PHOTO-FENTON OXIDATION OF AZO DYES IN TEXTILE WASTEWATERS IN THE PRESENCE OF FE/AC AND FE-TIO$_2$/AC CATALYSTS

ROHIT NAGARGOJE[#]; SUHEYDA ATALAY[*]; GULIN AYTIMUR ERSOZ[*]; BURCU PALAS[*]

[#]Department of Chemical Engineering
Institute of Chemical Technology, Mumbai, India

[*]Department of Chemical Engineering
Ege University, Izmir, Turkey

Abstract: Azo dyes are the most common type of the synthetic dyes, especially used in textile industry and they are seriously hazardous for the environment because of their resistance to biological and chemical degradation. In this study, removal of the azo dye, Procion Red MX-5B by using Photo-Fenton oxidation in presence of Fe/Activated Carbon and Fe-TiO$_2$/Activated Carbon catalysts was investigated and the catalytic performances of the catalysts were compared. The activated carbon, which was used as catalyst support, was prepared from walnut shells by using ZnCl$_2$ as chemical activation agent. As well as the comparison of the catalytic performances of the catalysts, the optimum reaction conditions were determined by varying the initial hydrogen peroxide concentration, catalyst loading, pH, and the initial dye concentration in presence of both the catalysts. According to the experimental results, the highest removal efficiencies were obtained in presence of Fe/AC catalyst. The optimum conditions were determined as 2 mM of initial hydrogen peroxide concentration, 0.25 g/L of catalyst loading and pH 3 when the initial dye concentration was 100 mg/L in presence of Fe/AC catalyst and 4 mM of initial hydrogen peroxide concentration, 0.25 g/L of catalyst loading and pH 4 in presence of Fe-TiO$_2$/AC catalyst. The decolorization and degradation efficiencies were evaluated as 97% and 55% in presence of Fe/AC catalyst and 87.5% and 20.2% at the optimum conditions.

1.INTRODUCTION

Textile mills are major consumers of water and one of the largest sectors causing intense water pollution and the textile wastewater contains a large variety of raw materials and reagents such as synthetic dyes and pigments (Blanco et al., 2012).

Azo dyes are the most commonly used synthetic dyes and the synthetic dyes are designed to be highly resistant to soap, water, light and oxidizing agents, so, they are resistant to the biological and chemical degradation. The release of the colored wastewater into water sources affects not only the aesthetics but also the water transparency and the gas solubility in water bodies and damages the environment and they may be toxic to flora and significantly reduce photosynthetic activity (Firmino et al., 2010, Khataee et al. 2013).

Azo dyes have been used increasingly in industries because of their easy and low cost synthesis compared to natural dyes. However, most azo dyes are known as toxic, carcinogenic, and mutagenic (Seesuriyachan, et al., 2007). Therefore removal of dyes before discharging them into natural water streams is crucial (Rodriguez-Couto, 2009).

Conventional treatment methods in the textile dyeing industry for color removal include coagulation, flocculation, and adsorption. Both coagulation and adsorption generate large amounts of sludge and waste which need further treatment for disposal. The limitations of conventional wastewater treatment methods can be overcome by the application of advanced oxidation processes through which highly oxidizing species like hydroxyl radicals are produced and these processes are extremely useful for substances resistant to conventional technologies (Abo-Farha, 2010, Zhou and He, 2007).

The most common AOPs comprises Fenton, Fenton-like, photo-Fenton processes, ozonation, electrochemical oxidation, photocatalysis, radiolysis and wet oxidation processes.

The photocatalytic degradation is a promising and effective technology for degrading organic compounds. In photocatalytic degradation inexpensive semiconductors are used and it can easily mineralize various recalcitrant organic compounds.

The basic steps for heterogeneous photocatalysis consist of initially transferring of the reactants in the liquid phase onto the catalyst surface followed by adsorption of the reactant on the catalyst surface, reaction in the adsorbed phase, desorption of the final product and finally removal of the final products in the liquid phase (Rauf et al.,2011).

The most common photocatalyst is TiO_2 due to its non-toxicity, high activity and high chemical stability and the effectiveness (Yoon et al., 2012). The TiO_2 catalysts have been improved by immobilization of them onto solid matrices such as activated carbon, zeolite and clay, recently. Amongst the catalyst support materials the activated carbon is preferable due to its high porosity and surface area, stability and fair prices (Rocha et al.,

2011). The activated carbon provides a large adsorption area for the target substance and makes the catalyst recovery step easier (Mahadwada et al., 2012, Yoon et al., 2012).

In literature, there are many studies on degradation and decolorization of azo dye containing wastewater, using both the conventional methods and various advanced oxidation methods including the photocatalytic degradation methods in presence of transition metal doped TiO_2 catalysts. However, the usage of organic waste based activated carbon as catalyst support in photocatalysis is an innovative approach.

In this context, the main objective of this study is to investigate the degradation and decolorization of the azo dye, Procion Red MX-5B by photo-fenton oxidation in presence of Fe-TiO_2/Activated carbon and Fe/Activated Carbon catalysts comparatively. In order to contribute the recovery of organic wastes, walnut shells were chosen to produce activated carbon which will be used as catalyst support. The activated carbon was produced from walnut shells by chemical activation method. By varying the initial hydrogen peroxide concentration, catalyst loading, pH, the initial dye concentration and the UV light intensity, the optimum reaction conditions were determined in photo-fenton process.

2. THEORETICAL BACKGROUND

Industrial wastewater is a global issue due to its high concentration of pollutants, especially recalcitrant organic compound. The discharge of industrial wastewater into the natural water resources has a remarkable negative effect on the environment and the human health. During the last century a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted in serious pollution problems (Yang et al., 2011).

Textile mills are major consumers of water and one of the largest sectors causing intense water pollution (Blanco, et al., 2012). The textile industry generates large quantities of wastewater from different steps of dyeing and finishing process and the textile wastewater is characterized by high content of dyestuff and high COD derived from additives (Kalra et al., 2011). Azo dyes are the most common and the largest group of dyes used in textile industry constituting 60–70% of all dyestuffs produced (Khehra et al., 2006).

2.1. Azo Dyes

Azo dyes are the most commonly used synthetic dyes in the textile, food, paper making, printing, leather, pharmaceutical and cosmetic industries and characterized by the nitrogen to nitrogen double bonds. They give bright, high intensity colours, much more so than the next most common dye class (anthraquinones). Their biggest advantage it their cost-effectiveness, which is due to the processes involved in manufacture.

The simplicity of the production reactions provides that the process can be scaled up or down very easily, which is always a key factor in the cost of chemicals. Energy requirements for the reaction are low, since most of the chemistry occurs at or below room temperature. The

environmental impact is reduced by the fact that all reactions are carried out in water, which is easy and cheap to obtain, clean and dispose of. As other dye classes become less viable from either an environmental or economic reasons, azo dyes become ever more attractive options. Procion Red MX-5B is classified as monoazo dye. Its chromophoric group is an azo double bond which absorbs light and affects visibility in water bodies. The molecular structure of MX-5B is given in Figure1.
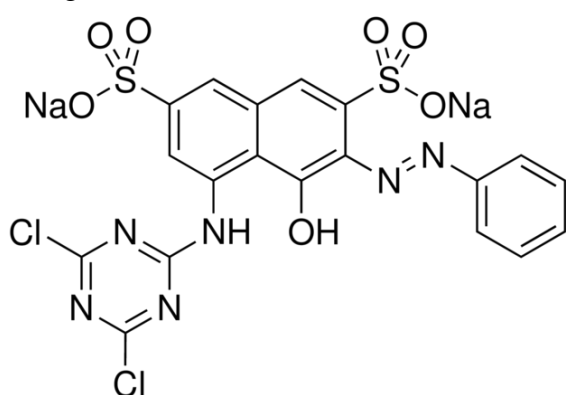
Figure 1. The molecular structure of the Procion Red MX-5B

The complex aromatic structures of the azo dyes, result in intense color in textile wastewater effluents. Color in the effluent, interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Rodriguez-Couto, 2009). Azo dyes, are also known as toxic, carcinogenic and mutagenic. The new environment regulations concerning textile products have banned the discharge of colored waste in natural water bodies. Therefore, an effective and economic treatment of effluents containing diversity of textile dyes has become a necessity for clean production technology for textile industries. (Khehra et al., 2006).

The conventional textile wastewater treatment methods comprising the flocculation, sedimentation, flotation, filtration, extraction and adsorption are usually costly, inefficient and often produce a high amount of secondary wastes. (Rache et al., 2013).

Recent progress in the removal of organics from wastewaters has led to the development of advanced oxidation processes (AOPs), which are in short based in the generation of extremely reactive species like hydroxyl and perhydroxyl radicals (HO• and HO$_2$• respectively). Among them, Photo-Fenton oxidation, based on the use of H$_2$O$_2$ and an iron catalyst under irradiation by UV-light, is used for the efficient degradation of a wide range of organic compounds, including azo dyes (Punzi et al., 2012).

## 2.2. Advanced Oxidation Processes

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant, in some cases producing chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed.

The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals (•OH), ozone, and chlorine.

Advanced oxidation processes (AOPs) are based on the generation of highly reactive radicals such as OH• capable of degrading a wide range of pollutants (Jonstrup et al., 2011). The AOP technique has drawn considerable attention from various quarters of scientific community as it is easy to handle and produces significantly less residuals as compared to the classical approaches. Amongst the many techniques employed in the AOP approach are the UV photolytic technique, Fenton process, photo-Fenton process, ozonation process, sonolysis, photocatalytic approach, biodegradation and the radiation induced degradation of dyes (Rauf et al., 2011).

2.2.1.Photocatalytic Degradation Processes

Various techniques are available for the elimination of dyes from wastewater and in particular photocatalysis is a more promising method. The basic steps for heterogeneous photocatalysis consist of initially transferring of the reactants in the liquid phase onto the catalyst surface followed by adsorption of the reactant on the catalyst surface, reaction in the adsorbed phase, desorption of the final product and finally removal of the final products in the liquid phase. (Rauf et al., 2011). The mechanism of the photocatalytic degradation is given in Figure 2.
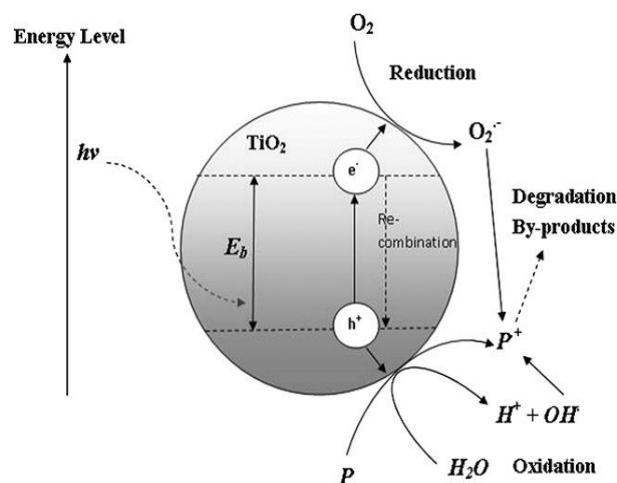
Figure 2. The mechanism of the photocatalytic degradation

Titanium dioxide is the most widely used photocatalyst owing to its efficiency, low cost, and chemical stability (Le et al., 2012). Recently, TiO_2 has been immobilized on different supports like glass beds, silica, activated carbon, biodegradable polymer and zeolites. Also, combining TiO_2 with the adsorption properties of organic molecules onto some adequate adsorbents increases the surface areas which lead to an enhancement of the reaction rate (Ilinoiu et al. 2013).

Using activated carbon as a catalyst support will help increase the photodegradation rate by progressively allowing an increased quantity of substrate to come in contact with the TiO_2 through means of adsorption. This is important because researchers have established that the oxidizing species generated by the photocatalyst, does not migrate very far from the active centers of the TiO_2 and therefore degradation takes place virtually on the catalyst surface. The synergistic effect can be explained 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, giving a complete photodegradation process (Puma et al., 2008).

3. LITERATURE SURVEY

In 2013, Sobana et al., studied the photocatalytic degradation of an azo dye Direct Yellow 4 (DY4) using Activated Carbon loaded ZnO (AC-ZnO) as a photocatalyst in aqueous solution investigated under solar irradiation. Among the activated carbons loaded from three different sources, commercial AC (ACSD) loaded ZnO was found to be more efficient in the degradation of Direct Yellow 4 (DY4) in solar light. The effects of operational parameters such as pH of the solution, amount of catalyst, initial dye concentration and effect of grinding for ACSD loading on photodegradation of DY4 were analyzed. The degradation of DY4 followed pseudo-first order kinetics according to the Langmuir–Hinshelwood model. Synergistic effect of ACSD-ZnO was shown by the synergistic factor of 2.0 (Sobana et al., 2013).

In 2013, Xu et al., synthesized Hydroxy-iron–aluminum pillared bentonite (H-Fe–Al-B) with ion exchange method. The photo-Fenton catalytic activity of H-Fe–Al-B was tested under different reaction condition using azocarmine B (ACB) as model pollutant under ultraviolet light (UV) irradiation. The effects of three operating variables, initial dye concentration, initial pH value and H$_2$O$_2$ concentration on the decolorization efficiency of ACB were optimized. The results showed that H-Fe–Al-B had high photocatalytic activity. The optimum conditions for ACB decolorization were dye concentration of 143.7 mg/L, pH of 4.2 and H$_2$O$_2$ concentration of 17.7 mM, respectively. The decolorization rate under the optimum conditions determined as 99.6% (Xu et al., 2013).

In 2012, Illinoiu et al., studied the hybrid material based on natural zeolite modified with nitrogen-doped TiO$_2$ photocatalyst (Z-TiO$_2$-N) synthesized by solid-state reaction under microwave-assisted hydrothermal conditions. The photocatalytic activity of Z-TiO$_2$-N photocatalyst under UV and VIS irradiation was determined for the degradation of Reactive Yellow 125 (RY 125) dye solution. The operational conditions using photocatalyst amount of 1 g/L at pH 3 were established as optimum conditions for photocatalytic application in RY 125 dye solution degradation. The experimental studies revealed that the degradation efficiency expressed in terms of decolorization, aromatic ring opening and mineralization depended strongly on the initial RY 125 dye solution concentrations. The photocatalyst exhibited a good performance for discoloration and aromatic-ring opening processes at all studied concentrations (25, 50 and 100 mg/L) but an effective mineralization was reached only for 25 mg/L RY 125 dye solution (Illinoiu et al., 2012).

In 2012, Punzi et al., compared efficiencies of homogeneous and heterogeneous photo-Fenton oxidation for treatment of azo dye containing synthetic textile wastewater. The influence of parameters such as the presence of NaCl

and starch was evaluated and optimal iron and H_2O_2 dosage determined. Complete decolorization of Remazol Red RR was achieved at all investigated NaCl and starch concentration. Mineralization, in terms of COD reduction, was 96% in the homogeneous and 93% in the heterogeneous reaction, but decreased with increasing NaCl and starch concentrations. The homogeneous oxidation showed the highest efficiency in treating synthetic wastewater containing Remazol Blue RR or a mixture of Remazol Red RR and Remazol Blue RR (Punzi et al., 2012).

In 2012, Sun et al., studied the photocatalytic degradation of organic pollutants in $TiO_2/UV/O_3$ system. TiO_2 nanotubes (TNTs) were prepared by hydrothermal treatment of P25 TiO_2 in NaOH solution. Adsorption and photocatalytic degradation of Brilliant Red X-3B (X3B), an anionic azo dye, in TiO_2 suspensions using O_2 and O_3 as oxidants, TNTs and P25 TiO_2 as photocatalysts, respectively. The maximum adsorption of X3B on the surface of TNTs was found to be 3 times higher than that of P25 TiO_2, and TNTs showed superior photocatalytic activity than P25 TiO_2 under identical conditions. Ozonation and photocatalytic oxidation were involved in the degradation of X3B in $TiO_2/UV/O_3$ system. However, only photocatalytic oxidation was responsible for the degradation of X3B in $TiO_2/UV/O_2$ system. Compared with O_2, O_3 is a more efficient oxidant in degradation of X3B in TiO_2/UV system (Sun et al., 2012).

In 2012, Zheng et al., studied on the TiO_2-coated activated carbon surface (TAs) composites prepared by a sol gel method with supercritical pretreatment. The photocatalytic degradation of acid yellow (AY) was investigated under UV radiation to estimate activity of catalysts and determine the kinetics. The effects of parameters including the initial concentration of AY, light intensity and TiO_2 content in catalysts were examined. The results indicate that TAs has a higher efficiency in decomposition of AY than P25, pure TiO_2 particles as well as the mixture of TiO_2 powder and active carbon. The photocatalytic degradation rate was found to follow the pseudo-first order kinetics with respect to the AY concentration (Zheng et al., 2012).

In 2011, Asilturk and Sener, studied the effect of activated carbon (AC) on the structural properties and photocatalytic activity of titanium dioxide was investigated. For this purpose, TiO_2-AC catalysts were prepared with varying weight percentages of AC and by hydrothermal and reflux methods. The physicochemical properties of the prepared catalysts, including crystallinity, particle size, thermal behavior, surface morphology, specific surface area and pore volume of the photocatalysts were investigated. Containment of AC into the catalysts in the varying proportions lead to increases both in the specific surface area and the particle size of the catalysts depending on the AC content and the method of the preparation. The synthesized catalysts were tested in UV-assisted degradation of Rhodamine B (RhB) in aqueous medium. The results demonstrated that the reflux method can be effective method for preparing the photocatalytic TiO_2-AC materials had a high photocatalytic activity for RhB removal (Asilturk and Sener, 2011).

In 2011, Le et al., studied TiO$_2$-anatase obtained directly by chemical vapor condensation (T-95), or from a commercial catalyst (P-25). TiO$_2$ nanoparticles and coconut shell activated carbon, CSAC, are mixed with mass ratios of 1/1 (CT-1, CP-1) and 2/1 (CT-2, CP-2), respectively. The catalyst obtained from the CVC process wasbetter than the commercial one in a comparison of the physico-chemical properties, and was also confirmed by the photocatalytic degradation of methylene blue (MB). The composited catalysts (CSAC/TiO$_2$) are better than CSAC or TiO$_2$ only. At the same TiO$_2$ to CSAC mass ratio, the MB removal efficiencies followed the trend: CT-2>CT-1>CP-2>CP-1> T-95>CSAC>P-25. Furthermore, the advantages of the CT-2 catalyst revealed its practical potential to treat pollutants (Le et al., 2011).

In 2009, Devi et al., investigated the usage of zero valent metallic iron (ZVMI) in the photo-Fenton process under UV light as a novel technique for the complete degradation of di azo dye Bismarck Brown (BB) in aqueous medium. The influence of various reaction parameters like concentration of oxidants, dye, iron powder and pH were investigated and optimum conditions were determined. Ammonium persulfate (APS) proved to be better oxidant in comparison with hydrogen peroxide for enhancing the degradation rate and effectively inhibited the precipitation of iron hydroxides at higher dosages of iron powder which was attributed to the acidity provided by APS which is crucial for Fenton process. The rate constant for the kinetics of degradation using various oxidation processes follows the order: Fe^0/APS/UV > Fe^0/H$_2$O$_2$/UV > Fe^0/APS/dark > Fe^0/UV > Fe^0/H$_2$O$_2$/ dark > Fe^0/dark > H$_2$O$_2$/UV > APS/UV (Devi et al., 2009).

In 2011, Lodha et al., studied direct photocatalytic degradation of rhodamine B (RB) reported by thiocyanate complex of iron and hydrogen peroxide. The rate determining parameters like, pH of the medium, concentration of the complex and dye, amount of H$_2$O$_2$, and light intensity on the degradation process were studied. The rate of photocatalytic degradation of the dye was observed spectrophotometrically and they found that it follows pseudo-first-order kinetics (Lodha et al., 2011).

In 2011, Mahmoodi et al., prepared immobilized composite photocatalyst, titania (TiO$_2$) nanoparticle/activated carbon (AC), and its photocatalytic activity on the degradation of textile dyes was tested. AC was prepared using Canola hull. Basic Red 18 (BR18) and Basic Red 46 (BR46) were used as model dyes. The effects of reaction parameters such as weight percent (wt.%) of activated carbon, pH, dye concentration and anions were investigated on dye degradation. Data showed that dyes were decolorized and degraded using the immobilized composite photocatalyst. Results showed that the immobilized composite photocatalyst with 2 wt.% of AC is the most effective novel immobilized composite photocatalyst to degrade textile dyes (Mahmoodi et al., 2011).

In 2011, Rauf et al., studied the degradation of azo dyes using transition metal doped TiO$_2$ as photocatalysts in aqueous solutions. The addition of these

dopants can alter the surface properties of TiO_2 catalyst such as surface acidity and surface area. The degradation of dyes depends on several parameters such as pH, catalyst concentration, substrate concentration and the nature of the doping substances. Depending on the structure of the azo dye, the major identified intermediates were hydroxylated derivatives, aromatic amines, naphthoquinone, phenolic compounds and several organic acids. The study also presents the literature findings on the available pathways and mechanisms of degradation of some azo dyes in the presence of metal doped TiO_2 catalysts (Rauf et al., 2011).

In 2011, Zhang et al., studied nano-TiO_2-supported activated carbon (TiO_2/AC) developed for the microwave (MW) degradation of an azo dye, methyl orange (MO), selected as a model contaminant in aqueous solution. The effects of selected process parameters such as supported TiO_2 content, MW irradiation time, initial MO concentration, catalyst dose, and solution pH on the degradation were investigated. The results showed that the supported TiO_2 on AC resulted in the production of hydroxyl radical (•OH) in aqueous solution under MW irradiation, which significantly enhanced the performance of AC/MW process for the degradation of MO. Also, the supported-TiO_2/AC displayed higher catalytic activity than AC alone under MW irradiation. By comparison, the supported-TiO_2/AC/MW process exhibited several advantages, including high degradation rate, short irradiation time, no residual intermediates and no secondary pollution (Zhang et al., 2011).

In 2010, Hussein and Abass, studied the photocatalytic decolorization of both the real and simulated textile wastewater under artificial source of irradiation using titanium dioxide and zinc oxide. The effects of various operational parameters such as catalyst amount, type of catalyst, type of reactor, type of dye, dye concentration, and temperature were investigated. Under optimal conditions, the extent of decolorization was about 100 %. The decolorization percentages differ with the difference in type of dye used in textile industry. The results indicate clearly that titanium dioxide and zinc oxide could be used successfully in photocatalytic treatments of textile industrial wastewater (Hussein and Abass, 2010).

In 2009, Akpan and Hameed, studied the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO_2-based photocatalysts. The experimental results showed that various parameters, such as the initial pH of the solution to be degraded, oxidizing agents, temperature at which the catalysts must be calcined, dopant content and catalyst loading influenced the photocatalytic degradation of any dye in wastewaters. It was also found out that sol–gel method is widely used in the production of TiO_2-based photocatalysts because of the advantage derived from its ability to synthesize nanosized crystallized powder of the photocatalysts of high purity at relatively low temperature (Akpan and Hameed, 2009).

In 2009, Elmorsi et al., investigated decolorization of the Mordant red 73 (MR73) azo dye in water in laboratory-scale experiments using UV/H_2O_2 and photo-Fenton treatments.

Photodegradation experiments were carried out in a stirred batch photoreactor equipped with a low-pressure mercury lamp as UV source. The effect of operating parameters such as pH, [H_2O_2], [dye] and the presence of inorganic salts ($NaNO_3$, NaCl and Na_2CO_3) were also investigated. The results indicated that dye degradation was dependent upon pH, [H_2O_2] and initial dye concentration. The presence of chloride ion led to large decreases in the photodegradation rate of MR73 while both nitrate and carbonate ions have a slight effect. The photo-Fenton treatment, in the presence of Fe powder as a source of Fe^{2+} ions, was highly efficient and resulted in 99% decolorization of the dye in 15 min. Mineralization of MR73 dye was investigated by determining chemical oxygen demand (COD). In a 3 h 65% of the dye was mineralized by the H_2O_2/UV process, while the photo-Fenton treatment was more efficient producing 85% mineralization over the same 3h period (Elmorsi et al., 2009).

In 2009, Khataee et al., studied the photocatalytic degradation of three commercial textile dyes (C.I. Acid Orange 10 (AO10), C.I. Acid Orange 12 (AO12) and C.I. Acid Orange 8 (AO8)) with different structure and different substitute groups has been investigated using supported TiO_2 photocatalyst under UV light irradiation. All the experiments were performed in a circulation photochemical reactor equipped with a 15 W UV lamp

emitted around 365 nm. The investigated photocatalyst was industrial Millennium PC-500 immobilized on glass plates by a heat attachment method. The results indicated that the photocatalytic decolorization kinetics of the dyes were in the order of AO10 >AO12 >AO8. The dye solutions could be completely decolorized and effectively mineralized, with an average overall TOC removal larger than 94% for a photocatalytic reaction time of 6 h. The kinetic of photocatalytic decolorization of the dyes was found to follow a first-order rate law (Khataee et al., 2009).

In 2009, Yang et al., studied the degradation of azo dye Acid Orange 7 (AO7) by three common peroxides, persulfate (PS), peroxymonosulfate (PMS) or hydrogen peroxide (H_2O_2) under various activation conditions, such as heat (25–80°C), UV light (254 nm), or anions (SO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-). The order of AO7 degradation efficiencies by heat activation was PS>PMS>H_2O_2. PS oxidation activated by heat was an effective degradation technology, while PMS and H_2O_2 are hardly activated. When assisted by UV, peroxides could all be activated and degrade AO7 quickly. The order is PS >H_2O_2 > PMS (Yang et al., 2009).

4. EXPERIMENTAL STUDY

The experimental study consists of 2 main parts including the decolorization and degradation of the Procion Red MX-5B by photo-fenton oxidation in presence of Fe-TiO_2/AC catalyst and in presence of Fe/AC catalyst comparatively.
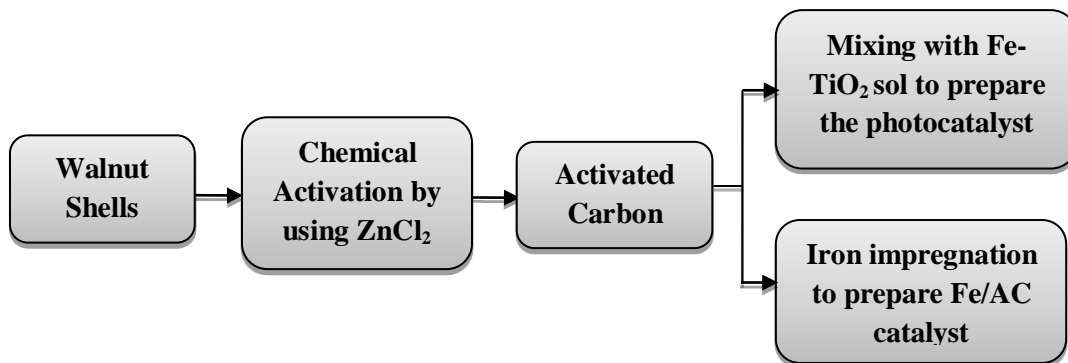
Figure 3: Preparation of Catalysts

4.1 Fe/AC and Fe-TiO$_2$/AC Catalysts

In the photo-fenton oxidation experiments, iron loaded activated carbon catalyst and iron-titanium dioxide coated activated carbon catalysts that had already been prepared in the previous studies were used. The activated carbon was prepared from walnut shells by chemical activation method by using zinc chloride as the chemical activation agent (Acharya et al., 2009, Aygün et al., 2003, Nowicki et al., 2010, Yang et al.,2010). The steps of the catalyst preparation are shown in Figure 3 above.

In order to prepare activated carbon from walnut shells, firstly the pre-treatment step comprising of crushing, milling, washing with distilled water and drying of the walnut shells was applied. Then the pretreated walnut shells were activated by treating with zinc chloride and carbonized at 800 ℃ under nitrogen gas flow. The steps of activated carbon catalyst support preparation are shown in Figure 4

Fe/AC Catalyst

After the activated carbon prepared, iron was impregnated on it by using Fe(NO$_3$)$_3$.9H$_2$O as metal precursor and in a ratio of Fe/Catalyst=1/10 by weight. Then, the catalysts were calcined at 200℃ in air atmosphere to remove the nitrates.

Fe-TiO$_2$/Activated Carbon Catalyst

The Fe-TiO$_2$/Activated carbon catalyst (photocatalyst) was prepared by sol-gel method. The preparation of the catalyst can be investigated in two steps. In the first step, Fe-TiO$_2$ sol was prepared and in the second step, this sol was mixed with activated carbon.

The Fe-TiO$_2$/AC catalyst was prepared in ratios of Fe/TiO$_2$=1% and Fe-TiO$_2$/AC=10% by wt. according to the procedure 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., 2012):
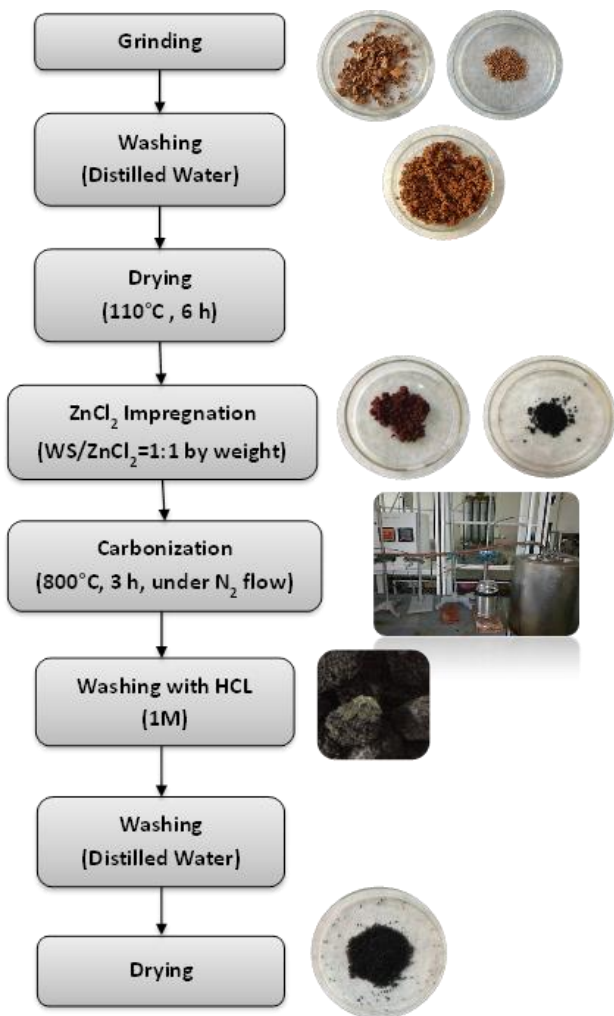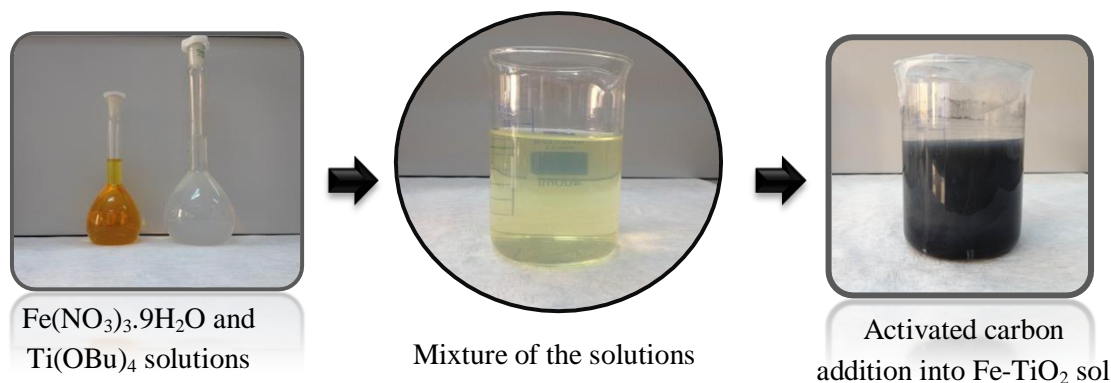
Figure 4. Steps of activated carbon catalyst support preparation

Fe-TiO₂ Sol Preparation

Ti(OBu)$_4$ was diluted in methanol solution

Fe(NO$_3$)$_3$.9H$_2$O was dissolved in methanol

Ti(OBu)$_4$ and Fe(NO$_3$)$_3$.9H$_2$O solutions were mixed.

pH of the mixture was adjusted to 7.

Fe-TiO₂ /Activated Carbon Preparation

The desired amount of activated carbon was added to the Fe-TiO$_2$ sol.

After Fe-TiO$_2$ sol coated on activated carbon the sol was changed into gel.

The support was vacuum dried and the obtained particles were heat treated at 250°C for 2 h in air.

Then the particles were treated at 500°C for 2 h under nitrogen flow.

4.2. Experimental Set-Up

The experimental set up mainly consists of a photo reactor, a magnetic stirrer and a cooler. The UV lamp was placed in a quartz tube in the photoreactor. The photoreactor was placed in a cabinet to avoid emissions of UV light. Water was circulated through the jacket to keep the constant reaction temperature. The samples were taken from the sample valve during the experiments.

Fe(NO$_3$)$_3$.9H$_2$O and Ti(OBu)$_4$ solutions

Mixture of the solutions

Activated carbon addition into Fe-TiO$_2$ sol

Figure 5. Preparation of Fe-TiO$_2$

The picture of the experimental set up is given in Figure 6.
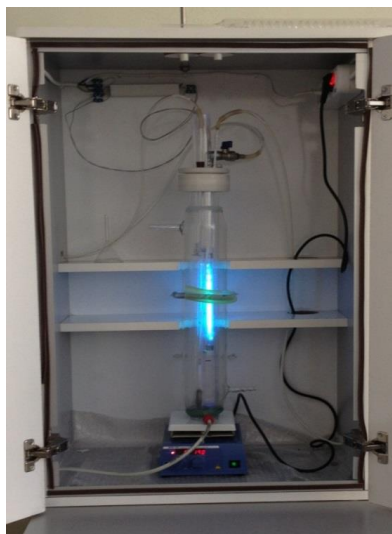

Figure 6. Experimental set up

4.3. Experiments

The photo-fenton oxidation experiments were carried out in presence of both the Fe/AC the Fe-TiO$_2$/AC catalysts. The effect of initial H$_2$O$_2$ concentration (2-8 mM), catalyst loading (0.05- 0.5 g/L), pH (3-7), initial dye concentration (100-150 mg/L) on the decolorization and the degradation efficiencies were investigated to determine the optimum reaction conditions. The parametric studies in presence of both of the catalysts were summarized in Figure 7.

4.4. Analysis

The analyses of both photo-fenton oxidation and the photocatalytic degradation experiments were performed with a UV-VIS spectrophotometer (Jasco UV-VIS Spectrophotometer Model 7800). The decolorization efficiencies were calculated from the absorbance values 538 nm which corresponds to the chromophore containing azo linkage.

The degradation was calculated from the absorbance values at 330 nm which indicated the degradation of the aromatic part of the azo dye.
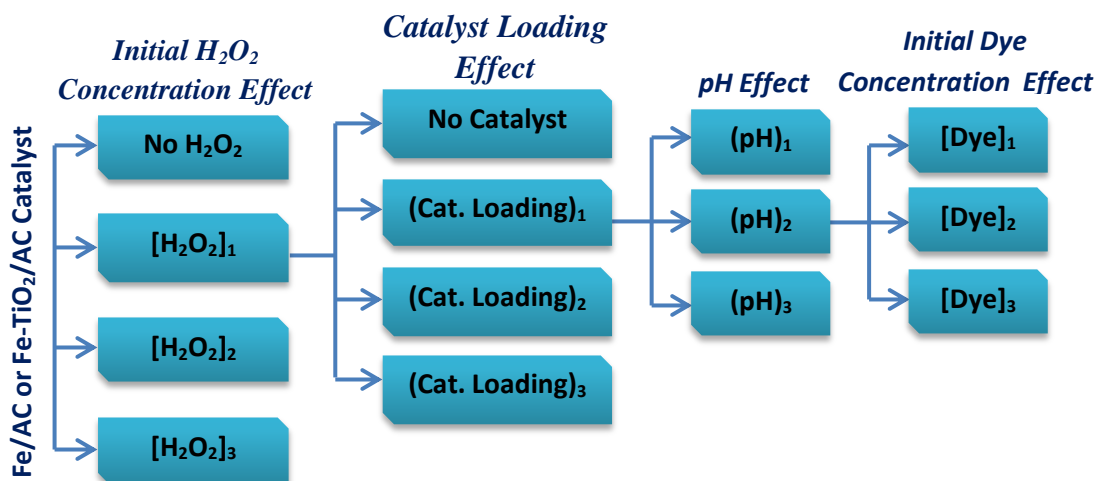

**Figure 7.** The parametric studies on photo-fenton oxidation of Procion Red MX-5B

5. RESULTS AND DISCUSSION

5.1. Photo-fenton Oxidation of Procion Red MX-5B in presence of Fe/AC Catalyst

In order to determine the optimum reaction conditions for photo-fenton oxidation of the azo dye, Procion Red MX-5B, the effect of initial H_2O_2 concentration, catalyst loading, pH, and initial dye concentration on the decolorization and the degradation efficiencies were investigated in presence of Fe/AC catalyst. The UV light intensity was 6 Watt in all the experiments.
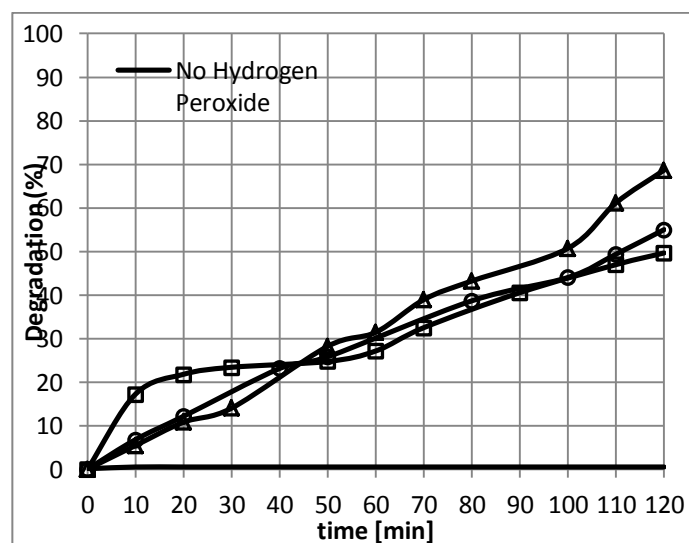
5.1.1. Effect of Initial Hydrogen Peroxide Concentration

The initial hydrogen peroxide concentration was varied as 2, 4 and 8 mM while the catalyst loading, pH, and the initial dye concentration were kept constant at 0.25 g/L, 3, 100 mg/L, respectively. In addition, an experiment without addition of H_2O_2 was performed. The initial hydrogen peroxide concentration effect on decolorization and degradation efficiencies are shown in Figure 8 and Figure 9, respectively.
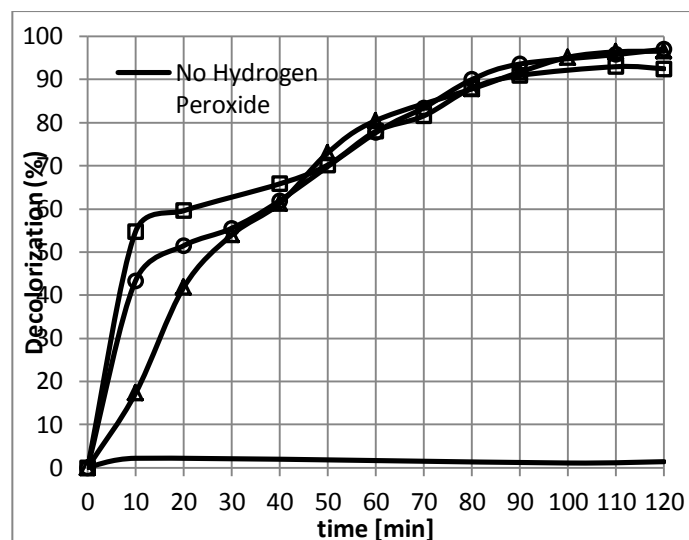
Figure 8. The initial hydrogen peroxide concentration effect on decolorization efficiency of the photo-fenton oxidation.

Reaction conditions: 0.25 g/L catalyst loading, [Dye]$_o$=100 mg/L, pH=3, 6 Watt UV lamp.

Figure 9. The initial hydrogen peroxide concentration effect on degradation efficiency of the photo-fenton oxidation.

Reaction conditions: 0.25 g/L catalyst loading, [Dye]$_o$=100 mg/L, pH=3, 6 Watt UV lamp.

As seen in both Figure 7 and 8, in the absence of H_2O_2, direct photolysis of the dye was resulted in no azo bond degradation nor decolorization. These results are in agreement with the literature (Elmorsi et al., 2010).

It is well known that, the hydrogen peroxide concentration affects the number of hydroxyl radicals generated, hence, affects the performance achieved in photo-fenton oxidation (Xu et al., 2013).

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

Although the maximum degradation efficiency was obtained when the initial hydrogen peroxide concentration was 8 mM (68.7 %), the decolorization efficiencies did not vary significantly with the increasing hydrogen peroxide concentration. As 2 mM of initial hydrogen peroxide concentration allows to almost complete decolorization (97 %) and 55 % degradation, 2 mM initial hydrogen peroxide concentration was determined as the optimum concentration.

So, in the further experiments to investigate the effect of catalyst loading, initial dye concentration and pH, the initial hydrogen peroxide concentration was kept constant at 2 mM.

5.1.2. Effect of Catalyst Loading

The catalyst loading was varied as 0.05, 0.1 and 0.25 g/L, while the initial hydrogen peroxide concentration, pH, the

initial dye concentration, were kept constant at 2 mM, 3, 100 mg/L, 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 10 and Figure 11, respectively.
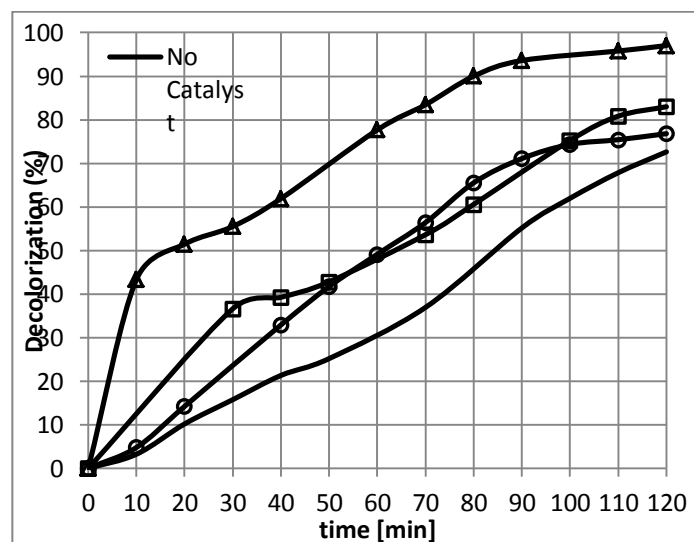
Figure 10. The catalyst loading effect on decolorization efficiency of the photo-fenton oxidation.
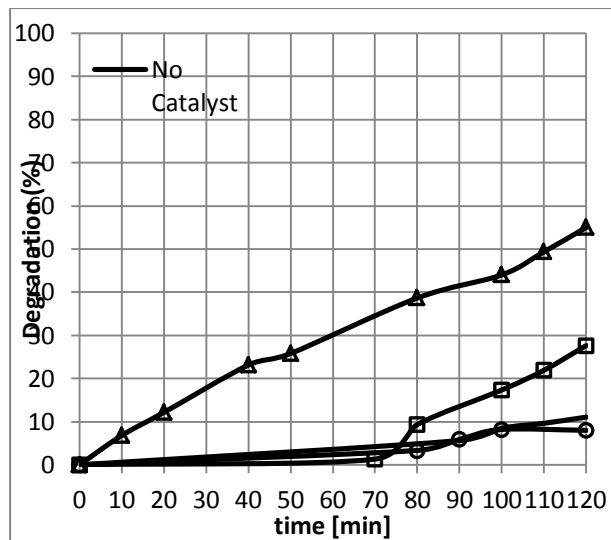*Reaction conditions: $[H_2O_2]_o=2$ mM, $[Dye]_o=100$ mg/L, pH=3, 6 Watt UV lamp.*

According to the results, 72.6% decolorization and 11.1% degradation efficiencies were obtained by the synergetic effect of hydrogen peroxide and UV light when there was no catalyst in the reaction medium.

The presence of the catalyst improved the efficiencies up to almost complete decolorization. Increasing the catalyst loading from 0.05 to 0.25 g/L increased the decolorization efficiency from 76.8% to 97%. The degradation and the

decolorization rates also increased as the catalyst loading increased.

The catalyst effect is more considerable in degradation efficiencies in comparison to decolorization efficiency. Increasing the catalyst loading from 0.05 to 0.25 g/L increased the degradation efficiencies from 8% to 55%.

Figure 11. The catalyst loading effect on degradation efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, $[Dye]_o=100$ mg/L, pH=3, 6 Watt UV lamp.

The reason of the improvement in the efficiencies can be explained that, as the catalyst loading increases, the number of photons and the dye molecules that can be adsorbed increases. Also, the density of the particles in the illumination area increases, therefore the decolorization and the degradation efficiencies are enhanced (Gümüş and Akbal, 2011).

Despite the advantages of using catalyst at high dosages, excess use of the catalyst may result in decrease in the efficiencies due to the, turbidity which hinders the penetration of UV light and the scavenger effect of the excessive Fe^{2+} ions (Devi et al., 2011).

As the maximum degradation and decolorization efficiencies were obtained when the catalyst loading was 0.25 g/L, this concentration was determined as the optimum condition.

So, in the further experiments to investigate the effects of initial dye concentration and pH the catalyst loading was kept constant at 0.25 g/L.

5.1.3. Effect of pH
The initial pH varied as 3, 5 and 7, while the initial hydrogen peroxide concentration, catalyst loading, and the initial dye concentration, were kept constant at 2 mM, 0.25 g/L, 100 mg/L, respectively.
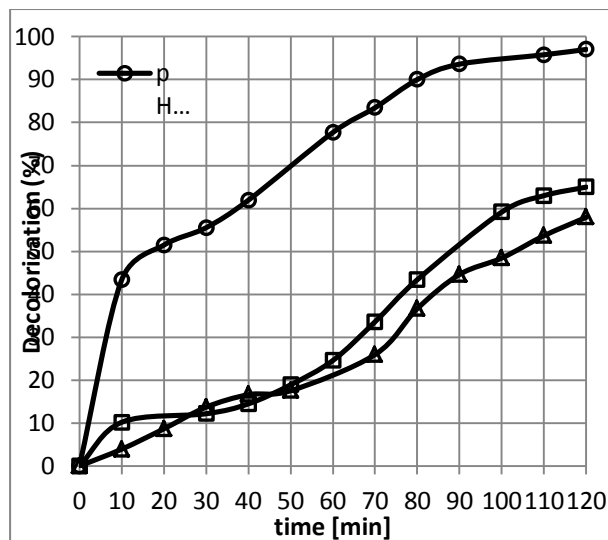
The pH effect on decolorization and degradation efficiencies are shown in Figure 12 and Figure 13, respectively.

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 decolorization efficiencies increased from 57.9% to 97%.

The reason of the increase in the efficiencies can be explained that, the hydroxyl radicals are generated efficiently under acidic conditions and at higher pH values, immobilized iron species can be transformed into less photoactive materials, such as $Fe(OH)_3$ (Elmorsi et al., 2010, Xu et al., 2013). Also, pH is an
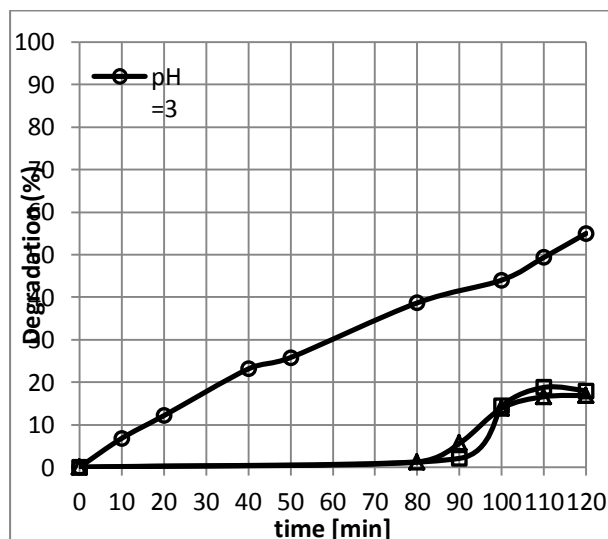
important parameter that affecting the adsorption of the dye molecules onto the photocatalyst due to the determination of the surface charge of the catalyst (Rauf et al., 2011).

Figure 12. The initial pH effect on decolorization efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0. 25 g/L of catalyst loading, $[Dye]_o=100$ mg/L, 6 Watt UV lamp.
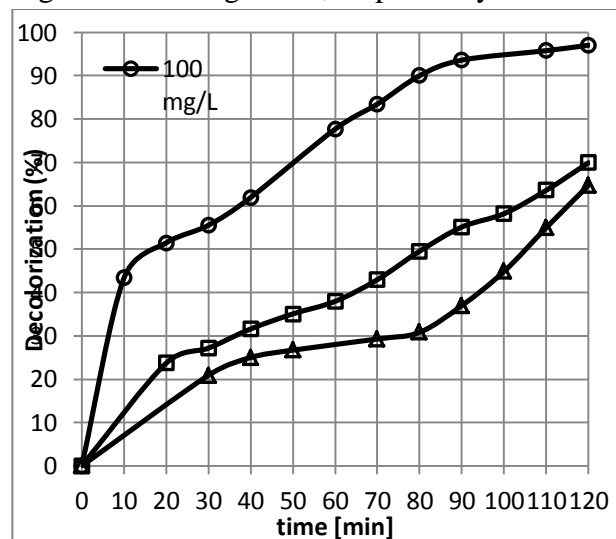

Figure 13. The initial pH effect on degradation efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0. 25 g/L of catalyst loading, $[Dye]_o=100$ mg/L, 6 Watt UV lamp.

As the maximum degradation and decolorization efficiencies were obtained when the initial pH was 3, this pH value was determined as the optimum condition. So, in the further experiments to investigate the effect of initial dye concentration, the initial pH was kept constant at 3.

5.1.4. Effect of the Initial Dye Concentration

The initial dye concentration was varied as 100, 125 and 150 mg/L, while the initial hydrogen peroxide concentration, catalyst loading and pH were kept constant at 2 mM, 0.25 g/L, 3, respectively. The initial dye concentration effect on decolorization and degradation efficiencies are shown in Figure 14 and Figure 15, respectively.
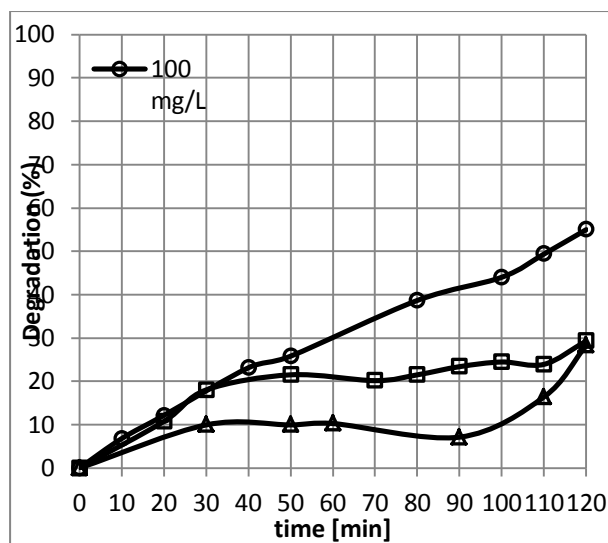

Figure 14. The initial dye concentration effect on decolorization efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0.25 g/L of catalyst loading, pH=3, 6 Watt UV lamp.

At initial stages of the decolorization and degradation, the removal rates decreased by increasing initial concentrations. The increase in dye concentration increases the number of dye molecules and competition with the hydroxyl radical concentration, so the removal rate decreases (Tekbaş et al., 2008).

Also, increasing the initial dye concentration decreased both the decolorization and the degradation efficiencies significantly. The decolorization efficiencies decreased from 97% to 69.9% when the initial dye concentration increased from 100 mg/L to 125 mg/L. However, a further increase in the dye concentration up to 150 mg/L resulted in only a slight decrease in decolorization efficiencies.

Figure 15. The initial dye concentration effect on degradation efficiency of the photo-fenton oxidation.

*Reaction conditions: [H$_2$O$_2$]$_o$=2 mM, 0. 25 g/L of catalyst loading, pH=3, 6 Watt UV lamp.*

The decrease in the efficiencies can be explained that, the hydroxyl radicals do not increase proportionally to the increase in dye concentration. Also, high dye concentration prevents the UV light penetration into the depth of the solution and the active centers on the catalyst surface is occupied by the dye molecules reducing the catalyst surface, result in decrease of the generation of hydroxyl radicals (Devi et al., 2011).

5.2. Photo-fenton Oxidation of Procion Red MX-5B in presence of Fe-TiO$_2$/AC Catalyst

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-TiO$_2$/AC catalyst were examined by varying the initial H$_2$O$_2$ concentration, catalyst loading, pH and the initial dye concentration in order to determine the optimum reaction conditions. In all the experiments, the UV light intensity was kept constant at 6 Watt.
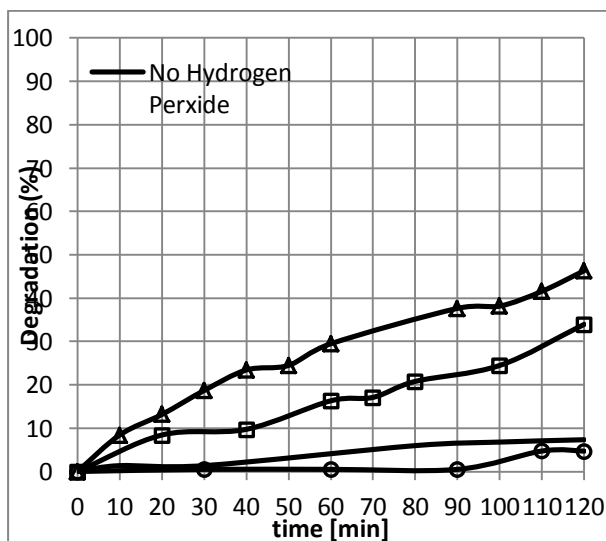
5.2.1. Effect of Initial Hydrogen Peroxide Concentration

2, 4 and 8 mM of initial hydrogen peroxide concentrations were examined while the catalyst loading, pH, and the initial dye concentration were kept constant at 0.25 g/L, 3, 100 mg/L respectively. In addition, an experiment without the presence of hydrogen peroxide was also carried out. The effect of initial H$_2$O$_2$ concentration on decolorization and degradation efficiencies are shown in Figure 16 and Figure 17, respectively.
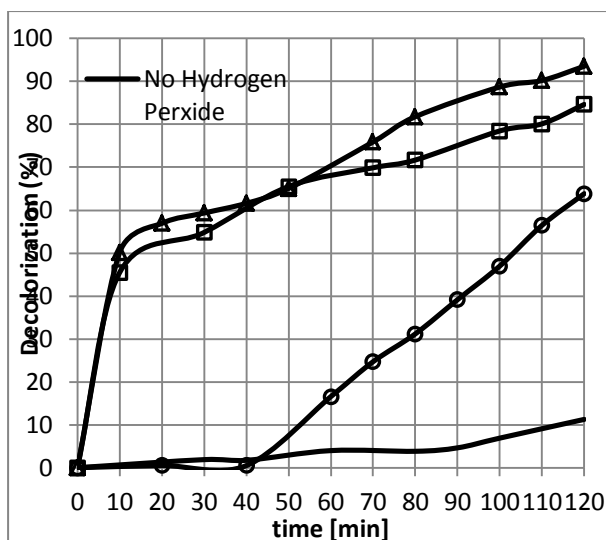
Figure 16. The initial hydrogen peroxide concentration effect on decolorization efficiency of the photocatalytic oxidation.

Reaction conditions: 0.25 g/L catalyst loading, [Dye]$_o$=100 mg/L, pH=3, 6 Watt UV lamp.

Figure 17. The initial hydrogen peroxide concentration effect on degradation efficiency of the photocatalytic oxidation.

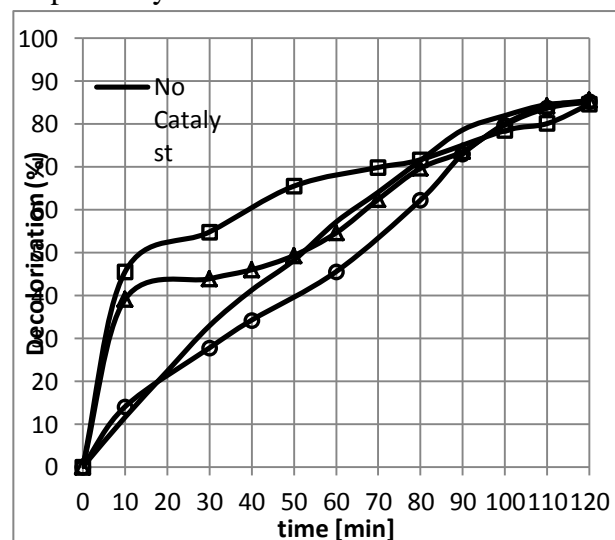*Reaction conditions: 0.25 g/L catalyst loading, [Dye]$_o$=100 mg/L, pH=3, 6 Watt UV lamp.*

According to the experimental results, addition of hydrogen peroxide up to 4 mM increased the decolorization and the degradation efficiencies to 84.6% and 33.9% respectively. A further increase in the initial hydrogen preroxide concentration did not resulted in a remarkable increase in decolorization and degradation rated and the efficiencies. So, the optimum initial hydrogen peroxide concentration was determined as 4 mM.

5.2.2. Effect of Catalyst Loading

The catalyst loading was varied as 0.1 and 0.25 and 0.5 g/L, while the initial hydrogen peroxide concentration, pH, the initial dye concentration, were kept constant at 2 mM, 3, and 100 mg/L, respectively. In addition, an experiment without addition of catalyst was performed.
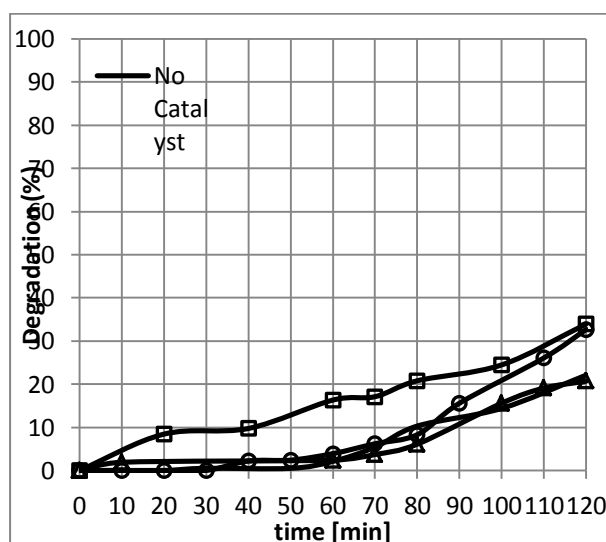
The catalyst loading effect on decolorization and degradation efficiencies are shown in Figure 18 and Figure 19, respectively.

Figure 18. The catalyst loading effect on decolorization efficiency of the photo-fenton oxidation.

According to the results, the catalyst loading has not a significant impact on the decolorization efficiencies. However, the catalyst amount was effective when the initial rates were considered. As the catalyst loading increased up to 0.25 g/L, the decolorization rates increased. In the first 10 minute of the reaction, the maximum decolorization was obtained as 43.9% when the catalyst loading was 0.25 g/L. A further increase in catalyst loading resulted in decrease in decolorization rates. When the degradation process was considered the degradation rates and efficiencies were increases with increasing catalyst loading up to 0.25 g/L. Above this catalyst loading, the rates and the efficiencies decreased. The reason of the decrease can be explained as the turbidity which preventing the penetration of UV light and the scavenger effect of the excessive iron ions (Devi et al., 2011).

As the maximum degradation efficiency and the maximum degradation and decolorization rates were obtained when the catalyst loading was 0.25 g/L, this concentration was determined as the optimum condition. So, in the further experiments to investigate the effects of initial dye concentration and pH the catalyst loading was kept constant at 0.25 g/L.

5.2.3. Effect of pH

The effect of pH on photocatalytic degradation was investigated in the pH range 3-5 while the initial hydrogen peroxide concentration, catalyst loading, and the initial dye concentration, were kept constant at 4 mM, 0.25 g/L, 100 mg/L, respectively.

The pH effect on decolorization and degradation efficiencies are shown in Figure 20 and Figure 21, respectively.

Figure 19. The catalyst loading effect on degradation efficiency of the photo-fenton oxidation.
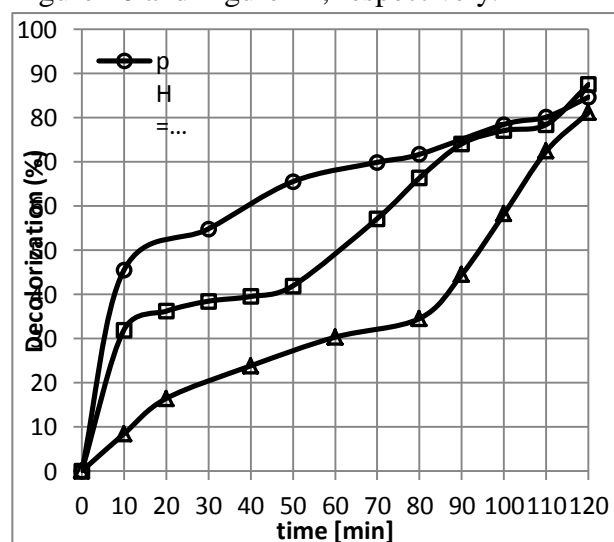
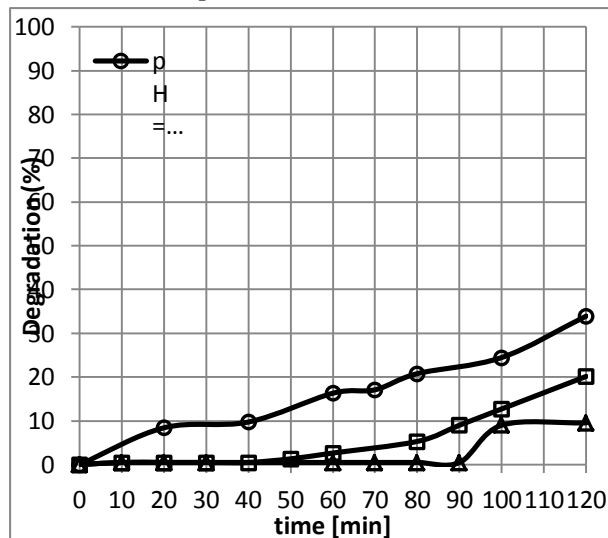**Figure 20.** The initial pH effect on decolorization efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0. 25 g/L of catalyst loading, $[Dye]_o=100$ mg/L, 6 Watt UV lamp.

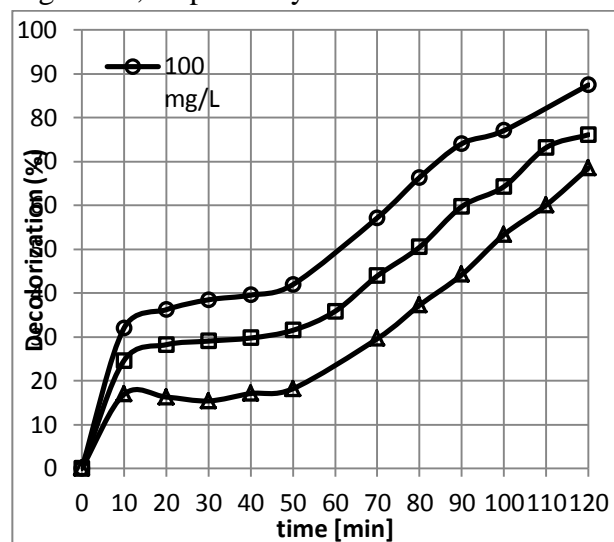**Figure 21.** The initial pH effect on degradation efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0. 25 g/L of catalyst loading, $[Dye]_o=100$ mg/L, 6 Watt UV lamp.

The experimental results show that as pH decreased from 5 to 3, the decolorization rates were increased remarkably. However, variation of pH has not a significant impact on the decolorization efficiencies. The maximum decolorization efficiency was evaluated as 87.5% at pH 4.

The degradation efficiencies and the rates increased with the decreasing pH. Although the maximum degradation efficiency was evaluated as 33.9% at pH 3, when both of the degradation and the decolorization efficiencies were considered, the optimum pH was determined as 4 not to work with so acidic reaction medium.

5.2.4. Effect of the Initial Dye Concentration

100, 125 and 150 mg/L of the initial dye concentrations were examined in order to determine how the initial dye concentration affected the removal efficiencies while the initial hydrogen peroxide concentration, catalyst loading and pH were kept constant at 4 mM, 0.25 g/L, and 4, respectively. The initial dye concentration effect on the removal efficiencies are shown in Figure 22 and Figure 23, respectively.

Figure 22. The initial dye concentration effect on decolorization efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0.25 g/L of catalyst loading, pH=3, 6 Watt UV lamp.

According to the experimental results, increasing the initial dye concentration decreased both the decolorization rates and the efficiencies as expected. The decolorization efficiencies decreased from 87.5% to 68.5% when the initial dye concentration increased from 100 mg/L to 150 mg/L. However, the initial dye

concentration has not a remarkable effect on the degradation efficiencies and the rates.

The reason of the decrease in decolorization efficiencies can be a result of the high concentration of dye molecules that restricted the penetration of the UV light into the solution. Also, hydroxyl radicals that were produced during the oxidation process were not sufficient to degrade high concentrations of the dye solution.
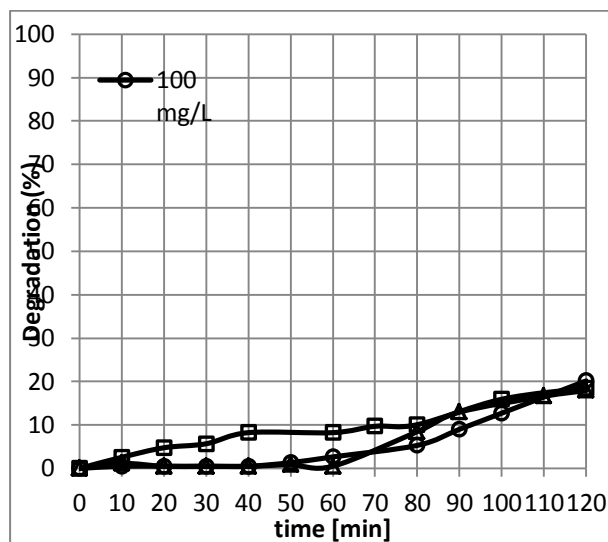

Figure 23. The initial dye concentration effect on degradation efficiency of the photo-fenton oxidation.

Reaction conditions: $[H_2O_2]_o=2$ mM, 0. 25 g/L of catalyst loading, pH=3, 6 Watt UV lamp.

6.0 CONCLUSIONS

The organic waste based Fe/Activated Carbon and Fe-TiO$_2$/Activated Carbon catalysts were found to be successful in degradation and the decolorization of the Procion Red MX-5B by using photo-fenton process. The activated carbon

which was used as catalyst support was prepared from walnut shells by chemical activation method to contribute the recovery of the organic wastes.

In the parametric studies, the effects of the initial hydrogen peroxide concentration, catalyst loading, pH and the initial dye concentration were investigated in presence of both of the catalysts in order to determine the optimum reaction conditions. A 6 Watt of UV lamp was used as the radiation source in the photocatalytic processes.

According to the parametric studies, the degradation and the decolorization efficiencies were generally increased with the increasing the initial hydrogen peroxide concentration. The increasing catalyst loading also improved both of the removal efficiencies and rates in presence of Fe/AC catalyst, however, the increasing Fe-TiO$_2$/AC catalyst amount resulted in only increase in decolorization rates and a slight increase in degradation efficiencies. pH has a remarkable impact on the removal efficiencies in presence of Fe/AC catalyst, as pH the decreased, the efficiencies were increased, but variation of pH from 3 to 5 in presence of Fe-TiO$_2$/AC catalyst had not a significant effect on the decolorization efficiencies, but, increased the degradation efficiencies. The increasing initial dye concentration decreased both of the removal efficiencies and the rates in presence of both of the catalysts.

The optimum conditions were determined as 2 mM of initial hydrogen peroxide concentration, 0.25 g/L of catalyst loading and pH 3 when the initial dye

concentration was 100 mg/L in presence of Fe/AC catalyst and the decolorization and the degradation efficiencies were evaluated as 97% and 55%, respectively. 4 mM of initial hydrogen peroxide concentration, 0.25 g/L of catalyst loading and pH 4 were determined as the optimum conditions in presence of Fe-TiO$_2$/AC catalyst and the decolorization and the degradation efficiencies were evaluated as 87.5% and 20.2% at these optimum conditions.

When catalytic performances of the Fe/AC and Fe-TiO$_2$/AC catalyst were compared, Fe/AC catalyst was determined as more efficient because the highest decolorization and the degradation efficiencies were obtained in presence of this catalyst at the optimum conditions. Figure 24 shows the decolorization of Procion Red MX-5B by photo-fenton oxidation in presence of Fe/AC catalyst.

The optimum degradation and the decolorization efficiencies at the optimum reaction conditions in presence of Fe/AC and Fe-TiO$_2$/AC catalysts are shown in Table 1:

Type of the Catalyst	Optimum Conditions	Optimum Degradation Efficiency (%)	Optimum Decolorization Efficiency (%)
Fe/AC	[Dye]$_o$=100 mg/L [H$_2$O$_2$]$_o$=2 mM 0.25 g/L catalyst loading pH=3	97	55
Fe-TiO$_2$/AC	[Dye]$_o$=100 mg/L [H$_2$O$_2$]$_o$=4 mM 0.25 g/L catalyst loading, pH=4	87.5	20.2

Table 1. The optimum conditions and efficiencies in presence of Fe/AC and Fe-TiO$_2$/AC catalysts for the photo-fenton oxidation processes
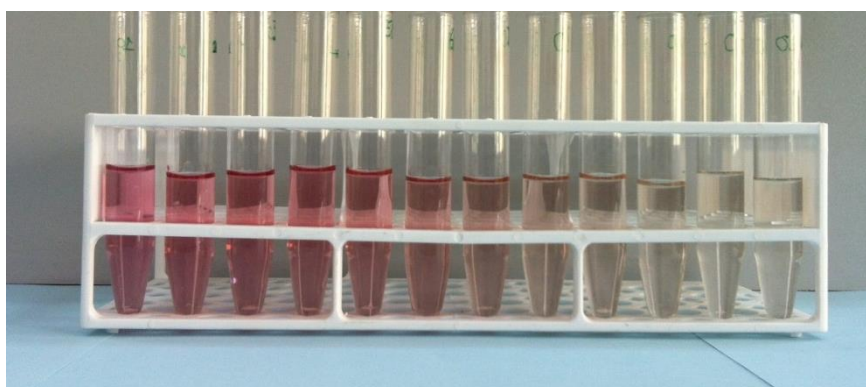
Figure 24. Decolorization of the azo dye, Procion Red MX-5B by photo-fenton oxidation

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