacity of the support. Combining TiO_2 with the adsorption properties of the catalyst support increases the surface areas which lead to an enhancement of the reaction rate (Ilinoiu et al. 2013).

Using activated carbon as a catalyst support improves the photo-oxidation rate by progressively allowing an enhanced quantity of substrate to come in contact with the TiO_2 through means of adsorption. This is of importance because the oxidizing species formed by the photocatalyst do not migrate very far from the active centers of the TiO_2 and therefore degradation takes place on the catalyst surface virtually. The synergistic effect can be expressed as an enhanced adsorption of the target pollutant onto the activated carbon phase followed closely by a transfer through an intermediate to the TiO_2 phase, resulting in complete photo-degradation process (Puma et al., 2008).

In this regard, in the photocatalytic oxidation part of this experimental study, iron-titania coated on activated carbon catalysts were used for the degradation and the decolorization of the azo dye, Procion Red MX-5B.

▪ Catalytic Wet Air Oxidation

Among the advanced oxidation process, wet air oxidation is one of the most efficient technologies to eliminate highly concentrated persistent, toxic and hazardous organic compounds, converting them CO₂ and H₂O under high temperature and high pressure using oxygen as the oxidant, without the emissions of NO_x, SO₂, HCl, dioxins, furans, and fly ash (Jing et al. 2012).

In wet oxidation reactions, the two commonly used oxidants have been oxygen (either molecular oxygen or in air) and hydrogen peroxide. The degradation mechanisms by wet oxidation are very complicated. The chemical reaction stage occurs mostly via free-radical reactions comprising initiation, propagation and termination reactions. The main reactions proposed in the degradation of organic substances (RH) are listed as follows (Zhou and He, 2006):



The efficient removal of pollutant applying wet air oxidation method require high pressure and temperature and, the severe reaction conditions may result in high installation costs and limits its industrial applications. Therefore, catalytic wet air oxidation (CWAO) has been developed using various catalysts in order to reduce the severity of the oxidation conditions (Roy et al., 2010).

By using a catalyst in wet air oxidation, higher oxidation rates are achieved and, this strongly improves the decomposition of organic pollutants under milder conditions of temperature and pressure, resulted in decrease in the operating costs (Ovejero et al., 2012, Levec and Pintar, 2007).

The catalysts that are used in catalytic wet oxidation processes can be classified as homogenous catalysts, noble metal catalysts, and, transition metal oxide catalysts. Besides them, carbon materials can also be used as catalyst

alternatively. Though the homogenous catalysts, such as copper and iron salts, shows very high catalytic performances in mineralization of organics, an additional metal separation step is required to remove or recover the metal ions from the treated effluent due to their toxicity.

Noble metal catalysts (Pt, Pd, Ru, Rh) and transition metal oxide catalysts (oxides of Cu, Ni, Mn, Fe, Co) are quite active and demonstrated to have high efficiency in the treatment of numerous pollutants present in industrial wastewater. However, their instability and fast deactivation via leaching of active phases limit the application areas of these catalysts. Deactivation due to the formation of carbonaceous deposits; oxygen poisoning and catalyst sintering are the other disadvantages of them (Keav et al., 2010, Kim and Ihm et al., 2011, Quintanilla et al., 2006, Roy et al., 2010).

Recently, various carbon materials such as, carbon xerogels, carbon foams, carbon fibers and activated carbon has been used in catalytic wet oxidation processes effectively due to the stability, high porosity and surface areas of the carbon materials. Activated carbon has been used as catalyst or catalyst support in catalytic wet air oxidation processes. In order to prevent loss of activated carbon it is important to work at temperatures below 150°C (Rocha et al., 2011, Rey et al., 2009)

Considering the advantages and the disadvantages of the various types of catalysts which have been utilized so far in catalytic wet air oxidation of organic pollutants, the usage of iron on activated carbon catalyst were found to be reasonable due to the synergetic effect of adsorption capacity of activated carbon and catalytic activity of iron, minimization of the metal leaching and ease of catalyst recovery.

Even though any study on the catalytic wet air oxidation of azo dyes in the presence of iron/activated carbon catalysts cannot be found in the literature, the high degradation and decolorization efficiencies obtained in the other advanced oxidation processes (e.g. catalytic wet peroxide oxidation) in the presence of these catalysts make them promising to be used in the catalytic wet air oxidation.

- **Activated carbon catalyst support**

Within the scope of this master thesis, iron over activated carbon and iron-titania coated on activated carbon catalysts were used for the degradation and the decolorization of Procion Red MX-5B in the advanced oxidation processes.

Activated carbon is a porous, amorphous carbon material which has a large internal surface area and high porosity. The most widely used commercial active carbons have a specific surface area varying from 800 to 1500 m² (Baseri et. al., 2012). Activated carbon can be prepared from a wide range of raw carbon resources, such as lignite, peat, coal and biomass resources, such as cherry, apricot stone, olive and peach stones, grape seeds, coconut shell, bagasse of fruits, shells of various nuts (walnut, almond peanut, pistachios, etc.) wood, sawdust and so on. Some of the carbon materials used for the activated carbon production is shown in Figure 2.3.



Figure 2.3. Raw materials used in activated carbon production

In this study, the activated carbons were prepared from the walnut shells in order to contribute the recovery of the agricultural wastes. This agricultural waste is considered as a suitable candidate for activated carbon preparation because of its relatively high carbon content and low ash and the high wide range of production and use in Turkey. Activated carbons are used mostly for adsorption in industry due to their large adsorption capacity, stability and relative ease of regeneration. Activated carbon increases the degradation rate of the target pollutant by progressively allowing an increasing quantity of substrate to come in contact with the catalyst through means of adsorption. Activated carbon will prove to be an excellent support in promoting the catalytic process in providing a synergistic effect by forming a common interface between both the activated carbon phase and the catalyst particle phase (Mahmoodi et al., 2011).

The activated carbons are prepared either physical or chemical methods. In the physical activation, the carbonized material is subjected to carbon dioxide, steam, or other oxidizing gases at higher temperatures. Carbon dioxide or steam corrodes the carbonaceous material to form a porous structure according to the following reactions (Yang and Qiu, 2010, Marsh, 2006):



In the chemical method, the starting material is impregnated with a chemical agent, acid (HNO_3 , H_3PO_4 , etc.), base (NaOH , KOH , etc.) or salt (ZnCl_2 , K_2CO_3 , etc.) and the blend is heated to a temperature of 400-800°C. Chemical activation reduces the formation of tar and other by products, thereby increasing carbon yield. The activation agents contribute to the development of internal microporous cavities resulting in an increased surface area (Martinez et al., 2006).

The chemically activated carbons are known to have much more developed surface area and porous structure than the activated carbons produced by the physical method). However, physical activation has several advantages over chemical activation as it is relatively an inexpensive and simple method. The advantages and the disadvantages of the physical and the chemical activation methods are summarized in Table 2.5 (Macia-Agullo et al., 2010, Nowicki et al., 2010).

Table 2.5. Comparison of the physical and chemical activation methods applied in activated carbon production.

	Physical Activation	Chemical Activation
Yield	Lower	Higher
Development of porosity	Lower	Higher
Activation Energy	Higher	Lower
Activation Time	Longer	Shorter
Usage of corrosive chemicals	No need to use	Uses corrosive agents
Washing stage	No washing stage	Washing the products

Considering both the advantages and the disadvantages of these activation methods, the activated carbons which used as catalyst support in advanced oxidation processes were prepared both the physical and several chemical

activation methods including nitric acid, zinc chloride and potassium hydroxide activations, comparatively.

2.2.3. Biological oxidation

Biotechnological approaches were proven to be effective in treatment of polluted wastewaters in an eco-friendly manner and at low cost. Microbial decolorization methods offer complete cleanup of wastewater in a natural way as it mostly reduce the color components to much simpler compounds such as carbon dioxide, ammonia, and water (Singh and Pakshirajan, 2010).

White-rot fungus has received significant attention in recent decades because of their natural ability to degrade lignin, which could also be useful in the treatment of organic pollutants, pulp and paper wastewater, and azo dye wastewater (Liang et al. 2012). The white rot fungus are superior to most of the biological methods because the use of bacteria in the treatment of dye effluents may lead to the formation of colorless aromatic amines, which are more toxic than the parent compounds resulting in limitation of the application areas of the bacterial treatment (Rodriguez-Couto, 2009).

The lignin degrading system of white rot fungi comprises various extracellular enzymes such as laccases, peroxidases and oxidases making them capable of degrading a wide range of organic pollutants like phenolic compounds and synthetic dyes (Kiran et al., 2012).

The white-rot fungi, particularly *Phanerochaete chrysosporium* and *Trametes versicolor* have been extensively studied for their ability to degrade a broad range of organic pollutants. They secrete nonspecific lignin-degrading enzymes such as lignin peroxidase (LiP), manganese peroxidase (MnP), laccases, and other oxidases which degrade the dyes almost non-selectively (Keharia and Madamwar, 2001).

Recently, of lignocellulosic wastes, which may contain significant concentrations of soluble carbohydrates and inducers of enzyme synthesis, has been used as support materials for the fungi to be immobilized on them and resource of nutrient in order to decrease the cost of the biological treatment.

The selection of a suitable organic waste for fungus growth and target enzyme synthesis is of importance in the development of an efficient biological treatment (Erden et al., 2009). In literature there is large number of alternatives to be used as immobilizing agent and nutrient resource. Some of the examples are pine shavings, wheat straw, rice hull, corn cob, sugarcane bagasse, fruit peelings, sunflower seed shell etc. In this study, walnut shells are selected to be used as immobilizing agents for *Phanerochaete chrysosporium* and *Trametes versicolor* in the removal of the azo dye Procion Red MX-5B.

3. LITERATURE SURVEY

In this section, recent advances in research areas focusing advanced oxidation of dyes in the presence of various catalysts, particularly metal loaded carbon catalysts were summarized. Also, innovative biological oxidation methods for dye decolorization were reviewed. Table 3.1 summarizes the review of the related studies in literature.

3.1. Advanced Oxidation Processes

3.1.1. Fenton like oxidation

In 2013, Yao et al., In 2012, Mesquita et al., in 2011, Duarte et al., in 2007, Ramirez et al. studied the Fenton like oxidation of several azo dyes in the presence of iron loaded activated carbon catalysts. Yao et al. examined the optimum reaction conditions for the oxidation of Reactive Red M-3BE in presence of activated carbon fiber catalyst (ACF). They compare the catalytic performances of activated carbon fibers in the presence of H_2O_2 and absent of H_2O_2 regarding the reaction conditions of pH 3 and 60°C. This dye was effectively removed in 30 min at rates higher than 98%. Mesquita et al. investigated the effect of several parameters like the initial pH, reaction temperature, initial concentrations of catalyst, H_2O_2 and initial Chicago Sky Blue concentration. The optimum conditions were determined as 50° C reaction temperature, 2.25 mM of initial H_2O_2 concentration at pH 3 for a 0.012 mM initial concentration of dye. Under optimal conditions, dye conversion and total organic carbon (TOC) removal were found as 88%, and 47% respectively. Duarte et al. investigated the most suitable reaction conditions for the Fenton-like oxidation of Orange II dye. They compare the catalytic performances of Norit RX3 Extra, Merck, Kynol catalysts. The optimum reaction conditions were determined as 30 ° C reaction temperature, initial at pH 3, for a 0.1 mM initial concentration of dye and the catalyst showing the highest catalytic performance was determined as N-Fe catalyst. TOC conversion values were found after 24 h as 61%, 25% and 25% for N-Fe, M-Fe and K-Fe respectively. The iron leaching values after 24 hour were also determined as 1.65%, 0.67%, and 0.89% for N-Fe, M-Fe and K-Fe respectively. Ramirez et al. investigated the influence of different reaction parameters such as, initial pH, temperature, the initial concentrations of Orange II

hydrogen peroxide using heterogeneous Fenton-like reaction. They determined the reaction conditions as 30°C reaction temperature, $[H_2O_2]_0 = 6 \text{ mM}$, initial pH=3 for an initial dye concentration of 0.1 Mm. They also compare the catalytic performances of activated carbon/Fe and carbon aerogel/Fe. The degradation of OII, removal of TOC, and iron leaching for values after 4 hour for activated carbon/Fe catalyst were 55%, 23% and 7.8% respectively and the same values for carbon aerogel/Fe catalyst were 94.6%, 58.8% and 10.0% respectively (Yao et al.,2013, Mesquita et al., 2012, Duarte et al.,2011, Ramirez et al., 2007).

In 2014, Ersöz, in 2013 Gan and Li., and in 2010, Daud et al studied the heterogeneous Fenton-Like of Reactive Black 5, Rhodamine B(RHB), and Acid Red 1, respectively. Ersöz investigated the influence of different reaction parameters such as, initial pH, temperature, the initial concentrations of Reactive black 5(RB5), initial hydrogen peroxide concentration, and catalyst dosage on the oxidative degradation of RB5 using iron(III) impregnated on rice husk ash as heterogeneous catalyst. The optimum conditions were determined as 30°C of reaction temperature, 0.5 g/L of catalyst loading, 4 mM of initial $[H_2O_2]_0$ concentration, at pH 3 for an initial dye concentration of 100 mg/L. The decolorization and degradation efficiencies were evaluated as 89.18% and 59.71 %, respectively at these optimum conditions. Gan and Li investigated the effect of several parameters including the initial pH, reaction temperature, catalyst dosage, and initial concentration of H_2O_2 on heterogeneous Fenton-like degradation of a Rhodamine B in the presence of rice hull based silica supported iron catalyst. The optimum conditions were determined as 323 K of reaction temperature, 3 of initial pH, initial $[H_2O_2]_0$ concentration of 0.98 mM, and 1g/cm^3 of catalyst dosage for an initial dye concentration of 50 mg/L. They observed about 75% of COD removal in 240 min and almost 100% decolorization in 10 min. Daud et al., also examined the optimum reaction conditions for the oxidation of Acid Red 1 in the presence of rice husk ash-based catalyst by heterogeneous Fenton like process. They reached 96% of dye decolorization efficiency at pH 2 and 30°C for 0.07 wt% of iron (III) oxide loading and 8 mM of initial hydrogen peroxide concentration (Ersöz, 2014, Gan and Li., 2013, Daud et al., 2010).

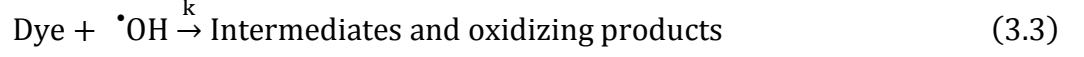
In 2010, Bouasla et al., in 2007, Behnajady et al. and Sun et al. studied the oxidation of Methyl Violet 6G, Acid Yellow 23 and Amido Black 10B by

homogeneous Fenton processes, respectively. Bouasla et al. investigated the effect of several parameters comprising the initial pH, reaction temperature, the initial concentrations of catalyst, H_2O_2 and methyl violet dye. They also compare the catalytic performances of FeSO_4 , FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ catalysts. The optimum conditions were determined as 30°C reaction temperature, initial $\text{pH} = 3$, $[\text{H}_2\text{O}_2]_0 = 2.1 \text{ mM}$, $[\text{Fe}^{2+}] = 0.06 \text{ mM}$ for a 0.06 mM initial concentration of dye in presence of FeSO_4 catalyst and the efficiency of degradation evaluated as 97.6% after 60 min. Behnajady et al. also examined the optimum reaction conditions for the oxidation of Acid Yellow 23 using Fenton process. They reached 98% of dye decolorization efficiency at $\text{pH} 3$ for 13.95 mg/L of initial Fe(II) concentration and 500 mg/L of initial hydrogen peroxide concentration. Sun et al. investigated the influence of different reaction parameters such as, initial pH, temperature, the initial concentrations of Amido Black 10B, hydrogen peroxide, and ferrous concentration on the oxidative degradation of Amido Black 10B. They determined the optimum conditions as 25°C of reaction temperature, $[\text{H}_2\text{O}_2]_0 = 0.50 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.025 \text{ mM}$, initial $\text{pH} = 3.5$ for an initial dye concentration of 50 mg/L and the degradation efficiency was evaluated as 99.25% at these optimum conditions (Bouasla et al., 2010, Behnajady et al., 2007, Sun et al., 2007).

According to these studies, homogeneous and heterogeneous Fenton processes are efficient treatment methods for decolorization of dyes. However, when the iron leaching and the sludge generation are considered besides the dye removal, the heterogeneous catalysts are more preferable instead of iron salts.

In the literature, the Fenton and Fenton like oxidation mechanism of the dyes and various aromatic compounds were investigated by many researchers (Sun et al., 2007, Liou, et al., 2007, Zhang et al., 2013, Ramirez et al., 2009). The kinetic study provides a basis for reactor design, scale-up and performance prediction thus encourages the industrial applications of this environmentally friendly treatment method.

According to the dye degradation and decolorization mechanisms proposed in literature, the decolorization mechanism of Procion Red MX-5B was derived in the following simplified form (Sun et al., 2007):



where the dye that is mentioned in the equation 3.3 is Procion Red MX-5B and the intermediates are any hydroxyl radical scavengers such as excess of ferrous ions, hydrogen peroxide, hydroperoxyl radical ($\text{HO}_2^\bullet$) and hydroxyl radical ($\bullet\text{OH}$) itself generated through the Fenton like reactions. k_f , k_g , and, k_c represent the reaction rate constants of conversion of ferric ion to ferrous ion, hydroxyl radical generation and hydroxyl radical consumption reactions, respectively.

The decolorization rate of Procion Red MX-5B according to equation 3.3 can be expressed as follows:

$$r_{\text{Dye}} = \frac{d[\text{Dye}]}{dt} = -k[\bullet\text{OH}]^m[\text{Dye}]^n \quad (3.5)$$

Assuming the dye decolorization reaction is an elementary reaction:

$$r_{\text{Dye}} = \frac{d[\text{Dye}]}{dt} = -k[\bullet\text{OH}][\text{Dye}] \quad (3.6)$$

Applying mass balances on $\bullet\text{OH}$, the rate equation for the generation and consumption of $\bullet\text{OH}$ is derived:

$$r_{\bullet\text{OH}} = \frac{d[\bullet\text{OH}]}{dt} = k_g[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k[\text{Dye}][\bullet\text{OH}] - \sum_{i=1}^n k_{c_i}[\text{I}_i][\bullet\text{OH}] \quad (3.7)$$

where I stands for the various intermediates scavenging the $\bullet\text{OH}$ radicals.

In kinetic modelling studies, when the reactive radical concentrations are concerned, generally Pseudo Steady State Hypothesis (PSSH) assumption is used (Liou, et al., 2007, Zhang et al., 2013, Ramirez et al., 2009). Since the amounts of Fe^{3+} and H_2O_2 added into the reaction medium were sufficient to keep the $[\bullet\text{OH}]$

at a fixed value, could be applied which indicated the change in concentration of $\bullet\text{OH}$ radical with respect to time was zero:

$$\frac{d[\bullet\text{OH}]}{dt} = 0 \quad (3.8)$$

Combining equations 3.7 and 3.8:

$$[\bullet\text{OH}] = \frac{k_g[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k[\text{Dye}] + \sum_{i=1} k_{c_i} [\text{I}_i]} \quad (3.9)$$

Substituting equation 3.9 into the equation 3.6:

$$\frac{d[\text{Dye}]}{dt} = -k \frac{k_g[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k[\text{Dye}] + \sum_{i=1} k_{c_i} [\text{I}_i]} [\text{Dye}] \quad (3.10)$$

Because the concentration of the dye is negligible when compared to the hydrogen peroxide concentration equation 3.10 is reduced to:

$$\frac{d[\text{Dye}]}{dt} = -\frac{kk_g[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{\sum_{i=1} k_{c_i} [\text{I}_i]} [\text{Dye}] \quad (3.11)$$

$$k_{\text{apparent}} = \frac{kk_g[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{\sum_{i=1} k_{c_i} [\text{I}_i]} \quad (3.12)$$

$$\frac{d[\text{Dye}]}{dt} = -k_{\text{apparent}} [\text{Dye}] \quad (3.13)$$

where k_{apparent} is pseudo first order reaction rate constant with respect to the Procion Red MX-5B concentration, and, is a function of initial concentrations of the reactants, Fe^{2+} (depending on Fe^{3+} in Fenton like oxidation), H_2O_2 , the dye, scavenger intermediates present in reaction medium and the reaction temperature.

$$k_{\text{apparent}} = f([\text{Dye}]_0, [\text{H}_2\text{O}_2]_0, [\text{Fe}^{2+}]_0, T) \quad (3.14)$$

The linearized form of the equation 3.14 is:

$$\ln\left(\frac{[\text{Dye}]_0}{[\text{Dye}]}\right) = k_{\text{apparent}} t \quad (3.15)$$

3.1.2. Photocatalytic oxidation and photo-Fenton like oxidation

In 2011, Mahadwad et al. and in 2012, Yoon et al. studied on photocatalytic degradation of azo dyes with Titanium dioxide (TiO_2) photocatalyst loaded onto activated carbon support. These experiments were carried out at room temperature. Mahadwad et al., studied the photocatalysis of Reactive Black 5 in presence of TiO_2 -Activated carbon catalysts. They obtained COD removal efficiencies of 85.04%, 88.26% and 84.73% in presence of TiO_2 , 20% $\text{TiO}_2\text{:AC}$ and 40% $\text{TiO}_2\text{:AC}$ catalysts, respectively, for catalyst loading of 800 mg/L. Yoon et al., studied the photocatalytic degradation of methly orange in presence of TiO_2 supported on spherical activated carbon catalysts which was a mixture of anatase and rutile in the weight ratio 8:2, and evaluated the maximum degradation efficiency as 98% under experimental conditions for photocatalyst dosage of 30 g/L, an initial MO concentration of 50 g/L, and an initial solution pH of 5.7, when the UV-C lamp was used as the light source (Mahadwad et al., 2011 & Yoon et al., 2012).

In 2013, Zeng et al. and In 2011, Mahmoodi et al., investigated TiO_2 -Activated Carbon produced from organic wastes as catalyst in photocatalytic degradation. Zeng et al. studied the degradation of Acid Yellow in presence of coconut shell based activated carbon catalyst support while Mahmoodi et al., studied degradation of Basic Red 18 and Basic Red 46 in presence of canola hull based activated carbon catalyst support. Zeng et al., varied initial dye concentration from 6 to 15 mg/L while UV light intensive was change from 10 to 40 mW/cm^2 and the reaction temperature was kept constant at 25°C. Results showed that the rate constants k_{app} of azo dye AY degradation are found as; 0.0049 min^{-1} for pure TiO_2 , 0.0057 min^{-1} for P25 0.0070 min^{-1} , for the mixture of TiO_2 and activated carbon and 0.0098 min^{-1} for TiO_2 -coated activated carbon surface (TAs). Mahmoodi et al., studied the photocatalytic degradation of azo dyes in presence of TiO_2 -Activated Carbon catalyst (2 wt.% of AC) with an initial H_2O_2 concentration 7.68 mM. The initial dye concentrations of Basic Red 18 and Basic Red 46 were 0.128 mM (at pH 5.5) and 0.120 mM (at pH 5.6), respectively. According to the experimental results 81.2 % and 76.2 % COD removal were obtained for Basic Red 18 and 46, respectively in 150 minutes (Zeng et al., 2011, Mahmoodi et al., 2011).

In 2010, Li et al., studied on treatment of the dye wastewater in the presence of Fe-doped TiO_2 coated on activated carbon by sol gel method. The optimum conditions for affecting the dye removal rate were investigated and 0.33% of Fe ion content, 6 g/L of catalyst loading, UV-lamp powers of 60 W (two lamps), flow rate of 300 mL/hr determined as the optimum values. The degradation efficiency of dye wastewater by four photo catalysts changed as follows: 0.33% FTA > TA > 0.33% FT > TiO_2 . The rate constant ($k = 0.0376$) in presence of 0.33% FTA was found to be higher than the sum of the rate constants of both TA (0.0205) and 0.33% FT (0.0166). An investigation of catalyst reuse revealed that the 0.33% FTA showed almost no deactivation in photocatalytic degradation. (Li et al., 2010).

In 2009, Khataee et al. studied on decolorization of various types of Acid Orange (AO10, AO12, AO8) azo dye solutions of 30 mg/L initial dye concentration at neutral pH in presence of TiO_2 nanoparticles on glass plates. An average overall TOC removal was larger than 94% for photocatalytic reaction time of 6 h. The amount of removal TOC is for AO10, AO12 and AO8 is 97.96%, 96.89% and 94.47%, respectively (Khataee et al., 2009).

In 2012, Chen et al. and in 2009 Akpan et al., studied photocatalytic degradation of various azo dyes in presence of pure TiO_2 . Chen et al., studied on photocatalytic degradation Remazol Black 5 (RB5) and Remazol Brilliant Orange (3R) and determined the optimum conditions as conducted at 1.0 mg/mL of photocatalyst loading, 0.1 mM of initial dye concentration, pH 2.0 and irradiation of 254 nm. By the addition of 20 mmol/mL of three electron acceptors, H_2O_2 , KBrO_3 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, the photocatalytic decolorization of RB5 and 3R dyes were increase by 54% and 35%, 59% and 41%, and 36% and 33%, respectively. Akpan et al., investigated effect of pH and catalyst amount on decolorization of the different azo dyes Fast Green FCF, Patent Blue VF, Methyl orange, BRL. The optimum values of pH and Fast Green FCF, Patent Blue VF, Methyl orange, BRL were determined as 4.4, 11, 2.5, and 7.2. The efficiencies of degradation evaluated for Fast Green FCF, Patent Blue VF, Methyl orange, BRL were %91, %92, %90.5 and 91.5, respectively (Chen et al., 2012, Akpan et al., 2009).

In 2009, Alaton et al., investigated treatment of synthetic wastewaters containing Acid Blue 193 and Reactive Black 39 and real wastewater containing Reactive Black 39 using Photo-Fenton-like process. Surface methodology was applied to discuss the effects of several process parameters such as Fe^{3+} , H_2O_2 concentrations, reaction time, and, initial chemical oxygen demand on treatment performance in terms of color, chemical oxygen demand and total organic carbon removal efficiencies. Optimum reaction conditions for AB 193 production wastewater were evaluated as $\text{Fe}^{3+}=1.5 \text{ mM}$; $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ and a reaction time of 45 min. Under these conditions, 98% color, 78% COD and 59% TOC removals were obtained (Alaton et al., 2009).

3.1.3. Catalytic wet air oxidation

In 2011, Türgay et al, investigated catalytic wet peroxide oxidation and anaerobic biological degradation of reactive azo dyes, Procion Red MX-5B and Reactive Black 5 as well as treating real wastewater. The objective of this research was to compare the chemical and biological treatment methods and to assess the impact of reaction parameters on treatment effectiveness. In the anaerobic process, the addition of microorganisms growing on forest residues, increasing the amount of yeast extract and the residence time enhanced the dye removal efficiencies. In the catalytic wet peroxide oxidation process, the reaction optimum reaction conditions were determined by 0.5g/L of catalyst (activated carbon) loading, 2mL H_2O_2 /300mL solution (35wt%), 80°C, pH=3, 2 hours of reaction time. Under the optimum conditions, 93% of the dye was removed. CWPO process was tested in treatment of real textile industry wastewater and 50% of dye removal was accomplished (Türgay et al., 2011).

In 2011, Jing et al., investigated the progress of catalytic wet air oxidation technology. Various heterogeneous catalysts including noble metals and metal oxides have been introduced. The advances in the research on wastewater treatment by CWAO process are summarized in aspects of reaction mechanism investigation, reaction kinetics study and catalyst development. It is pointed out that the preparation of active and stable catalysts, the investigation on reaction mechanisms and the study on reaction kinetics models are very important for the promotion of CWAO application (Jing et al., 2011).

In 2010, Nguyen et al., studied a simple and efficient method for the fabrication of magnetic Fe_2MO_4 activated carbons by impregnating the activated carbon with simultaneous magnetic precursor and carbon modifying agent followed by calcination. The catalytic activity for oxidation of methyl orange (MO) was evaluated. According to the results, catalytic activity of $\text{Fe}_2\text{MnO}_4/\text{AC-H}$ was higher than $\text{Fe}_3\text{O}_4/\text{AC-H}$ in the methyl orange oxidation. The influence of reaction parameters (pH, catalyst loading H_2O_2 dosage and initial methyl orange concentration) on degradation performance of the oxidation process was investigated. Reusability and stability and of selected catalyst were tested also (Nguyen et al., 2010).

3.2. Biological Oxidation

In 2012, Theeracha et al., compare the synthetic dye decolorization by whole cells and a laccase enriched extract from *Trametes versicolor* DSM11269. Using a laccase enzyme which was extracted from the fungal liquid culture supernatant, the anthraquinone derivative dyes (Alizarin Red S and Remazol Brilliant Blue R) were decolorized in three hours at 50°C by 55 and 70%, respectively. The azo compounds (Amaranth, Cibacron Brilliant Red 3B-A, Direct Blue 71 and Reactive Black 5), and the indigo molecule (Indigo Carmine), showed a higher resistance to decolorization (<10% in 6 h), though Amaranth, Reactive Black 5 and Indigo Carmine were efficiently decolorized by *T. versicolor* in agar plate assays (Theeracha et al., 2012).

In 2011, Enayatizamir et al., investigated biodegradation pathway and detoxification of the diazo dye Reactive Black 5 (RB5) by *Phanerochaete chrysosporium*. The fungus is immobilized on cubes of nylon sponge and on sunflower-seed shells (SS). A fixed-bed tubular bioreactor with dimensions of 20 cm height and 4.5 cm in internal diameter (working volume of 200 mL) was filled with 8 g of nylon cubes or 8 g of SS colonized by the fungus and kept at room temperature (25°C) and aeration rate of 0.5 vvm. In the case of nylon cultivation the glucose concentration of the culture medium composition was 2 g/L glucose and in case of sunflower-seed shells cultivation the culture medium contained no glucose. Dye was treated under non-sterile conditions in successive batches, increasing the dye concentration in each batch (15, 40, 60, 80 and 100 mg/L). The

bioreactor was poured out and filled with fresh medium and sterilized at the beginning of each batch. After 2–3 h the dye was added under non-sterile conditions. Samples which were collected from the middle part of the bioreactor were collected, centrifuged and analyzed. The sunflower-seed shells cultivation led to the best results with a decolorization percentage of 90.3% in 72 h for an initial RB5 concentration of 100 mg/L (Enayatzamir et al., 2011).

In 2009, Enayatzamir et al., investigated the simultaneous production of laccase and decolorization of the diazo dye Reactive Black 5 in a fixed-bed bioreactor. The production of laccase and the decolorization of the recalcitrant diazo dye Reactive Black 5 (RB5) by the white-rot fungus *Trametes pubescens* immobilized on stainless steel sponges in a fixed-bed reactor was studied. Fixed-bed tubular bioreactor consisted of a glass column with dimensions of 20 cm height and 4.5 cm in internal diameter (working volume of 200 ml). Air was supplied in a continuous way at 1 vvm, occasioning a gentle agitation of the culture medium. The bioreactor was filled with six stainless steel sponges colonized by *T. pubescens*. The decolorization the medium composition consists of 2 g/L glucose, dye (60 mg/L), 0.1mM acetate buffer (pH 4.5) and copper (0.5 mM). The medium was added to the bioreactor under non-sterilized conditions. The decolorization of RB5 occurred via two processes; bio sorption of the dye onto the fungal mycelium and degradation of dye by the laccase enzymes secreted by the fungus. RB5 decolorization was performed during four batches obtaining decolorization percentages 74%, 43% and 52% in 24 h for the first, third and four batch, respectively (Enayatzamir et al., 2009).

In 2008, Faraco et al., investigated decolorization of various textile dyes by the white-rot fungi *Pleurotus ostreatus* and *Phanerochaete chrysosporium*. Dyes used in the experiments are Acid blue 62, Acid red 299, Reactive blue 19 (Remazol Brilliant Blue R), Reactive black 5, Reactive red 4 Reactive yellow 81, Direct red 81(Congo Red), Direct blue 1 (Chicago Sky Blue), Direct black 38 (Chlorazol Black), Disperse blue 1, and Disperse yellow 3. Decolorization in liquid cultures was carried out in micro-titre plates with U bottom wells, using malt extract broth with different dye concentrations selected among 30, 150, 300, 600, 1000 ppm, on the basis of the ability of fungal strains to decolorize the dyes. Also, decolorization abilities by liquid cultures of fungi were investigated in 500

ml flasks. The percentage decolorization of the Remazol Black 5 by *P. ostreatus* in shaken flask for an initial dye concentration of 300 ppm is 90% in 10 days and the percentage decolorization of the Remazol Black 5 by *P. chrysosporium* in shaken flask for an initial dye concentration of 1000 ppm is 90% in 3 days. The percentage decolorization of the Reactive red 4 by *P. ostreatus* in shaken flask for an initial dye concentration of 30 ppm is 20% in 13 days and the percentage decolorization of the Reactive red 4 by *P. chrysosporium* in shaken flask for an initial dye concentration of 600 ppm is 100% in 6 days (Faraco et al., 2008).

Table 3.1. Literature survey on advanced oxidation and biological oxidation of dyes

		No	Reference	Dye	Catalyst	Results	
						Reaction Conditions/ Optimum Conditions	Degradation/ Decolorization/COD Removal/ TOC Removal/ Toxicity
FENTON LIKE OXIDATION	Fe/AC Catalysts	1	Yao et al. (2013)	Reactive Red M-3BE	Activated carbon fibers (supported ferric ion (Fe@ACFs) Fe@ACFs/H ₂ O ₂ base on activated carbon fibers	pH 3 60 °C	higher than 98% decolorization in 30 min The initial rate constants (k , min ⁻¹) of the reaction: 0.0531, 0.1094, 0.2129, and 0.3438 min ⁻¹ at 30, 40, 50, and 60 °C, respectively. Ea for RR M-3BE degradation: 45.66 KJ mol ⁻¹ .
		2	Mesquita et al. (2012)	Chicago Sky Blue (CSB)	Activated carbon Norit RX 3	50°C pH 3 [H ₂ O ₂] ₀ = 2.25 Mm W _{cat} /Q = 4.1 g min/mL [CSB] ₀ = 0.012 mM	Iron leaching: below 0.4 ppm At steady-state, a dye conversion of 88%, with a total organic carbon (TOC) removal of 47%
		3	Duarte et al. (2011)	Orange II (OII)	Iron loaded three different commercial activated carbons; Norit RX 3 Extra, Merck Kynol	30°C pH 3 [Dye] ₀ = 0.1 mM	TOC conversion values after 24 h: 61%, 25% and 25% for N-Fe, M-Fe and K-Fe respectively. The iron leaching values after 24 hour: 1.65%, 0.67%, and 0.89% for N-Fe, M-Fe and K-Fe respectively.
		4	Ramirez et al. (2007)	Orange II (OII)	Activated carbon/Fe Carbon aerogel/Fe	pH 3, 0.2 g/L catalyst amount, 6 mM H ₂ O ₂ concentration 30°C.	The decomposition of OII, removal of TOC, and iron leaching for values after 4 hour for activated carbon/Fe catalyst were 94.6%, 23% and 7.8% respectively. The same values for carbon aerogel/Fe catalyst were 55%, 58.8% and 10.0% respectively.

Table 3.1 (continued)

FENTON LIKE OXIDATION	Rice Husk Based Catalysts	5	Ersöz, (2014)	Reactive Black 5 (RB5)	Iron over rice husk ash	pH 3 30°C [H ₂ O ₂] ₀ = 4 mM [Dye] ₀ = 100 mg/L Catalyst loading=0.5 g/L	The best degradation efficiency %59.71 Decolorization efficiency (89.18%) Noticeably low the iron leaching
		6	Gan and Li, (2013)	Rhodamine B (RHB)	Rice-hull based silica supported iron	pH= 3, 323 K Catalyst dosage= 1.0 g/dm ³ [H ₂ O ₂]=0.98mmol [RHB]=50mg/L	Almost 100% decolorization within 10 min Activation energy (E): 82.53 kJ/mol .
	Homogeneous Fenton Catalysts	7	Bouasla et al. (2010)	Methyl violet 6B	Three different catalyst FeSO ₄ , FeCl ₃ Fe(NO ₃) ₃)	pH 3, 30°C [H ₂ O ₂]=2.1 mM [Fe ²⁺]= 0.06 mM [MV] ₀ =0.06 mM	Efficiency of degradation after 60 min of reaction, was 97.6%. DEcoloration of methyl violet by the Fe ²⁺ /H ₂ O ₂ system is faster than that obtained by the Fe ³⁺ /H ₂ O ₂ system
		8	Sun et al. (2007)	Amido Black 10B	Ferrous catalyst	pH =3.5, 25°C [H ₂ O ₂] ₀ = 0.50 mM [Fe ²⁺] ₀ = 0.025 mM [Dye] ₀ =50 mg/L	99.25% degradation efficiency was achieved after 60 min of reaction.
	Fe/TiO ₂ /AC	9	Li et al. (2010)	Azo dyes	Fe-TiO ₂ /AC,FA (Fe-doped TiO ₂ coated on activated carbon)	Fe ions content is 0.33%. Catalyst content is 6 g/L. UV-lamp poweris 60 W (two lamps) Flow rate were 300 mL/hr.	The degradation efficiency of dye wastewater by four photo catalysts changes as follows: FTA > TA > FT > TiO ₂ . The rate constant (k = 0.0376) of 0.33% FTA was found to be more than the sum of the rate constants of both TA (0.0205) and 0.33% FT (0.0166).
	Organic Waste Based AC	9	Mahmoodi et al (2011)	Basic Red 18 Basic Red 46	Titania over Canola hull based activated carbon support (2% wt. of AC)	7.68 mM of H ₂ O ₂ 0.128 mM of initial Basic Red 18 concentration 0.120 mM of initial Basic Red 46 concentration pH =5.6	In 150 min, 81.2% and 76.2% of COD removal for Basic Red 18 and Basic Red 46, respectively.

Table 3.1 (continued)

PHOTOCATALYTIC OXIDATION	Organic Waste Based AC	10	Zeng et al. (2013)	Acid Yellow (AY)	TiO₂-Coated Activated Carbon surface (TAs). Activated carbon was produced from coco nut shell	The initial content of AY was varied from 6 to 15 mg/L. The aerating rate of air is 38 mL/s. Reacting temperature: 25 °C. 40 mW/cm² UV light intensity	The rate constants k_{app} of AY degradation: 0.0049 min⁻¹ for pure TiO₂ 0.0057 min⁻¹ for P25 0.0070 min⁻¹ for the mixture of TiO₂ and active carbon 0.0098 min⁻¹ for TAs. The relation between the AY degradation rates follows the order of TiO₂ content from high to low: 4.2%, 5.1%, 3.0%, 6.8%, 1.6 %.
	TiO ₂ - AC	12	Yoon et al. (2012)	Methyl orange (MO)	TiO ₂ /SAC (TiO ₂ supported on spherical activated carbon)	A mixture of anatase and rutile in the weight ratio 8 : 2. Photocatalyst dosage of 30 g/L. An initial MO concentration of 50 mg/L An initial solution pH of 5.7.	The highest removal efficiency of 98%.
		13	Mahadwad et al. (2011)	Reactive Blak 5	TiO ₂ TiO ₂ -Activated carbon	Catalyst loading of 800 mg/L	COD removal efficiencies of 85.04%, 88.26% and 84.73% in presence of TiO ₂ , 20% TiO ₂ :AC and 40% TiO ₂ :AC catalysts, respectively,
	TiO ₂ -Fish Scale	14	Ho et al. (2012)	Methyl Orange	Fish scale (FS) loaded TiO ₂	Mass ratio of TiO₂/FS (90:10, 70:30 and 50:50) Photocatalyst loading (0.1, 0.3 and 0.5 g) Initial dye concentration (within 20 mg/L) Irridation time of 4 hour	TiO₂/FS of 90:10 composite showed highest photodegradation efficiency (61.1%). Photodegradation efficiencies of 50.4%, 37.9% and 1.9%, in the presence of TiO₂, TiO₂/FS of 70:30 and TiO₂/FS of 50:50 composites, respectively.

Table 3.1. (continued)

PHOTOCATALYTIC OXIDATION	TiO₂- Glass	15	Khataee et al. (2009)	Acid Orange 10 (AO10), Acid Orange 12 (AO12). Acid Orange 8 (AO8))	Immobilized TiO ₂ nanoparticles on glass plates activated	30 mg/l of initial dye concentrations. Natural pH.	The amount of removal TOC is for for AO10 is 97.96%, For AO12 is 96.89% For AO8 is 94.47%. The photocatalytic decolorization kinetics were in the order of AO10 >AO12 >AO8.
	Pure TiO₂	16	Chen et al. (2012)	Remazol Black 5 (RB5) and Remazol Brilliant Orange (3R)	Pure TiO ₂	1.0 mg/mL of photocatalyst loading, 0.1 mM of initial dye concentration, pH 2.0 and irradiation of 254 nm.	Addition of 20 mmol/mL of electron acceptors, H ₂ O ₂ , KBrO ₃ , and (NH ₄) ₂ S ₂ O ₈ increased the decolorization by 54% and 35%, 59% and 41%, and 36% and 33%, respectively.
		17	Akpan et al. (2009)	Fast Green FCF, Patent Blue VF, Methyl orange, BRL	Pure TiO ₂	The optimum values of pH and Fast Green FCF, Patent Blue VF, Methyl orange, BRL were determined as 4.4, 11, 2.5, and 7.2.	The efficiencies of degradation evaluated for Fast Green FCF, Patent Blue VF, Methyl orange, BRL were %91, %92, %90.5 and 91.5, respectively
	Iron	18	Alaton et al., (2009)	Acid Blue 193 Reactive Black 39	Fe ³⁺ Catalyst	Fe ³⁺ =1.5 mM; [H ₂ O ₂] = 35 mM Reaction time of 45 min.	98% color, 78% COD and 59% TOC removals were obtained
AOP&BIOLOGICAL PROCESS	CWPO & Microbial Process	19	Türgay et al. (2011)	Procion Red MX-5B Reactive Black 5	Activated carbon in CWPO process	0.5 g/L activated carbon loading with 2 mL H ₂ O ₂ /300mL solution (35 wt%), at 80°C, in 2 h with pH 3. Residence time (5-180 min) 300mL solution of a mixture of 200 mg/L of Procion Red MX-5B and 200 mg/L of Reactive Black 5 at atmospheric pressure with an air flow rate of 0.23 L/min	Approximately 93% of the dye removal The percentage of dye removal with real wastewater was 50%. In the chemical oxidation process, the reaction time is less than microbial process; however an acidic medium is used by adding some oxidizing agents.

Table 3.1 (continued)

BIOLOGICAL OXIDATION	<i>P.chrysosporium</i>	20	Enayatizamir et al. (2011)	Reactive Black 5	White rot fungi <i>Phanerochaete chrysosporium</i> Immobilized on, Sunflower seed shells (SS) and Nylon sponge	Fixed-bed tubular bioreactor with dimensions of 20 cm height and 4.5 cm in internal diameter (working volume of 200 mL) Dye concentration (15, 40, 60, 80 and 100 mg/L)	Decolouration percentage of 90.3% in 72 h for an initial RB5 concentration of 100 mg/L. For 80 mg/L RB5 concentration, $87 \pm 8.4 \%$ and $45 \pm 4.3 \%$ decolorization values are obtained with SS and nylon sponge immobilizers respectively, in 72 hours.
	<i>P.chrysosporium</i>	21	Faraco et al. (2008)	Acid blue 62 Acid red 299 Reactive blue 19 Reactive black 5 Reactive red 4 Reactive yellow 81 Direct red 81 Direct blue 1 Direct black 38 Disperse blue 1 Disperse yellow 3	White rot fungi, <i>Phanerochaete chrysosporium</i> and <i>Pleurotus ostreatus</i> .	Decolourization in liquid cultures was performed in; Micro-titre plates with U bottom wells and Flasks Initial dye concentrations (30, 150, 300, 600, 1000 ppm)	The percentage decolourization of the Remazol Black 5 by <i>P. ostreatus</i> -for an initial dye concentration of 300 ppm is 90% in 10 days - for an initial dye concentration of 1000 ppm is 90% in 3 days. Percentage decolourization of the Reactive red 4, -by <i>P. ostreatus</i> in shaken flask for an initial dye concentration of 30 ppm is 20% in 13 days. - by <i>P. chrysosporium</i> in shaken flask for an initial dye concentration of 600 ppm is 100% in 6 days.
	<i>T.pubescens</i>	22	Enayatizamir et al. (2011)	Reactive Black 5	White rot fungi, <i>Trametes pubescens</i> immobilized on stainless steel sponges	Fixed-bed tubular bioreactor with dimensions of 20 cm height and 4.5 cm in internal diameter (working volume of 200 mL) Dye concentrations (30 and 60 mg/L)	Decolouration percentages 74%, 43% and 52% in 24 h for the first, third and four batch, respectively.

3.3 Foreword to the Study

Liquid phase advanced oxidation of dyes over various catalysts and biological oxidation of dyes by innovative methods are reviewed in this section. The conclusions extracted from the literature survey assisted and guided in developing the structure and the experimental plan of the study.

The basic emerging concepts are related to the main objective of this study are listed below:

I. The Choice the Target Compound

Azo dyes are one of the most common pollutants found in industrial wastewaters, especially, in the effluents of textile industry. Turkey is among Europe's largest textile manufacturers. Therefore, textile industry wastewaters are one of the major water pollution sources in our country. They cause intense color in water bodies, and some of the types are reported to be mutagenic, carcinogenic and toxic.

Procion Red MX-5B is chosen as the model compound for azo dyes because of its high water solubility, high molecular weight and complex chemical structure. In addition to these, no any study is found in the literature investigating the degradation and decolorization of Procion Red MX-5B by several advanced and biological oxidation processes comparatively.

II. The Choice of the Treatment Methods

Advanced oxidation methods have a reputation for their effectiveness and innovative approaches to wastewater treatment in an environmentally friendly manner. There are many types of advanced oxidation methods including Fenton like oxidation, catalytic wet oxidation, super critical water oxidation, sonolysis, electrocatalysis, photocatalysis, ozonation, etc. Considering the adaptability to the industrial applications and the costs of these methods, Fenton like oxidation, photo-Fenton like oxidation, photocatalytic oxidation and CWAO methods are chosen to be used in this study.

Besides the advanced oxidation, an innovative biological oxidation method is also chosen to decolorize the azo dye solutions in order to compare the efficiencies of the chemical and natural oxidation methods.

III. The Choice of The Catalyst Type

In literature it is reported that the noble metals, metal salt and metal oxide catalysts are quite effective in oxidation of dyes. However, these catalysts suffer from deactivation and leaching. Usage of metal catalysts supported on various solid matrices is recommended to eliminate the deactivation and leaching. In this regard iron over activated carbon catalysts and iron-titania over activated carbon catalysts are chosen to be used in advanced oxidation of the azo dye, Procion Red MX-5B, due to the high catalytic activities of titania and iron, and, large surface area, porous structure and chemical stability of the activated carbon. The activated carbon is prepared from walnut shells in order to develop low cost catalysts derived from organic wastes and creating new usage areas for the recovery of the organic wastes.

IV. The choice of the Microorganism and the Immobilizing Agent

In the biological oxidation, the white rot fungi, *Phanerochaete chrysosporium* and *Trametes versicolor* are found to be good candidates to degrade and decolorize the azo dyes because of their destructive and non-selective enzymes such as lignin peroxidase, manganese peroxidase and laccase. The microorganisms are immobilized on walnut shells to supply a nutrient source as well as make the microorganism separation step easier after the treatment.

V. The choice of the Operating Conditions

At the end of the literature survey it is decided to investigate the advanced oxidation and the biological oxidation processes at the following conditions tabulated in Table 3.2.

VI. Kinetic Study

The kinetic study will be carried out for the most efficient oxidation method tested in the context of the study. The decolorization data recorded in the parametric study will be used. n^{th} order reaction kinetic models will be fitted to

the experimental data and regression analysis will be performed in order to derive the reaction rate equations. The activation energy will be calculated using the reaction rate constants evaluated at different reaction temperatures.

Table 3.2. Operating conditions for the oxidation methods

		Catalyst Loading g/L	[H ₂ O ₂] ₀ mM	pH	Temp. °C	Press. atm	Air flow rate l/min
AOPs	Fenton Like Oxidation	0-0.5	0-8	3-4	30-70	-	-
	Photocatalytic Oxidation and Photo-Fenton Oxidation	0-0.5	0-8	3-7	Room temp.	-	-
	Catalytic Wet Air Oxidation	0-0.5	-	7	50-90	1-3	0.61
			Concentration of the microorganism, g/100 mL			Glucose Concentration, g/L	
Biological oxidation	<i>T.versicolor</i>		0.5-4			1-4	
	<i>P. chrysosporium</i>		1			2	

4. EXPERIMENTAL

The experimental study carried out in this study can be investigated in two main sections including the Advanced Oxidation Processes and Biological Oxidation Process.

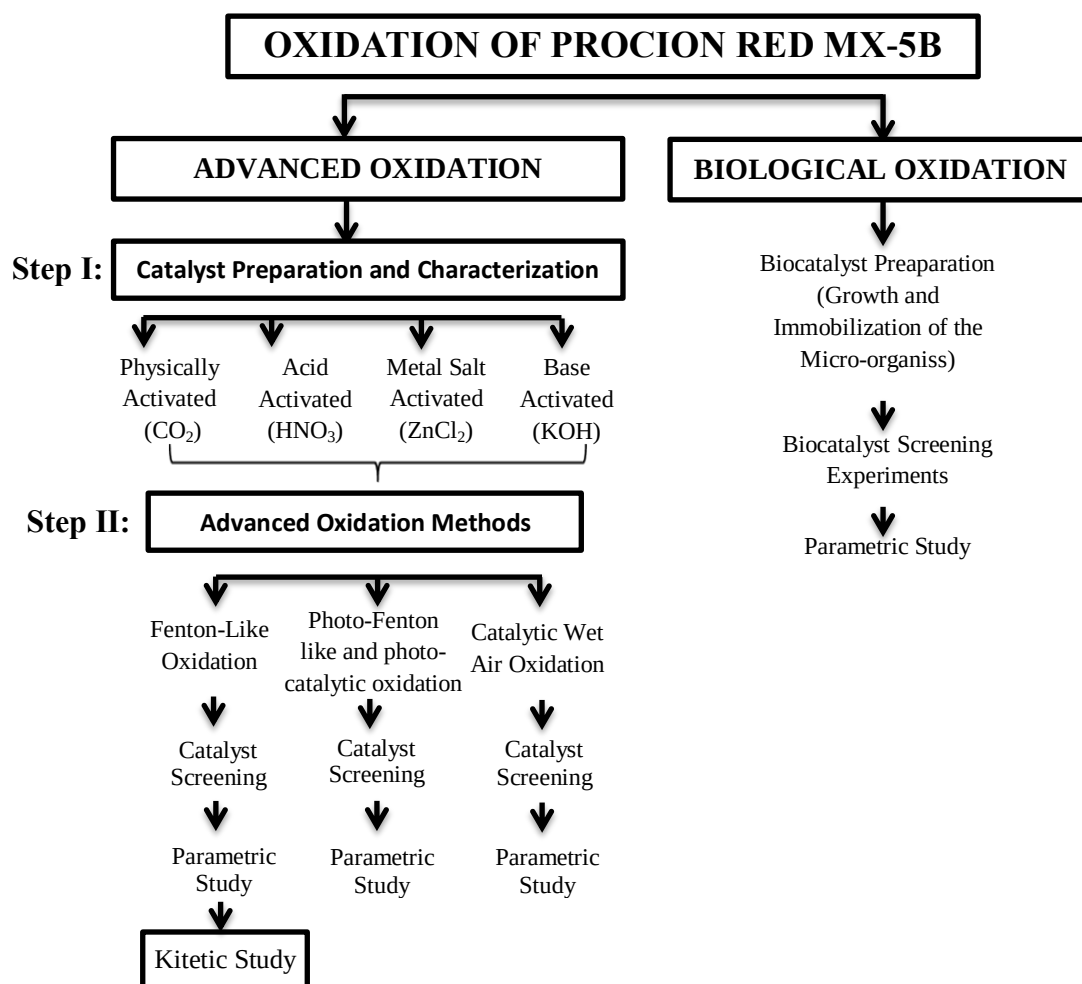


Figure 4.1. Stages of the Experimental Study

4.1 Advanced Oxidation Processes

Degradation and decolorization of the azo dye, Procion Red MX-5B were investigated by applying several advanced oxidation methods, including the Heterogeneous Fenton Like Oxidation (or Catalytic Wet Peroxide Oxidation), Catalytic Wet Air Oxidation and the Heterogeneous Photo-Fenton Like Oxidation in presence of innovative and environmentally friendly catalysts. The catalysts prepared in this study can be classified under two groups which are iron loaded activated carbon catalysts (Fe/AC) and Fe-TiO₂ loaded on activated carbon catalysts (Fe-TiO₂/AC).

4.1.1 Preparation of catalysts

4.1.1.1 Preparation of the activated carbons

Walnut shell based activated carbon was chosen as the catalyst support due to the porous structure, high surface area and chemical stability in order to obtain efficient catalysts as well as contributing the recovery of organic wastes.

The activated carbons were prepared from the walnut shells by applying both the physical and chemical activation methods. In the physical activation, carbon dioxide was used. In the chemical activation, three activation agents which consist of nitric acid (HNO_3), zinc chloride (ZnCl_2) and potassium hydroxide (KOH) were used to prepare different types of activated carbon and compare their performances as catalyst support in advanced oxidation process.

The physically activated carbon was denoted as P-AC in this study, while the nitric acid, zinc chloride and potassium hydroxide activated carbons were denoted as H-AC, Z-AC and K-AC, respectively.

▪ Pretreatment step

In order to prepare activated carbon from walnut shells, firstly the pre-treatment step comprising of crushing, milling, washing with distilled water and drying (at 110°C for 6 hours) of the walnut shells was applied (Yang and Qiu, 2010; Aygün et al., 2003). In Figure 4.2 steps of the pretreatment are given.

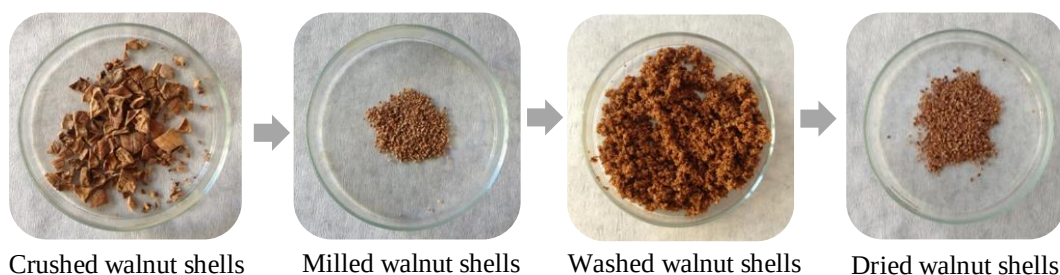


Figure 4.2. Pretreatment of walnut shells

After the pretreatment, carbonization and activation steps were applied. While the volatile compounds in the walnut shells were removed by carbonization, carbon yield was increased by the activation methods. The carbonization and activation system is shown in Figure 4.3.



Figure 4.3. Carbonization and activation process

▪ **Preparation of physically activated carbon**

Pre-treated walnut shells were carbonized under nitrogen gas flow at 400°C for 2 hours and activated under CO₂ gas flow at 800°C for 1 hour (Okutucu et al., 2011; Zhang et al., 2011; Nowicki et al., 2010). The carbonized form and physically activated carbons are presented in Figure 4.4.

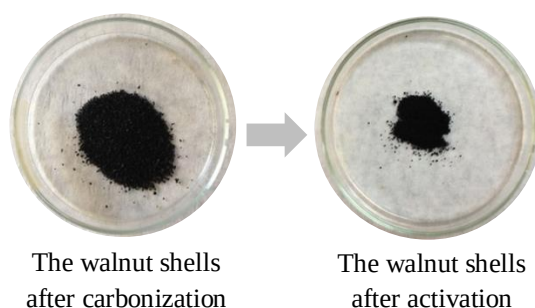


Figure 4.4 Physically activated walnut shells

▪ **Preparation of chemically activated carbons**

▫ *Nitric acid activated carbon preparation (Acid activation)*

Pre-treated walnut shells were carbonized at 800°C under nitrogen gas flow for 3 hours. The carbonizate was mixed with 6 M HNO₃ solution in a ratio of 1g walnut shell/10 mL HNO₃ at boiling point temperature of nitric acid (83 °C) continuously.

After all the acid was evaporated, the walnut shells were dried in oven. Then the acid treated walnut shells were washed with distilled water to increase the pH

until it reached neutral value (Ekpete and Horsfall, 2011; Mui et al., 2010; El-Sheikh et al., 2007). Figure 4.5 shows the steps of the nitric acid treatment.

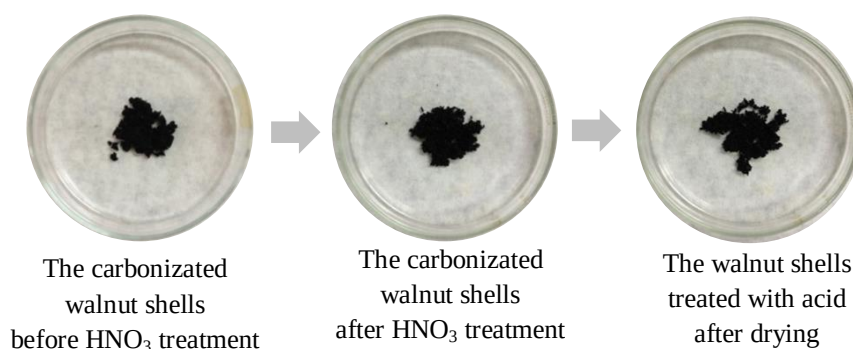


Figure 4.5 Nitric acid treatment of walnut shell based activated carbons

▫ *Zinc chloride activated carbon preparation (Metal salt activation)*

Pre-treated walnut shells were mixed with zinc chloride solution in ratio of walnut shell/ ZnCl_2 equals to 1:1 by weight. After drying, the mixture was carbonized at 800°C under nitrogen gas flow (to prevent combustion) for 3 hours. The carbonization products were washed with 1 M HCl to remove residual organic and mineral matters and washed with distilled water to increase the pH up to neutral value (Zabihi et al., 2010; Yang and Qiu, 2010; Acharya et al., 2009). Zinc chloride treatment of the walnut shells are presented in Figure 4.6.

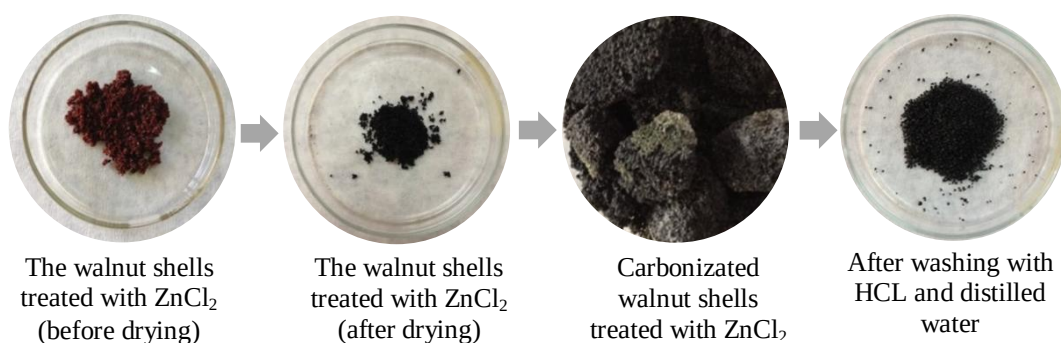


Figure 4.6 Zinc chloride activation of walnut shells

▫ *Potassium chloride activated carbon preparation (Base activation)*

Pre-treated walnut shells were mixed with KOH solution ratio of KOH/Walnut Shell equals to 1:1 by weight. After drying, the mixture was carbonized at 800°C under nitrogen gas flow for 3 hours. The carbonizate was

washed with HCl and then washed with distilled water (Choi et al., 2012; Bagheri and Abedi, 2009; Nowicki et al., 2010; Joseph et al., 2006). In 4.7 potassium hydroxide activation steps are shown.

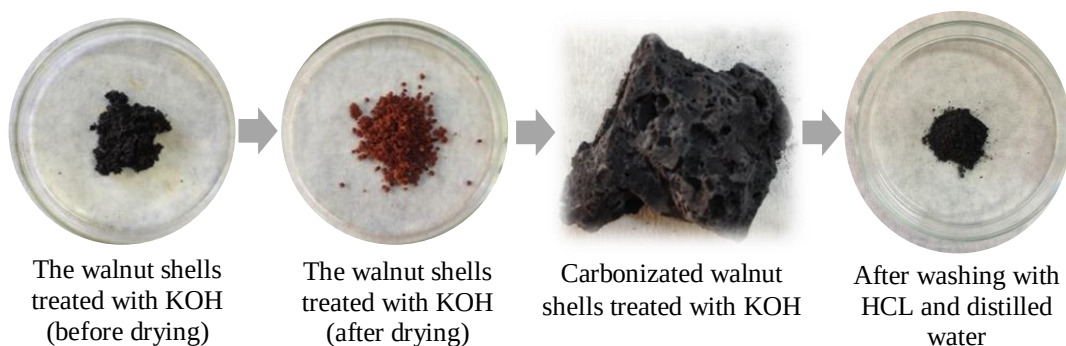


Figure 4.7. Potassium hydroxide activation of walnut shells

4.1.1.2 Metal impregnation

Two main groups of catalyst including the Fe/AC and Fe-TiO₂/AC were prepared applying iron impregnation and sol-gel methods.

▪ Iron impregnation method (for the preparation of Fe/AC catalysts)

Iron was impregnated on each of activated carbons (P-AC, H-AC, Z-AC and K-AC) by using Fe(NO₃)₃·9H₂O as metal precursor and it was impregnated in a ratio of Fe/Catalyst=1/10 by weight. Iron on activated carbon catalysts were represented by adding 'Fe/' in front of the corresponding activated carbon symbol (e.g. Fe/P-AC). After impregnation, the catalysts were calcined at 200°C in air atmosphere to remove the nitrates.

▪ Sol-gel method (for the preparation of Fe-TiO₂/AC catalysts)

The preparation of the photocatalyst (Fe-TiO₂/AC) can be investigated in two steps. In the first step Fe-TiO₂ sol was prepared and in the second step, the activated carbons were added into Fe-TiO₂ sol to form Fe-TiO₂/AC gel and the heat treatments were applied.

The Fe-TiO₂/AC catalyst was prepared in ratio of (Fe-TiO₂)/Catalyst is equal to 1/10 by wt. and Fe/TiO₂ is equal to 1/100 by wt. according to the procedures in literature (Huang et al., 2011; Kim et al., 2006; Li et al., 2010; Liu

et al., 2010; Tang et al., 2012; Zhao et al., 2010). The preparation of Fe-TiO₂ sol, addition of activated carbon and heat treatment steps are presented in Figure 4.8.

- Ti(OBu)₄ was diluted in methanol solution
- Fe(NO₃)₃·9H₂O was dissolved in methanol
- Ti(OBu)₄ and Fe(NO₃)₃·9H₂O solutions were mixed.
- pH of the mixture was adjusted to 7.
- The desired amount of activated carbon was added to the Fe-TiO₂ sol.
- After the Fe-TiO₂ sol coated on activated carbon was changed into gel form the support was vacuum dried at 90°C.
- The obtained particles were heat treated at 500°C for 2 h under nitrogen gas flow.

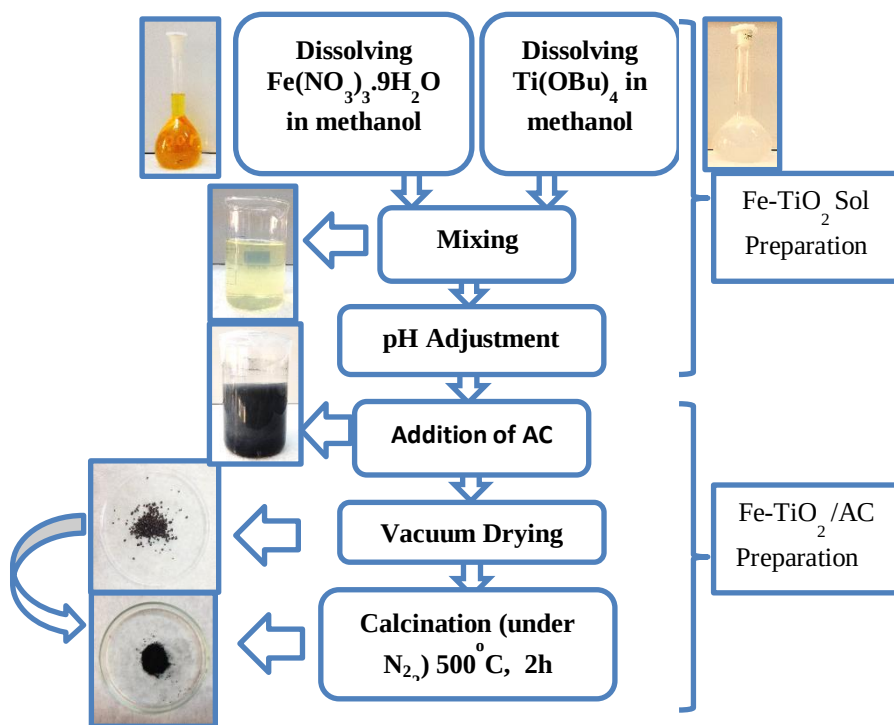


Figure 4.8 Preparation steps of Fe-TiO₂/Activated carbons

Iron-titania coated on activated carbon catalysts were denoted as adding ‘Fe-TiO₂/’ in front of the corresponding activated carbon symbol (e.g. Fe-TiO₂/P-AC) throughout this study.

4.1.2 Characterization of catalysts

Characterization of the catalyst supports (activated carbons) and the catalysts (Fe-TiO₂/AC and Fe/AC) were carried out in İzmir Yüksek Teknoloji Enstitüsü/Malzeme Araştırma Merkezi.

The morphology of the supports and catalysts was observed by a Phillips XL 30S FEG scanning electron microscope (SEM). Everhart-Thornley detector (ETD) was used to investigate the porous structures of the catalyst supports and Back-scattered electron detector (BSED) was used to determine the iron distribution on the catalyst surfaces. Also, the elemental distribution on the catalysts which showed the highest catalytic performances in the advanced oxidation processes was determined by the mapping method of the SEM analysis.

The phases and the crystal structures were studied using X-ray diffraction (XRD) analysis operating by a Philips X' Pert Pro and the XRD patterns of the catalysts were recorded in the angle range of $2\theta=5-80^\circ$.

Measurements of surface area, average pore size and micropore volume of the catalyst support and the catalyst which showed the highest catalytic performance in catalyst screening experiments were performed by a Micromeritics Gemini-2380 apparatus based on the Brunauer–Emmett–Teller (BET) method.

The point of zero charge analyses were performed to determine pH range in which each of the activated carbon surface is charged positively to attract the anionic dye molecules of Procion Red MX-5B so that a more efficient adsorption is achieved during the advanced oxidation treatments. Using 0.1 M NaOH or HCl, the solutions at initial pHs 5, 6, 7, 8, 9, and 10 were prepared. P-AC, H-AC, Z-AC and K-AC were added into these solutions. After the activated carbons kept 3 hours in these solutions, final pH measurements were carried out in every certain time intervals until the final pH was the same as the previous value. The initial and the final pHs of the solutions were plotted to determine the point of zero charges of each of the activated carbons (Orfao et al., 2006).

4.1.3 Experimental set-up and procedure

4.1.3.1 Experimental set-up and procedure for Fenton like process

The Fenton like experiments were carried out in 250 mL three necked volumetric flasks for 2 hours using a temperature controlled hot plate. The experimental system is illustrated in Figure 4.9.

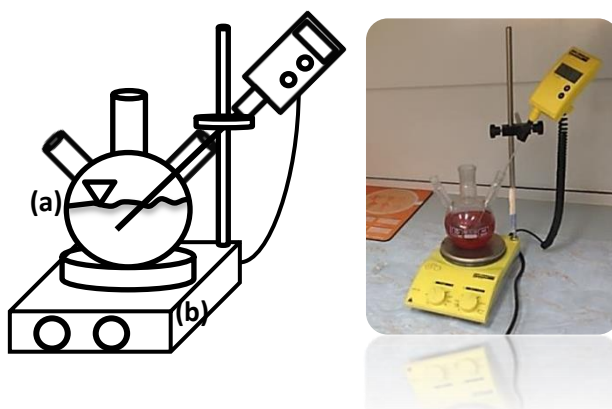


Figure 4.9. Experimental set up of Fenton like oxidation (a) three necked volumetric flasks, (b) temperature controlled hot plate stirrer

Initial pH of the dye solutions were adjusted to the desired value using dilute sulfuric acid and sodium hydroxide solutions. When the temperature reached the set value, hydrogen peroxide and catalyst were added into the reaction medium simultaneously. Samples were taken at regular intervals during the experiments in order to analyze the degradation and the decolorization efficiencies.

4.1.3.2 Experimental set-up and procedure for photo-Fenton like and photocatalytic oxidation processes

The experimental set up mainly consisted of a 850 mL of photoreactor, a magnetic stirrer and a cooler. There was a UV lamp in the quartz tube of the photoreactor. The photoreactor was installed in a cabinet to avoid emissions of UV light. A jacket, through which water was circulated, was placed around the reactor to maintain the desired reaction temperature. The photocatalytic experimental set up is presented in Figure 4.10.

In a typical experimental run, the initial pH of the dye solution was adjusted to the desired value. Certain amounts of hydrogen peroxide and the catalyst were added into the dye solution. After the solution was filled into the reactor the UV

lamp was turned on. The samples were taken at regular time intervals using a sample valve in order to analyze the degradation and the decolorization efficiencies of the dye with respect to time.

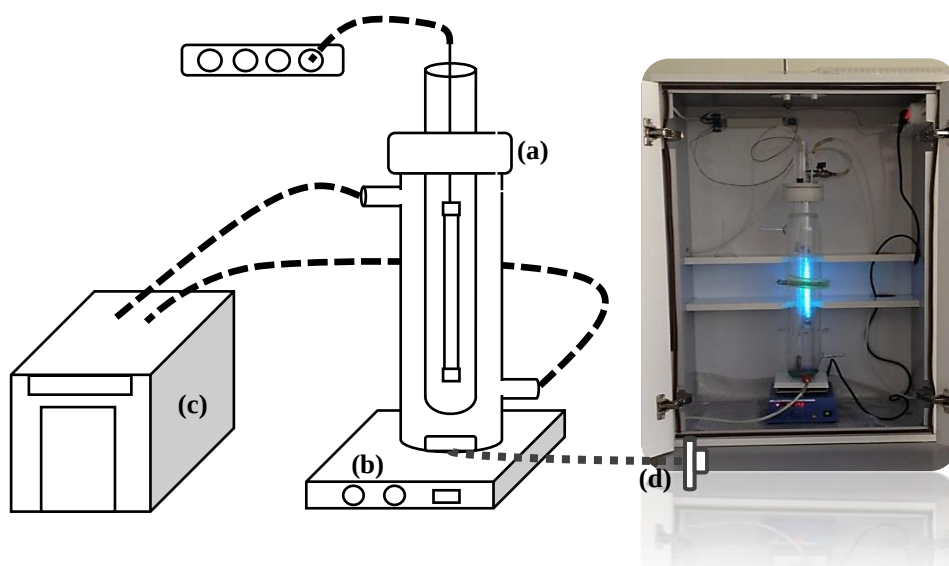


Figure 4.10. The experimental setup, (a) photoreactor, (b) magnetic stirrer, (c) circulator, (d) sample valve.

4.1.3.3 Experimental set-up and procedure for catalytic wet air oxidation processes

The CWAO reactions were performed as a semibatch process in a bubble column reactor of 500 mL volume ($h=0.5$ m; $D=0.35$ m), which is made of a stainless steel material. A schematic diagram of the experimental setup is illustrated in Figure 4.11.

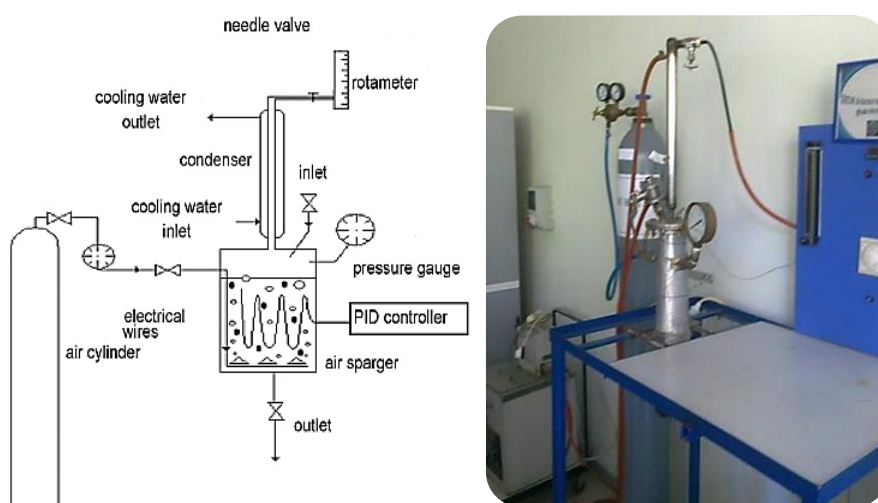


Figure 4.11. Experimental setup of CWAO process.

250 mL of dye solution was charged into the reactor and heated to the desired temperature by electrical wires wrapped around the reactor. The reaction temperature was controlled by a PID controller (1/32DIN temperature controller). In order to minimize the heat loss the reactor was insulated with glass wool. There was a condenser at the top of the reactor, which was used to condense the vapors formed during the reaction and send the condensate back to the reactor. Air was fed continuously and distributed in the reactor via a sparger placed at the bottom of the reactor. A rotameter (Sho-Rate) is used to adjust the flow rate of the air stream. Samples were taken and analyzed at the end of experiment.

4.1.4 Advanced oxidation experiments

4.1.4.1 Fenton like oxidation experiments

Prior to the parametric study, catalyst screening experiments were performed in order to determine which type of the catalyst showed the highest catalytic performance in Fenton like oxidation of Procion Red MX-5B. In these experiments, the initial dye concentration, the initial hydrogen peroxide concentration and pH was kept at 100 mg/L, 4 mM and 3 respectively, while the catalyst loading varied as 0.25 g/L and 0.5 g/L and the temperature was varied as 30 and 50 °C. The experimental plan of the catalyst screening experiments are given in Figure 4.12.

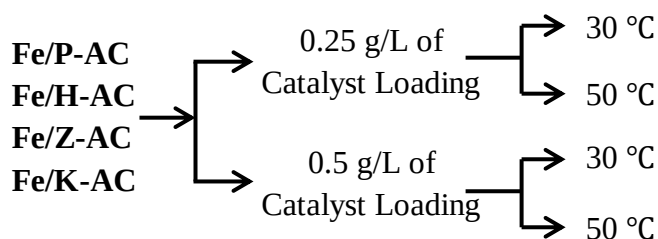


Figure 4.12. Catalyst screening experiments of Fenton like oxidation

In the parametric study, the influences of the initial hydrogen peroxide concentration, catalyst loading, initial pH, and temperature on the degradation and decolorization efficiencies and the rates were investigated in the presence of the catalyst showed the highest catalytic performance in the catalyst screening experiments. The initial dye concentration was kept at 100 mg/L. Parametric study is summarized in Table 4.1.

Table 4.1. Parametric Study on Fenton like oxidation

Reaction Parameter	
Initial Hydrogen Peroxide Concentration, mM ([Dye] ₀ =100 ppm, 0.1 g/L of catalyst loading, pH=3, T=50°C)	No H ₂ O ₂
	1
	4
	8
Catalyst Loading, g/L ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =4 mM, pH=3, T=50°C)	No Catalyst
	0.1
	0.25
	0.5
Initial pH ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =4 mM, 0.25 g/L of catalyst loading, T=50°C)	3
	3.5
	4
Reaction Temperature, °C ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =4 mM, 0.25 g/L of catalyst loading, pH=3)	30
	40
	50
	60
	70

After the most suitable catalyst and the optimum reaction conditions were determined, reusability of the catalyst was tested during three consecutive runs under the optimum experimental conditions.

4.1.4.2 Photo-Fenton like and photocatalytic oxidation experiments

Catalyst screening experiments were performed for both Fe/AC and Fe-TiO₂/AC types of catalysts. Prior to the photo-Fenton like (UV+H₂O₂+Catalyst) experiments, the photocatalytic oxidation (UV+Catalyst) abilities of Fe/AC and Fe-TiO₂/AC catalysts were tested in the absence of H₂O₂ varying the catalyst loadings.

In these experiments, the initial dye concentration and the initial pH were kept constant at 100 mg/L and 3, respectively, while the catalyst loading varied as 0.25 g/L and 0.5 g/L. The experimental plan of the catalyst screening experiments is presented in Figure 4.13.

The optimum reaction conditions for photo-Fenton like oxidation of azo dyes were determined in presence of the catalyst which showed the highest catalytic performance in the catalyst screening experiments.

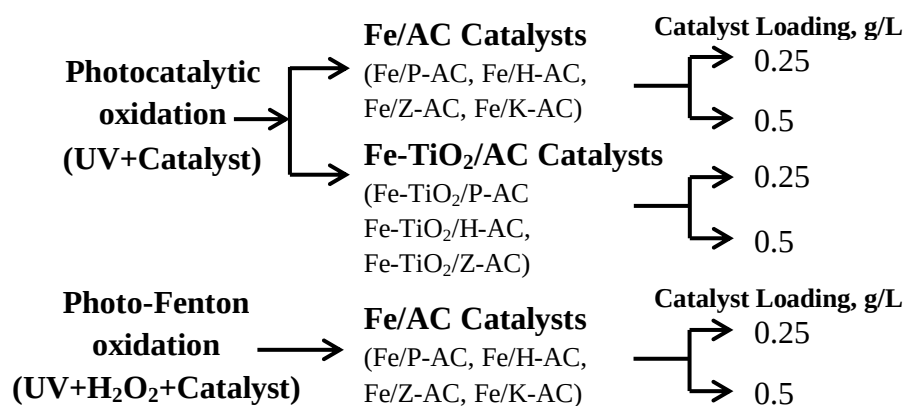


Figure 4.13. Catalyst screening experiments of photocatalytic and photo-Fenton like oxidation

Because the degradation and decolorization efficiencies recorded in the absence of H_2O_2 were very low in the presence of both Fe/AC and Fe-TiO₂/AC catalysts, the parametric study was carried out in the presence of hydrogen peroxide and Fe/AC catalysts which are easier and more inexpensive to prepare.

In the parametric study, the effects of catalyst loading, UV light intensity, pH and the initial H_2O_2 concentration on decolorization and the degradation were investigated. The parametric study is summarized in Table 4.2.

Table 4.2 Parametric study on photo-Fenton like oxidation

Reaction Parameter	
Catalyst Loading, g/L ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =4 mM, pH=3, UV light intensity=6 Watt)	No Catalyst
	0.1
	0.25
	0.5
Initial Hydrogen Peroxide Concentration, mM ([Dye] ₀ =100 ppm, 0.25 g/L of catalyst loading, pH=3, UV light intensity=6 Watt)	No H ₂ O ₂
	1
	4
	8
Initial pH ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =2 mM, 0.25 g/L of catalyst loading, UV Light intensity=6 Watt)	3
	5
	7
UV Light Intensity, Watt ([Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =2 mM, 0.25 g/L of catalyst loading, pH=3)	No UV light
	6
	8

4.1.4.3 Catalytic wet air oxidation experiments

The catalytic performances of the Fe/AC catalysts were tested in also CWAO process. The initial dye concentration, air flow rate and pH were kept

constant at 100 mg/L, 0.61 l/min and 7 respectively, while the temperature, pressure and the catalyst loadings were varied as 70 and 90°C, 1 and 3 atm, and, 0.25 g/L and 0.5 g/L, respectively. The catalyst screening experiments performed for catalytic wet air oxidation of Procion Red MX-5B is shown in Figure 4.14.

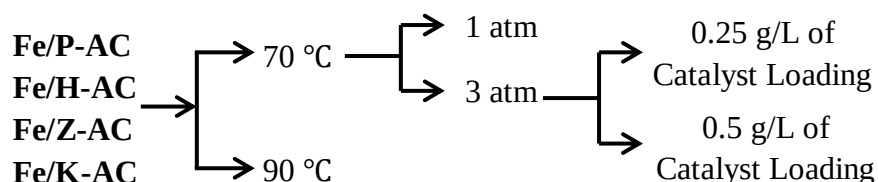


Figure 4.14. Catalyst screening experiments of catalytic wet air oxidation

In the parametric study the influences of the catalyst loading, reaction temperature and the pressure on dye removal efficiencies were investigated in presence of the most suitable catalyst to determine the optimum reaction conditions. The air flow rate and the initial pH were kept constant at 0.61 L/min and 7, respectively for an initial dye concentration of 100 ppm. The experimental plan of the parametric study is presented in Table 4.3.

Table 4.3 Parametric study on catalytic wet air oxidation

Reaction Parameter	
Catalyst Loading, g/L ([Dye] ₀ =100 ppm, pH=3, 0.61 L/min of air flow rate, P=1 atm, T=70 °C)	No Catalyst
	0.1
	0.25
	0.5
Temperature, °C ([Dye] ₀ =100 ppm, 0.25 g/L of catalyst loading, pH=3, 0.61 L/min of air flow rate, P=1 atm)	50
	70
	90
Pressure, atm ([Dye] ₀ =100 ppm, pH=3, 0.61 L/min of air flow rate, T=70 °C)	1
	2
	3

4.1.5. Analysis

4.1.5.1 Degradation and the decolorization analyses

The degradation and decolorization analyses were performed with a UV-VIS spectrophotometer (Shimadzu UV-VIS Spectrophotometer Model 1800).

The degradation efficiencies were calculated from the absorbance values at 330 nm indicating the degradation of the aromatic part of the azo dyes while the decolorization efficiencies were calculated from the absorbance values at

maximum wavelength (538 nm for Procion Red MX-5B) corresponding to the breakage of chromophore containing azo linkage (-N=N-) of the dye molecule. The decolorization and degradation efficiencies were calculated using the following equation:

$$\text{Degradation or Decolorization Efficiency} = \frac{A_0 - A_t}{A_0} \quad (4.1)$$

Where, A_0 is the initial absorbance and A_t is the absorbance at time t .

4.1.5.2 Metal leaching analysis

The iron content in the treated dye solution was evaluated in the presence of the most suitable catalysts under the optimum reaction conditions determined for the advanced oxidation processes tested in the present study. The iron leaching analyses were performed using an Atomic Absorption Spectrometer (Varian SpectrAA-10 Plus).

4.1.5.3 Toxicity tests

Toxicity tests were carried out in order to determine whether any toxic end products were generated during the advanced oxidation of the Procion Red MX-5B. These tests were performed by the comparison of the root lengths of the *Lepidium sativum* growing in the treated dye solution and distilled water.

The seeds of the *Lepidium sativum* were purchased from a local market. 5 mL of treated dye solution and distilled water (as control group) pipetted onto filter paper fitted into 9-cm of plastic petri dishes separately. 25 undamaged seeds were distributed uniformly on the dishes. The dishes were incubated in the dark at room temperature. At the end of the 96 hours, the lengths of the roots were measured growing in both of the mediums (Jonstrup et al., 2011, Almeida and Corso, 2014). The toxicity was evaluated according to the different methods derived from literature:

- **Method 1** (Nawanopparatsakul et al., 2012, Jonstrup et al. 2011)

$$\text{Growth Inhibition (or Root Elongation)} = (L_o - L_t) / L_o$$

L_o : Average root elongation in control medium (distilled water), cm

L_t : Average root elongation in treated medium, cm

- **Method 2** (Hoekstra et al., 2002)

$$\text{Relative Root Growth, \%} = (L_o/L_t) * 100$$

L_o : Average root elongation in control medium (distilled water), cm

L_t : Average root elongation in treated medium, cm

- **Method 3** (Ayhan et al., 2007)

$$\text{Absolute Growth Rate} = (L_{t1} - L_{t2}) / \Delta t$$

L_{t1} : Root length measured at time t_1 , cm

L_{t2} : Root length measured at time t_2 , cm t , day.

4.1.6. Kinetic Study

The kinetic study was performed by the data collected in the parametric study of the oxidation method which was determined as the most suitable one. The reaction rates were calculated at different temperatures by fitting the n^{th} order reaction rate models to the decolorization data obtained in parametric study. The reaction rate constants were derived at various reaction temperatures and the activation energy was calculated.

4.2. Biological Oxidation

In this section, two white rot fungi, *P. chrysosporium* and *T. versicolor* were tested to treat the solutions of Procion Red MX-5B. The microorganisms were immobilized on walnut shells to make the microorganism step easier. In order to choose the most suitable microorganism firstly the microorganism selection experiments were carried out. Then, the optimum reaction conditions were determined in the presence of the selected microorganism.

4.2.1. Growth of the microorganisms

P. chrysosporium and *T. versicolor* culture were maintained on potato dextrose agar (PDA) and malt extract agar plates at 37 °C and 26 °C, respectively, in darkness for 3 days. Agar plates were prepared by dissolving 39 g potato dextrose agar or 50 g of malt extract agar in 1 liter distilled water. Potato dextrose agar plates were sterilized at 121°C for 15 minutes and malt extract agars were sterilized at 115°C for 10 minutes. *P. chrysosporium* and *T. versicolor* cultures cultivated on the agar plates are presented in Figure 4.15.



Figure 4.15 Fungi cultures cultivated on agar plates

Inoculation and immobilization of the microorganisms on walnut shells were carried out in 1 L of round bottom glass flasks containing 2% malt extract broth by weight and sterilized walnut shell powder. The process was maintained under air atmosphere, in darkness, at 37 °C for *P. chrysosporium* and at 26 °C for *T. versicolor*, for 7 days. At the end of 7 days the immobilized microorganisms are filtered and stored in laboratory jars. In Figure 4.16 the inoculation and immobilization stages are given.

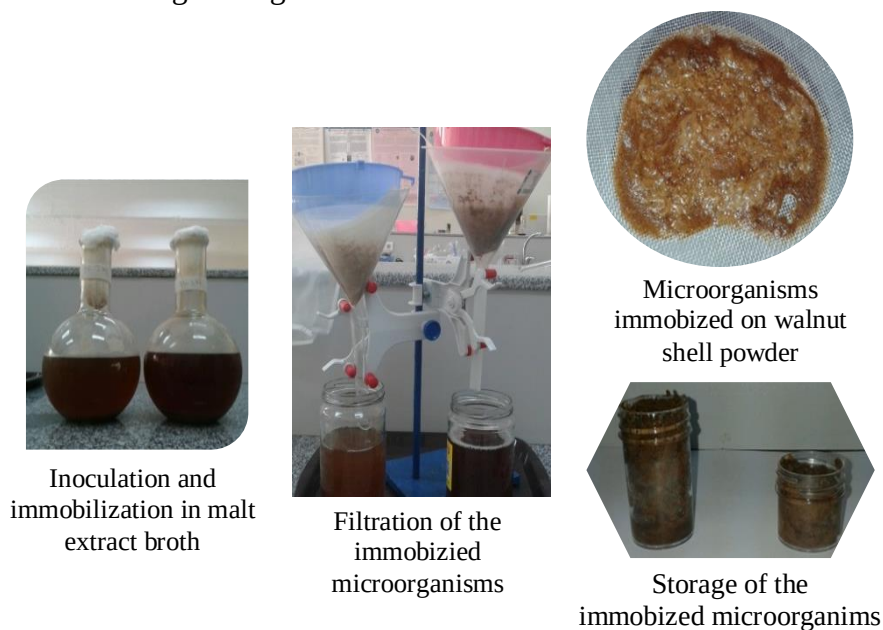


Figure 4.16 Inoculation and immobilization stages

4.2.2 Microorganism Selection Experiments

In order to compare the oxidation abilities of the *P. chrysosporium* and *T. versicolor*, the microorganisms are added into 50 mL of Procion Red-MX-5B solutions separately at a concentration of 1 gram of immobilized microorganism/100 mL. The initial concentration of Procion Red MX-5B

solutions were kept constant at 100 ppm. Besides using microorganisms alone, three sets of experiments also performed for both of the microorganisms, adding microorganism and 2 g/L of glucose; microorganism and 1 mM of H₂O₂; and, lastly, microorganism, 2 g/L of glucose and 1 mM of H₂O₂. The batch experiments were maintained at room temperature and 200 rpm of orbital shaking for 7 days. At the end of the experiments samples were taken to evaluate the degradation and decolorization efficiencies. The experimental plan was summarized in Table 4.4.

Table 4.4 Microorganism Selection Experiments

Using <i>P. chrysosporium</i>	Micro-organism alone
	Addition of Glucose
	Addition of H ₂ O ₂
	Addition of Glucose and H ₂ O ₂
Using <i>T. versicolor</i>	Micro-organism alone
	Addition of Glucose
	Addition of H ₂ O ₂
	Addition of Glucose and H ₂ O ₂

4.2.3. Experimental Set-up

The batch experiments were carried out in an orbital shaker at room temperature and 150 rpm using 50 mL of 100 ppm Procion Red MX-5B solutions. Samples are taken from the reaction medium at every 2 days. The experimental system is presented in Figure 4.17.



Figure 4.17 Experimental set up of biological oxidation

4.2.3. Parametric Study

After determination of the most suitable microorganism in the microorganism selection experiments, the influences of microorganism concentration and the glucose concentration were investigated in the presence of

the selected microorganism varying the microorganism concentration in the range of 0.5-2 g/100 mL and altering the initial glucose concentration between 1 and 4 g/L. The experimental plan is shown in Table 4.5.

Table 4.5 Parametric study on biological oxidation

Immobilized Microorganism Concentration, g/100 mL	No Microorganism
	0.5
	1
	2
Glucose Concentration, g/L	No Glucose
	1
	2
	4

4.2.4 Analysis

The dye removal efficiencies were evaluated using a UV-VIS spectrophotometer. The degradation efficiencies were calculated from the absorbance values recorded at 330 nm and the decolorization efficiencies were found using the absorbance valued monitored at 538 nm.

5. RESULTS AND DISCUSSION

5.1 Results and Discussion for Advanced Oxidation Processes

5.1.1 Characterization of the catalyst supports and catalysts

5.1.1.1 Scanning Electron Microscopy

Investigation of the surface morphology of the catalyst supports and catalysts prepared by different activation techniques was carried out by scanning electron microscopy (SEM). Everhart-Thornley detector (ETD) was used to record the SEM photographs of each of the catalyst support. In Figure 5.1 SEM photographs of the catalyst supports at 20000 times magnification is presented.

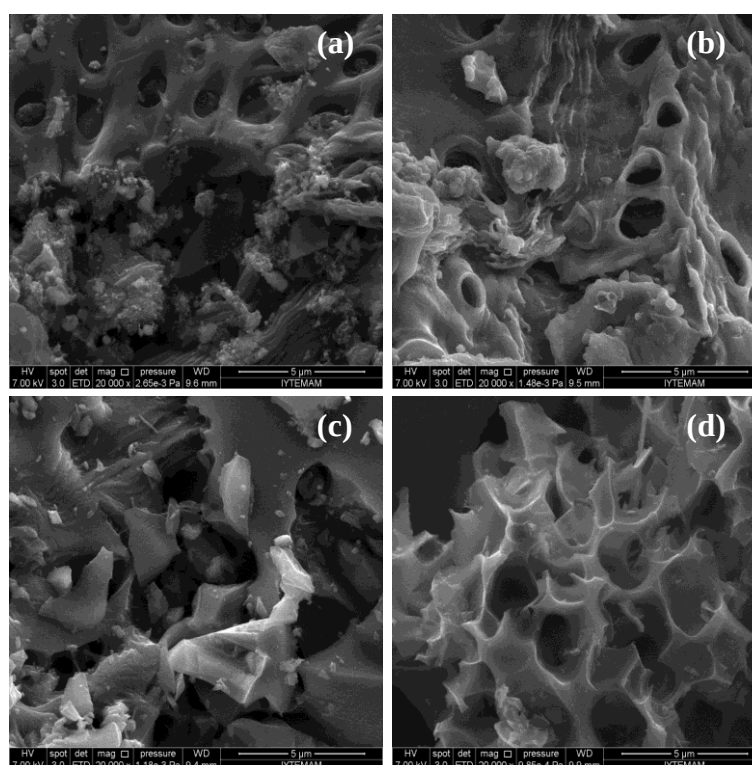


Figure 5.1. SEM photographs of the P-AC (a), H-AC (b), Z-AC (c), and, K-AC (d) at 20000 times magnification (with Everhart-Thornley Detector).

According to the SEM photographs, each of the activated carbon prepared has porous leading to large surface areas which make the adsorption capacity higher and hence iron impregnation efficiency increases.

The activated carbon textures differ with respect to the activation method. P-AC surface is full of cavities at different size and shapes developed due to the carbon monoxide and carbon reaction forming carbon monoxide. In the physical

activation either carbon dioxide or steam corrodes the carbonaceous material to form a porous structure (Marsh and Reinoso, 2006).

H-AC has heterogeneous porous texture. In the acidic treatment, the oxidizing agent nitric acid makes the pore walls of the activated carbon thinner resulting in opening the closed pores and widening existing pores (Huang et al., 2003). Besides, various surface oxygen complexes are formed on activated carbon due to the treatment with oxidizing agents. These oxygen complexes influence the surface area and pore texture of the activated carbon (Pradhan and Sandle, 1999).

Z-AC contains attached small particles over its surface constituting complex pore networks which were probably formed during the evaporation of ZnCl_2 in carbonization.

K-AC has a more homogeneous structure when compared to the other activated carbons. In the potassium hydroxide treatment, the primal pores formed due to the evaporation of the volatile compounds in the carbonization step are improved by the reaction between carbon and potassium hydroxide and new pores are also developed.

The surface morphology of the Fe/AC catalysts (Fe/P-AC, Fe/H-AC, Fe/Z-AC, and, Fe/K-AC) was examined using Back-Scattered electron detector (BSED) in order to detect the iron particles distributed on the activated carbon. The SEM photographs of the catalysts at 20000 times magnification were shown in Figure 5.2.

The lighter areas in the SEM photographs of the Fe/AC catalysts indicate the atoms having higher atomic number (iron atoms) and the darker areas shows the atoms having lower atomic number (carbon atoms). On Fe/K-AC surface the iron particles cannot be detected because probably the iron ions occupied the interior sites of the pores instead of placing on the surface. Gray colored areas on the micrograph of Fe/Z-AC might be interpreted as iron film formation on the activated carbon surface. Different tones of gray represent the various phases of iron. Iron particles are observed clearly on the Fe/P-AC surface.

The iron dispersion on the catalyst surfaces can be observed more clearly by the mapping method of the scanning electron microscopy. In Figure 5.3, the

elemental distribution on the Fe/K-AC which is determined as the most suitable catalyst in the Fenton like and photo-Fenton like oxidation, and Fe/Z-AC which is found to be the most suitable catalyst in the catalytic wet air oxidation process are shown.

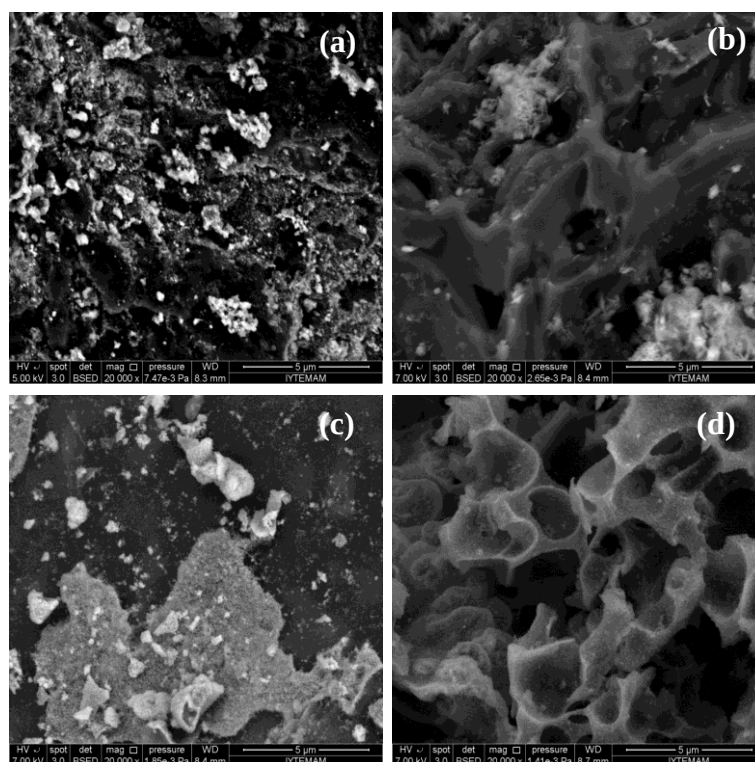


Figure 5.2. SEM photographs of the Fe/P-AC (a), Fe/H-AC (b), Fe/Z-AC (c), and, Fe/K-AC (d) at 20000 times magnification (with Back-Scattered Electron Detector).

The micrographs show that a homogeneous distribution was accomplished in the iron impregnation step. Oxygen content can be a result of the surface groups formed on the activated carbon surface during the chemical activation of the walnut shells.

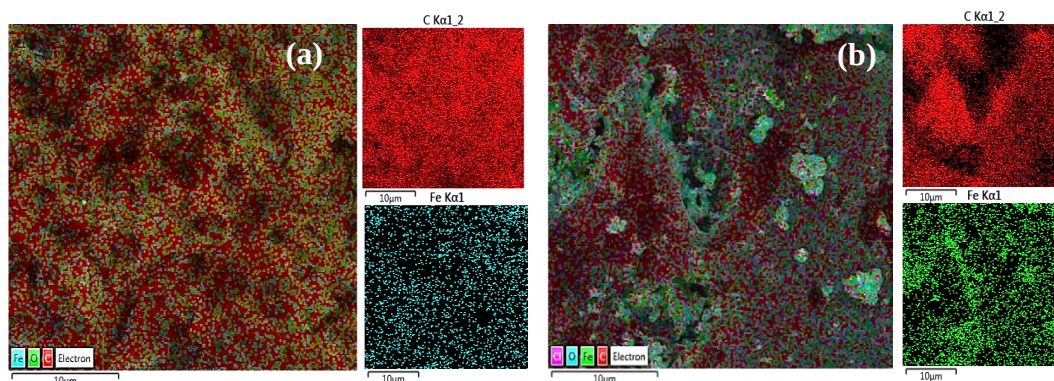


Figure 5.3. SEM/Mapping photographs of the Fe/K-AC (a) and Fe/Z-AC (b).

The surface morphology of the Fe-TiO₂/AC types of catalysts was studied by scanning electron microscopy (SEM) using Back-Scattered electron detector (BSED) in order to demonstrate the presence of the TiO₂ and iron particles distributed on the activated carbon. The SEM photographs of the Fe-TiO₂/AC catalysts are shown in Figure 5.4.

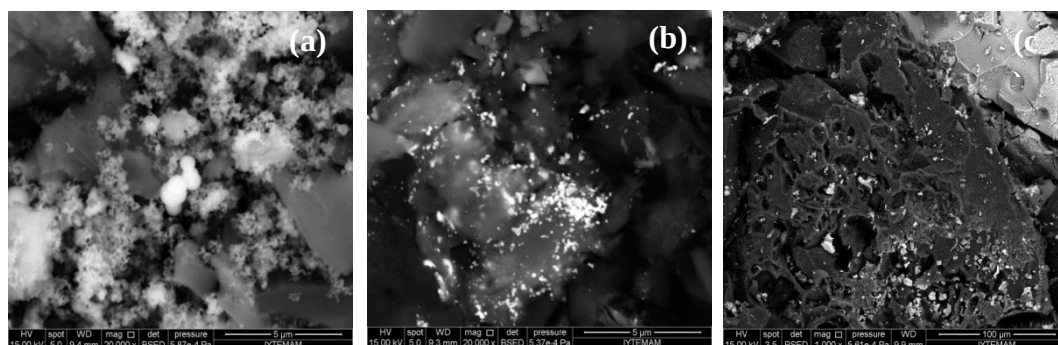


Figure 5.4. SEM photographs of the Fe-TiO₂/P-AC (a), Fe-TiO₂/H-AC (b), and, Fe-TiO₂/Z-AC (c) at 20000 times magnification (with Back-Scattered Electron Detector).

The lightest colored areas in the SEM photographs indicate the atoms having the highest atomic number (iron atoms), the darker areas shows the atoms having moderate atomic number (titanium atoms) and the darkest colored areas represents atoms having smallest atomic number (carbon atoms).

5.1.1.2 X-Ray Diffractometry Analysis

The phases and the amorphous/crystal structures of the activated carbons and the catalysts prepared by different activation methods were analyzed by X-Ray Diffractometry (XRD). The XRD patterns of the activated carbons and catalysts are shown in Figure 5.5 and 5.6, respectively.

The low peak intensities in the XRD patterns indicate that no large sizes of crystals are formed. Smooth diffraction peaks at around $2\theta = 26^\circ$ associated to the (002) plane spacing of graphite were observed. Having no diffraction peaks corresponding to the inorganic components indicates a successful carbonization process was achieved during the activated carbon preparation (Duarte et al, 2011).

After iron impregnation, the same diffraction peaks of graphite at $2\theta = 26^\circ$ were recorded in Fe/AC patterns. The iron particles in the catalysts cannot be detected because the impregnated iron ions are well distributed in the catalyst,

and, the individual iron ions are probably so small to detect. Ramirez et al. also reported the similar peaks of graphite in the XRD patterns of iron loaded carbon based catalysts. They did not observed any peaks corresponding to the iron phases when carbon aerogel was used and observed only peaks with very low intensity when activated carbon was used as catalyst support (Ramirez et al., 2007).

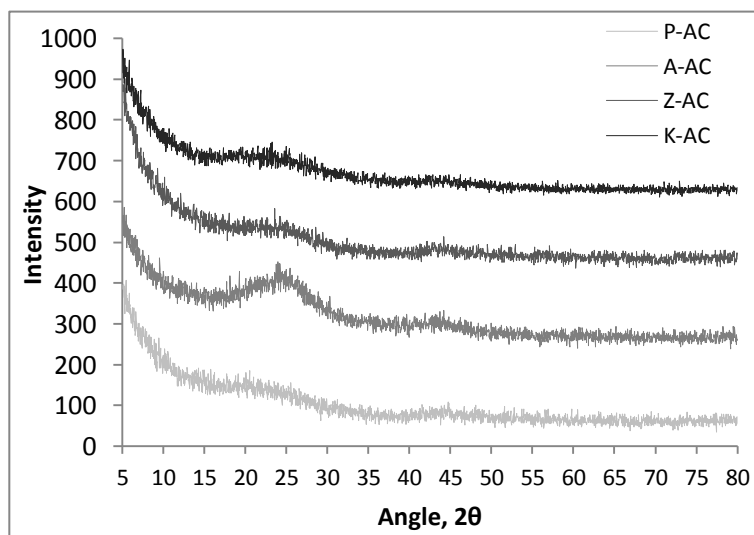


Figure 5.5. XRD patterns of the P-AC, H-AC, Z-AC, and, K-AC.

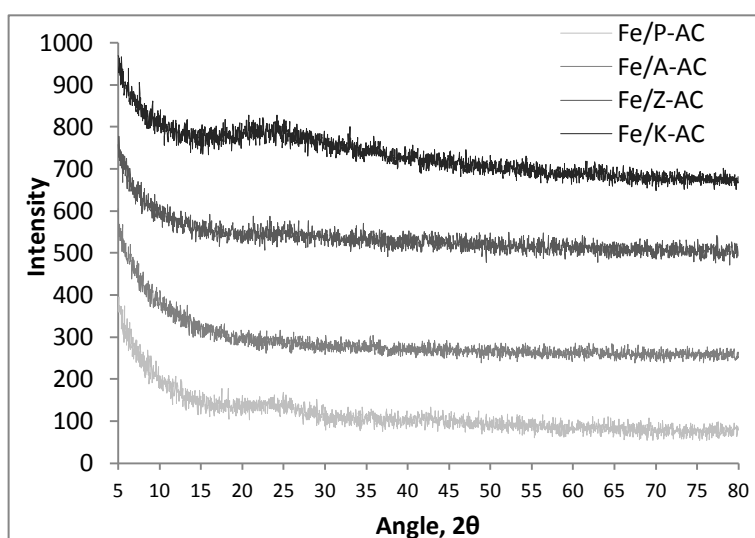


Figure 5.6. XRD patterns of the Fe/P-AC, Fe/H-AC, Fe/Z-AC, and, Fe/K-AC.

The phases of the Fe-TiO₂/AC catalysts prepared by various activation methods were investigated by X-Ray Diffractometry (XRD). The XRD patterns of the catalysts are presented in Figure 5.7.

The diffraction peaks at around $2\theta = 25^\circ$ and $2\theta = 48^\circ$ which are associated to the anatase (1 0 1) and (2 0 0) planes of titanium dioxide were observed respectively. Anatase phase has much higher photocatalytic activity than rutile phase. Besides, diffraction peak at around $2\theta = 26^\circ$ indicating the graphite (0 0 2) plane was also recorded in the XRD patterns of Fe-TiO₂/AC catalysts.

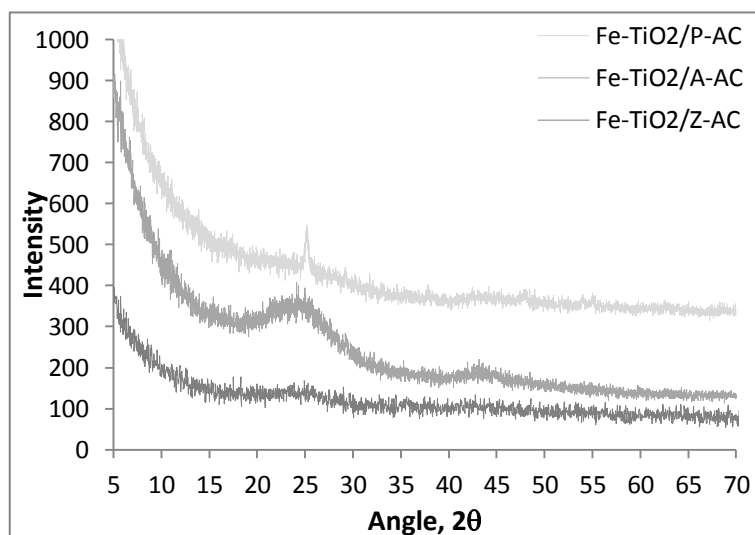


Figure 5.7 XRD patterns of the Fe-TiO₂/P-AC, Fe-TiO₂/H-AC, and, Fe-TiO₂/Z-AC.

5.1.1.3 Surface area and pore size measurements

The surface area (BET, Langmuir and t-Plot), pore volume and pore size measurements were carried out for only the catalyst supports and the corresponding catalysts which showed the highest catalytic performance in advanced oxidation processes (K-AC and Fe/K-AC in Fenton like and photo-Fenton like oxidation, Z-AC and Fe/Z-AC in catalytic wet air oxidation). The results of BET analysis obtained for the most suitable catalyst supports and catalysts are tabulated in Table 5.1.

Table 5.1. Surface area measurements of the selected catalyst supports and the catalysts

	Surface Area, m ² /g				t-Plot Micropore Volume, cm ³ /g	Average Pore Size, Å
	BET	Langmuir	t-Plot Micropore	t-Plot External		
K-AC	961.06	1207.36	828.33	132.72	0.3676	18.62
Fe/K-AC	724.86	911.9	593.73	131.12	0.2632	20.48
Z-AC	1370.3	1771.36	321.77	1048.53	0.1345	18.76
Fe/Z-AC	1143.2	1477.44	271.42	871.78	0.1137	19.08

According to the measurements, the BET surface areas were found to be 961.06 and 1370.3 m²/g for K-AC and Z-AC, respectively. When these results were compared to the surface areas of the organic waste based activated carbons in literature, it can be concluded that the activated carbons prepared in this study have large surface areas. Table 5.2 presents some of examples for the BET surface areas and the average pore sizes of the activated carbons reported in literature which were prepared under similar activation conditions.

Table 5.2. BET surface areas of the activated carbons in literature, which were prepared from the organic wastes.

	Organic Waste	Activation Conditions	BET Surface Area, m ² /g	Reference
K-AC	Walnut Shell	700°C, Weight Ratio=1:1	502	Jahangiri et al., 2012
	Kenaf Fiber	700°C Impregnation ratio=1.4	525.5	Chowdhury et al., 2011
	Cashew Nut Shell	700°C, Impregnation ratio=1.4	984	Kumar et al., 2011
Z-AC	Walnut Shell	C:ZnCl ₂ =1:1	803.74	Zahibi et al. 2010
	Rice Husk Sugarcane Bagasse	700°C, ZnCl ₂ :Rice Husk=1:1 ZnCl ₂ :Sug.Bag=1:1	674 (rice husk) 750 (sug. bag.)	Kalderisa et al., 2008
	Pine Cone	500°C, Weight Ratio=1:1	1462	Duman et al., 2009

The average pore sizes of the activated carbons (1.86-2.05 nm) show that they have microporous structures (if pore diameter < 2 nm: microporous; 2 < pore diameter < 50 nm: mezoporous; pore diameter > 50 nm: macroporous) which are suitable to metal impregnation and to use as catalyst support.

After the iron impregnation on the catalyst supports, the BET surface areas of the activated carbons were decreased from 961.06 m²/g to 724.86 m²/g for K-AC, and, from 1370.3 m²/g to 1143.2 m²/g for Z-AC. This may be due to the pores occupied by the iron ions. Because of the same reason, the micropore areas were also decreased and this resulted in the increase in the average pore size.

5.1.2 Point of zero charge analysis

The point of zero charge (pzc), describes the condition when the electrical charge density on a surface is zero. The surface functional groups and pH_{pzc} characterize the acidity or basicity of the adsorbent, type of activated carbon, and

the net surface charge of the carbon in solution. The influence of the functional groups of activated carbon determines pH_{pzc} which is the pH at which the net surface charge on carbon was zero. At $pH < pH_{pzc}$, the carbon surface has a net positive charge, while at $pH > pH_{pzc}$ the surface has a net negative charge (Al-Degs et al., 2007).

In this study, the removal of an anionic dye, Procion Red MX-5B was investigated in the presence of activated carbon catalyst supports. In order to accomplish high adsorption capacity, the activated carbon surfaces and the dye should be charged at opposite signs.

Therefore, the pH range in which the activated carbon surfaces were charged positively was determined by the point of zero charge analysis carried out for each of the activated carbon. The pH_{pzc} analysis of the activated carbons prepared in this study is given in Figure 5.8.

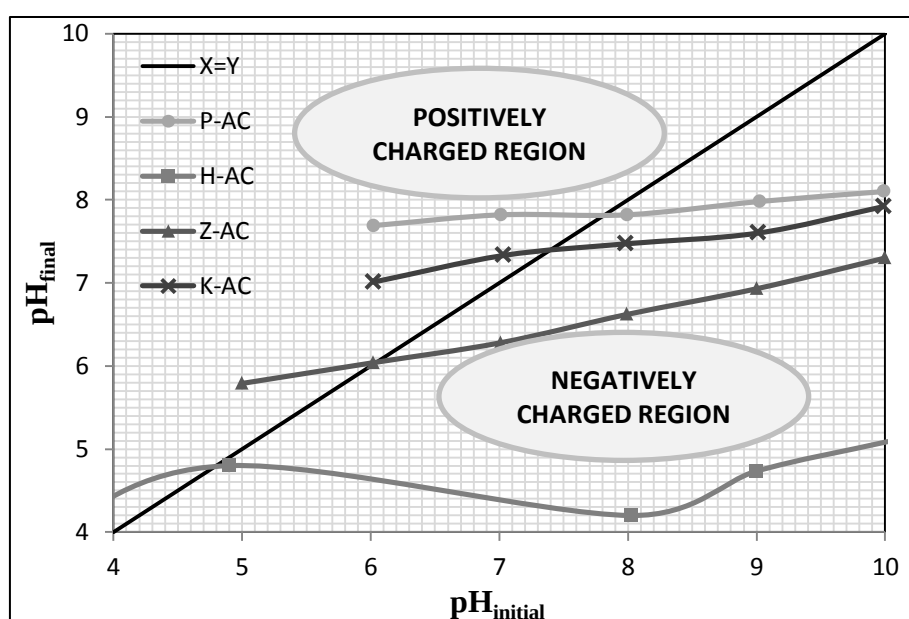


Figure 5.8. Point Zero Charge Analysis

According to the results, point of zero charge was determined pH 7.8, 4.8, 6 and 7.4 for Fe/P-AC, Fe/H-AC, Fe/Z-AC, and Fe/K-AC respectively.

The pH should be lower than the point of zero charge, pH_{pzc} of the activated carbon in order to maximize adsorption of an anionic substance. So, in the advanced oxidation processes the operating pHs were kept below the pH_{pzc} of the related activated carbon support.

5.1.3 Fenton like oxidation

5.1.3.1 Catalyst screening for Fenton like oxidation

The catalytic performances of Fe/AC catalysts prepared applying physical and three chemical activation methods and were tested in the catalyst screening experiments. In these experiments, the initial H_2O_2 concentration and the initial pH were kept constant at 4 mM and 3, respectively, for the degradation and the decolorization of dye solutions at initial concentration of 100 ppm. The catalyst loading and the reaction temperature were varied as 0.25-0.5 g/L and 30 and 50°C. Figure 5.9 and 5.10 show the degradation and the decolorization efficiencies, respectively, which were recorded in the presence of different catalysts.

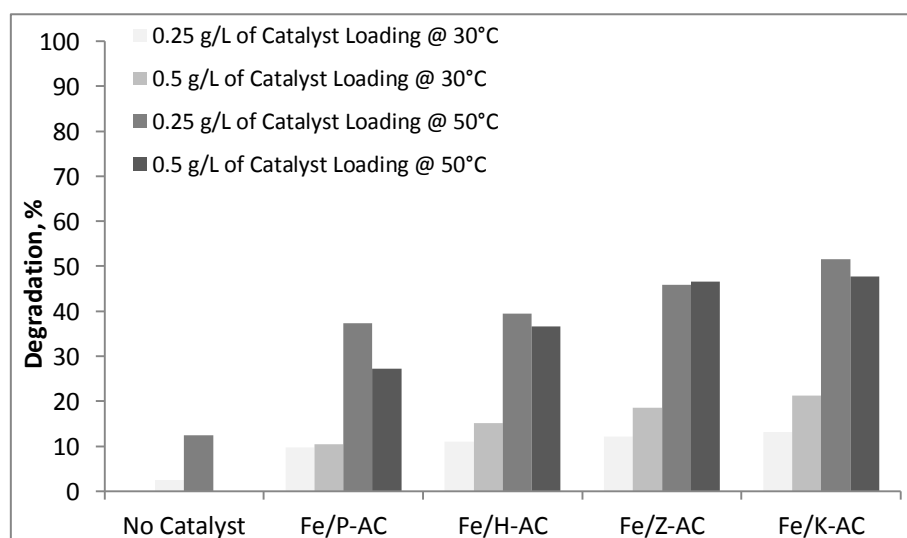


Figure 5.9. Degradation of Procion Red MX-5B by Fenton like oxidation in the presence of different catalyst supports. Reaction conditions: $[\text{Dye}]_0=100$ ppm, $[\text{H}_2\text{O}_2]_0=4$ mM, and, initial pH of 3.

Firstly, the ability of the H_2O_2 to degrade the Procion Red MX-5B was investigated in the absence of the any of the heterogeneous catalysts. When there is no catalyst in the reaction medium, the degradation efficiencies at 30 and 50°C were evaluated as 2.4% and 12.5%, respectively. The addition of catalyst resulted in increase in the degradation efficiencies up to 13.2% at 30 °C for the catalyst loadings of 0.25 g/L. The increase in catalyst dosage at low reaction temperature improved the dye removal. Up to 21.3% degradation was accomplished when the catalyst loadings were 0.5 g/L at 30°C.

Raising the temperature enhances the generation of hydroxyl radicals. The degradation efficiencies recorded at 50°C were considerably higher than those of

obtained at 30°C. At 50°C and 0.25 g/L of catalyst loadings the highest dye removal efficiencies were achieved. Under these conditions, dye degradation performances of the catalysts are ranked from the lowest to highest as follows: Fe/P-AC (37.4%) < Fe/H-AC (39.5%) < Fe/Z-AC (45.8%) < Fe/K-AC (51.6%). However, a further increase in the catalyst loadings at 50°C resulted in slight decrease in the degradation efficiencies due to the self-scavenging effect of iron ions and the parallel possible reactions.

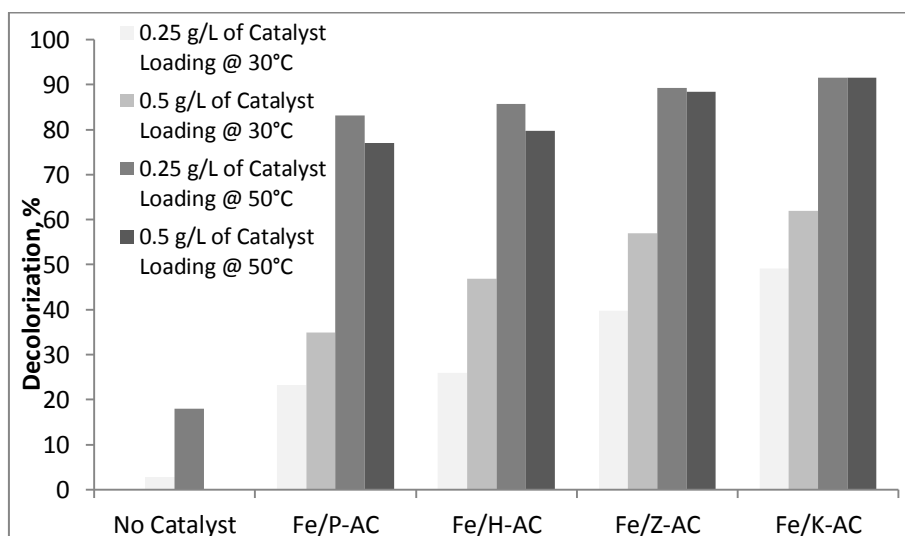


Figure 5.10. Decolorization of Procion Red MX-5B by Fenton like oxidation in the presence of different catalyst supports. Reaction conditions: [Dye]₀=100 ppm, [H₂O₂]₀=4 mM, and, initial pH of 3.

In the absence of any catalyst the 2.7% and 18% decolorization efficiencies were accomplished at 30 and 50 °C, respectively. As well as degradation efficiencies, the decolorization efficiencies were also enhanced with the addition of catalysts. At 30°C, the minimum and the maximum decolorization efficiencies were recorded as 34.9% and 62% in the presence of P-AC and K-AC, respectively.

The decolorization efficiencies were improved in the presence of the each of the catalysts when the reaction temperature was increased to 50 °C. At this temperature the highest decolorization efficiencies were accomplished for the catalyst loadings of 0.25 g/L. The decolorization performances of the catalysts are ranked from the lowest to highest under as follows: Fe/P-AC (83.1%) < Fe/H-AC (85.7%) < Fe/Z-AC (89.2%) < Fe/K-AC (91.6%). Increasing the catalyst loadings

to 0.5 g/L at 50°C, decreased the decolorization efficiencies slightly in the presence of the each of the catalysts tested.

Because the highest degradation and the decolorization efficiencies were obtained in the presence of Fe/K-AC catalyst under all the conditions of the catalyst screening experiments, this catalyst was determined as the most suitable one for the Fenton like oxidation of the Procion Red MX-5B.

5.1.3.2 Determination of the optimum reaction conditions for Fenton like oxidation

In the parametric study, the effects of initial hydrogen peroxide concentration, catalyst loading, pH and temperature degradation and decolorization efficiencies were performed in presence of Fe/K-AC catalyst which showed the highest catalytic performance in the catalyst screening experiments. The initial Procion Red MX-5B was kept constant at 100 ppm during the parametric study.

▪ Effect of hydrogen peroxide concentration

Determination of an optimum hydrogen peroxide concentration for the degradation of Procion Red MX-5B by Fenton oxidation is of importance because hydrogen peroxide plays role as an oxidizing agent. The effect of the initial H_2O_2 concentration was investigated in a H_2O_2 concentration range between 2 and 8 mM, while the catalyst loading, temperature and pH were kept constant at 0.1 g/L, 50°C and 3, respectively. In addition, an experimental set without addition of H_2O_2 was carried out. The degradation and the decolorization profiles changing with respect to the initial H_2O_2 concentration are given in Figure 5.11 and 5.12, respectively.

In the presence of the catalyst alone in the reaction medium, approximately no degradation and decolorization were recorded. It means neither oxidation nor adsorption of the dye was accomplished. The reason of the dye could not be adsorbed onto the activated carbon can be explained that Procion Red MX-5B molecules are too big to be occupied in the pores of the activated carbon. Addition of H_2O_2 resulted in generation of hydroxyl radicals via decomposition of the H_2O_2 into $\bullet\text{OH}$, thus, oxidation of the dye.

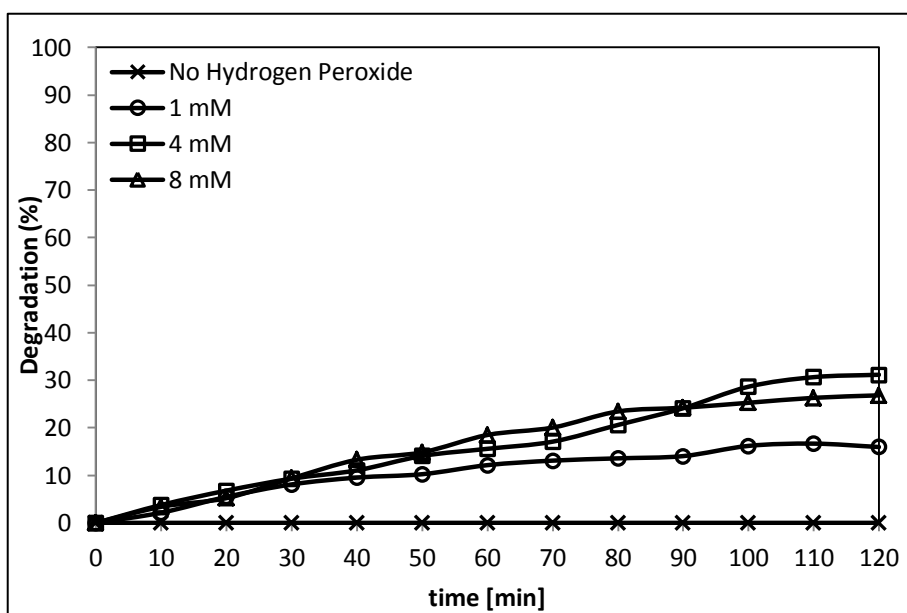


Figure 5.11. Effect of the initial hydrogen peroxide concentration on degradation. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.1 g/L catalyst loading, 50°C, pH= 3.

At low H_2O_2 concentration (1 mM), the degradation efficiency was evaluated as 16% whereas it is increased to 31% at moderate H_2O_2 concentration (4 mM). A further increase in H_2O_2 concentration did not enhanced the degradation efficiencies. Therefore, the optimum H_2O_2 concentration was determined as 4 mM.

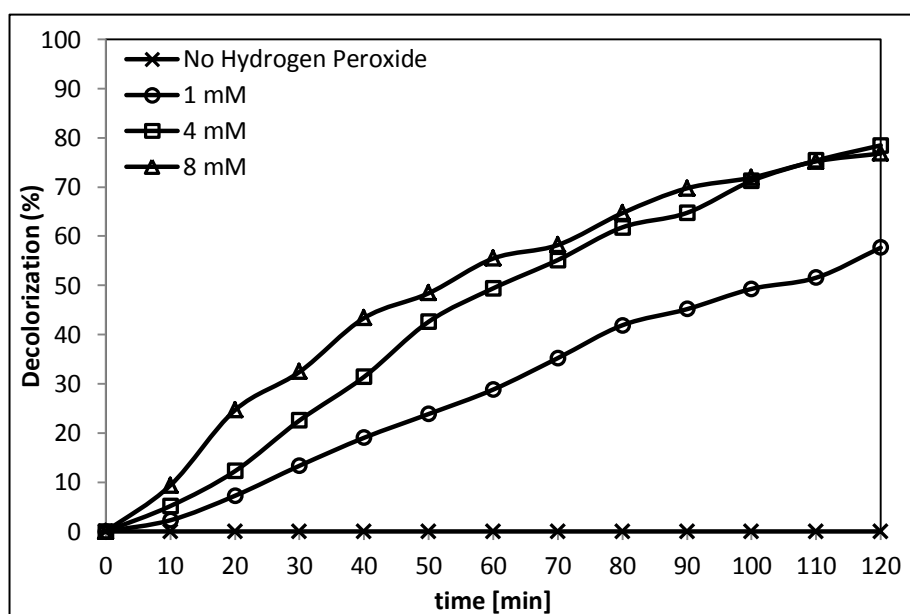


Figure 5.12. Effect of the initial hydrogen peroxide concentration on decolorization. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.1 g/L catalyst loading, 50°C, pH= 3.

Increasing the initial H_2O_2 concentration up to 4 mM resulted in improvement of decolorization rates and efficiencies. At this H_2O_2 concentration

78% decolorization efficiency was achieved. Above 4 mM, the decolorization rates and efficiencies were not enhanced anymore. Scavenging of the hydroxyl radicals may occur when excess amount H_2O_2 is used due to the following reaction (Gan and Li, 2013):



▪ Effect of catalyst loading

In order to examine the influence of the catalyst loading on the decolorization and degradation of Procion Red MX-5B, different catalyst loadings between 0.1-0.5 g/L were examined while the initial hydrogen peroxide concentration, temperature and pH were kept constant at 4 mM, 50°C and 3, respectively. Additionally, an experiment in the absence of catalyst was performed. The effect of catalyst loading on degradation and decolorization are shown in Figure 5.13 and 5.14, respectively.

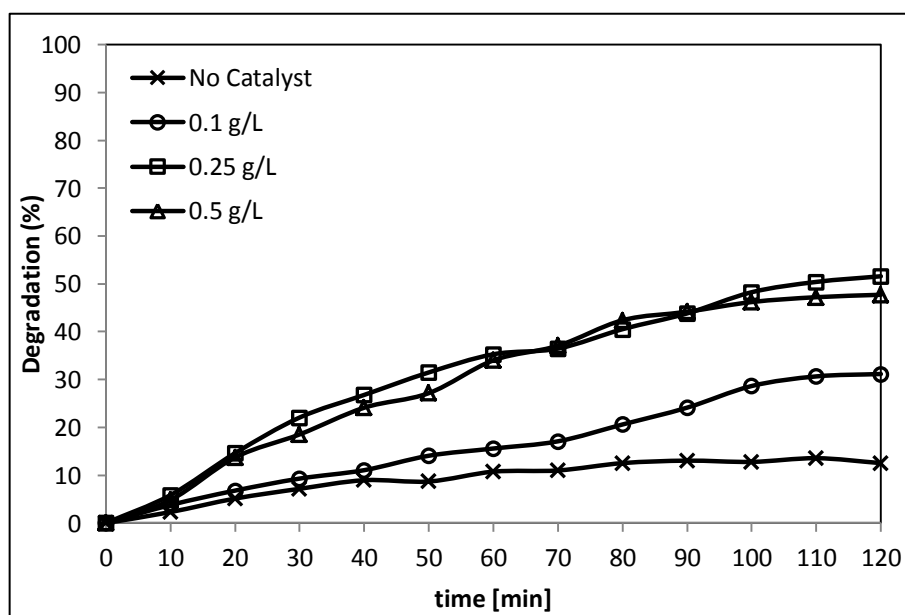


Figure 5.13. Effect of catalyst loading on decolorization. Reaction conditions: $[\text{Dye}]_0 = 100$ mg/L, $[\text{H}_2\text{O}_2]_0 = 4$ mM, 50°C, pH= 3

In the absence of the catalyst, 13% and 18% degradation and decolorization was achieved. Addition of the catalyst improved of the dye oxidation rates and efficiencies up to a catalyst loading of 0.25 g/L. Raising the catalyst dosage contributes to the increase in the number of the active sites on the

catalyst surface, thus, accelerates the generation of hydroxyl radicals (Panda et al., 2011).

When the catalyst loading was 0.25 g/L, the degradation and the decolorization efficiencies were evaluated as 52% and 92%, respectively. Above this loading, no considerable influence on the dye removal efficiencies were observed.

This is possibly due to the initiation of the recombination reactions between Fe^{2+} and $\cdot\text{OH}$. In other words, very high concentration of Fe^{2+} could lead to the self-scavenging of $\cdot\text{OH}$ radicals and decreases the dye degradation rate (Ertugay and Acar, 2013).

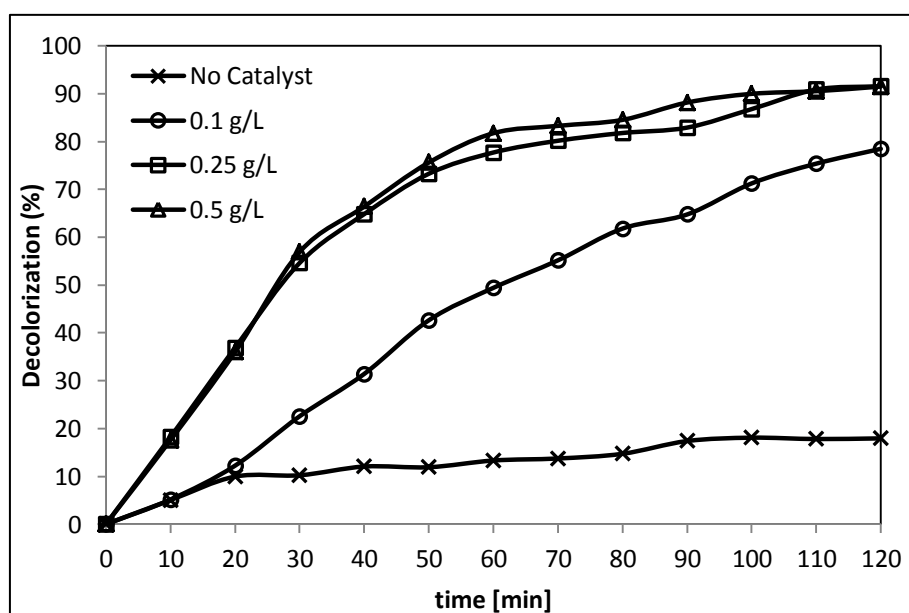


Figure 5.14. Effect of catalyst loading on decolorization. Reaction conditions: $[\text{Dye}]_0 = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$, 50°C , $\text{pH} = 3$



As there was no significant increase in efficiencies above 0.25 g/L, the optimum catalyst loading was determined as 0.25 g/L.

▪ Effect of pH

The initial pHs of 3, 3.5, 4 were tested to analyze the effect of pH on dye removal whereas the catalyst loading, initial hydrogen concentration and

temperature were kept constant at 0.25 g/L, 4 mM, and 50°C respectively. The results are presented in Figure 5.15 and Figure 5.16.

The initial pH values were selected under the point of zero charge (pH_{pzc}) of the K-AC which was determined at $\text{pH}=7.4$ previously. Under pH_{pzc} the activated carbon surface charges positively to attract the anionic Procion Red MX-5B molecules.

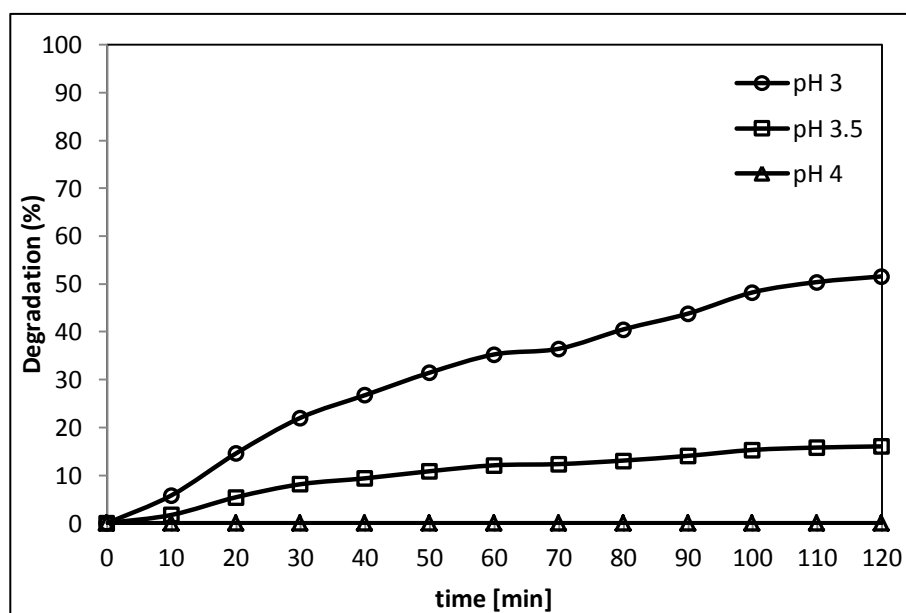


Figure 5.15. Effect of catalyst loading on degradation. Reaction conditions: $[\text{Dye}]_0=100$ mg/L, 0.25 g/L of catalyst loading, $[\text{H}_2\text{O}_2]_0=4$ mM, 50°C.

The pH of the reaction mixture affects the oxidation efficiencies intensively because a change in pH of the solution involves a variation of the concentration of ferrous ions. At pH 3, the degradation and the decolorization efficiencies of the dye were evaluated as 52% and 92% respectively.

Increasing the pH from 3 to 4 resulted in a dramatic decrease in both degradation and decolorization efficiencies and the rates of the dye. At pH 4, only 20% of decolorization efficiency was accomplished and no degradation was observed at the end of 2 hours.

Several reasons might be responsible for the low dye removal efficiencies accomplished in the less acidic mediums. Above the optimum pH there may be a possible decomposition of H_2O_2 into water and oxygen and reduction in the oxidation ability due to the fact that H_2O_2 is unstable at higher pHs.

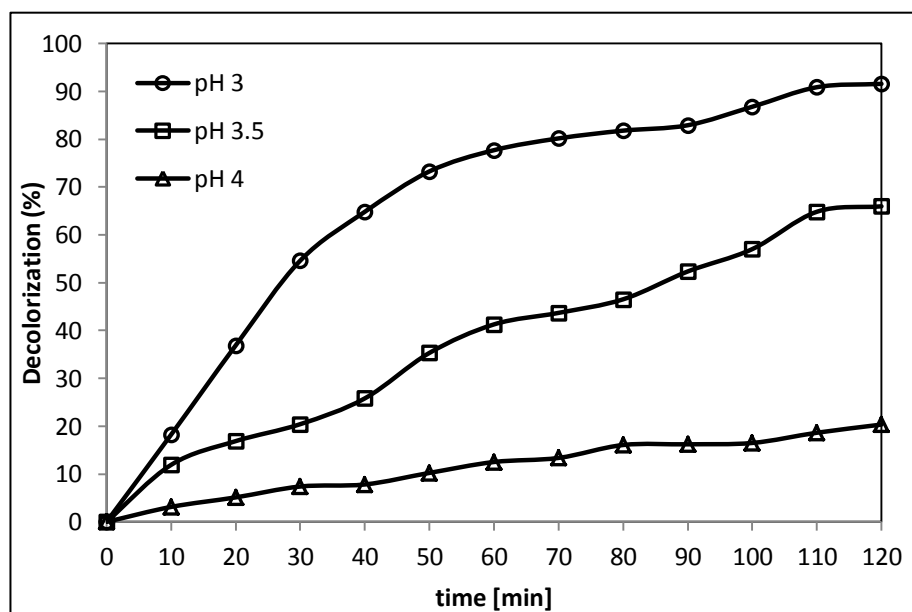


Figure 5.16. Effect of catalyst loading on decolorization. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.25 g/L of catalyst loading, $[H_2O_2]_0 = 4$ mM, 50°C .

▪ Effect of temperature

The impact of temperature on the degradation and the decolorization of Procion Red MX-5B were studied setting the reaction temperatures to 30, 40, 50, 60 and 70°C while the remaining parameters were kept at the determined optimum values. The degradation and the decolorization efficiencies are given as function of time in Figure 5.17 and 5.18, respectively.

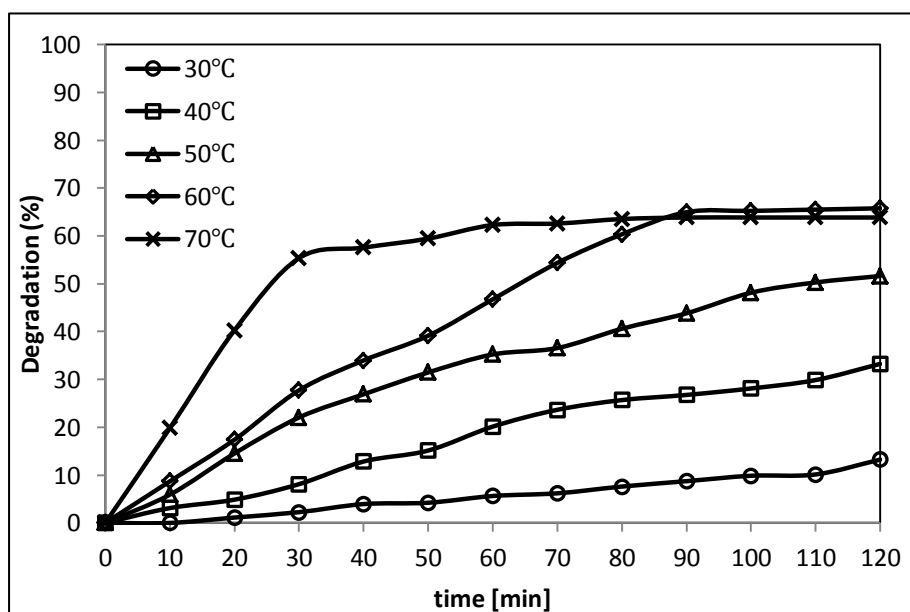


Figure 5.17. Effect of temperature on degradation. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.25 g/L of catalyst loading, $[H_2O_2]_0 = 4$ mM, 3 of pH.

The influence of temperature on degradation and decolorization rates is of significance because reaction between hydrogen peroxide and any form of ferrous/ferric iron improved with raising temperature which results in acceleration of oxidation.

According to Figure 5.17 and Figure 5.18, the higher the reaction temperature was the more rapid degradation and decolorization was. In the first half hour of the reaction the degradation efficiencies were recorded as 2.3%, 8.1%, 22%, 27.7% and 55.3% at 30, 40, 50, 60 and 70 °C, respectively, while the decolorization efficiencies were evaluated as 12.3%, 29.6%, 55%, 62.8% and 91%, respectively. Hence it can be concluded that the temperature was more effective on dye decolorization in comparison with the degradation.

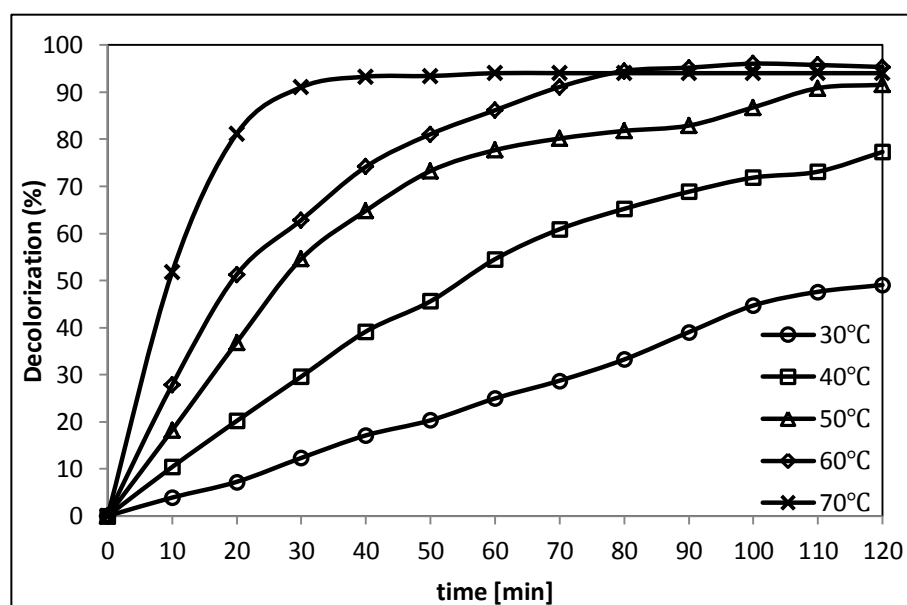


Figure 5.18. Effect of temperature on decolorization. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.25 g/L of catalyst loading, $[H_2O_2]_0 = 4$ mM, 3 of pH.

Though higher temperatures enhances the dye removal efficiencies at the beginning of the reaction, the difference in dye removal efficiencies decreased as time passes and the especially in the second hour of the reaction time the temperature effect was not very considerable.

Because dye removal efficiencies recorded at the end of two hours increased slightly above 50 °C, this temperature was determined to be the optimum operating condition.

5.1.3.3 Reusability of the catalyst and iron leaching analysis

The reusability of the catalyst and metal leaching analyses are significant from the economical and the environmental point of view. The reusability tests were carried out during three consecutive runs using the recovered catalysts which were used in the Fenton like oxidation experiments under optimum conditions.

The catalysts were recovered by filtration, washing with distilled water for several times and drying. The dye removal efficiencies obtained for the first, second and the third usage of the catalyst are presented in Figure 5.19 and 5.20.

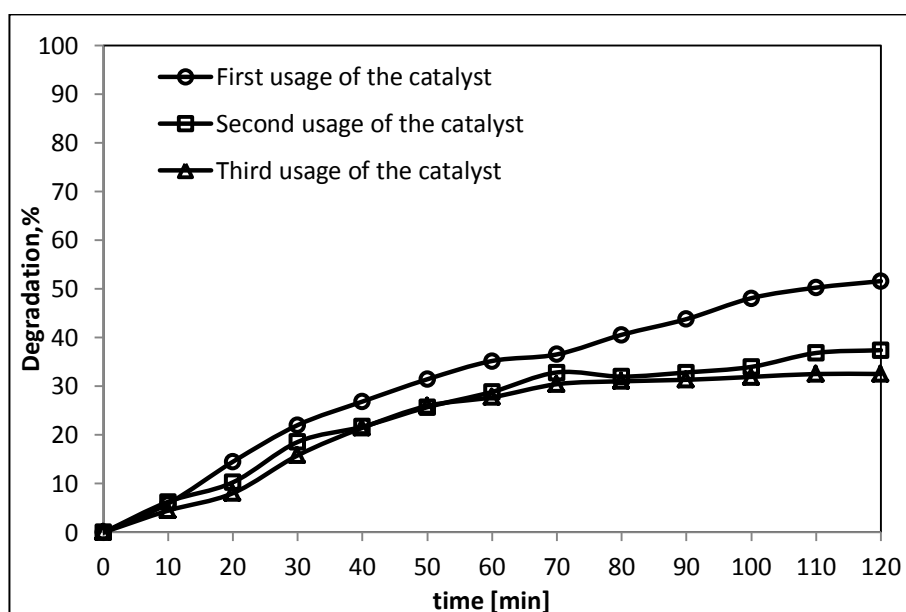


Figure 5.19. The degradation of the Procion Red MX-5B in the presence of recovered catalysts. Reaction conditions: $[Dye]_0 = 100$ mg/L, $[H_2O_2]_0 = 4$ mM, 0.25 g/L catalyst loading, pH 3, $T = 50^\circ\text{C}$.

The experimental results presents that the catalyst showed activity decay after each reuse due to the possible reduction of the catalyst surface area, catalyst poisoning and loss of active phase via leaching.

The degradation and decolorization efficiencies accomplished with fresh catalyst and the reused catalysts for the second and third times were 51.6 and 91.6%, 37.4 and 84.4%, and, 32.5 and 80.9%, respectively.

According to the iron leaching analyses, the fresh catalyst showed good stability with a leaching of 1.23 ppm which satisfies the European Union directives of 2 mg/L. However for the second and the third reuse of the catalyst the 2.22, and 2.63 mg/L of iron leaching were measured, respectively.

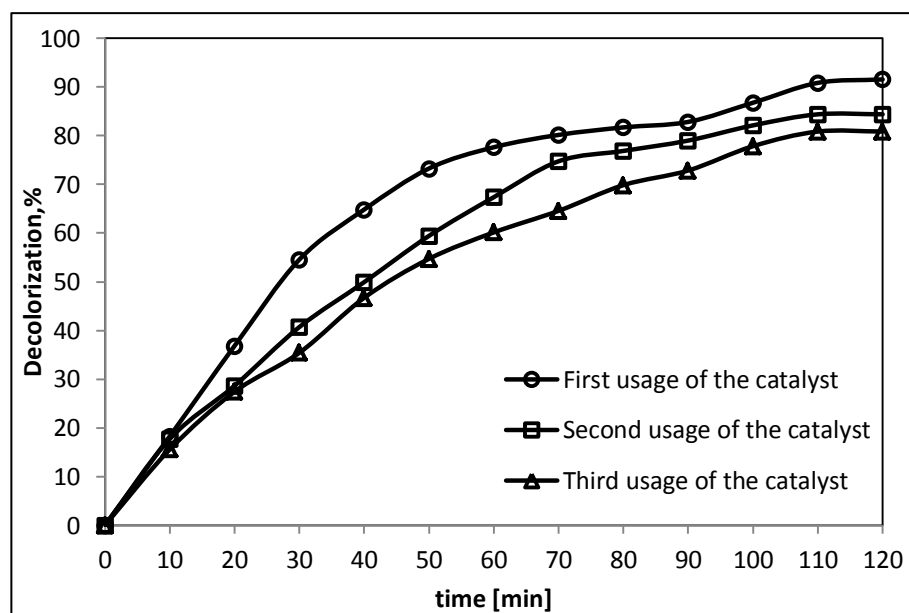


Figure 5.20. The decolorization of the Procion Red MX-5B in the presence of recovered catalysts. Reaction conditions: $[Dye]_0 = 100$ mg/L, $[H_2O_2]_0 = 4$ mM, 0.25 g/L catalyst loading, pH 3, $T = 50^\circ\text{C}$.

5.1.3.4 Toxicity tests

The toxicity analyses were performed with the comparison of the root lengths of the *Lepidium sativum* growing in the treated dye solution and the distilled water.

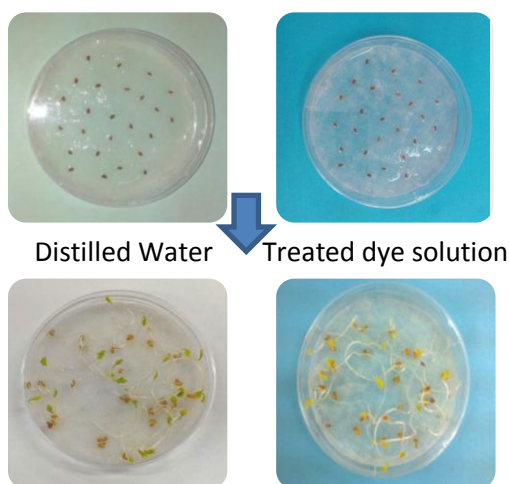
In order to determine whether the Fenton like oxidation process is effective in decreasing the toxicity of the dye or toxic compounds were generated as end products in the Fenton-like oxidation process, the inhibition in root growth, relative root growth and the absolute growth rate were calculated according to the formulas derived from the literature.

The results are tabulated in Table 5.3 and the photographs of the growing seeds are shown in Figure 5.21.

According to the assessment of the toxicity tests no toxic by-products were formed at the end of the Fenton like treatment since the growth inhibition in the treated dye solution is only 1.1% with respect to the growth rate evaluated in the distilled water. The lower the growth inhibition the lower the toxicity is; which leads to high root growth rate in treated dye solution.

Table 5.3. Results of the toxicity tests of Fenton like oxidation

Mean Length of the <i>Lepidium sativum</i> Roots Growing in Different Mediums after 96 hours, [cm] (Visioli et al., 2013, Aydın and Kara, 2006)		
Distilled Water	Treated Dye Solution at Optimum Reaction Conditions	
4.85	4.80	
Evaluation of the Toxicity		
Method 1 Nawanopparatsakul et al., 2012, Begum et al., 2010.	Method 2 Hoekstra et al., 2002	Method 3 Ayhan et al., 2007
Growth inhibition in the treated dye solution,%= $((4.85-4.80)/4.85)*100 = 1\%$	Relative Root Growth, %, in the treated dye solution = $(4.80/4.85)*100 = 99\%$	Absolute Growth Rate in the treated dye solution= $(4.80-0)/4 = 1.2 \text{ cm/day}$

**Figure 5.21.** *Lepidium sativum* seeds growing in distilled water and treated dye solutions

5.1.4. Photocatalytic oxidation and photo-Fenton like oxidations

The photocatalytic methods tested in this study experiments consist of photocatalytic oxidation which carried out in the absence of H_2O_2 assessing the performances of the catalysts only, and, the photo-Fenton like oxidation through which H_2O_2 and iron containing the catalysts were added into the reaction medium.

5.1.4.1 Catalyst screening

Procion Red MX-5B was degraded and decolorized by the photocatalytic oxidation and Photo-Fenton like oxidations in presence of iron loaded activated carbon (Fe/AC) and Fe-TiO₂ coated on activated carbon (Fe-TiO₂/AC) catalysts.

▪ Catalyst Screening in the presence of Fe- and Fe-TiO₂ Loaded Activated Carbon Catalysts – Photocatalytic Oxidation

In this step of catalyst screening experiments, the photocatalytic performances of Fe-TiO₂/AC and Fe/AC catalysts prepared by different activation methods were compared in the absence of H₂O₂ changing the catalyst loading from 0.25 to 0.5 g/L. Figure 5.22 shows the degradation and the decolorization performances of the Fe-TiO₂/AC catalysts, and in Figure 5.23 the catalytic performances of the Fe/AC catalysts are compared.

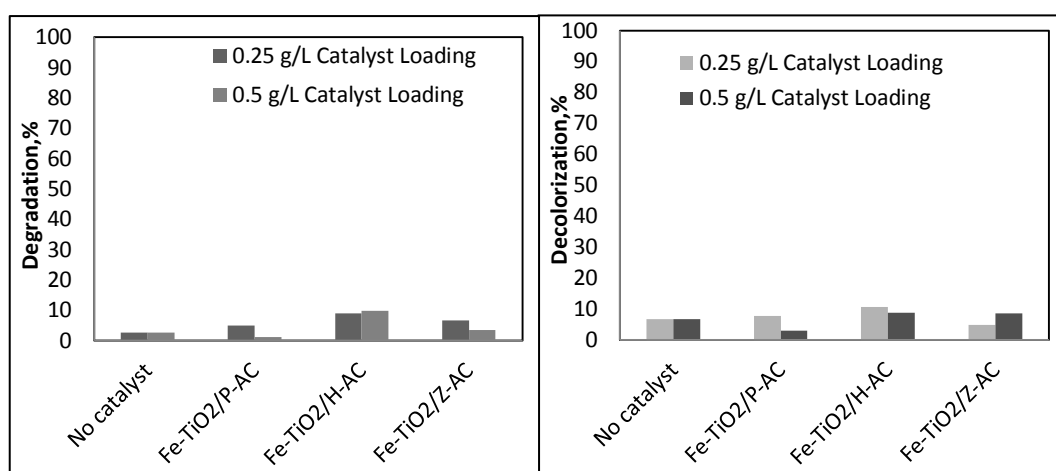


Figure 5.22. Comparison of the photocatalytic performances of Fe-TiO₂/AC catalysts. Reaction conditions: [Dye]₀=100 ppm, UV light intensity 6 W, pH 3

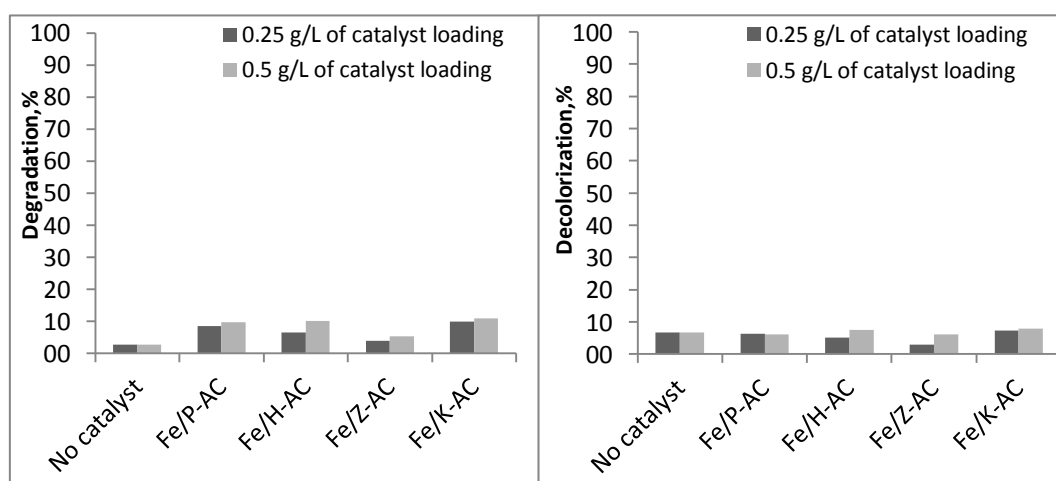


Figure 5.23. Comparison of the photocatalytic performances of Fe/AC catalysts. Reaction conditions: [Dye]₀=100 ppm, UV light intensity 6 W, 3 of pH.

According to the catalyst screening experiments, in the presence of types of the Fe-TiO₂/AC and Fe/AC catalysts, the degradation and the decolorization

efficiencies were recorded up to 11 %. Because TiO_2 content in the catalyst did not resulted in any enhancement in the dye removal efficiencies, the catalyst screening experiments were continued with using Fe/AC catalysts in the presence of H_2O_2 .

▪ **Catalyst Screening in the presence of H_2O_2 and Fe Loaded Activated Carbon Catalysts – Photo-Fenton Like Oxidation**

The photo-Fenton like oxidation activities of the Fe/AC catalysts were examined in the presence of H_2O_2 altering the catalyst loading from 0.25 to 0.5 g/L. The degradation and the decolorization efficiencies are given in Figure 5.24 and 5.25.

Applying 0.25 g/L of catalyst loading, the lowest and highest degradation efficiencies were evaluated as 34.2% and 50% whereas the decolorization efficiencies were 74.7 % and 88.3% in the presence of the Fe/P-AC and Fe/K-AC, respectively. When the catalyst loading increased to 0.5 g/L, the dye removal efficiencies improved slightly and the maximum degradation and the decolorization efficiencies reached to 59% of degradation and 92% of decolorization, in the presence of Fe/K-AC catalyst. So, the parametric study experiments in which the optimum reaction conditions were determined were continued with using the base activated carbon catalyst.

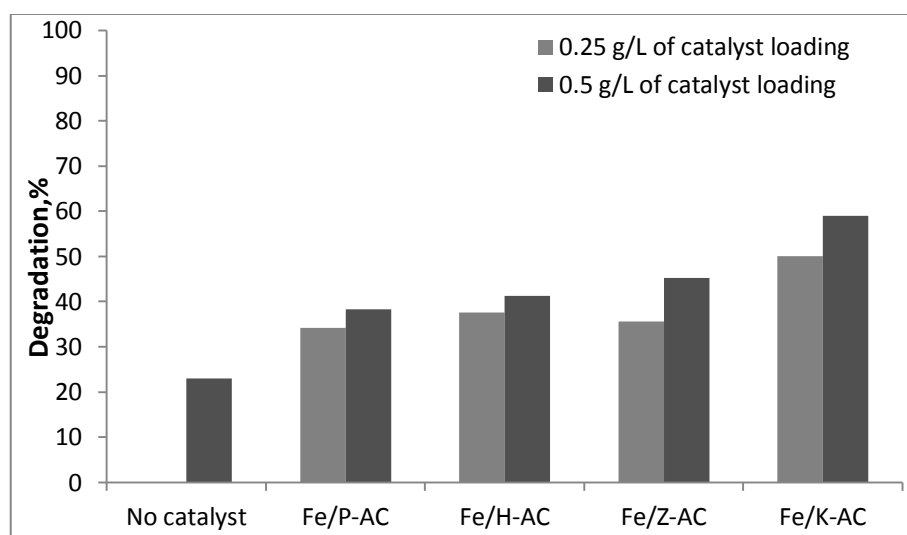


Figure 5.24. Comparison of the degradation performances of Fe/AC catalysts on photo-Fenton like oxidation. Reaction conditions: $[\text{Dye}]_0 = 100$ ppm, $[\text{H}_2\text{O}_2]_0 = 2$ mM, UV light intensity of 6 W, 3 of pH.

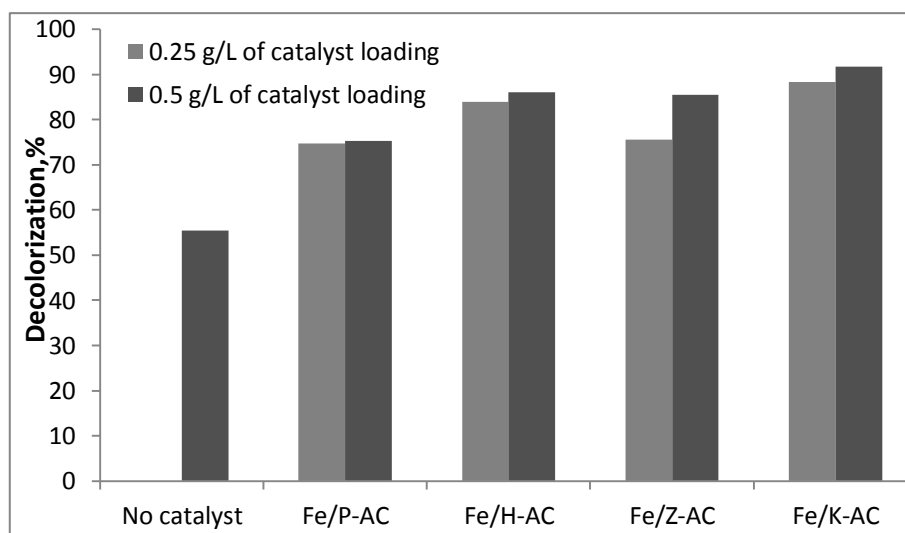


Figure 5.25. Comparison of the decolorization performances of Fe/AC catalysts on photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, $[H_2O_2]_0=2$ mM, UV light intensity of 6 W, 3 of pH.

5.1.4.2 Determination of the optimum reaction conditions for photo-Fenton like oxidation

The effects of several parameters on decolorization and the degradation of the azo dye, Procion Red MX-5B in photo-Fenton oxidation in presence of Fe/K-AC catalyst were examined by varying catalyst loading, the initial H_2O_2 concentration, pH and UV light intensity in order to determine the optimum reaction conditions. In all the experiments the initial dye concentration was kept constant at 100 ppm.

▪ Effect of Catalyst Loading

The catalyst loading was varied between 0.1 and 0.5 g/L, while the initial hydrogen peroxide concentration, pH, and UV light intensity were fixed at 2 mM, 3, and 6 Watt, respectively. In addition, an experiment without addition of catalyst was performed. The catalyst loading effect on decolorization and degradation efficiencies are shown in Figure 5.26 and 5.27, respectively.

According to the results, 23% degradation and 55.5% decolorization efficiencies were achieved by the synergetic effect of hydrogen peroxide and UV light when there was no catalyst in the reaction medium. The photodegradation efficiencies enhanced with the increase in the amount of photocatalyst. This can be explained by the increase in the active sites when the quantity of the

photocatalyst increases, which is a characteristic of heterogeneous photocatalysts. (Djaneye-Boundjou et al., 2012).

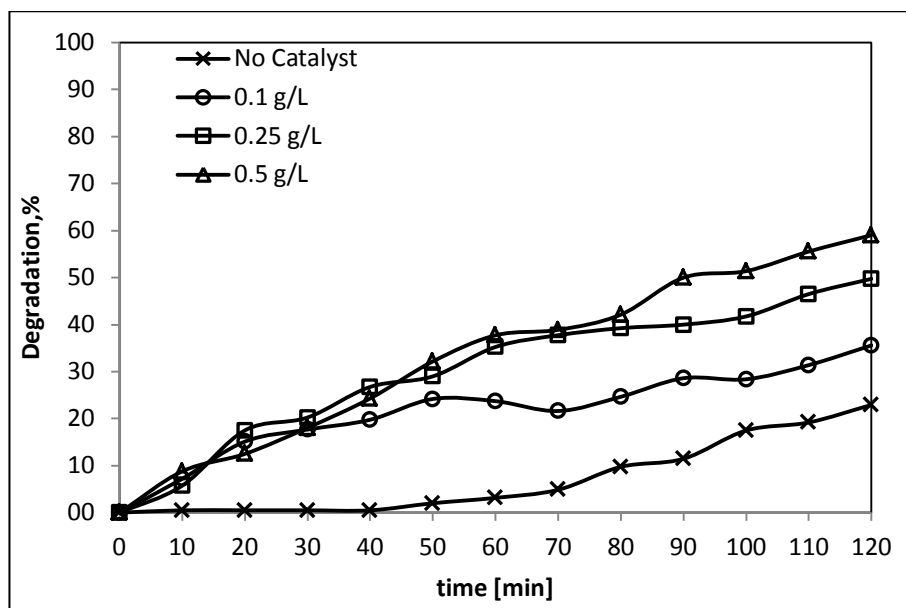


Figure 5.26. The catalyst loading effect on degradation of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, $[H_2O_2]_0=2$ mM, UV light intensity 6 W, pH 3.

Increasing the catalyst loading from 0.1 to 0.5 g/L raised the degradation efficiencies from 35.6%, to 59.0%. The decolorization efficiencies observed for catalyst loading of 0.1, 0.25 to 0.5 g/L of were 77.2%, 88.3% and 91.6%, respectively.

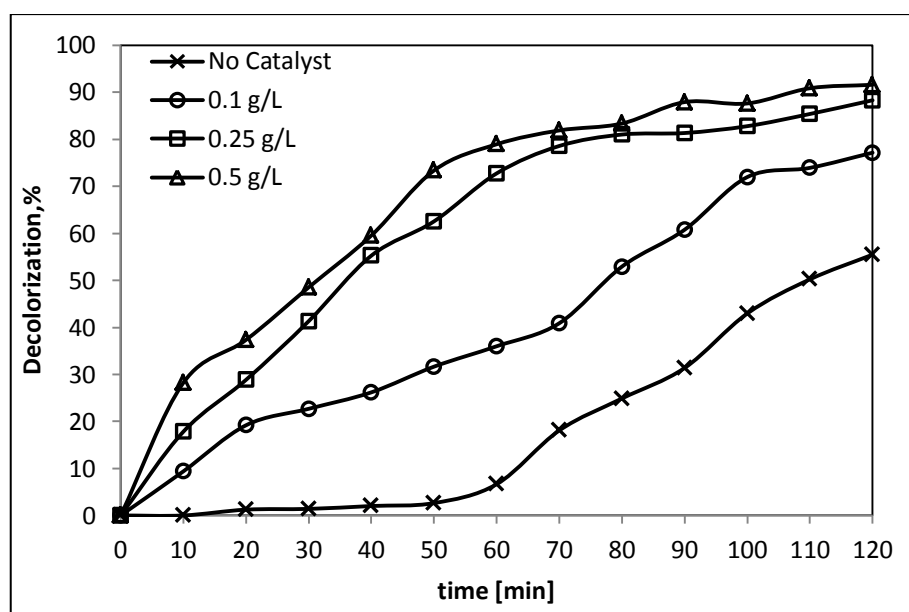


Figure 5.27. The catalyst loading effect on decolorization of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, $[H_2O_2]_0=2$ mM, UV light intensity 6 W, pH 3.

The increase of catalyst concentration above the optimum may result in the agglomeration of catalyst particles, hence the part of the catalyst surface become unavailable for photon absorption, and degradation rate decrease. The excess catalyst prevent the illumination leading to the reduction of generation of the $\bullet\text{OH}$ radicals (Akpan et al., 2009).

Even though the maximum degradation and decolorization efficiencies were obtained when the catalyst loading was 0.5 g/L, the increase when the amount varied from 0.1 to 0.25 g/L was significantly higher than the variation from 0.25 to 0.5 g/L and hence catalyst loading of 0.25 g/L was determined as the optimum value.

▪ Effect of Initial Hydrogen Peroxide Concentration

1, 2 and 4 mM of initial hydrogen peroxide concentration were tested while the catalyst loading, pH and the UV light intensity were kept constant at 0.25 g/L, 3, and 6 W, respectively. In addition, an experiment without addition of hydrogen peroxide was performed. The influence of the initial hydrogen peroxide concentration effect on decolorization and degradation are presented in Figure 5.28 and 5.29, respectively.

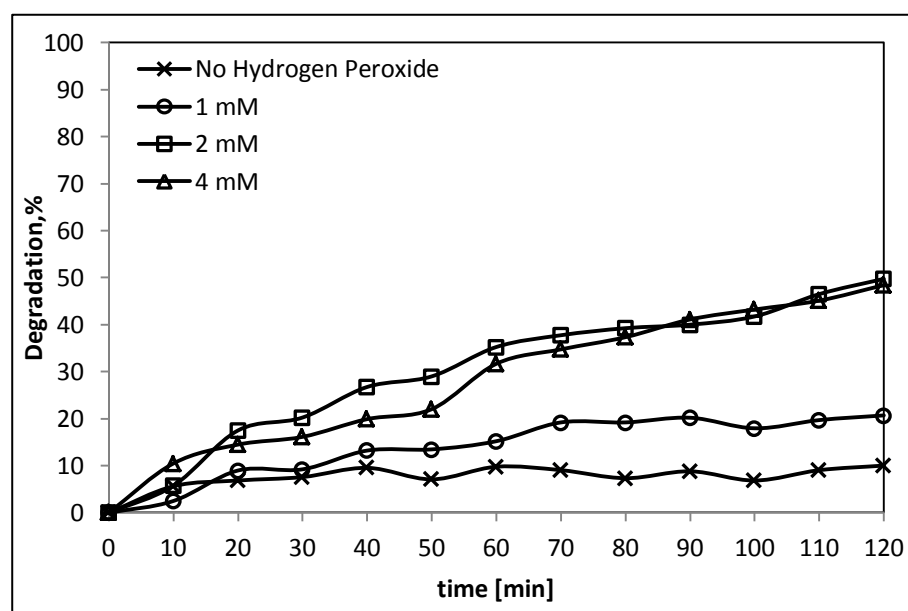


Figure 5.28. The initial H_2O_2 concentration effect on degradation of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[\text{Dye}]_0=100$ ppm, 0.25 g/L catalyst loading, pH 3, UV light intensity 6 W.

As can be noticed from the results, generation of the hydroxyl radicals by addition of hydrogen peroxide significantly enhanced both the degradation and decolorization.

Removal efficiency increases as the dose of H_2O_2 is increased up to a certain critical value after which the efficiency starts to decrease. Above the optimum concentration of H_2O_2 , scavenging of $\text{HO}\cdot$ radicals will occur, as expressed by the following equations (Ramirez et al., 2010);



The dye removal efficiencies enhanced up to 2 mM of H_2O_2 loading. The maximum degradation and the decolorization efficiencies were evaluated as 49.8% and 88.3%, respectively, at this H_2O_2 concentration. A further addition of H_2O_2 resulted in decrease in efficiencies due to the scavenging effect of the excess hydroxyl radicals. Thus, 2 mM was determined to be the optimum H_2O_2 loading.

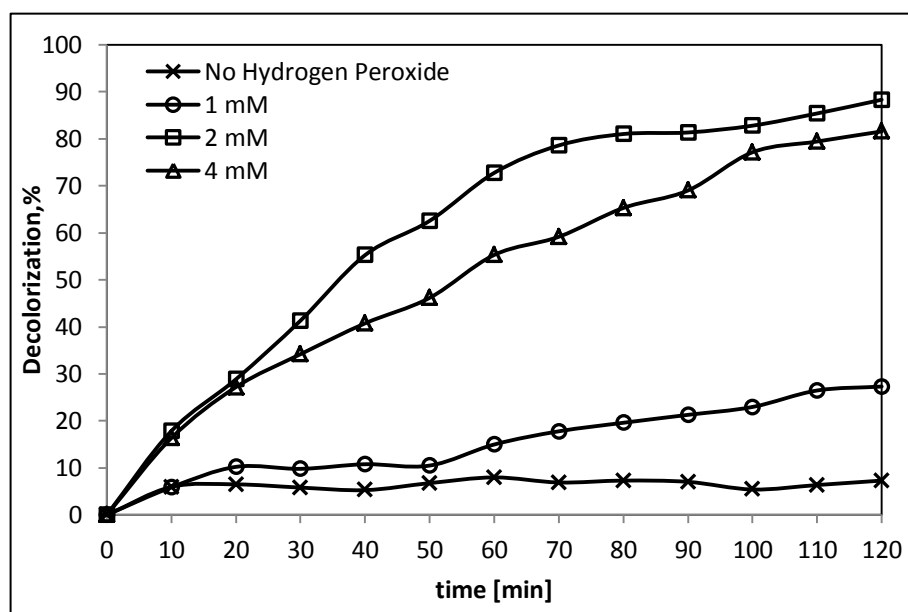


Figure 5.29. The initial H_2O_2 concentration effect on decolorization of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[\text{Dye}]_0=100$ ppm, 0.25 g/L catalyst loading, pH 3, UV light intensity 6 W.

▪ Effect of pH

The initial pH changed as 3, 5 and 7, which are below the point of zero charge (pH_{pzc}) of the K-AC which was determined at $\text{pH}=7.4$ previously. The

initial hydrogen peroxide concentration, catalyst loading, and, UV light intensity were fixed at 2 mM, 0.25 g/L, and, 6W respectively. The degradation and the decolorization profiles changing with the initial pH are shown in Figure 5.30 and 5.31, respectively.

According to the experimental results, the decolorization and the degradation efficiencies and rates increased with decreasing pH remarkably. When the initial pH was decreased from 7 to 3, the degradation efficiencies were increased from 5% to 49.8% whereas the decolorization efficiencies improved from 20.8% to 88.3%.

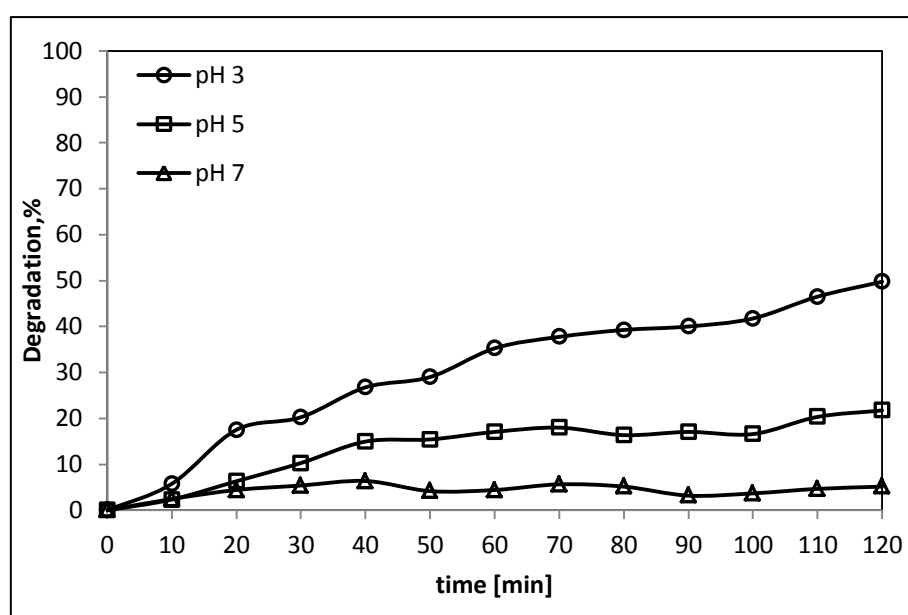


Figure 5.30. The initial pH effect on degradation of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0 = 100$ ppm, 0.25 g/L catalyst loading, $[H_2O_2]_0 = 2$ mM, UV light intensity of 6 W.

The reason of the increase in the efficiencies can be explained that, the hydroxyl radicals are generated efficiently under acidic conditions. At higher pH values, immobilized iron species can be transformed into less photoactive materials, such as $Fe(OH)_3$, and the higher values of pH favor the dissociation of H_2O_2 to form HO_2 (Nesic et al., 2013).

As the maximum degradation and decolorization efficiencies were obtained when the initial pH was 3, this pH value was determined as the optimum condition.

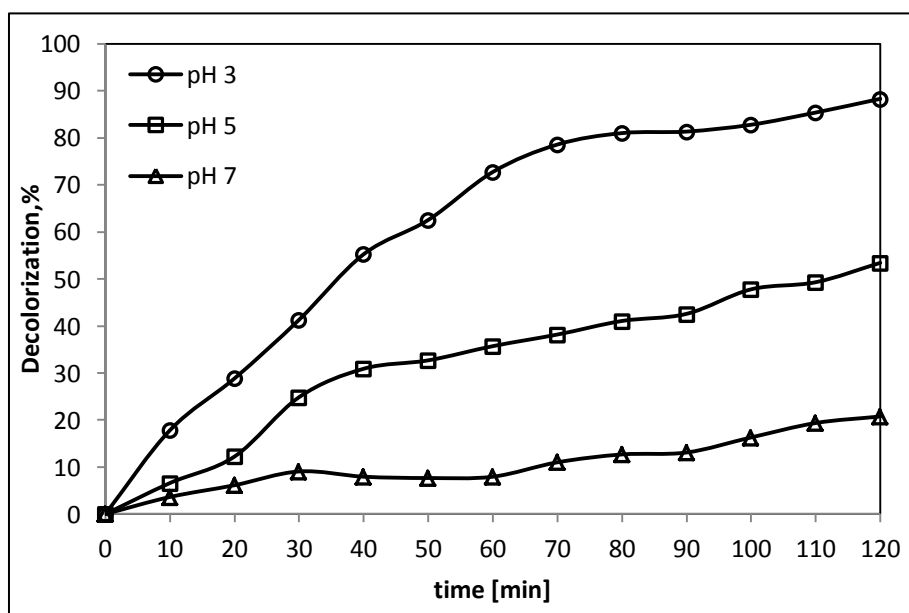


Figure 5.31. The initial pH effect on decolorization of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, 0.25 g/L catalyst loading, $[H_2O_2]_0=2$ mM, UV light intensity of 6 W.

▪ Effect of the UV Light Intensity

The UV light intensity was changed as 6 and 8 W, while catalyst loading, the initial hydrogen peroxide concentration, pH, the initial dye concentration, were kept constant at 0.25g/L, 2 mM, 3, and 100 mg/L, respectively. In addition, set of experiment was carried out in the absence of UV light. The impact of UV light intensity on decolorization and degradation efficiencies is shown in Figure 5.32 and 5.33, respectively.

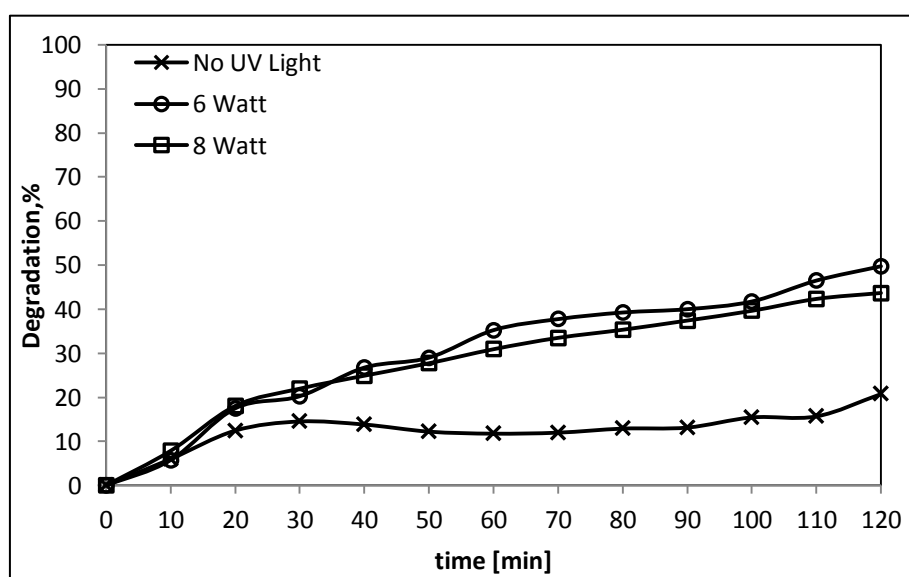


Figure 5.32. The UV light intensity effect on degradation of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, 0.25 g/L catalyst loading, $[H_2O_2]_0=2$ mM, 3 of pH.

The presence of UV light was essential in the photo-Fenton like oxidation since only 20.7% degradation and 35.2% decolorization were achieved in the absence of UV. Under UV light, the degradation and the decolorization efficiencies increased to 49.8% and 88.3% when the light intensity was 6 Watt.

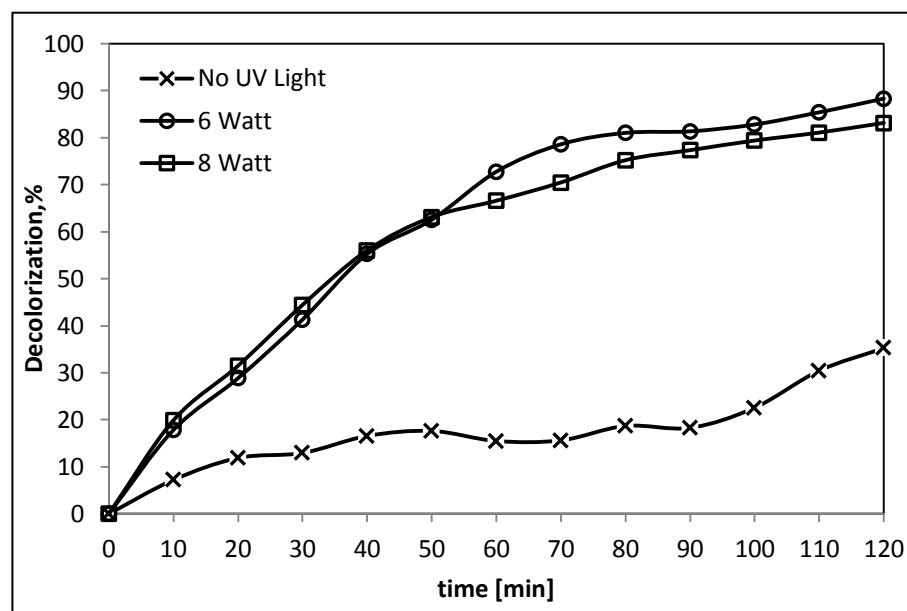


Figure 5.33. The UV light intensity effect on decolorization of Procion Red MX-5B in photo-Fenton like oxidation. Reaction conditions: $[Dye]_0=100$ ppm, 0.25 g/L catalyst loading, $[H_2O_2]_0=2$ mM, 3 of pH.

Though the presence of the UV light was of importance, the light intensity was not effective in dye removal. A further increase in UV light intensity up to 8 Watt did not result in enhancement of the dye removal efficiencies. Therefore, 6 Watt of UV light intensity was determined as the optimum condition.

5.1.4.3 Iron leaching analysis

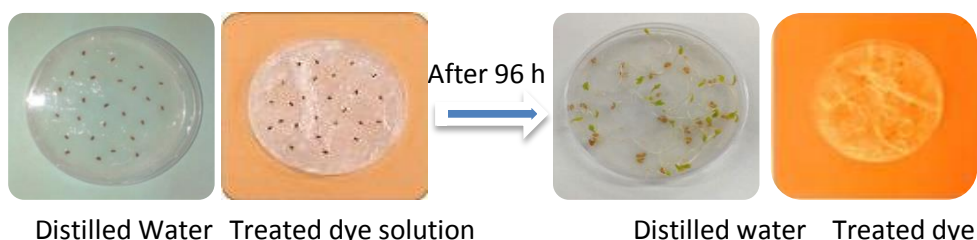
According to the iron leaching analysis, the iron concentration in the treated dye solution under the optimum reaction conditions was determined as 1.98 ppm which was below the European Union directives of 2 ppm (Ramirez et al., 2007).

5.1.4.4 Toxicity tests

The same calculation methods were applied as in the toxicity analysis of the Fenton like oxidation. The results are presented in Table 5.7 and Figure 5.34.

Table 5.7. Results of the toxicity tests of photo-Fenton like oxidation

Mean Length of the <i>Lepidium satium</i> Roots Growing in Different Mediums after 96 hours, [cm] (Visioli et al., 2013, Aydın and Kara, 2006)		
Distilled Water		Treated Dye Solution at Optimum Reaction Conditions
4.85		4.82
Calculation of the Toxicity		
Method 1 Nawanopparatsakul et al., 2012, Begum et al., 2010.	Method 2 Hoekstra et al., 2002	Method 3 Ayhan et al., 2007
Growth inhibition in the treated dye solution, % = $((4.85-4.82)/4.85)*100 = 0.6\%$	Relative Root Growth, %, in the treated dye solution = $(4.82/4.85)*100 = 99.4\%$	Absolute Growth Rate in the treated dye solution = $(4.82-0)/4 = 1.2 \text{ cm/day}$

**Figure 5.34.** Toxicity tests of the photo-Fenton like oxidation of the Procion Red MX-5B.

According to the toxicity tests, no remarkable growth inhibition was observed in the dye solution treated by photo-Fenton like oxidation, indicating that dye is decomposed into non-toxic end products at the end of the photo-Fenton like oxidation. In several studies researchers have found that the low growth inhibition rates were obtained after photo-Fenton treatment of dyes. Jonstrup et al., evaluated 16% of growth inhibition after photo-Fenton like oxidation of Remazol Red RR at the end of 2 hours (Jonstrup et al., 2011).

5.1.5. Catalytic wet air oxidation

5.1.5.1. Catalyst screening experiments

The catalyst screening experiments were performed to determine which type of the catalyst showed the highest catalytic performance on catalytic wet air oxidation. In these experiments, the initial dye concentration, air flow rate and pH was kept at 100 mg/L, 0.61 l/min and 7 respectively, while the catalyst loading, temperature and the pressure varied as 0.25 g/L and 0.5 g/L, 70 and 90°C, 1 and 3 atm, respectively. Figure 5.35 and 5.36 show the comparison of the catalytic

performances of the different catalysts on degradation and the decolorization of Procion Red MX-5B, respectively.

According to the experimental results, when the catalyst loading was 0.25 g/L at 70°C reaction temperature under 1 atm pressure, the lowest and the highest degradation efficiencies were obtained in presence of base activated carbon catalyst support (12.9 %) and in presence of zinc chloride and physically activated carbon catalyst support (14.3%), respectively. At the same conditions, the lowest and the highest decolorization efficiencies were obtained in presence of acid activated carbon catalyst support (3.1%) and in presence of zinc chloride activated carbon catalyst support (7.3 %), respectively.

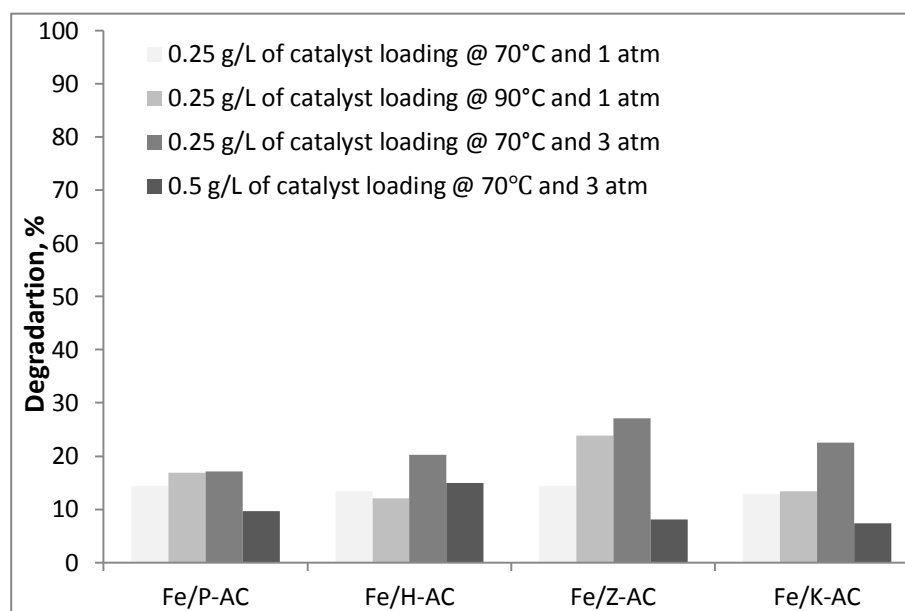


Figure 5.35. Comparison of the catalytic performances of different types of catalysts for degradation of Procion Red MX-5B in CWAQ process. Reaction conditions: [Dye]₀=100 mg/L, P=1 atm, pH=7.

As the temperature increased from 70 to 90°C, generally only insignificant increases were observed in the dye removal efficiencies. When the pressure was increased from 1 to 3 atm at 70 °C loading 0.25 g/L of catalyst, all the degradation and the decolorization efficiencies were enhanced.

The catalytic wet air oxidation of Procion Red MX-5B in the presence of Fe/AC catalysts was much less efficient in comparison with the Fenton like and photo-Fenton like processes and the highest degradation and the decolorization

efficiencies were recorded as 13.9% and 27.1%, respectively, using the zinc chloride activated catalyst at 70 °C and 1 atm.

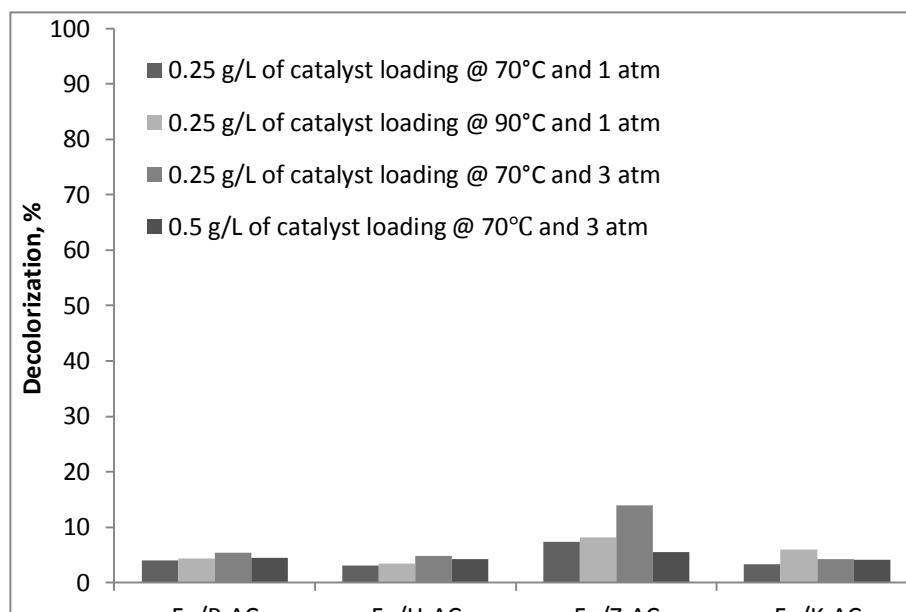


Figure 5.36. Comparison of the catalytic performances of different types of catalysts for decolorization of Procion Red MX-5B in CWAQ process. Reaction conditions: $[Dye]_0=100$ mg/L, $P=1$ atm, $pH=7$

Raising the catalyst loading up to 0.5 g/L at these conditions resulted in a decrease in the dye oxidation efficiencies. Because the zinc chloride showed relatively the highest catalytic performance in catalytic wet air oxidation of Procion Red MX-5B, in the parametric study this catalyst was used to determine the optimum reaction conditions.

5.1.5.2 Determination of the optimum reaction conditions for catalytic wet air oxidation

The influence of catalyst loading, reaction temperature and pressure on the degradation and decolorization of the Procion Red MX-5B was investigated in presence of zinc chloride activated carbon catalyst in the parametric study.

▪ Effect of Catalyst Loading

The catalyst loading was varied as 0.1, 0.25, 0.5 g/L, while the initial dye concentration, pressure, temperature, pH and the air flow rate were kept constant at 0.1 g/L, 1 atm, 70°C, 7 and 0.61 L/min, respectively. Figure 5.37 shows the influence of the catalyst loading on the dye removal efficiencies.

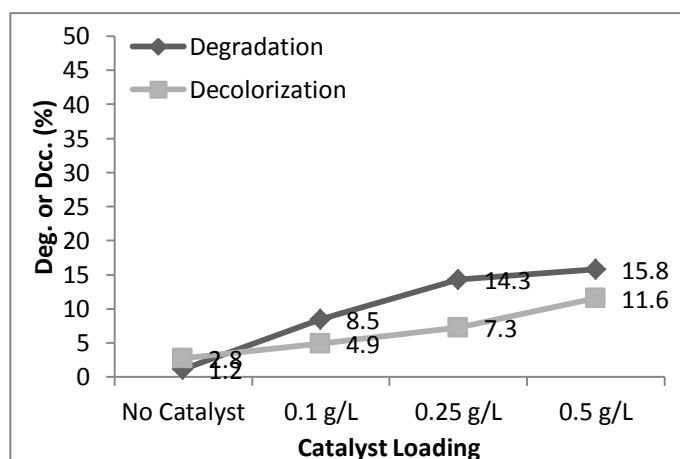


Figure 5.37. Catalyst loading effect on degradation and decolorization efficiencies of Procion Red MX-5B in CWAQ process. Reaction conditions: $[Dye]_0=100$ mg/L, $T=70^\circ\text{C}$, $P=1$ atm, $pH=7$, and, $F=0.61$ L/min.

According to the experimental results, when the catalyst loading is increased from 0.1 to 0.5 g/L, the degradation efficiency increased from 8.5% to 15.8% and the decolorization efficiency increased from 4.9% to 11.6%. The optimum catalyst loading was determined as 0.25 g/L as there was not any remarkable increase in degradation efficiencies above this value.

▪ Effect of Temperature

In this study, 50, 70 and 90°C of reaction temperatures were examined while the initial dye concentration, catalyst loading, pressure, pH and the air flow rate were kept constant at 0.1 g/L, 0.25 g/L, 1 atm, 7 and 0.61 L/min, respectively. Figure 5.39 shows how the temperature affected the dye removal efficiencies.

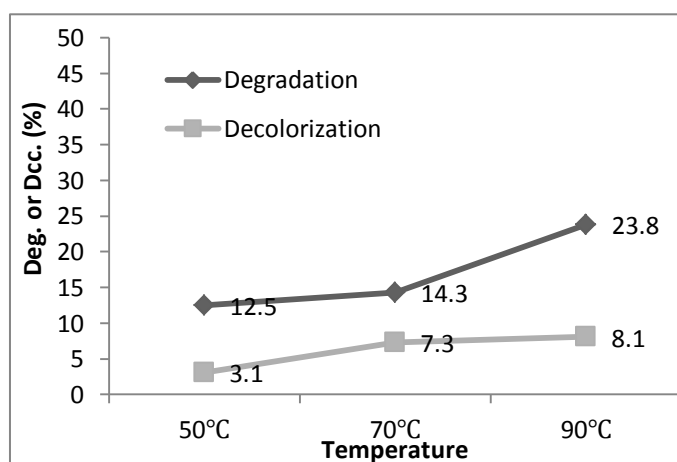


Figure 5.38. Temperature effect on degradation and decolorization efficiencies of Procion Red MX-5B in CWAQ process. Reaction conditions: $[Dye]_0=100$ mg/L, 0.25 g/L of catalyst loading, $P=1$ atm, $pH=7$, and, $F=0.61$ L/min.

The experimental results show that, the higher the reaction temperature was, the higher the degradation and the decolorization efficiencies of the dye were. As the reaction temperature increased from 50 °C to 90 °C the degradation and the decolorization efficiencies increased up to 23.8% and 8.1%, respectively. Although increasing the temperature has a positive effect on dye removal, operating costs also increase with the increasing heat requirement, so, moderate temperatures are more preferable.

▪ Effect of Pressure

In order to examine the pressure effect on dye removal, 1, 2 and 3 atm of reaction pressures were tested while the initial dye concentration, catalyst loading, temperature, pH and the air flow rate were kept constant at 0.1 g/L, 0.25 g/L, and 70°C, 7 and 0.61 L/min, respectively. The results are presented in Figure 5.39.

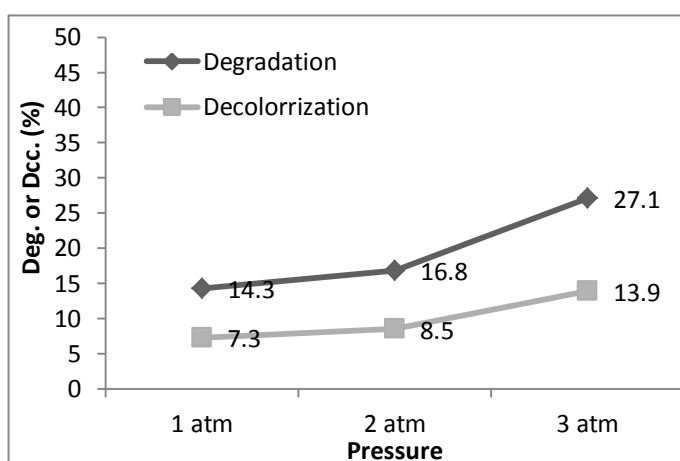


Figure 5.39. Pressure effect on degradation and decolorization efficiencies of Procion Red MX-5B in CWAQ process. Reaction conditions: $[Dye]_0 = 100$ mg/L, 0.25 g/L of catalyst loading, 70°C, pH=7, and, $F = 0.61$ L/min.

The experimental results showed that, as the reaction pressure increased dye removal efficiencies also increased. This could be explained that, at high temperatures and pressures the solubility of oxygen increases and as the oxygen concentration in the liquid phase increases, the contact between oxygen and organic matter is promoted which results in enhancement the oxidation process and increases the removal efficiencies. The maximum degradation and the decolorization efficiencies were evaluated as 27.1% and 13.9% when the pressure was 3 atm.

5.2. Biological Oxidation

In the biological oxidation, firstly the biocatalyst screening experiments were carried out to decide which fungus was more effective in dye removal. After the selection of the microorganism, a parametric study was performed to investigate the effects of the reaction parameters on dye removal efficiencies and to determine the optimum reaction conditions.

5.2.1 Biocatalyst Screening

Prior to determination of the optimum reaction conditions, the most suitable microorganism was selected in the biocatalyst screening experiments. In these experiments, azo dye degradation and decolorization performances of the *T. versicolor* and *P. chrysosporium* were compared both in the presence and in the absence of glucose and H₂O₂. The initial Procion Red MX-5B concentration was fixed at 100 ppm and the experiments were carried out at room temperature and 200 rpm shaking. The results are shown in Figure 5.40 and 5.41.

▫ *Using microorganism alone*

In order to compare the performances of the fungi, firstly, *T.versicolor* and *P. chrysosporium* were added into the dye solutions separately, at a concentration of 1g microorganism/100 mL dye solution. According to the results, at the end of the 1 week, no considerable dye removal was observed.

▫ *Using microorganism and glucose*

Addition of 2 g/L glucose into reaction medium, improved the decolorization efficiencies remarkably. 52.7% and 11.7% decolorization efficiencies were achieved with *T. versicolor* and *P. chrysosporium*, respectively. Nevertheless, the effect of glucose on degradation was not of significance. The degradation efficiencies were improved up to 5.1% using *T. versicolor*.

The white rot fungi secrete several lignin degrading enzymes such as peroxidases. It is reported that during the lignin degradation reactions the white rot fungi produces H₂O₂ (Kelley and Reddy, 1986). Some of enzymes they secrete have iron at the catalytic center, which slowly decomposes of hydrogen peroxide resulting in generation of hydroxyl radicals (Kato et al., 2014).

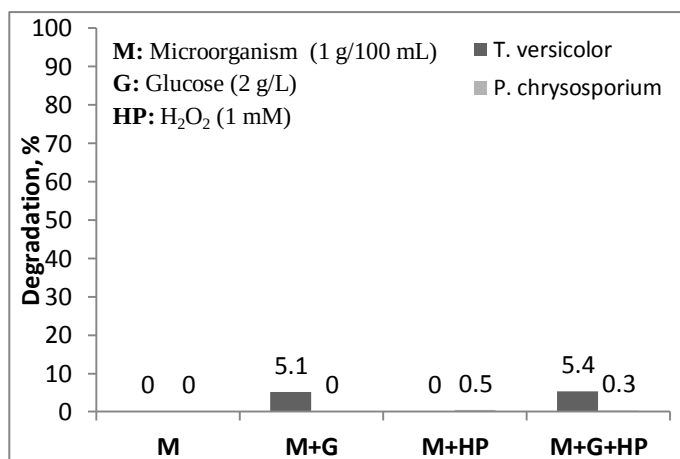


Figure 5.40. Degradation efficiencies evaluated in biocatalyst screening experiments in the presence of T.versicolor and P. chrysosporium. Reaction conditions: [Dye]₀=100 ppm, at room temperature and 200 rpm shaking.

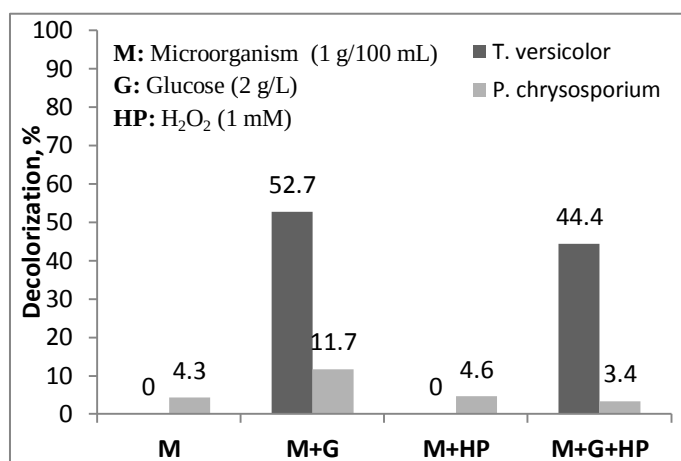


Figure 5.41. Decolorization efficiencies evaluated in biocatalyst screening experiments in the presence of T.versicolor and P. chrysosporium. Reaction conditions: [Dye]₀=100 ppm, at room temperature and 200 rpm shaking.

▫ *Using microorganism and H₂O₂*

In biological systems, hydroxyl radicals can be produced by one-electron reduction of H₂O₂ in two types of reactions. In the first type (Fenton reaction) H₂O₂ is reduced by Fe(II) or other reduced transition metals, to produce hydroxyl radicals. In the second reaction type, (iron-catalyzed Haber-Weiss reaction) superoxide reduces Fe(III) to Fe(II) which reduces H₂O₂ to form hydroxyl radicals (Forney et al., 1982).

In order to increase the hydroxyl radical formation, 1 mM of H₂O₂ was added into the reaction medium the presence and in the absence of glucose.

However, the extra addition of H_2O_2 decreased the decolorization efficiencies, probably, due to the scavenger effect of excess H_2O_2 . For instance, the decolorization efficiency was decreased from 52.7 to 44.4% when 1 mM of H_2O_2 was used together with *Trametes versicolor* in glucose containing reaction medium.

Because the highest dye removal efficiencies were accomplished in the presence of *T. versicolor*, this fungus was selected as the most suitable biocatalyst in oxidizing of Procion Red MX-5B. The parametric study was performed using the selected fungus.

5.2.2. Parametric Study

In the parametric study the influence of glucose and microorganism concentration on the dye degradation and decolorization were investigated in the presence of *T. versicolor* immobilized on walnut shells. Prior to determination of the optimum microorganism concentration, a set of experiments was performed varying the glucose concentration from 1 g/L to 4 g/L keeping the microorganism concentration at 1 g/100 mL. 50 mL of dye solutions at 100 ppm concentration were used. The experiments were carried out at room temperature and 200 ppm shaking for 1 week. The glucose impact on dye removal efficiencies is presented in Figure 5.42.

The enzyme secretion depends on nutrient limitation either nitrogen or carbon sources. The most common and usable carbon source is glucose (Kapdan et al., 2000). The results indicate that glucose was essential for removal of Procion Red MX-5B since in the absence of glucose neither degradation nor decolorization was achieved in 1 week. Increasing the glucose concentration up to 2 g/L enhances the degradation and decolorization, though a further increase in glucose concentration results in reduction of the dye removal efficiencies.

The reason of the decrease in the dye removal efficiencies can be explained that, in contrast to a nitrogen sources, excess glucose may inhibit decolorization activity because the consumed glucose is converted to organic acid which decrease pH and therefore inhibiting the cell growth and decolorization activity (Chen et al., 2003).

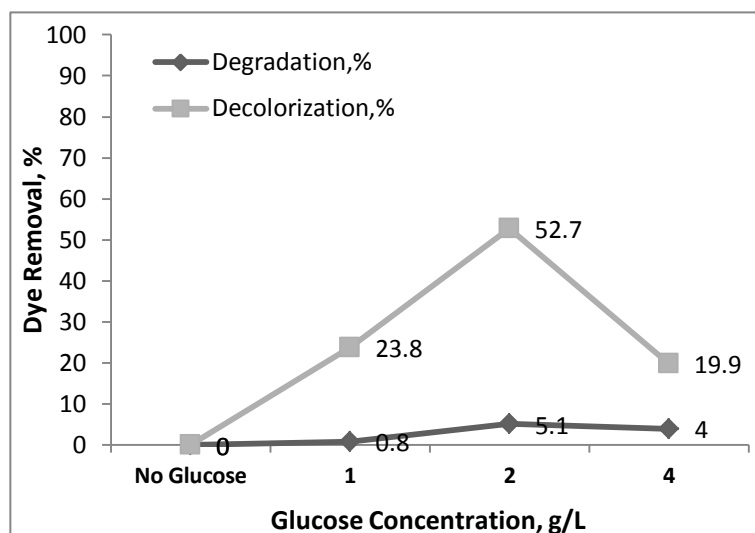


Figure 5.42. The influence of glucose concentration on dye removal efficiencies. Reaction conditions: $[Dye]_0=100$ ppm, 1 g/100 mL microorganism concentration, at room temperature and 200 rpm shaking.

Since, the dye removal efficiencies declined above 2 g/L glucose concentration this concentration was determined as the optimum condition.

The influence of the microorganism concentration on dye removal efficiencies was assessed changing the microorganism concentration between 1 g/100 and 2 g/100 mL fixing the glucose concentration at 2 g/L. The results are shown in Figure 5.43.

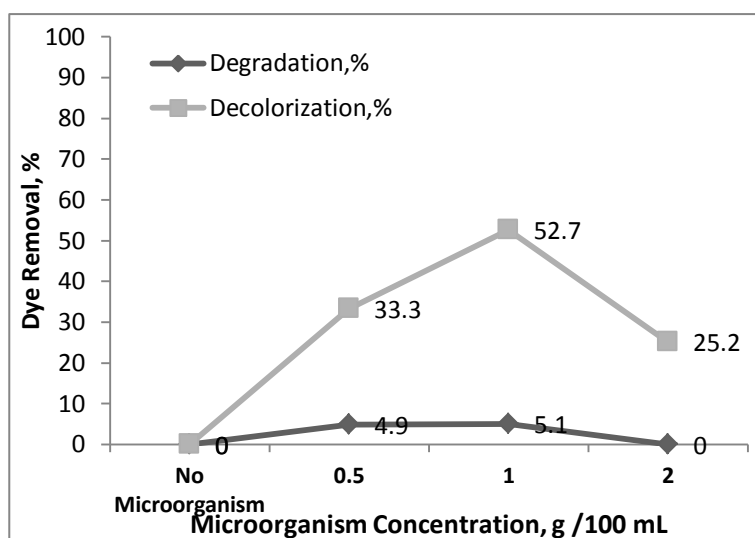


Figure 5.43. The influence of microorganism concentration on dye removal efficiencies. Reaction conditions: $[Dye]_0=100$ ppm, 2g/L glucose concentration, at room temperature and 200 rpm shaking.

The microorganism, *T. versicolor* secretes lignin degrading enzymes such as laccase, lignin peroxidase and manganese peroxidase which also have the ability of decomposing of organic compound in a wide variety. According to the

experimental results, the decolorization efficiency of Procion Red MX-5B was increased up to 33.3% and 52.7% when the microorganism concentration was 0.5 and 1 g/100 mL, respectively, while the presence of the microorganisms was not effective in degradation of Procion Red MX-5B. Above 1 g/100 mL microorganism, the dye removal was decreased due to the possible scarce of nutrient source or toxic products generated in during the enzymatic reactions.

6. GENERAL CONSIDERATIONS

The azo dye, Procion Red MX-5B was degraded and decolorized using several advanced oxidation methods and biological oxidation comparatively. Fenton like oxidation, photo-Fenton like oxidation, photocatalytic oxidation and catalytic wet air oxidation were tested in the context of the advanced oxidation part of the study. Iron impregnated activated carbon catalysts were used in advanced oxidation processes. The activated carbon supports were prepared from walnut shells applying physical and various chemical activation methods. The characterization results of the catalyst show that the catalysts have porous structures leading to large surface areas.

The highest dye removal efficiencies evaluated at the determined optimum reaction conditions for each of the oxidation method are presented in Table 6.1. Among the oxidation methods tested in the study, the maximum degradation and decolorization of Procion Red MX-5B was achieved using Fenton like and photo Fenton like oxidation in the presence of KOH activated carbon catalysts. The toxicity tests showed that no toxic by-products were formed in the Fenton and photo Fenton treatment. CWAO and photocatalytic oxidation performed in the absence of hydrogen peroxide were not effective on degradation and decolorization of Procion Red MX-5B. In comparison to photo Fenton like oxidation, higher degradation and decolorization efficiencies were achieved in Fenton like oxidation. However, less amount of oxidizing agent (H_2O_2) was sufficient to reach the optimum dye removal efficiencies in photo Fenton like oxidation due to the presence of UV light.

In the biological oxidation two white rot fungi, *T. versicolor* and *P. chrysosporium* were immobilized on walnut shells and their dye removal performances were tested in biological oxidation process. The decolorization ability of *T. versicolor* was superior to the other fungi, and in the presence of this fungus, 52.7% decolorization of Procion Red MX-5B was accomplished in one week. It is concluded that the advanced oxidation process are much more effective than the biological oxidation considering the reaction times and the degradation and decolorization efficiencies.

Fenton like oxidation was assessed as the most suitable method to degrade and decolorize Procion Red MX-5B amongst the oxidation methods tested in this study because of the highest dye removal efficiencies, and its potential to adaptability to industrial applications due to the simplicity and low cost. Therefore, the kinetic study was carried out for the Fenton like oxidation of Procion Red MX-5B.

Table 6.1. Maximum dye removal efficiencies achieved in the each chemical and biological oxidation process

Type of the Method	Catalyst Type	Optimum Conditions	Optimum Degradation Efficiency (%)	Optimum Decolorization Efficiency (%)
FENTON LIKE OXIDATION	Fe/K-AC	[Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =4 mM, 0.25 g/L of catalyst loading, initial pH=3, T= 50°C	51.6	91.6
PHOTO-FENTON LIKE OXIDATION	Fe/K-AC	[Dye] ₀ =100 ppm, [H ₂ O ₂] ₀ =2 mM, 0.25 g/L of catalyst loading, initial pH=3, 6 Watt of UV Light Intensity	50	88.3
PHOTO-CATALYTIC OXIDATION	Fe/K-AC	[Dye] ₀ =100 ppm, [0.25 g/L of catalyst loading, initial pH=3, 6 Watt of UV Light Intensity	10	7
CATALYTIC WET AIR OXIDATION	Fe/Z-AC	[Dye] ₀ =100 ppm, 0.25 g/L of catalyst loading, initial pH=7, T= 70°C, P=3 atm, 0.61 L/min air flow rate	27.1	13.9
BIOLOGICAL OXIDATION	<i>T. versicolor</i>	[Dye] ₀ =100 ppm, 1g/100 mL microorganism concentration, 2 g/L glucose concentration, room temperature, 200 rpm shaking, 1 week	5.1	52.7
	<i>P. chrysosporium</i>	[Dye] ₀ =100 ppm, 1g/100 mL microorganism concentration, 2 g/L glucose concentration, room temperature, 200 rpm shaking, 1 week	0	11.7

7. KINETIC STUDY

The kinetic study was performed using the decolorization data obtained in the parametric study on Fenton like oxidation performed at different reaction temperatures. The decolorization data comprise the concentration values of Procion Red MX-5B with respect to time under the optimum reaction conditions.

In order to derive the reaction rate equations, experimental data first were analyzed qualitatively. From Figure 5.18, it is apparent that the decolorization was faster at the beginning of the reaction and getting slower as time passed.

At low and moderate reaction temperatures the progression of color removal rate is different from that at high reaction temperatures. Up to 60 °C the decolorization increased steadily as the time increased during 2 hours. Nevertheless, at 70°C, the decolorization reached its maximum value in a shorter time.

In order to utilize the dye decolorization results in industrial applications at large scale, kinetic modelling is needed. Various reaction rate models such as n^{th} order models comprising first, second, pseudo-first and pseudo-second order models, Behnajady-Modirshahla-Ghanbary (BMG) model Fermi's equation, etc. has been tested in the kinetic studies found in literature in order to express dye decolorization kinetics (Ertugay and Acar, 2013, Rache et al., 2013, Karataş et al, 2012, Sun et al., 2009). Among these models, pseudo-first order reaction model is often determined to be the most suitable model elucidating the Fenton like oxidation of dyes (Dorraj et al., 2015, Idel-aouad et al, 2011, Chang and Chern, 2010, Huang et al., 2009).

Considering the literature survey on dye decolorization kinetics, first order or pseudo-first order reaction kinetics was proposed to express the Fenton like oxidation of Procion Red MX-5B. Pseudo-first order reaction model is represented by:

$$\frac{dC}{dt} = -k_{\text{app}} \cdot C \quad (7.1)$$

where; C is the concentration of Procion Red MX-5B [mg/l], k_{app} is the kinetic rate constant [min^{-1}], and, t is the reaction time.

k_{app} is depend on the reaction temperature, initial concentrations of the dye, hydrogen peroxide and the catalyst, therefore, it is a function of these parameters (Ramirez et al., 2009):

$$k_{app} = f(T, [\text{Dye}]_o, [\text{H}_2\text{O}_2]_o, [\text{Catalyst}]_o) \quad (7.2)$$

By integrating and linearizing, the following equation is obtained,

$$\ln \frac{C_o}{C_t} = k_{app} t \quad (7.3)$$

The graphical representation of reaction rate constants and the regression coefficients calculated at different reaction temperatures according the pseudo-first order reaction rate model are shown in Figure 7.1.

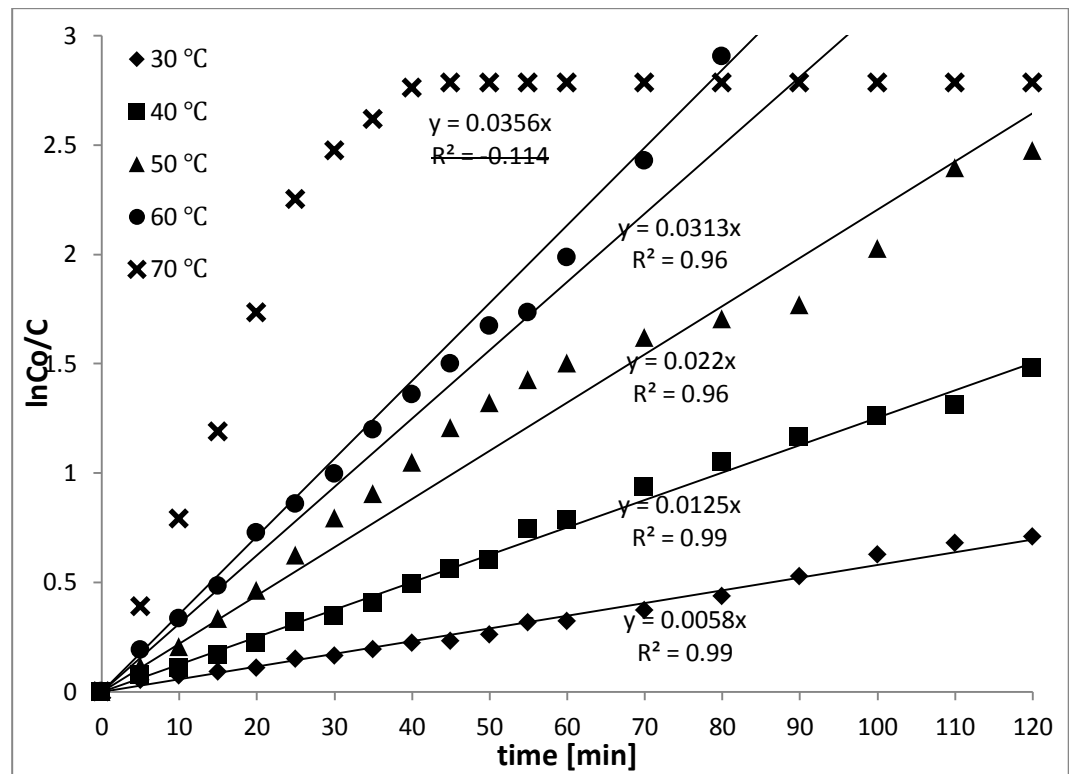


Figure 7.1. Determination of the rate constants and regression coefficients according to the pseudo-first order model. Reaction conditions: $[\text{Dye}]_o = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_o = 4 \text{ mM}$, 0.25 g/L of catalyst loading, 3 of pH, $T = 30\text{--}70 \text{ }^\circ\text{C}$.

From Figure 7.1, it is apparent that the dye decolorization reaction fits the pseudo-first order model well at 30, 40, 50 and 60 °C. The pseudo-first order

reaction rate constants at 30, 40, 50, and 60 and were evaluated to be 0.0058, 0.0125, 0.022, and, 0.0313, min^{-1} , respectively, and the regression coefficients were in the range of 0.96-0.99. The increase in the reaction rates with respect to the rise in temperature suggests that the transfer of the reactants to the catalyst surface, the reaction, and, the transfer of the end products from the catalyst surface are favored by the high reaction temperatures (Karthikeyan et al, 2011).

However, pseudo-first order model is not adequate for 70 °C because the dye concentration values remained almost the same after 35 minutes and the reaction reached steady state after this point. In order to derive a suitable kinetic model at 70°C, Behnajady-Modirshahla-Ghanbary (BMG) model was tested.

The pseudo first order reaction rate constants and the corresponding regression coefficients calculated at various reaction temperatures are listed in Table 7.1.

Table 7.1. Pseudo first order reaction rate constants and the corresponding regression coefficients

	Reaction Rate Constant, min^{-1}	Regression Coefficient, R^2
30 °C	0.0058	0.99
40 °C	0.0125	0.99
50 °C	0.0220	0.96
60 °C	0.0313	0.96
70 °C	-	-

▪ Behnajady-Modirshahla-Ghanbary (BMG) model

The decolorization data obtained at 70 °C was fitted to BGM model which allows expressing the decrease in reaction rates during the oxidation process (Behnajady et al, 2007):

$$\frac{C}{C_0} = 1 - \frac{t}{m + bt} \quad (7.4)$$

where; C is the concentration of the dye [mg/l], b and m are two characteristic constants relating to the reaction kinetics and oxidation capacities, and, t is the reaction time.

In order to solve the constants the equation (7.3) was linearized:

$$\frac{t}{1 - C/C_0} = m + bt \quad (7.5)$$

For 70 °C of reaction temperature, m and b constants were determined by plotting t vs. $\frac{t}{1 - C/C_0}$. The graphical representation is shown in Figure 7.2.

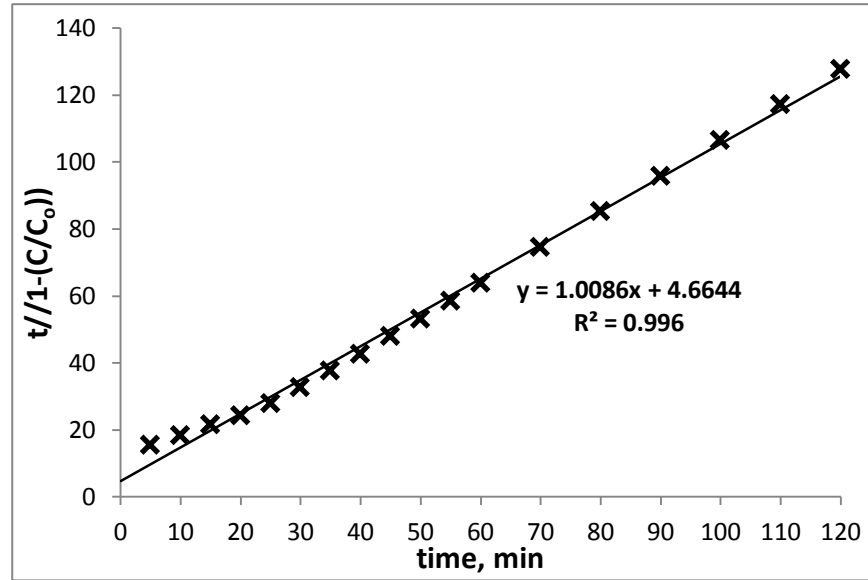


Figure 7.2. Determination of the m and b constants according to BMG model. Reaction conditions: [Dye]₀=100 mg/L, [H₂O₂]₀=4 mM, 0.25 g/L of catalyst loading, 3 of pH, T=70°C.

According to Figure 7.2, the decolorization data at 70 °C fitted BMG model well with a regression coefficient of 0.996. m and b values were found as 4.6644 and 1.0086, respectively. Substituting the m and b constants in equation (7.4) the corrected concentration values were calculated and the reaction rates were determined by taking the derivative of the equation (7.4):

$$\frac{C}{C_0} = 1 - \frac{t}{4.6644 + 1.0086t} \quad (7.6)$$

$$\frac{dC/C_0}{dt} = \frac{-m}{(m + bt)^2} \quad (7.6)$$

$$-r = -\frac{dC}{dt} = 100 \frac{4.6644}{(4.6644 + 1.0086t)^2} \quad \frac{\text{mg}}{\text{lmin}} \quad (7.7)$$

In order to find the reaction rate constant at 70 °C, the pseudo-second order reaction rate model was proposed:

$$\frac{dC}{dt} = -k_{app} \cdot C^2 \quad (7.8)$$

After linearization, equation (7.8) takes the form of;

$$\frac{1}{C} = \frac{1}{C_0} + k_{app}t \quad (7.9)$$

The reciprocal of the corrected concentration values and the reaction time were plotted according to the second order reaction rate model and shown in Figure 7.3. From the Figure 7.3, the order of the reaction was determined to be 2 due to the high regression coefficient and reaction rate constant was found to be 0.0018 L/mg.min.

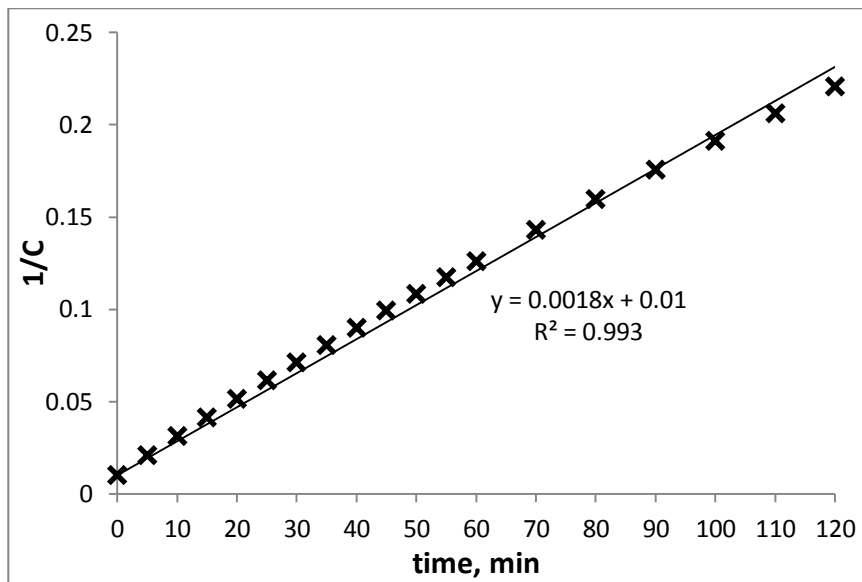


Figure 7.3. Corrected reaction rates calculated at 70°C according to the 2nd order reaction kinetics. Reaction conditions: [Dye]₀=100 mg/L, [H₂O₂]₀=4 mM, 0.25 g/L of catalyst loading, 3 of pH, T=70°C.

Because the dye oxidation reactions generally followed pseudo-first order reaction kinetics (for 30, 40, 50 and 60 °C), the activation energy was evaluated using the pseudo-first order reaction rate constants. The activation energy and the pre-exponential factor were calculated according to the linearized form of the Arrhenius equation:

$$k = Ae^{\left(-\frac{E}{RT}\right)} \quad (7.8)$$

$$\ln k = \ln A - \frac{E}{R} \frac{1}{T} \quad (7.9)$$

where A [min^{-1}] is the pre-exponential (frequency) factor, E [J/mole] is the activation energy, R [J/mol.K] is the ideal gas constant ($R=8.314$ J/mol.K), and T [K] is the reaction temperature. Figure 7.4 presents the Arrhenius plot of decolorization of the azo dye from which the kinetic parameters calculated.

There is a good linear relationship in the plot of $1/T$ vs. $\ln k$ for the reaction rate model proposed. From the Figure 7.4., the activation energy and the pre-exponential factor were evaluated as 47.36 kJ/mol and $9.19 \times 10^5 \text{ min}^{-1}$, respectively.

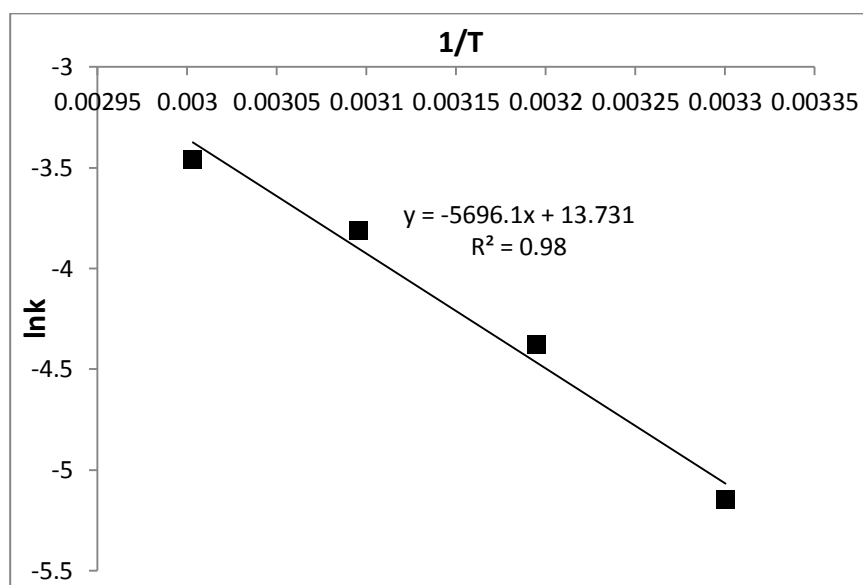


Figure 7.4. Arrhenius plot of the Fenton like oxidation of Procion Red MX-5B based on the first order reaction kinetics in the temperature range of 30-60°C.

The high regression coefficients evaluated according to the pseudo-first order reaction model indicated that the Fenton like oxidation of Procion Red MX-5B in the presence of selected Fe-KOH catalyst followed the pseudo first order kinetics. Therefore the Arrhenius form of the Procion Red MX-5B decolorization based on first order kinetics is described as:

$$k = 9.19 \times 10^5 \exp\left(\frac{-47.36 \times 10^3}{R \times T \text{ [K]}}\right) (\text{min}^{-1}) \quad (7.8)$$

The activation energies reported for the heterogeneous Fenton like oxidations of the azo dyes in literature are generally very close to or higher than the activated energy calculated in this work. For instance, Ramirez at al., claimed that the activation energy for oxidation of Orange II in the presence of iron over

carbon aerogel catalyst was 56.1 kJ/mol in the temperature range of 30-70°C. Gan and Li evaluated 82.53 kJ/mol of activation energy necessary to oxidize Rhodamine B in the presence of rice husk based silica supported iron catalyst in the temperature range of 30-50 °C (Ramirez et al., 2007, Gan and Li, 2013). Table 7.2 summarizes the literature survey on activation energies evaluated for Fenton like oxidation of dyes.

Table 7.2. Comparison of the activation energies found in literature

Reference	Dye	Catalyst	Temp. Range, °C	Act. Energy, kJ/mole
Ramirez et al., 2007	Orange II	Iron over carbon aerogel	30-70	56.1
Gan and Li., 2013	Rhodamine B	Rice hull based silica supported iron	30-50	82.53

According to the kinetic study on Fenton like oxidation of Procion Red MX-5B in the presence of Fe-KOH catalysts, the dye oxidation follows the first order kinetics up to 60 °C. Nevertheless, above 60 °C, the dye oxidation follows the second order reaction kinetics.

8. CONCLUSIONS

The conclusions extracted from the experimental study can be investigated in two main sections involving the advanced oxidation and biological oxidation sections.

8.1. Advanced Oxidation

The iron impregnated activated carbon catalysts which were prepared from walnut shells by chemical and physical activation methods were found to be successful in degradation and the decolorization the Procion Red MX-5B by using advanced oxidation processes.

▪ *Catalyst Characterization*

The catalyst and the catalyst supports were characterized by SEM, XRD and BET analyses. The SEM micrographs of the catalyst support and the catalyst show that each of the activated carbon prepared by different chemical and physical activation methods have porous textures resulting in large surface areas and good iron distribution. According to the XRD patterns, the iron activated carbon support and the catalyst has amorphous structures and no any impurities were found in the catalyst structure which means a successful carbonization and activation step.

The highest decolorization and degradation efficiencies were obtained with base activated catalyst (Fe/K-AC) in Fenton like and photo-Fenton like oxidations and using zinc chloride activated catalyst (Fe/Z-AC) in CWAQ. The surface areas and the average pore sizes of these catalyst measured BET method. According to the measurements, the BET surface areas were evaluated as 961.06 and 1370.3 m²/g for K-AC and Z-AC, respectively. When these results were compared to the surface areas of the organic waste based activated carbons in literature, it can be concluded that the activated carbons prepared in this study have generally larger or similar surface areas.

▪ *Fenton Like Oxidation*

Prior to the parametric study in which the optimum reaction conditions were determined, catalyst screening experiments were performed to select the

most suitable catalyst. Fe/K-AC was determined to be the most suitable catalyst. The optimum conditions were determined by 4 mM of initial H_2O_2 concentration, 0.25 g/L of catalyst loading, 3 of initial pH and temperature of 50°C , and the degradation and the decolorization efficiencies were evaluated as 51.6% and 91.6% at these optimum conditions.

The reusability tests showed that, the degradation efficiencies decreased from 51.6% (in the presence of fresh catalyst) to 37.4% and 32.5% and the decolorization efficiencies decreased from 91.6% to 84.4% and 80.9% in the second and third use of the recovered catalysts, respectively.

The iron leaching study shows that the iron concentration in the treated dye solution in the presence of the fresh catalyst was 1.23 ppm and it increased up to 2.22 and 2.63 ppm in the second and third use of the recovered catalysts, respectively. Thus the catalyst showed good chemical stability since the iron leaching was noticeably low. According to the toxicity analyses, the inhibition in the root growth was %1.1.

▪ *Photocatalytic and Photo-Fenton Like Oxidation*

In the catalyst screening experiments, the photocatalytic performances of Fe/AC and Fe-TiO₂/AC catalysts which were prepared by different activation methods (physical activation method and chemical methods including HNO_3 , ZnCl_2 and KOH activations) were compared both in the presence and in the absence of H_2O_2 by changing the catalyst loading from 0.25 to 0.5 g/L.

In presence of the iron-titania coated on activated carbon catalysts the degradation and the decolorization efficiencies were below 11%. So, the catalyst screening experiments were performed using Fe/Activated Carbon catalyst. According to the results of catalyst screening experiments, the highest decolorization and degradation efficiencies were obtained in presence of base activated catalyst.

The optimum reaction conditions were determined as 0.25 g/L for catalyst loading, 2 mM for initial H_2O_2 concentration, 3 of pH and 6 W of UV light intensity in the presence of KOH activated catalyst (Fe/K-AC). The degradation

and the decolorization efficiencies were evaluated as 50% and 88.3% at these optimum conditions.

The catalyst showed good chemical stability in the photo-Fenton like oxidation since the iron leaching was 1.98 ppm which was below the European Union directives of 2 ppm. The results of toxicity analysis show that the inhibition of the root of *Lepidium sativum* growth in the treated dye solutions was 0.6 %.

▪ Catalytic Wet Air Oxidation

In the catalyst screening experiments Fe/Z-AC was selected as the most suitable catalyst and the parametric study was carried out in the presence of this catalyst. Although the complete degradation and decolorization of the dye couldn't be achieved, this environmentally friendly method and the catalyst derived from the organic wastes found to be promising for the further parametric studies.

According the experimental results, dye removal efficiencies were increased with the increasing catalyst loading, temperature, pressure and the air flow rate. The maximum degradation and the decolorization efficiencies were evaluated as 27.1 % and 13.9 %, respectively, when the catalyst loading, temperature, pressure and air flow rate were 0.25 g/L, 70°C, 3 atm and 0.61 L/min, respectively, for an initial dye concentration of 100 ppm.

▪ Kinetic Study

The kinetic study was carried out for the Fenton like oxidation of Procion Red MX-5B which was determined as the most suitable oxidation method considering the high dye removal efficiencies and simplicity of this method. Pseudo-first order reaction kinetics was fitted to the decolorization data obtained in the parametric study of the Fenton like oxidation up to 60°C. The rate equations for decolorization at 30, 40, 50, and 60 °C were as follows:

$$-r = 0.0058 C \quad \text{at } 30^\circ \text{C} \quad (8.1)$$

$$-r = 0.0125 C \quad \text{at } 40^\circ \text{C} \quad (8.2)$$

$$-r = 0.0220 C \quad \text{at } 50^\circ \text{C} \quad (8.3)$$

$$-r = 0.0313 C \quad \text{at } 60^\circ \text{C} \quad (8.4)$$

where $-r$, mg/lmin is the decolorization rate of Procion Red MX-5, and C , mg/l is concentration of Procion Red MX-5B.

The decolorization data obtained at 70 °C was corrected according to the Behnajady-Modirshahla-Ghanbary (BMG) model. The decolorization data was fitted to pseudo-second order reaction kinetics and the decolorization rate equation at 70 °C was found to be;

$$-r = 1.8 \times 10^{-3} C^2 \quad \text{at } 70^\circ \text{C} \quad (8.5)$$

Because the dye decolorization reaction kinetics followed the pseudo-first order reaction kinetics generally, the activation energy and the pre-exponential factor was calculated using to the pseudo-first order reaction rates constants and found as 47.36 kJ/mol and $9.19 \times 10^5 \text{ min}^{-1}$, respectively.

8.2. Biological Oxidation

In the biological oxidation, the white rot fungi, *Trametes versicolor* and *Phanerochaete chrysosporium* immobilized on walnut shells was used to degrade and decolorize the Procion Red MX-5B. In the microorganism selection experiments, *T. versicolor* was determined the most suitable fungus. In the parametric study the optimum microorganism concentration and glucose concentration were determined as 1 g/100 mL and 2 g/L, respectively, at room temperature and 200 rpm shaking. The biological oxidation was not effective in dye degradation, only 5.1% degradation was achieved under the optimum reaction conditions, in the presence of *T. versicolor*, which was selected as the most suitable microorganism in biocatalyst screening experiments. Nevertheless, this fungus was effective in dye decolorization, 52.7% of Procion Red MX-5B was decolorized at the end of 1 week.

When the advanced oxidation and biological oxidation methods tested in the study were compared, a much more rapid dye removal was accomplished at higher removal efficiencies by the application of photo-Fenton like and Fenton like oxidation methods. Advanced oxidation methods have also some advantages over the biological oxidation methods such as ease of handling the process and acceptable operating costs.

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RESUME**Res. Assist. BURCU PALAS****CONTACT INFORMATION**

Address: Ege University/ Faculty of Engineering/ Department of Chemical Engineering

Phone: 02323114051

E-mail: burcu.palas@ege.edu.tr

EDUCATIONAL BACKGROUND

2011-2015: M.Sc.

Ege University/ Faculty of Engineering/ Department of Chemical Engineering

2007-2011: B.Sc.

Ege University/ Faculty of Engineering/ Department of Chemical Engineering

2002-2006: High School

Bornova Anatolian High School

PROJECTS

2012-2015: Researcher/ Ege University-Scientific Research Project

“Azo Boyar Madde İçeren Atıksuların Sabit Yataklı Reaktörde Biyolojik Oksidasyon ile Arıtılması” (12 MÜH 068)

2015- : Researcher/ Ege University-Scientific Research Project

“Azo Boyar Maddelerin Perovskit Tipi Katalizörler Varlığında Fenton Benzeri Yöntemi ile Giderimi” (15 MÜH 030)

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G.Ersöz, **B.Palas**, Ceviz Kabuğu Kullanılarak Sulu Çözeltilerden Azo Boyaların İleri Oksidasyon Yöntemleri İle Giderimi, Türkiye İnnovasyon Haftası 2014, 29-30 Mayıs 2014, İzmir.