

**PRETREATMENT OF SIMULATED ACID DYE BATHS
BY FENTON'S REAGENT**

**M Sc. Thesis by
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(501031813)**

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ABBREVIATIONS

ATM	: American Textile Manufacturers Institute
UNEP	: United Nations Environment Programme
EPA	: Environmental Protection Agency
FFTA	: Foundation of the Flexographic Technical Association
COD	: Chemical Oxygen Demand (mg/L)
AOX	: Halogenated Organics
BOD	: Biochemical Oxygen Demand (mg/L)
VOC's	: Volatile Organic Compounds
HAP	: Hazardous Air Pollutants
ITKB	: General Secretariat of Istanbul Textile & Apparel Exporters' Associations
SME	: Small and Medium Scale Enterprises
GDP	: Gross Domestic Product
TL	: Turkish Lira
SBR	: Sequencing Batch Reactor
UF	: Ultrafiltration
NF	: Nanofiltration
RO	: Reverse Osmosis
AOP	: Advanced Oxidation Processes
STP	: Standard Temperature and Pressure
UV	: Ultraviolet
TOC	: Total Organic Carbon (mg/L)
IAWPRC	: International Association on Water Pollution Research and Control
MLVSS	: Mixed Liquor Suspended Solids (mg/L)
ISO	: International Standardization Institute
OUR	: Oxygen Uptake Rate (mg L ⁻¹ h ⁻¹)
F/M	: Food to Microorganism ratio (mg COD/mg MLVSS.d ⁻¹)
EC	: Effective Concentration
VSS	: Volatile Suspended Solids (mg/L)
WWTP	: Wastewater Treatment Plant
SS	: Suspended Solids (mg/L)

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PRETREATMENT OF SIMULATED ACID DYE BATHS BY FENTON'S REAGENT

SUMMARY

The textile dyeing industry generates huge volumes of colored effluents with medium to high chemical oxygen demand (COD), total dissolved solids (TDS), heavy metals and nonionic surfactants. Apart from the aesthetic deterioration and hindrance of light penetration in the ecosystem caused by color, some dyes and their degradation products are potentially toxic or even carcinogenic in character. As a consequence, it is essential to treat dye house effluent prior to discharge into publicly owned treatment works and/or receiving water bodies.

It is known that biological treatment of dye house effluent is not very effective unless dye bath effluents are separated and pretreated before they are combined with the rest of the waste streams. Advanced Oxidation Processes (AOP) based on the oxidative degradation of organic compounds using hydroxyl radical ($\cdot\text{OH}$) are alternative methods for chemical pre-treatment of recalcitrant wastewater. Among a number of AOP, the Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) is one of the most effective and successfully employed processes applied for the chemical pre-treatment of textile wastewater. Fenton's reagent is usually applied at acidic pH ($\approx 2.5-3.5$), thus making it the treatment of choice when the natural pH of acid dye-bath effluents is considered.

In the present study, the treatability of two simulated acid dye-bath effluents (DB I and DB II) via Fenton's reagent was investigated. Reaction pH, initial Fe^{2+} and H_2O_2 concentrations, as well as process temperature ($20^\circ\text{C} < T < 70^\circ\text{C}$) were first optimized in terms of COD and color removal. The optimum conditions for acid DB I were determined as $\text{Fe}^{2+} = 2\text{ mM}$, $\text{H}_2\text{O}_2 = 30\text{ mM}$ and $\text{pH} = 3$ at $T = 50^\circ\text{C}$ and likewise as $\text{Fe}^{2+} = 10\text{ mM}$, $\text{H}_2\text{O}_2 = 30\text{ mM}$ and $\text{pH} = 3$ at $T = 60^\circ\text{C}$ for DB II, resulting in up to 32 % COD removal and complete decolorization for both acid dye-baths. Kinetic studies were carried out to determine the pseudo first order reaction rate constants and activation energies for H_2O_2 and COD abatement. The ratio of reaction rate constants with respect to increasing temperature for both dye baths was found almost constant as $0.1 \pm 0.05\text{ min}^{-1}/\text{min}^{-1}$, indicating that a positive relationship existed between COD removal and H_2O_2 consumption. The activation energies for COD and H_2O_2 abatement kinetics were determined as 5.8 kJ/mol and 9.5 kJ/mol for DB I and as 12.4 kJ/mol and 9.8 kJ/mol for DB II, respectively, which showed that DB II was more difficult to treat than DB I. The toxicity and biodegradability of the raw and chemically pre-treated effluents at optimized experimental conditions were also questioned by means of an activated sludge inhibition test and soluble inert COD determination, respectively.

The EC_{50} value for DBI was found as 311 mg/L COD for a test duration of 30 min and an F/M ratio of 0.19 mg COD/ mg MLVSS. d⁻¹, whereas Fenton pre-treated DBI exhibited no inhibition under the same conditions. Raw and treated DB II exhibited no inhibition for a test duration of 30 min and an F/M ratio of 0.20 mg COD/ mg MLVSS. d⁻¹.

Inert COD results have shown that the Fenton pre-treated DB I had soluble inert COD content of 110 mg/L COD which was significantly higher than that of raw DB I having almost completely biodegradable nature. The inert COD tests for the raw and Fenton pre-treated DB II showed that both are almost biodegradable in nature having soluble inert COD contents of 4 mg/L COD and 12 mg/L COD respectively.

Sİ MÜLE EDİ LMİ Ş ASİ T BOYA BANYOLARIN FENTON REAKTANI İ LE ÖN ARI TI M

ÖZET

Tekstil endüstrisi ol dukça büyük hacı mlerde, yüksek KOİ, topla mç özün müş madde, ağır metal ve ani yonik yüzeyaktif maddeler içeren ç ıkış suları üret mektedir. Estetik açı dan ol uşt urdu ğ u kirlen me ve ışı ğ ın ekosisteme ulaş ması nı engelle mesi ni n yanı sıra, bazı boyar maddeler ve bunların bozun malarıyla ol uş an ürünler potansi yel toksik hatta kanserojen ol abil mektedir. Bunun sonucunda, boyahane ç ıkış suları nın evsel atıksu arıtma tesislerine ve/veya alıcı ortama deş arj edil me den önce ön- arıtı marı ş arttır.

Boyahane atıksularının ayrı ele alınarak, di ğ er atıksularla birleşt iril me den önce ön- arıtı m dan geçiril me meleri halinde biyolojik olarak arıtıl maları nın ol anaklı ol madı ğ ı bilin mektedir. Organik maddelerin hidroksil radikali ($\cdot OH$) ile oksidatif arıtı m na dayanan İleri Oksidasyon Prosesleri (İ OP), arıtı maya dirençli atıksuların kimyasal ön- arıtı m iç in etkili bir yöntemdir. Birçok İ OP arasında Fenton reaktanı (Fe^{2+}/ H_2O_2), tekstil atıksularının kimyasal ön- arıtı mında en etkili ve başarılı yöntem olarak bilin mektedir. Fenton reaktanı, uygulandı ğ asidik pH ($\approx 2.5-3.5$) ve asit boya banyolarının doğal pH'sı göz önüne alınd ı ğ ında, uygun bir arıtı m seçene ğ i ol abil mektedir.

Bu çalış mada, hazırlanmış iki asit boya banyosu atıksularının Fenton reaktanı ile arıtılabilirlikleri araştırılmış tır. Reaksiyon pH'sı, Fe^{2+} ve H_2O_2 konsantrasyonlarının yanı sıra, deney sıcaklıkları ($20^\circ C < T < 70^\circ C$), KOİ veren k gideri mleri göz önüne alarak opti mize edil miş tir. Boya Banyo I için opti mum koşullar $Fe^{2+} = 2$ mM, $H_2O_2 = 30$ mM, pH = 3 ve $T = 50^\circ C$ aynı şekilde Boya Banyo II için ise $Fe^{2+} = 10$ mM, $H_2O_2 = 30$ mM, pH = 3 ve $T = 60^\circ C$ olarak bulunmuşt ur. Fenton ön- arıtı m ile her iki asit boya banyoda, %32 KOİ gideri mi ve %100'e varan renk gideri mi göz len miş tir. Ayrıca ön- arıtı m tabi tutulan Boya Banyolarda biyolojik arıtılabilirlikteki iyileş me de araştırılmış tır. H_2O_2 and KOİ gideri mlerinin birinci derece hız sabitlerini ve aktivasyon enerjilerini bul mak üzere zamanı karşı (kinetik) çalış malar yürüt ülmüşt ü. Reaksiyon hız sabitlerinin artan sıcaklı ğ a karşılık 0.1 ± 0.05 min⁻¹/min⁻¹ değ erinde sabit kalarak KOİ gideri mi ve H_2O_2 'teki azal ma arasında pozitif bir ilişki ol du ğ u gör ülmüşt ü. KOİ gideri mleri için aktivasyon enerjileri DB I ve DB II için 5.8 kJ/ mol ve 9.5 kJ/ mol, H_2O_2 gideri mleri için de 12.4 kJ/ mol ve 9.8 kJ/ mol olarak hesaplanmış; DB II'nin DB I'den daha zor arıtıldı ğ ı bulunmuşt ur. Ham ve ön- arıtı m tabi tutulmuş boya banyoların biyolojik arıtılabilirlikleri ISO 8192 Aktif Ç amur İnhibisyon Testi ve çözünmüş inert KOİ tayini ile sorgulanmış tır. DB I için 30 dak. test süresi ve 0.19 mg KOİ/ mg UAKM gün⁻¹ değ erinde F/M de, EC₅₀ değ erı 311 mg/ L KOİ bulunmakla birlikte, aynı koşullarda arıtılmış DB I hiçbir inhibisyon etki si gösterme miş tir. Ham ve arıtılmış DB II örnekleri de 30 dak. test

süresi ve $0.20 \text{ mg KOI} / \text{mg UAKM gün}^{-1}$ değeri nde F/ M de, i n h i b i s y o n e t k i s i göster n e m i ş t i r.

Inert KOI test sonuçları, ön-arıtıl mış DB I'in $110 \text{ mg} / \text{L KOI}$ değeri ile, t a m a m n a yakı nı biyolojik olarak ayrışabilen h a m DB I' den oldukça yüksek bir i n e r t KOI' ye sahip ol du ğ u n u göster m i ş t i r. H a m ve ön-arıtıl mış DB II'nin ise, ölçülen KOI değerleri, sırasıyla, $4 \text{ mg} / \text{L KOI}$ ve $12 \text{ mg} / \text{L KOI}$ göz önüne alınarak, her i k i s i n i n he n e n h e n e n t a m m y l a biyolojik olarak ayrışabilir d u k l a r ı göz l e n m i ş t i r.

1. INTRODUCTION

The textile industry is one of the highest wastewater generating sectors, involving the addition of a vast variety of chemicals at different stages of production. Dyeing process and the dyestuffs constitute a major share in the overall textile processing. The annual production of dyestuffs amount to over 700,000 tons worldwide of which 10 to 15 percent appear in the effluents from dyeing operations. Biological treatment systems, alone, prove unsatisfactory for the treatment of the dyestuffs and even having a non-toxic nature, they often require to be subjected to pre-treatment in separate flows using destructive chemical oxidation techniques. Among them the Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process, usually applied at acidic pH ($\approx 2.5 - 3.5$), was selected for investigating the treatability of two exhausted acid dyebaths which come out as an absolute treatment alternative when the operating conditions i.e. pH and temperature of these acid dyebaths are considered as well as the advantages of the Fenton process in terms of cost, ease of operation and availability. For this purpose, two acid dyebaths, i.e. one containing a metal (chromium) complex dye and acetic acid as the assisting chemical and another one bearing three acid dyes, and an ester based and oxyethylene derivative as dye auxiliary chemicals, were simulated in accordance with the actual factory spent dyebath conditions with maximum possible residual concentrations of the dyes and assisting chemicals.

The first part of the experimental work involves the optimization of Fe^{2+} iron (1 - 10 mM) and H_2O_2 (10 - 100 mM) concentration as well as reaction pH (2 - 5). In the second part of the study, a kinetic evaluation of the Fenton process at different operating temperatures ($T = 20 - 70^\circ\text{C}$) was investigated to assess the thermal improvement of COD and color removal and to determine activation energies for H_2O_2 and COD abatement. Finally, the effect of Fenton's pre-treatment on acute toxicity based Activated Sludge Inhibition Test - ISO 8192 and changes in the inert COD fraction of the acid dyebaths were examined.

2 THEORETICAL BACKGROUND

2.1 Textile Industry

2.1.1 History

The textile industry is one of the oldest in the world. The oldest known textiles, which date back to about 5000 B.C., are scraps of linen cloth found in Egyptian caves. The industry was primarily a family and domestic one until the early part of the 1500s when the first factory system was established. It wasn't until the Industrial Revolution in England, in the 18th century, that power machines for spinning and weaving were invented. In 1769 when Richard Arkwright's spinning frame with variable speed rollers was patented, water power replaced manual power (Neefus, 1982).

The twentieth century has seen the development of the first man-made fibers (rayon was first produced in 1910). Although natural fibers (wool, cotton, silk, and linen) are still used extensively today, they are more expensive and are often mixed with man-made fibers such as polyester, the most widely used synthetic fiber. In addition, segments of the textile industry have become highly automated and computerized (ATM, 1997).

2.1.2 Introduction

In terms of its output or production and employment, the textile industry is one of the largest industries in the world (UNEP, 1994). The textile industry is comprised of a diverse, fragmented group of establishments that produce and/or process textile-related products (fiber, yarn, fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibers; transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related

products; and dye and finish these materials at various stages of production (EPA, 2001).

The process of converting raw fibers into finished apparel and nonapparel textile products is complex; thus, most textile mills specialize. Little overlap occurs between knitting and weaving or among production of manmade, cotton, and wool fabrics. The primary focus of this section is on weaving and knitting operations, with a brief mention of processes used to make carpets (EPA, 2001).

Operations typically vary in scale from large mechanized plants to small scale traditional units but all are characterized by the vast quantity of water required (textile manufacturing is one of the largest industrial users of process water: >100 liters per kg of finished product) and by the variety of chemicals used in a long sequence of wet processing stages that generate many waste arisings. Variations in the fabric profiles also produce wide fluctuations in flow rates and waste concentration (UNEP, 1994).

In its broadest sense, the textile industry includes the production of yarn, fabric, and finished goods which may be summarized as four production stages; (i) yarn formation, (ii) fabric formation, (iii) wet processing and (iv) fabrication. These stages are presented in the process flowchart shown in Figure 2.1.

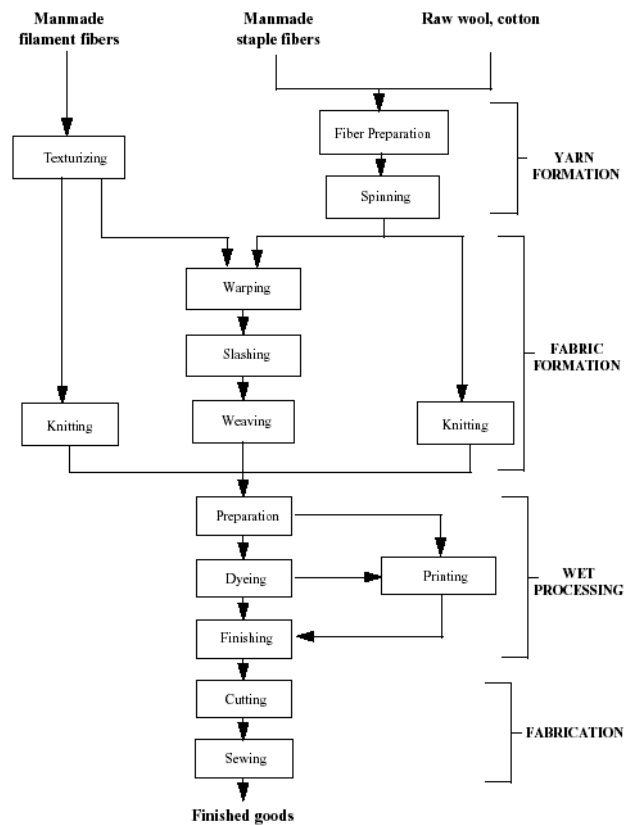


Figure 2.1: Typical Textile Processing Flow Chart (EPA 2001)

2.1.3 Wet Processing

Woven and knit fabrics cannot be processed into apparel and other finished goods until the fabrics have passed through several water-intensive wet processing stages. Wet processing enhances the appearance, durability, and serviceability of fabrics by converting undyed and unfinished goods, known as gray or greige goods, into finished consumers' goods. Also collectively known as finishing, wet processing has been broken down into four stages in this section for simplification: fabric preparation, dyeing, printing, and finishing. These stages, shown in Figure 1.2, involve treating gray goods with chemical baths and often require additional washing, rinsing, and drying steps. Note that some of these steps may be optional depending on the style of fabric being manufactured.

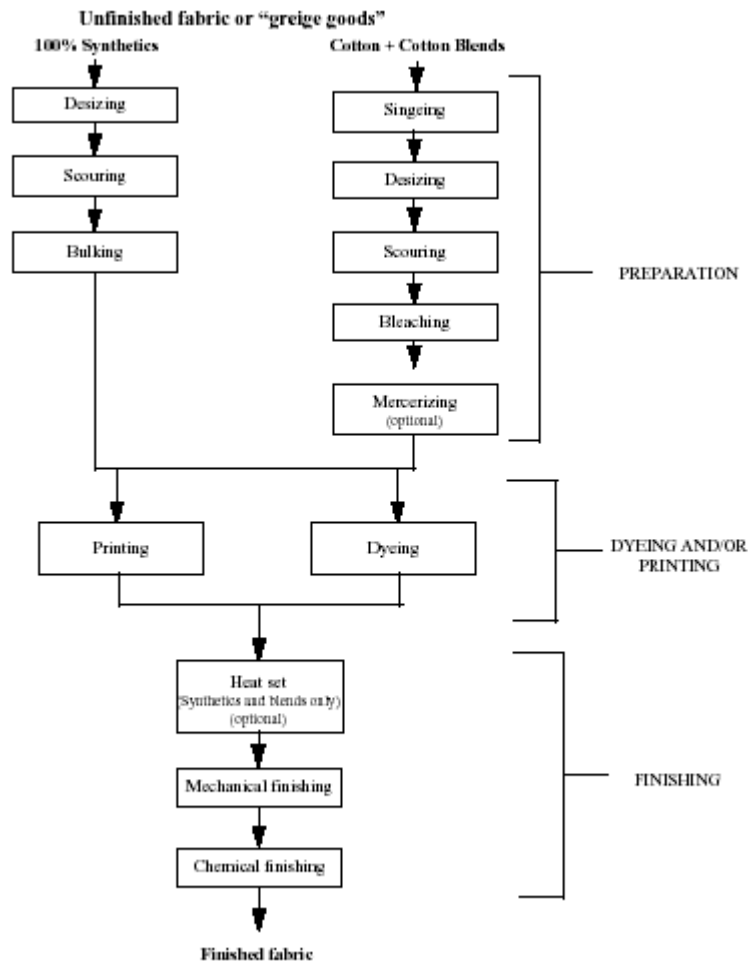


Figure 2.2: Typical Wet Processing Steps for Fabrics

In terms of waste generation and environmental impacts, wet processing is the most significant textile operation. Methods used vary greatly depending on end-products and applications, site-specific manufacturing practices, and fiber type. Natural fibers typically require more processing steps than manmade fibers. For most wool products and some manmade products, the yarn is dyed before weaving; thus, the pattern is woven into the fabric. Processing methods may also differ based on the final properties desired, such as tensile strength, flexibility, uniformity, and luster (Snowden- Swan, 1995).

Most manufactured textiles are shipped from textile mills to commission dyeing and finishing shops for wet processing although some firms have integrated wet processing into their operations. A wide range of equipment is used for textile dyeing and finishing (EPA, 1996). Much of the waste generated from the industry is produced during the wet processing stages. Relatively large volumes of wastewater

are generated, containing a wide range of contaminants that must be treated prior to disposal. Significant quantities of energy are spent heating and cooling chemical baths and drying fabrics and yarns (Snowden-Swan, 1995).

2.1.4 Dyeing

Dyeing processes may take place at any of several stages of the manufacturing process (fibers, yarn, piece-dyeing) to add color and intricacy to textiles and increase the product value. Today, textiles can be dyed with almost any color to achieve a variety of aesthetic and functional purposes. Most dyeing is performed either by the finishing division of vertically integrated textile companies, or by specialty dye houses. Specialty dye houses operate either on a commission basis or purchase greige goods and finish them before selling them to apparel and other product manufacturers.

Each dyeing process requires different amounts of dye per unit of fabric to be dyed. This is significant since color and salts in wastewater from spent dyes are often a pollution concern for textile facilities. In addition, less dye used results in energy conservation and chemical savings. Stock dyeing is used to dye fibers. Top dyeing is used to dye combed wool sliver.

2.1.4.1 Dyes and Their Classification

Textiles are dyed using a wide range of dyestuffs, techniques, and equipment. A dye is used to impart color to materials of which it becomes an integral part. Dyes used by the textile industry are largely synthetic, typically derived from coal tar and petroleum based intermediates. Dyes are sold as powders, granules, pastes, and liquid dispersions, with concentrations of active ingredients ranging typically from 20 to 80 percent.

An aromatic ring structure coupled with a side chain is usually required for resonance and thus to impart color. Resonance structures that cause displacement or appearance of absorption bands in the visible spectrum of light are responsible for color. Correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A

chromophore group is a color giver and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo ($-N=N-$); carbonyl ($=C=O$); carbon ($=C=C=$); carbon-nitrogen ($>C=NH$ or $-CH=N-$); nitroso ($-NO$ or $N-OH$); nitro ($-NO_2$ or $=NO-OH$); and sulfur ($>C=S$, and other carbon-sulfur groups). The chromogen-chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are an amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives. These auxochromes are important in the use classification of dyes (World Bank, 1998).

Dyes may be classified in several ways, according to chemical constitution, application class and end use. Chemical classification is based on chromogen. For example, nitro dyes have the chromophore $-NO_2$. The primary classification of dyes is based on the fibers to which they can be applied and the chemical nature of each dye. Table 1.1 lists the major dye classes, fixation rates and the types of fibers for which they have an affinity.

Affinity is an important factor in determining dye exhaust but one that resists generalizations. Each dye class is generally applicable to (or has affinity for) specific types of fibers. Individual dyes within dye classes, however, can show large variations in affinity. Therefore, 'typical' exhaustion data provide only general guidelines. It is seen that reactive dyes have rather low rates of fixation while the highest fixation rates are achieved with basic dyes.

Typical values for affinity, bath ratio, and exhaust are:

K (affinity) = 50 to 1 000 various dye/fiber combinations

L (bath ratio) = 5 to 50 for various equipment

E (exhaustion) = 0.50 to 1.00 (50- to 100-percent exhaustion)

K (affinity) is a partition coefficient, or the ratio of the concentration of the dye in solution to the concentration of the dye in the substrate, at equilibrium i.e.:

$$K = C^f / C \quad (2.1)$$

Where:

C^f = concentration of dye in fiber at equilibrium

C^s = concentration of dye in solution at equilibrium

An important relationship is:

$$E = K / (K + L) \quad (2.2)$$

This equation implies that when L increases, E decreases and more color is discharged. The effect is more pronounced on low-affinity dyes (i.e., when K is low). When K decreases, the dye remains in the solution and the color in the wastewater increases, especially if L is high.

Factors that companies consider when selecting a dye include the type of fibers being dyed, desired shade, dyeing uniformity, and fastness (desired stability or resistance of stock or colorants to influences such as light, alkali, etc) (FFTA, 1991).

Most commonly in use today are the reactive and direct types for cotton dyeing, disperse types for polyester dyeing and acid dyes for nylon dyeing. Vat dyes, such as indigo, are also commonly used for cotton and other cellulosic fibers. Reactive dyes react with fiber molecules to form covalent bonds. Direct dyes can color fabric directly with one operation and without the aid of an affixing agent. Direct dyes are the simplest dyes to apply and the cheapest in their initial and application costs although there are tradeoffs in the dyes' shade range and wetfastness. Direct and reactive dyes have a fixation rate of 70 to 95 percent and 50 to 80 percent, respectively. A variety of auxiliary chemicals may be used during dyeing to assist in dye absorption and fixation in the fibers. Disperse dyes, with fixation rates of 80 to 92 percent; require additional factors, such as dye carriers, pressure, and heat, to penetrate synthetic fibers (Snowden-Swan, 1995; ATM, 1997).

Table 2 1: Major dye classes, fixation rates and types of fibers for which they have affinity

Dye Class	Description	Method	Fibers typically applied to	Typical Fixation (%)	Typical Pollutants Associated with Various Dyes
Acid	Water-soluble anionic compounds	Exhaust/ Back Continuous (carpet)	Wool, nylon	80 - 93	Color, organic acids, unfixed dyes
Basic	Water-soluble, applied in weakly acidic dyebaths, very bright	Exhaust/ Back	Acrylic, some polyesters	97 - 98	N A
Direct	Water-soluble anionic compounds, can be applied directly to cellulose without mordants (or metals like Cr and Cu)	Exhaust/ Back Continuous	Cotton, rayon, other cellulose	70 - 95	Color, salt, unfixed dye, cationic fixing agents, surfactant, defoamer, leveling and retarding agents, finish, diluents
Disperse	Water insoluble	High temperature, Exhaust Continuous	Polyester, Acetate, other synthetics	80 - 92	Color, organic acids, carriers, leveling agents, phosphates, defoamer, lubricants, dispersants, delustrants, diluents
Reactive	Water-soluble, anionic compounds, largest dye class	Exhaust/ Back Cold pad batch/ Continuous	Cotton, other cellulose, wool	50 - 80	Color, salt, alkali, unfixed dye, surfactant, defoamer, finish, diluents
Sulfur	Organic compounds containing sulfur or sodium sulfide	Continuous	Cotton, other cellulose	60 - 70	Color, alkali, unfixed dye, oxidizing agent, reducing agent
Vat	Cl dest dyes, more chemically complex, water insoluble	Exhaust Package Continuous	Cotton, other cellulose	80 - 95	Color, alkali, unfixed dye, oxidizing agent, reducing agent

2.1.4.2 Dyeing With Acid Dyes

Most acid dyes are sodium salts of organic sulfonic acids and the anion is the active colored component. There are a few of acid dyes containing carboxyl groups. The acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath (Bus, 1999).

The most significant assistant in the application of these acid dyes onto the desired fabric is the acid added to the dye bath which promotes dye exhaustion. Many acid dyes will not exhaust at all unless the dye bath has been acidified. Both the amount of dye adsorbed on the fiber and the rate of exhaustion is dependent upon the acidity of the dye bath. The acid strength and concentration used are carefully selected depending on the acid dye molecular size. The smaller the dye structure, the more acid or stronger acid is required to have a lower pH. However, exhaustion of high affinity dyes at higher rate or at low pH would cause uneven dyeing because of the difficulty of the dye migration which is necessary to have an even dyeing results.

The acid dyes are relatively easy to dissolve in water because of the presence of water solubilizing groups. However, there is also the possibility of undissolved particles becoming deposited on the goods. The required amount of dyestuff is dissolved in water better through a pasting step, preferably with a small amount of anionic wetting agent.

Acid dyes are used for dyeing of mainly nylon fibers, as well as wool, silk and modified acrylics. Acid dyeing of nylon results in ionic bonds or salt links between the dye molecules and the polymer. The terminal amino group, $-NH_2$ of nylon provides the dye site where the ionic link is formed. The dyeing of nylon with acid dyes can be represented as follows:



Nylon polymer with terminal amino group Hydronium ion nylon polymer with + charged terminal amino group



Nylon polymer with + charged dye anion ionic link formed
terminal amino group

In addition to dominant ionic bonds, hydrogen bonds and Vander Waals forces play a role in the bonding between the other part of the colored anion and the fiber. Usually, large dye molecular structure will have a higher affinity to the fiber and better wetfastness.

Salt is usually control the evenness of dyeing with large molecule dyes. Gaubert's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is usually used as a levelling agent. It acts as a retarding agent. When dissolved in water, sodium sulfate will dissociate and generate SO_4^{2-} anion. These smaller anions in the dye liquor are attracted more quickly than the larger dye anions, DSO_3^+ , to the positively charged nylon fibers, nylon NH_3^+ . The dye anions moving at a much slower rate will gradually replace the sulfate anion on the dye sites due to the high affinity of their molecular structure, resulting in a much more even dyeing (Fan et al., 2004).

2.1.4.3 Methods of Dyeing

Dyeing can be performed using continuous or batch processes. In batch dyeing a certain amount of textile substrate, usually 100 to 1,000 kilograms, is loaded into a dyeing machine and brought to equilibrium or near equilibrium with a solution containing the dye. Because the dyes have an affinity for the fibers, the dye molecules leave the dye solution and enter the fibers over a period of minutes to hours, depending on the type of dye and fabric used. Auxiliary chemicals and controlled dyebath conditions (mainly temperature) accelerate and optimize the action. The dye is fixed in the fiber using heat and/or chemicals, and the tinted textile substrate is washed to remove unfixed dyes and chemicals. Common methods of batch, or exhaust, dyeing include beam, beck, jet, and jig processing. Pad dyeing can be performed by either batch or continuous processes.

In continuous dyeing processes, textiles are fed continuously into a dye range at speeds usually between 50 and 250 meters per minute. Continuous dyeing accounts for about 60 percent of total yardage of product dyed in the industry (Snowden-Swan, 1995). To be economical, this may require the dyer to process 10,000 meters of textiles or more per color, although specialty ranges are now being designed to run as little as 2,000 meters economically.

Continuous dyeing processes typically consist of dye application, dye fixation with chemicals or heat, and washing. Dye fixation is a measure of the amount of the percentage of dye in a bath that will fix to the fibers of the textile material. Dye fixation on the fiber occurs much more rapidly in continuous dyeing than in batch dyeing.

2.1.5 Finishing

Finishing encompasses chemical or mechanical treatments performed on fiber, yarn, or fabric to improve appearance, texture, or performance. Mechanical finishes can involve brushing, ironing or other physical treatments used to increase the luster and feel of textiles. Application of chemical finishes to textiles can impart a variety of properties ranging from decreasing static cling to increasing flame resistance. The most common chemical finishes are those that ease fabric care, such as the permanent-press, soil-release, and stain-resistant finishes and the anti-microbial finishes. Chemical finishes are usually followed by drying, curing and cooling steps. Application of chemical finishes is often done in conjunction with mechanical finishing steps (Snowden-Swan, 1995).

2.1.6 Textile Industry's Profile

The textile processing industry is characterized by its fairly high specific water consumption ($\approx 2000 \text{ m}^3/\text{day}$) and its large amount of wastewater discharges. Due to processing in aqueous solutions or suspensions, wastewater is by far the dominating waste stream. However, due to the nature of the textile industry, it is difficult to define specific limits for the water use and wastewater flow rates. The technique used for a certain fabric - such as wool or cotton mostly affects both wastewater quality and quantity. The specific wastewater discharge, for example, varies according to the production method, between 110 m^3 and 180 m^3 per ton of fabric. The organic loads from textile effluents range between 2.5 - 800 kg COD per ton of fabric which corresponds to a range of 150 - 5000 mg/l COD (Gürürlü et al., 1990).

The textile industry is chemical intensive; wastewater from textile processing contains bath residues from preparation, dyeing, finishing, application of sizing

and other operations. Reduction of chemical usage, and substitution of less harmful chemicals for traditional ones, is a primary goal of the industry.

The composition of raw mixed wastewater in textile processing industry may be briefly characterized as follows (Schönberger and Kaps, 1994):

- Medium to high strength COD (organic load), mainly from the desizing and dye printing stages
- intense coloring caused by large amounts of unfixed remaining dyes
- high temperatures, since many reactions require high temperatures
- pollution with organic materials corresponds in average to the pollution of domestic wastewater. In case of employing water-saving techniques, it can be higher
- high conductivity because of the salt character of many textile auxiliaries
- high AOX-, sulphide- and heavy metal concentrations due to chlorinated bleaching agents and halogen-, sulfur- or heavy metal contained in dyes in some cases
- high phosphate contents, when polyphosphates for conditioning are added because of the use of hard process water

More specifically, these large volumes of wastes include wash water from preparation and continuous dyeing alkaline waste from preparation, and batch dye waste containing large amounts of salt, acid, or alkali. Primary sources of biological oxygen demand (BOD) include waste chemicals or batch dumps, starch sizing agents, knitting oils, and degradable surfactants. Wet processing operations, including preparation, dyeing and finishing generate the majority of textile wastewater. Types of wastewater include cleaning water, process water, non-contact cooling water, and stormwater.

One other source of wastewater pollutants of the industry is the Desizing or the process of removing size chemicals from textiles. In this process, large quantities of size used in weaving processes are typically discarded. Figures from the US show that more than 90 percent of the size used by the U.S textile industry, or 90,000 tons, is disposed of in the effluent stream. The remaining 10 percent is recycled (EPA, 1997). Desizing processes is claimed to often contribute up to 50 percent of the BOD load in wastewater from wet processing (Snowden-Swan, 1995).

Finishing processes typically generate wastewater containing natural and synthetic polymers and a range of other potentially toxic substances (Snowden-Swan, 1995). Pollution from peroxide bleaching normally is not a major concern. In most cases, scouring has removed impurities in the goods, so the only by-product of the peroxide reaction is water. The major pollution issues in the bleaching process are chemical handling, water conservation, and high pH.

Hazardous waste generated by textile manufacturers results primarily from the use of solvents in cleaning knit goods (ATM, 1997). Solvents may be used in some scouring or equipment cleaning operations, however, more often scouring processes are aqueous-based and cleaning materials involve mineral spirits or other chemicals (ATM, 1997). In addition, Table 1.2 summarizes the typical pollutant releases associated with various textile manufacturing processes.

Table 2.2: Potential Emissions from major textile processes (EPA, 1996)

Process	Air Emission	Waste water
Fiber preparation	Little or no emission generated	Little or no wastewater generated
Yarn spinning	Little or no emission generated	Little or no wastewater generated
Sizing	VOC's	BOD, COD, metals; cleaning waste; size
Weaving	Little or no emission generated	Little or no wastewater generated
Desizing	Little or no emission generated	BOD from water-soluble desizes; synthetic size; lubricants; biocides; antistatic compounds
Scouring	VOC's from glycol ethers and solvents	Disinfectants and insecticide residues; NaOH; detergents; fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents
Dyeing	VOC's	Metals; salts; surfactants; organic processing assistants; cationic materials; color; BOD, COD, temperature; sulfide; acidity/alkalinity; aquatic toxicity; spent solvents
Printing	Solvents; acetic acid from dyeing; combustion gases; particulate matter	Suspended solids; urea; solvents; color; metals; heat; BOD, foam
Finishing	VOC's; formaldehyde vapors; combustion gases; particulate matter	BOD, COD, suspended solids; toxics; spent solvents

Many textile mills have few or no metals in their effluent, but whenever metals are present, they may include metals such as copper, cadmium, chromium, nickel, and zinc. Sources of metals found in textile mill effluents may include fiber, incoming water, dyes, plumbing, and chemical impurities.

Although the textile industry is a relatively minor source of HAP (Hazardous Air Pollutants) compared with other manufacturing industries, air emissions have been identified as the second greatest pollution problem (after aqueous effluent) for the industry. Because many different types of commodity and specialty chemicals are used to manufacture textiles, characterization and management of air emissions for textile mills is a challenging responsibility.

Emissions comprise both point sources and fugitive emissions. Point sources include high-temperature coating, drying, and curing ovens, which emit volatile organic compounds (VOCs); boilers, which are a source of particulates, nitrous oxides, and sulfur dioxide; and bulk storage tanks for commodity and specialty chemicals. Fugitive air emissions result from spills, solvent-based cleaning, wastewater treatment plant operation, and warehouses used to store finished fabric.

Solid waste is the largest waste stream produced (by volume) following aqueous effluent. The quantity of solid waste generated depends on the size and type of textile operation, the nature of the waste, and the efficiency of the machinery used. Not surprisingly, solid waste generation varies widely among mills. According to a 1994 survey conducted by the ATM, total monthly solid waste generation for the 290 facilities surveyed was more than 51,000 tons per month.

2.1.6.1 The Problem of Residual Dyes in Textile Effluents

Dyeing operations generate a large portion of the industry's total wastewater. Dyes and pigments from printing and dyeing operations are the principal sources of color in textile effluent (EPA 1996). Dyes and pigments are highly colored materials used in relatively small quantities (a few percent or less of the weight of the substrate) to impart color to textile materials for aesthetic or functional purposes. In typical dyeing and printing processes, 50 to 100 percent of the color is fixed on the fiber, as shown in Table 6. The remainder is discarded in the form of spent dye baths or in wastewater

from subsequent textile-washing operations (EPA, 1996). The primary source of wastewater in dyeing operations is spent dyebath and washwater. Such wastewater typically contains by-products, residual dye, and auxiliary chemicals. Additional pollutants include cleaning solvents, such as oxalic acid.

Of the 700,000 tons of dyes produced annually worldwide, about 10 to 15 percent of the dye is disposed of in effluent from dyeing operations (Snowden-Swan, 1995). However, dyes in wastewater may be chemically bound to fabric fibers (ATM, 1997). The average wastewater generation from a dyeing facility is estimated at between 3800 and 7500 m³ per day. Dyeing and rinsing processes for disperse dyeing generate about 50 to 130 liters of wastewater per kg of product. Similar processes for reactive and direct dyeing generate even more wastewater, about 100 to 150 liters per kg of product (Snowden-Swan, 1995).

Several authors have identified salts in textile-dyeing wastewater as a potential problem area (EPA, 1996). Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile wet processes. Salt is used mostly to assist the exhaustion of ionic dyes, particularly anionic dyes, such as direct and fiber reactive dyes on cotton. Some dyes require as much as 250 - 300 g/l of salt to have high dye exhaustion from the dyebath to the target textile materials (Fan et al., 2004). Typical cotton batch dyeing operations use quantities of salt that range from 20 percent to 80 percent of the weight of goods dyed, and the usual salt concentration in such wastewater is 2,000 ppm to 3,000 ppm.

Common salt (sodium chloride) and Glauber's salt (sodium sulfate) constitute the majority of total salt use. Other salts used as raw materials or formed in textile processes include Epsom salt (magnesium chloride), potassium chloride, and others in low concentrations.

Dyes may contain metals such as zinc, nickel, chromium, and cobalt (ATM, 1997). In some dyes, these metals are functional (i.e., they form an integral part of the dye molecule) as one component in the dye chromophore; however, in most dyes, metals are simply impurities generated during dye manufacture. For example, mercury or other metals may be used as catalysts in the manufacture of certain dyes and may be

present as by-products (EPA 1996). These metal ions, after entering the environment can cause serious health problems and environmental pollution.

Previous studies have claimed that the effluents from textile dyeing industries contain a variety of chemicals and dyes, which are carcinogenic and mutagenic (Mithukumar et al., 2005). The aquatic toxicity of textile industry wastewater varies considerably among production facilities. The sources of aquatic toxicity can include salt, surfactants, ionic metals and their complexed metals therein, toxic organic chemicals, biocides, and toxic anions (EPA 1996; ATM, 1997). Most textile dyes have low aquatic toxicity. On the other hand, surfactants and related compounds, such as detergents, emulsifiers, dispersants, are used in almost every textile process and can be an important contributor to effluent aquatic toxicity, BOD and foaming (EPA 1996).

2.2 Textile Industry in Turkey

As a quality cotton-producing country, Turkey has an integrated and diversified production in all sub-sectors of the textile industry, produces and exports all types of yarn, fabric, clothing, household textiles and other ready-made products.

The industrialization efforts of the sixties and seventies gave birth to the modern textile industry in Turkey. At the beginning this sector operated as small workshops. In time the sector showed rapid development and during the seventies began exporting. Currently it is one of the most important sectors in the Turkish economy in terms of GDP, employment and exports. The share of this sector in the country's GDP was around 10 % and the sector's share of employment in total employment in the country was 20 %. Its share of production in total industrial production of the country was around 40 % according to the ITKB figures (ITKB 2003).

In the light of the textile sector of Turkey and the developments in the exportation of textile products, it is evident that the share of investments in the textile sector has increased compared to the investments in other sectors. For instance, while the total investment (with current prices) in the scope of incentive certificate in the textile and garment sectors was 631 trillion TL in 2000, it increased up to one quadrillion TL in 2001.

Today, Turkey is one of the most important textile and clothing producers and exporters in the world. The total export values of textile and apparel products was declared to be 46,877,598,000 USD (April 2004) by the Undersecretariat of External Trade and the share of Turkey in the world market was stated to be 32.2 % (ITKB, 2003).

80 % of the garment industry is composed of SMEs and a large part of it is making commission production. However, the textile sector is mainly composed of big sized firms. The number of firms in this sector is approximately 40 thousand and 1/4 of them are active exporters. Approximately 1/4 of the 500 large industrial organizations are in the textile and garment industry. The number of companies with foreign capital is 294. 93 of these companies are in the textile and 201 are in the ready-made clothing sector. A large number of garment firms are in Marmara region and textile firms are concentrated mainly in Southeast Anatolia, Mediterranean, Aegean and Marmara regions. The biggest share in manufacturing is that of the textile sector.

The biggest shares in manufacturing sector belong to weaving and garment sub-sectors in order of importance. 9,563 Investment Incentive Certificates were issued in the weaving and garment sub-sectors (ITKB, 2003).

Total fixed investment amount of these certificates is 10,736,500 millions TL in the weaving and garment sub-sectors. Meanwhile, the number of the employees predicted in these certificates is 822,664 (ITKB, 2003).

2.3 Conventional Textile Wastewater Treatment

A variety of physical, chemical, and/or biological processes have been used to treat textile effluents. Physical and/or chemical treatment processes including coagulation/flocculation (Koprivanac et al., 1993), adsorption (Ramakrishna et al., 1997), flotation (Lin and Lo, 1996), and oxidation reduction including Fenton's reagent (Kwi et al., 2000) have been effective in eliminating most of the pollutants of concern. Conventional aerobic biological treatment processes can successfully degrade the organic matter present in textile waste waters; nevertheless, these systems usually exhibit a relatively low color and nutrient removal potential. On the other

hand, anaerobic treatment may be promising in enhancing dye color reduction (Vandeviere et al., 1998). Conventional biological treatment systems processes cannot address the nutrient removal issue adequately, beyond the limits of satisfying metabolic requirements of the biomass involved.

Sequencing batch reactor (SBR) technology served as an attractive solution, particularly when land availability as well as flexibility and simplicity of operation are of concern. SBRs have been traditionally employed in the biodegradation of organic compounds from municipal and industrial wastewaters. The potential of SBR systems in removing organic matter, nutrients and color from textile wastewaters have been realized in the recent years. Several studies were conducted to assess the efficiency of SBR systems as single process or in conjunction with chemical treatment either before or after biological treatment (Fongsatitkul et al., 2004).

Commonly employed methods for color removal such as adsorption, coagulation-flocculation, oxidation and electrochemical methods are quite expensive and have operational problems (Lin and Peng, 1996; Ramakrishna and Vraraghavan, 1997).

Biological treatment of dye-containing wastewater is considered unsatisfactory because of the low efficiency and low reaction rate of the treatment. Consequently, dye wastewater is usually treated using physical and chemical methods (Chang et al., 2003). Flocculation and activated carbon adsorption have been used to treat dye-containing wastewater. However, sludge generation and adsorbent regeneration are the principal weakness of these processes (Slokar and Mijcen Le Marechal, 1998).

2.4 Advanced Textile Wastewater Treatment

Processes such as coagulation, carbon adsorption and biological treatment, used currently for the purification of textile dyeing wastewater can be employed for the treatment of printing wastewater. The physical-chemical processes alone were not, however, considered appropriate for the treatment of wastewater, because of their high costs and due to the fact that they are not effective to meet the required levels. Membrane processes are very promising advanced treatment methods for colour removal as well as for reducing the volume of wastewater generated and recovering and recycling valuable components from the waste stream. Several approaches have

been proposed to implement membrane processes in the treatment of textile wastewater from different production streams.

Ultrafiltration (UF) is effective for the removal of particles and macromolecules and does not decolourise the waste stream. Nanofiltration (NF) allows the separation of low molecular weight organic compounds and divalent salts, with an appreciable softening effect. Reverse osmosis (RO) is suitable for removing ions and larger species from dye bath effluents. The reverse osmosis membrane also removes the colour and desalinates the waste stream considerably (NaCl retention of 93%), however, the retention for the reactive dyes is somewhat lower in the nanofiltration process (Šostar et al., 2005)

2.5 Advanced Oxidation Processes (AOP)

2.5.1. Basic Principles of AOP

Among chemical processes, the advanced oxidation process (AOP) has been used to reduce the organic load or toxicity of different waters and wastewaters. In general, AOP are defined as oxidation processes, which generate hydroxyl radicals ($\cdot\text{OH}$) in sufficient quantity to affect water and wastewater treatment (Huang et al., 1993). The hydroxyl radical is one of the most reactive free radicals and one of the strongest oxidants, which have a high electrochemical reduction potential ($\cdot\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$ $E_0 = 2.33 \text{ mV, STP}$). Many systems can be classified as AOP based on the generation of $\cdot\text{OH}$ and most of them use a combination of two oxidants (e.g., O_3 plus H_2O_2); catalyst plus oxidant (e.g., $\text{Fe}^{2+} + \text{H}_2\text{O}_2$); oxidant plus irradiation (e.g., H_2O_2 plus solar or near (long) UV); oxidant plus photo-catalyst (e.g., H_2O_2 plus TiO_2 plus UV); oxidant plus ultrasound (e.g., H_2O_2 plus ultrasound) for the generation of $\cdot\text{OH}$. The formed radicals react with organic materials breaking them down gradually in a stepwise process. The major AOPs are classified into O_3 , UV-C/ O_3 , UV-C/ H_2O_2 , UV-A/ TiO_2 , Fe^{2+} or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (Fenton or Fenton like processes) and UV-A or UV-C/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ processes (photo-Fenton process), depending on the method of $\cdot\text{OH}$ production.

The advantage of AOPs is that they effectively destroy the organic compounds, converting them mainly to carbon dioxide and water (Leggini et al., 1993). In particular, the homogeneous (photo) catalytic treatment using the dissolved iron such as the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and UV-A or UV-C $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ processes are known to be suitable for the treatment of wastewaters, with high concentrations of organics, due to their high performance and competitive economy.

There are various examples of AOP studies in the literature with many industrial wastes. Below are some examples, which investigate the efficiencies of different AOP for textile applications.

2.5.2 Applications of AOP in the Textile Industry

There are hundreds of citations in the literature regarding the treatment of textile dyes with AOP and it is quite important to mention these studies herein.

Oğuz et al. (2004) studied the dye and COD removal from ozonation of synthetic wastewater containing Bonaplex Red CR-L dye in a semi-batch reactor as functions of initial dye concentration (400, 600, 800 and 1000 mg/L), temperature (18, 40 and 70 °C), ozone-air flow rate (5, 10 and 15 L min⁻¹), pH (3, 6, 9.3 and 12) and ozone generation percentage (0.7, 1.1 and 1.4 %). They found that the dye removal from synthetic wastewater in excess of 99% was obtained at an oxidation time of 15 min. The efficiencies of COD removal were between 56 and 35% at an oxidation time of 30 min. At the end of the study, it was concluded that ozonation is an efficient process for dye removal from synthetic wastewater of Bonaplex Red CR-L, but alone ozonation was not an efficient method to remove all the COD from the textile wastewater.

Saeniro et al. (2004) concluded that the commercial azo dye C.I. Reactive Orange 4 in its reactive and hydrolysed forms can be efficiently photodegraded, using commercial samples of TiO_2 as a photocatalyst and sunlight was also very effective as a light source.

Degradation of commercial reactive dyestuffs by heterogeneous and homogeneous AOPs resulted in higher treatment efficiencies in terms of color, TOC, COD (Arslan and Balcioglu, 1999; Arslan et al., 2001).

Common problems among all the AOPs are the high demand of electrical energy for devices such as ozonizers, UV lamps, ultrasounds, and/or consumption of chemical reagents which results in rather high treatment costs (Yediler et al., 2003).

The only exception is the Fenton's process. In such a process, in fact, under acidic condition, a $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ mixture produces $\cdot\text{OH}$ radicals in a very cost-effective way. The major advantages of the Fenton's reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) are: (i) both iron and hydrogen peroxide are cheap and non-toxic; (ii) there is no mass transfer limitation due to its homogeneous catalytic nature; (iii) there is no form of energy involved as catalyst; (vi) the process is technologically simple.

Because of these features, Fenton's process has been applied in many fields including recalcitrant wastewater and/or landfill leachates treatment.

2.5.3 Fenton Processes

Fenton-type reactions using H_2O_2 as an oxidant in the presence of iron ions at acidic pH have been among the most common homogeneous systems.

Reported first by H. J. H. Fenton in 1894 for its ability to oxidize various organic compounds dissolved in water, Fenton's reagent is an aqueous solution of hydrogen peroxide and ferrous ions. The ferrous ion acts as a homogeneous catalyst, while the hydrogen peroxide serves the role of the oxidant.

Among the different AOP, Fenton's reagent has been used for different treatment processes because of its ease of operation and low cost. A wide variety of Fenton's reagent applications have been reported, such as treatment of textile wastewaters, treatment of industrial wastewaters of pharmaceutical origin, treatment of acid manufacturing wastewater, reduction of polynuclear aromatic hydrocarbons in water, treatment of brines or treatment of paper pulp manufacturing effluents (Martinez et al., 2003).

The Fenton and photo-Fenton reaction using Fe^{2+} , H_2O_2 and UV light have been shown to be effective in mineralizing several recalcitrant pollutants like PCBs, chlorinated herbicides, phenolic wastes, chlorophenols, perhalogenated alkanes, dye effluents and many other wastewaters of different origin (Pignatello and Chapa,

1994; Pignatello and Sun, 1995; Huston and Pignatello, 1996; Arslan et al., 1999; Huston and Pignatello, 1999, Kang and Chang, 1997, Eisenhauer, 1964; Barbeni et al., 1987).

2.5.3.1. Homogeneous Processes

The reaction between dissolved Fe^{2+} and hydrogen peroxide in acidic aqueous solution leads to oxidation of Fe^{2+} to Fe^{3+} and is thought to form the highly reactive hydroxyl radical ($\cdot\text{OH}$). The reaction is spontaneous and can occur without the influence of light (Wadley and White, 2004).

The mechanism of the Fenton process was first proposed by Haber and Weiss 40 years after the discovery of Fenton's reagent (Haber and Weiss, 1934). It has been further elucidated by others (Symons and Gutteridge, 1998).

The principal inorganic reactions which are considered common to the Fenton reaction system represent the interactions among various inorganic species including $\cdot\text{OH}$, H_2O_2 , $\text{Q}^\cdot$, H_2Q , Fe^{2+} and Fe^{3+} as shown in Eqs. (5.1) - (5.18), respectively,





These reactions listed above presents some of the multiple parallel processes that occur immediately after $^\bullet\text{OH}$ generation by Reaction (2.1). The relevance of each reaction in the mechanism is equally dependant of their reaction rate constant (k) and the concentration of each participating species. The $^\bullet\text{OH}$ scavenging by Fe^{2+} and H_2O_2 is shown in Reactions (2.2) and (2.3). The hydroperoxyl radicals ($\text{HOO}^\bullet$) generated from Reaction (2.2) may be transformed to superoxide radical ($\text{O}_2^{\bullet-}$) according to Reaction (2.4). Since the pK_a of this reaction is 4.8, this process is favored at basic pH while the equilibrium is shifted towards $\text{HOO}^\bullet$ at acidic pH. As

shown in Reactions (2.5) and (2.6), and depending on the reaction pH either $\text{O}_2^{\cdot-}$ or $\text{HOO}^\cdot$ are linked to the pathways of oxygen generation via reaction with Fe^{2+} and Fe^{3+} , respectively. Oxygen is also generated during the termination reaction of $\text{HOO}^\cdot$, which also results in H_2O_2 regeneration (Reaction 2.11). $\text{HOO}^\cdot$ is also generated via reaction of Fe^{3+} and H_2O_2 as shown in Reaction (2.8). Reaction (2.10) is a termination reaction for $^\cdot\text{OH}$ which regenerates H_2O_2 . On the other hand, Reactions (2.12) to (2.18) are the reactions between the organic compounds (R-H), organic radicals ($\text{R}^\cdot$) and $^\cdot\text{OH}$ which involve $^\cdot\text{OH}$ attack on a R-H substrate present in the system (i.e., acid dyes), and therefore the corresponding reaction rates are a function of the substrate properties. The outcome of Reaction (2.12) results in the generation of $\text{R}^\cdot$, which are responsible for a series of further reactions. Some of them include scavenging of $^\cdot\text{OH}$ (Reaction 2.13) and Fenton components (Reactions 2.14 and 2.15), Fe^{2+} regeneration (Reaction 2.16), and formation of other products by reaction with oxygen (Reaction 2.17) or other $\text{R}^\cdot$ radicals via termination reactions. Another case is the reaction between $\text{R}^\cdot$ and $^\cdot\text{OH}$ (Reaction 2.13), which constitutes a termination reaction for both radicals.

According to the values presented above, the Fenton reaction (Reaction 2.1) exhibits one of the lowest k values among the reactions of this mechanism. This indicates that Reaction (2.1) plays a major role only at the beginning of the process, at a time when only Fe^{2+} , H_2O_2 and the substrate are present. Shortly after the hydroxyl radicals are produced, the parallel mechanisms described by Reactions (2.2)-(2.1) become influential in this process depending on their reaction rate constant values.

These equations show that iron acts like a catalyst, however since the reduction of Fe^{3+} is generally much slower than the oxidation of Fe^{2+} , iron exists mainly in the Fe^{3+} form in these systems (Ragnatello, 1992).

In the so called Fenton Processes the iron can initially be in the form of either Fe^{2+} or Fe^{3+} . The initial degradation rate is slower for $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ than for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ since, in the former case, Fe^{3+} must be reduced to Fe^{2+} before hydroxyl radicals (or ferryl species) are produced (Wadley and White, 2004).

2.5.3.2 Photo-Fenton Processes

When irradiated with light of suitable wavelength ($\lambda = 180$ to 400 nm), i.e. ultraviolet and some visible light, Fe^{3+} can catalyze the formation of hydroxyl radicals (or ferryl species):



This is called the photo-Fenton reaction and is followed by reaction (5.1). The $\cdot\text{OH}$ production is determined by the availability of light and H_2O_2 .

The modified photo-Fenton processes include complexation of the Fe^{2+} with a carboxylic acid anion such as oxalate. The ferrioxalate complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is highly photo-reactive and the reduction of Fe^{3+} to Fe^{2+} can occur at a wavelength further into the visible spectrum (about 550 nm) (Hslop and Bolton, 1999).

Numerous transition metal ions and their complexes in their lower oxidation states, such as Cu(I), Cr(II), Co(II) and Ti(III) have the oxidative features of the Fenton reaction.

2.5.3.3 Heterogeneous Processes

The source of iron used as a catalyst for the Fenton process can be a solid surface, including iron containing minerals or iron coated silica particles (sand), as well as iron adsorbed onto zeolites or ion exchange membranes.

The dark heterogeneous Fenton process (Fe^{3+} oxide/ H_2O_2 /dark) makes use of a particulate mineral oxide catalyst usually goethite ($\alpha\text{-FeOOH}$) and an oxidant, usually hydrogen peroxide. Oxidation of organic compounds is carried out by the hydroxyl radical, which is thought to be produced through the interaction of hydrogen peroxide with the surface sites on the goethite where the oxidation reaction occurs as well. The advantages of the heterogeneous Fenton processes include the application over extended periods without requiring regeneration or replacement, preventing the production of large volumes of non-reusable ferric hydroxide sludge, increased hydroxyl radical generation at pH between 5 to 9.

The heterogeneous Fenton processes also may take place in the presence of light as heterogeneous photo-Fenton processes.

2.5.4 Factors Affecting the Fenton Process

Many parameters, such as the initial concentrations of ferric salt and hydrogen peroxide, the ratio of initial iron to hydrogen peroxide concentrations, pH, light intensity and temperature, can influence the efficiency of the Fenton and Fenton-like processes.

2.5.4.1 pH

pH is probably the most important control variable in the Fenton process. As indicated in Eqn. (5.1), the amount of $\text{HO}^\bullet$ generated by the Fenton process is affected by the pH. The hydroxyl radicals can be efficiently formed especially under acidic conditions between pH 2 and 4. At higher pH iron may precipitate (Kiwit et al., 1993; Pulgarin and Kiwit, 1996). The inactivity of Fenton's reagent at $\text{pH} > 4$ has also been attributed to faster decomposition of H_2O_2 to water and oxygen through the reaction (5.20) (Pulgarin and Kiwit, 1996), oxidation of Fe^{2+} by an oxidant other than H_2O_2 (Kuo, 1992), or the reaction between Fe^{2+} and H_2O_2 not producing hydroxyl radicals in this pH region.



The optimum pH range for the treatment of certain xenobiotics and industrial effluents with Fenton is $\text{pH} = 2 - 5$ (Casero et al., 1997, Kwon et al., 1999, Perez et al., 2002, Ghaly et al., 2001, Kang et al., 2002). This may be explained with the fact that the iron species are mostly soluble in the pH range 2 - 5, and hence able to act as active catalysts during the Fenton treatment (Figure 2.3).

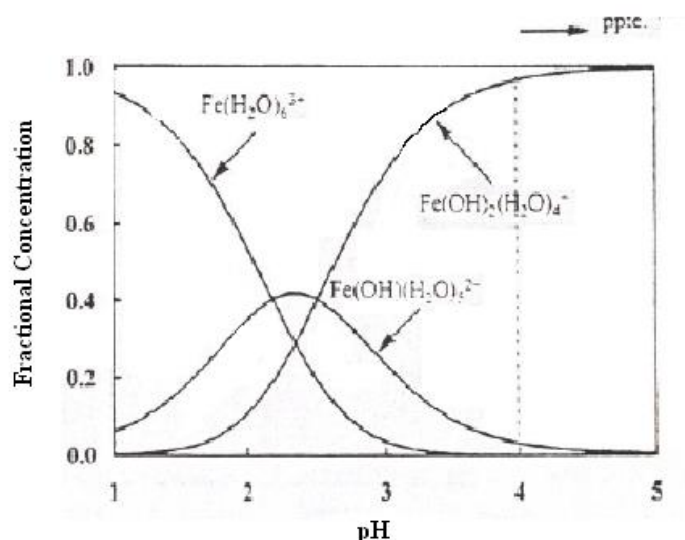


Figure 2.3: Variation of concentration of monomeric Fe(III) and Fe(III)-hydroxo species as a function of pH (Safarzadeh Amiri et al., 1996)

Pignatello (1992) had reported that photo-Fenton reaction is optimum at pH 2.8. The reason may be due to the fact that the main species $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ at $\text{pH} = 2 - 3$ (Refer to Table 5.1) is the one with the largest molar absorption coefficient and quantum yield for $\cdot\text{OH}$ production, along with higher Fe^{2+} regeneration ability in the range 280 - 370 nm as described in the following part; effect of light intensity.

Table 2.3: Hydrated iron (III) species in solution as a function of pH (Safarzadeh-Amiri et al., 1996)

Dominant Fe^{3+} species	pH range
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	1 - 2
$\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$	2 - 3
$\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+$	3 - 4

2.5.4.2 Light Intensity

The rate of degradation of organic pollutants by Fenton reaction is increased when an irradiation source is present. The positive effect of irradiation on the degradation rate is due to the photoreduction of Fe^{3+} to Fe^{2+} ions (photochemical regeneration of Fe^{2+}), that can further react with more H_2O_2 . It has been proven that the irradiation of $\text{Fe}^{3+} + \text{H}_2\text{O}_2$, also called Fenton-like reaction, enhances the rate of oxidant production, through the involvement of high valence Fe intermediates responsible for

the direct attack to organic matter (Boss mann et al., 1998, Pignatello et al., 1999). Absorption of visible light by the complex formed between Fe^{3+} and H_2O_2 seems to be the cause of formation of such high valence Fe based oxidants. Another mechanism is believed to be the photoexcitation of the complexes formed between Fe^{3+} and organic matter. The molar absorption coefficients of such complexes and the quantum yields of their reaction of photolysis are even larger than the values for Fe^{3+} aquo complexes (Boss man et al., 1998).

2.5.4.3 Temperature

The effect of temperature on the Fenton reactions has been studied by many researchers (Lunar et al., 2000; Gob et al., 2001, Sagawe et al., 2001. Lee and Yoon (2004) investigated the thermal enhancement of the formation of $\cdot\text{OH}$ by the $\text{hv}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system (including the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system) with reaction temperatures ranging from 25 to 50 °C. Particularly, the thermal enhancement of $\text{Fe}(\text{OH})^{2+}$ photolysis which is the most significant step in the $\text{hv}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system was effectively explained by two factors; (1) the variation of the $\text{Fe}(\text{OH})^{2+}$ concentration with temperature, and (2) the temperature dependence of the quantum yield for $\text{Fe}(\text{OH})^{2+}$ photolysis (measured activation energy/ 11.4 kJ mol⁻¹). Although in both the UV-A/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems, elevated temperatures enhanced the formation of $\cdot\text{OH}$, the thermal enhancement was much higher in the dark $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system than the UV-A/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system. Furthermore, it was found that the relative thermal enhancement of the formation of $\cdot\text{OH}$ in the presence of $\cdot\text{OH}$ scavengers (tert-butyl alcohol) was magnified in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system but was not in the $\text{hv}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system.

2.6 Treatment of Textile Dyes Using Fenton's Reagent

The Fenton's reagent has received particular attention for the treatment of textile wastewaters in the recent years. The Fenton's reagent works effectively for recalcitrance, color and inert COD removal for dye house effluents. The Fenton process has been proposed for the degradation of dye pollutants (Kang et al., 2002; Feng et al., 2003; Swaminathan et al., 2003, Tang, 1996).

A study by Xiang-Rong et al., 2004 investigated the degradation of 20 different dyes in aqueous solutions by the Fenton process was performed. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased greatly, while the color and TOC removals of the latter two types were lower. The efficiencies of three oxidation processes, including $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ were compared and the results showed that the oxidation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ was the strongest. The former four types of dyes were decolorized and their TOC values were decreased significantly, while the color and TOC removals of the latter two types were lower. It was also found that the Fenton process could be used to enhance biotreatment of the dye wastewater in the sewage treatment plant.

Swaminathan et al. (2003) have studied the Fenton's reaction for the decolorization and degradation of two commercial dyes viz., Red MB, Blue MR and H-acid, a dye intermediate used in chemical industries for the synthesis of direct, reactive and azo dyes. Maximum color and COD removal was obtained for Red MB, H-acid and Blue MR at 10-25 mg/l of Fe^{2+} dose and 400-500 mg/l of H_2O_2 dose at pH 3.0. The initial oxidation reaction was found to fit into first order rate kinetics and the rate of oxidation of H-acid was higher than the other dyes. It was found that the dye degradation proceeded through cleavage of the substituent group due to the release of chloride and sulfate from the Fenton's treated Red MB dye and sulfate from H-acid and Blue MR.

Yediler et al., 2003 have studied the degradation of two azo reactive dyes, C.I. Reactive Yellow 84 (RY(+)) and C.I. Reactive Red 120 (RR120)) by photo-Fenton and Fenton-like oxidation. The effective system conditions were found to be pH of 3, hydrogen peroxide-to-iron molar ratio of 20:1 and UV or solar irradiation. The color removal efficiency at the optimum conditions during different Fenton-like processes was also evaluated. The results showed that the color removal of RY84 after 15 min reaction time follows the decreasing order: solar/ $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ > UV/ $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ > UV/ $\text{Cu}(\text{II})/\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ > UV/ $\text{Fe}(\text{III})\text{oxalate}/\text{H}_2\text{O}_2$ > UV/ $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ > dark/ $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ > solar/ $\text{Fe}(\text{III})\text{oxalate}/\text{H}_2\text{O}_2$ > UV/ H_2O_2 > UV/ $\text{Fe}(\text{II})$ = UV. During the same reaction period the relative order for RR120 removal rate was slightly different: solar/ $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ > UV/ $\text{Fe}(\text{II})/\text{H}_2\text{O}_2$ > UV/ $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ =

UV/ Cu(II)/ Fe(III)/ H_2O_2 > UV/ Fe(III)oxalate/ H_2O_2 = UV/ H_2O_2 > UV. The toxic potential of the dye's degradation was investigated by the bioluminescence test using the LUM St ox 300 instrument and results were expressed as the percent inhibition of the luminescence of the bacteria *Vibrio fischeri* (Yediler et al., 2003).

The oxidative degradation of two direct dyes, Blue 2B (B54) and Red 12B (R31) in aqueous solution has been studied using Fenton's reagent by Malik et al. (2003). Results showed that dyes are decomposed in a two-stage reaction. In the first stage, dyes are decomposed rapidly, and somewhat less rapidly in the second stage. The effects of different system variables like initial pH of the medium, initial concentrations of the dye, Fe^{2+} and H_2O_2 , reaction temperature, and added Cl^- and SO_4^{2-} ions have been investigated. The degradation rate is strongly dependent on the initial concentrations of the dye, Fe^{2+} and H_2O_2 . The results indicated that the B54 and R31 can be most effectively oxidized in an aqueous medium of pH 3 at an initial $[Fe^{2+}]:[H_2O_2]:[dye]$ ratio of 1:32.9:2.4 and 1:16.5:1.8 (mM, respectively). At the optimum initial ratio of $[Fe^{2+}]:[H_2O_2]:[dye]$, 97% degradation can be achieved in 30 min at a temperature of 30 °C and 70% removal of initial chemical oxygen demand (COD) is achieved after 60 min. The degradation of both the dyes obeys first order rate kinetics with respect to the concentration of the dye in the second stage of oxidation. The results will be useful in designing wastewater treatment plants.

A study by Lio et al. (2003) used the Fenton process was to explore the possibility of treating explosives, namely 2,4,6-trinitrophenol (PA), ammonium picronitrate (AP), 2,4-dinitrofluorene (DNT), methyl-2,4,6-trinitrophenyl nitramine (Tetryl) and 2,4,6-Trinitrofluorene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The photo-Fenton process was also conducted to compare its oxidation efficiency with the Fenton process. Results showed that oxidation efficiencies in Fenton system were in the following sequence: DNT>PA>AP>TNT>Tetryl>RDX>HMX. They found that the degradation of the explosives obeyed a pseudo-first-order behavior and; for all explosives, the oxidation rates significantly increased with increasing the concentration of Fe(II), as well as illumination with UV light.

2.7. Effects of Industrial Pollutants on the Biological Activated Sludge Treatment Process

There are different approaches that may be used to evaluate the biological treatability of industrial pollutants. Among them, the most widely used ones are the determination of the 'BOD₅/COD' ratio, utilization of respirometric methods (measurement of oxygen uptake rates) and COD fractionation of wastewaters (Perkins et al., 2001, Arslan-Alaton, 2003, Xiao et al., 2002, Orhon et al., 1999, Tünay et al., 1990, Gümürli et al., 1990).

There exist many examples in the literature studying the effect of Fenton treatment on the improvement of bio-treatability. For example, Lopez et al. investigated the effectiveness of the Fenton's reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+$) for the pre-treatment of a municipal landfill leachate with the objective of improving its overall biodegradability, evaluated in terms of BOD₅/COD ratio, up to a value compatible with biological treatment. BOD₅/COD ratio of the leachate could be increased from 0.2 $[(2300/10540)=0.2]$, the initial value, up to 0.5 the minimum value compatible with a subsequent biological post-treatment.

For instance, Chamorro et al. (2001) studied the use of Fenton's reagent to improve organic chemical biodegradability with different organic compounds (formic acid, phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene). It was seen that the ratios of BOD₅/COD while initially being near zero, increased to approximately 0.4 after partial oxidation of these toxic compounds with the Fenton treatment and Fenton pre-treatment with subsequent low-cost biological treatment was proposed to be an effective alternative.

In the present study, Activated Sludge Inhibition Test (ISO 8192) was used to assess the acute effects of the raw and pre-treated dyebath effluents on the activated sludge microorganisms and the soluble inert COD fractions were determined in order to evaluate the improvement of biological treatability of these spent dyebaths.

2.7.1. Acute Inhibitory Effects on Sewage Sludge

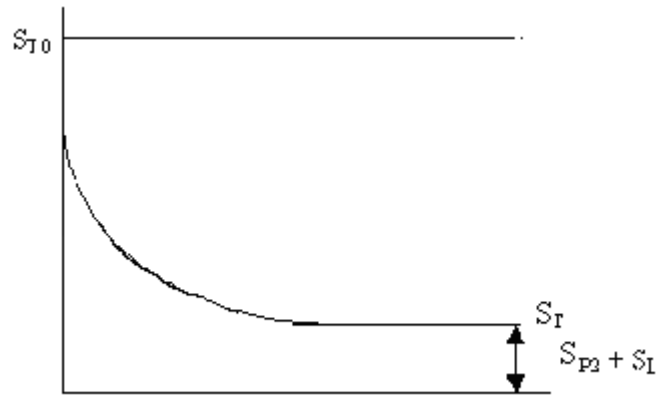
The Activated Sludge Inhibition test relies on the measurement of Dissolved Oxygen (DO) in the samples containing varying dilutions of the test compound in contact with synthetically grown activated sludge, in order to calculate the corresponding Oxygen Uptake rates (OUR). The reduction in OUR with time, relative to the blank containing only the synthetic feed, is explained with the inhibitory effect of the test compound exerted on the activated sludge microorganisms.

It should be noted that the activated sludge inhibition test is not a biodegradability test but it is a toxicity test that is used to study the acute toxic/inhibitory effect of pollutants on WWTP's.

2.7.2. Determination of the Inert COD in Industrial Effluents

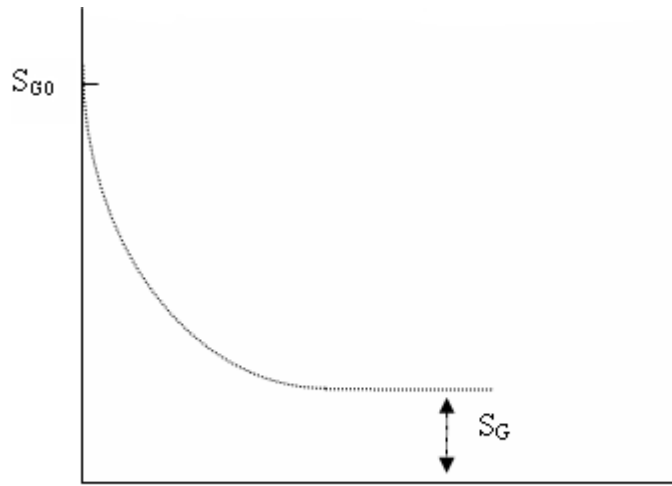
The importance of soluble inert COD content (S_i) of the influent wastewater has been emphasized by many researchers in the literature. There are several methods available for the determination of this component (Ekama et al., 1986; Henze et al. 1987). However these methods are not able to differentiate the soluble inert organic substances from the soluble inert microbial end products as a major disadvantage. Other procedures based solely on the measurement of COD allowed the direct experimental determination of soluble inert organic substances in the influent (Kappeler and Gujer, 1992; Ghon et al., 1994).

The method proposed by Germirli et al., 1993 involves the monitoring of COD in the soluble wastewater reactor and the glucose reactor of equivalent soluble COD content both seeded with minimal biomass (10-50 mg MLVSS/L) previously acclimated to the wastewater and the glucose substrate. These reactors eventually reach a stable threshold obtained from the COD measurements after consumption of the total biodegradable substrate and ultimate mineralization of the biomass. The inert COD profiles to be obtained by this method are presented in Figure 2.4.



Time (days)

(a) Raw Wastewater Reactor



Time (days)

(b) Glucose Reactor

Figure 2.4: Inert COD Profiles (Gerritsli, 1993)

The method assumes that the residual soluble COD in the wastewater reactor is equal to the sum of soluble inert COD (S_I) and residual soluble microbial end products generated in the reactor.

$$S_T = S_I + S_{P2} \quad (2.25)$$

The amount of residual soluble microbial end products generated in the reactor is always a fraction (Y_{SP}) of the degradable COD content of the initial COD (S_{S0}) which is calculated from the glucose reactor with the assumption that $Y_{PS(\text{wastewater})} \approx Y_{PS(\text{glucose})}$ (2.26).

$$Y_{PS} = S_{PG} / S_{G0} \quad (2.26)$$

This allows the calculation of S_I from the following two equations with two unknowns:

$$S_{S0} + S_I = S_{T0} \quad (2.27)$$

$$Y_{PS} S_{S0} + S_I = S_T \quad (2.28)$$

S_{PG} : residual soluble microbial end products generated in glucose reactor (mg/L)

S_{P2} : residual soluble microbial end products generated in wastewater reactor (mg/L)

S_{G0} : initial soluble COD of glucose reactor (mg/L)

S_{T0} : initial soluble COD of wastewater reactor (mg/L)

S_{S0} : initial soluble biodegradable COD in wastewater reactor (mg/L)

S_T : final soluble COD of wastewater reactor (mg/L)

S_I : initial soluble inert COD of wastewater (mg/L)

Y_{PS} : fraction of biodegradable COD converted into soluble inert metabolic products (mg cell COD/mg COD)

This method has been applied in the present study to determine the soluble inert COD fractions in the investigated acid dye baths to examine the effect of Fenton's pre-treatment on the improvement of bio-treatability which is important in terms of effectiveness of the preceding biological treatment.

3. MATERIALS AND METHODS

3.1. Materials

In the present study, Fenton's treatment of acid dyebath effluents was investigated because of two major facts which were; the high COD content and the low pH of the acid dyebaths which the Fenton's treatment fits best in terms of the removal efficiencies for COD as well as the color.

3.1.1. Textile Acid Dyebaths

Two different textile acid dye-bath compositions were used in this study. The commercial dyes and dye assisting chemicals to form two dyebaths were obtained from a local textile finishing factory. The dyebaths were prepared exactly as they are used in the factory to simulate real acid dyeing bath compositions. Theoretically, acid dye materials are well attained on the targeted fabric and only 10 - 20 % of the dye remains in the dyebaths. However in this study, it was assumed that the dye components of the simulated dyebath compositions totally remained unfixed and appeared in the exhausted dyebaths in order to observe the worst case, and the dyebaths were prepared accordingly.

Dyebath I was composed of a metal-complex dye (Nortalan Black MRX) and acetic acid as the assisting chemical. This dyebath was used for nylon dyeing in the factory.

Dyebath II consisted of 3 different acid dyes (Telon Gelb A3RL, Telon Bleu GL, Telon Rot F2BL) and 2 assisting chemicals. The dye assisting chemicals are an acid donor (Ruco Acid GBK); an ester-based chemical and a leveling agent (Laugal TP).

The compositions of the two dyebaths are provided in Table 3.1 and Table 3.2.

Table 3 1: Exhausted Acid Dyebath I Composition

Dye Stuff (CI Index)	Trade name	Company	Chemical nature	Conc. (ng/l)
Acid Yellow 242	Telon Gelb A3RL	Dystar	Azo	30
Acid Red 360	Telon Rot F2BL	Dystar	Azo	30
Acid Blue 264	Telon Blau GL	Dystar	Antrachinon	30
Assisting Chemicals				
	Laugal TP	Erca spa	Oxyethylene derivative w/ amine & sulphonic prop Ester	1500
	Ruco Acid GBK	Rudolf Chemie		500
COD = 2747 ± 33 ng/L				

Table 3 2: Exhausted Acid Dyebath II Composition

Dye Stuff (CI Index)	Trade name	Company	Chemical nature	Conc. (ng/l)
Metal Complex Black	Neutrilan Black MRX	Yorkshire Chemicals	Cr(III) complex, azo, sulphonate groups	350
Assisting Chemicals				
Acetic Acid			CH ₃ COOH Weak acid	1500
COD = 1752 ± 21 ng/L				

The reason why Fenton pre-treatment was chosen for this study was that the acid dyes are widely applied in textile dye houses world-wide and they have the highest shares in Turkey among other dyes. The dye-bath formulations studied are frequently being used for nylon dyeing in the factory.

3.1.2 Reagents and Supplies

All chemicals used were reagent grade and obtained from Fluka, Aldrich, Merck or Riedel depending upon the price and availability.

More specifically, the chemicals used for the Fenton pre-treatment were; reagent grade hydrogen peroxide (35 % v/v, Fluka), ferrous iron sulfate hepta hydrate (Fe(SO₄).7H₂O Merck), sodium hydroxide pure pellets (NaOH Merck), Catalase

(from *Micrococcus lysodeikticus*, 1 AU destroys 1 μmol H_2O_2 at pH = 7 RTP, 100181 U ml, Huka), reagent grade Sulfuric acid (H_2SO_4 , Merck).

Reagents used for the H_2O_2 determination were; potassium iodide solution (1% w/v), Ammonium molybdate solution (9 grams ammonium molybdate in 10 ml & NH_4OH and diluted to 100 ml), sulfuric acid solution (one part H_2SO_4 - 98% of four parts distilled water), starch indicator, sodium thiosulfate (0.1 N).

3.2 Experimental Procedure

3.2.1 Fenton Experiments

The simulated acid dye bath effluents used in the optimization, kinetic and inhibition studies were prepared by dissolving the dyes and dye assisting chemicals in hot ($\sim 80^\circ\text{C}$) distilled water and stirring for about three hours to mix well using a temperature controllable magnetic stirrer (Yellowline MST Basic, IKA-WERKE).

Appropriate amount of Fenton reagents were taken from the stock solution of 11.42 M H_2O_2 (35 % w/w) solution to yield the desired H_2O_2 concentrations in the experiment medium and likewise, the evaluated Fe^{2+} concentrations were attained in the solution taken from the 0.36 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (10 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml) stock solution.

The pH of the medium was adjusted to the desired value before starting the experiment with concentrated (6 N) NaOH and H_2SO_4 solutions. Magnetic stirrers were used to attain a constant mixing intensity of 300 rpm during the experiments.

The reaction was assumed to start with the addition of Fe^{2+} almost simultaneously with the addition of H_2O_2 . After the selected reaction time, usually set as 30 min for preliminary optimization experiments, the experiment was ceased with the addition of NaOH to increase the pH around 10 - 11 where Fe^{2+} would no longer stay in solution and precipitate as iron sludge ($\text{Fe}(\text{OH})_3$).

Samples were taken for the measurement of remaining color and the COD of the dye baths after enough time passed for the settling of iron sludge from the solution. Before measuring COD, the remaining H_2O_2 in solution was checked with H_2O_2

strips. The samples having H_2O_2 concentrations above 10 mg/l were digested with appropriate amounts of catalase in order to prevent the interference with the COD determination.

3.2.1.1. Preliminary Optimization Experiments

The optimization experiments for the two dyebaths were carried out at ambient temperature (20°C) for different concentrations of Fe^{2+} (1 - 10 mM), H_2O_2 (10 - 100 mM) and at different pH values (pH = 2 - 5). Experiments were conducted as described in Fenton experiments. The experimental scheme consisted of monitoring the removal of COD and color of the dyebaths after 30 minutes of reaction time.

3.2.1.2. Kinetic Experiments

The kinetic studies were conducted for both simulated acid dyebath effluents at different temperatures in order to evaluate the temperature effects on the COD and color removal kinetics together with the consumption of H_2O_2 . All of the kinetic experiments were run at pH = 3 for 90 minutes in 2 L beakers with an amount of 1 L of dyebaths. The temperature of the experiment medium was kept constant automatically with a temperature probe included in the heater-magnetic stirrer.

Samples of 25 ml were withdrawn at $t = 0, 2, 5, 10, 20, 30, 40, 60, 75, 90$ min. time intervals. 15 ml of the sample was poured in glass test tubes with appropriate drops of NaOH to increase the pH to 10 - 11 and catalase was added immediately to each sample to destroy the residual H_2O_2 to prevent its possible interference with COD measurements. The supernatants taken from the test tubes were analyzed for COD and color likewise the optimization studies. In separate experiments where H_2O_2 abatement was followed at varying temperatures, catalase was not added for H_2O_2 determination. The remaining 10 ml was poured to 50 ml beakers and again appropriate drops of NaOH were added to stop the reaction. After filtering from 0.45 μ filter papers to another beaker, the remaining concentrations were determined by titration against sodium thiosulfate.

3.2.2 Analytical Procedure

3.2.2.1 COD Measurement

COD measurements were conducted in accordance with the ISO 6060 (1986) by the titrimetric open reflux method.

3.2.2.2 Color Measurement

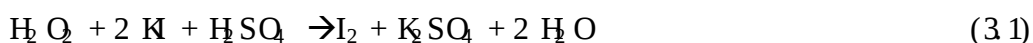
In this study, color was referred to as the measured absorbency which is the measure of how much light is absorbed by a substance compared with a blank (clear, colorless water). Color of the solution is related to the wavelength of light absorbed by the solution. Since solutions which absorb visible light are generally colored, they are good candidates for analysis via spectrophotometry.

The absorbance of the raw and pre-treated samples were performed on a spectrophotometer (Novaspec II, Pharmacia LKB) which uses wavelengths of light ranging from 350 nm to 900 nm. For the multicolor Dyebath I the absorbencies were measured at the three specific wavelengths of 436, 525, 620 nm corresponding to perceived colors yellow, red and blue, respectively, which are the selected wavelengths for the discharge standards for color in the German Guidelines (Gaehtel et al., 1994). The Turkish legislation currently has no discharge standard for color; however, within the framework of the adoption of the European Union Acquis these standards will also be adopted. For Dyebath II, the color measurements were done at the wavelength yielding maximum absorption bands. Absorbance measurements were performed with 1 cm optical path length disposable cells.

3.2.2.3 Determination of Hydrogen Peroxide

Residual hydrogen peroxide was determined by molybdate-catalyzed potassium iodide titration method (Korrmann et al., 1988).

H₂O₂ oxidizes iodide to iodine in the presence of acid and molybdate catalyst. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator.





10 ml samples are transferred to 50 ml small beakers and filtered from 0.45 µm filter papers with the help of 20 ml syringes. Then 5 ml of sulfuric acid, 3 ml of KI solution, 3 drops of ammonium molybdate and 2-3 drops of starch indicator is added respectively. The sample is titrated with 0.1 N sodium thiosulfate until the dark blue color just disappears.

The H_2O_2 concentration in the sample is calculated via the following formula:

$$H_2O_2 \text{ (mg/l)} = \frac{V_t \times N \times MW_{H_2O_2}}{V_s} \quad (3.3)$$

V_t : Volume of titrant (ml)

N : Normality of titrant (0.1 N)

V_s : Volume of sample (ml)

$MW_{H_2O_2}$: Molecular weight of H_2O_2 (mg/mol) (= 34.000 mg/mol)

3.2.2.4 Activated Sludge Inhibition Test

Activated sludge inhibition tests were conducted in accordance with a test procedure described in ISO 8192. All experiments were run at a constant temperature of 20 ± 2 °C. The heterotrophic mass used in the activated sludge inhibition test was fed with a synthetic wastewater (SWW) to simulate municipal wastewater as described in Table 3.3.

Table 3.3: Synthetic Domestic Wastewater Solution ($COD_{ot} = 30,000$ mg/L)

Reagent	(g/L)
Peptone	16
Meat extract	11
Urea	3
NaCl	0.7
$CaCl_2 \cdot 2H_2O$	0.4
$MgSO_4 \cdot 7H_2O$	0.2
K_2HPO_4	2.8

The samples were diluted with appropriate amounts of SWW ($COD_{s\text{ WW}} = 500 - 1000$ mg/L) to obtain a series of different dye bath COD fractions thereby keeping a

constant total COD in the dyebath + S W W effluent mixture. S W W as well as raw and pre-treated dyebath effluent samples were aerated for 30 min in test beakers containing proper amounts of activated sludge being previously acclimated to S W W. The F/ M (Food-to- Microorganisms) ratio was set between 0.19 - 0.20 mg COD/ mg ML VSS. d⁻¹ (ML VSS = 600 - 900 mg/ L). The decrease in dissolved oxygen concentration (in mg/ L) in the blank synthetic wastewater (S W W) as well as in different dilutions of raw and pre-treated dyebath effluent samples was monitored for 2 - 4 min using a WTW Oxi Dig 2000 model oxygen meter. Oxygen uptake rates (OUR) (expressed in mg/ L h⁻¹) in the blank (S W W) and diluted dyebath effluent samples were calculated based on the linear part of decreasing dissolved oxygen concentration curves as a function of the aeration (i.e. biological treatment) time. Percent inhibition of OUR, i.e. I_{OUR}, for every tested sample dilution, was calculated using the following equation;

$$I_{OUR} (\%) = [(R_B - R_T) \times 100] / R_B \quad (3.4)$$

where R_T is the oxygen uptake rate in the sample effluent mixture; R_B is the oxygen uptake rate in the blank sample (i.e. in S W W). The I_{OUR} values were thereafter plotted against ln COD's (natural logarithm of the CODs at different acid dyebath effluent dilutions) of acid dyebath effluents. The COD content of raw and pre-treated dyebath effluents resulting in 50 % decrease in OUR (i.e. EC₅₀ value; in mg/ L) was calculated by interpolation of the ln COD versus percent I_{OUR} plots obtained for different dyebath effluent samples.

The heterotrophic sludge sensitivity was checked by means of a reference test chemical (3,5-dichlorophenol). Its EC₅₀ value (5-30 mg/ L) was reconfirmed by applying the above indicated ISO 8192 test procedure and found as 29 mg/ L.

3.2.2.5 Determination of the Soluble Inert COD

The soluble inert COD fractions were determined for both the raw and Fermenton pre-treated dyebaths in accordance with the procedure described by Orhon et al. (1999). 2l-batch reactors which were constantly aerated were used. All reactors were initially seeded with 50 mg VSS/ L of acclimated biomass. The seeding was intentionally kept minimal to avoid interferences to carry over of endogenous residues. The acclimated

biomass for each of the raw and pre-treated dyebaths were obtained from the mixed liquor of the fill and draw reactors fed with 50 % dyebath effluents and 50 % glucose solutions (initial seed obtained from WWTP of the textile finishing factory). Each run for the inert COD determination of dyebath effluents was continued for 50 days until all biological activity was completed and no appreciable COD change was detected. The experiments were conducted at room temperature and at a pH range of 7.0 - 8.0.

The buffer and nutrient solutions containing trace elements (Mg, Mn, Fe, Zn and Ca) and compounds to supply the nutrients, nitrogen and phosphorus are herein called Solution A and Solution B (Table 3.4). Appropriate amounts of Solution A and Solution B for dilutions (10 ml Solution A and Solution B for 1000 mg/L COD) were added to all reactors to eliminate the effects of nutrient limitation and to buffer the reactors for possible pH variations.

Table 3.4: Formulations of nutrient and buffer solutions

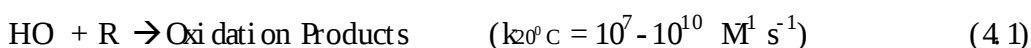
Solution A		Solution B	
Reagent	(g/L)	Reagent	(g/L)
K ₂ HPO ₄	320	MgSO ₄ ·7H ₂ O	15
KH ₂ PO ₄	160	FeSO ₄ ·7H ₂ O	0.5
NH ₄ Cl	120	ZnSO ₄ ·7H ₂ O	0.5
		MnSO ₄ ·3H ₂ O	0.5
		CaCl ₂	2.0

The soluble COD was defined as the filtrate through 0.45 µm glass fiber filters, also used in the determination of VSS and SS parameters.

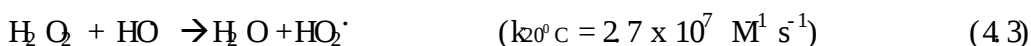
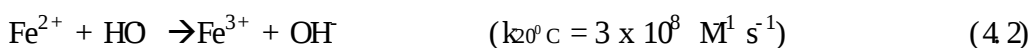
4 RESULTS AND DISCUSSION

4.1 Pretreatment with Fenton's Reagent - Optimization Experiments

Referring to the Fenton process, it is well known that higher hydrogen peroxide to substrate ratios result in more extensive substrate degradation, while higher concentrations of iron ions yield faster rates. However, in order to maximize the effectiveness of the process, it is preliminarily necessary to determine the optimum operational $\text{Fe}^{2+} : \text{H}_2\text{O}_2$ mass ratio. As previously described, Fenton's reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} + \text{HO}\cdot$) is used to produce the hydroxyl radicals necessary to oxidize organic substances (R) according to the following reaction (Huang et al., 1993):



Particular attention must be paid to Fe^{2+} and H_2O_2 concentrations in order to avoid the following undesired $\text{HO}\cdot$ scavenging reactions occurring in the presence of an excess of each of the two reagents (Tang and Huang, 1997, Hueh et al., 2004).



Previous studies, in fact, have demonstrated that the highest oxidation efficiency is achieved by reaction (4.1) when neither Fe^{2+} nor H_2O_2 is overdosed, so that the maximum amount of $\text{HO}\cdot$ is available for the oxidation of organic compounds (Tang and Huang, 1997). In other words, an optimal molar ratio between H_2O_2 and Fe^{2+} ($\text{Fe}^{2+} : \text{H}_2\text{O}_2$) must be fixed in order to minimize scavenging effects.

In the presence of excess Fe^{2+} , reaction (4.2) predominates over reaction (4.1). Therefore, the higher the Fe^{2+} concentration, the lower the amount of $\text{HO}\cdot$ radicals available to oxidize organic matter according to reaction (4.1).

4.1.1. Effect of Initial Ferrous Iron Concentration

In order to determine the optimum Fe^{2+} and H_2O_2 concentrations, a set of experiments was carried out for the exhausted acid dyebaths while progressively increasing the concentration of Fe^{2+} (0.5 - 10 mM) maintaining the concentration of H_2O_2 constant at an arbitrary value of 30 mM. According to previous studies (Malik and Saha, 2003; Burbano, 2005), all the experiments were carried out at a fixed reaction time of 30 min and an initial pH of 3.0.

4.1.1.1. Dyebath I

Percent COD removal efficiencies obtained after 30 min treatment at varying Fe^{2+} concentrations is presented in Figure 4.1. The iron concentrations studied were in the range 0.5 - 20 mM as 0.5, 1, 2, 3, 4, 5, 7.5, 10, 15, 20 mM respectively. Control samples with only hydrogen peroxide were also tested for COD removals.

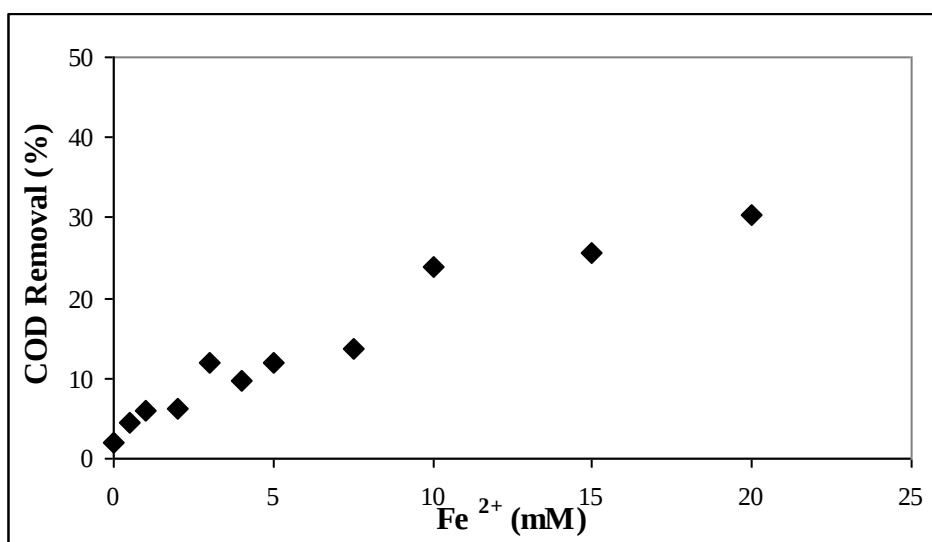


Figure 4.1. Effect of Fe^{2+} concentration on COD removal for DBI ($\text{H}_2\text{O}_2 = 30$ mM, pH = 3, $t = 30$ min; $\text{COD}_0 = 2741$ mg/L)

It may be observed from the figure that COD removal increased with increasing iron concentrations. Only, after 10 mM the COD removal did not increase significantly.

Percent color removal efficiencies at the predefined wavelengths may be observed from Figure 4.2. Color removal could not be observed for the iron concentrations of 0.5, 1 and 2 mM, hence not shown in the figure. The color removal showed a similar

trend to the COD removal. Accordingly, the optimum iron concentration was chosen to be 10 mM for DBI corresponding to 24 % COD removal ($COD_0 = 2741 \text{ mg/L}$).

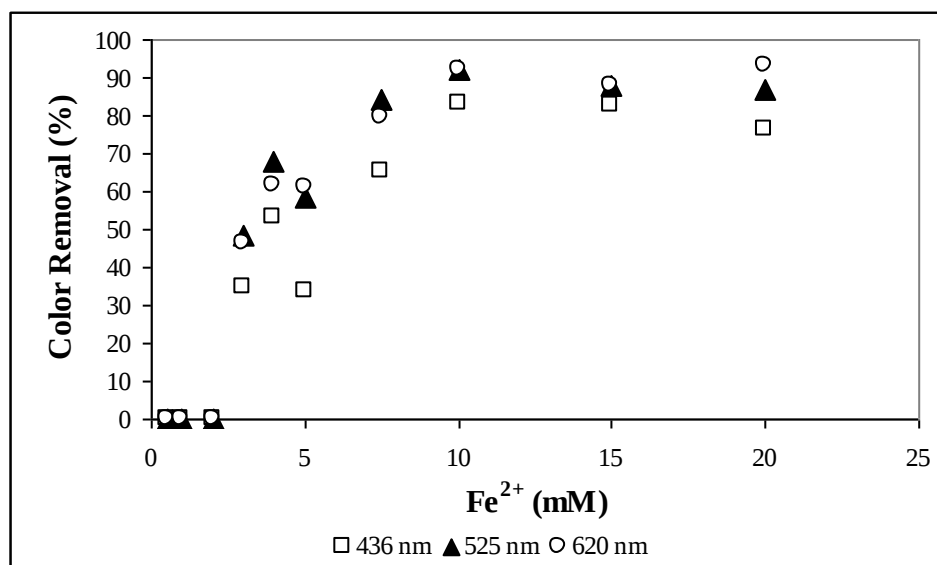


Figure 4.2 Effect of Fe^{2+} concentration on color (absorbance) removal for DBI ($H_2O_2 = 30 \text{ mM}$, $pH = 3$, $t = 30 \text{ min}$; $COD_0 = 2741 \text{ mg/L}$; $A_{436, 0} = 0.833 \text{ cm}^{-1}$; $A_{525, 0} = 0.612 \text{ 1/cm}$; $A_{620, 0} = 0.28 \text{ 1/cm}$)

The results for the optimization of initial Fe^{2+} concentration are presented in Table 4.1.

Table 4.1: Effect of Fe^{2+} dose on COD and Colour Removal Efficiency for DBI. ($H_2O_2 = 30 \text{ mM}$, $pH = 3$; Reaction duration = 30 min; $COD_0 = 2746 \text{ mg/L}$; $A_{436, 0} = 0.833 \text{ cm}^{-1}$; $A_{525, 0} = 0.612 \text{ cm}^{-1}$; $A_{620, 0} = 0.28 \text{ cm}^{-1}$)

Fe^{2+} Concentration (mM)	COD		Color			
	Final COD (mg/L)	Removal Efficiency (%)	Final Absorbance (cm^{-1}) at $\lambda = 436, 525, 620$ nm			Removal Efficiency (%) at $\lambda =$ 620 nm
			436	525	620	
0	2692	2	-*	-	-	-
0.5	2621	5	-	-	-	-
1	2582	6	-	0.498	0.273	-
2	2573	6	-	0.520	0.215	-
3	2419	12	0.544	0.315	0.150	46
4	2477	10	0.389	0.196	0.108	61
5	2419	12	0.554	0.253	0.109	61
7.5	2371	14	0.29	0.097	0.057	80
10	2107	23	0.14	0.049	0.022	92
15	2189	26	0.241	0.091	0.040	88
20	2078	30	0.203	0.065	0.019	93

*: no removal observed

4.1.1.2 Dyebath II

The COD removal efficiencies achieved after 30 min. Fenton's treatment are depicted in Figure 4.3. The iron concentrations studied were in the range 0.25 - 6 mM. 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 mM as Fe^{2+} . Control samples were also tested for COD removal without the addition of iron. The results obtained in terms of COD removal are presented in Figure 4.3.

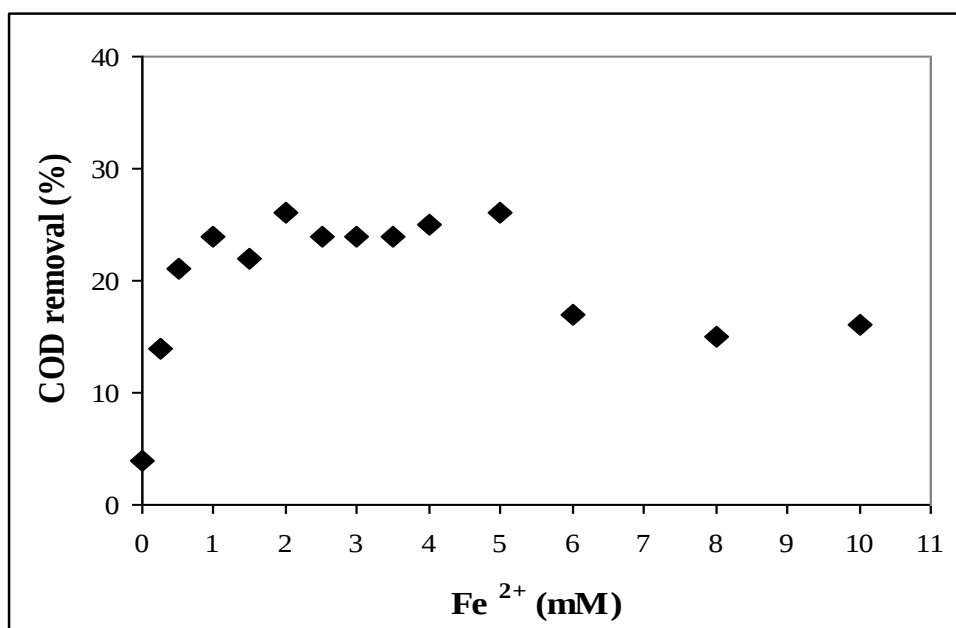


Figure 4.3 Effect of Fe^{2+} concentration COD removal for DB II ($\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$, $\text{COD}_0 = 1705 \text{ mg/L}$)

It may be observed from the figure that the COD removal was not enhanced significantly with increasing iron concentrations from 1 mM up to 5 mM with the exception of 2 mM where there happens to be a slight peak of 26 % COD removal ($\text{COD}_0 = 1705 \text{ mg/L}$). It was observed that COD removal decreased significantly above 5 mM of Fe^{2+} concentration.

This may be explained as accepted in the literature that, in the presence of an excess of Fe^{2+} , reaction (4.2) predominates over reaction (4.1). Therefore, the higher the Fe^{2+} concentration, the lower the amount of OH available to oxidize organic matter according to reaction (1) (Lopez et al., 2004).

The reduction in color with different Fe^{2+} concentrations for DB II is presented in Figure 4.4.

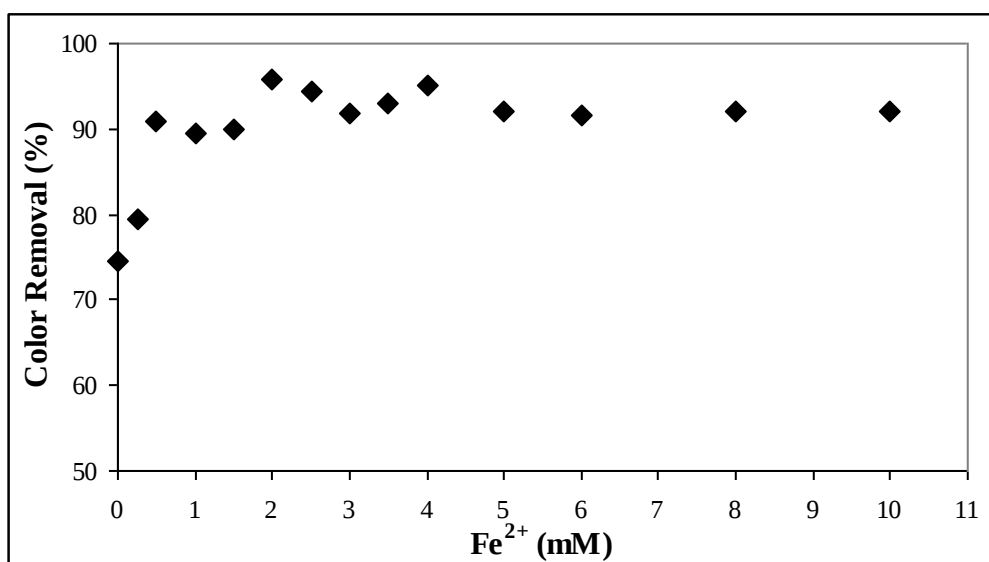


Figure 4.4 Effect of Fe^{2+} concentration on color abatement for DB II ($\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$, $\text{COD}_0 = 1705 \text{ mg/L}$, $A_{569,0} = 7.32 \text{ cm}^{-1}$)

The color removal proved to be constant above an iron concentration of 2 mM Fe^{2+} which corresponded to a removal by 90 %. Accordingly the optimum Fe^{2+} concentration was selected as 2 mM for the proceeding experiments.

The experimental results are summarized in Table 4.2

Table 4.2: Effect of Fe^{2+} concentration on COD and Colour Removal Efficiency for DB II. ($\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, Reaction duration = 30 min , $\text{COD}_0 = 1705 \text{ mg/L}$, $A_{569,0} = 7.32 \text{ cm}^{-1}$)

Fe^{2+} Concentration (mM)	COD		Color	
	Final COD (mg/L)	Removal Efficiency (%)	Final Absorbance (cm^{-1}) at 569 nm	Removal Efficiency (%)
0	1688	1	7.31	-
0.25	1466	14	1.858	75
0.5	1345	21	1.51	80
1	1296	24	0.81	91
1.5	1330	22	0.765	90
2	1262	26	0.727	90
2.5	1296	24	0.313	96
3	1296	24	0.416	94
3.5	1296	24	0.602	92
4	1279	25	0.52	93
5	1262	26	0.361	95
6	1483	17	0.58	92
8	1449	15	0.57	92
10	1432	16	0.58	92

4.1.2 Effect of Initial Hydrogen Peroxide Concentration

4.1.2.1 Dyebath I

The effect of H_2O_2 concentration on treatment efficiency was investigated by trying different concentrations of H_2O_2 at the optimum Fe^{2+} concentration found as 10 mM and $\text{pH}=3$. The H_2O_2 concentration range was selected to be 10 - 100 mM as 10, 20, 25, 30, 35, 40, 50, 75, 100 mM of H_2O_2 respectively. A separate control experiment was conducted to observe the effect of Fe^{2+} in the absence of H_2O_2 .

The results are shown in Figure 4.5 in terms of percent COD removals.

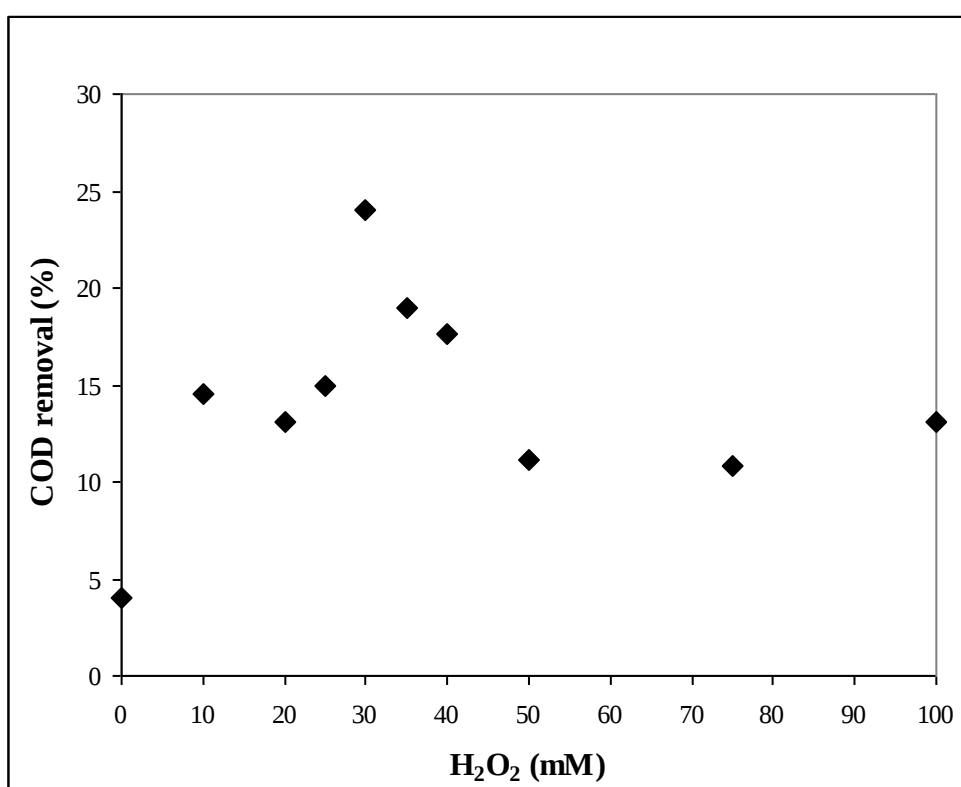


Figure 4.5 Effect of H_2O_2 dose on COD abatement for DBI (Fe^{2+} =10 mM, $\text{pH}=3$, $t=30$ min; $\text{COD}_0 = 2745$ mg/L)

As can be seen in Figure 4.5, the highest percent COD removal efficiency was found as 24 % for the H_2O_2 concentration of 30 mM ($\text{COD}_0 = 2745$ mg/L).

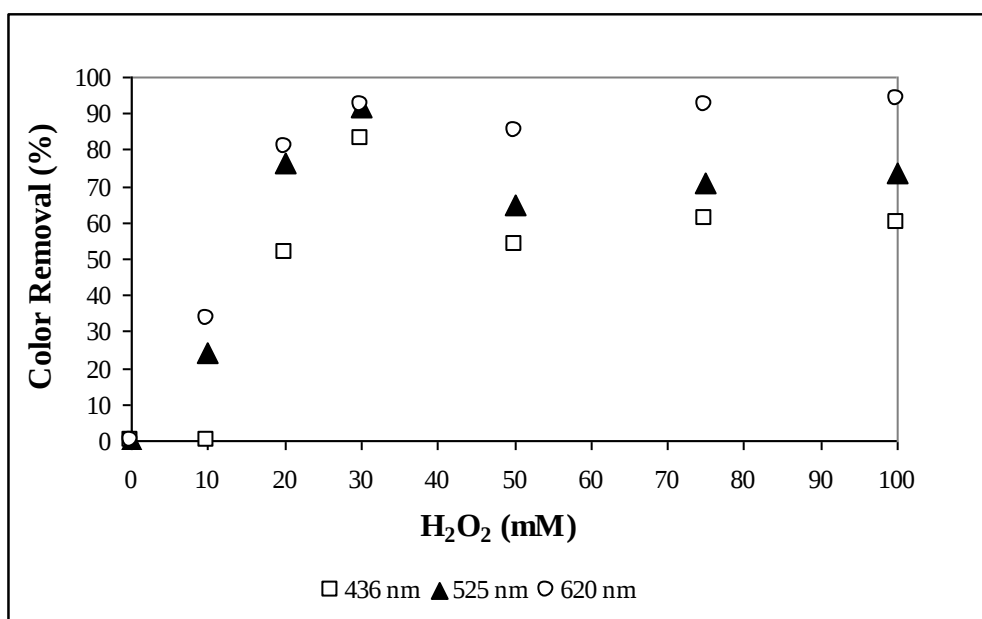


Figure 4.6 Effect of H_2O_2 concentration on color removal for DBI ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{pH} = 3$; $t = 30 \text{ min}$; $A_{436,0} = 0.833 \text{ cm}^{-1}$; $A_{525,0} = 0.612 \text{ cm}^{-1}$; $A_{620,0} = 0.28 \text{ cm}^{-1}$)

The color removal efficiencies may be observed from Figure 4.6. There was no color removal with H_2O_2 concentrations less than 20 mM and the removal efficiency did not increase with dosages higher than 30 mM. Therefore the optimum H_2O_2 concentration was observed to be 30 mM for DBI.

The results of the experiments are presented in Table 4.3.

Table 4.3: Effect of the initial H_2O_2 concentration on COD and Color Removal Efficiency for DBI. ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{pH} = 3$; Reaction duration = 30 min; $\text{COD}_0 = 2745 \text{ ng/L}$; $A_{620,0} = 0.28 \text{ cm}^{-1}$)

H_2O_2 Concentration (mM)	COD		Color	
	Final COD (ng/L)	Removal Efficiency (%)	Final Absorbance (cm^{-1}) at $\lambda = 620 \text{ nm}$	Removal Efficiency (%)
0	2636	4	0.267	5
10	2347	15	0.186	34
20	2386	13	0.054	81
25	2405	15	-	-
30	2086	24	0.022	92
35	2290	19	-	-
40	2328	18	-	-
50	2438	11	0.042	85
75	2448	11	0.022	92
100	2386	13	0.017	94

4.1.2.2 Dyebath II

The experiments were carried out with the optimum Fe^{2+} concentration found as 2 mM and for the H_2O_2 concentration range = 10 - 60 mM as 10, 15, 20, 30, 40, 50, 60 mM respectively. The results are presented in Table 4.4 and in a single graph with corresponding COD and color removal percentages (Figure 4.7). Color is referred to as absorbance at 569 nm. It is evident from the figure that both the COD and color removal remained stagnant above H_2O_2 concentration of 30 mM. Hence the optimum H_2O_2 concentration was found to be 30 mM with a corresponding COD removal efficiency of 26 % ($\text{COD}_0 = 1677 \text{ mg/L}$).

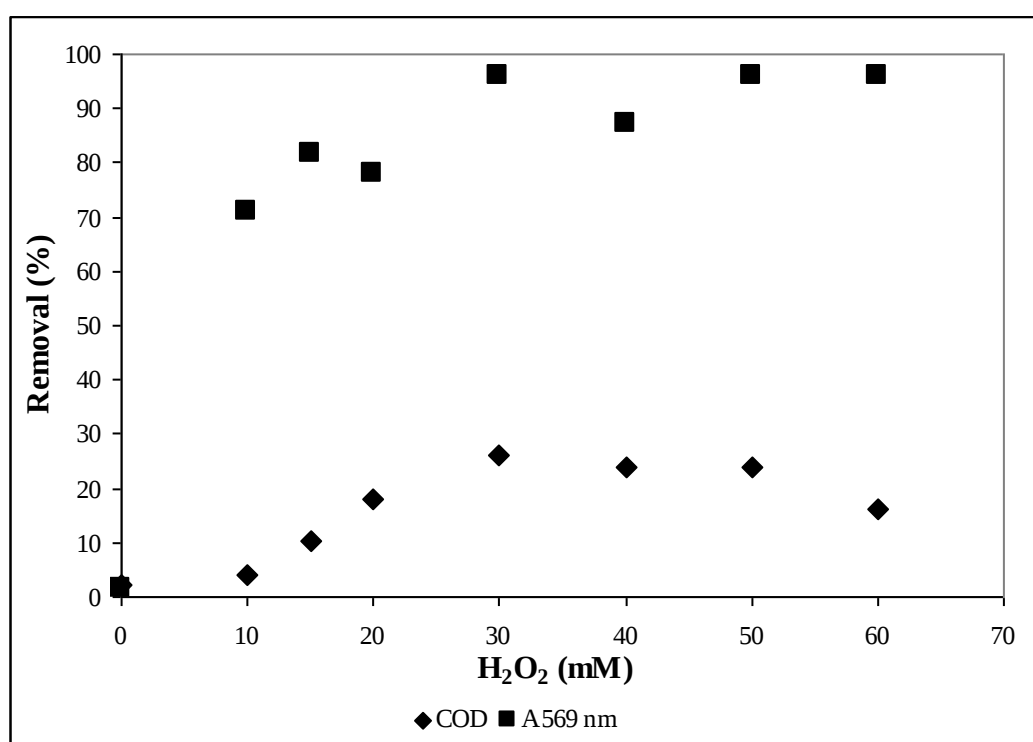


Figure 4.7. Effect of initial H_2O_2 concentration on COD and color removal for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$; $\text{COD}_0 = 1677 \text{ mg/L}$; $A_{569, 0} = 7.32 \text{ cm}^{-1}$)

The results of the experiments that evaluated the effect of initial H_2O_2 concentration are presented in Table 4.4.

Table 4.4: Effect of H_2O_2 concentration on COD and Colour Removal Efficiency for DB II. ($Fe^{2+} = 2 \text{ mM}$, $pH = 3$; Reaction duration = 30 min; $COD_0 = 1677 \text{ mg/L}$, $A_{569, 0} = 7.32 \text{ cm}^{-1}$)

H_2O_2 Concentration (mM)	COD		Colour	
	Final COD (mg/L)	Removal Efficiency (%)	Final Absorbance (cm^{-1}) at 569 nm	Removal Efficiency (%)
0	1643	2	-	-
10	1608	4	2.122	71
15	1506	10	1.341	82
20	1375	18	1.61	78
30	1157	31	0.293	96
40	1258	25	0.952	87
50	1266	25	0.294	96

It was found that the optimum molar $Fe^{2+} : H_2O_2$ ratio for the Dyebath I and Dyebath II were 1:3 and 1:15 respectively. However, many similar molar ratios of the initial Fe^{2+} to H_2O_2 concentrations for the Fenton reaction have been reported in the literature. For example 1:3 for phenol (Eisenhauer, 1964); 1:4 for chlorobiphenyls (Sedlak and Andren, 1991), 1:11 for 2,4-dichlorophenol (Tang and Huang, 1996).

Martinez et al. (2003) have reported the optimized values of H_2O_2 and Fe^{2+} concentrations as 3 and 0.3 M respectively, for an extremely polluted pharmaceutical wastewater ($COD_0 = 362,000 \text{ mg/l}$). They have achieved a COD global reduction of 56 %

Among the studies investigating the effectiveness of Fenton reactions on the treatment of dyes, Neamtu et al. (2003), have reported a value of 20:1 for the molar ratio of $H_2O_2 : Fe^{2+}$ for the oxidation of commercial reactive azo dye aqueous solutions.

4.1.3 Effect of pH

As indicated in the previous sections pH has a significant effect on the Fenton reactions and the most suitable pH range for the removal of various organics was $pH = 2 - 5$ (Lunar et al., 2000, Perez et al., 2002, Ghaly et al., 2001, Kang et al., 2002). The effect of pH on Fenton's treatment of the exhausted dyebaths was studied also in terms of COD and colour removal efficiencies obtained after 30 min at optimum Fe^{2+} and H_2O_2 concentrations. The studied pH values ranged between $pH = 2 - 5$ as $pH = 2, 2.5, 3, 3.5, 4, 4.5, 5$

4.1.3.1 Dyebath I

The obtained plots of COD and Color (absorbance at 620 nm) removal for Dyebath I at different pH values are presented in Figure 4.8 and Figure 4.9, respectively.

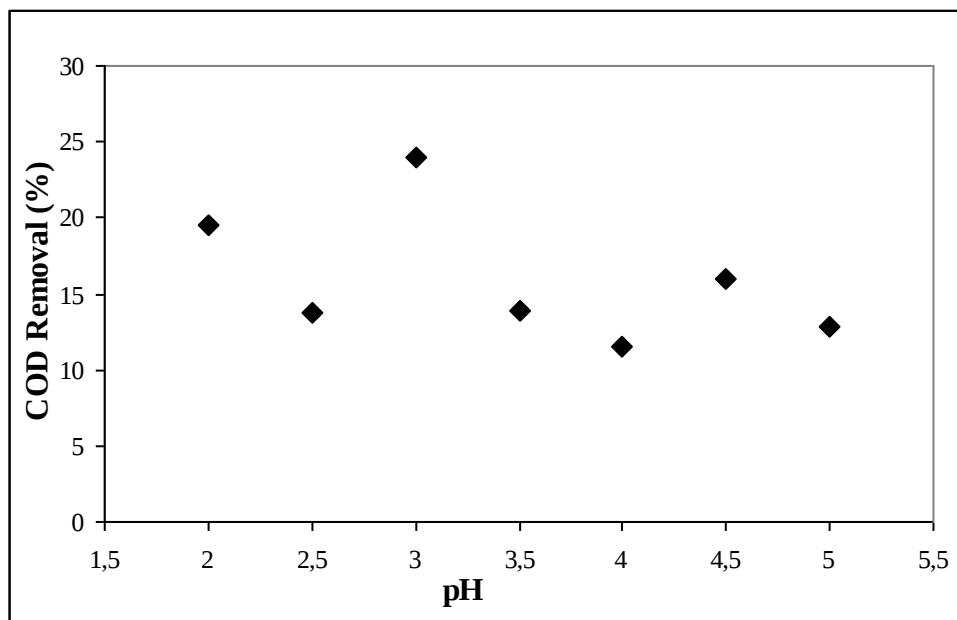


Figure 4.8: Effect of pH on COD removal efficiencies for DBI ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $t = 30 \text{ min}$, $\text{COD}_0 = 2731 \text{ mg/L}$)

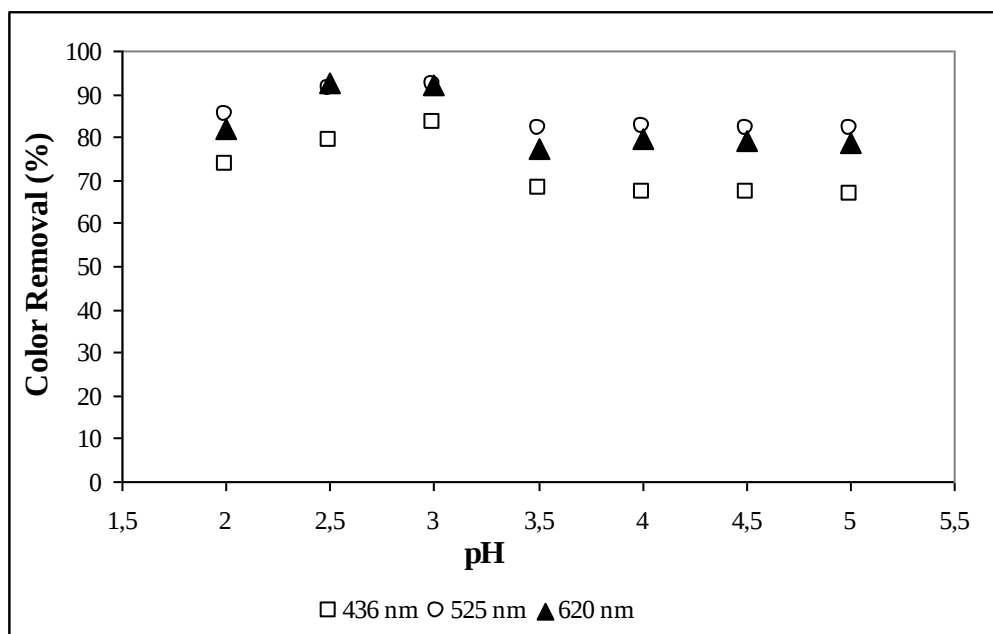


Figure 4.9: Effect of pH on color removal efficiencies for DBI ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $t = 30 \text{ min}$, $\text{COD}_0 = 2731 \text{ mg/L}$; $A_{436,0} = 0.833 \text{ cm}^{-1}$; $A_{525,0} = 0.612 \text{ cm}^{-1}$; $A_{620,0} = 0.28 \text{ cm}^{-1}$)

As can be observed from Figures 4.8 and 4.9, the optimum pH in terms of COD and color removal efficiencies was selected as pH = 3.

The experimental results are summarized in Table 4.5.

Table 4.5: Effect of pH on COD and Color Removal Efficiency for DBI. ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, Reaction duration = 30 min, $\text{COD}_0 = 2731 \text{ mg/L}$; $A_{620,0} = 0.28 \text{ cm}^{-1}$)

pH	COD		Color	
	Final COD (mg/L)	Removal Efficiency (%)	Final Absorbance (cm^{-1}) at 620 nm	Removal Efficiency (%)
2	2185	20	0.05	82
2.5	2349	14	0.021	93
3	2076	24	0.022	92
3.5	2348	14	0.064	77
4	2403	12	0.057	80
4.5	2294	16	0.058	79
5	2376	13	0.06	79

4.1.3.2 Dye bath II

The results obtained from the pH optimization experiments in terms of COD and color removal efficiencies illustrated in the Figures 4.10 and 4.11, after 30 min reaction time at optimum Fe^{2+} and H_2O_2 concentrations of 2 mM and 30 mM respectively.

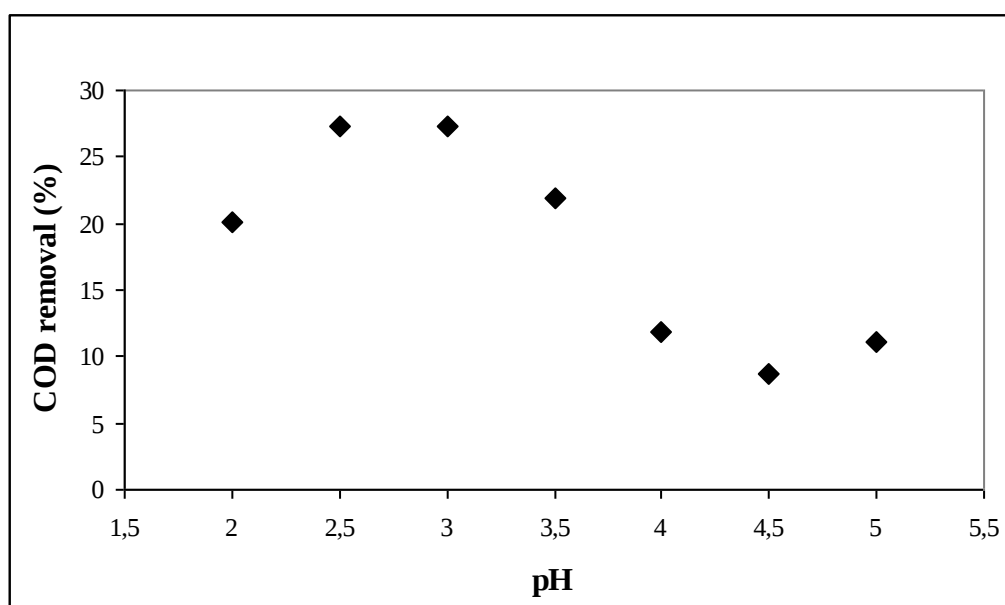


Figure 4.10: Effect of pH on COD removal efficiencies for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $t = 30 \text{ min}$, $\text{COD}_0 = 1677 \text{ mg/L}$)

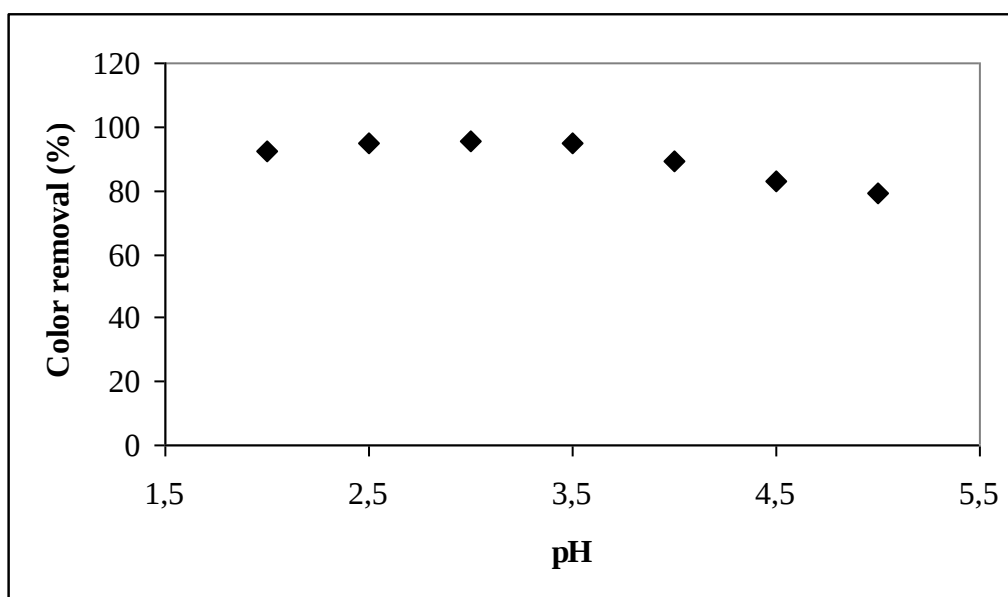


Figure 4 11: Effect of pH on Color removal efficiencies for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $t = 30 \text{ min}$, $\text{COD}_0 = 1677 \text{ ng/L}$, $A_{569,0} = 7.32 \text{ cm}^{-1}$)

The color removal for Dyebath II at varying pH was observed to be constant between pH = 2 - 5

The optimum pH for the effective removal of COD and color was found to be pH = 3 for both Dyebath I and Dyebath II. It is important to note that pH = 3 is the nearest pH value to the original pH values of the exhausted acid dyebaths which are pH = 3.5 and pH = 4.5 for the dyebaths I and II respectively.

Similarly, Neamtu et al. (2003) and Tang and Chen (1996) have also shown the results for degradation of azo reactive dyes, C.I. Reactive Yellow 84 and C.I. Reactive Red 120 by Fenton reactions as pH = 3 and pH = 2 respectively. Color removal of synthetic dye wastewater by Fenton's and photo-Fenton's reaction was achieved at pH range 3 - 4 (Solozhenko et al., 1995; Deng et al., 2000).

The experimental results obtained are summarized in Table 4.6

Table 4.6: Effect of pH on COD and Colour Removal Efficiency for DB II. ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, Reaction duration = 30 min, $\text{COD}_0 = 1677 \text{ ng/L}$, $A_{569,0} = 7.32 \text{ cm}^{-1}$)

pH	COD		Col or	
	Fi nal COD (ng/ L)	Re moval Effi ciency (%)	Fi nal Absorbance (cm^{-1}) At 569 nm	Re moval Effi ciency (%)
2	1341	20	0.578	92
2.5	1219	27	0.385	95
3	1219	27	0.341	95
3.5	1309	22	0.355	95
4	1478	12	0.789	89
4.5	1530	9	1.230	83
5	1491	11	1.536	79

4.2 Kinetic Studies

4.2.1. Effect on Temperature on COD and Colour Removals, and Fate of H_2O_2

Recently, several studies have reported that in the (dark or photo) Fe^{3+} (or Fe^{2+})/ H_2O_2 system, increased reaction temperature can enhance system reactivity (in terms of target compound removal, COD or TOC) (Lunar et al., 2000; Gob et al., 2001). Sagawe et al. (2001) have also demonstrated the possibility of a combined photochemically and thermally enhanced photoreactive Fenton system utilizing solar infrared as an energy source. The results presented in the literature have shown that in the case of photochemically and thermally enhanced Fenton systems, the removal rate of target compounds (i.e., 4-nitrophenol) could be increased to more than 100 times that of the dark Fe^{3+} (or Fe^{2+})/ H_2O_2 systems. However, some researchers pointed out that the increased reaction temperature might cause a decrease in the utilization of oxidant (H_2O_2), that is, an increase in the ratio of H_2O_2 consumed to the amount of target material removed (increase of $[\Delta\text{H}_2\text{O}_2] = [\Delta\text{COD or TOC}]$) (Dutta et al., 2001). In most cases, the thermal enhancement of target compound removal was reported (Lopez et al., 2004; Lee et al., 2002; Torrades et al., 2003; Perez et al., 2002; Lee and Yoon, 2004).

In this study, kinetic experiments were conducted in order to examine the effect of dye bath temperature on COD, colour and H_2O_2 abatement rates towards the modeling of Fenton's Reagent. It was aimed to determine the fate of COD and H_2O_2 with varying temperatures for the two dye baths. The main reason for the consideration of

the kinetic evaluation was that the acid dye baths are usually applied at elevated temperatures at around 80 °C

The selected temperature range for the investigation was between 20 °C and 70 °C for both of the dye baths. The kinetic experiments were run as described in the Methods section

4.2.1.1 Dye bath I

Dye bath I was treated with Fenton's Reagent at the predetermined optimum reaction conditions $\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$ and at $\text{pH} = 3$ for the temperatures of $T = 20, 30, 40, 45, 50, 55, 60 \text{ }^\circ\text{C}$ for 90 min.

Figure 4.12 summarizes the COD abatement kinetics obtained for Dye bath I at varying temperatures.

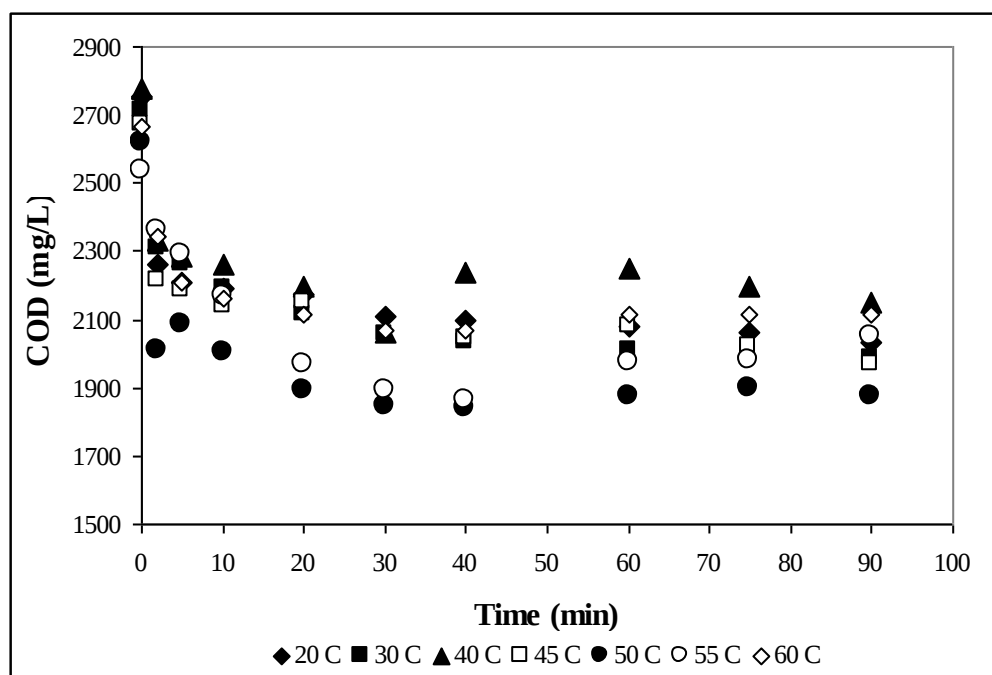


Figure 4.12: COD abatement kinetic for DBI at different temperatures at optimum conditions ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 90 \text{ min}$)

It was observed from Figure 4.12 that the COD removal did not continue after 30 min reaction time. It is also important to note that the difference of COD removal with increasing temperature is more detectable in the first minutes of the Fenton reaction.

The effect of temperature on COD removal efficiencies after 30 min reaction time is summarized in Figure 4.13.

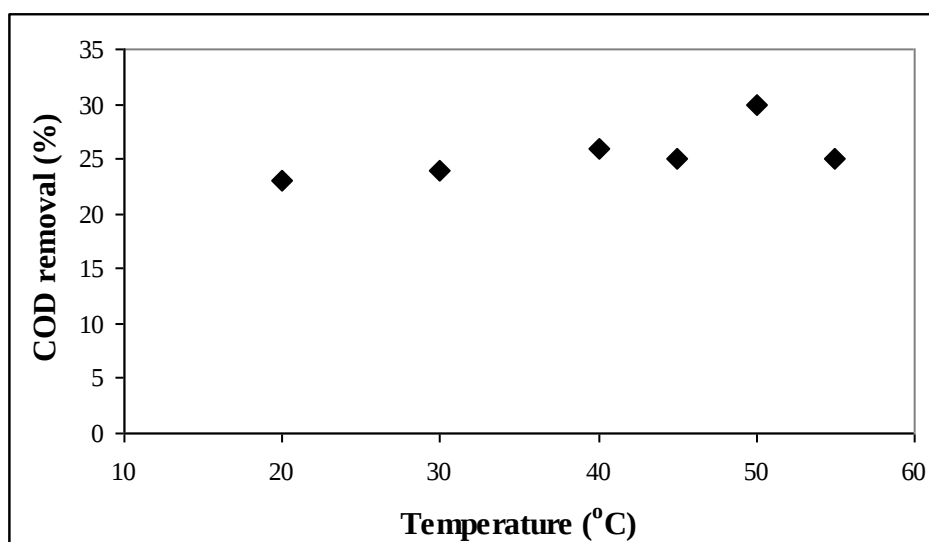


Figure 4.13: Effect of Temperature on COD removal efficiencies for DBI ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$; $\text{COD}_0 = 2616 \text{ mg/L}$)

It was observed that the highest COD removal efficiency was obtained at $T = 50^\circ\text{C}$ as 30 % with a final COD value of 1843 mg/L after 30 minutes of reaction time.

The residual H_2O_2 concentration was also determined at varying temperatures in parallel samples taken for the determination of remaining COD. Figure 4.14 presents the residual H_2O_2 concentrations in the dye bath solutions with increasing temperatures.

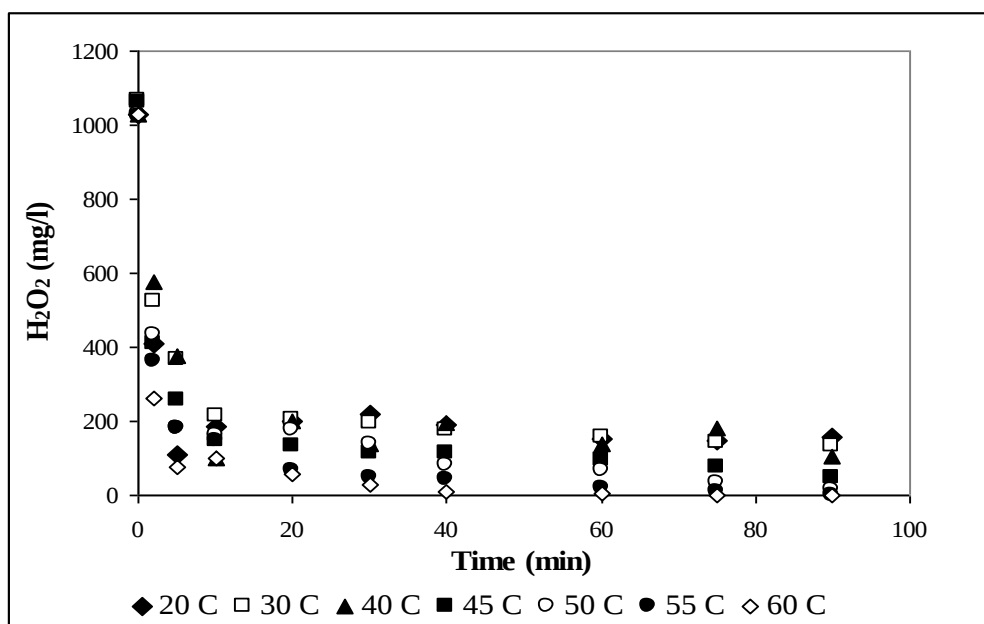


Figure 4.14: H_2O_2 consumption for DBI at different temperatures at optimum conditions ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 90 \text{ min}$)

The color abatement kinetics were again observed at wavelengths of 436, 525 and 620 nm for Dyebath I. It was decided to show the results obtained at the best representative wavelength which was 620 nm (Figure 4.15).

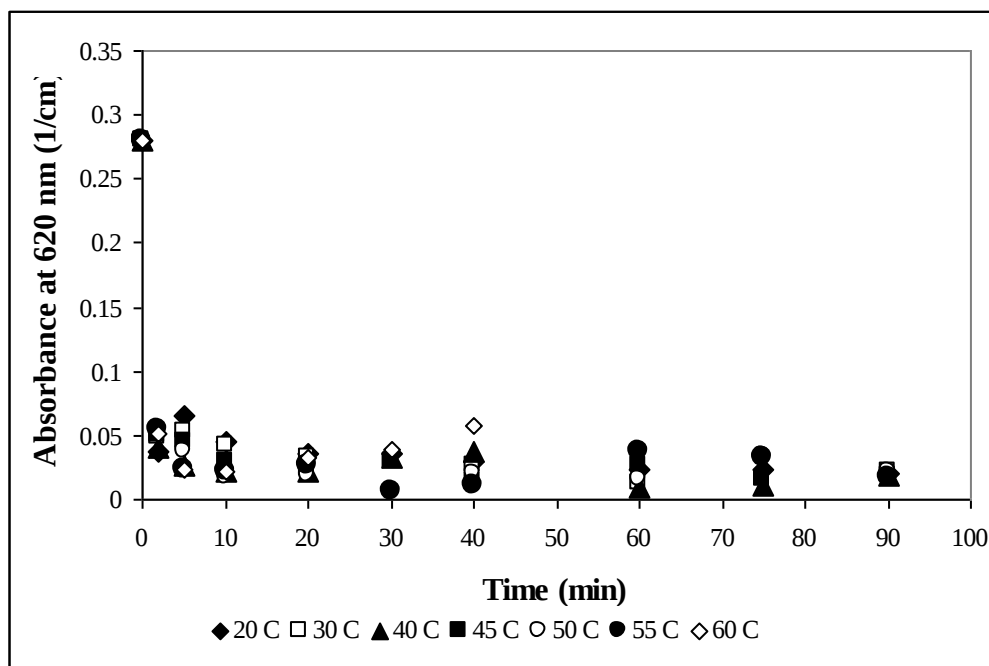


Figure 4.15: Color removal for DBI at different temperatures at optimum reaction conditions ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 90 \text{ min}$, $A_{620,0} = 0.28 \text{ cm}^{-1}$)

The effect of temperature on color removal was summarized in Figure 4.16.

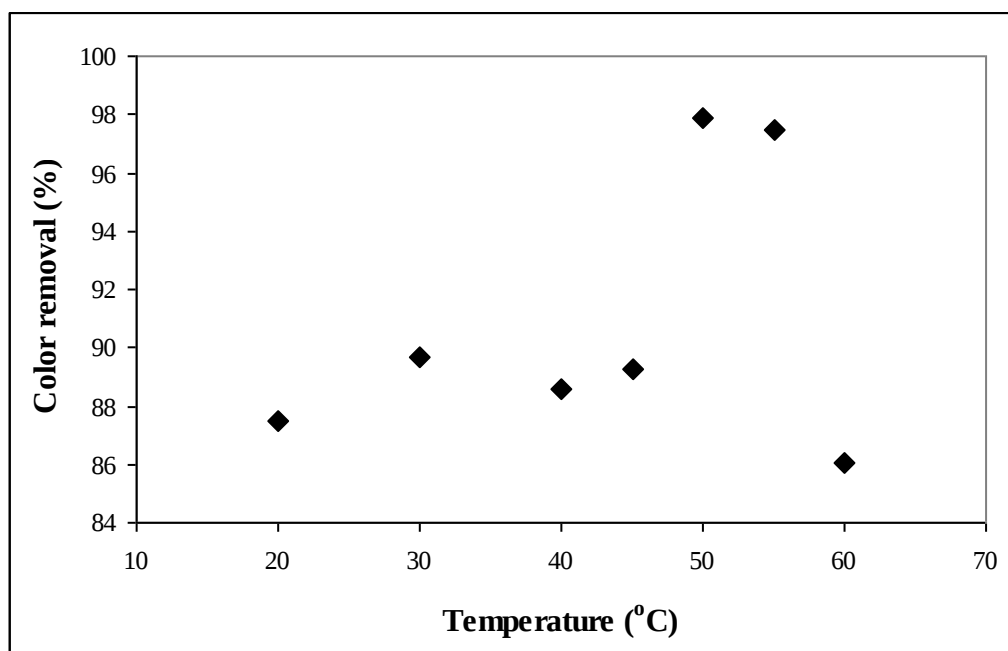


Figure 4.16: Effect of Temperature on color removal efficiencies for DBI ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$, $A_{620,0} = 0.28 \text{ cm}^{-1}$)

It may be observed from Figure 4.16 that the highest color removal (99 %) was achieved at 50 °C

4.2.1.2 Dyebath II

Dyebath II was also treated with the Fenton's reagent at optimum process conditions determined as $\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$ and $\text{pH} = 3$ for 90 min reaction time. The studied Dyebath temperatures were $T = 20, 30, 40, 50, 60$ and 70°C . The results are presented in terms of COD abatement kinetic and overall COD removal efficiencies, as well as remaining H_2O_2 and color (absorbance at 569 nm) as in the case of Dyebath I.

The COD removal efficiencies and COD removal efficiencies for Dyebath II are presented in the Figures below (Figure 4.17).

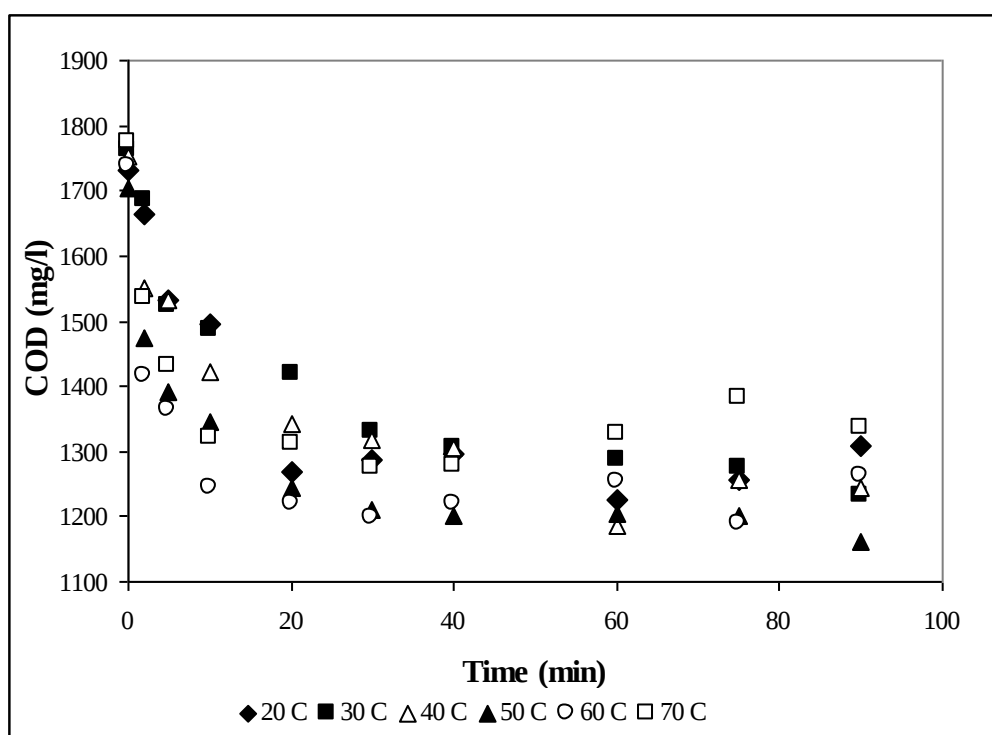


Figure 4.17: COD abatement kinetics at varying temperatures for DB II at optimum reaction conditions ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 90 \text{ min}$)

Figure 4.18 provides an overview of the overall COD removal efficiencies obtained after 30 min for the Dyebath II under the predetermined experimental conditions, pointing out the best experiment temperature as 60 °C in terms of COD removal.

It is also evident from Figure 4.18 that the difference in COD removals observed at 20 °C and 60 °C is more significant at the beginning of the reaction i.e. first 30 min.

For instance, after 10 min reaction time COD removal is only 14 % for $T = 20^{\circ}\text{C}$ but already at 28 % at $T = 60^{\circ}\text{C}$ indicating that the reaction is almost complete.

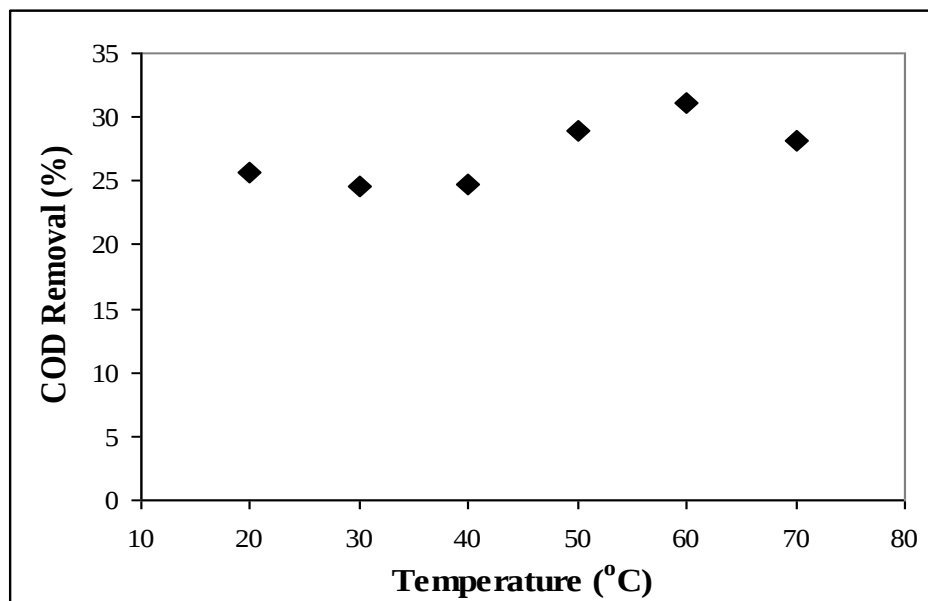


Figure 4 18: Effect of Temperature on COD removal efficiencies for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$)

It was observed that the best COD removal for Dyebath II was obtained at $T = 60^{\circ}\text{C}$ with a removal efficiency of 31 % and a final COD of 1197 mg/L ($\text{COD}_0 = 1738 \text{ mg/L}$) after 30 minutes of reaction time.

The H_2O_2 abatement kinetics for Dyebath is presented in Figure 4 19.

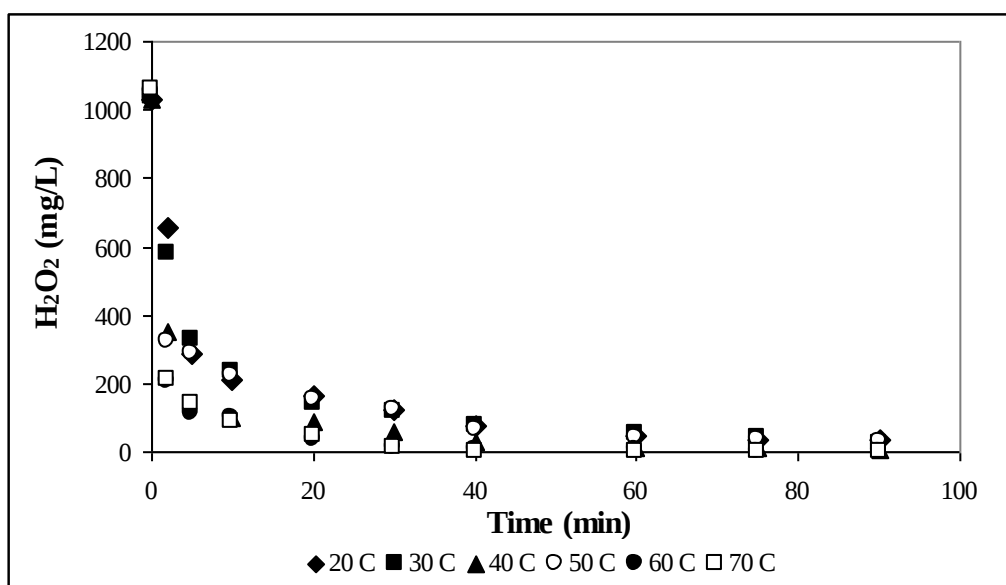


Figure 4 19: Fate of H_2O_2 for DBII at different temperatures at optimum conditions ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 90 \text{ min}$)

It was observed that the remaining H_2O_2 with time decreased with increasing temperatures indicating higher reaction rates up to $T = 60^\circ C$. At $T = 60^\circ C$ the H_2O_2 consumption was practically the same as $T = 70^\circ C$ (H_2O_2 consumed = 99 % of the initial concentration) for 90 min.

The color abatement obtained for Dyebath II for 90 min reaction time at 569 nm wavelength at varying temperatures is illustrated in Figure 4.20.

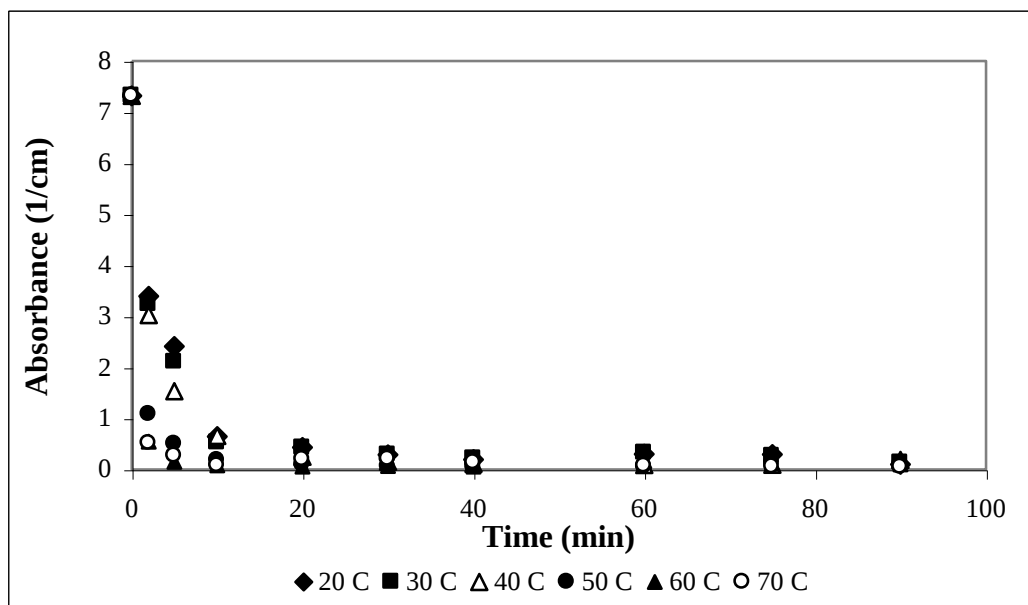


Figure 4.20: Color removal for DB II at different temperatures at optimum conditions at $\lambda = 569\text{ nm}$ ($Fe^{2+} = 2\text{ mM}$, $H_2O_2 = 30\text{ mM}$, $pH = 3$, $t = 90\text{ min}$)

It was observed that the color removal was faster during the first 10 min of the Fenton reaction at elevated temperatures, as in the case of COD removal. However, almost the same efficiencies were observed for color abatement after a reaction time of 90 min.

The effect of temperature on color removal for Dyebath II for a reaction duration of 30 min is presented in the Figure 4.21.

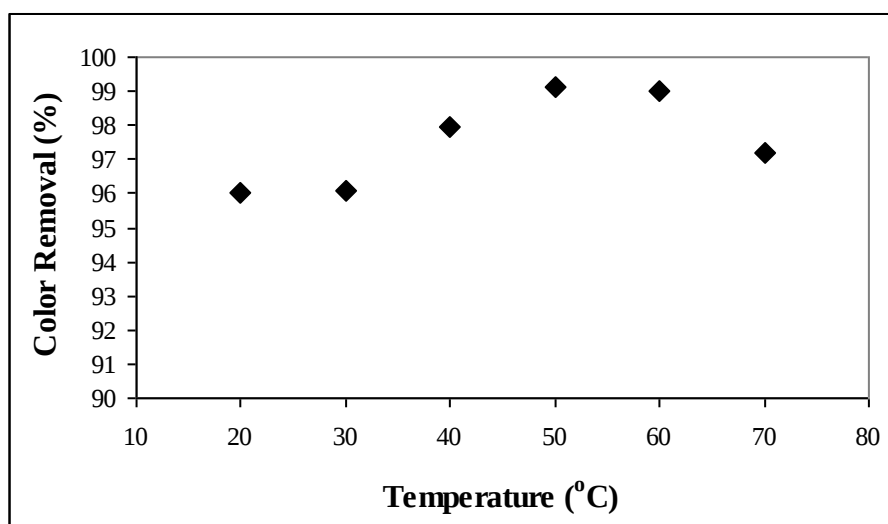


Figure 4.21: Effect of Temperature on color removal efficiencies for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$)

From Figure 4.21, it is evident that high color removal values (all above 95 %) were obtained even at lower temperatures, however, the highest color removals were achieved at temperatures around 50 - 60 °C

4.2.2 Determination of Reaction Rate Constants

It was previously reported that the rate of the oxidation reaction depends on the concentration of hydroxyl free radical, reaction conditions and pH (Pignatello, 1992; Zhu et al., 1996; Bossmann et al., 1998).

Previous studies have shown that during Fenton's oxidation, color removal of dyes were faster than COD removal (Kang and Chang, 1997). The reason was claimed to be the formation of stable intermediate products, which require longer time for further oxidation. Arslan et al. (2001) reported, on photocatalytic treatment of simulated dye effluents, that decolorization was faster than COD and TOC removal. Their studies indicated that decolorization due to the electrophilic attack of the chromophoric groups by $\cdot\text{OH}$ might be a primary step and COD and TOC removal indicating the ultimate oxidation of the wastewater. During solar photocatalytic degradation of two dyes, color removal after 3 h exposure was 100 % and 88 % and the corresponding TOC removal was 81 % and 42 % respectively. TOC removal increased on increase in exposure time (Wang, 2000).

Deng et al. (2000) reported that the decolorization of reactive dyes by photo-Fenton system was dependent on the molecular structure of the dyes. The susceptibility of

azo dyes to decolorization by Fe^{3+} -EDTA- H_2O_2 oxidation is affected by the substituent on the phenolic ring (Namand Tratnyek, 2000). Their study revealed that the dyes substituted with halogen atoms were oxidized to a greater extent than the corresponding methyl or methoxy groups.

The reaction rate constants determined for the degradation of dyes by oxidation processes range between 0.1 - 0.4 min^{-1} . There are examples in the literature for the degradation of several dyes such as 0.0875 min^{-1} for a reactive azo dye CI. Reactive Yellow 84 treated with dark Fenton, 0.2060 min^{-1} for Acid Orange 8, 0.4182 for Acid Blue 74, 0.1098 for Methyl Orange (Neamt u et al., 2003, Aleboyeh et al., 2003).

The reported values for observed first and initial reaction rates for several organics with Fenton systems include $1.54 \times 10^3 \text{ s}^{-1}$ for nitrobenzene (Fe^{2+} : H_2O_2 = 7 mM: 3 mM $T = 25^\circ\text{C}$ $t = 60 \text{ min}$), 26 L/mg min for cork cooking wastewater (Fe^{2+} : H_2O_2 = 1 mM: 5 mM $T = 30^\circ\text{C}$ $t = 30 \text{ min}$ $T = 30^\circ\text{C}$) (Rodriguez et al., 2003, Guedes et al., 2003).

In this study it was aimed to determine the reaction rate constants for the two dyebaths treated with Fenton's reagent at optimum experimental conditions (initial Fe^{2+} and H_2O_2 concentrations and pH of the medium) in terms of COD, H_2O_2 and color removal.

The pseudo-first order reaction rates (k_{COD} and $k_{\text{H}_2\text{O}_2}$, in min^{-1}) for COD removal and H_2O_2 consumption were determined.

4.2.2.1 Dyebath I

The results obtained for Dyebath I under optimum conditions ($\text{Fe}^{2+} = 10 \text{ mM}$ $\text{H}_2\text{O}_2 = 30 \text{ mM}$ $\text{pH} = 3$; $t = 30 \text{ min}$) at different temperatures ($T = 20, 30, 40, 45, 50, 55, 60^\circ\text{C}$) are summarized in Table 4.7.

Table 4 7: Summary of reaction rate constants for COD color and H_2O_2 for DBI ($Fe^{2+} = 10 \text{ mM}$, $H_2O_2 = 30 \text{ mM}$, $pH = 3$; $t = 30 \text{ min}$; $COD_0 = 2747 \pm 33 \text{ ng/L}$)

T (°C)	COD removal (%)	Final COD (ng/L)	$k_{COD} (\text{min}^{-1})$	R^2	$k_{H_2O_2} (\text{min}^{-1})$	R^2
20	23	2109	0.0204	0.95	0.152	0.90
30	24	2056	0.0214	0.90	0.148	0.92
40	26	2061	0.0205	0.90	0.198	0.96
45	25	1872	0.0224	0.88	0.272	0.91
50	30	1843	0.0268	0.90	0.344	0.99
55	25	1895	0.0198	0.90	0.338	0.95
60	22	2070	0.0210	0.85	0.231	0.85

Figure 4.22 illustrates the pseudo-first order reaction rate constants obtained for the COD removal at different experimental temperatures under the optimum experimental conditions determined for the initial Fe^{2+} and H_2O_2 concentrations and the pH of the medium.

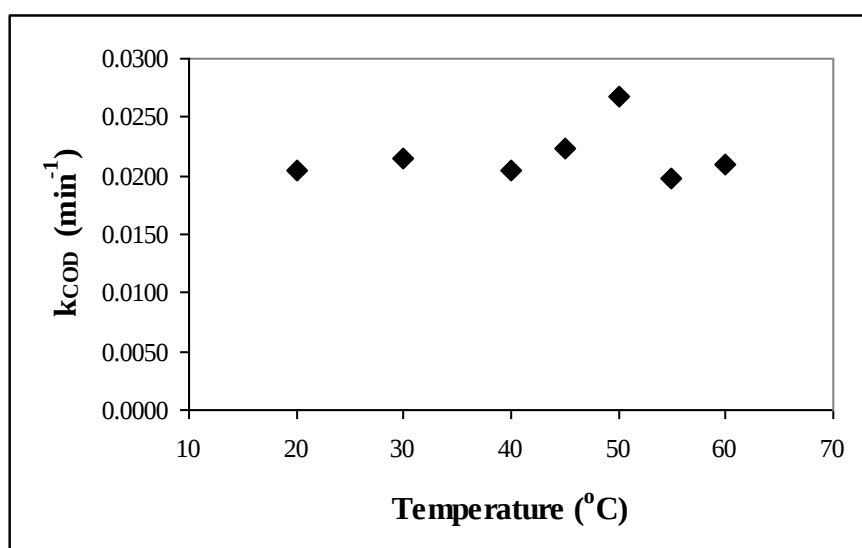


Figure 4.22: Effect of Temperature on pseudo-first order reaction constant for COD abatement (k_{COD}) for DBI ($Fe^{2+} = 10 \text{ mM}$, $H_2O_2 = 30 \text{ mM}$, $pH = 3$; $t = 30 \text{ min}$, $COD_0 = 2747 \pm 33 \text{ ng/L}$)

It may be observed from Figure 4.22 more clearly that the fastest reaction took place at 50°C which is consistent with the data obtained from COD removal for the Dyebath I as the best COD removal was again observed at 50°C after 30 min reaction time.

The pseudo-first order reaction rate constants obtained for the H_2O_2 consumption at varying temperatures under the optimum experimental conditions are presented in Figure 4.23.

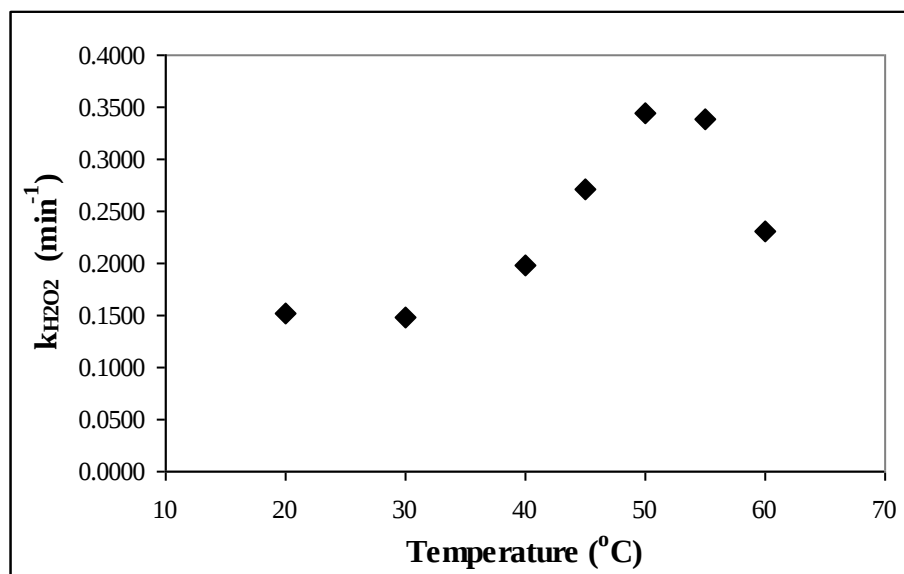


Figure 4.23: Effect of Temperature on pseudo-first order reaction constant for H_2O_2 abatement ($k_{\text{H}_2\text{O}_2}$) for DB I ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$)

It may be observed from Figure 4.23 that the pseudo-first order reaction rates for H_2O_2 consumption followed the same trend with the COD removal efficiencies and the pseudo-first order reaction rate constants obtained at different temperatures, pointing 50°C for the fastest H_2O_2 decomposition.

It was observed that the pseudo-first order rate constant both had the highest values at 50°C and tended to decrease at temperatures above proving that 50°C was the optimum temperature for COD removal for the Dyebath I.

Figure 4.24 illustrates the ratio of the pseudo-first order reaction rates for the COD removal to H_2O_2 consumption against the temperature.

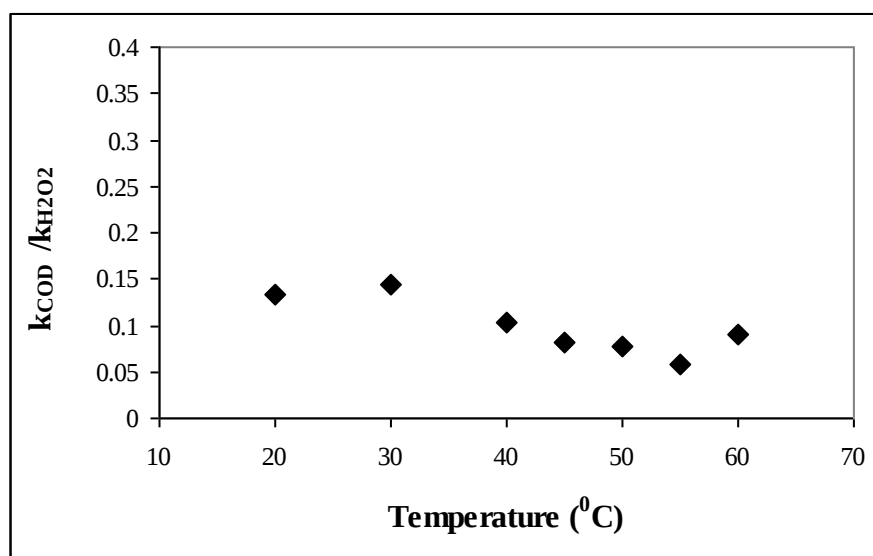


Figure 4.24: Effect of temperature on ratio of pseudo-first order reaction rates of COD removal and H_2O_2 consumption for DB I ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$)

As expected, the ratio of pseudo-first order reaction rate constants for COD and H_2O_2 abatement is almost constant at around $0.1 \text{ min}^{-1} / \text{min}^{-1}$ against the increasing temperature. This indicates that the observed COD removal is directly related to the H_2O_2 decomposition to form the $\text{HO}^\bullet$ radicals, which actually are the responsible oxidizing agents.

4.2.2.2 Dyebath II

The results obtained for Dyebath II at optimum experimental conditions ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$; $t = 30 \text{ min}$) and different temperatures ($T = 20, 30, 40, 50, 60, 70^\circ\text{C}$) are summarized in Table 4.8

Table 4.8 Summary of reaction rate constants for COD, color and H_2O_2 for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$; $t = 30 \text{ min}$; $\text{COD}_0 = 1752 \pm 21 \text{ ng/L}$)

T (°C)	COD removal (%)	Final COD (ng/l)	k_{COD} (1/min)	R^2	$k_{\text{H}_2\text{O}_2}$ (1/min)	R^2
20	26	1288	0.0248	0.99	0.255	0.99
30	25	1328	0.0296	0.99	0.228	0.99
40	25	1319	0.0271	0.99	0.524	0.99
50	29	1210	0.0404	0.99	0.261	0.99
60	31	1197	0.0456	0.90	0.430	0.90
70	28	1274	0.0295	0.93	0.387	0.85

Figure 4.25 illustrates the variations of the pseudo-first order reaction rate constants with the increase in the temperature.

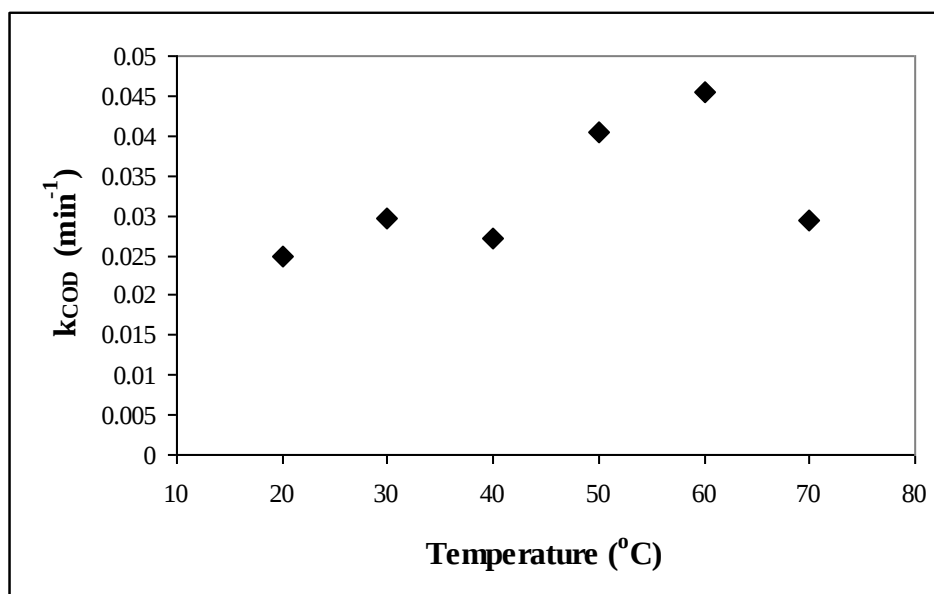


Figure 4.25: Effect of Temperature on pseudo-first order reaction constants (k_{COD}) for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$)

It is seen that the maximum value obtained is at 60°C , which coincides with the best COD removal efficiency obtained for Dyebath II.

The variation of the ratio of pseudo-first order reaction rate constants of COD removal to H_2O_2 consumption against temperature is illustrated in Figure 4.26.

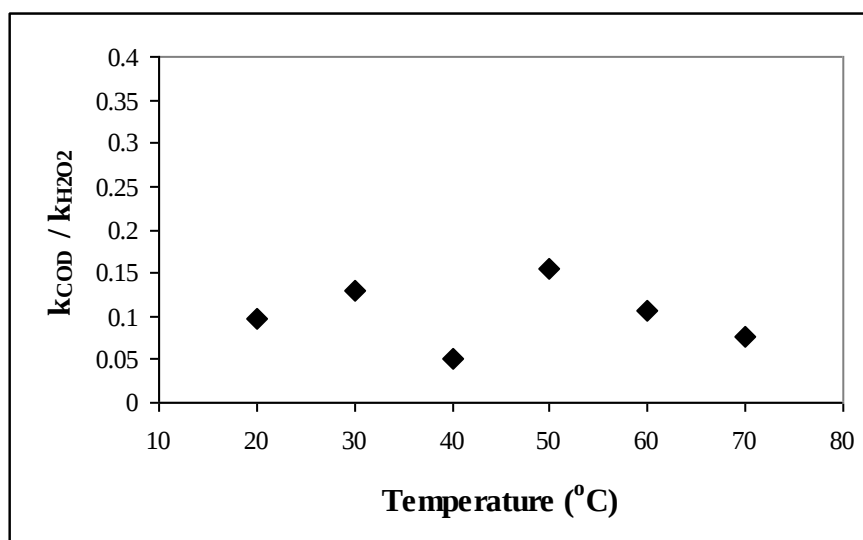


Figure 4.26: Effect of temperature on the ratio of first order COD and H_2O_2 abatement rates for DB II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $t = 30 \text{ min}$, $\text{pH} = 3$)

It may be observed that, as in the case of Dyebath I, the ratio of the pseudo-first order reaction rate constants is almost constant again at around $0.1 \text{ min}^{-1}/\text{min}^{-1}$ with varying temperatures indicating that the removal of COD was achieved parallel to the consumption rate of H_2O_2 .

4.2.3 Determination of Activation Energies (E_a)

The activation energies were calculated from the Arrhenius equation and the results are shown in Figures 4.27 - 4.30, by plotting the observed pseudo-first order COD and H_2O_2 abatement rate constants versus the reciprocal of the absolute temperatures. The magnitude of the activation energy reflected the extent of the temperature dependence of COD and H_2O_2 abatement.

The activation energies for the COD removal and H_2O_2 consumption reactions with Fenton's treatment were derived for DB I and II from the kinetic studies and the pseudo-first order reaction rates as provided in the previous section.

The rate constant k is affected by the temperature and this dependence may be represented by the Arrhenius equation:

$$k = A e^{-E_a/RT} \quad (4.5)$$

where;

k : pseudo-first order reaction constant (min^{-1})

E_a : Activation energy (J/mol)

R : Ideal Gas constant = $8.314 \text{ J/mol} \cdot \text{K}$

T : Absolute temperature in (K)

A : Frequency factor ($1/\text{min}$)

and the Frequency factor A is assumed to be independent of temperature. Taking the natural logarithm of this equation gives:

$$\ln k = \ln A - E_a/(RT) \quad (4.6)$$

or

$$\ln k = -E_a/(RT) + \text{constant} \quad (4.7)$$

or

$$\ln k = -(E_a/R)(1/T) + \text{constant} \quad (4.8)$$

Equation 4.8 indicates that if the plot of $\ln k$ vs. $1/T$ is a straight line, the slope is E_a/R . These equations provide the basis for the experimental determination of E_a .

Examples for the E_a values found in the literature for various degradation reactions involved in the Fenton and Fenton-like systems ranged between 9 and 42 kJ/mol (Lee and Yoon, 2004). Therefore, all these elementary reactions have relatively low temperature dependence over the temperature range 10-50 °C (i.e., of less than a factor of 10). The Fenton reaction (4.1), which becomes the initiation reaction when ferrous salt is used as an iron source, has an activation energy of 36 kJ/mol (Hogg et al., 1954).

Reported values for the activation energies of Fenton reactions with organic species range between 60 - 70 (Rodríguez et al., 2003, Guedes et al., 2003).

The activation energy E_a for H_2O_2 decomposition is $E_a \approx 23$ kJ/mol for the fermentative and $E_a \approx 76$ kJ/mol for the thermal decomposition process.

4.2.3.1 Dyebath I

The activation energy for the degradation of COD for Dyebath I was calculated via the plot of $\ln k_{COD}$ vs $1/T$ which is presented in Figure 4.27.

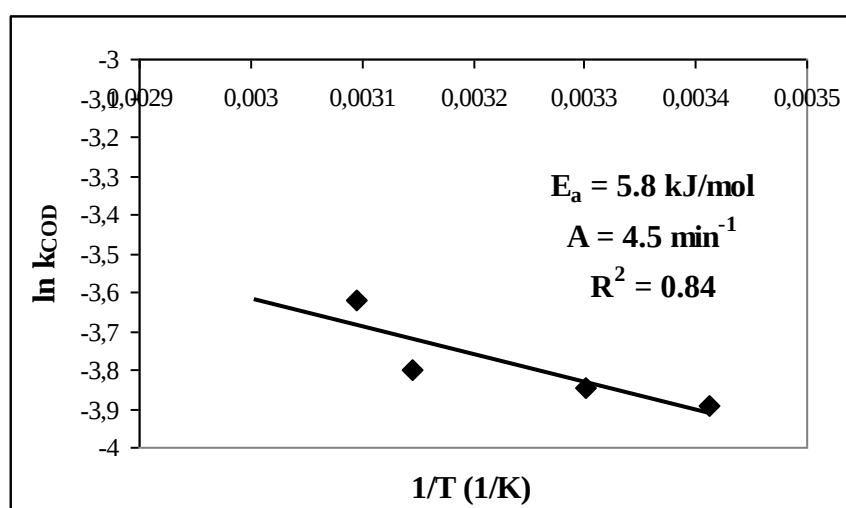


Figure 4.27: Plot of $\ln k_{COD}$ vs $1/T$ for Dyebath I ($Fe^{2+} = 10$ mM, $H_2O_2 = 30$ mM, pH = 3, t = 30 min)

From this plot the slope was read to be 705, which corresponds to E_a/R and accordingly the activation energy of the COD removal reaction for Dyebath I was calculated as $E_a = 5.8 \text{ kJ/mol}$.

The activation energies for the H_2O_2 abatement reactions were also calculated likewise from the $\ln k_{\text{H}_2\text{O}_2}$ vs $1/T$ plot (Figure 4.28).

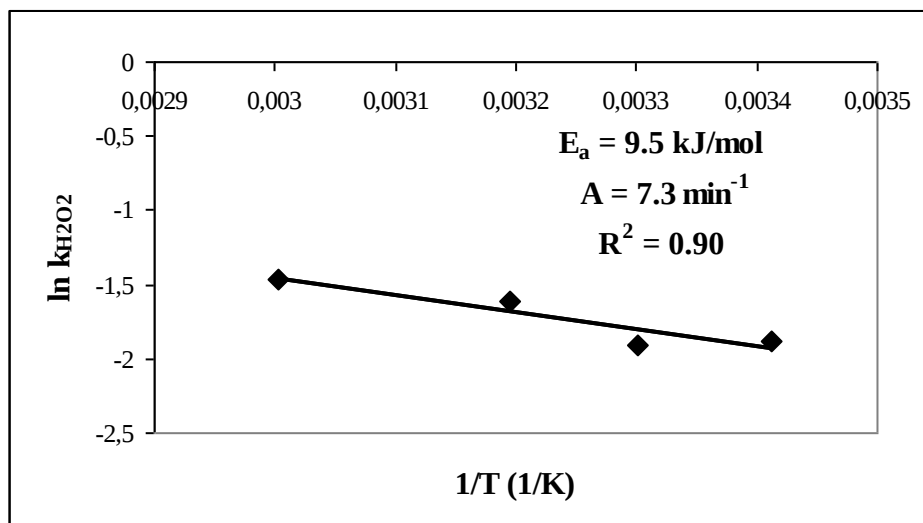


Figure 4.28: Plot of $\ln k_{\text{H}_2\text{O}_2}$ vs $1/T$ for Dyebath I ($\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$)

The activation energy of the H_2O_2 degradation reaction was found as 9.5 kJ/mol . It may be concluded that the H_2O_2 abatement in case of Fenton pre-treatment of DBI was chemical oxidative decomposition. Hence, the possibility of thermal H_2O_2 decomposition can be ruled out.

4.2.3.2 Dyebath II

Similarly, the activation energy for the degradation of COD was calculated. The plot of $\ln k_{\text{COD}}$ vs $1/T$ drawn for Dyebath II is presented in Figure 4.29.

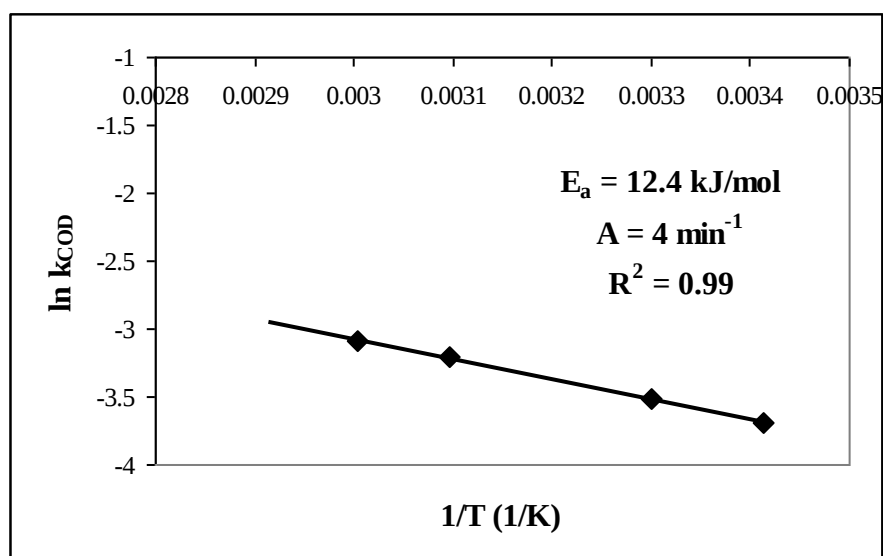


Figure 4.29: Plot of $\ln k_{\text{COD}}$ vs $1/T$ for Dyebath II ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$)

From this plot the slope was read to be 653 and accordingly the activation energy of the COD removal reaction for Dyebath II was calculated as $E_a = 12.4 \text{ kJ/mol}$.

The activation energies for the H_2O_2 consumption reactions were calculated from the $\ln k_{\text{H}_2\text{O}_2}$ vs $1/T$ plot presented in Figure 4.30.

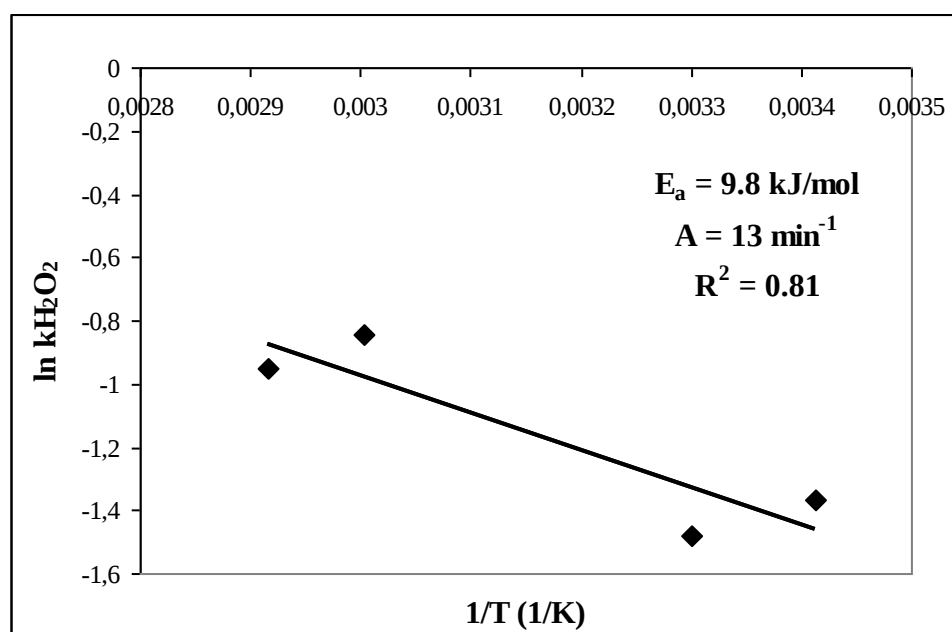


Figure 4.30: Plot of $\ln k_{\text{H}_2\text{O}_2}$ vs $1/T$ for Dyebath I ($\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$, $\text{pH} = 3$, $t = 30 \text{ min}$)

The activation energy of the H_2O_2 degradation reaction was found as 9.8 kJ/mol .

4.3 Determination of Effects on Biodegradability

The effects of Fenton's pre-treatment of simulated acid dyebath effluents on subsequent biological wastewater treatment systems were assessed via Activated Sludge Inhibition Test (ISO 8192) and soluble inert COD determination.

Before presenting the results of the bio-treatability studies, it is important to demonstrate the COD contribution of the studied acid dyebaths (the dyeing process) to the overall COD load of the plant before and after Fenton pre-treatment. It was assumed that the average, raw textile wastewater flow rate from common textile factory is 2000 m³/day and the contribution of the dyeing process to this flow is 500 m³/day at its max. (Table 4.9).

Table 4.9: Textile Operations Process Profiles

Process	Flow (m ³ /day)
Preparation (scouring/bleaching)	550
Dyeing	500
Rinsing	750
Finishing	200
Total	2000

The COD contributions of the dyebaths to the total effluent were calculated considering the above mentioned volumetric fractions as presented in Table 4.10.

Table 4.10: COD contributions of the dyebaths before and after treatment

COD Contribution (mg/l)	Before Treatment		After Treatment	
	DB I	DB II	DB I	DB II
	687	438	443	300

It was observed that the organic load from DB I and DB II before Fenton pre-treatment were 687 mg/L and 438 mg/L as COD, respectively. After the Fenton pre-treatment these have fallen to values of 438 mg/L and 300 mg/L as COD respectively.

4.3.1. Activated Sludge Inhibition Tests

The activated sludge inhibition test was carried out to assess the acute toxicity effects of the raw and Fenton pre-treated dyebaths to activated sludge microorganisms, acclimated to S.W.W. which were not previously exposed to dyebath formulations. by measuring the oxygen uptake rates in samples containing the unacclimated sludge subjected to synthetic wastewater only as described in the previous section. It was

decided to keep the F/M ratio constant at around 0.19 - 0.20 mg COD/ mg MLVSS. d⁻¹ for the experiments carried out with the raw and pre-treated Dyebaths I and II. Different dyebath COD dilutions (fractions of COD from dyebath) were tested which summed up to the same total COD value together with the COD coming from the synthetic wastewater solution. The COD contributions from the synthetic wastewater solution were kept above 250 mg/ L in order to prevent interferences arising from the substrate limitation. The percent inhibition values were calculated as described in the previous section and plotted against the $\ln$ COD values of the dilutions tested. The corresponding EC_{50} (in mg/ L COD) values were determined by interpolation.

4.3.1.1 Dyebath I

The EC_{50} values were found for the raw and the Fenton pre-treated dyebath for 30 min. at the previously optimized Fenton conditions as determined before ($[Fe^{2+}]_0 = 10$ mM, $[H_2O_2]_0 = 30$ mM, pH = 3; T = 50 °C). The F/M value was 0.19 mg COD/ mg MLVSS. d⁻¹ for the experiments carried out with Dyebath I.

For the raw dyebath samples, the total COD value was kept at 700 mg/ L. Figure 4.31 provides the plot obtained for raw Dyebath I.

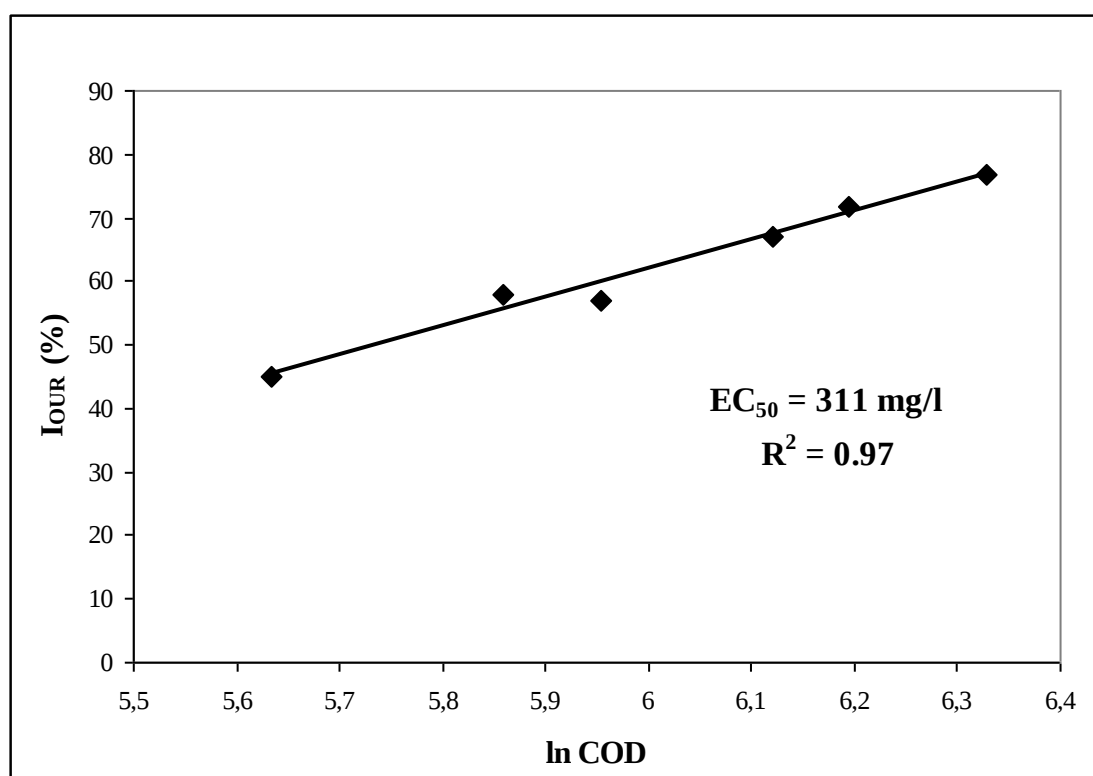


Figure 4.31: The Inhibition (%) vs. $\ln$ COD plot for Dyebath I ($F/M = 0.19$ mg COD/ mg MLVSS. d⁻¹)

The $EC_{50(t=30 \text{ min})}$ was found as 311 mg/L COD. The COD contribution of the DBI in the overall wastewater of the textile plant without the Fenton pre-treatment was estimated as 687 mg/L COD, which indicates that it will exhibit significant toxicity on the activated sludge microorganisms.

The same test procedure was applied for the treated ($Fe^{2+} = 10 \text{ mM}$, $H_2O_2 = 30 \text{ mM}$, $pH = 3$; $T = 50^\circ C$; $t = 30 \text{ min}$) samples of Dyebath I ($F/M = 0.19 \text{ mg COD/mg MLVSS.d}^{-1}$) no relative inhibition was observed in measured oxygen uptake rates as compared with synthetic wastewater after one hour test duration.

It may be concluded that the inhibition of the Dyebath I on activated sludge microorganisms was totally removed after the Fenton treatment.

4.3.1.2 Dyebath II

The EC_{50} values were also determined for the raw and Fenton pre-treated Dyebath II samples. However, with an exceptional condition where acetic acid was eliminated from the dyebath composition since in the first try it was not possible to observe any inhibition effects within 3 hours (max. defined by the test procedure) due to the readily biodegradable nature of the acetic acid. Since the COD value of the dyebath was reduced significantly after the elimination of acetic acid, it was decided to provide a fixed COD concentration from the synthetic wastewater solution while changing the volumetric percentage of the dyebath in the test sample. The F/M value was $0.19 \text{ mg COD/mg MLVSS.d}^{-1}$ for the experiments carried out with Dyebath II. The OURs calculated for the samples containing the raw dyebath were above the OURs obtained for the blanks during 1-hour test duration even for the highest possible volumetric ratio of the dyebath in the overall wastewater, which was selected as 20% (by volume). Similarly, the results obtained from the Fenton pre-treated samples run at the same F/M shown no inhibition on the measured OURs during 1-hr test duration. It was concluded that Dyebath II has no inhibitory effects on the activated sludge microorganisms.

4.3.2 Determination of Soluble Inert COD

The soluble inert fractions of the raw and Fenton pre-treated dye baths were determined according to the procedure proposed by Gerçirli et al., 1993. The soluble

inert fractions were calculated from the measured initial and final soluble COD data points of the raw and pre-treated DB I and DB II reactors.

4.3.2.1. Dye Bath I

The reduction in COD values in the bio-reactors initially fed with raw and treated Dye Bath I were followed until they reach down to a certain residual COD

The raw wastewater reactor was initially fed with the diluted Dye Bath I sample having 2045 mg/L COD (dilution = 25 %) which decreased to 95 mg/L after 45 days, whereas the glucose reactor initially at 1475 mg/L COD decreased to 65 mg/L COD. It may be observed that the COD reduction in the raw Dye Bath I was much more rapid than Fenton pre-treated Dye Bath I, reaching to the same COD value as the reactor containing only glucose after 20 days. However, they both revealed a COD removal efficiency of 95 % after 41 days.

The COD abatement with respect to time for the raw and Fenton pre-treated Dye Bath I (Table 4.11) is shown in Figure 4.32.

Table 4.11: Results of soluble inert COD test for DB I

Time (d)	COD (mg/L)			
	DB I Raw	DB I Raw Glucose	DB I Treated	DB I Treated Glucose
0	2045	1475	1337	1680
6	1124	689	1065	765
11	786	416	895	527
19	252	315	787	157
21	231	203	657	96
23	194	186	603	82
28	137	145	376	51
32	113	103	177	39
34	95	74	151	35
38	91	65	133	30
41	97	67	135	34
45	95	65	135	34

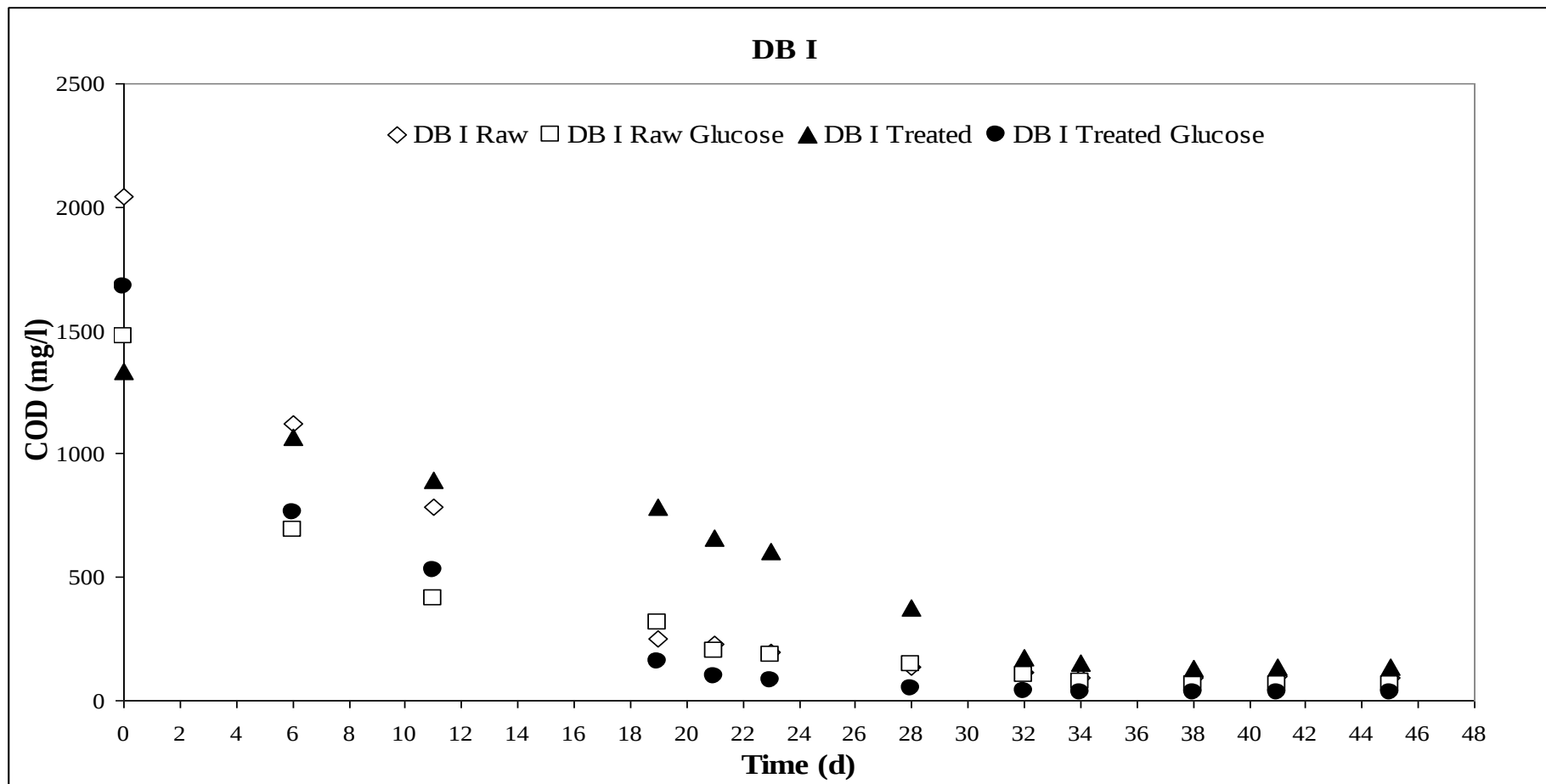


Figure 4.32: Inert COD profiles of raw and Fenton pre-treated Dye Bath I

The results of the COD fractionation tests for the raw and Fenton pre-treated Dye Bath I are outlined in Table 4 12

Table 4 12: Results of inert COD determination tests for raw and pre-treated DB I

DB I	S_{G0} (ng/ L)	S_{PG} (ng/ L)	S_{T0} (ng/ L)	S_T (ng/ L)	Y_{SP}	S_{S0} (ng/ L)	S_I (ng/ L)
Raw	1475	65	2045	95	0.0441	2040	5
Pre-treated	1680	34	1337	135	0.0202	1227	110

The results obtained from the inert COD determination test were corrected according to the actual COD values of the raw and pre-treated dye baths (Table 4 13).

Table 4 13: COD fractions of raw and pretreated DB I

DB I	COD (ng/ L)	S_P (ng/ L)	S_{S0} (ng/ L)	S_I (ng/ L)	S_I (%)
Raw	2750	121	2743	7	0.25
Pre-treated	1925	29	1406	115	6

The results indicated that Fenton pre-treated Dye Bath I had a significantly greater inert COD content of 115 mg/ L COD than the raw Dye Bath I, which only had an inert COD of 7 mg/ L. The reason for this may be attributed to the fact that in some cases the generation of more recalcitrant compounds than the initial compound subjected to oxidation is possible.

4.3.2.2 Dye Bath II

The reduction in COD values in the bi o-reactors fed with raw and treated Dye Bath II was followed for the same time interval of 45 days until the plateau was reached for the residual COD.

The raw dye bath reactor was initially fed with 1636 mg/ L COD which decreased to 75 mg/ L, whereas the glucose reactor initially at 1530 mg/ L COD decreased to 65 mg/ L COD. The COD removal efficiencies were 95 % and 96 % for the raw and Fenton pre-treated Dye Bath II, respectively. The results of the soluble inert COD test is depicted in Table 4. 14

Table 4 14: Results of soluble inert COD test for DB II

Time (d)	COD (mg/ l)			
	DB II Raw	DB II Raw Glucose	DB II Treated	DB II Treated Glucose
0	1636	1530	1117	1320
6	1123	821	635	611
11	865	603	431	298
19	566	283	126	31
21	423	194	85	32
23	386	165	78	28
28	256	124	53	25
32	133	99	39	22
34	114	85	34	23
38	87	71	35	26
41	76	68	37	30
45	75	65	35	30

COD removal in the test reactors is shown in Figure 4 37.

It may be observed that the COD reduction in the raw Dye Bath II took place at a significantly faster rate than the Fermenter pre-treated Dye Bath II.

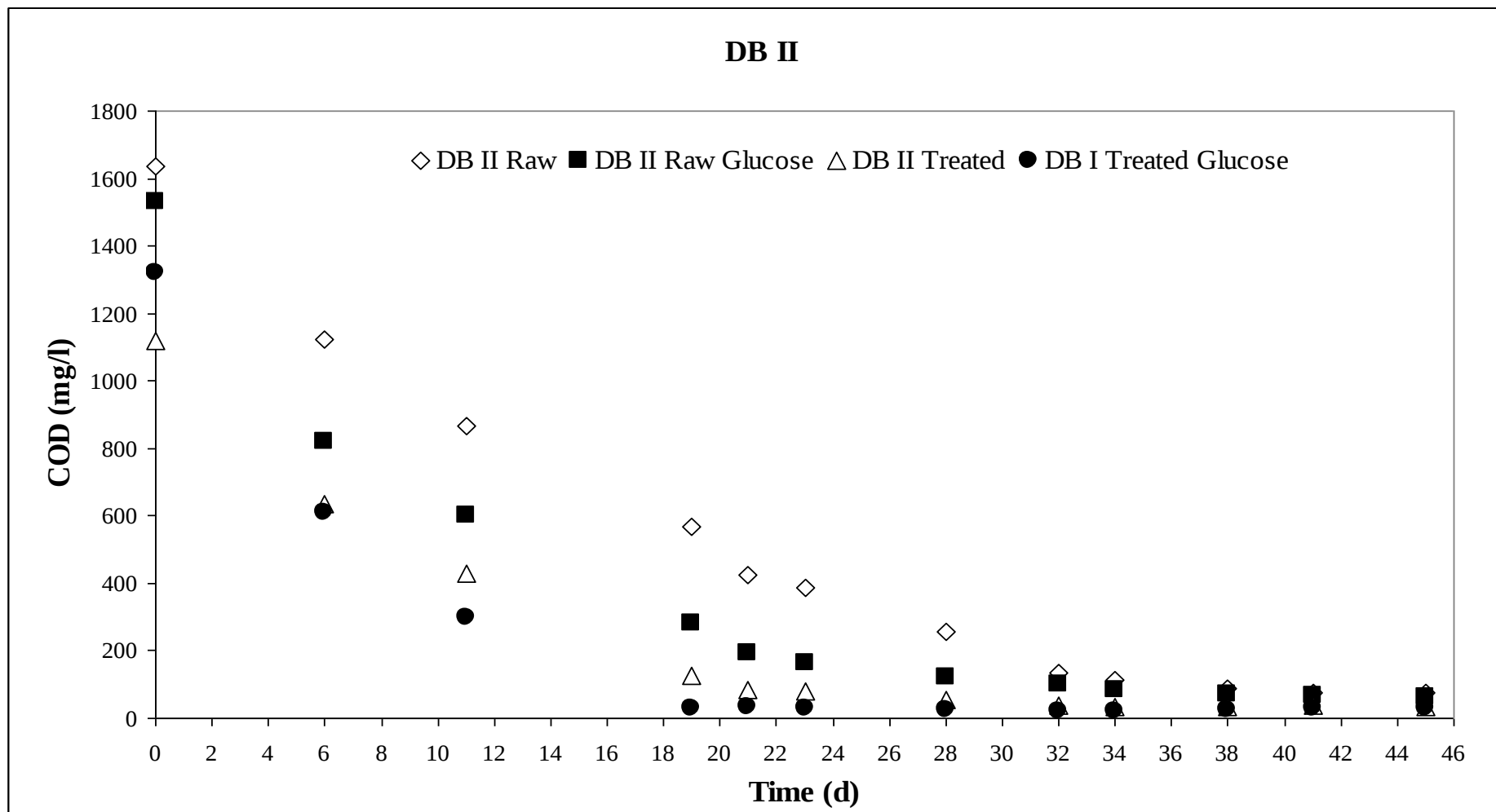


Figure 4.33: Inert COD Profiles of raw and Fenton pre-treated Dye Bath II

The results of the COD fractionation tests for the raw and Fenton pre-treated Dye Bath I are outlined in Table 4 15.

Table 4 15: Results of inert COD determination tests for raw and pre-treated DB II

DB II	S _{G0} (ng/ L)	S _{PG} (ng/ L)	S _{T0} (ng/ L)	S _T (ng/ L)	Y _{SP}	S _{S0} (ng/ L)	S _I (ng/ L)
Raw	1530	65	1636	75	0.0425	1630	6
Pre-treated	1320	30	1117	35	0.0227	1107	10

The results obtained from the inert COD determination test were again corrected according to the actual COD values of the raw and pre-treated dye baths (Table 4.16).

Table 4 16: COD fractions of raw and pretreated DB II

DB II	COD (ng/ L)	S _P (ng/ L)	S _{S0} (ng/ L)	S _I (ng/ L)	S _I (%)
Raw	1730	73	1723	6	0.35
Pre-treated	1211	27	1200	11	1

The results indicated that, Fenton pre-treated Dye Bath II had an inert COD fraction of 11 mg/ L COD, which was slightly higher than the inert COD fraction of the raw Dye Bath I, which was 6 mg/ L COD.

5. CONCLUSIONS

In this study, the effects of Fenton's pre-treatment on two different acid dye bath formulations, DB I and DB II were investigated in terms of the observed COD and color removal efficiencies. The following conclusions may be drawn from the study:

1. Optimum experimental conditions for the simulated exhausted acid dye baths; DB I and DB II were; $\text{Fe}^{2+} = 10 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$ and $\text{pH} = 3$ and $\text{Fe}^{2+} = 2 \text{ mM}$, $\text{H}_2\text{O}_2 = 30 \text{ mM}$ and $\text{pH} = 3$; which yielded overall COD removal efficiencies of 23 % and 26 % respectively. The corresponding color removal efficiencies were 92 % and 90 %
2. The observed effects of increasing temperature showed that the COD removal improved from 23 to 30 % from 20°C to 50°C for DB I, and from 26 to 31 % from 20°C to 60°C for DB II. It was observed for both dye baths that above a certain temperature, the COD removal did not show any further improvement confirming an optimum for temperature for the Fenton pre-treatment.
3. The pseudo-first order reaction rate constants for COD removal for DB I increased by 35 % from 0.020 min^{-1} to 0.027 min^{-1} by increasing temperature from 20°C to 50°C ; and the pseudo-first order reaction rate constants for COD removal for DB II increased by 84 % from 0.025 min^{-1} to 0.046 min^{-1} by increasing temperature from 20°C to 60°C
4. For both dye baths, COD content decreased more markedly in the first minutes of reaction, with a subsequent smaller reaction rate.
5. The pseudo-first order reaction rate constants for H_2O_2 consumption for DB I increased from 0.15 min^{-1} to 0.34 min^{-1} by increasing temperature from 20°C to 50°C and for DB II from 0.26 min^{-1} to 0.43 min^{-1} by increasing temperature from 20°C to 60°C

6. The relationship between COD removal and H_2O_2 consumption was found to be directly proportional with values of $k_{COD}/k_{H_2O_2}$ with respect to temperature nearly constant at around $0.1 \text{ min}^{-1}/\text{min}^{-1}$.
7. The E_a values obtained from the COD removal kinetics for DB I and DB II were 5.8 kJ/mol and 12.4 kJ/mol , respectively.
8. The E_a values obtained from the H_2O_2 abatement kinetics for DB I and DB II were 9.5 kJ/mol and 9.8 kJ/mol , respectively. There was no thermal decomposition.
9. The EC_{50} value obtained for the raw DB I from activated sludge inhibition test was 311 mg/L as COD, whereas the pre-treated samples of DB I exerted no inhibition, which indicated that acute inhibitory effect of DB I was totally removed with Fenton's pre-treatment.
10. The raw and pre-treated DB II (dye ingredients only) exhibited no inhibition.
11. The COD contributions of the raw and Fenton pre-treated dye baths to the overall textile wastewater effluent were calculated as 687 mg/L and 438 mg/L for DB I, and 443 mg/L and 300 mg/L for DB II.
12. It was observed that raw DB I was more rapidly biodegraded compared to the pre-treated DB I. The soluble inert COD fractions of the raw and Fenton pre-treated DB I were 7 mg/L and 115 mg/L , respectively, indicating that Fenton pre-treatment generated more recalcitrant compounds than the original spent DB I formulation.
13. It was again observed that raw DB II was more rapidly biodegraded compared to the pre-treated DB II. The soluble inert COD results for the raw and Fenton pre-treated DB II were 6 mg/L and 11 mg/L , respectively, indicating that the raw as well as the pre-treated dye bath effluents were almost entirely biodegradable in nature.

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