

**TREATMENT OF AN AZO DYE AND AZO DYE PRODUCTION
WASTEWATERS WITH FENTON-LIKE AND PHOTO-FENTON-LIKE
ADVANCED OXIDATION PROCESSES**

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Programme: Environmental Science and Engineering

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JUNE 2008

**AZO BOYAR MADDENİN VE AZO BOYAR MADDE ÜRETİMİ
ATIKSULARININ FENTON-BENZERİ VE FOTO-FENTON-BENZERİ
İLERİ OKSİDASYON PROSESLERİ İLE ARITIMI**

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ABBREVIATIONS

AR	: Acid Red
AB	: Acid Blue
RB	: Reactive Black
RO	: Reverse Osmosis
RSM	: Response Surface Methodology
CCD	: Central Composite Design
ANOVA	: Analysis of Variance
EPA	: Environmental Protection Agency
GDP	: Gross Domestic Product
AOPs	: Advanced Oxidation Processes
C.I.	: Citation Index
AU	: Activity Unit
ww	: Wastewater
UV	: Ultraviolet
VIS	: Visible
US	: Ultrasound
WAO	: Wet Air Oxidation
SCWO	: Supercritical Water Oxidation

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LIST OF SYMBOLS

COD	: Chemical Oxygen Demand (mg/L)
TOC	: Total Organic Carbon (mg/L)
TC	: Total Carbon (mg/L)
BOD	: Biochemical Oxygen Demand (mg/L)
k	: Reaction Rate Constant
K	: Equilibrium Constant
TSS	: Total Suspended Solids (mg/L)
$\lambda_{\max}$	: The wavelength at which maximum absorbance occurs
A_{497}	: Absorbance at 497 nm (1/cm)
A_{576}	: Absorbance at 576 nm (1/cm)
R^2	: Correlation Coefficient
DF	: Degrees of Freedom
Prob>F	: Probability Value
F-value	: Fisher variation ratio
•OH	: Hydroxyl radical
HO₂•	: Hydroperoxyl radical
COD₀	: Initial Chemical Oxygen Demand (mg/L)
H₂O_{2,0}	: Initial Hydrogen Peroxide Concentration (mM)
pH₀	: Initial pH
Fe³⁺₀	: Initial Ferric Ion Concentration (mM)
[Fe³⁺]	: Ferric Ion Concentration (mM)
[H₂O₂]	: Hydrogen Peroxide Concentration (mM)
t_r	: Reaction Time (min)

TREATMENT OF AN AZO DYE AND AZO DYE PRODUCTION WASTEWATERS WITH FENTON-LIKE AND PHOTO-FENTON-LIKE ADVANCED OXIDATION PROCESSES

SUMMARY

Textile acid dyes and wastewater from the acid dyeing process are both well-known for their intense color and recalcitrant nature. Recent studies indicate that several advanced oxidation processes (AOPs) could be a good alternative for treating colored aromatics. Among them Fe-based AOPs recently received great attention because of their high efficiency in the oxidation of dyestuff, ease of operation and relatively low cost. With these facts in the mind, first part of the present study aimed at investigating color and organic carbon (TOC) removal from 100 mg/L aqueous Acid Red 183 solution using Fenton-like, photo-Fenton-like and ferrioxalate-photo-Fenton-like processes. According to the experimental findings, the Fenton-like process (optimum working conditions: $\text{pH}_0=2.8$; $\text{Fe}^{3+}_{,0}=3 \text{ mM}$; $\text{H}_2\text{O}_{2,0}=30 \text{ mM}$) resulted in practically complete color (98%) and partial TOC removal (56%); while UV-A assisted Fenton-like treatment proceeded significantly faster. For instance at $\text{pH}_0=2.8$, $\text{Fe}^{3+}_{,0}=0.3 \text{ mM}$ and $\text{H}_2\text{O}_{2,0}=30 \text{ mM}$, 48% color and 14% TOC removals were achieved after 20 min photo-Fenton-like oxidation instead of 23% color and 6% TOC removal obtained with Fenton-like treatment. On the other hand ferrioxalate-photo-Fenton-like treatment found to be an unattractive alternative from both color and organic carbon removal points of view.

Dye production effluents generally are difficult to be treated due to versatile constitutions such as raw materials, intermediates, auxiliary chemicals and some residual dyes resulting strong color, high chemical oxygen demand (COD) and low biodegradability. In the second part of the study, treatability of synthetic azo dye production wastewaters (Acid Blue 193 and Reactive Black 39) simulating the effluent generated from dye synthesis reactor washing, and a real dye production effluent from reverse osmosis membrane separation of an azo dye (Reactive Black 39), via photo-Fenton-like process was investigated. Response Surface Methodology (RSM) was employed for evaluation of individual and interaction effects of several process parameters (initial Fe^{3+} , H_2O_2 and COD concentrations and reaction time) on treatment performance in terms of color, COD and TOC removals. RSM was also utilized for process optimization. Optimized variables for synthetic Acid Blue 193 production wastewater found to be $\text{Fe}^{3+}=1.5 \text{ mM}$, $\text{H}_2\text{O}_2=35 \text{ mM}$ and reaction time = 45 min, for COD $\leq 200 \text{ mg/L}$. Under these conditions 98% color, 78% COD and

59% TOC removals were experimentally obtained and fitted well to the model predictions. The same model satisfactorily described the photo-Fenton-like treatment of synthetic Reactive Black 39 production wastewater. On the other hand, in case of reverse osmosis effluent of Reactive Black 39 production, experimentally achieved color, COD and TOC removal rates were considerably lower than the model predictions. The dramatic decrease in the treatment efficiency was attributable to the high chloride (i.e. a well known $\bullet\text{OH}$ scavenger) content of reverse osmosis effluent as compared with synthetic wastewaters.

AZO BOYAR MADDENİN VE AZO BOYAR MADDE ÜRETİMİ ATIKSULARININ FENTON-BENZERİ VE FOTO-FENTON BENZERİ İLERİ OKSİDASYON PROSESLERİ İLE ARITIMI

ÖZET

Asit boyar maddeler ve asit boyama prosesinden kaynaklanan atıksular yoğun renge sahip ve biyolojik arıtmaya dirençli yapıdadır. Son yıllarda çeşitli ileri oksidasyon proseslerinin aromatik yapıdaki boya moleküllerinin arıtımında başarılı olduğu kanıtlanmıştır. İleri oksidasyon proseslerinden Fenton ve foto-Fenton tipi prosesler boya moleküllerinin oksidasyonundaki başarıları, işletimlerinin kolaylığı ve göreceli olarak düşük maliyetleri ile dikkat çekmektedir. Bu çalışmanın ilk kısmında 100 mg/L konsantrasyonundaki sulu Asit Kırmızı 183 çözeltisinden Fenton-benzeri, foto-Fenton-benzeri ve demiroksalat-foto-Fenton-benzeri prosesleri ile renk ve toplam organik karbon (TOK) giderimi incelenmiştir. Deneysel sonuçlara göre, optimum koşullarda ($\text{pH}_0=2.8$; $\text{Fe}^{3+}_{0,0}=3 \text{ mM}$; $\text{H}_2\text{O}_{2,0}=30 \text{ mM}$) Fenton-benzeri oksidasyon ile neredeyse tam bir renk (%98) ve kısmi bir TOK (%56) giderimi sağlanmış olup, UV-A kullanımıyla (foto-Fenton-benzeri proses) giderim verimi ve hızı artmıştır. Örnek olarak $\text{pH}_0=2.8$, $\text{Fe}^{3+}_{0,0}=0.3 \text{ mM}$ and $\text{H}_2\text{O}_{2,0}=30 \text{ mM}$ koşullarında foto-Fenton-benzeri prosesle 20 dakika sonunda %48 renk ve %14 TOK giderimi sağlanmışken, Fenton-benzeri oksidasyonda aynı süre sonunda elde edilen giderimler %23 renk ve % 6 TOK şeklindedir. Demiroksalat-foto-Fenton-benzeri proses ise renk ve organik karbon giderimleri bakımından iyi bir alternatif olarak görünmemektedir.

Boya üretimi atıksuları içerdikleri ham maddeler, ara ürünler, yardımcı kimyasallar ve kalıntı boyalar dolayısıyla yoğun renge ve yüksek kimyasal oksijen ihtiyacına sahip biyolojik olarak zor ayrışabilir nitelikte atıksulardır. Bu çalışmanın ikinci kısmında, boya sentez reaktörlerinin yıkanması sırasında meydana gelen atıksuyu temsil eden sentetik boya üretimi atıksularının ve reaktif boya madde sentezi ters osmoz çıkış suyunun foto-Fenton-benzeri proses ile arıtılabilirliği incelenmiştir. Seçilen proses parametrelerinin (başlangıç Fe^{3+} , H_2O_2 ve KOİ konsantrasyonları ile reaksiyon süresi) renk, KOİ ve TOK giderimleri üzerindeki etkilerinin belirlenmesi ve proses optimizasyonu amacıyla yüzey cevap metodu kullanılmıştır. 200 mg/L KOİ'ye sahip sentetik Asit Mavi 193 üretimi atıksuyu için optimum işletme parametreleri; 1.5 mM Fe^{3+} , 35 mM H_2O_2 ve 45 dakika reaksiyon süresi olarak bulunmuştur. Bu koşullar altında deneysel olarak elde edilen renk, KOİ ve TOK giderimleri sırasıyla %98, %78 ve %59'dur. Elde edilen deneysel sonuçlar model tahminleri ile uyumludur. Aynı model sentetik Reaktif Siyah 39 üretimi atıksuyunun

foto-Fenton benzeri oksidasyonla arıtımına da başarılı bir şekilde uygulanmıştır. Ancak Reaktif Siyah 39 sentezi ters osmoz atıksuyunun arıtımında elde edilen giderim verimleri model tahminlerinin oldukça altında kalmıştır. Arıtma performansındaki bu düşüşün sebebi gerçek atıksuyun yüksek klorür içeriğidir. Klorür iyonlarının $\bullet\text{OH}$ radikali ile reaksiyonu sonucu ortamdaki radikal miktarı azalmakta, bu da organik madde oksidasyon verimini düşürmektedir.

1. INTRODUCTION

Textile industry has become one of the major sources of severe pollution problems in the world because of the increased demand for textile products. It is one of the highest water consumers among different industrial sectors and produces 50-100 L wastewater/kg of finished product (Manu and Chaudhari, 2002). The processes involved in textile industries are generally classified as spinning, sizing, scouring, kiering, desizing, bleaching, dyeing and finishing (Dos Santos et al., 2007). Textile wastewater is chemically very complex in nature as it contains a mixture of colorants (dyes and pigments) and various organic as well as inorganic compounds along with high concentrations of heavy metals, total dissolved solids, and medium-to-high chemical oxygen demand as well as low-to-medium biochemical oxygen demand (Sharma et al., 2007).

Among the processes mentioned above, textile dyeing, a combined process of bleaching and coloring, is the most water consuming and chemically intensive process. Dyeing generates high quantities of wastewaters ($\approx 2000 \text{ m}^3/\text{d}$) and it constitutes a major pollution problem due to the variety and complexity of chemicals employed. (Arslan-Alaton et al., 2008) Effluent from textile dyeing contains high amounts of total dissolved solids, sodium chloride, sodium sulphate and potentially carcinogenic residuals of certain dye bath auxiliaries (mainly aryl sulphonate based formulations) and unfixed dyestuff at significant concentrations (Ranganathan et al., 2007). As a consequence of low fixation efficiencies of dyes onto textile fibers, colored wastewater is produced containing up to 250 mg/L of waste (exhausted) dyes. Colored wastewater is particularly associated with textile azo dyes. Due to their stability and recalcitrant nature, azo dyes are poorly degradable by conventional wastewater treatment processes that involve chemicals or activated sludge (İnce and Gönenç, 1997; Pagga and Brown, 1986). The dyes released into the environment can lead to acute effects on exposed organisms because of the potential toxicity of their anaerobic degradation products, abnormal coloration and reduction in photosynthesis since they absorb the light that enters the water (Kornaros and Lyberatos, 2006;

Chung and Cerniglia, 1992). The presence of unnatural colors is unaesthetic and tends to be associated with contamination in public perception (Nunez et al., 2007).

Methods for decolorization of textile effluents have received considerable attention in recent years. Different combinations of biological, chemical and physical methods are valid as conventional methods for dealing with textile effluents (Koby et al., 2003). Biological degradation of dye molecules is in most cases impossible (Meyer, 1981), resulting in the persistence of high levels of dye accumulation (Talarposhti et al., 2001). Furthermore, potential degradation products may equally be of toxic/recalcitrant nature. Chemical precipitation, adsorption and more recently several advanced oxidation processes (AOPs) have been employed for the treatment of textile wastewater. Among them, especially ozonation, heterogeneous photocatalytic treatment, Fenton and photo-Fenton oxidation, ultraviolet (UV) irradiation and electrochemical oxidation have been proven particularly effective for the treatment of biologically-difficult-to-treat industrial wastewater and colored (textile) effluent (Chatzisyneon et al., 2006).

The AOPs such as Fenton and photo-Fenton processes (İnce and Gönenç, 1997), $\text{H}_2\text{O}_2/\text{UV-C}$ processes (Arslan and Balçioğlu, 1999; Kuo, 1992) and TiO_2 -mediated heterogeneous photocatalysis (Kuo and Ho, 2001) have gained major attention for the treatment of dyes and dyehouse effluent in the last two decades. Especially Fenton and photo-Fenton type treatment methods are very promising since they have high efficiency in the oxidation of miscellaneous organics, including the colored aromatics and can be successfully applied to treat dye and textile wastewaters with high reaction yields and low treatment costs (Arslan-Alaton and Teksoy, 2007). Fenton's reaction involves hydrogen peroxide (H_2O_2) and a ferrous iron (Fe^{2+}) catalyst. Hydroxyl radicals ($\bullet\text{OH}$) are generated by the catalytic decomposition of H_2O_2 in acidic media and react quickly and non-selectively with most organic compounds. Decomposition of H_2O_2 can also be catalyzed by ferric ions, which is called Fenton-like oxidation ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$). Photo-Fenton oxidation is the photochemically enhanced version of Fenton and Fenton-like processes. In photo-Fenton systems, UV radiation is added to Fenton's reagent, which causes an increase in the efficiency of $\bullet\text{OH}$ formation (Nunez et al., 2007; Carneiro et al., 2007; Safarzadeh-Amiri et al., 1997). Another type of reaction enhancement is made by applying the ferrioxalate complex as the iron source in the photo-Fenton oxidation,

which is known as the ferrioxalate-photo-Fenton process. Ferrioxalate-photo-Fenton oxidation further benefits from solar radiation since ferrioxalate strongly absorbs light at longer wavelengths and generates ($\bullet\text{OH}$) at high quantum yields (Nunez et al., 2007; Safarzadeh-Amiri et al., 1997).

As compared with the Fenton process, the dark Fenton-like process has been investigated in relatively few studies, although its efficiency is thought to be practically identical to that of the Fenton process due to the fact that rate-limiting step of Fe-based advanced oxidation processes is the relatively slow catalytic reaction between ferric ion and hydrogen peroxide (Safarzadeh-Amiri et al., 1996). In other words, Fenton reagent ultimately behaves like the Fenton-like reagent. In photo-Fenton reaction, selecting Fe^{3+} as an iron source instead of Fe^{2+} , have an advantage of benefiting more from the irradiation at the beginning stage of the reaction. Fe-based AOPs are working at acidic pH's (typically 2-5) which is a range close to the application pH of acid dyes onto polyamide fibers (pH 3-5) (Arslan-Alaton and Teksoy, 2007). Thus, acid dyes and acid dyebath effluents are ideal candidates for Fenton-type oxidative treatment.

Considering these facts, in the first part of the present study, decolorization and mineralization of a commercial textile acid dye, namely Acid Red 183 (AR 183), by Fenton-like, photo-Fenton-like and ferrioxalate-photo-Fenton-like processes were investigated. These three Fe-based AOPs were compared according to their decolorization and organic matter degradation efficiencies of the model pollutant. The effect of selected process parameters (initial reaction pH and Fe^{3+} concentration) on Fenton-like oxidation efficiency was particularly investigated. Color (absorbance at the maximum, typical absorption band of the dye) and total organic carbon (TOC) concentrations were determined in order to state and compare the treatment performances.

In the second part of the study, photo-Fenton-like oxidation experiments were conducted with wastewaters from azo dye manufacturing. Although photochemical AOPs are known to be not feasible for the treatment of combined dye manufacturing (production) wastewater due to its high UV absorbance; some waste streams could be separated from the main effluent and treated efficiently by these methods. Among the several streams created in dye production process, wastewater from reactor washing and reverse osmosis effluent/outflows are thought to be quite suitable for

photochemical treatment such as photo-Fenton type oxidations, with their relatively low strength and slightly acidic pH. Separate treatment of these dye-containing streams with suitable AOPs leads to a decrease in the volume of the remaining effluent and reduces its pollutant load, hence contributing to the wastewater management in dye production. With these motivations, present work aimed at evaluating the treatability of synthetic dye production wastewaters, simulating the effluent generated from dye synthesis reactor washing, and a real effluent from reverse osmosis membrane separation of dye, via photo-Fenton-like process.

The photo-Fenton type processes are affected by numerous parameters such as iron catalyst concentration, hydrogen peroxide oxidant concentration, pH, initial pollutant concentration. The majority of the studies concerned with the effect of these process variables on the treatment efficiency and reaction kinetics were performed using a rather one-factor-at-a-time approach, where one parameter was varied thereby keeping the others constant. However, the process parameters may involve synergistic effects, as a result of complex interactions between these process variables. Hence, the application of conventional experimental process optimization approach is not adequate since it is very time consuming, and does not necessarily allow correct optimization of the process. To overcome these drawbacks, experimental process optimization should be based on statistical design tools. In the design and statistical evaluation of experiments, Response Surface Methodology (RSM) can be used for process optimization and prediction of the interaction between process variables, reducing the number of trials and thus the time and associated costs spent for conducting these experiments (Alim et al, 2008). RSM has already proven to be a reliable statistical tool in the investigation of chemical treatment processes (Myers and Montgomery, 2002).

With these facts in the mind, in the second part of the study RSM was applied to assess the individual and interaction effects of several operating parameters on treatment efficiency. Central Composite Design (CCD), which is a widely used form of RSM, was employed to evaluate the effect of initial Fe, H_2O_2 and COD concentrations and reaction time on color, COD and TOC removal efficiencies of synthetic Acid Blue 193 (AB 193) production wastewater. Selected process parameters were optimized to obtain maximum color, COD and TOC abatements and model predictions were experimentally validated.

In addition to acid dye production wastewater, photo-Fenton-like oxidation of synthetic Reactive Black 39 (RB 39) production wastewater and reverse osmosis (RO) effluent of RB 39 production was also performed under optimized conditions. In this context, applicability of the model predictions on photo-Fenton-like treatment of a 'reactive' type of dye production wastewater was investigated, as well as exploring the applicability of the process in practice, i.e. to real dye production effluent.

2. THEORETICAL BACKGROUND

2.1. Textile Industry

Textile industry is primarily concerned with the design or manufacture of clothing as well as distribution and use of textiles. Textile is a flexible material comprised of a network of natural or artificial fibers and come from four main sources: animal, plant, mineral and synthetic. The processes involved in textile industries are spinning, sizing, scouring, kiering, desizing, bleaching, dyeing and finishing (Dos Santos et al., 2007; EPA, 1997).

Spinning (yarn production) is the process of creating yarn from various raw fiber materials. Grouping and twisting operations are applied to the separate fibers to bind them into a long, stronger yarn (EPA, 1997).

Sizing is the first preparation step, in which several agents are added to provide strength to the fibers and minimize breakage (Dos Santos et al., 2007). Sizing agents, such as starch, polyvinyl alcohol and carboxymethyl cellulose, form a film around the yarn or individual fibres, and increase its weight, crispness, and luster (Encyclopedia Britannica-textile sizing, 2008).

Desizing employed to remove sizing materials from the warp yarns, prior to fabric formation. The major methods for fabric manufacture are weaving and knitting (Dos Santos et al., 2007).

Next step is the scouring which removes impurities from the fibers by using alkali solution (commonly sodium hydroxide) to breakdown natural oils, fats, waxes and surfactants, as well as to emulsify and suspend impurities in the scouring bath (Dos Santos et al., 2007; EPA, 1997).

Bleaching used to remove unwanted color from the fibers by using chemicals such as sodium hypochlorite and hydrogen peroxide (Dos Santos et al., 2007).

Mercerizing is a continuous chemical process used to increase dye-ability, lustre and fiber appearance. A concentrated alkaline solution (a solution of caustic soda) is

applied at this step. Then caustic is removed by several washes under tension (EPA, 1997).

Dyeing is the process of adding color and intricacy to the fibers and increase the product value. Dyeing of textile is achieved using a wide range of dyestuffs, techniques and equipment and requires large volumes of water not only in the dyebath, but also during the rinsing step (Dos Santos et al., 2007; EPA, 1997).

Finishing is the final process to impart the required end use finishes to the fabric. At this step, chemical or mechanical treatments performed on fiber, yarn or fabric to improve appearance, texture or performance (EPA, 1997).

The textile industry is the largest and one of the first established industries in Turkey. It plays an integral role in the Turkish economy, providing about 10% of Gross Domestic Product (GDP), 18% of industrial production, 20% of manufacturing labour force and 32% of Turkish export earnings (ITKIB, 2003). It is one of the mightiest water consuming sectors, between 25 and 250 m³ per ton of product depending on the processes and the largest consumer of colorants for various dyeing, printing and finishing processes (Chacon et al., 2006; Gonçalves et al., 2005). Textile industry and its wastewaters have become one of the main sources of severe pollution problems worldwide, with the increased demand for textile products.

2.2. Textile Dyes

Dyes are substances that possess high coloration degree and are, in general, employed in the textile, pharmaceutical, cosmetics, plastics, photographic, paper and food industry (Zollinger, 1991). Textile dyeing is the process of imparting color to a textile material in loose fiber, yarn, cloth or garment form by treatment with a dye. It is concerned with carbon-based compounds that can be dissolved in appropriate solvents, usually water. The primary source of dye has been nature, with the dyes derived from animals or plants. In the last 150 years, artificial dyes have been produced to achieve a broader range of colors, and to make the dyes more stable to washing and general use. Different classes of dye are applied for different types of fiber and at different stages of the textile production process (Wikipedia-dyeing, 2008; Zollinger, 1991)

Over 700,000 tons and approximately 10,000 types of dyes and pigments are produced yearly worldwide (Carneiro et al., 2007). Among them, azo dyes constitute the largest and the most important class of commercial dyes with ~70% by weight (Zollinger, 1991). Approximately 12% of the dyes are lost in wastewater annually during manufacturing and processing operations (Arslan et al., 2000).

2.2.1. Classification of Dyes

Since there are lots of textile dyes that have developed over the years with its typical chemical structures and commercial names, classifying them into any particular category is a quite uphill task. Dyes could be categorized according to source of their materials, chromophore nature and nuclear structure as well as an industrial classification could be done.

The most general categorization is based on the source from which dye is made. According to this classification, dyes are divided into two groups as natural dyes originated from plants, animal and minerals and man-made synthetic dyes (dyes & pigments-types of dyes, 2008).

In chemical classification; dyes can be grouped according to the nature of their chromophore, a group of atoms responsible for the dye color. The most important chromophores are azo, carbonyl, methine, nitro and quinoid groups. In addition to chromophores, dye molecule includes electron withdrawing or donating substituents that cause or intensify the color of the chromophores, called auxochromes (Christie, 2001). The most important auxochromes are amine, carboxyl, sulfonate and hydroxyl (Welham, 2000).

In case of an industrial classification that is made by considering the dye performances in dyeing processes; textile dyestuffs can be broadly split into groups as azo, reactive, acid, basic, direct, mordant (chrome), disperse, vat, sulphur, oxidation and solvent dyes. These groups can be clubbed together into three categories according to the fiber types they applied, as dyes for cellulose fibers, protein fibers and synthetic fibers (dyes & pigments-textile dyes, 2008).

Brief information about the textile dyestuff, grouped according to the industrial classification, was presented below. Azo dyes and azo dye synthesis were explained in a more detailed manner as well as the acid dyes and acid dyeing process, since this

study is mainly focused on the photochemical oxidation of an aqueous acid dye solution and azo dye production wastewaters.

2.2.1.1. Azo Dyes

The azo dyes, characterized by an azo group ($-N=N-$), constitute the largest and the most important class of commercial dyes used in textile industry for dyeing several natural and synthetic materials (Lucas and Peres, 2007; Chacon et al., 2006). Azo group of dyes represents about 70% of the dyes produced annually in the world and colored wastewater is particularly associated with their presence (Dos Santos et al., 2007, Zollinger, 1991).

The general formula for making an azo dye requires two organic compounds; a coupling component which is an aromatic ring compound (benzene or naphthalene) and a diazo component. Most of the azo dyes contain only one azo group, but some contain two (disazo), three (trisazo) or more (Christie, 2001).

In theory, azo dyes can supply a complete rainbow of colors, but yellow/red dyes are more common as blue/brown dyes. They have fair to good fastness properties. Due to the processes involved in their manufacture, azo dyes have an advantage of being cost-effective (Christie, 2001). Many types of azo dyes are valid such as acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulfur dyes, each of them has a unique chemistry, structure and particular way of bonding.

Azo Dye Synthesis

Azo dye synthesis is mainly composed of two steps. First step involves diazotisation; the process by which an aromatic primary amine is converted to a diazonium compound. In diazotization, sodium nitrite is added to a solution of the amine in aqueous acid solution at low temperature ($0-5^{\circ}\text{C}$). Reaction of the amine with nitrous acid results in formation of a nitrosamine. Tautomerization (removal of a hydrogen from one part of the molecule, and the addition of a hydrogen to a different part of the molecule) and loss of water converts nitrosamine to the diazonium salt. After the diazonium salt is obtained, it reacted with a coupling component (i.e. a phenol, aromatic amine), and form the stable azo dye (Sci-tech Encyclopedia, 2008). These coupling components may also include additional azo groups, chelated metal ions and charged organic groups as well as the aryl unit (Zoorob and Caruso, 1997).

Most of the azo dyes contain only one azo group, but some contain two or more. For preparing an disazo dye containing two azo group, first diazotised aromatic amines are coupled with couplers containing diazotizable amino groups and aminomonoazo dye is obtained. Then this resultant azo dye diazotized and coupled with final components (Blus, 1999).

Salt and other impurities need to be removed before dyes are dried for producing saleable powder. The conventional process applied for purification of dye is as follows: After the chemical synthesis of dye, it is precipitated from the aqueous solution using salt. The slurry is passed through a filter press. The filter retains the dye, and the filtrate is removed. The retained dye is collected and dried in ovens. The dried dye is then pulverized to produce a powder for sale (Yu et al., 2001).

2.2.1.2. Acid Dyes

Acid dyes are one of the most widely applied textile dye classes and have the highest market share in the Turkish polyamide dyeing sector (Arslan-Alaton and Teksoy, 2007). They can be applicable to natural fibers like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. Acid type of dyes are water-soluble anionic molecules, which are named for the acid used in dyeing process and for the types of bonds they form to the fiber. Dye molecule contains two groups of atoms; one acidic, such as a carboxylic group, and one color-producing, such as an azo or nitro group (Wikipedia-acid dye, 2008; Encyclopedia Britannica-acid dye, 2008)

Acid dyes are thought to fix to fibers by ionic bonding, hydrogen bonding and Van der Waals forces. Since they are generally present in the form of sodium salts of the sulfonic or carboxylic acids, they are in solution anionic. Animal protein fibers and synthetic nylon fibers contain many cationic sites, therefore there is an attraction of anionic dye molecule to a cationic site on the fiber. The strength (fastness) of this bond is related to the desire/ chemistry of the dye to remain dissolved in water over fixation to the fiber (Wikipedia-acid dye, 2008). In addition to textile industry, they are also used in paints, inks, plastics and leather.

Acid Dyeing Process and Dye Assisting Chemicals

The acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath. Ionic bonds or salt links are formed between positively charged terminal group on polymer and dye anion. In addition to the dominant ionic bonds, hydrogen

bonds and Van der Waals forces play a role in the bonding. Those additional bondings occur between the other part of the colored anion and the fiber (Fan et al., 2004).

In conventional acid dyeing processes, textile material is immersed into a dyeing-bath comprising dye as well as the agents for dispersing and fixing the dye to the textile material. The dyeing bath is subsequently heated, during dyeing of the textile material and maintained at a second temperature close to the boiling point of the dyeing-bath. By this way dye molecules exit the bath and get attach to the fibers (European Patent 1333119, 2003).

Acid is used to promote dyeing exhaustion. Acidity of the bath influences both the amount of dye adsorbed by fiber and the rate of exhaustion. Acid strength and concentration are determined depending on acid dye molecular size. Usually, small dye molecular structure has lower affinity to the fiber as compared to large dye, and more acid or stronger acid is required for dyeing with small molecule acid dyes (Fan et al., 2004).

In order to control the evenness of dyeing; salts (i.e. sodium sulfate, sodium chloride), which produce anions smaller than the dye anion when dissolved in liquor, are used as a retarding agent. These anions are attracted more quickly to the fibers as compared to the dye anions that are moving at a slower rate. Dye anions will gradually replace the smaller anion due to their high affinity to fiber which leads to a much more even dyeing (Fan et al., 2004). Although enhancing the evenness of dyeing, dye leveling and/or retarding agents usually have disadvantages including increased initial expense and higher cost to treat the spent dyeing bath (United States Patent 5318598, 1994).

2.2.1.3. Reactive Dyes

Between the several azo dyes, the most used are the 'reactive' type, making up approximately 30% of the total dye market. Reactive dyes have high water solubility and characteristic brightness and used for the coloration of the cellulosic fibers (Pearce et al., 2003).

In a reactive dye, chromophore (azo group) contains a substituent that is activated and allowed to directly react to the surface of the substrate (Wikipedia-reactive dye, 2008). This reactive group forms a covalent bond with OH⁻, NH⁻, or SH⁻ groups in

fibers (cotton, wool, silk, nylon) in an alkaline dyebath (Dos Santos et al., 2007). Since reactive dyes have a low degree of fixation, color is a problem in dyeing wastewater. As much as 50% of the dye might be lost in the dyebath effluent. Dye hydrolysis, bounding of dye functional groups to water rather than cellulose, is another reason of residual reactive dyes in dyehouse wastewater (Dos Santos et al., 2007; Pearce et al., 2003).

2.2.1.4. Basic Dyes

Basic dyes are water soluble dyes that are cationic and so will react with the negatively charged materials. Basic dyes possess cationic functional groups such as -NR_3^+ or =NR_2^+ and their primary mechanism of staining is by ionic bonding (Stains File-Basic dyes, 2008). This group of dyes works well on acrylics having anionic groups attached to polymer. The anionic sites on acrylics make them suitable for dyeing with cationic dyes, since there will be a strong ionic interaction between dye and polymer (in effect, the opposite of the acid dye-protein fiber interaction) (Christie, 2001).

2.2.1.5. Direct Dyes

Direct dyes are water soluble dyes which have a high affinity for cellulose fibers (cotton or rayon etc.) and are taken up directly. Their flat shape and their length enable them to lie along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds (Stains File-direct dyes, 2008). Although washfastness of direct dyes is poor, it may be improved by after treatment (Encyclopedia Britannica-direct dye, 2008).

2.2.1.6. Mordant Dyes

This class of dyes requires a mordant, a substance of organic or inorganic origin improving the fastness of the dye against water, light and perspiration e.g., dyes with metal chelating groups. The most commonly used mordant dyes have hydroxyl and carboxyl groups and are negatively charged thus could be accepted as a subgroup of acid dyes. Some cationic mordant dyes possessing amino groups are also present (Stains File-Mordant dyes, 2008). Most natural dyes are mordant. Synthetic mordant dyes, or chrome dyes comprise some 30% of dyes used for wool, and are especially useful for black and navy shades (Wikipedia-dye, 2008)

2.2.1.7. Disperse Dyes

Dispersed dyes are mainly used in dyeing polyesters and have a minor use in dyeing cellulose acetates and polyamides. These types of dyes are fairly hydrophilic and have low solubility in water. General structure of dye molecule is small, planar and non-ionic, with attached polar functional groups. Dye molecules interact with the polymer by forming dispersed particles. Shape of the dye molecule makes it easier for the dye to slide between the polymer chains, under pressure and high temperature. Disperse dyes are quite volatile, and tend to sublime out of the polymer at sufficiently high temperatures (Christie, 2001).

2.2.1.8. Vat Dyes

Water insoluble vat dyes are used particularly on cellulosic fibers (cotton). They are incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkaline form, which has an affinity for the textile fiber. After dyeing, fabric is oxidized and original insoluble dye is regenerated (Wordweb online-Vat dye, 2008). The indigo color of the blue jeans is one of the most important members of this group. Natural indigo, which probably the oldest dye known to man, extracted from the plant “*Indigofera tinctoria*” and used by the Egyptians in 200 BC (Wikipedia-indigo dye, 2008).

2.2.1.9. Sulfur dyes

Sulfur dyes are the biggest volume dyes manufactured for cotton. Similarly to the vat dyes, sulfur dyes must be reduced to their leuco forms before application. The dyes are absorbed by cotton from an alkaline solution of sodium sulfide and are insolubilised within the fibre by oxidation. Due to the high polluting nature of the let out dye-baths, slowly sulfur dyes are being phased out (Wikipedia - sulfur dye, 2008; Christie, 2001)

2.2.1.10. Oxidation Dyes

Oxidation dyes are primarily aromatic compounds that belong to three major chemical families of diamines, aminophenols (amino naphthols) and phenols or naphthols. They are generally colorless, and are typically a low molecular weight product. These type of dyes fall into two categories, oxidation base (primary

intermediate) and coupler (secondary intermediate). To generate color using these products, at least one of type of each must be combined with a suitable oxidant under alkaline conditions (Christie, 2001).

2.2.1.11. Solvent Dyes

Solvent dyes are the class of dyes that gets soluble in organic solvents. It is usually used as a solution in an organic solvent. Solvent dye molecules are typically nonpolar or little polar and they do not ionize. They are insoluble in water. Many of the solvent dyes are azo dyes which have lost the ability of ionizing due to some molecular rearrangement. In the process they gained the ability to dissolve in non-polar materials such as triglycerides (Jacson Colorchem - solvent dyes, 2008; Wikipedia-Solvent dye, 2008).

2.3. Environmental Properties of Textile Dyeing and Finishing Effluents

Textile wastewater is a mixture of various organic compounds employed as cleaning solvents, plasticizers, sequestering agents, tannins, dye carriers, leveling agents, dispersing agents, etc. and colorants. Beside the higher chemical and biological oxygen demand, it also contains high concentrations of heavy metals and total dissolved solids. Thus, it is chemically very complex in nature (Sharma et al., 2007).

Textile dyeing and finishing industry, which grew at faster rate in the developing countries due to cheaper labour and less stringent waste disposal norms, is one of the major polluters among the industrial sectors, considering the volume and chemical composition of the effluent discharge (Carneiro et al., 2007; Sharma et al., 2007). Wastewater from the textile preparation, dyeing and finishing is known for its strong and intense color, high dissolved solids content, low BOD, medium COD content and hence can be categorized as medium-strength wastewater. Their low BOD/COD ratio indicates the large amount of nonbiodegradable organic matter (Al-Kdasi et al., 2004).

Colored textile effluents contain dye and dye intermediates with high degree of aromaticity and low-biodegradability and their release into the aquatic system results in the environmental risk (Noorjahan et al., 2003). In addition to the residuals of dye bath auxiliaries and unfixed dyestuff, textile dyeing and finishing effluent also

contains high amounts of total dissolved solids, sodium chloride and sodium sulphate (Ranganathan et al., 2007).

Many dyes are difficult to fade due to their complex structure and synthetic origin and release of them to natural environments is described as very problematic to aquatic ecosystem (Carneiro et al., 2007). They are biorecalcitrant due to their aromatic structure and their discharge can result in the formation of toxic aromatic amines under anaerobic conditions in receiving media and contaminate the soil and groundwater (Voyksner et al., 1993).

It is known that large amounts of azo dyes entering activated sludge treatment plants, will pass through unchanged and will be discharged into the environment together with their precursors and potentially carcinogenic degradation. Without adequate treatment, these toxic and/or mutagenic dyes and their breakdown products can remain in the environment for an extended period of time (Dos Santos et al., 2007).

Discharge of untreated dyeing effluent will also cause aesthetic problems in natural water currents. Apart from the unpleasant effect of the color presence, dyes strongly absorb sunlight, thus hindering the photosynthetic activity of aquatic plants and impending all ecosystem (Nunez et al., 2007). Beside the adverse environmental effects mentioned, color and toxicity of dyes also influence the efficiency of some water treatment techniques (Carneiro et al., 2007).

It should also be noted that temperature of effluents from textile dyeing and finishing industry is unusually high compared to most industrial wastewaters. During the dyeing process, rinse water temperatures up to 90 °C could be encountered (Perez et al., 2002). Thus, direct discharge of the effluents may cause temperature changes in receiving body and threaten the aquatic life.

2.3.1. Environmental Properties of Acid Dyebath Effluent

Acid dyes, one of the most extensively applied textile dye classes world-wide, are quite problematic pollutants as they tend to pass through conventional decolorization systems unaffected. The dyeing process takes place at acidic pH (pH 3-5) and around boiling temperature thus resulting in an effluent with low pH and high temperature (Arslan-Alaton and Teksoy, 2007; Çapar et al. 2006 a). In addition to the acids used to promote dyeing exhaustion, acid dyeing wastewater contains salts utilized for neutralizing the zeta potential of the fiber, bases for pH control and brightly colored

dyes for dyeing the fiber (Işık and Sponza, 2006; Fan et al., 2004). In general, these wastewaters are characterized by high chemical oxygen demand and high dissolved solids with an average color load (Çapar et al. 2006 a).

Since fixation rates of acid dyes are considerably high, dye concentrations of the effluents are relatively low. However, some acid dyes are among the most hazardous azo dyes due to the release of carcinogenic amines and have toxic properties. Moreover, residual auxiliary chemicals may also create toxic effects for the aquatic life. Therefore, it is essential to apply an adequate treatment for these wastewaters before discharging into the receiving environment (Çapar et al., 2006 b).

2.4. Environmental Properties of Azo Dye Manufacturing Effluent

The manufacturing of azo dyes creates wastes that are discarded as wastewater and solid residues. Dye manufacturing wastewater generally includes remaining dye, as well as intermediate products and unreacted raw materials (i.e. aromatic amines with alkyl-, halogen-, nitro-, hydroxyl-, sulfonic acid- substituents, salts like sodium nitrite and sodium chloride) (Sci-tech Encyclopedia, 2008; Kornaros and Lyberatos, 2006).

The effluent is normally characterized by high chemical oxygen demand, suspended solids and intense color (Kornaros and Lyberatos, 2006; Kang et al., 1999). Several waste streams that are variable in composition and strength are generated during dye synthesis process. COD concentration of the combined dye manufacturing effluent is around 2000-3000 mg/L. BOD/COD ratio of the wastewater is quite low, implying that it contains large amount of non-biodegradable organic matter (Kornaros and Lyberatos, 2006; Kim et al., 2005).

The dyes and other intermediates can be reduced in the environment to produce carcinogenic compounds (such as naphthylamines, substituted phenylamines, benzidine analogs) as well as causing unnatural coloration (Voyksner et al., 1993). Industries generally adding NaOCl in the final polishing step to remove effluent color forms chlorinated by-products, damaging severely the surface water and ecological environment (Shu et al., 2006). The effluent may also contain unchelated metals (i.e. cobalt, chromium, copper) resulting from the production of metal-complexed dyes. Most of these metals are known as important pollutants and can be

toxic to many organisms even in trace amounts. Turkish receiving water discharge standards for dye, dye raw materials and dye assisting materials production industry effluents were presented in Table 2.1 (Water Pollution Control Regulation, 2004). As can be seen, this regulation does not contain limitation for color parameter, despite its significant adverse impacts on environment.

Table 2.1: Receiving water discharge standards for chemical dye, dye raw materials and dye assisting materials production industry

Parameters	Composite Sample (Taken in 2 hours)	Composite Sample (Taken in 24 hours)
COD (mg/L)	200	150
TSS (mg/L)	60	40
Cr ⁶⁺ (mg/L)	0.5	0.3
Cd (mg/L)	-	0.2
Zn (mg/L)	4	3
Total Cr (mg/L)	2	1
Pb (mg/L)	2	1
Fe (mg/L)	30	-
Total CN ⁻ (mg/L)	2	1
Fish Toxicity Test	6	3
pH	6-9	6-9

Chemical composition of dye production wastewater is usually subject to daily and seasonal changes resulting in high variations of color and organic matter content in effluents. Sponza (2006) analyzed the samples taken from the effluent of the treatment plant of a chemical dye production industry in Turkey, for chemical, biochemical and toxicity parameters during 9 months from May 1997 to February 1998. The existing treatment plant consisted from a mechanical, chemical and biological treatment. It has been reported that, fluctuating COD values are higher than the permissible discharge limits in most of the measurement period. In addition to the exceeding organic matter content, presence of moderately and minor acute toxicity found via conventional and enrichment toxicity tests. The existent cause of toxicity was found to be the combined and synergistic effect of color, metals (Cr⁶⁺, Cd²⁺, Pb²⁺, Fe³⁺ and Zn²⁺) and total hydrocarbon present in the wastewater.

2.5. Treatment of Textile Dyeing Effluents

Various combinations of biological and physical-chemical treatment techniques are used as conventional methods for dealing with dye containing textile effluents. However conventional methods such as chemical coagulation/flocculation or membrane separation (ultrafiltration, reverse osmosis) are not effective in decolorization of the dyehouse effluents since they provide only a phase transfer of dyes and produce large quantities of sludge, besides being quite costly (Lucas and Peres, 2007). Elimination by activated carbon adsorption is also inefficient treatment method because of the highly soluble and hydrophilic structure of most dyes. Furthermore, color removal with biological treatment is not an effective solution due to the complex and recalcitrant nature of the azo dyes that resist to biodegradation (Carliell et al., 1996).

Recent studies indicate that several advanced oxidation processes (AOPs) could be a good alternative for treating colored aromatics (Carneiro et al., 2007). Among the various AOPs; treatment with ozone (often combined with H_2O_2 , UV-C or both), H_2O_2 /UV systems, Fenton and photo-Fenton type oxidations, heterogeneous photocatalytic oxidation (mediated by TiO_2 , ZnO , CdS , etc), electrochemical processes, sonolysis (ultrasound irradiation), wet air oxidation and supercritical water oxidation have been reported in literature as effective for the degradation of azo dyes (Papadopoulos et al., 2007; Chatzisyneon et al., 2006). Therefore in the treatment of textile wastewater, AOPs have more recently been used for selective removal of the more bioresistant fractions (i.e. dyebath effluents) and their conversion to readily biodegradable intermediates that can subsequently be treated biologically.

Most of the AOPs mentioned including ozonation, Fe-based oxidation, H_2O_2 /UV systems, heterogeneous photocatalysis and ultrasound treatment involve the production of strongly oxidizing agents, mainly hydroxyl radical ($\bullet\text{OH}$). Generated $\bullet\text{OH}$ react rapidly and non-selectively with most of the organic compounds including biologically-difficult-to-degrade ones (dyes, pesticides etc.) and efficiently decompose them (Huang et al., 2007). Especially oxidation of dyes and textile effluents with Fenton and photo-Fenton type AOPs has recently received great attention because of their high efficiency in the oxidation of dyestuff, ease of operation and low cost (Bigda, 1995).

2.5.1. Treatment of Acid Dyes and Acid Dyeing Wastewater

Like the other types of textile azo dyes, AOPs are frequently used as a treatment method for dealing with acid dyeing wastewater. Fenton and photo-Fenton type oxidations are one of the most effective and widely used AOPs in the degradation of acid dyes. As well as their efficiency in the dye decomposition, Fe-based AOPs' working pH (2-5) is almost same with the application pH (3-5) of acid dyes on polyamide fibers, which makes them an economical solution for the treatment of acid dyebath effluent (Arslan-Alaton and Teksoy, 2007).

In addition to Fe-based oxidation processes, ozonation, H₂O₂/UV systems and their combinations are the other AOPs applied to the wastewater containing acid type of dyes (Muthukumar et al., 2005; Muthukumar et al., 2004).

2.6. Treatment of Dye Manufacturing Wastewaters

Pollutant parameters of major interest in the treatment of dye manufacturing process wastewaters are chemical oxygen demand, salinity and color (Kim et al., 2005). Various combinations of conventional treatment processes, including physical and chemical methods (coagulation/flocculation, adsorption on activated carbon, polymer and mineral sorbents, reverse osmosis, chemical oxidation, filtration and electrochemical treatments) as well as biological treatments have been used for the treatment of dye manufacturing wastewaters (Kornaros and Lyberatos, 2006).

Since environmental characteristics of the dye manufacturing wastewater is not suitable for direct application of biological oxidation due to the biorecalcitrant nature of dyes and dye intermediates, biological treatment units are generally combined with a pretreatment method to reduce the pollutant loading and improve the efficiency of the system (Yu-Li et al., 2006).

In the treatment of dye manufacturing wastewater, coagulation/flocculation and adsorption are the most commonly used techniques; however transferring the problem from aqueous to solid phase. Both methods have some drawbacks like final disposal of the created sludge or regenerating the adsorbent material (Shu et al., 2006).

Oxidative degradation by chlorine and ozone are the other important alternatives for dealing with the dye manufacturing effluents. Although chlorine is a powerful oxidant, chlorination has a disadvantage of generating carcinogenic by-products and started to be phased out (Sarasa et al., 1998). On the other hand, ozonation and its combination with coagulation are still valid as effective treatment methods, providing efficient color removal (Sarasa et al., 1998; Yu-Li et al., 2006).

In addition to ozonation, H₂O₂-based AOPs such as Fenton type oxidations have been employed to degrade successfully dyes and intermediates in the manufacturing effluent (Kang et al., 1999). However, only few studies are available in literature related with the application of AOPs on dye manufacturing wastewater, whereas many works have been reported about the textile dyeing effluents (Kornaros and Lyberatos, 2006).

In general, photochemical AOPs are not efficient solution for the treatment of combined dye manufacturing wastewater due to its high UV absorbance resulting from the high concentrations of pollutants (Safarzadeh-Amiri et al., 1997). However, as aforementioned several waste streams having different strength were created during dye production process. Among them, some streams (i.e. wastewater generated from the reactor washing, reverse osmosis effluent/outflows) are quite suitable for the photochemical treatment with their relatively lower pollution load (COD $\leq$ 500 mg/L) despite their intense color.

2.7. Advanced Oxidation Processes

Destructive oxidation of dyes and textile effluents has received considerable attention since colored aromatic compounds have proven to be treated effectively by a variety of AOPs (Carneiro et al., 2007). Information about the AOPs frequently applied for treating dye-containing wastewater, was presented below.

2.7.1. Ozonation

Ozone is a quite powerful oxidizing agent because of its instability. Although the original purpose of ozone oxidation is disinfection of potable water, it can also be successfully used for treatment of biologically difficult-to-degrade pollutants, preoxidation of industrial wastewater and post-treatment & disinfection of secondary treated domestic and industrial effluents (Glaze et al., 1987).

In aqueous solutions, ozone reacts with organic compounds dissolved in water through either direct attack of the molecular ozone or indirect attack by free radicals i.e. hydroxyl radical ($\bullet\text{OH}$). These different reaction pathways result in different oxidation products and are controlled by different types of kinetics (Tizaoui, 2008). Direct ozonation prevails at $\text{pH} < 4$. Between pH s 4-9 both mechanism are present and above $\text{pH} > 9$ radical oxidation dominates (Staehelin and Hoignè, 1985). Brief description of ozone reaction mechanisms were given below.

Direct Ozone Oxidation

Ozone is mainly available as molecular ozone under acidic pH conditions and direct molecular oxidation reactions dominate (Arslan-Alaton and Alaton, 2007). In direct attack, molecular ozone reacts with the organic compounds having specific functional groups through electrophillic, nucleophilic or cycloaddition reactions (Staehelin and Hoignè, 1985). The direct ozone oxidation of organic compounds is more selective than the radical oxidation and has a slow reaction rate constant, typically in the range of $k = 1$ to $1000 \text{ M}^{-1} \text{ s}^{-1}$ (Tizaoui, 2008).

Indirect Ozone Oxidation

Ozone is unstable in water and it decomposes to highly reactive secondary oxidants such as $\bullet\text{OH}$, $\text{HO}_2\bullet$, $\text{HO}_3\bullet$, and $\text{HO}_4\bullet$, which start a free-radical reaction mechanism (Hoigne and Bader, 1976). The produced radicals react instantly ($k = 10^8$ - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$) with most of the pollutants and degrade them (Tizaoui, 2008). Radical oxidation is less selective compared to direct oxidation and it dominates under basic conditions. The radical pathway is influenced by the type of dissolved substances in water.

In recent years, ozone oxidation stands out as potential decolorization process of colored effluents since both direct and indirect pathways are able to break down the chromophore groups with conjugated double bonds which are responsible for color. Ozonation is widely used for the treatment of dyes and provides effective color reduction. However COD removal efficiency of dyes via ozonation is generally lower than the efficiency of Fe-based AOPs. (Dos Santos et al., 2007; Swaminathan et al., 2005)

Rate-limiting step in the ozone oxidation of wastewaters has been reported in literature as the mass transfer from the gas phase to the aqueous medium (Swaminathan et al., 2005). Since ozonation is an expensive process, kinetic

parameters of the oxidation reaction of the target pollutant need to be determined in order to assess the feasibility of its use in treatment.

2.7.2. UV Photolysis of Ozone

Photons in the UV spectrum decompose ozone into oxygen and hydrogen peroxide in the presence of water. Hydrogen peroxide then reacts with UV radiation or ozone to form the hydroxyl radical. Oxidation of organic molecules occurs due to the reaction with hydroxyl radicals, molecular ozone and direct photolysis. Commonly used radiation wavelength is 254 nm since ozone is at its maximum absorption efficiency at this wavelength (EPA, 1998). Combined O₃/UV process has typically higher removal efficiency than ozone and UV alone.

2.7.3. Hydrogen peroxide/Ozone

In an H₂O₂/O₃ system, referred to as peroxone, H₂O₂ is used in conjunction with O₃ to enhance the generation of hydroxyl radicals. Reaction of O₃ with hydroperoxide ion (the conjugate base of hydrogen peroxide) initiates the chain reactions that results in the generation of hydroxyl radicals (reaction 2.1). The overall reaction is represented by reaction 2.2 (Tizaoui, 2008).



The combined H₂O₂/O₃ process has been demonstrated to be more effective at decolorization than O₃ or H₂O₂ alone and applicable for direct, metal-complex or disperse dyes (Strickland and Perkins, 1995; Slokar and Marechal, 1998).

2.7.4. Hydrogen peroxide/UV

In the hydrogen peroxide/UV system, highly reactive hydroxyl radicals (•OH) are generated by the direct photolysis of hydrogen peroxide. These radicals attack the organic pollutant and breaks down them as this is the case for the other radical oxidation processes. Hydrogen peroxide has its maximum absorption efficiency at about 220 nm wavelength, which is lower than ozone's (EPA, 1998). However, many of the wastewaters having moderate to high concentrations of pollutants shows a high absorbance below 300 nm, which means hydrogen peroxide/UV treatment

will be inefficient due to the poor absorption of the UV photons by hydrogen peroxide (Safarzadeh-Amiri et al., 1997).

2.7.5. Heterogeneous Photocatalytic Oxidation

Heterogeneous photocatalysis is one of the AOPs which involves a photocatalytic reaction proceeding on the surface of a semiconductor (Demeestere et al., 2005). Radiation stimulates valence band electrons in the semiconductor and excited electrons jump to the conduction band leaving holes in the valence band. Redox reactions occur between the electrons and holes and the organic/inorganic pollutants present in water. Holes react with water and/or hydroxyl ions to produce hydroxyl radicals ($\bullet\text{OH}$) or directly oxidize pollutants, while electrons react with dissolved O_2 or other electron acceptors to form additional $\bullet\text{OH}$ (Arslan et al., 2000).

TiO_2 , ZnO and CdS are the most commonly employed photocatalysts. Especially TiO_2 has become the bench mark catalyst because of its high photocatalytic activity as compared to other semiconductors (Lathasree et al., 2004). ZnO is a suitable alternative to TiO_2 and has been reported as more efficient in some applications (Daneshvar et al., 2004).

Recently, use of heterogeneous photocatalysis in combination with biological treatment has been considered as a cost-effective alternative for the treatment of colored wastewater (Hu et al., 2003). The process can be performed at ambient temperatures and pressures and has an advantage that no chemical oxidants have to be employed (Demeestere et al., 2005). Major restrictions of heterogeneous photocatalytic oxidation are the necessity to remove the catalyst after treatment and the limited surface area of semiconductors (Arslan et al., 2000).

2.7.6. Electrochemical Processes

Electrochemical processes (electrolysis and electrocoagulation) have been proposed as one of the effective methods for treating wastewaters containing non-biodegradable organic compounds, such as colored textile effluents (Vlyssides et al., 2000; Naumczyk et al., 1996).

Electrolysis process includes direct or indirect electrolysis. In direct electrolysis, organic pollutants are oxidized on inert electrodes without the involvement of other substances. Many anode materials have been tested in direct oxidation and anodes

made of graphite, Pt, TiO₂, IrO₂, PbO₂, SnO₂, Ti-based alloys and boron-doped diamond electrodes reported as effective in mineralization of pollutants (Chatzisymeon et al., 2006). Beside direct process, organic pollutants can be oxidized by the indirect electrolysis which involves redox reagents (e.g. hypochlorite ions, ozone, hydrogen peroxide) generated in situ (Panizza and Cerisola, 2001).

Electrochemistry has recently been used to produce hydroxyl radicals ($\bullet\text{OH}$) by generating Fenton reagent in the bulk of the solution, which is known as electro-Fenton process. The system involves either addition of ferrous iron or reduction of ferric iron electrochemically, with the simultaneous electrochemical production of hydrogen peroxide upon the reduction of oxygen on several electrodes (mercury pool, graphite, vitreous carbon or carbon-polytetrafluoroethylene O₂-fed cathodes) (Kuşvuran et al., 2004; Ventura et al., 2002).

Another electrochemically based method is electrocoagulation, which removes pollutants from aqueous media by introducing highly charged polymeric metal hydroxide (aluminium or iron hydroxide) species. These species neutralize the electrostatic charges on particles and promote agglomeration or coagulation. Resultant flocs are separated from aqueous phase either by precipitation or floatation (Kobya et al., 2003). In recent years, electrocoagulation has been considered as an effective alternative for treating dye-containing wastewater. The electrogenerated flocs separate rapidly and remove color and turbidity from the effluent. Major limitation of the process is its high initial capital cost (Kobya et al., 2003; Lin and Peng, 1994).

2.7.7. Sonolysis

Decomposition of pollutants by ultrasonic irradiation of the liquid, namely sonolysis, is a relatively new method which has drawn attention especially for its decolorization effects. Two pathways occur when ultrasound (US) is applied to the liquid: (1) direct break down of chemical bonds of the pollutant and (2) generation of hydroxyl radicals ($\bullet\text{OH}$) by dissociation of water molecules in cavitation bubbles (He et al., 2007). The efficiency of pollutant degradation is directly depends on the efficiency of $\bullet\text{OH}$ diffusion into the aqueous phase (Tezcanlı-Guyer and İnce, 2003).

Sonolysis process is generally combined with an additional AOP, since degradation rates are slow for practical uses, when it is applied alone. In order to enhance the

destruction rate of the pollutants, combinations of ultrasonic irradiation with O_3 , O_3 /UV, TiO_2 /UV, Fenton reaction, Fe^{3+} /UV have been employed (Okitsu et al., 2008). Sonocatalysis can take the place of photocatalysis in case the reaction medium is not transparent (Bejarano-Perez and Suarez-Herrera, 2007).

2.7.8. Wet Air Oxidation

Wet air oxidation (WAO) is a process of subcritical oxidation of organic matter in aqueous phase using air or pure oxygen as oxidant, at elevated temperatures (100–350 °C) and at pressures ranging from 0.5 to 20MPa. In WAO processes, increased temperatures and pressures raise the concentration of dissolved oxygen and enhance the contact between the molecular oxygen and organic matter and thus improve the oxidation rate (Kuşvuran et al., 2004). Although this method can be used with reasonable effectiveness to remove color and COD from dye-containing wastewater, it requires high temperatures (200-300 °C) and high pressures (sometimes over 10 MPa) to achieve acceptable removal rates. Coupled use of WAO with catalysts (such as the metal salts) allows less extreme conditions to be required (Chang et al., 2003). In the literature, the treatment efficiencies for various dyes by using WAO and catalytic WAO vary in between 50 and 90% (as COD or TOC removal), at the residence times of 30–240 min (Söğüt and Akgün, 2007). WAO involves high first investment capital; however the operating cost of the system is not much as compared with the other chemical techniques (Kuşvuran et al., 2004).

2.7.9. Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is a thermal oxidation process that occurs in an aqueous medium at temperatures and pressures above mixture's thermodynamic critical point, which are 374 °C and 22.1 MPa for pure water, respectively (Söğüt and Akgün, 2007). Under this conditions water becomes a fluid with unique properties and behaves as a low-polarity, largely unassociated solvent, in which molecular oxygen and many organic compounds are totally miscible (wikipedia-supercritical water oxidation, 2008). This process can be seen as a further development of the wet air oxidation, occurring at temperatures up to 350 °C and pressures up to 20 MPa. In a traditional SCWO treatment system, wastewater is combined with oxidizer at elevated pressure (>22 MPa) and temperature (500-600) during residence times of 1-100 seconds. For most wastes, these conditions are sufficient to destroy organic

substances into CO₂ and H₂O with conversion rates of 99-100% (Söğüt and Akgün, 2007; Kritzer and Dinjus, 2001).

SCWO can effectively treat a wide variety of industrial wastes including textile dyes in a significantly short residence times. However, it is an expensive technology due to its operation at high temperature and pressure, as well as the substantial amount of power required to pressurize the oxygenating reagent (Söğüt and Akgün, 2007; Matsumura et al., 2002). Technical problems of reactor corrosion and salt precipitation are the major restrictions that have hindered the industrial application of the process (Kritzer and Dinjus, 2001).

2.7.10. Fe-based Oxidation Processes

2.7.10.1. Fenton Oxidation

The dark reaction of Fe²⁺ with H₂O₂ is called Fenton's reaction and was first observed by Fenton in 1894. It is a homogeneous catalytic oxidation process that generates hydroxyl radicals (•OH) under acidic conditions as represented by the following equation (Barbeni et al., 1987; Walling, 1975; Fenton, 1894).



•OH generated by the catalytic decomposition of H₂O₂, can either react with Fe²⁺ to produce Fe³⁺;



or attack the organic molecules present in solution (Safarzadeh-Amiri et al., 1997);



The unselective •OH are capable of reacting quickly with most of the organic compounds including biologically-difficult-to-degrade ones (dyes, pesticides etc.), and decompose them by H-abstraction and addition to C=C unsaturated bonds (Huang et al., 2007; Lucas and Peres, 2007).

Due to the capacity of the Fenton's reagent to oxidize many classes of organic compounds, attention has turned to its possible application in oxidative treatments of contaminated water in recent decades. Since it is an effective way of producing •OH in a spontaneous dark reaction, it is widely used as a suitable treatment method for concentrated wastewater including recalcitrant dye molecules (Jeong and Yoon,

2005; Hislop and Bolton, 1999). In addition to the efficiency of the reaction, iron is a non-toxic element and separable with coagulation, while H₂O₂ has infinite solubility, easy to handle, environmentally safe and usually consumed during degradation (Carneiro et al., 2007).

Fenton process is favored by acidic pH conditions (2-5) with a distinct optimum range of pH=2.8-3.0 (Pignatello, 1992). However, as the solution pH is higher in many cases, the necessity to acidify the reaction medium limits the applicability of the Fenton process in practice. Besides the strict acidic limitation, a lot of iron sludge is produced at the end of the reaction which needs further treatment (Jeong and Yoon, 2005).

Although numerous organic pollutants can be treated by Fenton's reagent, it is observed that starting pollutant is partially transformed to intermediate products showing resistance to further oxidation, instead of complete mineralization. This may result due to the complexation of the intermediates with Fe³⁺ and/or some competitive reactions utilizing •OH (Safarzadeh-Amiri et al., 1997).

2.7.10.2. Fenton-like Oxidation

The decomposition of H₂O₂ is also catalyzed by an externally added and/or in-situ formed transition metal ion such as Fe³⁺ which is generally known as the Fenton-like oxidation (reaction 2.6). Fe²⁺ regeneration by the Fenton-like process gives rise to a free radical mediated, catalytic reaction mechanism (Nunez et al., 2007; Emilio et al., 2002; Safarzadeh-Amiri et al., 1997):



The initial rate of decomposition of H₂O₂ and the rate of oxidation of organic solutes are slower using Fe³⁺/ H₂O₂ than Fe²⁺/ H₂O₂ due to the lower reactivity of ferric ion toward hydrogen peroxide. Hydroperoxyl radical (HO₂•), which is more selective and slow in organic matter oxidation, generated in the first stage of the Fenton-like

process instead of $\bullet\text{OH}$ (reaction 2.7). However, extent and the overall rate of degradation achieved are same for both (Perez et al., 2002; Safarzadeh-Amiri et al., 1997; Pignatello, 1992).

Since the rate-limiting step of Fe-based advanced oxidation processes is the relatively slow catalytic reaction between ferric ion and hydrogen peroxide (reaction 2.6), it is believed that the main pollutant degradation initiated by the Fenton's reagent is a Fenton-like catalyzed degradation process. In other words, Fenton's reagent is actually a Fenton-like process in the presence of excessive amount of H_2O_2 (Safarzadeh-Amiri et al., 1996; Pignatello, 1992).

Fenton-like process is also effective at acidic pH conditions with an optimum about 2.8-3.0 (Pignatello, 1992). Major drawbacks of the process are same with the Fenton oxidation: pH limitation and excess sludge problem. Extent of mineralization achieved with Fenton-like reagent was reported about 40-60%, similarly to the Fenton process, depending on the amount of iron, hydrogen peroxide and the solution temperature (Safarzadeh-Amiri et al., 1997). Despite being an effective way of $\bullet\text{OH}$ production, relatively fewer studies has been reported about the Fenton-like oxidation of dyes as compared with Fenton process.

2.7.10.3. Photo-Fenton Oxidation

The photochemically enhanced version of Fenton and Fenton-like processes is well known as photo-Fenton oxidation as given below (Huang et al., 2007; Safarzadeh-Amiri et al., 1996; Pignatello, 1992);



The above reaction results in the continuous support of Fe^{2+} iron for the Fenton reaction shown in reaction 2.3, thus enhancing the $\text{Fe}^{2+/3+}$ cycle and providing additional $\bullet\text{OH}$ (provided that H_2O_2 is being present at sufficient amounts). $\bullet\text{OH}$ and Fe^{2+} are produced via photoreduction of Fe^{3+} to Fe^{2+} (reaction 2.11) with the highest quantum yield of 0.14 (mol Fe^{2+} produced/mol photon absorbed) observed at the wavelength 313 nm. This reaction is a strong function of the irradiation wavelength (e.g. the emission band of the light source) and pH, decreasing dramatically with increasing pH and wavelength (Safarzadeh-Amiri et al., 1997; Safarzadeh-Amiri et al., 1996).

The initial oxidation of organic pollutants produces intermediates, which can react with ferric ion and generate photochemically active complexes. Photolysis of these complexes results in production of Fe(II), organic radicals (R•) and CO₂:



The radical R• can react with oxygen and degrade further, leading to additional enhancement in destruction rate of organic molecules (Safarzadeh-Amiri et al., 1997; Safarzadeh-Amiri et al., 1996).

Besides the photoreduction of ferric ion and Fe(III)-organic intermediate complexes, some direct photolysis of hydrogen peroxide also occurs as represented by reaction 2.13 (Huang et al., 2007):



However, since hydrogen peroxide significantly absorbs UV at wavelengths < 300 nm, which is a range also strongly absorbed by contaminants, contribution of this reaction to the photodegradation is negligible (Safarzadeh-Amiri et al., 1997).

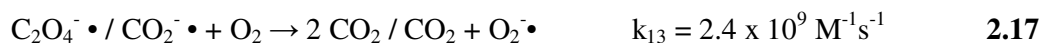
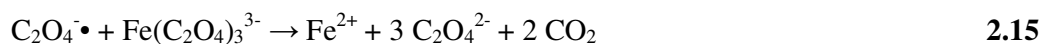
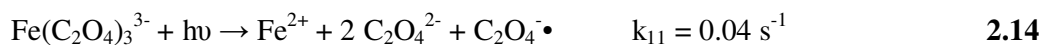
It is proved that rate of organic pollutant destruction and the extent of mineralization via Fenton type oxidation process are improved by irradiation with UV and even visible light due to the increase in •OH formation efficiency and photochemistry of iron complexes aforementioned (Safarzadeh-Amiri et al., 1996; Ruppert et al., 1993; Sedlak et al., 1987). Hence, light enhanced Fenton reaction has attracted increasing attention in the oxidation of variety of organic compounds including dyes (Nogueira et al., 2005).

Since the rate of organic matter degradation is improved significantly by light irradiation, the use of photo-Fenton reagent would be beneficial in cases where reaction time is limiting factor. However, it should be considered that efficiency of the photo-Fenton process directly depends on the UV absorbance of the waste stream. UV light-mediated treatment is only useful and economical for the wastewater with low to moderate concentrations of pollutants with low UV absorbance, since light absorption by Fe²⁺ is hindered in the presence of highly absorbing wastewater and •OH scavenging reactions occur due to the high concentrations of hydrogen peroxide, dissolved non-organic matter and other scavengers (Safarzadeh-Amiri et al., 1997).

Like the dark Fe-based AOPs, photochemically assisted Fenton process works at acidic pH conditions with an optimum range of pH=2.8-3.0 (Nunez et al., 2007). Thus there is a need for pH adjustment prior to treatment since the pH of the waste stream is higher in many cases. On the other hand, production of iron sludge is decreased as compared with dark process, since improvement in reaction efficiency reduces the required amount of iron catalyst.

2.7.10.4. Ferrioxalate Mediated Photo-Fenton Oxidation

Applying ferrioxalate in the photo-Fenton oxidation is known as the ferrioxalate photo-Fenton advanced oxidation process. The ferrioxalate complex is the best known and most extensively studied example of Fe(III)-polycarboxylate complexes and a popular chemical actinometer that is widely employed to measure light intensity (Hatchard and Parker, 1956). UV-VIS irradiation of ferrioxalate in acidic to slightly acidic solutions (pH= 3-5) has been suggested to proceed as follows (Huang et al., 2007; Safarzadeh-Amiri et al., 1997):



Fe^{2+} produced via reactions 2.14 and 2.15 with a high quantum yield of 1.0-1.2 over the range of 250-480 nm irradiation. In air saturated solution at acidic pH, the intermediate oxalate radical reacts with molecular oxygen and generates the $\text{O}_2^{\bullet-}$ radical (reaction 2.17), which participates in the formation of hydrogen peroxide. Generated ferrous ions can react with hydrogen peroxide present in solution to produce hydroxyl radicals (reaction 2.3).

The rate of degradation of organic compounds and extent of mineralization via photo-Fenton process is improved by the use of ferrioxalate due to:

1. The high quantum yield of Fe^{2+} generation over a broad range of irradiation wavelength (250-480 nm). Since the ratio of photoformed $\bullet\text{OH}$ to Fe^{2+} ions is about unity, irradiation of ferrioxalate results in the formation of at least one $\bullet\text{OH}$ radical for every quantum of light energy absorbed (Emilio et al., 2002; Safarzadeh-Amiri et al., 1997).
2. More efficient utilization of UV-VIS irradiation due to the strong absorption of ferrioxalate up to 500 nm, which also makes a large portion of the solar spectrum available (Nogueira et al., 2005; Safarzadeh-Amiri et al., 1997)
3. Formation of Fe^{2+} -oxalate complexes that reacts very quickly with hydrogen peroxide to generate $\bullet\text{OH}$, beside the Fe^{2+} ion (Safarzadeh-Amiri et al., 1997, Safarzadeh-Amiri et al., 1996).
4. Effect of ferrioxalate utilization on the critical process parameter of pH. Available pH range for the photo-Fenton reaction is greatly extended because of the strong complexation of oxalate with iron (Jeong and Yoon, 2005).

Use of ferrioxalate in photo-Fenton process has been suggested as a possible alternative due to the enhancement in the degradation of some organics pollutants. Moreover, allowing benefit from solar light make it more economical as compared to the processes using artificial UV radiation (Lucas and Peres, 2007; Nogueira et al., 2005; Emilio et al., 2002). On the other hand, addition of oxalate has been considered as the disadvantage of the process due to the increase of carbon load in the system (Nogueira et al., 2005).

2.8. Fenton-like and Photo-Fenton Treatment of Textile Dyes

Treatment of Dyes with Homogenous Fenton-like and Photo-Fenton-like Systems

Homogenous Fenton and photo-Fenton type processes, where the catalyst of iron ions are dissolved in water, are known to be very efficient for degradation of non-biodegradable dyes with a high rate of oxidation reaction. Many researchers have investigated treatability of textile dyes with homogenous Fe-based systems.

Wang (2008) studied Fenton and Fenton-like oxidation of a typical azo dye, Acid Black 1, under neutral pH conditions. Initial rate of dye degradation in Fenton oxidation was found to be faster than Fenton-like oxidation but the extent of degradation achieved for the two systems was similar after 100 min treatment. The kinetics of Fenton oxidation was described by a combined pseudo-first-order kinetic model while the Fenton-like reaction followed comparatively simpler, pseudo-first-order kinetics. Results indicated that, degradation rate was strongly dependent on the initial concentrations of Fe^{2+} or Fe^{3+} , H_2O_2 and initial pH of the solution.

Visible light-assisted photo-Fenton-like oxidation of a mono-azo dye, Acid Red 88, has been carried out by Madhavan et al. (2008) in presence of Cu^{2+} or Fe^{3+} ions as the catalyst and oxone (as an alternative oxidant to H_2O_2). Decolorization of Acid Red 88 in Cu^{2+} /oxone system was found to follow zero-order kinetics with respect to the dye and first-order kinetics when Fe^{3+} /oxone system was employed. In both the cases, the decolorization of dye was found to be accelerated with increasing concentrations of metal-ions in solution. A rapid decolorization and TOC removal rates obtained with Fe^{3+} reveal Fe^{3+} as the efficient catalyst over Cu^{2+} ion for the photocatalyzed degradation of Acid Red 88 in presence of oxone.

Aguiar and Ferraz (2007) used several phenol derivatives in combination with Fenton-like reagent ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Cu}^{2+}/\text{H}_2\text{O}_2$) in the degradation of an azure dye, Azure B. The reaction system composed of 3-hydroxyanthranilic acid/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was able to degrade Azure B at higher levels than the conventional Fenton reaction (87% and 75% of decolorization after 20 min reaction, respectively). On the other hand, gallic and syringic acids, catechol and vanillin induced Azure B degradations remained lower as compared with conventional Fenton reaction. Azure B was not degraded in the presence of 10% (v/v) methanol or ethanol, which are $\bullet\text{OH}$ radical scavengers.

Ntampeglitis et al. (2006) investigated decolorization kinetics of three commercially used Procion H-ex1 dyes using a Fenton-like reagent in their study. The effect of the major system parameters (pH, concentrations of H_2O_2 , Fe^{3+} and dye) on the kinetics was determined. Experimental results indicated that at an optimum range of parameters, the mineralization rate is very slow for the Fenton-like process whereas it increases significantly for the photo-Fenton-like process. Also

increase in biodegradability, which is expressed by the BOD/COD ratio, found to be higher in photo-Fenton-like case as compared with dark Fenton-like.

Study of Hsueh et al. (2005) assessed Fenton and Fenton-like reactions at low iron concentration ($\leq 10\text{mg/L}$) to oxidize three commercial azo dyes, namely Red MX-5B, Reactive Black 5 and Orange G. Experimental results indicated that both of the Fenton and Fenton-like processes can achieve complete decolorization. Effect of Fe^{2+} , Fe^{3+} and H_2O_2 concentrations as well as the solution pH on reaction efficiency was investigated and it has been found that increasing dose of iron enhances the dye decolorization whereas high levels of H_2O_2 appear to reduce dye decolorization because of the scavenging effect.

Fernandez et al. (2004) studied treatment of azo-dye Orange II, using oxone in solutions with Co^{2+} ions, in the dark and under light. Results indicated that photobleaching of the dye under Xe-light was faster than the dark process. The beneficial effect of O_2 during the mineralization of Orange II due to the formation of peroxide radicals was noticed when solutions containing Co^{2+} /oxone were purged with O_2 as is the case in Fenton-like reactions.

The study of Neamtu et al. (2003) evaluated the degradation of Reactive Yellow 84 and Reactive Red 120 reactive dyes by photo-Fenton and Fenton-like oxidation processes. The effects of different reaction parameters on treatment efficiency were assessed and effective system conditions were found to be pH of 3, hydrogen peroxide-to-iron molar ratio of 20:1 and UV or solar irradiation.

Treatment of Dyes with Heterogeneous Fenton-like and Photo-Fenton-like Systems

As aforementioned, homogenous Fenton and photo-Fenton systems are very efficient methods of organic wastewater treatment with high rates of oxidation. However homogenous systems suffer from the tight range of pH and difficulties in catalyst separation and reuse at the end of the treatment (Chen and Zhu, 2006). To overcome these drawbacks, heterogeneous catalysts for Fenton and photo-Fenton type processes were developed.

In heterogeneous systems, the catalyst loaded with irons can be reused for further runs and range of reaction pH is extended, in addition to the minimization of the sludge containing Fe ions (Cheng et al., 2004; Feng et al., 2004). In this context, the degradation of organic contaminants using heterogeneous Fenton and photo-Fenton

catalysts might be preferable in some cases; such as the in situ remediation of contaminated groundwater and soils, where the initial acidification may be costly and destructive (Hanna et al., 2008). The ideal heterogeneous catalyst should be cheap, suitable for wide range of pH, has good catalytic activity and low catalyst leaching (Chen and Zhu, 2006). On the other hand it should be noted that the rate of organic matter oxidation with heterogeneous systems is generally slower as compared with the homogenous process, due to the mass transfer limitation.

Decolorization of an anthraquinone dye, Reactive Brilliant Blue by hydrogen peroxide was examined by Chen et al. (2008) using Fe-containing NaY and ZSM-5 zeolites as heterogeneous Fenton-like catalysts. The results showed that Fe-containing zeolites generally exhibited similar or better catalytic efficiency compared with homogeneous Fenton reagent, with Fe-containing ZSM-5 being more efficient. Under the conditions of initial pH 2.5, 30.0 mM H_2O_2 and 4.0 g/L ZSM-5 catalyst, 250 mg/L dye could be decolorized over 90% within 20 min.

Hanna et al. (2008) studied the catalytic activity of four mineral oxides (quartz/amorphous iron(III) oxide $\{Q_1\}$, quartz/maghemite $\{Q_2\}$, quartz/magnetite $\{Q_3\}$ and quartz/goethite $\{Q_4\}$) by employing methyl red as a model compound for the Fenton-like oxidation at pH 5 and 7. It was found that catalytic activities of the synthesized mixed oxides followed the order $Q_4 > Q_1 > Q_2 > Q_3$ at pH 5, while the trend is modified as $Q_4 > Q_3 > Q_1 > Q_2$, at pH 7.

Photo-assisted Fenton mineralization of an azo dye Acid Violet 7 was studied by Muthuvel and Swaminathan (2007) using a Fe^{3+} loaded Al_2O_3 as a heterogeneous catalyst in the presence of H_2O_2 and UV-A light. The photocatalytic activity of the heterogeneous process was compared with its corresponding homogenous system. Initial dye degradation rate was found to be faster in homogenous process whereas the time taken for complete degradation was almost the same for both systems.

Souza et al. (2007) investigated the decomposition of a basic dye, methylene blue, using a thermal treated limonite (a natural ore comprised of hydrated iron (III) oxides) under H_2 flow. Results showed that the main iron oxides phases in the thermal treated material were goethite and magnetite. Methylene blue was successively oxidized, indicating that the efficient generation of highly reactive hydroxyl radicals ($\bullet\text{OH}$) from the reaction of H_2O_2 on the catalysts surface.

The study of Ramirez et al. (2007) evaluated the degradation and mineralization of Orange II solutions, using catalysts based on pillared saponite clay impregnated with several iron salts (Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate). The experimental results exhibit that these solids present good properties for the treatment of dye, allowing to reach, in the best conditions and after 4 h of oxidation, 99% of dye degradation with 91% of TOC reduction (at 70 °C).

The study of Ferraz et al. (2007) investigated the reactivity of the heterogeneous Fenton system $\text{H}_2\text{O}_2/\text{HCOOH}$ over an iron oxide surface. A reactive textile dye Drimaren Red was used as a model pollutant. Experimental results showed that HCOOH and H_2O_2 interact to produce the pair $\text{H}_2\text{O}_2/\text{HCOOH}$ which leads to the formation of $\bullet\text{OH}$ radical more strongly than H_2O_2 alone, thus enhancing the degradation of the reactive dye.

In the study of Chen and Zhu (2006), Hydroxyl-Fe-pillared bentonite was used as a solid catalyst for photo-Fenton treatment of azo-dye Orange II. Almost 100% discoloration and more than 60% TOC removal could be achieved after 120 minutes treatment. Hydroxyl-Fe-pillared bentonite catalyst showed good stability during dye degradation in a wide range of pH (3.0–9.5), because of its strong surface acidity.

The photodegradation of azo dye Orange I using heterogeneous iron oxide-oxalate complex system in the presence of UV-A light was studied by Lei et al. (2006). Five iron oxides including γ -FeOOH, IO-250, IO-320, IO-420 and IO-520 were employed. The experimental results indicated that the degradation of Orange I depends strongly on the types of iron oxides, the initial pH value, the initial concentration of oxalate and dye. At the optimal oxalate concentrations, the heterogeneous system utilizing γ -FeOOH showed the best performance in dye degradation.

In the study of Li et al. (2006) Fe pillared bentonite and Al-Fe pillared bentonite were employed as heterogeneous catalysts for the photo-Fenton treatment of azo dye X-3B. The photocatalytic activities of the heterogeneous catalysts were compared with their corresponding homogenous Fenton reagent at the same experimental conditions. It was found that both of the heterogeneous processes showed higher photocatalytic activity than their corresponding homogeneous process.

Lv et al. (2005) assessed the degradation of cationic and anionic dyes using ferric species immobilized on different ionic exchange resins, in the presence of H_2O_2 and visible light irradiation. It was found that for the photodegradation of cationic dyes (malachite green and methylene blue), the immobilized catalyst on a strongly or weakly cationic resin was much more effective than the catalyst supported on an anionic resin, whereas an opposite order in the catalyst activity was observed for the photodegradation of anionic dyes (phloxine and X3B).

Moura et al. (2005) studied the degradation of methylene blue via heterogeneous Fenton system based on $\text{Fe}^0/\text{Fe}_3\text{O}_4$, Fe^0 , Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ composites, to investigate the effect of the $\text{Fe}^{+2}_{\text{surf}}$ species on the oxide surface. It was found that the combination of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ produces a novel and active heterogeneous system in the degradation of the model pollutant.

Degradation of azo dye Orange II using nanostructured catalysts (Fe^{3+} -doped TiO_2 and bentonite clay-based Fe nanocomposite (Fe-B)) have been assessed by Feng et al. (2004). The nanostructured Fe-B catalyst showed a good catalytic activity in the discoloration and mineralization of Orange II in the presence of UV-C light (254 nm) and H_2O_2 at an initial solution pH of 6.60, with negligible leaching of Fe ions from the nanocatalyst.

The study of Feng et al. (2003) illustrates the possibility of photo-assisted degradation of an azo dye Orange II using laponite RD clay-based Fe nanocomposite in the presence of H_2O_2 and UV light (254 nm). Complete discoloration of Orange II was achieved in 45 min whereas mineralization of the dye undergoes a slower kinetics than decoloration (70% TOC removal in 90 minutes).

Treatment of Dyes with Hybrid Systems including Fenton-Like or Photo-Fenton Reagents

Use of Fenton-like/photo-Fenton-like reagents in combination with ozone or TiO_2 mediated heterogeneous photocatalysis, for the degradation of dye molecules have been investigated in several scientific studies.

Wu (2008) assessed the decolorization of Reactive Red 2 using ozone-related, Fenton-like-related and ozone/Fenton-like hybrid systems in his study. The decolorization rate constants were found to be consistent with pseudo-first-order kinetics and they followed the order of $\text{UV}/\text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{3+}$ (5.78 h^{-1}) > $\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$

$(5.33 \text{ h}^{-1}) > \text{UV/ H}_2\text{O}_2/\text{Fe}^{3+} (4.59 \text{ h}^{-1}) > \text{UV/ H}_2\text{O}_2 (4.08 \text{ h}^{-1}) > \text{UV/ O}_3 (2.91 \text{ h}^{-1}) = \text{O}_3 (2.91 \text{ h}^{-1}) \geq \text{UV/ O}_3/\text{Fe}^{3+} (2.90 \text{ h}^{-1}) > \text{O}_3/\text{Fe}^{3+} (2.42 \text{ h}^{-1}) > \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{3+} (2.03 \text{ h}^{-1}) > \text{O}_3/\text{H}_2\text{O}_2 (1.42 \text{ h}^{-1})$, at pH = 7.

A combined homogeneous and heterogeneous photocatalytic decolorization and degradation of an azo dye Reactive Orange 4 have been carried out by Selvam et al. (2007) using ferrous sulphate/ferrioxalate with H_2O_2 and TiO_2 -P25 nanoparticles. UV/ferrioxalate/ H_2O_2 / TiO_2 system found to be the most efficient among all the combinations. Efficiency of the UV/ Fe^{3+} / H_2O_2 / TiO_2 process was also higher than the efficiencies of individual photo-Fenton and UV/ TiO_2 -P25 processes.

The degradation of Acid Red 88 azo dye in water was studied by Dominguez et al. (2005) using 21 oxidation processes, which could be grouped in three categories: processes deriving from the heterogeneous photocatalysis (using TiO_2), oxidation systems based on Fenton-type reactions (homogeneous photocatalysis) and processes based on the application of ozone. Among the investigated processes, O_3/TiO_2 system obtained the fastest decolorization with 95% color removal in only 3 min. On the other hand, taking into account the TOC and COD reductions, ozone-photo-Fenton system could be considered as the most effective process with 60% and 82% removal efficiencies respectively, within a 1 hr treatment time.

The effects of Fe^{3+} species on the photocatalytic degradation of azo dye Acid Red 1 in TiO_2 aqueous suspensions under irradiation in the 315–400 nm range have been studied by Mrowetz and Selli (2004). The initial increase of the photocatalytic degradation rate observed in water suspensions containing Fe^{3+} aquo ions was attributed to the increased amount of dye adsorbed on the iron(III)-modified semiconductor surface.

Kositzi et al. (2004) compared the efficiency of photo-Fenton-like system with two different TiO_2 modifications with oxidants (H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$) in decolorization and dissolved organic content reduction of two selected synthetic textile wastewater. The photo-Fenton-like process is found to be considerably faster than TiO_2 /oxidant system in both types of wastewater.

Lee et al. (2003) investigated the photodegradation of an acid dye, Acid Red 114 in the presence of Fe^{3+} , TiO_2 particles, and H_2O_2 . The effect of initial pH and Fe^{3+} , TiO_2 , H_2O_2 concentrations on reaction rate were studied and it was found that dye

removal was increased with the increasing Fe^{3+} , H_2O_2 and TiO_2 concentrations. The removal rate at pH 2.5 was found to be higher than any other; pH 3.5, 5.5, and 8.5.

Ferrioxalate mediated Photo-Fenton-like Treatment of Dyes

Studies about application of ferrioxalate in the photo-Fenton reaction to degrade textile dyes were also available in the related scientific literature. Monteagudo et al. (2008) investigated decolorization and mineralization of the azo dye Orange II solutions by solar photo-Fenton and ferrioxalate-assisted solar photo-Fenton processes. The results reveal that the addition of oxalic acid to solar photo-Fenton system improves the photocatalytic efficiency since ferrioxalate complexes absorb strongly and a higher portion of the solar spectrum can be used. Ferrioxalate-assisted solar photo-Fenton processes permits the use of an iron concentration below the discharge legal limit according to European Union (2 ppm) and oxalic acid can be used to pH adjustment, reducing the operation costs of Fe removal and chemicals. Duran et al. (2008) was also compared solar photo-Fenton and ferrioxalate assisted solar photo-Fenton processes in degradation of Reactive Blue 4 solutions. The ferrioxalate mediated process again found to be increasing the degradation rate of Reactive Blue 4, due to the reasons aforementioned.

Carnerio et al. (2007) investigated oxidation of Reactive Blue 4 by ferrioxalate-photo-Fenton process. The effect of initial dye, ferrioxalate and H_2O_2 concentrations on the dye degradation was investigated and best treatment performance was obtained using 1.0 mM ferrioxalate and 10 mM of H_2O_2 . Under these experimental conditions, TOC and color removal efficiencies were found to be 80% and 100%, for 0.1 mM RB 4 in 35 minutes of solar irradiation.

The study of Huang et al. (2007) examined the treatment of Reactive Black B, using ferrioxalate in the presence of hydrogen peroxide with UV irradiation. Treatment efficiencies of ferrioxalate/ H_2O_2 /UV and Fe^{3+} / H_2O_2 /UV processes were compared. Experimental results indicated that applying oxalate increases both the Reactive Black B removal efficiency and the COD removal from 68% and 21% to 99.8% and 71%, respectively.

Lucas and Peres (2007) investigated the photodegradation of an azo dye Reactive Black 5 via Fenton/UV-C and ferrioxalate/ H_2O_2 /solar light processes. Fenton/UV-C process found to be more efficient than the ferrioxalate/ H_2O_2 /solar light system in

both decolorization and mineralization of the reactive dye. 98.1% color and 46.4% TOC reduction could be achieved with Fenton/UV-C after 30 minutes treatment, while the color and TOC removal efficiencies of ferrioxalate/H₂O₂/solar light were found to be 93.2% and 29.6%, respectively.

Study of Nogueira et al. (2005) assessed the influence of iron sources, Fe(NO₃)₃ and ferrioxalate, on the photo-Fenton degradation efficiency of the dye malachite green. Experimental results indicated that degradation of the dye showed a slight improvement when ferrioxalate was used as an iron source.

2.9. RSM Applications in the Treatment of Dyes and Textile Effluents

RSM has been recently applied as a statistical tool for evaluation of individual and interaction effects of several operating parameters on treatment of dyes and dye-containing wastewater. Since RSM has proven to be a reliable statistical tool in the investigation of chemical treatment processes (Myers and Montgomery, 2002), it is widely utilized for optimization of the process parameters in AOPs, where a large number of variables influencing the system feature.

Monteagudo et al. (2008) employed RSM in the optimization of decolorization and mineralization of Orange II solutions by solar photo-Fenton and ferrioxalate-assisted solar photo-Fenton reactions. The effect of initial Fe(II), oxalic acid, H₂O₂ and dye concentrations and solution pH on color, TOC and COD removal efficiencies were investigated. Optimum conditions were found to be [H₂O₂] = 450 ppm, [Fe(II)] = 1.6 ppm, [Orange II] = 25 ppm, pH 3 for solar photo-Fenton system and [H₂O₂] = 120 ppm, [Fe(II)] = 2 ppm, [Orange II] = 25 ppm, pH 3.25, [H₂C₂O₄] = 13.3 ppm for ferrioxalate assisted solar photo-Fenton system. Under these optimum conditions, ferrioxalate assisted process showed a better treatment performance in terms of COD and TOC removals.

Aleboyeh et al. (2008) aimed to apply RSM in the optimization of Acid Red 14 decolorization by electrocoagulation process. Simple and combined effects of current density, time of electrolysis and initial pH on the color removal efficiency was evaluated. The optimum current density, time of electrolysis and initial pH of the solution were found to be 102 A/m², 4.47 min and 7.27, respectively. Under the optimal conditions, 91% color removal was obtained.

Rauf et al. (2008) investigated decolorization of Acid Red 94 via UV radiation in the presence of H_2O_2 . RSM was employed to assess the interactive effects of dye and H_2O_2 concentration and pH, on decolorization efficiency. The maximum dye decolorization was determined as 90% with 0.005 mM dye, at optimum 0.042 M H_2O_2 and optimum pH 6.6.

Körbahtı and Rauf (2008 a) applied RSM in order to evaluate the effect of dye and H_2O_2 concentrations and pH in the photolytic degradation of Basic Red 2 via UV radiation in the presence of H_2O_2 . A maximum of 85% dye degradation was determined with 5 μM BR2 and 1.67mM H_2O_2 at pH 7.6.

Körbahtı and Tanyolaç (2008) assessed the effects of pollution load, applied potential, electrolyte concentration, reaction temperature and reaction time in the electrochemical oxidation of simulated textile wastewater. In a specific batch run under the optimum conditions predicted by RSM; COD, color and turbidity removals were realized as 61.6%, 99.6% and 66.4%, respectively.

The study of Sleiman et al. (2007) evaluated the photocatalytic degradation of an azo dye Metanil Yellow using TiO_2 as photocatalyst under UV irradiation. An experimental design based on RSM was applied with the aim of evaluating the individual and interaction effects of dye concentration, TiO_2 concentration, pH and light flux on the treatment efficiency and optimizing the operational conditions for the removal of dye.

The study of Caliman et al. (2007) assessed the photocatalytic degradation of Alcian Blue 8 GX dye in aqueous suspensions containing the commercial catalyst TiO_2 -P25. The effect of catalyst and oxidizing agent concentration, initial pH of the solution and UV exposure time upon the rate of photocatalytic degradation was assessed by the use of the RSM. At the optimum conditions (H_2O_2 concentration = 191.6 mg/L, pH 5.26, t = 26.3 min of irradiation) 100% conversion was achieved.

Cho and Zoh (2007) applied RSM in the optimization of photocatalytic degradation of Reactive Red 120 in their study. The reactions were mathematically described as the function of TiO_2 amount, dye concentration and UV intensity. 100% color and 67.27% TOC removal was achieved under the optimized conditions.

Study of Körbahtı and Rauf (2008 b) assessed decolorization of toluidine blue in the presence of UV radiation and heterogeneous hybrid catalyst (titanium oxide

impregnated with vanadium oxide). The optimum removal conditions were determined as 26.5 mg/20 mL V_2O_5/TiO_2 catalyst concentration at pH 7.7, and complete decolorization was achieved at 50 μ M TB concentration under these conditions.

Secula et al. (2008) employed RSM for optimization of the photocatalytic decolorization of a simulated dyestuff effluent containing the azo dye Reactive Black 5. The reactions were mathematically described as the function of the independent parameters of TiO_2 , Fe^{3+} and H_2O_2 concentrations. Under the optimum conditions established, the performance of 99.3% color removal was experimentally reached.

RSM was used by Körbahtı (2007) in order to evaluate the interactive effects of process parameters in the electrochemical treatment of textile dye wastewater, containing Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes. Complete dye removal was obtained under optimized conditions of 6.7 mA/cm², 5.9 mA/cm² and 5.4 mA/cm² current density and 3.1 g/L, 2.5 g/L and 2.8 g/L electrolyte concentration for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive textile dyes, respectively.

Körbahtı et al. (2007) investigated the electrochemical oxidation of water-based paint wastewater and used RSM to assess the individual and interaction effects of potential difference, reaction temperature and electrolyte concentration on COD, color and turbidity removal efficiencies. At the optimum conditions (8V potential difference, 30 °C reaction temperature and 35 g/L external electrolyte concentration) complete color and turbidity removals and 51.8% COD removal were achieved.

The decolorization of a strong colored azo dye solution of cationic red X-GRL by wet air oxidation was studied by Lei et al. (2007). RSM was used to investigate the effect of pH, temperature and oxygen amount on dye degradation. Under the optimum reaction conditions, 97% color removal could be achieved experimentally.

An experimental design based on RSM was applied by Sudarjanto et al. (2006) to evaluate the interactive effects of UV irradiation time, initial H_2O_2 dosage and recirculation ratio of the system on decolorization efficiency of the integrated chemical–biological treatment system (advanced oxidation by UV/ H_2O_2 followed by aerobic biodegradation). Maximal color degradation performance of 99% was

obtained under the optimum conditions of 30 min UV irradiation, 500 mg/L H_2O_2 and no recirculation.

Arantes et al. (2006) studied the decolorization of a biodegradation-resistant polymeric dye by chelator-mediated Fenton reactions. Central Composite Design was performed with the aim of evaluating the effects of chelator, Fe^{3+} , H_2O_2 concentrations and pH and optimizing the dye decolorization. At optimum conditions complete decolorization and chemical degradation of the 150 mg/L dye was observed in 3 hr.

Liu and Chiou (2005) studied the decolorization of Reactive Red 239 by TiO_2 with UV light. RSM was applied to optimize four independent parameters, UV light intensity, the concentration of TiO_2 , initial pH and stirring speed, in the photocatalytic degradation process of the dye. At optimized conditions (UV light intensity, 16.08 W/m^2 ; TiO_2 concentration, 3.06 g/L; initial pH, 2.64; stirring speed, 880 rpm) the maximal decolorization efficiency of 99.82% was achieved.

Muthukumar et al. (2004) studied the effect of ozone treatment for Acid Red 88 dye effluent and used RSM to optimize the parameters of salt concentration, pH and reaction time on color and COD removal efficiency. The increasing decoloration efficiency is obtained with increasing treatment time and decreasing salt concentration. At neutral pH, the efficiency of ozone found to be low in terms of decoloration when compared with that at acidic and alkaline pH.

Fernandez et al. (2004) used RSM to investigate the effect of pH and H_2O_2 addition on the decolorization and mineralization of Orange II in a photoreactor using TiO_2 -coated glass rings as immobilized photocatalyst. The results showed that decolorization is optimal at low pH values and does not significantly depend on the H_2O_2 concentration within the experimental ranges.

Lizama et al. (2002) studied photocatalytic discoloration of Reactive Blue 19 in aqueous suspensions containing TiO_2 or ZnO as catalysts. RSM was applied to evaluate the interactive effects of pH, amount of catalyst and dye concentration on process efficiency and for process optimization. Under optimized conditions, ZnO showed greater degradation activity than TiO_2 .

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Acid Red 183

Chromium(III)-complex mono azo dye Acid Red 183 (AR 183) was selected as the model dye pollutant due to its well-known molecular structure and other physicochemical features (its Cr content, relatively low molecular weight, etc.). AR 183 was purchased from Sigma Aldrich and used as received, without any purification. Dye has a molecular formula of $C_{16}H_{11}ClCrNa_2O_8S_2 \cdot nCr(III)$ with the following physicochemical properties: molecular weight = $584.84 \text{ g mol}^{-1}$, C.I. Number = 18800 and $\lambda_{\text{max}} = 497 \text{ nm}$. Its molecular structure is depicted in Figure 3.1. Stock dye solution was obtained by dissolving 2-3 g solid dye in 1000 mL distilled water. 100 mg/L aqueous acid dye solutions were prepared by diluting the stock solution for the individual experiments. The initial concentration of AR 183 fixed as 100 mg/L in all experiments, being a typical concentration of acid dyes in real textile wastewaters (Neamtu et al., 2002). 100 mg/L aqueous dye solution has 50 mg/L COD, 13 mg/L TOC and 1.00 cm^{-1} absorbance at λ_{max} .

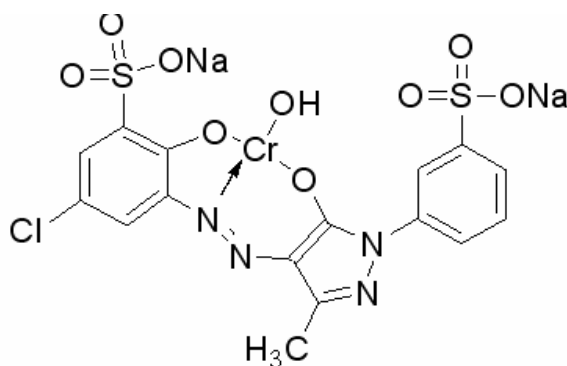


Figure 3.1: Molecular structure of AR 183

3.1.2. Azo Dye Production Wastewaters

Synthetic Acid Blue 193 (AB 193) and Reactive Black 39 (RB 39) production wastewaters were prepared to simulate the effluent from dye synthesis reactor washing. To attain uniformity throughout the optimization experiments, synthetic wastewaters were obtained dissolving the synthesized, raw dye formulations (prior to purification) supplied by a local dye manufacturing company, in distilled water. Synthetic AB 193 production wastewater samples were prepared daily to attain final CODs of 100, 150, 200, 250 and 300 mg/L in the reaction solutions. The studied COD range (100-300 mg/L) was selected considering the process conditions in the dye manufacturing plant (SETAŞ Chemical Company, 2007), while increments of 50 mg/L were determined according to the RSM. Synthetic RB 39 production wastewater was prepared as its COD would be ≤ 200 mg/L, so that optimum photo-Fenton-like conditions determined for initial CODs 150-200 mg/L could be applied. Molecular structures of the chromium(III)-complex diazo dye AB 193 and diazo dye RB 39 were displayed in Figure 3.2.

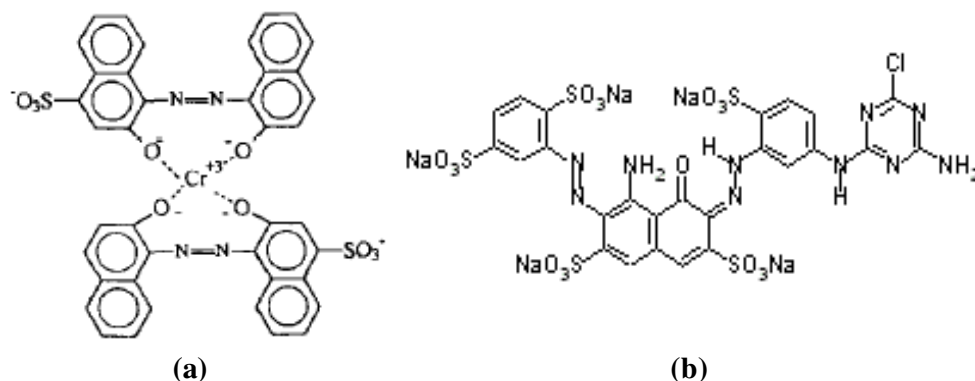


Figure 3.2: Molecular structure of AB 193 (a) and RB 39 (b)

Real dye production wastewater was obtained from a tank containing the filtrate produced in reverse osmosis membrane separation (a process for dye purification) of RB 39. Reverse osmosis (RO) effluent was diluted three times using distilled water in order to have a COD concentration ≤ 200 mg/L. In this way, optimum photo-Fenton-like conditions determined for initial CODs 150-200 mg/L could be applied. Diluted wastewater characteristics were given in Table 3.1 together with the environmental characteristics of synthetic AB 193 and RB 39 dye production wastewaters.

Table 3.1: Environmental characteristics of azo dye production wastewaters

Parameter	Synthetic AB 193 production ww (COD = 200 mg/L)	Synthetic RB 39 production ww (COD = 195 mg/L)	RO effluent of RB 39 production (COD = 165 mg/L)
Absorbance, $\lambda_{\max}$ (cm ⁻¹)	3.512 at 576 nm	9.310 at 611 nm	4.792 at 611 nm
TOC (mg/L)	65	72	66
Cl ⁻ (mg/L)	130	190	3500
pH	6.0	6.0	5.8

3.1.3. Reagents

35% w/v (11.42 M) H₂O₂ (hydrogen peroxide) purchased from Fluka, was stored in a cool room and used as received without any dilution. The iron catalyst source was prepared for daily use by dissolving Fe(NO₃)₃·9H₂O (ferric nitrate nona hydrate), purchased from Fluka, in distilled water to obtain a 10% (w:v) stock solution. In the ferrioxalate-photo-Fenton-like experiments, Fluka-grade K₂(C₂O₄)·H₂O (potassium oxalate monohydrate) was used as the oxalate source and 10% w:v potassium oxalate solution was also prepared daily. Residual (unreacted) H₂O₂ was determined using Peroxide Quant test strips (Aldrich) and Catalase enzyme (from *Micrococcus lyseidicticus*; 1 activity unit (AU) destroys 1 μ mol H₂O₂ at pH = 7 RTP, 200181 AU/mL, Fluka) was employed in order to destroy remaining H₂O₂. Nitric acid and sodium hydroxide solutions of several different molarities were prepared from concentrated, reagent grade HNO₃ (Merck) and NaOH (Merck) solutions by dissolving them in distilled water, and used for pH adjustment at any stage of the experiments.

3.2. Fenton-like and Photo-Fenton-like Treatment

3.2.1. Fenton-like Treatment

Fenton-like oxidation of 500 mL, 100 mg/L aqueous AR 183 was carried out in a 600 mL-capacity pyrex reaction vessel shown in Figure 3.3(a) as follows; first, acid dye solution was prepared daily from the stock solution mentioned above and its pH was adjusted prior to reaction. Then, Fe³⁺ catalyst was added to the reaction vessel which was continuously stirred at a rate of 200 rpm and a sample t=0 was taken. Then dye degradation was started by adding the H₂O₂ to the vessel and samples were taken at regular time intervals during the reaction for up to 40 min. Approximately

25 ml of sample was collected at each time and nearly 5 ml of it was spent for absorbance measurements. The color (absorbance at the peak absorption band for AR 183, e.g. 497 nm) of the sample was measured immediately, whereas the remaining portion was collected in a polyethylene (PE) bottle for TOC measurement. For that purpose, the Fenton-like reaction was ceased by increasing the sample pH to 6-8. In order to make this pH increase immediately after the sample was taken, 0.5-1 mL, 6 M NaOH solution was dropped into all sample bottles previously.

3.2.2. Photo-Fenton-like Treatment

Photo-Fenton-like oxidation of aqueous AR 183 solution and dye production wastewaters were carried out using cylindrical pyrex glass reaction vessels containing 100 mL solution. Irradiation was performed with a 150 W black light bulb UV-A lamp, emitting radiation between 310-390 nm with a maximum emission band at 360 nm. The lamp has an incident light flux of 2.6×10^{-5} Einstein min^{-1} , determined by ferrioxalate actinometry (Hatchard and Parker, 1956). The photoreactor was located inside a box (60×40×55 cm) with its three inner sides covered by mirrors so that the irradiation influx could be well distributed across the reaction vessel (Figure 3.3(b)). Ferric ion was added to the pH adjusted dye solution and a sample $t=0$ was taken under continuous stirring of the vessel at 100 rpm. Then reaction solution was located under the lamp which was turned on 20 min before the start of the reaction to obtain constant light emission, and dye degradation was initiated by the addition of a proper amount of H_2O_2 . Samples were taken regularly during the course of the photochemical experiments for up to 60 min. In order to avoid changes in irradiated volume; the reaction was restarted after each sampling period. Absorbance measurements were done immediately after the samples were taken while COD and TOC values were determined after application of the procedure mentioned in the Fenton-like experiments (pH adjustment followed by filtration).

Ferrioxalate-photo-Fenton-like oxidation of AR 183 solution was performed following the same procedure as the photo-Fenton-like oxidation; with the exception that potassium oxalate was mixed with the ferric iron source at an oxalate to ferric iron molar ratio of 3:1 and thereafter added to the reaction solution.

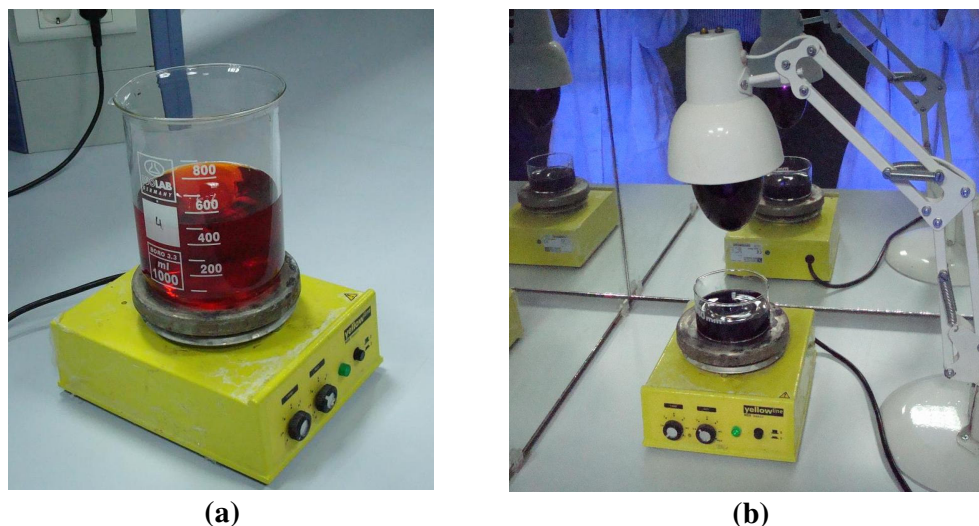


Figure 3.3: Fenton-like reactor (a) and photo-reactor (b)

3.3. Analytical Procedures

All measurements were done at least in duplicate. In the experiments involving AR 183 solution, color and TOC parameters were measured to follow treatment efficiency since the COD content of the aqueous dye solution was too low (< 50 mg/L) to be followed correctly. The photo-Fenton-like treatment efficiency of the synthetic and real azo dye production wastewaters were assessed in terms of color, COD and TOC removal.

3.3.1. Color Measurements

Color was measured in untreated and treated AR 183 solutions in terms of absorbance units at 497 nm ($\lambda_{\max}$), using a Novespec II/Pharmacia LKB colorimeter and 1 cm optical path length reusable glass cells without any pretreatment (i.e. pH-adjustment, filtration) due to the fact that color abatement proceeded very rapidly.

Color of the synthetic and real dye production wastewaters was determined again on the Novespec II/Pharmacia LKB colorimeter and without any pretreatment, at the wavelengths ($\lambda_{\max}$) of 576 nm for synthetic AB 193 production wastewater and 611 nm for synthetic RB 39 production wastewater as well as real RO effluent of RB 39.

The $\lambda_{\max}$ values, at which maximum absorbance in the spectrum occurs, were determined prior to the experiments, using 1 cm optical path length quartz cell with Perkin-Elmer lambda 25 model spectrophotometer.

3.3.2. TOC Measurements

Total organic carbon (TOC) of the aqueous AR 183 solution and dye production wastewaters was determined as a measure of changes in the organic carbon content (extent of mineralization) of the untreated and treated samples. Sample pH was adjusted to between 6-8 prior to TOC analysis as to ensure good $\text{Fe}(\text{OH})_3$ settling. Settled $\text{Fe}(\text{OH})_3$ sludge was removed by filtering the samples through 45 μm -membrane filters (provided by Millipore). The TOC of the sample filtrates was measured on a Shimadzu TC (total carbon) V_{PCN} carbon analyzer equipped with an auto sampler.

3.3.3. COD Measurements

Chemical Oxygen Demand (COD) is defined as the quantity of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD analysis of the untreated and treated synthetic azo dye production wastewaters were conducted according to ISO 6060 (1989) by the closed reflux titrimetric method, while COD of the RO effluent was determined in accordance with DIN 38 409 H 41-2 (Deutsche Normen, 1980) by the open reflux titrimetric method, due to its high chloride content (3500 mg/L). Prior to COD measurement, iron was removed from the sample by $\text{Fe}(\text{OH})_3$ precipitation obtained via pH adjustment (6-8) and filtration through 45 μm -membrane (Millipore) filters. Moreover residual H_2O_2 was destroyed using Catalase enzyme, to avoid the interference which results in misleading measurements.

3.3.4. pH Measurements

In order to determine the pH at any stage of the experiments, a Thermo Orion model 520 pH-meter was employed.

3.4. Experimental Design

An experimental design based on the Response Surface Methodology (RSM) was applied to evaluate the interactive effects of selected process parameters on synthetic AB 193 production wastewater treatment efficiency and optimizing the operating conditions of the treatment process.

RSM is a statistical method useful for the optimization of chemical reactions and/or industrial processes and widely used for the experimental designs (Myers and Montgomery, 2002). The method was introduced by G. E. P. Box and K. B. Wilson in 1951 (Wikipedia-response surface methodology, 2008). In such situations where multiple variables may influence the outputs, it is utilized for exploring the relationships between the outputs and the input variables and optimizing the processes or products (Baş and Boyacı, 2007; Giovanni, 1983). The output is called the response and the input variables are called independent variables.

The main idea of RSM is to use a set of designed experiments to obtain an optimal response. To do this, method employs a low-order polynomial equation in a pre-determined region of the independent variables, which will later be analyzed to locate the optimum values of independent variables for the best response (Ceylan et al. 2008). The optimization of a process by RSM is a faster method for gathering research results than classical one-factor-at-a-time approach since it allows the evaluation of the effect of multiple variables and their interactions on the output variables with reduced number of trials (Alim et al, 2008).

In the present study, Central Composite Design (CDD), which is a widely used form of RSM was employed for the optimization of the photocatalytic process. CDD is an experimental design for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment (Wikipedia-central composite design, 2008). It is an ideal design tool for sequential experimentation and allows testing the lack of fit when an adequate number of experimental values are available (Myers and Montgomery, 2002). In this study, four-factorial and five-level CDD consisting of 26 experimental runs was performed, including two replications at the center point. Initial Fe^{3+} and H_2O_2 concentrations, initial COD of the synthetic AB production wastewater and reaction time were considered as variables (independent factors) while percent color, COD and TOC removal efficiencies were considered as responses (dependent factors). The real values of independent factors and their variation limits were determined basing on the related scientific literature and experimental results obtained in preliminary aqueous AR 183 degradation experiments and were given in Table 3.2. All 26 experimental runs of central composite design were performed in accordance with Table 3.3.

Table 3.2: Experimental range and levels of independent process variables

Process Variables	Code	Real Values of the Coded Levels				
		-2	-1	0	1	2
Initial Fe^{3+} concentration (mM)	X_1	0.5	1.5	2.5	3.5	4.5
Initial H_2O_2 concentration (mM)	X_2	25	35	45	55	65
Reaction time (min)	X_3	0	15	30	45	60
Initial COD concentration (mg/L)	X_4	100	150	200	250	300

Table 3.3: Experimental runs indicated by the model for independent parameters of initial Fe^{3+} , H_2O_2 and COD concentrations and reaction time

	X_1	X_2	X_3	X_4
RUN	Fe^{3+} (mM)	H_2O_2 (mM)	Time (min)	COD (mg/L)
1	1.5	55	15	250
2	2.5	45	30	200
3	2.5	65	30	200
4	2.5	45	30	100
5	2.5	45	0	200
6	3.5	55	15	150
7	3.5	35	45	250
8	4.5	45	30	200
9	3.5	55	45	250
10	3.5	55	45	150
11	1.5	35	45	250
12	1.5	55	15	150
13	1.5	55	45	250
14	1.5	35	15	150
15	3.5	55	15	250
16	2.5	25	30	200
17	2.5	45	60	200
18	3.5	35	45	150
19	0.5	45	30	200
20	3.5	35	15	250
21	2.5	45	30	200
22	2.5	45	30	300
23	1.5	35	45	150
24	1.5	35	15	250
25	3.5	35	15	150
26	1.5	55	45	150

The above described model was also run, selecting $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio as an independent process parameter, instead of individual parameters of Fe^{3+} and H_2O_2 concentrations, in order to evaluate the effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio on treatment performance (color, COD and TOC removal efficiencies) and to obtain an optimum $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio. In Fe-based AOPs, it is important to determine a pollutant specific optimum ratio between H_2O_2 and $\text{Fe}^{2+}/\text{Fe}^{3+}$, since $\bullet\text{OH}$ -scavenging reactions decreasing the oxidation efficiency occur in the presence of an excess of one of the two reagents (Arslan-Alaton and Teksoy, 2007). Table 3.4 shows the experimental design considering the reaction time (A_1), initial COD of the solution (A_2) and $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio (A_3) as the independent variables. The values of A_3 were obtained dividing Fe^{3+} concentrations (X_1) by H_2O_2 concentrations (X_2).

Table 3.4: Experimental runs indicated by the model for independent parameters of reaction time, initial COD and $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio

	A_1	A_2	A_3
RUN	Time (min)	COD (mg/L)	$\text{Fe}^{3+}:\text{H}_2\text{O}_2$ (mM:mM)
1	15	250	0.027
2	30	200	0.056
3	30	200	0.038
4	30	100	0.056
5	0	200	0.056
6	15	150	0.064
7	45	250	0.100
8	30	200	0.100
9	45	250	0.064
10	45	150	0.064
11	45	250	0.043
12	15	150	0.027
13	45	250	0.027
14	15	150	0.043
15	15	250	0.064
16	30	200	0.100
17	60	200	0.056
18	45	150	0.100
19	30	200	0.011
20	15	250	0.100
21	30	200	0.056
22	30	300	0.056
23	45	150	0.043
24	15	250	0.043
25	15	150	0.100
26	45	150	0.027

3.5. Data Analysis

Experimental data were analyzed using Design-Expert 6.0.7 program including ANOVA and fitted to a second-order polynomial model (quadratic polynomial). The following function was employed to attain the interaction between the dependent and independent variables (Cho and Zoh, 2007; Sudarjanto et al.,2006):

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad 3.1$$

In this equation, Y represents the predicted response variable, X_i are the independent variables, b_0 is the constant coefficient and b_i , b_{ii} and b_{ij} are the interaction coefficients.

The quality of the fit of polynomial model was expressed by the value of correlation coefficient (R^2). R^2 provides a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions and it is always between 0 and 1. The closer the R^2 is to 1, the better it predicts the response. (Haaland, 1989)

The model F-value, probability value and adequate precision are the indicators showing the significance and adequacy of the employed model. The model F-value (Fisher variation ratio) is a statistically valid measure of how well the factors describe the variation in the data about its mean. The higher the F-value is from unity, the more certain it is that the factors explain adequately the variation in the data about its mean, and the estimated factor effects are real. (Liu and Chiou, 2005) Probability value (Prob>F) expresses the probability of seeing the observed F-value if the null hypothesis is true (Design-Expert 6.0.7 User's Guide, 2008). It is used to test the significance of the coefficients and beneficial for understanding the pattern of the mutual interactions between the test variables. The smaller the Prob>F, the better significance of the corresponding coefficient (Khuri and Cornell, 1987). Adequate precision measures the signal to noise ratio and a ratio greater than 4 is generally desirable for sound models (Design-Expert 6.0.7 User's Guide, 2008).

The two dimensional contour plots and three dimensional response surface plots, demonstrating the interaction of responses and process variables, were also developed using the same software.

3.6. Optimization Procedure

Simultaneous consideration of multiple responses involves first building an appropriate response surface model for each surface, and then trying to find a set of operating conditions that in some sense optimizes all responses or at least keeps them in desired ranges (Myers and Montgomery, 2002).

The optimal values of the process parameters were obtained by a module in Design-Expert 6.0.7 software, searching for a combination of factor levels that simultaneously satisfy for the requirements placed on each of the responses and factors (Körbahtı et al., 2007). In order to optimize the process, desired goals for each of the response and process parameter should be determined first. These goals can be “maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only)”. In the present study, desired goals were chosen to “maximize” the percent color, COD and TOC removals, while process parameters of initial Fe^{3+} and H_2O_2 concentrations and reaction time were selected to be “within the range”. Then, these individual goals were combined into an overall desirability function by the software for maximization to find the best local maximum (Design-Expert 6.0.7 User’s Guide, 2008).

In the optimization of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio for AB 193 production wastewater having an initial COD of 200 mg/L, independent parameters (reaction time and molar $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio) were chosen as “within the range” again, while desired goals for the response variables (percent color, COD and TOC removal) were kept as “maximize”.

4. RESULTS AND DISCUSSION

4.1. Treatability of Aqueous AR 183 Solution Using Fenton-Like and Photo-Fenton-Like Processes

In the first part of the study, decolorization and mineralization of 100 mg/L aqueous Acid Red 183 (AR 183) solution by Fenton-like, photo-Fenton-like and ferrioxalate-photo-Fenton-like processes were investigated. Fenton-like experiments were conducted at different Fe^{3+} concentrations and initial pHs in order to evaluate the effect of selected process parameters on the treatment efficiency. Photo-Fenton-like and ferrioxalate-photo-Fenton-like oxidations were carried out under the specified experimental conditions, determined basing on the dark Fenton-like experiments. Color and total organic carbon (TOC) concentrations were followed to state and compare the treatment performances of these three Fe-based AOPs.

4.1.1. Effect of Initial Fe^{3+} Concentration

Fe^{3+} concentration has an integral role in the rate and efficiency of the Fenton-like reaction, since it catalyzes the decomposition of H_2O_2 to produce hydroxyl radicals ($\bullet\text{OH}$). $\bullet\text{OH}$ reacts with organic compounds and initiates the degradative oxidation reactions (Safarzadeh-Amiri et al., 1997). To investigate the effect of initial Fe^{3+} concentration on AR 183 oxidation efficiency via Fenton-like reagents, a set of Fenton-like experiments was performed with varying Fe^{3+} concentrations ranging between 0.1-3.0 mM and a fixed initial dye and H_2O_2 concentration (at $\text{pH}_0 = 2.8$, e.g. the optimum pH of Fenton-like processes). The applied initial H_2O_2 concentration was selected basing on the previous experimental findings and preliminary optimization experiments conducted by Arslan-Alaton and Teksoy (2007). It was chosen as 30 mM, an amount that is by far sufficient for the oxidation of the selected dye concentration, but still not too high as to avoid free radical scavenging reactions of H_2O_2 (Tang and Huang, 1996). Likewise, it has also been reported in the scientific literature that Fe^{3+} addition in the range of 1.5-3.0 mM significantly accelerates the (dark) Fenton-like process (Arslan-Alaton et al., 2008;

Arslan-Alaton and Teksoy, 2007). Due to the fact that the recommended $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio is around 1:10 (Dominguez et al., 2005; Neamtu et al., 2003); 30 mM H_2O_2 was considered as the most appropriate concentration for the experimental series. Experimental results were displayed in Figure 4.1 and 4.2 in terms of color and TOC abatement rates, respectively. Percent color and TOC removal efficiencies obtained at different Fe^{3+} concentrations after 20 min Fenton-like treatment were presented in Figure 4.3.

Color Removal

From Figure 4.1 it may be observed that color removal increased by the increasing initial Fe^{3+} concentration, as expected. 98% color removal was achieved after 40 min treatment at the highest examined Fe^{3+} concentration (3.0 mM) with a sharp decrease in the absorbance parameter within the first minutes of the reaction. On the other hand, color abatement exhibited a retardation period at the lower studied Fe^{3+} concentrations. Obviously, curves representing color removal with respect to treatment time at varying Fe^{3+} concentrations as shown in Figure 4.1 did not fit to any reaction kinetic.

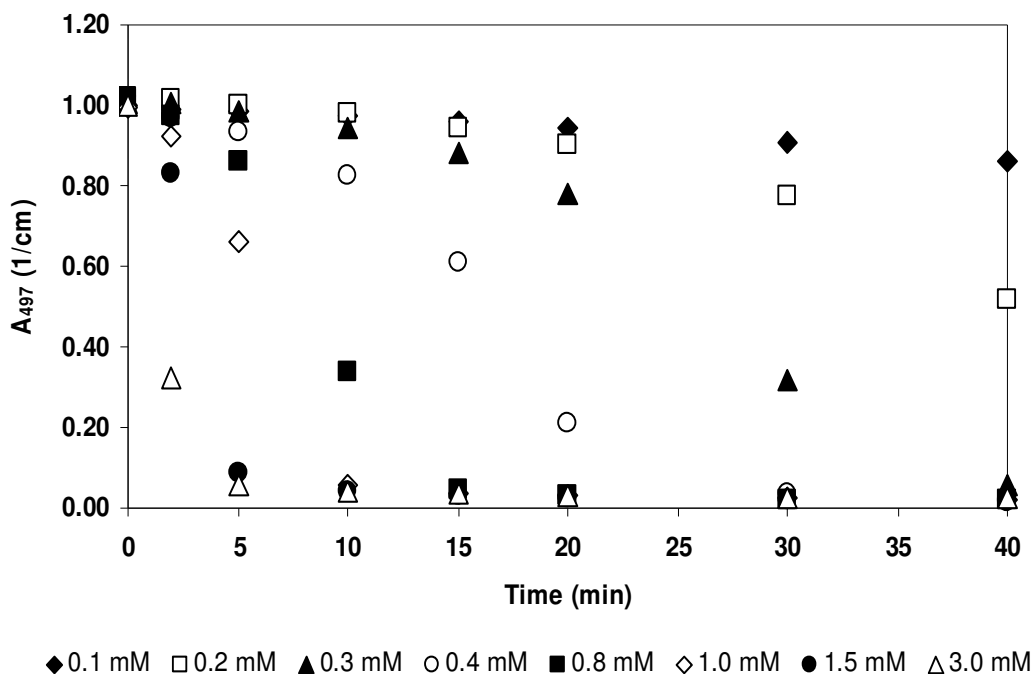


Figure 4.1: Color removals obtained for 100 mg/L aqueous AR 183 at different Fe^{3+} concentrations. Experimental conditions: H_2O_2 ,o = 30 mM; $\text{pH}_0 = 2.8$.

Figure 4.1 reveals that color removal efficiency was relatively low at Fe^{3+} concentrations below 0.3 mM. A significant increase in removal efficiency was observed when the Fe^{3+} concentration was raised to 0.4 mM, and 97% removal was achieved after 20 min treatment when the Fe^{3+} concentration exceeded 0.8 mM. As can be clearly seen in Figure 4.3, the increase in decolorization efficiency practically stopped after 0.8 mM Fe^{3+} , indicating that this particular Fe^{3+} concentration can be accepted as the optimum dose for decoloration under the specified experimental conditions.

TOC Removal

From Figure 4.2 it is evident that at least 3 mM Fe^{3+} was required to obtain a significant reduction in the dye's TOC content (56% TOC removal after 40 min treatment). Unsurprisingly, TOC removal efficiency decreased with decreasing Fe^{3+} concentration. As can be seen in Figure 4.3, TOC removal efficiency was always less than 30% when the Fe^{3+} concentration was ≤ 1.0 mM, and increased to 31% and 53% for 1.5 mM and 3 mM Fe^{3+} , respectively. Naturally, TOC removal was not as distinct as color removal since complete mineralization of dye molecules is rather limited and the TOC parameter only elucidates the mineralization (ultimate oxidation) step of the reaction. It is expected that the dye molecules mostly decomposed to intermediate oxidation products (aromatics with different functional groupings, carboxylic acids, etc.) during Fenton-like oxidation. From Figure 4.2 it can be observed that TOC values diminished faster within the first minutes of the reaction that is attributable to H_2O_2 depletion (Perez et al., 2002), completion of the fast decoloration reaction, as well as the accumulation of advanced oxidation intermediates that react with the free radicals at relatively slower rates than the dye molecules. Consequently TOC abatement rates decreased with the passage of time.

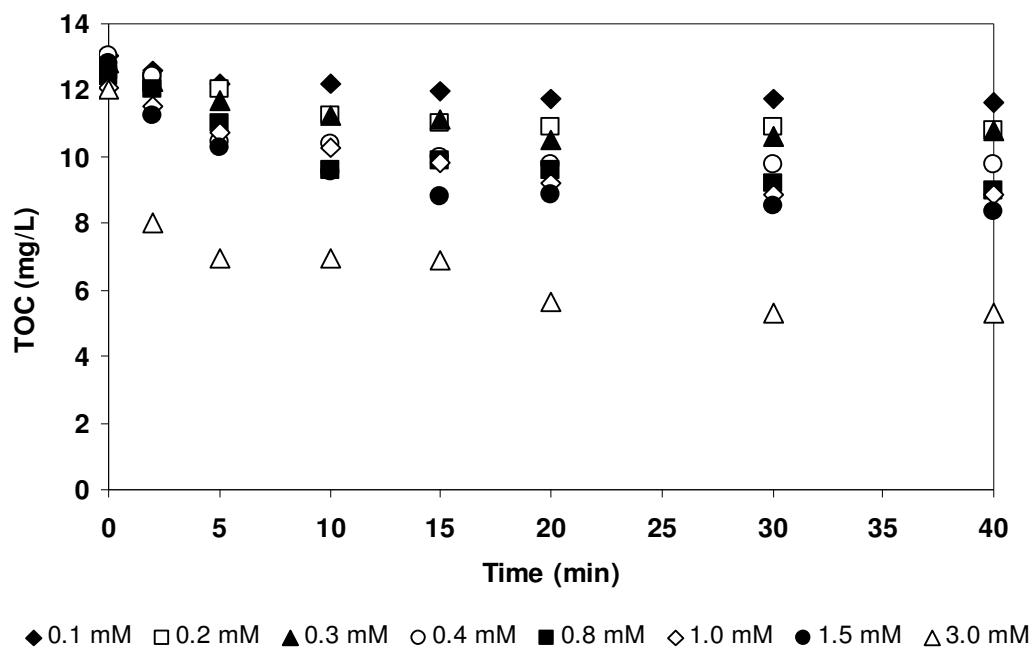


Figure 4.2: TOC removals obtained for 100 mg/L aqueous AR 183 at different Fe^{3+} concentrations. Experimental conditions: $\text{H}_2\text{O}_{2,0} = 30 \text{ mM}$; $\text{pH}_0 = 2.8$.

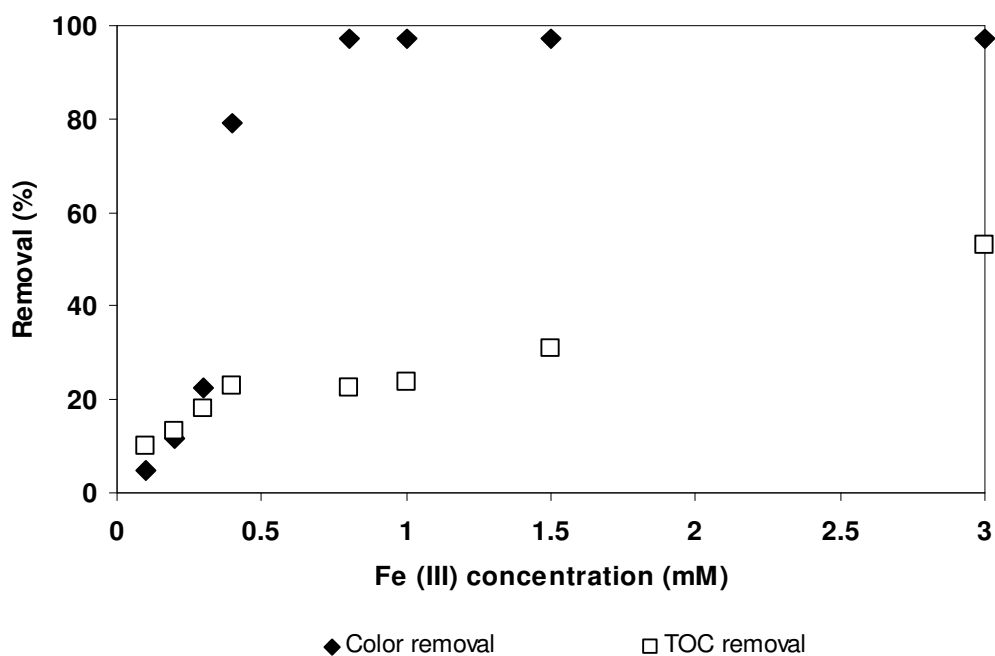


Figure 4.3: Percent color and TOC removal efficiencies obtained for 100 mg/L aqueous AR 183 at different Fe^{3+} concentrations. Experimental conditions: $\text{H}_2\text{O}_{2,0} = 30 \text{ mM}$; $\text{pH}_0 = 2.8$.

4.1.2. Effect of Initial pH

Fenton-like oxidation rate is a strong function of solvent (water) pH and being favored by the acidic pH conditions (2-5) with an optimum range of pH=2.8-3.0 (Pignatello, 1992). In the present investigation, the effect of initial pH on the degradation of 100 mg/L aqueous AR 183 by the Fenton-like process was also investigated. Experiments were carried out at initial pH's varying 2-7 (other experimental conditions were fixed at $\text{Fe}^{3+}_{,0} = 0.8 \text{ mM}$, $\text{H}_2\text{O}_2_{,0} = 30 \text{ mM}$) and the obtained results were depicted in terms of color and TOC abatement rates.

Color Removal

As expected, highest color removal was observed at around $\text{pH}_0 = 2.8$ at which Fenton-like treatment has proven to be highly efficient (see Figure 4.4). On the other hand, there existed a noticeable color reduction still at the initial pH's of 5, 6 and 7, that are known as inappropriate for the Fenton reaction. Likewise, color abatement rates were relatively slow at $\text{pH}_0 = 2.5$ still being close to the optimum Fenton pH. Both of the quite unexpected results can be explained by the step-wise, pH-dependent hydrolysis reactions of Fe^{3+} taking place right after the addition of Fe^{3+} to the aqueous reaction medium (Safarzadeh-Amiri et al., 1996). Following equations are related to the behavior of Fe^{3+} in pure water (Snoeyink and Jenkins, 1980);



From the above equations it can be inferred that Fe^{3+} hydrolysis causes H^+ ion release, leading to Fenton-like reactions occurring at lower pH's than the initially adjusted pH. Since pH is a logarithmic measure of hydrogen ion concentration, the same amount of hydrogen ion release results larger decreases in higher pH's. Hydrolyze reactions also indicate the prompt formation of different ferric hydroxo species play an important role in dark and photochemically assisted Fenton-like processes when the pH exceeds 2. In other words, ferric hydroxo-complexes display a ligand-to-metal charge-transfer (LMCT) absorption band that is thought to be

responsible for the performance of Fenton-like and especially photo-Fenton-like reactions (Safarzadeh-Amiri et al., 1996).

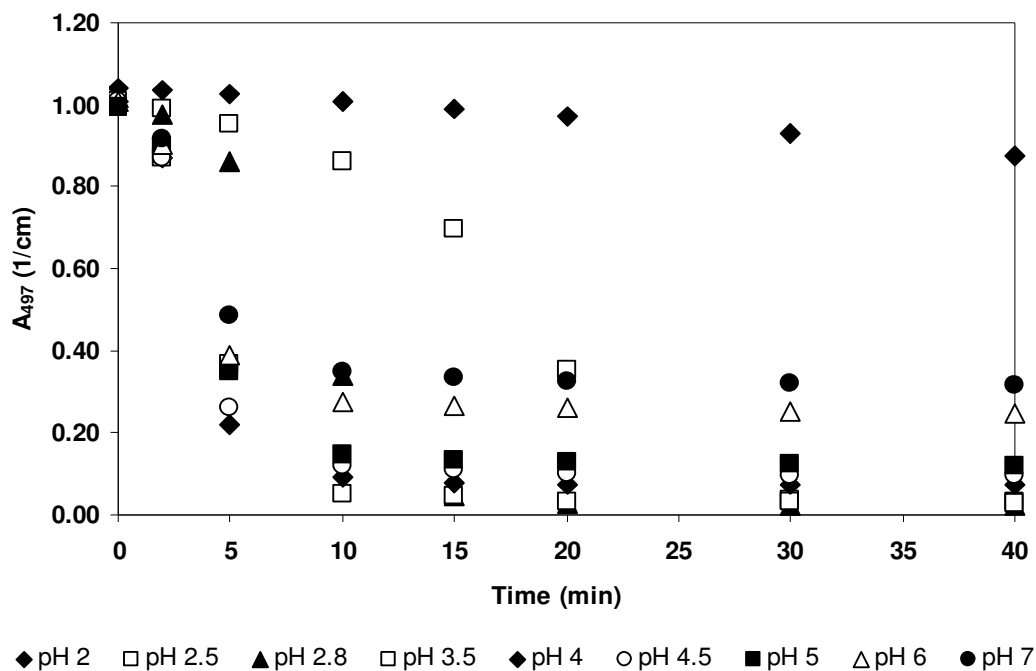


Figure 4.4: Color removals obtained for 100 mg/L aqueous AR 183 at different initial pH's. Experimental conditions: $\text{Fe}^{3+}_{,0} = 0.8 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 30 \text{ mM}$.

TOC Removal

Figure 4.5 reveals that TOC removal showed a parallel trend with color abatement, exhibiting the same highest and lowest removal efficiencies at $\text{pH}_0=2.8$ and $\text{pH}_0=2$, respectively. As expected, TOC removal efficiencies were low as compared with color removal, and closer to each other. Percent color and TOC removal efficiencies obtained after 20 minute Fenton-like treatment at different initial pH's were presented in Figure 4.6. TOC removal was found 20% at the initial pH's 2, 6 and 7, and achieved its maximum value (29%) in the pH range 2.8 - 4.5, where the pH immediately dropped to the values 2.6-3.1 after Fe^{3+} addition to the aqueous dye solution, indicating that in this particular pH range AR 183 oxidation via Fenton-like process exhibited a maximum performance. It is also important to note here that the pH range 3-5 is also the recommended application pH for nylon dyeing with acid dye formulations (Arslan-Alaton and Teksoy, 2007).

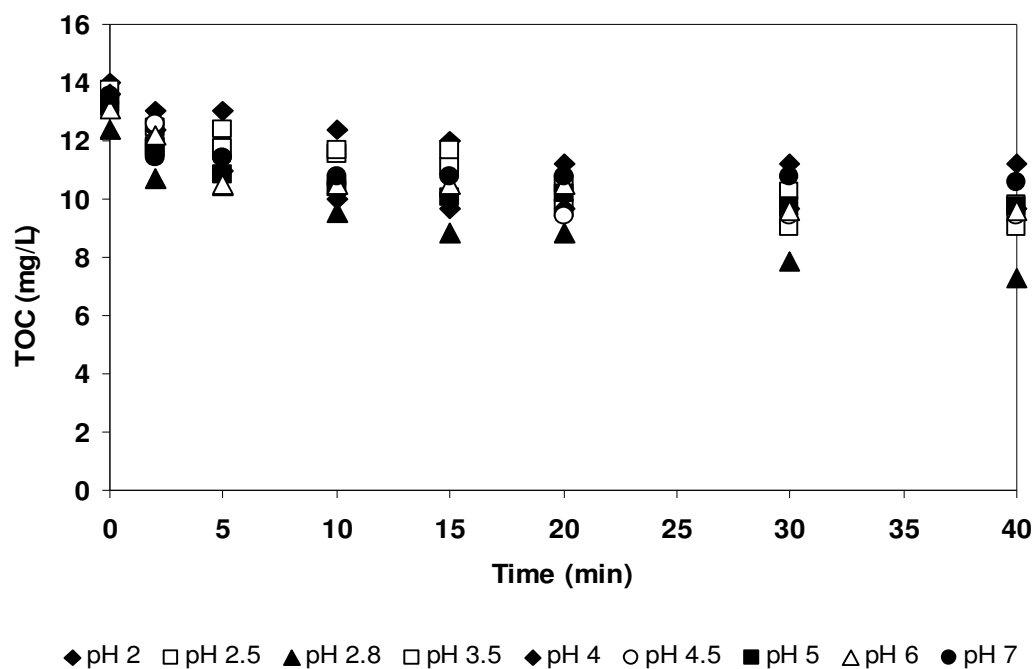


Figure 4.5: TOC removals obtained for 100 mg/L aqueous AR 183 at different initial pH's. Experimental conditions: $\text{Fe}^{3+}_{,0} = 0.8 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 30 \text{ mM}$.

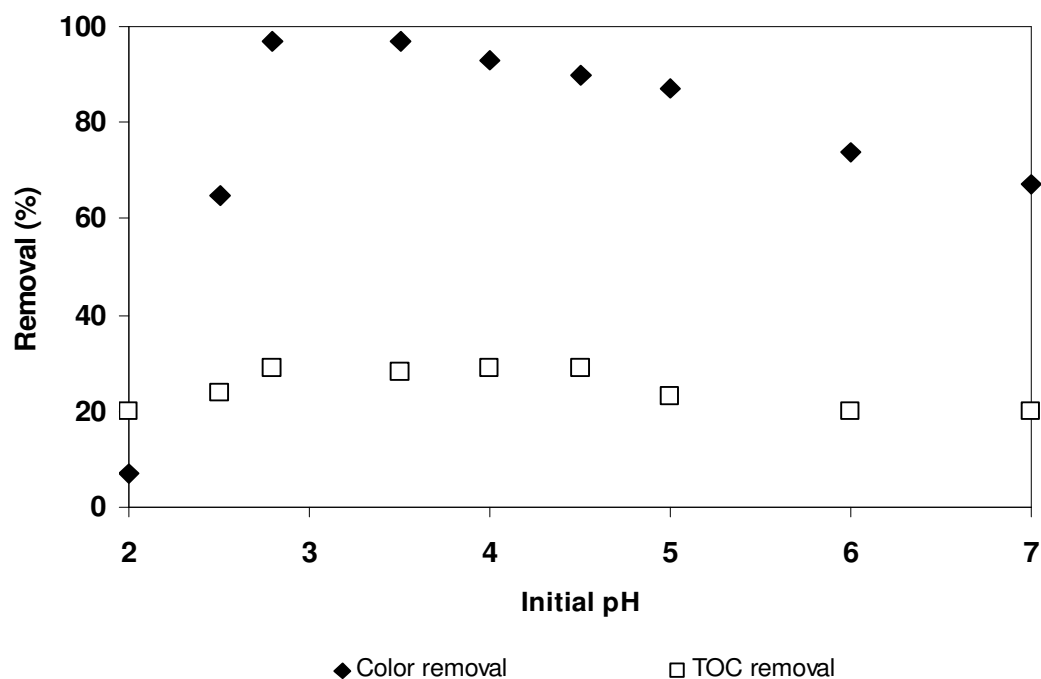


Figure 4.6: Percent color and TOC removal efficiencies obtained for 100 mg/L aqueous AR 183 at different initial pH's. Experimental conditions: $\text{Fe}^{3+}_{,0} = 0.8 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 30 \text{ mM}$.

4.1.3. Effect of UV-A Light

Photo-Fenton-like experiments were conducted in order to examine the effect of UV-A light irradiation on Fenton-like oxidation of aqueous AR 183. Considering the maximum emission band of our light source at 350 nm, a quantum yield of approximately 0.017 mol Fe^{2+} /mol photon is theoretically expected for Fe^{2+} formation via photochemical reduction of Fe^{3+} (Safarzadeh-Amiri et al., 1996). In order to observe the enhancement brought about by UV-A light irradiation, an initial Fe^{3+} concentration of only 0.3 mM was applied, at which the dark Fenton-like treatment would provide a rather low color and TOC removal efficiency.

Color Removal

Decolorization achieved with photo-Fenton-like treatment was illustrated in Figure 4.7 together with the Fenton-like experiment. The accelerating effect of UV-A irradiation on color abatement rate can be observed from the figure.

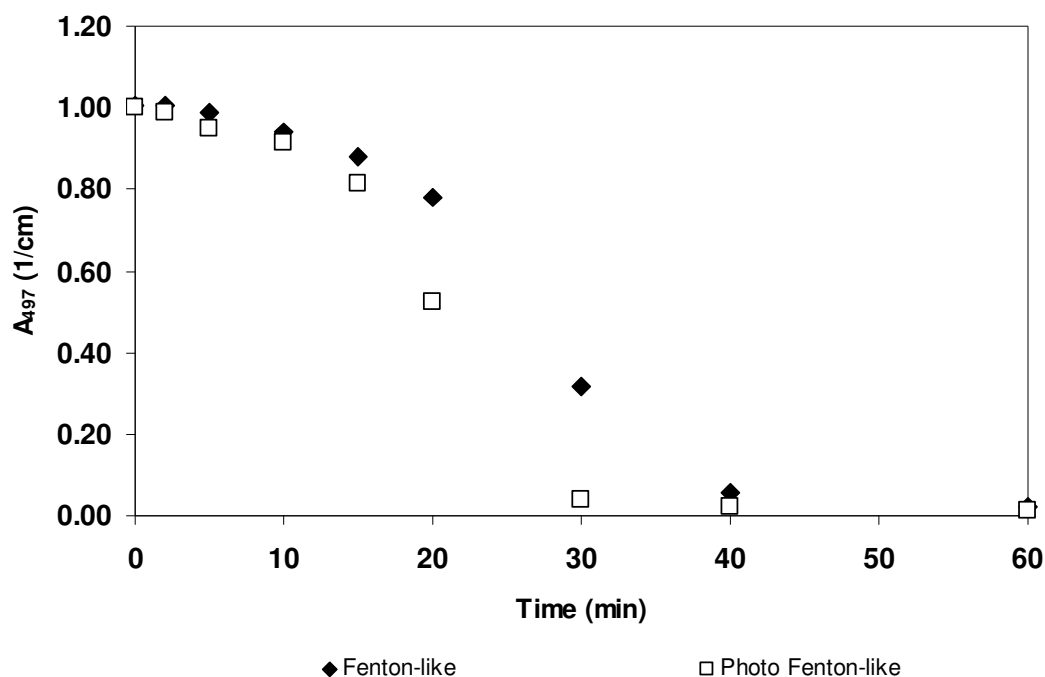


Figure 4.7: Color abatement rates observed for 100 mg/L aqueous AR 183 during Fenton-like and photo-Fenton-like processes. Experimental conditions: $\text{Fe}^{3+}_{,0} = 0.3$ mM; $\text{H}_2\text{O}_{2,0} = 30$ mM; $\text{pH}_0 = 2.8$.

Color removal reached 48% after 20 min oxidation in the presence of UV-A light, whereas the dark Fenton-like treatment resulted in only about 23% color removal under otherwise same experimental conditions. However after 40 min treatment time, the Fenton-like reaction nearly caught the photo-Fenton-like process since the color removal was practically complete after this time period. Since the rate of dye degradation was considerably accelerated with the application of UV-A light, the use of photo-Fenton-like reagent would be beneficial in cases where reaction time is limiting factor.

TOC Removal

UV-A light enhancement of AR 183 degradation via Fenton-like treatment was also noticeable in terms of TOC as shown in Figure 4.8. Although TOC removals were quite low as compared to decolorization efficiencies, it is evident that 14% instead of 6% TOC reduction was found for the photo-Fenton-like process after 20 min reaction. TOC removal reached 32% after 40 min photo-Fenton-like treatment, whereas Fenton-like advanced oxidation could only provide 12% TOC reduction in the same time period at otherwise same reaction conditions.

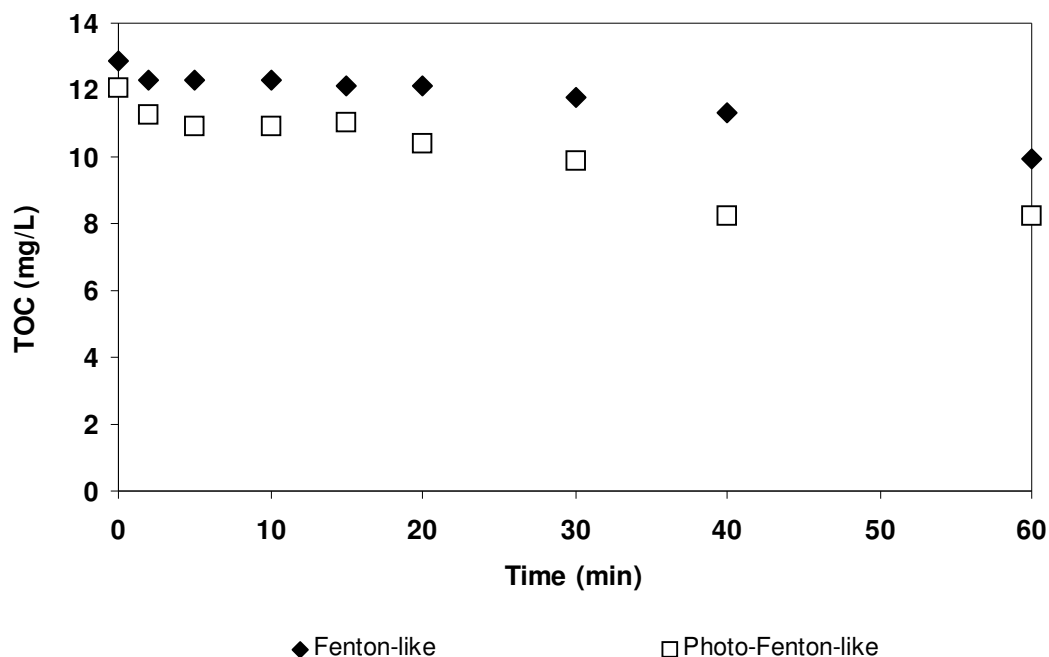


Figure 4.8: TOC abatement rates observed for 100 mg/L aqueous AR 183 during Fenton-like and photo-Fenton-like processes. Experimental conditions: $\text{Fe}^{3+}_{,0} = 0.3$ mM; $\text{H}_2\text{O}_{2,0} = 30$ mM; $\text{pH}_0 = 2.8$.

Separate control experiments were run with 100 mg/L aqueous AR 183 solution using H_2O_2 (30 mM) only, UV-A only, and Fe^{3+} (0.3 mM) combined with UV-A (in the absence of H_2O_2) to observe the effect of oxidant, UV-A and UV-A-induced Fe^{3+} photoreduction on the extend of dye degradation. In other words, these experiments were carried out to check the treatability of AR 183 solution with the individual components of Fenton-like and photo-Fenton-like oxidation systems. Results have indicated that no significant color and TOC elimination was observed in the experiments conducted with H_2O_2 and UV-A alone. In the case of Fe^{3+} + UV-A, very slight color reduction not exceeding 2% was obtained after 40 min treatment with negligible TOC removal. Thus, by these control experiments it was proven that dye degradation particularly proceeded via $\bullet\text{OH}$ that were mainly produced in the Fenton-like reaction.

4.1.4. Effect of Oxalate Addition

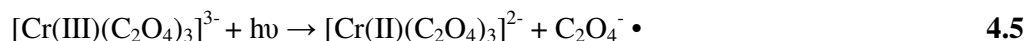
The oxidation of aqueous AR 183 solution via photo-Fenton-like process mediated by ferrioxalate, the oldest and best-known photoactive example of Fe(III)-polycarboxylate complexes (Hatchard and Parker, 1956), was investigated under UV-A irradiation. Former studies indicated that the photolytic/photocatalytic degradation of some organics can be enhanced in the presence of ferrioxalate that strongly absorbs light quanta at longer wavelengths and generates $\bullet\text{OH}$ at higher quantum yields than the photo-Fenton process (about 1.0-1.2 and independent of emission wavelength in the range of 250-480 nm) (Safarzadeh-Amiri et al., 1997; Safarzadeh-Amiri et al., 1996). Ferrioxalate-photo-Fenton-like experiments were carried out at the initial Fe^{3+} concentrations which were selected as 0.3 and 0.8 mM, to make an expressive comparison between the reaction rates. Fe^{3+} : $\text{K}_2\text{C}_2\text{O}_4$ molar ratio was taken as 1:3, which is a typical proportion given in the related scientific literature (Huang et al., 2007; Emilio et al., 2002). Obtained experimental results were displayed in Figure 4.9 and 4.10 in terms of color and TOC removals, respectively.

Color Removal

From Figure 4.9 it is clear that the ferrioxalate-photo-Fenton-like process did not result in the expected rate enhancement in color abatement. Color removal rates were significantly retarded at both studied Fe^{3+} concentrations. For instance, at 0.3 mM

Fe^{3+} concentration, color removal was only 33% after 40 min oxidation in the presence of ferrioxalate, whereas nearly complete color removal (98%) was achieved with the photo-Fenton-like process for the same treatment period and under otherwise identical reaction conditions (see Figure 4.7). Even with dark Fenton-like oxidation, considerably higher color reduction (94%) was obtained with 0.3 mM Fe^{3+} after 40 min treatment.

Decrease in removal efficiency may be observed due to the competition of organic carbon resulting from the oxalate addition (i.e. additional TOC = 21.6 mg/L for 0.9 mM $\text{C}_2\text{O}_4^{2-}$) with AR 183, for $\bullet\text{OH}$ in dye degradation. Besides this competition reaction, it might be speculated that Cr(III) ions, originated from the structure of AR 183 (the Cr^{3+} content of the original Cr(III) complex azo dye was determined as 4.5 mg/L) and was almost completely released at acidic pH (released amount was quantified as 3.8 mg/L) as free Cr^{3+} , have a strong tendency to bind to oxygen-containing functional groups and form complexes with ligands, including oxalate, and hence might be responsible for the observed retardation in dye degradation. Only limited information about the photoreduction of thermally stable $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ complexes induced by ultraviolet irradiation (254 nm) and under vacuum, is available. The overall quantum yield of this photoredox reaction was found to be very low and dependent on pH (favored at neutral pH), O_2 and substrate concentrations (Mytych et al., 2005);



The above indicated reaction may compete with reactions 2.14-2.17, leading to a significant reduction in Fe^{2+} formation that directly affects $\bullet\text{OH}$ production rate via Fenton reaction.

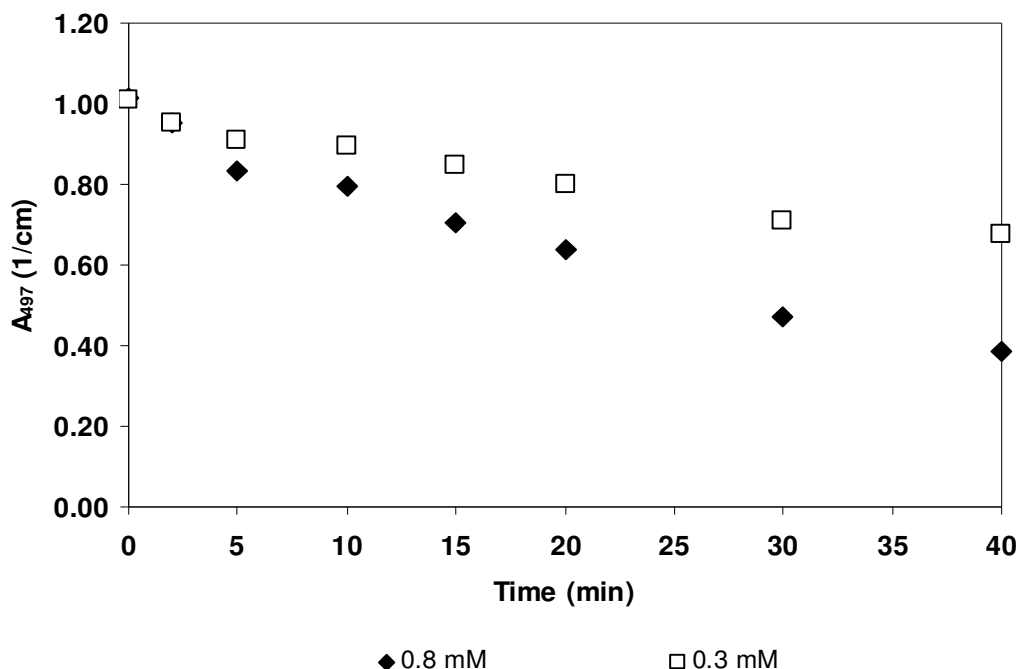


Figure 4.9: Color abatement rates observed for 100 mg/L aqueous AR 183 during ferrioxalate-photo-Fenton-like process at two different initial Fe^{3+} (0.3, 0.8 mM) and $\text{C}_2\text{O}_4^{2-}$ (0.9, 2.4 mM) concentrations. Experimental conditions: $\text{H}_2\text{O}_{2,o} = 30 \text{ mM}$; $\text{pH}_0 = 2.8$.

As expected, color removal efficiencies increased with the increase in the applied Fe^{3+} concentration from 0.3 to 0.8 mM. However, this effect also brought about a higher overall TOC value of the reaction solution, since the oxalate concentration was raised parallel to Fe^{3+} concentration (see Figure 4.10).

TOC Removal

Figure 4.10 demonstrates TOC abatement rates observed during ferrioxalate-photo-Fenton-like oxidation of aqueous AR 183 in the presence of 0.3 and 0.8 mM Fe^{3+} . Herein it should be emphasized that when the Fe^{3+} concentration was increased to 0.8 mM, the oxalate concentration was also elevated automatically from 0.9 mM to 2.4 mM as to maintain the 1:3 molar ratio of $\text{Fe}^{3+}:\text{C}_2\text{O}_4^{2-}$. The sudden increase in the TOC levels directly after $t=0$ (e.g. addition of the ferrioxalate reagent) was a consequence of the surplus organic carbon coming from oxalate anions.

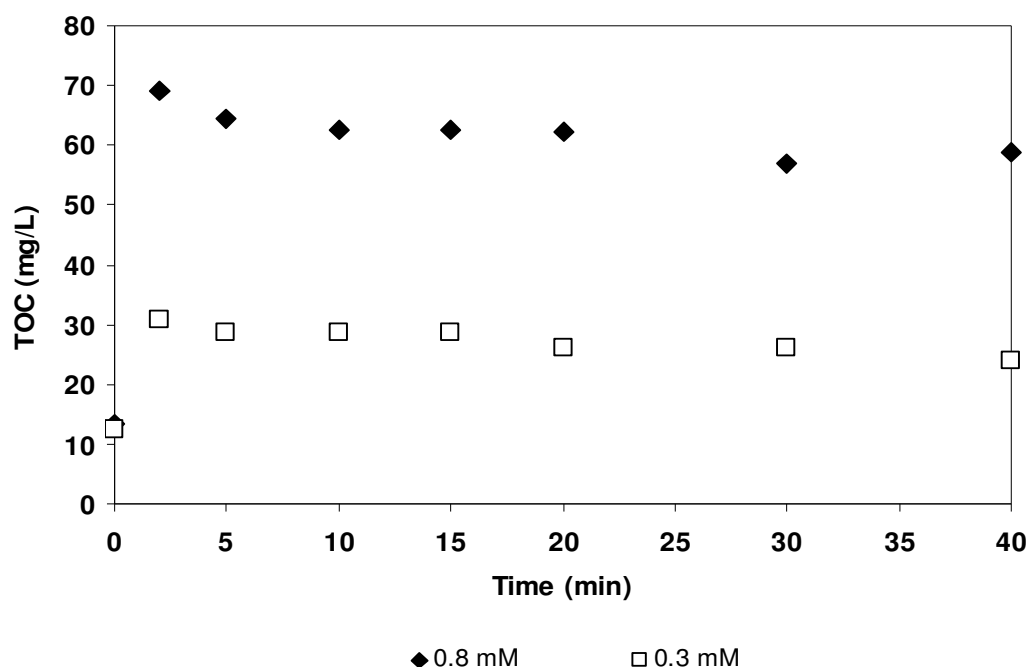


Figure 4.10: TOC abatement rates observed for 100 mg/L aqueous AR 183 during ferrioxalate-photo-Fenton-like process at two different initial Fe^{3+} (0.3, 0.8 mM) and $\text{C}_2\text{O}_4^{2-}$ (0.9, 2.4 mM) concentrations. Experimental conditions: $\text{H}_2\text{O}_{2,o} = 30 \text{ mM}$; $\text{pH}_0 = 2.8$.

TOC removal during the ferrioxalate-photo-Fenton-like reaction was gradually observed in both cases due to both oxalate as well as acid dye degradation that cannot be distinguished from each other. From Figure 4.10 it is evident that upon application of the ferrioxalate-photo-Fenton-like process, a rise in TOC was obtained instead of TOC reduction, in overall. A delay in decoloration accompanied with an increase in TOC concentration rendering this oxidation process quite unattractive for alternative AR 183 treatment.

4.2. Treatability of Azo (Acid and Reactive) Dye Production Wastewaters Using Photo-Fenton-Like Process: Optimization through RSM

In order to investigate the treatability of azo dye production wastewater by photo-Fenton-like process, oxidation experiments were run with synthetic wastewater, simulating Acid Blue 193 (AB 193) production effluent. Central Composite Design (CCD), a frequently used form of Response Surface Methodology (RSM), was employed with the aim of evaluating the effects of the selected process parameters (initial Fe^{3+} , H_2O_2 and COD concentrations and reaction time) on the process

performance. The process parameters of initial Fe^{3+} and H_2O_2 concentrations and reaction time were optimized by the experimental factorial design to obtain maximum percent color, COD and TOC removals. In order to validate the adequacy of the model predictions, a verification experiment was conducted with synthetic AB 193 production wastewater under the optimum process conditions determined by the model. Synthetic Reactive Black 39 (RB 39) production wastewater and real reverse osmosis (RO) effluent of RB 39 were also subjected to Photo-Fenton-like oxidation under these optimum conditions.

4.2.1. Photo-Fenton-like Oxidation of Synthetic AB 193 Production Wastewater

4.2.1.1. Experimental Design

Synthetic AB 193 production wastewater was prepared at varying COD's (100-300 mg/L) and subjected to photo-Fenton-like treatment in accordance with the experimental runs indicated by the model. Table 4.1 shows the four-factorial and five-level central composite design with the experimentally achieved color, COD and TOC removal efficiencies.

Table 4.1: Central Composite Design for RSM and experimentally obtained percent removal efficiencies

	X₁	X₂	X₃	X₄	Y₁	Y₂	Y₃
Trial no.	Initial Fe³⁺ (mM)	Initial H₂O₂ (mM)	Reaction Time (min)	Initial COD (mg/L)	Color Removal (%)	COD Removal (%)	TOC Removal (%)
1	1.5	55	15	250	96	45	32
2	2.5	45	30	200	97	78	51
3	2.5	65	30	200	98	78	49
4	2.5	45	30	100	98	73	78
5	2.5	45	0	200	36	49	31
6	3.5	55	15	150	97	78	48
7	3.5	35	45	250	96	78	55
8	4.5	45	30	200	97	83	53
9	3.5	55	45	250	98	84	57
10	3.5	55	45	150	99	80	59
11	1.5	35	45	250	98	74	49
12	1.5	55	15	150	98	70	48
13	1.5	55	45	250	98	63	39
14	1.5	35	15	150	96	73	43
15	3.5	55	15	250	97	81	51
16	2.5	25	30	200	96	81	48
17	2.5	45	60	200	98	83	74
18	3.5	35	45	150	97	83	60
19	0.5	45	30	200	97	77	51
20	3.5	35	15	250	95	76	44
21	2.5	45	30	200	97	78	51
22	2.5	45	30	300	98	81	50
23	1.5	35	45	150	98	80	74
24	1.5	35	15	250	96	64	31
25	3.5	35	15	150	95	76	55
26	1.5	55	45	150	98	76	60

Based on these results, an empirical relationship between the responses (Y_1 , Y_2 and Y_3) and independent variables (X_1 , X_2 , X_3 and X_4) were attained and expressed by the second-order polynomial equations. Approximating functions of Synthetic AB 193 production wastewater degradation were presented below, first in terms of coded factors and then actual factors, for color, COD and TOC removals, respectively.

$$\text{Color Removal (\%)} = 97.27 - 0.19 \times X_1 + 0.57 \times X_2 + 5.70 \times X_3 - 0.19 \times X_4 + 1.21 \times (X_1)^2 + 1.07 \times (X_2)^2 - 6.35 \times (X_3)^2 + 1.28 \times (X_4)^2 + 0.34 \times X_1 \times X_2 - 0.012 \times X_1 \times X_3 - 0.055 \times X_1 \times X_4 - 0.17 \times X_2 \times X_3 - 0.13 \times X_2 \times X_4 + 0.034 \times X_3 \times X_4$$

4.6

where, $-2 \leq X_i \leq 2$

$$\text{Color Removal (\%)} = 108.38271 - 7.52042 \times \text{Fe}^{3+} - 0.90554 \times \text{H}_2\text{O}_2 + 2.11956 \times t_r - 0.19504 \times \text{COD} + 1.20729 \times (\text{Fe}^{3+})^2 + 0.010723 \times (\text{H}_2\text{O}_2)^2 - 0.028240 \times (t_r)^2 + 5.11417 \times 10^{-4} \times \text{COD}^2 + 0.034125 \times \text{Fe}^{3+} \times \text{H}_2\text{O}_2 - 8.33333 \times 10^{-4} \times \text{Fe}^{3+} \times t_r - 1.1 \times 10^{-3} \times \text{Fe}^{3+} \times \text{COD} - 1.15 \times 10^{-3} \times \text{H}_2\text{O}_2 \times t_r - 2.65 \times 10^{-4} \times \text{H}_2\text{O}_2 \times \text{COD} + 4.5 \times 10^{-5} \times t_r \times \text{COD}$$

4.7

where, $0.5 \text{ mM} \leq [\text{Fe}^{3+}] \leq 4.5 \text{ mM}$; $25 \text{ mM} \leq [\text{H}_2\text{O}_2] \leq 65 \text{ mM}$; $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $0 \text{ min} \leq t_r \leq 60 \text{ min}$.

$$\text{COD Removal (\%)} = 77.56 + 4.32 \times X_1 - 1.32 \times X_2 + 5.03 \times X_3 - 1.56 \times X_4 + 0.20 \times (X_1)^2 + 0.23 \times (X_2)^2 - 3.20 \times (X_3)^2 - 0.42 \times (X_4)^2 + 2.94 \times X_1 \times X_2 - 1.69 \times X_1 \times X_3 + 3.41 \times X_1 \times X_4 + 0.11 \times X_2 \times X_3 - 0.59 \times X_2 \times X_4 + 0.67 \times X_3 \times X_4$$

4.8

where, $-2 \leq X_i \leq 2$

$$\text{COD Removal (\%)} = 109.71042 - 20.15354 \times \text{Fe}^{3+} - 0.86098 \times \text{H}_2\text{O}_2 + 1.25633 \times t_r - 0.10762 \times \text{COD} + 0.20365 \times (\text{Fe}^{3+})^2 + 2.32396 \times 10^{-3} \times (\text{H}_2\text{O}_2)^2 - 0.0142 \times (t_r)^2 - 1.68542 \times 10^{-4} \times \text{COD}^2 + 0.29356 \times \text{Fe}^{3+} \times \text{H}_2\text{O}_2 - 0.11279 \times \text{Fe}^{3+} \times t_r + 0.068163 \times \text{Fe}^{3+} \times \text{COD} + 7.625 \times 10^{-4} \times \text{H}_2\text{O}_2 \times t_r - 1.18625 \times 10^{-3} \times \text{H}_2\text{O}_2 \times \text{COD} + 8.92500 \times 10^{-4} \times t_r \times \text{COD}$$

4.9

where, $0.5 \text{ mM} \leq [\text{Fe}^{3+}] \leq 4.5 \text{ mM}$; $25 \text{ mM} \leq [\text{H}_2\text{O}_2] \leq 65 \text{ mM}$; $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $0 \text{ min} \leq t_r \leq 60 \text{ min}$.

$$\text{TOC Removal (\%)} = 51.29 + 2.30 \times X_1 - 0.68 \times X_2 + 7.74 \times X_3 - 5.98 \times X_4 - 0.45 \times (X_1)^2 - 1.38 \times (X_2)^2 - 0.42 \times (X_3)^2 + 2.51 \times (X_4)^2 + 1.06 \times X_1 \times X_2 - 2.19 \times X_1 \times X_3 + 3.69 \times X_1 \times X_4 - 1.65 \times X_2 \times X_3 + 0.98 \times X_2 \times X_4 - 1.11 \times X_3 \times X_4$$

4.10

where, $-2 \leq X_i \leq 2$

$$\text{TOC Removal (\%)} = 96.61344 - 10.63333 \times \text{Fe}^{3+} + 0.84571 \times \text{H}_2\text{O}_2 + 1.78315 \times t_r - 0.74934 \times \text{COD} - 0.44531 \times (\text{Fe}^{3+})^2 - 0.013791 \times (\text{H}_2\text{O}_2)^2 - 1.85694 \times 10^{-3} \times (t_r)^2 + 1.00438 \times 10^{-3} \times \text{COD}^2 + 0.10631 \times \text{Fe}^{3+} \times \text{H}_2\text{O}_2 - 0.14596 \times \text{Fe}^{3+} \times t_r + 0.073763 \times \text{Fe}^{3+} \times \text{COD} - 0.010996 \times \text{H}_2\text{O}_2 \times t_r + 1.95625 \times 10^{-3} \times \text{H}_2\text{O}_2 \times \text{COD} - 1.47917 \times 10^{-3} \times t_r \times \text{COD}$$

4.11

where, $0.5 \text{ mM} \leq [\text{Fe}^{3+}] \leq 4.5 \text{ mM}$; $25 \text{ mM} \leq [\text{H}_2\text{O}_2] \leq 65 \text{ mM}$; $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $0 \text{ min} \leq t_r \leq 60 \text{ min}$.

The model adequacy check is an important part of the data analysis procedure as the approximating model functions would give poor or misleading results if the fit is inadequate (Körbahtı and Rauf, 2008 a). A test procedure called Analysis of Variance (ANOVA), based on a decomposition of the total variability in the response variable, is employed to confirm the significance and adequacy of the established quadratic response surface model (Myers and Montgomery, 2002). Table 4.2 shows the ANOVA results of the model for percent color, COD and TOC removals. The mean squares were obtained by dividing the sum of squares of each of the two sources of variation, the model and the error (residual) variance, by the respective degrees of freedom (DF). The Fisher variation ratio (model F-value) was calculated by dividing the model mean square by residual mean square (Liu and Chiou, 2005).

Table 4.2: ANOVA results of the quadratic model for photo-Fenton-like degradation of synthetic AB 193 production wastewater (independent parameters: initial Fe^{3+} , H_2O_2 and COD concentrations and reaction time)

	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob>F
Color Removal	Model	2173.04	14	155.22	1.21	0.3807
	Residual	1410.88	11	128.26		
	Lack of Fit	1410.88	10	141.09		
	Pure Error	0.00	1	0.00		
	$R^2 = 0.6063$, Adequate precision = 4.920					
COD Removal	Model	1811.46	14	129.39	2.74	0.050
	Residual	520.16	11	47.29		
	Lack of Fit	520.16	10	52.02		
	Pure Error	0.00	1	0.00		
	$R^2 = 0.7769$, Adequate precision = 6.565					
TOC Removal	Model	3099.00	14	221.36	6.70	0.0016
	Residual	363.58	11	33.05		
	Lack of Fit	363.58	10	36.36		
	Pure Error	0.00	1	0.00		
	$R^2 = 0.8950$, Adequate precision = 10.179					

The Model F-value of 2.74 for COD removal and 6.70 for TOC removal indicate that there is a 5.00% and 0.16% chance that a "Model F-Value" this large could occur due to noise, respectively. Values of "Prob > F" less than 0.0500 imply that the model is significant, whereas the values greater than 0.1000 are usually considered as insignificant. Probability values (Prob > F) of 0.05 and 0.0016 denote the employed models are significant for percent COD and TOC removals, respectively. On the other hand in terms of color removal, the model F-value of 1.21 and a high probability value (Prob>F = 0.3807) reveal that the model is not significant relative to noise. There is a 38.07 % chance that a "Model F-value" this large could occur due to noise.

R^2 value of the response variables followed the order of $R^2_{(\text{TOC Rem})} > R^2_{(\text{COD Rem})} > R^2_{(\text{Color Rem})}$. The highest R^2 of the TOC removal efficiency denotes that only 10.5% of the total variation could not be represented by the empirical model, which expresses a good quadratic fit. On the other hand, nearly 40% of the total variation could not be explained by the model in case of color removal, having a relatively lower R^2 value of 0.6063.

The adequate precision ratios of 4.920, 6.565 and 10.179 (for color, COD and TOC removals, respectively) indicate an adequate signal for all response variables where they measure the signal to noise ratio; a ratio > 4 is desirable.

As it is understood from the ANOVA test, the model application explained the reaction well and can be used to navigate the design space for percent COD and TOC removal efficiencies. On the other hand, a distinct prediction could not be done by the model equation in case of color removal. This is not surprising since color abatement occurs quite rapid and promptly as compared with COD and TOC removals and nearly complete decolorization could be achieved under all experimental conditions, independent from the reactant concentrations (Fe^{3+} and H_2O_2) and initial COD of the solution.

The percent removals predicted by the model were compared with the experimental results in Appendix A, Table A.1. The predicted and actual values were close to each other for COD and TOC removal efficiencies, indicating a correspondence between the mathematical model and experiment.

As well as the ANOVA results of the quadratic model, ANOVA of the independent factors were also obtained by the Design-Expert software and depicted in Table 4.3. A Prob>F value less than 0.05 indicates that this factor has a significant effect on the response. As it is obvious from Table 4.3, reaction time (X_3) was the only factor that has a significant effect on all response variables. On the other hand, percent color, COD and TOC removals were not affected significantly from the varying H_2O_2 concentration (X_2) within the specified experimental range of 25-65 mM. Smaller Prob>F values of Fe^{3+} concentration (X_1) indicate a more significant effect on percent COD and TOC removals as compared with H_2O_2 , proving that catalyst concentration is the reaction rate limiting factor, in the presence of sufficient amount of oxidant (Arslan-Alaton and Teksoy, 2007). According to the results, mineralization efficiency was also significantly affected from the initial COD concentration (X_4) of the wastewater (organic load).

Table 4.3: ANOVA results for model terms (independent parameters: initial Fe^{3+} , H_2O_2 and COD concentrations and reaction time)

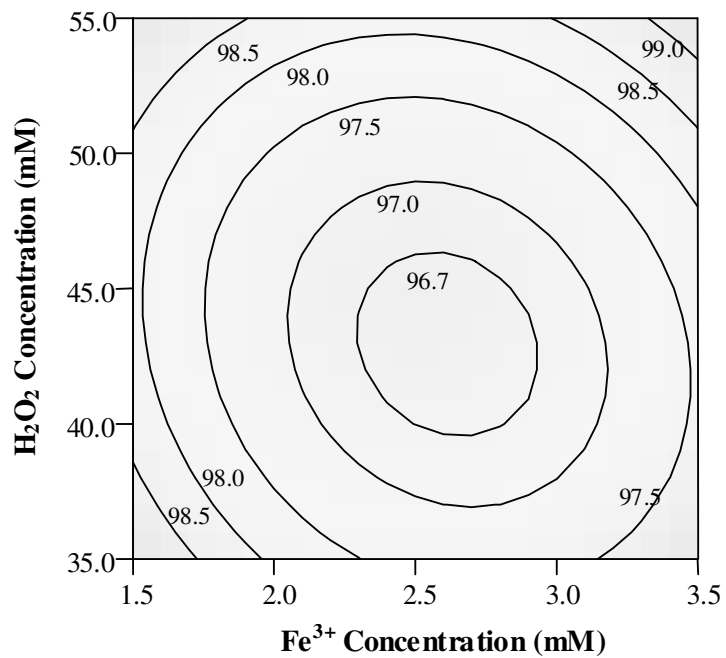
	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob>F
Color Removal	X ₁	0.90	1	0.90	6.994×10^{-3}	0.9349
	X ₂	7.89	1	7.89	0.062	0.8087
	X ₃	781.13	1	781.13	6.09	0.0312
	X ₄	0.87	1	0.87	6.755×10^{-3}	0.9360
	(X ₁) ²	25.44	1	25.44	0.20	0.6647
	(X ₂) ²	20.27	1	20.27	0.16	0.7000
	(X ₃) ²	704.69	1	704.69	5.49	0.0389
	(X ₄) ²	28.53	1	28.53	0.22	0.6464
	X ₁ X ₂	1.86	1	1.86	0.015	0.9062
	X ₁ X ₃	2.50×10^{-3}	1	2.50×10^{-3}	1.949×10^{-5}	0.9966
	X ₁ X ₄	0.048	1	0.048	3.774×10^{-4}	0.9848
	X ₂ X ₃	0.48	1	0.48	3.712×10^{-3}	0.9525
	X ₂ X ₄	0.28	1	0.28	2.190×10^{-3}	0.9635
	X ₃ X ₄	0.018	1	0.018	1.421×10^{-4}	0.9907
COD Removal	X ₁	448.68	1	448.68	9.49	0.0105
	X ₂	42.00	1	42.00	0.89	0.3662
	X ₃	606.52	1	606.52	12.83	0.0043
	X ₄	58.56	1	58.56	1.24	0.2895
	(X ₁) ²	0.72	1	0.72	0.015	0.9038
	(X ₂) ²	0.94	1	0.94	0.020	0.8903
	(X ₃) ²	178.19	1	178.19	3.77	0.0783
	(X ₄) ²	3.10	1	3.10	0.066	0.8027
	X ₁ X ₂	137.89	1	137.89	2.92	0.1157
	X ₁ X ₃	45.80	1	45.80	0.97	0.3462
	X ₁ X ₄	185.85	1	185.85	3.93	0.0730
	X ₂ X ₃	0.21	1	0.21	4.426×10^{-3}	0.9481
	X ₂ X ₄	5.63	1	5.63	0.12	0.7366
	X ₃ X ₄	7.17	1	7.17	0.15	0.7044
TOC Removal	X ₁	126.73	1	126.73	3.83	0.0761
	X ₂	11.19	1	11.19	0.34	0.5723
	X ₃	1438.87	1	1438.87	43.53	0.0001
	X ₄	857.17	1	857.17	25.93	0.0003
	(X ₁) ²	3.46	1	3.46	0.10	0.7523
	(X ₂) ²	33.20	1	33.20	1.00	0.3378
	(X ₃) ²	3.05	1	3.05	0.092	0.7671
	(X ₄) ²	110.05	1	110.05	3.33	0.0953
	X ₁ X ₂	18.08	1	18.08	0.55	0.4750
	X ₁ X ₃	76.69	1	76.69	2.32	0.1559
	X ₁ X ₄	217.64	1	217.64	6.58	0.0262
	X ₂ X ₃	43.53	1	43.53	1.32	0.2755
	X ₂ X ₄	15.31	1	15.31	0.46	0.5102
	X ₃ X ₄	19.69	1	19.69	0.60	0.4565

4.2.1.2. Response Surface and Contour Plots for Color, COD and TOC Removals

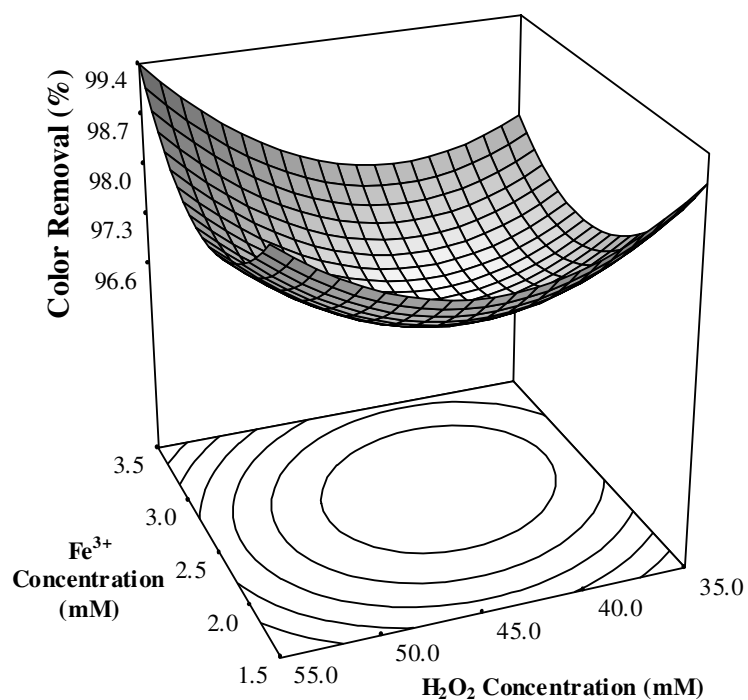
The 3-D response surface and 2-D contour plots for the predicted responses were also obtained by the Design-Expert software, based on the model polynomial functions to assess the change of the response surface. The interaction of the response variables and process parameters can be understood from these plots (Figures 4.11-4.19). Since the model had four factors, two factors were held constant for each diagram while the other two varied within the experimental ranges.

Effect of Fe^{3+} and H_2O_2 Concentrations on Percent Color Removal

Figure 4.11 illustrates the effect of initial Fe^{3+} and H_2O_2 concentrations upon color removal efficiencies, at constant reaction time and initial COD concentration (45 min and 200 mg/L, respectively). As it is obvious from the contour (a) and response surface (b) plots, color removal efficiency has its minimum, when the concentrations of both reactants were kept around their medium values within the specified range. The efficiency started to increase as coming closer to the corners of the plot. Independent from the reactant concentrations, pretty high color abatements ($\geq 97\%$) were achieved after 45 minutes of treatment, with the efficiencies quite close to each other. The plots of the color removal are in accordance with the ANOVA results, indicating that initial concentrations of Fe^{3+} and H_2O_2 did not have a significant effect on this response variable (Table 4.3).



(a)



(b)

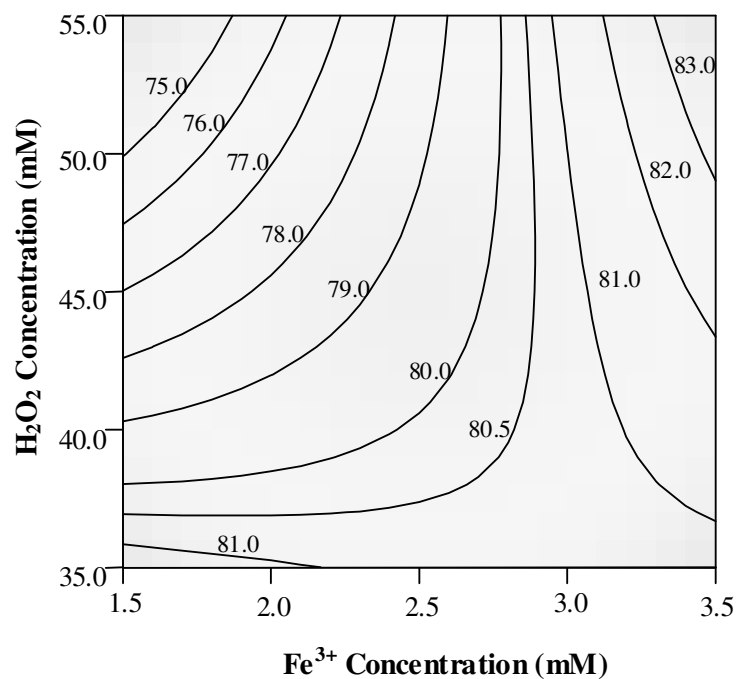
Figure 4.11: Contour (a) and response surface (b) plots of color removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and H_2O_2 concentrations; at 45 min reaction time and 200 mg/L initial COD

Effect of Fe^{3+} and H_2O_2 Concentrations on Percent COD Removal

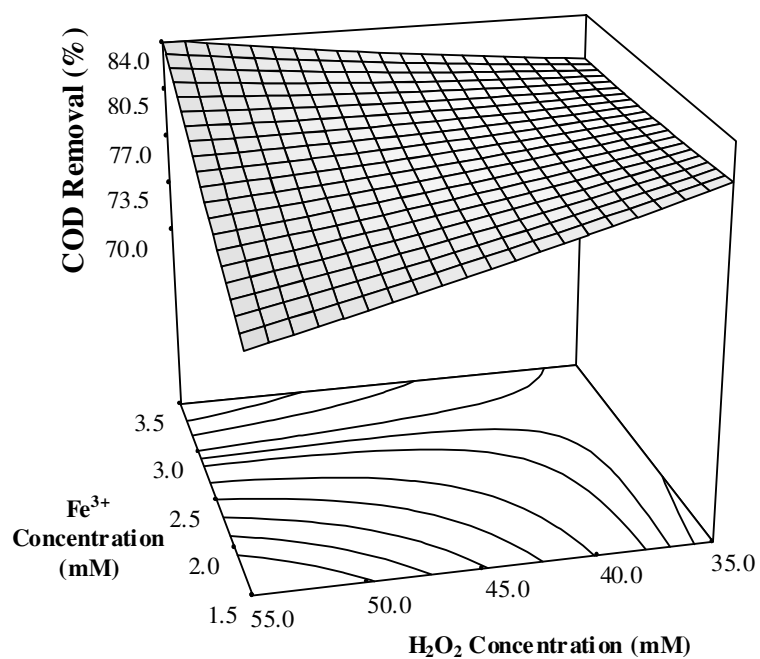
In Figure 4.12, the effect of initial Fe^{3+} and H_2O_2 concentrations upon COD abatement was shown while reaction time was kept constant at 45 min with $\text{COD}_0 = 200 \text{ mg/L}$. The contour (a) and response surface (b) plots reveal that at lower Fe^{3+} concentrations, an increase in H_2O_2 concentration appears to reduce the COD removal efficiency. This reduction was probably due to the well-known $\bullet\text{OH}$ scavenging effect of excessive H_2O_2 , which can be expressed by the following reaction (Tang and Huang, 1996);



On the other hand, when higher amounts of Fe^{3+} were available; COD removal increased with increasing oxidant concentration, and reached its maximum value (>83%) when both of the reactants were kept in their highest concentrations. For instance, provided that a COD removal of $\leq 81\%$ is desired, using low amounts of both Fe^{3+} and H_2O_2 reactants is a better option from both environmental and economical points of view. However if higher COD removal efficiencies are desired, Fe^{3+} and H_2O_2 concentrations should be kept more than 3 mM and 50 mM, respectively, revealing that a pollutant specific $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ range should be determined to achieve high COD removals (Arslan-Alaton and Teksoy, 2007; Tang and Huang, 1996).



(a)

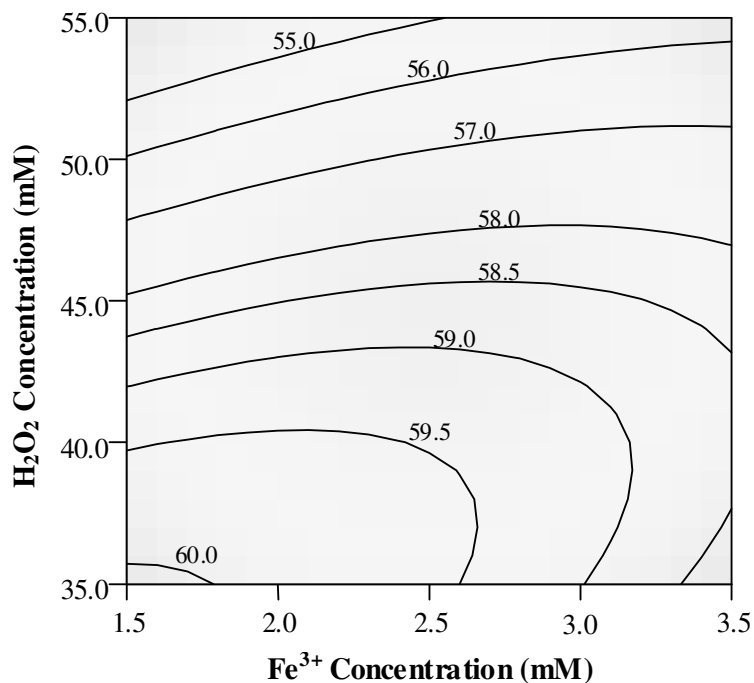


(b)

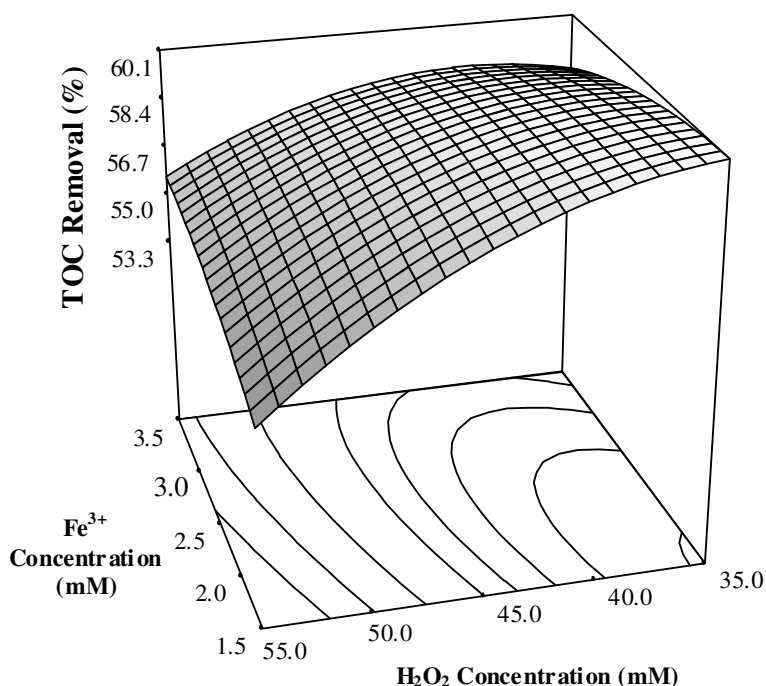
Figure 4.12: Contour (a) and response surface (b) plots of COD removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and H_2O_2 concentrations; at 45 min reaction time and 200 mg/L initial COD

Effect of Fe^{3+} and H_2O_2 Concentrations on Percent TOC Removal

In Figure 4.13, TOC removal was given as a function of H_2O_2 and Fe^{3+} concentrations, at constant reaction time (45 min) and COD concentration (200 mg/L). As it is obvious from the contour (a) and response surface (b) plots, TOC abatement reached its peak value (60%) when concentrations of the both reactants were kept at their minimum. Degradation percent decreased with increasing H_2O_2 concentration, whereas Fe^{3+} concentration did not have a significant impact on TOC removal efficiency. Minimum TOC removal was observed at the top left-hand of the contour plot (a), in the presence of low Fe^{+3} (1.5 mM) concentrations with excessive H_2O_2 (55 mM), due to the radical scavenging effect aforementioned. Hence, selection of the correct Fenton/Fenton-like reagent load is an important aspect that should be considered during the treatment process, which is also reported by several researchers (Monteagudo et al., 2008; Duran et al., 2008; Perez-Moya et al., 2007). In our case, keeping concentrations of the Fe^{+3} and H_2O_2 reagents around 1.5 mM and 35 mM is preferable for higher treatment performance as well as the cost effectiveness due to lower chemical consumption.



(a)

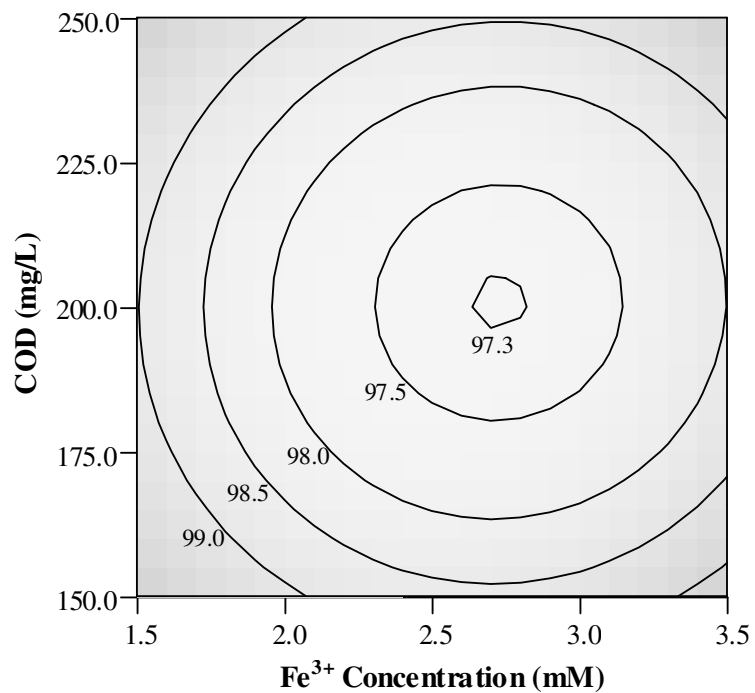


(b)

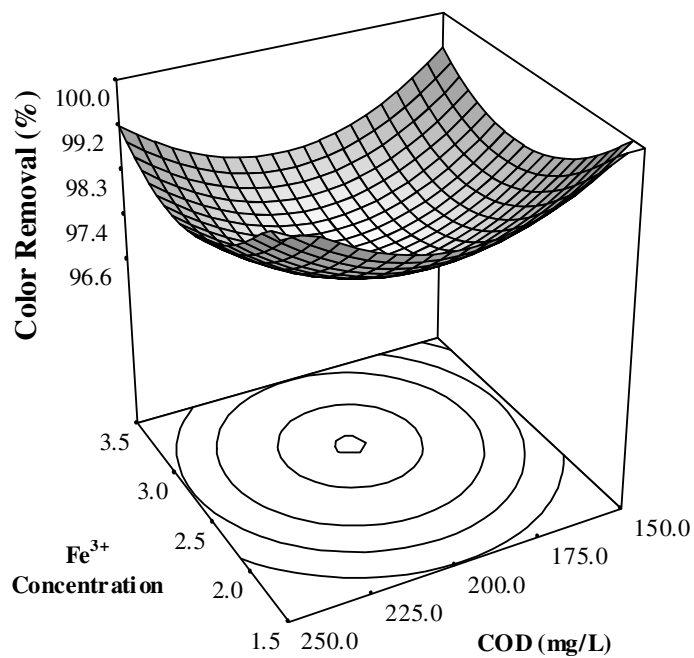
Figure 4.13: Contour (a) and response surface (b) plots of TOC removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and H_2O_2 concentrations; at 45 min reaction time and 200 mg/L initial COD

Effect of Fe^{3+} Concentration and Initial COD on Percent Color Removal

Color removal efficiency as a function of Fe^{3+} catalyst concentration and initial COD of synthetic AB 193 production wastewater was depicted in Figure 4.14 (a-b), while reaction time and initial H_2O_2 concentration were kept constant at 45 min and 35 mM, respectively. High removal efficiency (97-99%) was obtained at all conditions, implying that changes in Fe^{3+} and COD parameters within the specified range does not have a significant impact on color abatement.



(a)



(b)

Figure 4.14: Contour (a) and response surface (b) plots of color removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and COD concentrations; at 45 min reaction time and 35 mM initial H_2O_2 concentration

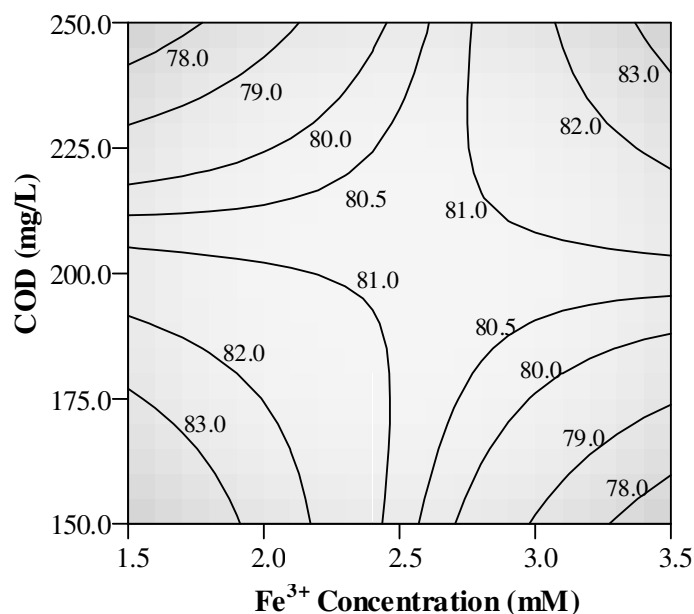
Effect of Fe³⁺ Concentration and Initial COD on Percent COD Removal

Figure 4.15 (a-b) shows the interaction of the initial Fe³⁺ and COD concentrations, at constant reaction time and H₂O₂ concentration (45 min and 35 mM, respectively). When initial COD of the dye solution was around 150 mg/L, at least 83% COD removal could be obtained with 1.5 mM Fe³⁺ concentration. An increase in Fe³⁺ concentration significantly retarded COD abatement at CODs ≤ 200 mg/L, which may be attributed to the free radical scavenging effect of excessive iron represented by the following equation (Tang and Huang, 1996):

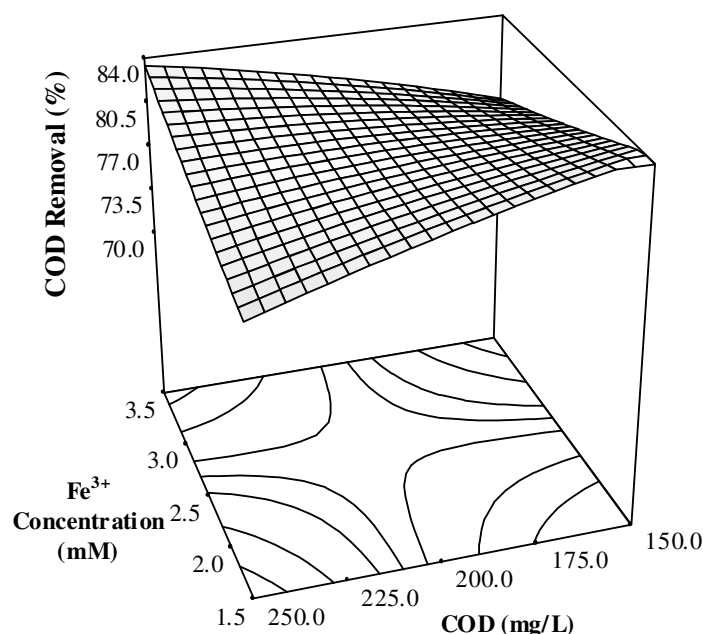


Negative effect of increasing catalyst concentration was also observed by Giroto et al. (2006), which evaluates Photo-Fenton degradation of polyvinyl alcohol using an empirical model based on neural networks.

As it is evident from the contour plot, increase in Fe³⁺ concentration improved COD removal efficiency at higher pollution loads (COD > 200 mg/L), indicating that effects of iron and hydrogen peroxide depend on the organic matter concentration, which is also reported in the study of Giroto et al. (2006). For instance, Fe³⁺ concentration should be increased up to 3.5 mM, to obtain 83% COD reduction with the solution having 250 mg/L initial COD, revealing that wastewaters of higher strength require elevated concentrations of reactant to be oxidized.



(a)



(b)

Figure 4.15: Contour (a) and response surface (b) plots of COD removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and COD concentrations; at 45 min reaction time and 35 mM initial H_2O_2 concentration

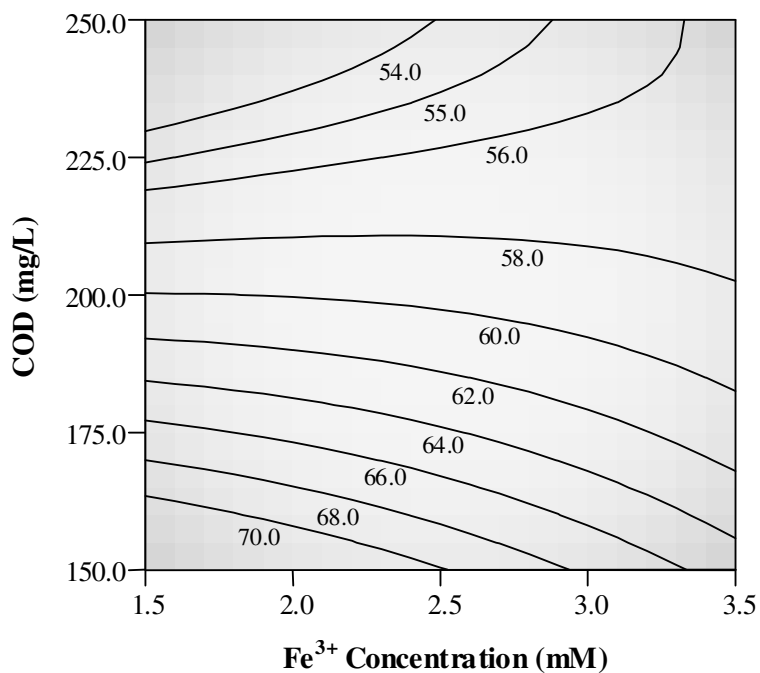
Effect of Fe^{3+} Concentration and Initial COD on Percent TOC Removal

Figure 4.16 displays the TOC removal efficiencies as a function of initial Fe^{3+} and COD concentrations, while reaction time and H_2O_2 concentration were fixed at 45 min and 35 mM, respectively. As it is evident from the contour (a) and response surface (b) plots, TOC removal was at its peak value while both of the process variables were kept in their minimum. With the increase in the input COD, percent TOC removal decreased from 70% to 54%, indicating that the process performance was strongly dependent on the pollution load.

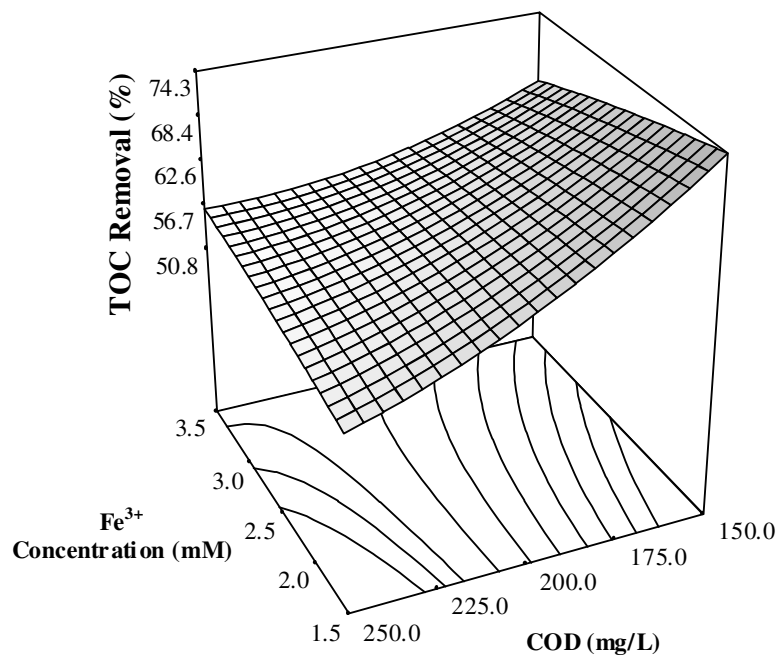
In AOPs, pseudo-first order kinetic is applicable for the oxidation rate, provided that sufficient amounts of oxidant and catalyst are available in the reaction medium. In such a case, oxidation rate shows an increase with the increasing input COD and TOC. However in related studies, it was demonstrated that removal efficiencies reduced with the increasing organic load (Balcioğlu and Arslan, 2001), revealing that at least one of the reactant was insufficient (rate-limiting). As can be seen from Figure 4.16 (a-b), percent TOC removal decreased at elevated input CODs; denoting

that mineralization of synthetic AB 193 production wastewater could not be represented by the pseudo-first order kinetics, probably due to the rate limiting concentration of oxidant (35 mM).

As it is evident from contour and response surface plots, increase in Fe^{3+} concentration slightly enhanced the TOC removal at higher initial CODs, as this was the case for COD abatement. On the other hand at initial CODs < 200 mg/L, TOC removal somewhat decreased with the increasing Fe^{3+} concentration due to the radical scavenging impact of excess iron, aforementioned. However, effect of Fe^{3+} concentration on TOC removal was less significant as compared with the initial COD, which was also expressed by the higher Prob>F value in the ANOVA results (Table 4.3).



(a)

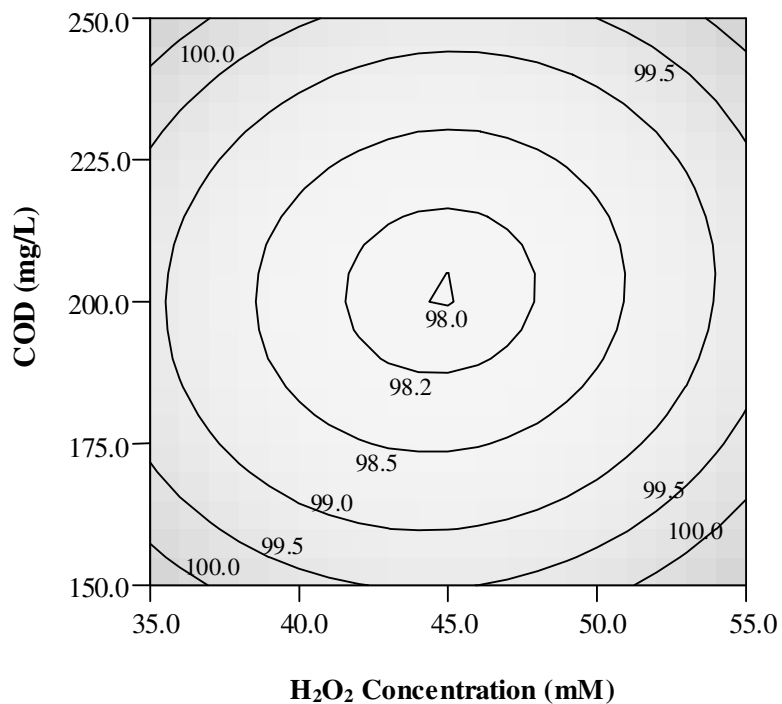


(b)

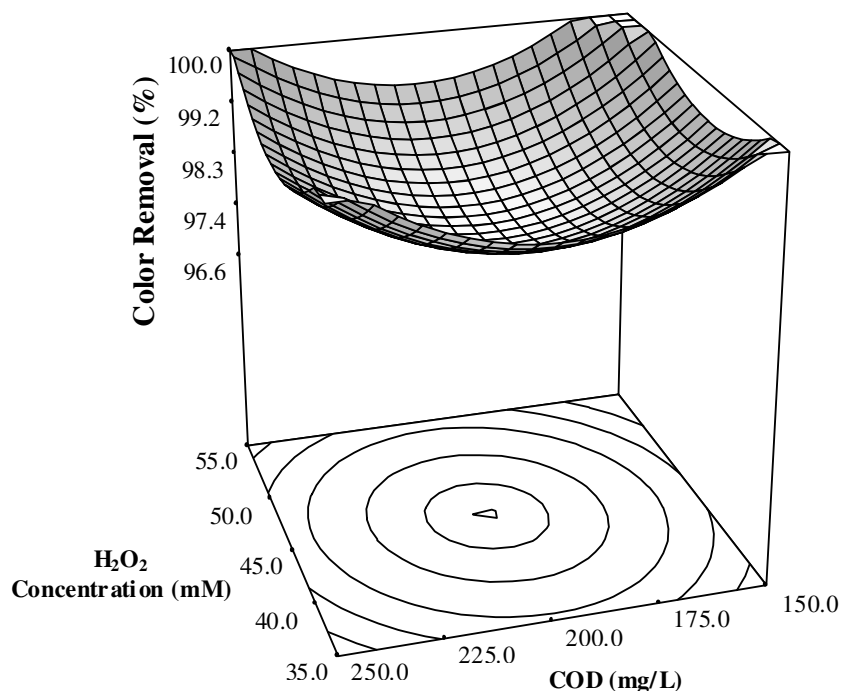
Figure 4.16: Contour (a) and response surface (b) plots of TOC removal from synthetic AB 193 production wastewater as a function of initial Fe^{3+} and COD concentrations; at 45 min reaction time and 35 mM initial H_2O_2 concentration

Effect of H_2O_2 Concentration and Initial COD on Percent Color Removal

Figure 4.17 (a-b) displays the effect of H_2O_2 concentration and initial COD upon the color reduction. As it is obvious from the contour plot (a), at 1.5 mM Fe^{3+} and 45 min reaction time, at least 98% color abatement was obtained, independent from the oxidant concentration and initial COD content of the solution.



(a)

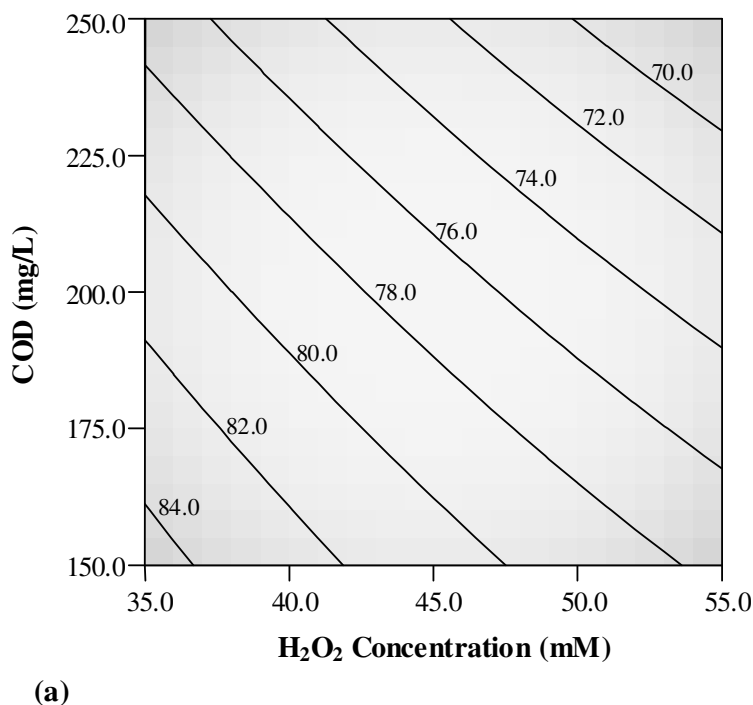


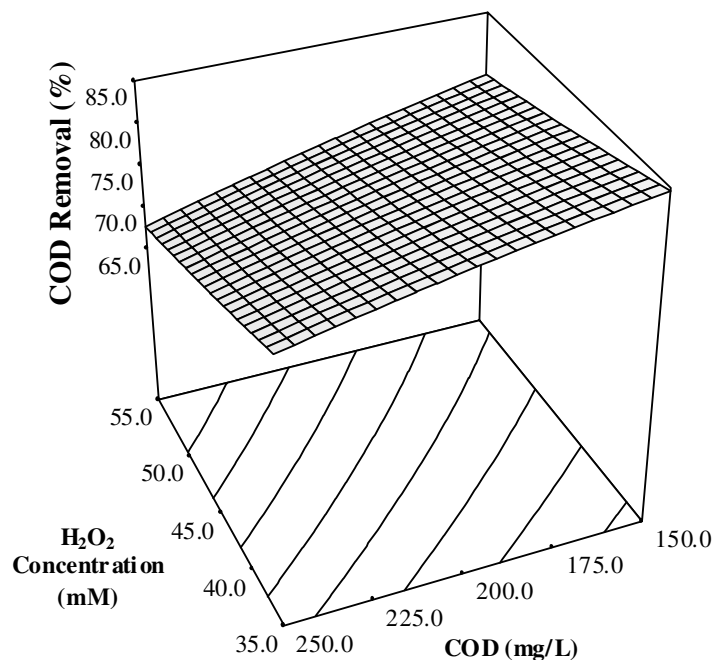
(b)

Figure 4.17: Contour (a) and response surface (b) plots of color removal from synthetic AB 193 production wastewater as a function of initial H₂O₂ and COD concentrations; at 45 min reaction time and 1.5 mM initial Fe³⁺ concentration

Effect of H_2O_2 Concentration and Initial COD on Percent COD Removal

Figure 4.18 are the contour (a) and response surface (b) plots showing the estimate COD removal efficiency over the H_2O_2 and COD variables when reaction time and Fe^{3+} concentration were kept constant at 45 min and 1.5 mM, respectively. As can be understood from both of the figures, increasing H_2O_2 concentration had a negative effect on COD abatement at all initial CODs in the studied range, indicating that 35 mM was by far sufficient for the oxidation of simulated dye production effluent. As aforementioned, efficiency decrease was probably due to the inhibitory (free radical scavenging) effect of excessive H_2O_2 on the advanced oxidation reaction. Increase in the COD of synthetic AB 193 production wastewater also led to a significant reduction in COD removal efficiency. COD abatement was below 70% when both of the independent parameters were kept at their maximum, whereas at least 84% removal could be achieved at a H_2O_2 concentration < 35 mM for an initial COD of 150 mg/L. The significance of the effect of H_2O_2 concentration and initial COD parameters on percent COD removal are close to each other as can also be understood from their Prob>F values (Table 4.3).



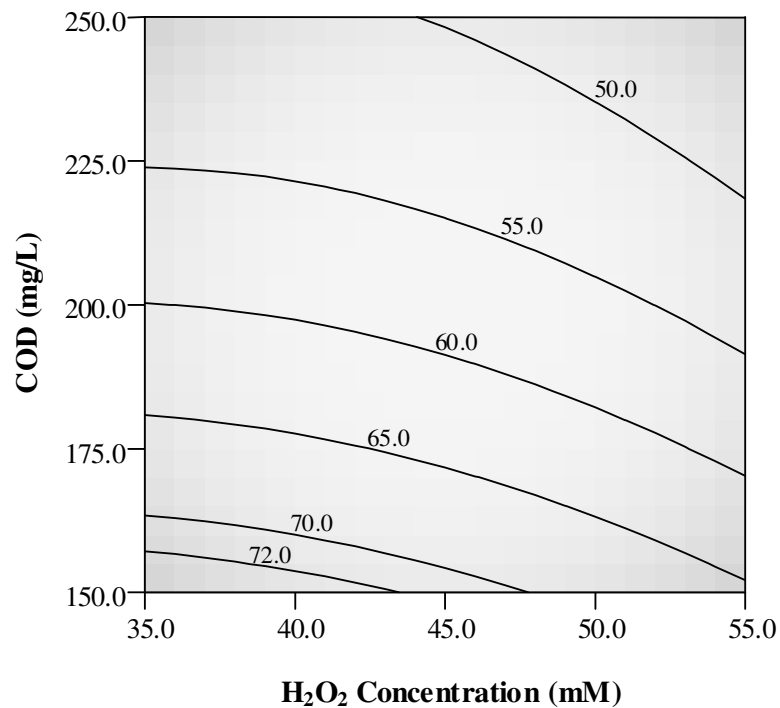


(b)

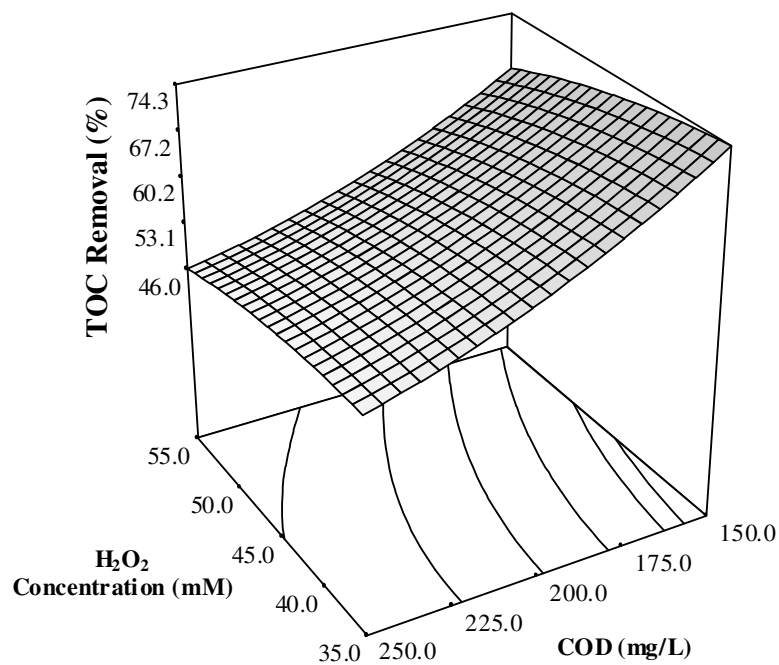
Figure 4.18: Contour (a) and response surface (b) plots of COD removal from synthetic AB 193 production wastewater as a function of initial H_2O_2 and COD concentrations; at 45 min reaction time and 1.5 mM initial Fe^{3+} concentration

Effect of H_2O_2 Concentration and Initial COD on Percent TOC Removal

Figure 4.19 displays the response contour (a) and surface plots (b) for TOC removal as a function of H_2O_2 concentrations and initial CODs, at 45 min reaction time and initial Fe^{3+} of 1.5 mM. Most efficient TOC removal (>72%) occurred when both of the independent parameters were kept minimum in the studied range. Similar to the case in COD abatement (see Figure 4.18), considerable decrease in percent TOC removal was observed with the increase in initial COD load, at all initial H_2O_2 concentrations; indicating that pseudo-first order kinetics can not be applicable for COD and TOC removal rates, probably due to the rate-limiting concentration of Fe^{3+} (1.5 mM). As it is evident from the Figure 4.19, increasing H_2O_2 concentration also reduced the TOC removal efficiency. However, effect of H_2O_2 concentration on response parameter was less significant as compared with initial COD of the wastewater, which was also denoted by the Prob>F values of (Table 4.3).



(a)



(b)

Figure 4.19: Contour (a) and response surface (b) plots of TOC removal from synthetic AB 193 production wastewater as a function of initial H_2O_2 and COD concentrations; at 45 min reaction time and 1.5 mM initial Fe^{3+} concentration

4.2.1.3. Optimization of the Photo-Fenton-like Process for Synthetic AB 193 Production Wastewater Treatment

Searching for optimum conditions for desirable responses is one of the main objectives of RSM. In case of multiple responses, the model searches for a set of operating conditions that in some sense maximizes all responses or at least keeps them in the desired ranges (Myers and Montgomery, 2002). In this study, optimal values of the process parameters were established by a module in the Design-Expert software, using approximating functions of percent color, COD and TOC removals. For process optimization, the desired goals in terms of color, COD and TOC removal efficiencies were defined as “maximize” to obtain the maximum treatment performance, while the process parameters of initial Fe^{3+} and H_2O_2 concentrations and reaction time were selected to be “in the range”. The optimization results of the independent process parameters were obtained for solutions having different initial CODs (organic loads).

The optimized variables at initial CODs of 150, 200 and 250 mg/L, a typical COD range for wastewater generated in dye synthesis reactor washing (SETAŞ Chemical Company, 2007); were given in Table 4.4 for the highest desirability. The removal efficiencies obtained under these optimum conditions were also shown in the same table.

Table 4.4: Optimization results of photo-Fenton-like treatment of synthetic AB 193 production wastewater

Initial COD (mg/L)	Fe^{3+} conc. (mM)	H_2O_2 conc. (mM)	Rxn. time (min)	Color Rem. (%)	COD Rem. (%)	TOC Rem. (%)	Desirability
150	1.5	35	45	100	85	74	0.98
200	1.5	35	45	99	81	60	0.84
250	3.5	44	45	99	84	57	0.83

As can be seen from Table 4.4, optimized variables for 200 mg/L initial COD were obtained as $\text{Fe}^{3+} = 1.5$ mM, $\text{H}_2\text{O}_2 = 35$ mM and reaction time = 45 min to achieve maximum color, COD and TOC removal efficiencies. Under these optimum conditions, 99% color removal, 81% COD removal and 60% TOC removal were foreseen by the program. For lower initial CODs (150 mg/L), optimization results

were found to be identical to the values predicted for 200 mg/L COD. On the other hand, when initial COD of the solution was increased up to 250 mg/L, optimized concentrations of Fe^{3+} and H_2O_2 also raised, indicating that higher strength wastewater involves elevated concentrations of Fenton-like reagent to achieve maximum treatment performance in terms of color, COD and TOC abatements.

4.2.1.4. Application of Optimized Photo-Fenton-like Conditions on Synthetic AB 193 Production Wastewater

Experiments were conducted with synthetic AB 193 production wastewater employing UV-A only, H_2O_2 only, H_2O_2 with UV-A and Fe^{3+} combined with UV-A, to find out the effect of the individual components of photo-Fenton-like process on organic matter degradation. Dark Fenton-like experiment was also carried out to investigate its efficiency in the treatment of synthetic acid dye production wastewater and comparing the process performance with photo-Fenton-like process. In these experiments, initial concentrations of reactants were used at their optimum conditions determined for photo-Fenton-like treatment, in order to make an expressive comparison between the treatment performances of all studied processes. Color, COD and TOC abatements achieved with control experiments as well as Fenton-like oxidation, were illustrated in Figure 4.20-4.22, together with the photo-Fenton-like experiment.

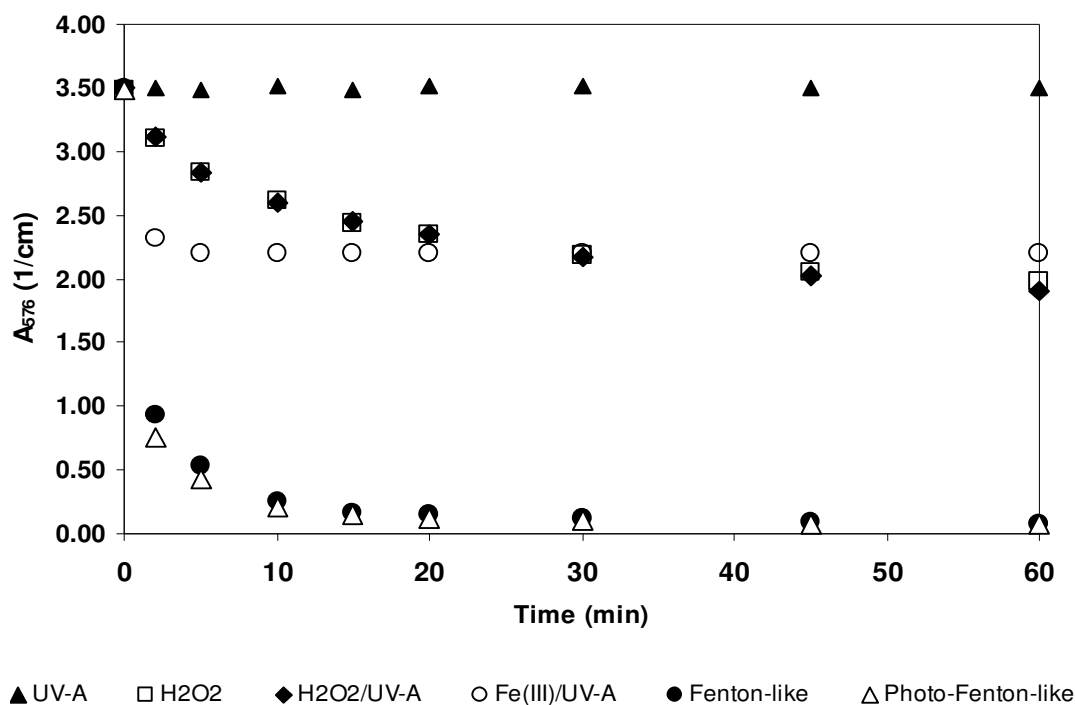


Figure 4.20: Color removals observed for synthetic AB 193 production wastewater at $\text{COD}_0 = 200 \text{ mg/L}$, $\text{Fe}^{3+}_{,0} = 1.5 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 35 \text{ mM}$; $\text{pH}_0 = 2.8$.

As can be seen from Figure 4.20, no decoloration was obtained in the experiment carried out with UV-A alone. On the other hand, color removal efficiencies after 60 minutes of treatment were measured as 43% and 45% via H_2O_2 alone and H_2O_2 combined with UV-A, respectively. In case of UV-A induced Fe^{3+} photoreduction, color sharply reduced within the first minutes after Fe addition, but then reduction ceased and color abatement remained at a constant value of 37%. The percent color removals obtained by the individual reactants of photo-Fenton-like process indicate that the chromophore group of AB 193 could be easily broken down even by H_2O_2 alone and $\bullet\text{OH}$ formed during photoreduction of Fe^{3+} in the $\text{Fe}^{3+}/\text{UV-A}$ process. However as it is obvious from the Figure 4.20, final effluents still have relatively high absorbance values at the end of 60 min exposure to H_2O_2 alone, H_2O_2 with UV-A and Fe^{3+} with UV-A, which requires further treatment.

In case of Fenton-like treatment, decolorization rate was slightly lower as compared with the light mediated process, in first minutes of the reaction. After 20 min treatment time, color removal with Fenton-like oxidation nearly caught the photo-Fenton-like process. Hence, use of $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-A}$ reagent could be preferable for

decoloration, only if reaction time is a strict limiting factor. Otherwise dark process seems to be a more cost-effective alternative in terms of energy consumption.

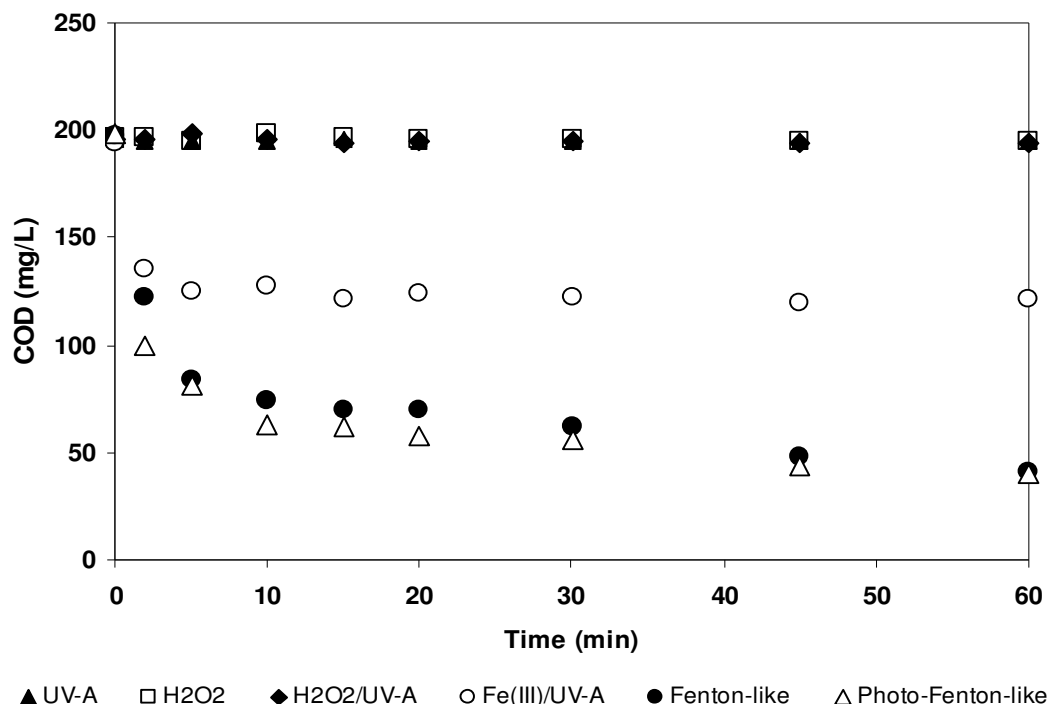


Figure 4.21: COD removals observed for synthetic AB 193 production wastewater at $\text{COD}_0 = 200 \text{ mg/L}$, $\text{Fe}^{3+}_{,0} = 1.5 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 35 \text{ mM}$; $\text{pH}_0 = 2.8$.

Figures 4.21 indicated that no significant COD elimination was obtained in the experiments performed with UV-A alone, H_2O_2 alone and H_2O_2 in combination with UV-A. On the other hand, partial COD abatement was observed in case of $\text{Fe}^{3+}/\text{UV-A}$, mainly resulting from the adsorption of organic molecules on settled $\text{Fe}(\text{OH})_3$. Photodegradation was not the primary mechanism in organic matter degradation, as it is understood from the relatively small difference between the COD contents of the filtrate of the sample taken just after the addition of Fe^{3+} , and filtrate of the sample $t=60$.

COD reduction was slightly slower with Fenton-like process as compared with photo-Fenton-like, but then Fenton-like treatment reached the efficiency of light mediated process, as this was the case for color removal. However, the time required for dark process to achieve the same COD abatement with photo-Fenton-like oxidation was 60 min, whereas 20 min was sufficient for decolorization (see Figure 4.20).

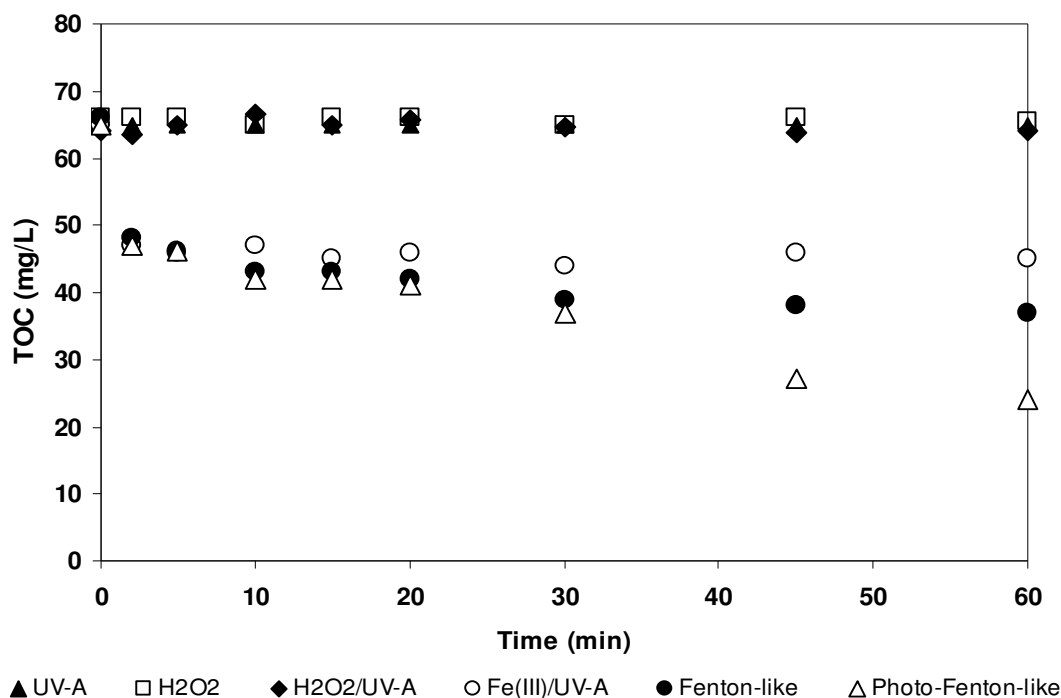


Figure 4.22: TOC removals observed for synthetic AB 193 production wastewater at $\text{COD}_0 = 200 \text{ mg/L}$, $\text{Fe}^{3+}_{,0} = 1.5 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 35 \text{ mM}$; $\text{pH}_0 = 2.8$.

As it is evident from Figure 4.22, no TOC removal could be achieved with the application of UV-A, H_2O_2 and $\text{H}_2\text{O}_2/\text{UV-A}$ processes. In UV-A induced Fe^{3+} photoreduction, significant TOC removal was observed due to the adsorption onto $\text{Fe}(\text{OH})_3$ flocs, as this was the case for COD. These control experiments proved that, organic matter degradation was mainly achieved by the catalytic decomposition of H_2O_2 in the presence of Fe^{3+} and UV-A light, rather than the individual components of the system.

TOC abatements observed with Fenton-like and photo-Fenton-like processes were close to each other during the first 30 minutes of the reaction as can be seen from Figure 4.22. However after this period, mineralization rate was accelerated in the presence of UV-A light, whereas it seems to be practically completed in dark reaction. TOC of the wastewater found to be 37 mg/L after 60 min treatment with Fenton-like process indicating 44% abatement, while it was measured as 24 mg/L in case of photo-Fenton-like oxidation revealing a TOC removal of 63%. The efficiency increase in the presence of UV-A light could be attributed to the photolysis of ferric ion-organic intermediate complexes. Some of the intermediates generated by

the decomposition of organic pollutants might have reacted with ferric ion to produce complexes as represented by reaction 2.12, which results in an increased rate of mineralization as the reaction progresses. Similar behavior was also reported for destruction of different types of organics by Pignatello (1992) and Safarzadeh-Amiri et al. (1996). They have shown that mineralization of organics with photo-Fenton oxidation can be divided into two stages. The first stage is dominated by oxidation with hydroxyl radicals (reaction 2.5), whereas second stage of oxidation is likely the result of the photochemistry of iron complexes (reaction 2.12).

4.2.1.5. Model Verification

Experimentally obtained removal efficiencies for photo-Fenton-like oxidation of synthetic AB 193 production wastewater ($\text{COD}_0 = 200 \text{ mg/L}$) under optimum conditions, were compared with the values predicted by the model to confirm the validity of the optimization procedure (Table 4.5).

Table 4.5: Predicted and experimentally obtained removal efficiencies for synthetic AB 193 production wastewater ($\text{COD}_0 = 200 \text{ mg/L}$) at optimum operation conditions ($\text{Fe}^{3+}_{,0} = 1.5 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 35 \text{ mM}$; reaction time = 45 min)

Responses	Model Predictions	Experimental Results
Color Removal (%)	99	98
COD Removal (%)	81	78
TOC Removal (%)	60	59

As can be seen from the table, actual and predicted removal efficiencies were close to each other, indicating the optimal removal efficiencies estimated by the empirical model were well validated by the additional experimental results. These results implicate that the optimization using a RSM based on the CCD can save the time and effort by the estimation of the optimum conditions of the maximum treatment efficiency.

4.2.1.6. Effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio on Process Performance: Evaluation using RSM

In Fe-based AOPs, molar ratio of the oxidant and iron source is an important process parameter since undesired $\bullet\text{OH}$ -scavenging reactions (reaction 4.12 and 4.13) occur in the presence of an excess of one of the two reagents, resulting in a reduction in the

amount of available $\bullet\text{OH}$, hence the oxidation efficiency. A pollutant specific optimum ratio between H_2O_2 and $\text{Fe}^{2+}/\text{Fe}^{3+}$ must be determined in order to minimize these scavenging effects (Arslan-Alaton and Teksoy, 2007; Arslan-Alaton et al., 2008). For this purpose, RSM was employed to attain an optimum $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio for photo-Fenton-like treatment of synthetic AB 193 production wastewater. This time independent process parameters were selected to be the reaction time (A_1), initial COD concentration (A_2) and $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio (A_3), while response variables were kept same as percent color, COD and TOC removals. Based on the experimental factorial design (Table 3.4), regression equations that show the correlation between removal efficiencies and process variables were derived by the model. These model equations were presented below first in terms of coded factors and then actual factors.

$$\text{Color Removal (\%)} = 100.60 + 5.87 \times A_1 - 0.19 \times A_2 - 1.78 \times A_3 - 6.98 \times (A_1)^2 + 0.65 \times (A_2)^2 + 1.28 \times (A_3)^2 + 0.034 \times A_1 \times A_2 - 0.72 \times A_1 \times A_3 - 0.018 \times A_2 \times A_3$$

4.14

where; $-2 \leq A_i \leq 2$

$$\text{Color Removal (\%)} = 73.40086 + 2.28396 \times t_r - 0.10868 \times \text{COD} - 42.95798 \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) - 0.031036 \times (t_r)^2 + 2.59752 \times 10^{-4} \times (\text{COD})^2 + 423.98633 \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2)^2 + 4.50000 \times 10^{-5} \times t_r \times \text{COD} - 0.87511 \times t_r \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) - 6.46437 \times 10^{-3} \times \text{COD} \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2)$$

4.15

where; $0 \text{ min} \leq t_r \leq 60 \text{ min}$, $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $1/90 \leq \text{Fe}^{3+}:\text{H}_2\text{O}_2 \leq 1/10$

$$\text{COD Removal (\%)} = 78.35 + 5.74 \times A_1 - 2.79 \times A_2 + 13.50 \times A_3 - 3.85 \times (A_1)^2 - 1.08 \times (A_2)^2 - 8.51 \times (A_3)^2 + 0.67 \times A_1 \times A_2 - 3.11 \times A_1 \times A_3 + 5.35 \times A_2 \times A_3$$

4.16

where; $-2 \leq A_i \leq 2$

$$\begin{aligned} \text{COD Removal (\%)} = & 46.38733 + 1.40196 \times t_r + 2.53074 \times 10^{-3} \times \text{COD} + 222.56091 \\ & \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) - 0.017128 \times (t_r)^2 - 4.32008 \times 10^{-4} \times (\text{COD})^2 - 2813.76409 \times \\ & (\text{Fe}^{3+}:\text{H}_2\text{O}_2)^2 + 8.92500 \times 10^{-4} \times t_r \times \text{COD} - 3.77418 \times t_r \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) + 1.94663 \times \\ & \text{COD} \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) \end{aligned}$$

4.17

where; $0 \text{ min} \leq t_r \leq 60 \text{ min}$, $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $1/90 \leq \text{Fe}^{3+}:\text{H}_2\text{O}_2 \leq 1/10$

$$\begin{aligned} \text{TOC Removal (\%)} = & 48.65 + 8.48 \times A_1 - 7.16 \times A_2 + 6.94 \times A_3 - 0.12 \times (A_1)^2 + 2.81 \\ & \times (A_2)^2 - 4.42 \times (A_3)^2 - 1.11 \times A_1 \times A_2 - 3.18 \times A_1 \times A_3 + 5.14 \times A_2 \times A_3 \end{aligned}$$

4.18

where; $-2 \leq A_i \leq 2$

$$\begin{aligned} \text{TOC Removal (\%)} = & 98.91662 + 1.06640 \times t_r - 0.63239 \times \text{COD} - 0.84959 \times \\ & (\text{Fe}^{3+}:\text{H}_2\text{O}_2) - 5.34272 \times 10^{-4} \times (t_r)^2 + 1.12342 \times 10^{-3} \times (\text{COD})^2 - 1461.04940 \times \\ & (\text{Fe}^{3+}:\text{H}_2\text{O}_2)^2 - 1.47917 \times 10^{-3} \times t_r \times \text{COD} - 3.85510 \times t_r \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) + 1.87067 \times \\ & \text{COD} \times (\text{Fe}^{3+}:\text{H}_2\text{O}_2) \end{aligned}$$

4.19

where; $0 \text{ min} \leq t_r \leq 60 \text{ min}$, $100 \text{ mg/L} \leq \text{COD} \leq 300 \text{ mg/L}$ and $1/90 \leq \text{Fe}^{3+}:\text{H}_2\text{O}_2 \leq 1/10$

ANOVA results showing the significance and adequacy of these quadratic models were displayed in Table 4.6.

Table 4.6: ANOVA results of the quadratic model for photo-Fenton-like degradation of synthetic AB 193 production wastewater (independent parameters: reaction time, initial COD and $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio)

	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob>F
Color Removal	Model	2139.57	9	237.73	2.63	0.0438
	Residual	1444.36	16	90.27		
	Lack of Fit	1443.23	14	103.09	183.27	0.0054
	Pure Error	1.13	2	0.56		
	$R^2 = 0.5970$, Adequate precision = 7.189					
COD Removal	Model	1566.37	9	174.04	3.64	0.0119
	Residual	765.25	16	47.83		
	Lack of Fit	763.84	14	54.56	77.32	0.0128
	Pure Error	1.41	2	0.71		
	$R^2 = 0.6718$, Adequate precision = 6.810					
TOC Removal	Model	2823.98	9	313.78	7.86	0.0002
	Residual	638.60	16	39.91		
	Lack of Fit	625.49	14	44.68	6.82	0.1351
	Pure Error	13.11	2	6.55		
	$R^2 = 0.8156$, Adequate precision = 10.724					

R^2 value of the response variables followed the order of $R^2_{(\text{TOC Rem})} > R^2_{(\text{COD Rem})} > R^2_{(\text{Color Rem})}$ as this is the case when Fe^{3+} and H_2O_2 concentrations were considered as individual parameters, instead of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio. Relatively high R^2 for TOC removal indicates a good fit of the model, where at least 0.80 is suggested (Joglekar and May, 1987). On the other hand, for color and COD removal efficiencies lower values of R^2 denote that 40.3% and 32.8% of the total variation could not be represented by the empirical models. The low Prob>F values of 0.0438, 0.0119 and 0.0002 imply the quadratic models are significant for color, COD and TOC removal percents, respectively. The adequate precision ratios indicate an adequate signal for all responses since a ratio greater than 4 is desirable for sound models.

ANOVA results of the model terms indicating the significance of each term on response variable were also obtained by the model and displayed in Table 4.7. A Prob>F value less than 0.05 indicates that factor has a significant effect on the response.

Table 4.7: ANOVA results for model terms (independent parameters: reaction time, initial COD and $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio)

	Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	Prob>F
Color Removal	A ₁	626.00	1	626.00	6.93	0.0181
	A ₂	0.63	1	0.63	6.953×10^{-3}	0.9346
	A ₃	6.20	1	6.20	0.069	0.7966
	(A ₁) ²	1059.84	1	1059.84	11.74	0.0035
	(A ₂) ²	9.17	1	9.17	0.10	0.7541
	(A ₃) ²	2.02	1	2.02	0.022	0.8830
	A ₁ A ₂	0.018	1	0.018	2.019×10^{-4}	0.9888
	A ₁ A ₃	2.06	1	2.06	0.023	0.8817
	A ₂ A ₃	1.251×10^{-3}	1	1.251×10^{-3}	1.386×10^{-5}	0.9971
COD Removal	A ₁	599.19	1	599.19	12.53	0.0027
	A ₂	141.86	1	141.86	2.97	0.1043
	A ₃	357.05	1	357.05	7.47	0.0148
	(A ₁) ²	322.78	1	322.78	6.75	0.0194
	(A ₂) ²	25.35	1	25.35	0.53	0.4771
	(A ₃) ²	88.87	1	88.87	1.86	0.1917
	A ₁ A ₂	7.17	1	7.17	0.15	0.7037
	A ₁ A ₃	38.37	1	38.37	0.80	0.3837
	A ₂ A ₃	113.43	1	113.43	2.37	0.1431
TOC Removal	A ₁	1304.45	1	1304.45	32.68	< 0.0001
	A ₂	931.23	1	931.23	23.33	0.0002
	A ₃	94.32	1	94.32	2.36	0.1438
	(A ₁) ²	0.31	1	0.31	7.869×10^{-3}	0.9304
	(A ₂) ²	171.44	1	171.44	4.30	0.0547
	(A ₃) ²	23.96	1	23.96	0.60	0.4498
	A ₁ A ₂	19.69	1	19.69	0.49	0.4925
	A ₁ A ₃	40.04	1	40.04	1.00	0.3315
	A ₂ A ₃	104.75	1	104.75	2.62	0.1248

As can be understood from Table 4.7, reaction time (A₁) found to be the most significant factor affecting percent color, COD and TOC removals, similar to the case where Fe^{3+} and H_2O_2 concentrations were considered as individual parameters. Quite small Prob>F value of initial COD (A₂) indicates input organic load was highly significant to TOC removal efficiency, while $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio (A₃) seems to be significant to the response of COD removal.

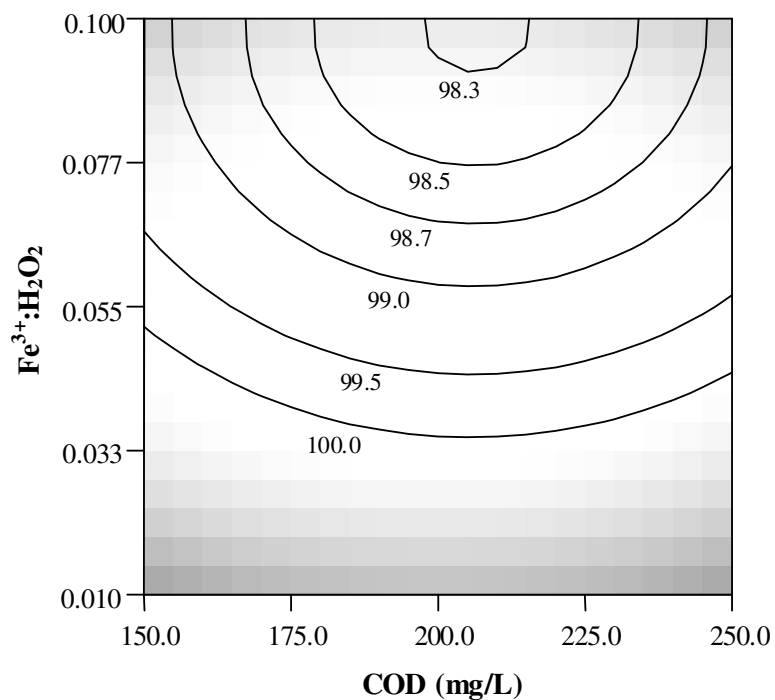
The model predictions for each run were presented in Appendix A, Table A.2 together with the experimentally achieved percent removals. As can be seen from the table, predicted and actual values of percent removals were closer to each other in

case of COD and especially TOC, indicating a correspondence between empirical model and experiment.

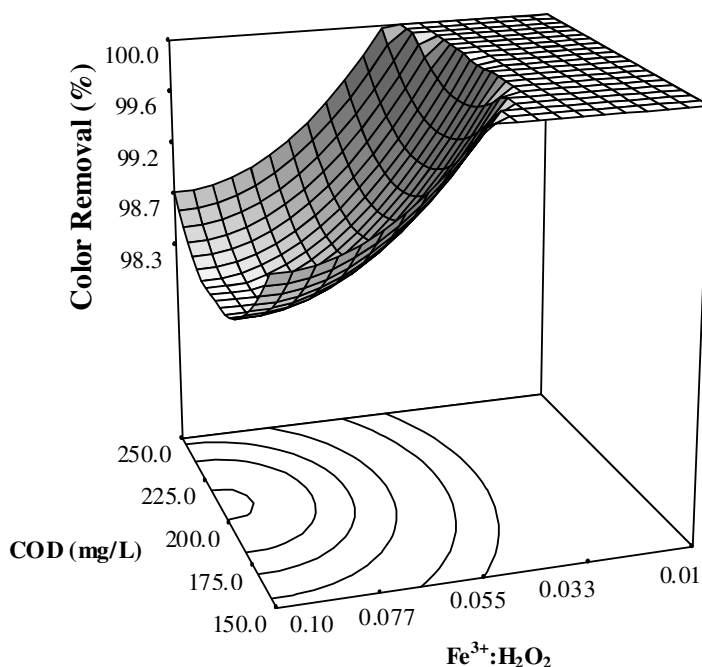
The response surface and contour plots displaying the interaction of the responses and process parameters were shown in Figures 4.23-4.25. In the plots of the quadratic models, one variable kept at central level while the other two varying within the experimental ranges.

Effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ Ratio and Initial COD on Percent Color Removal

Figure 4.23 (a-b) demonstrates the effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio and initial COD of the solution on color removal efficiency at a constant reaction time (45 min). As can be seen, variation of the initial COD within the range of 150-250 mg/L, does not have a significant impact on color removal, while increase in $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio slightly reduces the efficiency. Nearly complete color abatement (>98%) were achieved after 45 minutes of treatment, under all investigated conditions.



(a)

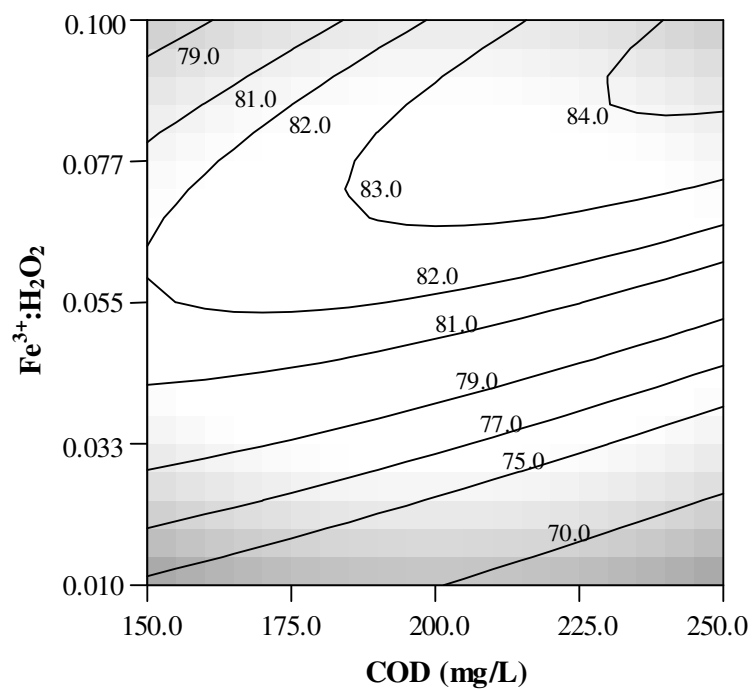


(b)

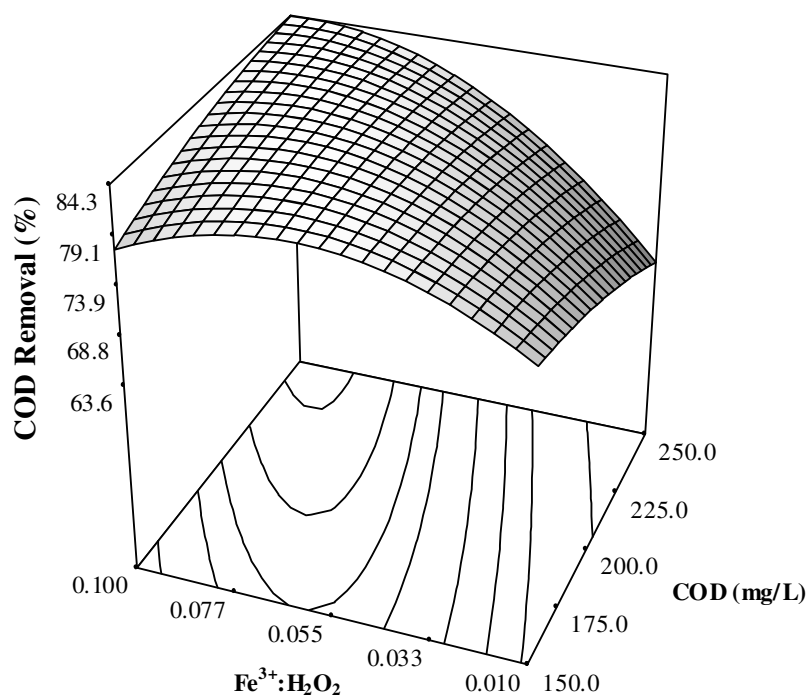
Figure 4.23: Contour (a) and response surface (b) plots of color removal from synthetic AB 193 production wastewater as a function of initial $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio and initial COD concentration; at 45 min reaction time

Effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ Ratio and Initial COD on Percent COD Removal

Figure 4.24 are contour (a) and response surface (b) plots showing the estimate COD removal efficiency over the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio and initial COD variables, at 45 min reaction time. While initial COD of the solution was around 150 mg/L, most efficient COD removal was obtained at the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio about 0.06. However in case of greater initial CODs (i.e. 250 mg/L), COD removal efficiency reached its highest value when $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio was kept around 0.1, indicating that optimum ratio of reactants is specific for the strength of the wastewater.



(a)

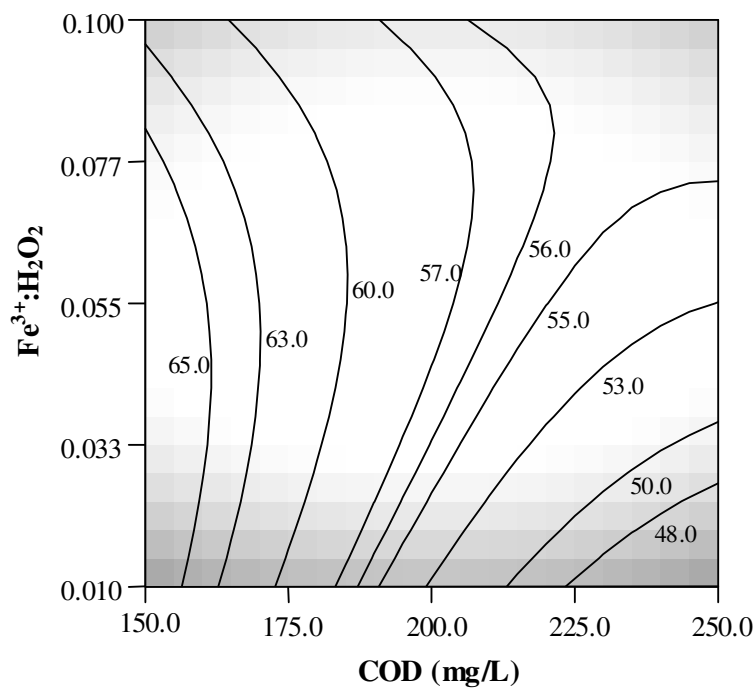


(b)

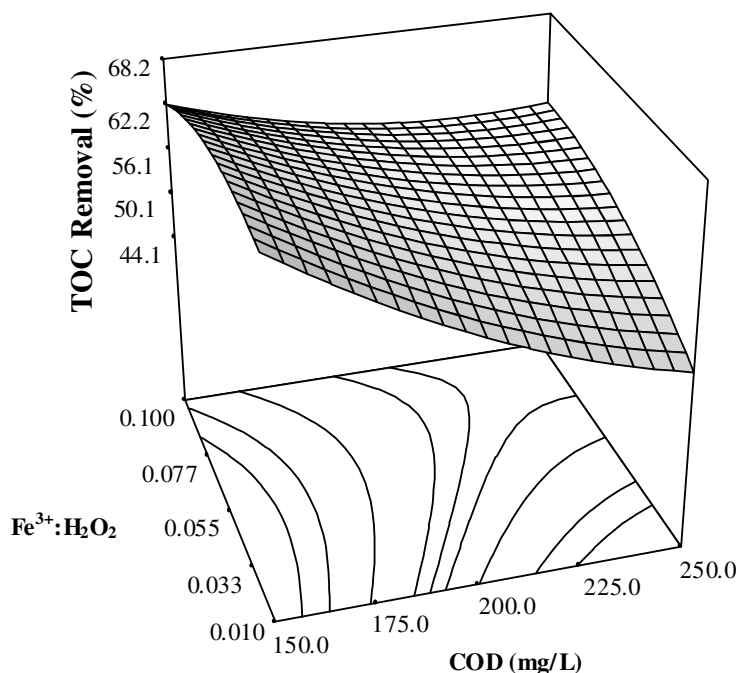
Figure 4.24: Contour (a) and response surface (b) plots of COD removal from synthetic AB 193 production wastewater as a function of initial $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio and initial COD concentration; at 45 min reaction time

Effect of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ Ratio and Initial COD on Percent TOC Removal

Figure 4.25 display the contour (a) and response surface (b) plots of the TOC removal as a function of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio and initial COD concentration, at constant reaction time of 45 min. As can be seen from the contour plot, at initial CODs less than 200 mg/L, change in $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio did not have a significant impact on TOC removal. However, when initial COD of the solution was greater than 200 mg/L, TOC abatement was enhanced with the raise in $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio, similar to the case in COD removal. Independent from the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio, TOC removal efficiency was adversely affected from the increasing COD loads.



(a)



(b)

Figure 4.25: Contour (a) and response surface (b) plots of TOC removal from synthetic AB 193 production wastewater as a function of initial $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio and initial COD concentration; at 45 min reaction time

The results were optimized by Design-Expert software using the approximating functions 4.14-4.19. Desired goals for the response variables (color, COD and TOC removal efficiencies) were chosen as “maximize”, while independent parameters of $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio and reaction time were defined to be “in the range”. The optimization results for initial COD of 200 mg/L were obtained as 0.073 $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio and 45 min reaction time, with the desirability of 0.83. At these optimum conditions, model predicted 99% color, 83% COD and 58% TOC removal could be achieved.

The optimal value of reaction time was found to be identical to the case, at which Fe^{3+} and H_2O_2 concentrations were considered as individual parameters. However optimized molar ratio of 0.073 is different from 0.043; calculated by dividing the optimum concentrations of Fe^{3+} (1.5 mM) by H_2O_2 (35 mM), which were determined in the previous part of the study. According to the results of the run considering $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio as an independent parameter, if Fe^{3+} concentration is selected again 1.5 mM, corresponding H_2O_2 concentration should be around 20 mM instead

of 35 mM, to obtain a molar ratio of 0.073. Considering that treatment efficiency was also high at the H_2O_2 concentration of 25 mM, 0.073 might be the real optimum molar ratio for COD's ≤ 200 mg/L.

4.2.2. Photo-Fenton-like Oxidation of Synthetic RB 39 Production Wastewater and Reverse Osmosis Effluent from RB 39 Production

Synthetic RB 39 production wastewater and reverse osmosis (RO) effluent of RB 39 production were also subjected to photo-Fenton-like treatment under the optimum conditions determined for acid dye production wastewater. In this way, validity of the predicted optimums was checked for the reactive type of dye production effluent. As aforementioned, optimal operation conditions were determined as $\text{Fe}^{3+}=1.5$ mM, $\text{H}_2\text{O}_2=35$ mM and reaction time=45 min for solutions having initial COD = 150-200 mg/L. Predicted and experimentally obtained response variables under this conditions were shown in Table 4.8. Predicted and actual color, COD and TOC removal efficiencies were also shown in Figure 4.26-4.28 as a function of reaction time.

Table 4.8: Predicted and experimentally obtained removal efficiencies at optimum operation conditions for synthetic RB 39 production wastewater and RO effluent of RB 39 production

Responses	Synthetic RB 39 production ww (initial COD = 195 mg/L)		RO effluent of RB 39 production (initial COD = 165 mg/L)	
	Model predictions	Experimental results	Model predictions	Experimental results
Color removal (%)	99	100	100	100
COD removal (%)	82	84	84	69
TOC removal (%)	61	53	70	37
Desirability	0.85		0.94	

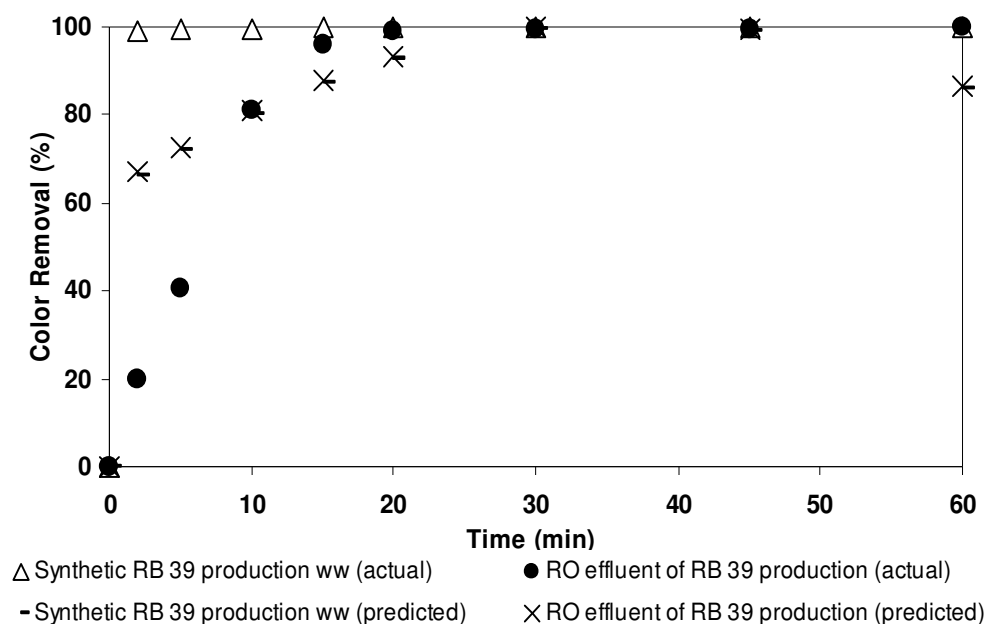


Figure 4.26: Predicted and experimentally achieved color abatements for synthetic RB 39 production wastewater ($COD_o = 195$ mg/L) and RO effluent of RB production ($COD_o = 165$ mg/L) during photo-Fenton-like oxidation. Experimental conditions: $Fe^{3+}_{,o} = 1.5$ mM; $H_2O_{2,o} = 35$ mM; $pH_o = 2.8$

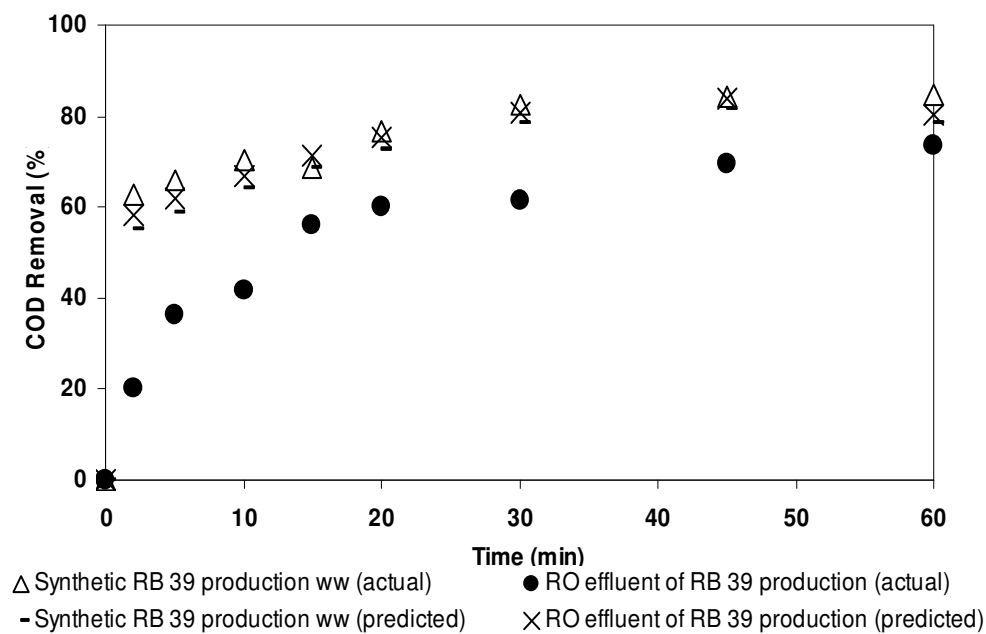


Figure 4.27: Predicted and experimentally achieved COD abatements for synthetic RB 39 production wastewater ($COD_o = 195$ mg/L) and RO effluent of RB production ($COD_o = 165$ mg/L) during photo-Fenton-like oxidation. Experimental conditions: $Fe^{3+}_{,o} = 1.5$ mM; $H_2O_{2,o} = 35$ mM; $pH_o = 2.8$

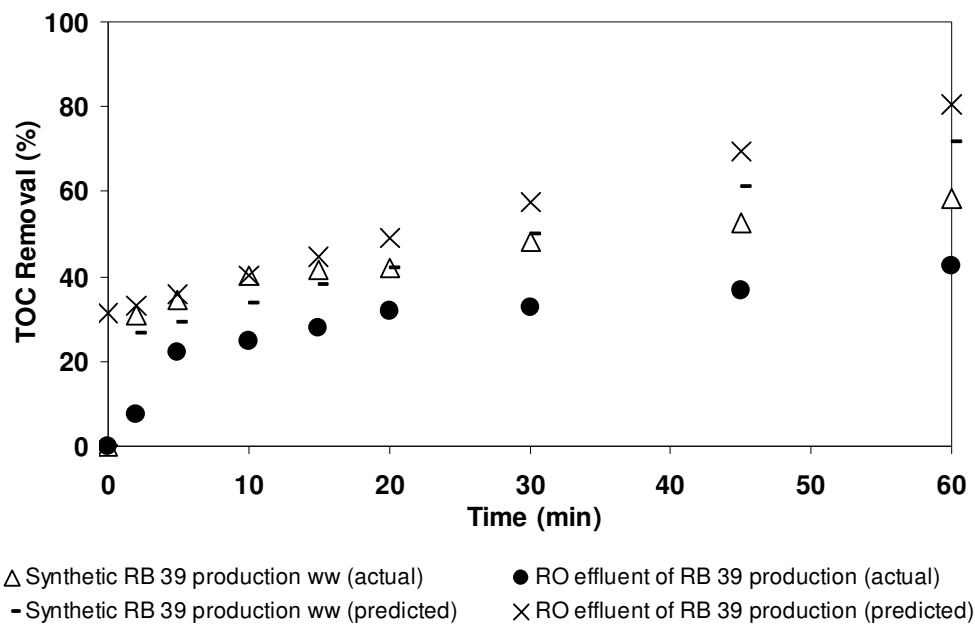


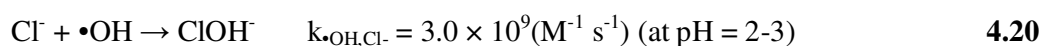
Figure 4.28: Predicted and experimentally achieved TOC abatements for synthetic RB 39 production wastewater ($\text{COD}_0 = 195 \text{ mg/L}$) and RO effluent of RB production ($\text{COD}_0 = 165 \text{ mg/L}$) during photo-Fenton-like oxidation. Experimental conditions: $\text{Fe}^{3+}_{,0} = 1.5 \text{ mM}$; $\text{H}_2\text{O}_{2,0} = 35 \text{ mM}$; $\text{pH}_0 = 2.8$

As can be seen from Table 4.8, for synthetic RB 39 production wastewater, experimentally achieved percent color and COD abatements (100% and 84%, respectively) were slightly higher than the 99% color and 82% COD removal percents predicted by the model, which speculatively is due to differences in molecular structures and/or concentrations of the chromium complex disazo dye AB 193 and the disazo dye RB 39 dye content of the dye production wastewaters. On the other hand, TOC removal efficiency for synthetic RB 39 production wastewater remained lower in actual case with 53%, as compared with the model prediction of 61%, revealing that to achieve a complete mineralization is a harder task for RB 39 than AB 193, as a consequence of differences in molecular weight and structure.

In case of RO effluent; predicted color removal efficiency (100%) was experimentally achieved in 45 min photo-Fenton-like treatment, however showed a significant retardation as compared to color removal in the synthetic reactive dye production wastewater (Figure 4.26). COD and TOC removals after 45 min treatment were found considerably lower than estimated by the model predictions (Table 4.8). Dramatic decrease in treatment performance can be also understood from Figures

4.27 and 4.28 showing the percent COD and TOC removals as a function of reaction time.

The efficiency decrease in case of RO effluent was attributable to its high chloride concentration as compared with synthetic azo dye production wastewaters (see Table 3.1). It is reported in many studies that $\bullet\text{OH}$ concentration is affected by the impurities present in the water such as inorganic anions like chloride. Chloride ion reacts with the $\bullet\text{OH}$ at acidic pH conditions as represented by the equation 4.17 (Evgenidou et al., 2007; Kiwi et al., 2000).



Hence the radical scavenging effect of Cl^- significantly reduces the organic matter oxidation rate and thus the treatment performance.

5. SUMMARY AND CONCLUSIONS

5.1. Treatability of Aqueous AR 183 Solution Using Fenton-like and Photo-like Processes

Due to their recalcitrant nature, textile azo dyes can not be effectively degraded with conventional wastewater treatment processes. In order to prevent the adverse effect on environment resulting from their release, several chemical and physicochemical processes have been employed in the past. Among them, Fenton and photo-Fenton type advanced oxidation processes has received great attention due to their high rate and efficiency in the oxidation of dyestuff, ease of operation and relatively low operating costs. These processes are known to be quite advantageous especially for the treatment of acid dyes and acid dyebath effluent since their working pH's (2-5) is a range being close to the application pH of acid dyes onto polyamide fibers (pH 3-5). On the other hand, Fenton-like treatment involving Fe^{3+} instead of Fe^{2+} ions as the iron catalyst source was relatively less explored for the degradation of textile dyes. With these facts in mind, in first part of the study 100 mg/L aqueous AR 183 solution was treated via Fenton-like, photo-Fenton-like and ferrioxalate-photo-Fenton-like processes to evaluate their efficiency and feasibility in color and TOC reduction from the dye solution. The following results and conclusions were obtained from the study:

- Increasing Fe^{3+} concentration exerted a positive effect on color and TOC removals, via Fenton-like reaction. This is an expected result, since increase in the concentration of the iron catalyst accelerates the decomposition of H_2O_2 to produce radicals, hence enhancing the organic matter degradation.
- The most efficient initial pH range for Fenton-like oxidation was established as 2.8-3.5 both in terms of color and TOC removal. Hydrolysis reactions of Fe^{3+} occurring after its addition to the aqueous reaction medium, reduce the initially adjusted pH of the solution. Hence significant color and partial TOC

abatements were obtained at the initial pHs 5-7 which are known as unsuitable for Fenton type AOPs.

- The color removal rate and degree of mineralization were improved with UV-A light irradiation. Color removal reached 48% after 20 min oxidation in the presence of light, which was more than twice of the 23% removal achieved by dark Fenton-like treatment under otherwise same experimental conditions. 14% TOC reduction was found for the photo-Fenton-like process in 20 min, whereas 6% removal was achieved with dark process. Therefore, treatment of AR 183 with photo-Fenton-like process can be recommended if rapid color removal is required with a partial organic carbon reduction.
- The ferrioxalate-photo-Fenton-like process did not show the expected improving effect on treatment efficiency and the results for color removal were even worse than those obtained by the dark Fenton-like process. The rather unexpected inhibitory effect of oxalate on dye degradation might be explained by the competition of the additional organic carbon (resulting from oxalate) with the dye molecules for hydroxyl radicals and the formation of Cr(III)-oxalate complexes between the Cr(III) ions released from the acid dye structure and oxalate, leading to a dramatic decrease in photocatalytically induced hydroxyl radical production. TOC values also showed an increase because of the organic carbon coming from the oxalate anions. Thus, it is evident that the use of oxalate in photo-Fenton-like treatment of AR 183 is meaningless from both color and organic carbon removal points of view.
- No significant color and TOC abatement was obtained in the control experiments carried out with individual components of Fenton-like and photo-Fenton-like processes, revealing that AR 183 degradation mainly proceeded via $\bullet\text{OH}$ generated by the Fe^{3+} catalyzed decomposition of H_2O_2 .

5.2. Treatability of Azo Dye Production Wastewaters Using Photo-like Processes

The disposal of dye plant effluent with toxic and non-biodegradable organic compounds is always a matter of great concern since they are considered as a quite dangerous source of environmental pollution. During dye manufacturing, several waste streams that are variable in composition and strength were created. Among

them; wastewater generated from the dye synthesis reactor washing and reverse osmosis effluent/outflows are considered to be suitable for photochemical oxidation, with their relatively low strength and slightly acidic pH. With these facts in the mind, second part of the study aimed at investigating the treatability of azo dye production wastewaters via photo-Fenton-like oxidation. For this purpose, synthetic AB 193 and RB 39 production wastewaters and a real dye production effluent (RO effluent of RB 39 production) were employed as model pollutants. Response Surface Methodology (RSM) was applied to assess the individual and interaction effects of several operating parameters on color, COD and TOC removal efficiencies, as well as for optimizing the process parameters to obtain maximum treatment performance. Once after the experimental runs indicated by the model were conducted with synthetic AB 193 production wastewater and results were obtained, model gave polynomial equations expressing the empirical relationship between the responses and process variables. These model polynomial functions were later analyzed to locate the optimum values of independent variables for the best response. The conclusions drawn from the second part of study were given below:

- ANOVA results of the approximating functions for model wastewater indicated that RSM explained the reactions well for COD and TOC removals, and can be used to navigate the design space. However, a distinct prediction could not be done by the employed model for color removal, probably due to the inappropriate reaction time interval used in Central Composite Design (0, 15, 30, 45 and 60 min). Since color abatement occurs quite rapid as compared with COD and TOC, selecting a narrower range for reaction time variable might result in more fitting predictions for color removal.
- Concordant to the developed empirical models, reaction time (X_3) was the only parameter that has a significant influence on all response variables, revealing that insufficient time results in a decrease of treatment efficiency, no matter which are the values of other process parameters. Effect of initial Fe^{3+} concentration (X_1) was more significant to the responses of COD and TOC removals as compared with the initial H_2O_2 concentration (X_2), indicating that Fe^{3+} catalyst was the rate-limiting reagent for oxidation of synthetic AB 193 production wastewater.

- Reduction of the oxidation efficiency was observed due to $\bullet\text{OH}$ -scavenging reactions in the presence of an excess of one of the two Fenton-like reagents. Hence, selection of the correct reagent load is extremely important to achieve high treatment efficiencies.
- Optimized variables for the solution having 200 mg/L initial COD were obtained as follows: $\text{Fe}^{3+} = 1.5 \text{ mM}$, $\text{H}_2\text{O}_2 = 35 \text{ mM}$ and reaction time = 45 min for maximum color, COD and TOC abatements. For initial CODs less than 200 mg/L (i.e. 150 mg/L), optimal values of the independent parameters were same, whereas concentrations of Fe^{3+} and H_2O_2 increased up to 3.5 mM and 44 mM, in case of 250 mg/L initial COD.
- Under the optimum conditions, model predicted that 99% color, 81% COD and 60% TOC removal could be achieved by the photo-Fenton-like process, for synthetic AB 193 production wastewater having 200 mg/L initial COD. RSM predictions were well validated by the additional experimental data, achieving up to 98%, 78% and 59% color, COD and TOC removals, respectively. These results demonstrate the usefulness of the RSM in predicting the system performance.
- The control experiments conducted with UV-A only, H_2O_2 only, H_2O_2 with UV-A and Fe^{3+} combined with UV-A demonstrated that most of the color, COD and TOC removals were obtained via $\bullet\text{OH}$ -initiated oxidation.
- Dark Fenton-like oxidation of synthetic AB 193 production wastewater achieved color and COD abatement efficiencies close to the photo-Fenton-like's, although removal rates were a bit slower. However in case of TOC abatement, second stage of oxidation (degradation of intermediate products) was provided by photo-Fenton-like process, leading to a higher extent of mineralization as compared with dark process. For instance, observed TOC abatement after 60 min treatment was 44% with dark reaction, while it was 63% in the presence of UV-A light.
- RSM was also utilized to obtain optimum $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio for photo-Fenton-like treatment of synthetic AB 193 production wastewater. Maximum color, COD and TOC removals for the wastewater having 200 mg/L initial

COD were achieved as 99%, 83% and 58% respectively, at optimal conditions of 0.073 Fe^{3+} : H_2O_2 ratio and 45 min reaction time.

- In photo-Fenton-like treatment of synthetic RB 39 production wastewater, 100% color, 84% COD and 53% TOC abatements were experimentally obtained under the optimum conditions ($\text{Fe}^{3+} = 1.5 \text{ mM}$, $\text{H}_2\text{O}_2 = 35 \text{ mM}$ and reaction time = 45 min) for $\text{COD} \leq 200 \text{ mg/L}$, which were slightly higher than the model predictions in terms of color and COD. On the other hand, experimentally achieved TOC abatement was lower than the predicted value of 61%, denoting that complete mineralization of RB 39 production wastewater is more difficult than AB 193 production wastewater, which is probably due to the differences in molecular weight & structure and concentration of the dyes, as well as the type and concentration of other dye production wastewater ingredients.
- For RO effluent of RB 39 production, experimentally achieved 69% COD and 37% TOC abatements under optimum conditions ($\text{Fe}^{3+} = 1.5 \text{ mM}$, $\text{H}_2\text{O}_2 = 35 \text{ mM}$ and reaction time = 45 min) for $\text{COD} \leq 200 \text{ mg/L}$ were considerably lower than the model predictions of 84% COD and 70% TOC removal, as well as the retardation observed in decolorization. The significant decrease in the treatment efficiency was mainly attributed to the high chloride concentration ($\text{Cl}^- = 3500 \text{ mg/L}$) of RO effluent, which caused $\bullet\text{OH}$ scavenging reactions.
- Photo-Fenton-like oxidation process was found to be very effective in the treatment of suitable waste streams from acid and reactive dye production, and can be suggested for obtaining almost complete decolorization with significant COD and TOC abatements. However, it is recommended to determine the chloride content of the wastewater prior to application of such a photochemical process, since treatment efficiency is considerably reduced in case of high chloride concentrations.

6. REFERENCES

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APPENDIX

APPENDIX A. Central Composite Design for RSM and the Predicted and Experimentally Achieved Removal Efficiencies

Table A.1: Four-factorial and five-level central composite design for RSM and the predicted and experimentally achieved removal efficiencies

	X_1	X_2	X_3	X_4	Y_1		Y_2		Y_3	
Trial no.	Fe^{3+} (mM)	H_2O_2 (mM)	Time (min)	COD (mg/L)	Color Removal (%)		COD Removal (%)		TOC Removal (%)	
					Actual	Predicted	Actual	Predicted	Actual	Predicted
1	1.5	55	15	250	96	89	45	53	32	32
2	2.5	45	30	200	97	97	78	78	51	51
3	2.5	65	30	200	98	>100	78	76	49	44
4	2.5	45	30	100	98	>100	73	79	78	73
5	2.5	45	0	200	36	60	49	55	31	34
6	3.5	55	15	150	97	90	78	76	48	51
7	3.5	35	45	250	96	99	78	83	55	56
8	4.5	45	30	200	97	>100	83	87	53	54
9	3.5	55	45	250	98	100	84	86	57	56
10	3.5	55	45	150	99	>100	80	82	59	61
11	1.5	35	45	250	98	100	74	77	49	51
12	1.5	55	15	150	98	90	70	65	48	47
13	1.5	55	45	250	98	100	63	68	39	46
14	1.5	35	15	150	96	89	73	73	43	49
15	3.5	55	15	250	97	89	81	77	51	50
16	2.5	25	30	200	96	100	81	81	48	47
17	2.5	45	60	200	98	83	83	75	74	65
18	3.5	35	45	150	97	99	83	77	60	65
19	0.5	45	30	200	97	>100	77	70	51	45
20	3.5	35	15	250	95	87	76	76	44	44
21	2.5	45	30	200	97	97	78	78	51	51
22	2.5	45	30	300	98	>100	81	73	50	49
23	1.5	35	45	150	98	100	80	85	74	74
24	1.5	35	15	250	96	89	64	63	31	30
25	3.5	35	15	150	95	88	76	72	55	48
26	1.5	55	45	150	98	>100	76	78	60	66

Table A.2: Three-factorial and five-level central composite design for RSM and the predicted and experimentally achieved removal efficiencies

	A ₁	A ₂	A ₃	B ₁		B ₂		B ₃	
Trial no.	Time (min)	COD (mg/L)	Fe ³⁺ :H ₂ O ₂	Color Removal (%)		COD Removal (%)		TOC Removal (%)	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
1	15	250	0.027	96	89	45	56	32	31
2	30	200	0.056	97	100	78	81	51	50
3	30	200	0.038	98	>100	78	77	49	48
4	30	100	0.056	98	>100	73	80	78	73
5	0	200	0.056	36	61	49	55	31	34
6	15	150	0.064	97	88	78	74	48	50
7	45	250	0.100	96	99	78	84	55	56
8	30	200	0.100	97	100	83	83	53	51
9	45	250	0.064	98	99	84	81	57	54
10	45	150	0.064	99	100	80	82	59	67
11	45	250	0.043	98	100	74	76	49	51
12	15	150	0.027	98	89	70	67	48	47
13	45	250	0.027	98	>100	63	71	39	48
14	15	150	0.043	96	89	73	71	43	49
15	15	250	0.064	97	88	81	71	51	41
16	30	200	0.100	96	100	81	83	48	51
17	60	200	0.056	98	84	83	76	74	65
18	45	150	0.100	97	99	83	78	60	62
19	30	200	0.011	97	>100	77	67	51	43
20	15	250	0.100	95	88	76	78	44	48
21	30	200	0.056	97	100	78	81	51	50
22	30	300	0.056	98	>100	81	73	50	49
23	45	150	0.043	98	100	80	81	74	68
24	15	250	0.043	96	88	64	63	31	36
25	15	150	0.100	95	89	76	74	55	49
26	45	150	0.027	98	>100	76	79	60	68

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