

**REUSE OF TEXTILE DYE BATHS BY TREATMENT WITH
ADVANCED OXIDATION**

by

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B.S. in Env. E., Yıldız Technical University, 1995

Submitted to the Institute of Environmental Sciences in partial fulfillment

of the requirements for the degree of

Master of Sciences

in

Environmental Technology

Boğaziçi University

1998

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ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my thesis supervisor Prof. Dr. Nilsun İnce for her encouraging attitude, valuable guidance, support and patience throughout this study.

Financial support for this research is supported by B.U. Research Fund, project number 97HY103 and is greatly acknowledged.

I wish to thank to PISA Boya Fabrikası A.Ş., especially Mehmet Ali İnce and Berrin Kadıhasanoğlu for their help and tolerance during the study.

I am indebted to my friends İzzet Apikyan and Ebru Z. Aktürk for their encouragement and friendly support.

I am also thankful to jury members, Prof. Dr. Ömer Saygın and Assist. Prof. Dr. Neylan Dirilgen for their constructive criticisms and suggestions.

Finally, I owe special thanks to my dear family and fiancée Öncü Güyer for their extreme patience, support and love.

ABSTRACT

The urgent need to conserve, recycle, and reuse the limited water resources of the earth has forced mankind to research and develop new methods and technologies for treating and managing used waters from process, cooling and/or rinse facilities of industrial applications. This is especially important in textile dyeing and finishing industries, where huge amounts of water are consumed in dyeing and washing/rinsing of the fabrics.

The purpose of this study was to investigate the reusability of dyebath effluents in a textile batch dyeing process, by a homogeneous advanced oxidation system, involving H_2O_2 and ferrous sulfate in the presence and absence of UV-light.

Synthetic dye bath effluents were prepared using a reactive azo-dye, Procion Red HE-7B, which was selected as a model compound for its wide use in the industry. Effectiveness of the system was tested by monitoring the degree of color and total organic carbon degradation. Parameters such as chemical oxygen demand and total dissolved solids were also monitored. Reusability of the treated water was tested in a dyehouse with various azo dyes.

Under the experimental conditions employed, it was found that complete color removal and 71% total organic carbon degradation is possible in 20 min of UV irradiation. The treated effluent was found to be reusable in cotton batch dyeing, yielding satisfactory dye quality on the fabric.

Estimated cost of reusing dyebath effluents after treatment with the proposed technique was found to be 1.54 per m^3 . The corresponding cost of using commercial water supply was estimated to be 2.42 per m^3 .

ÖZET

Dünyanın sınırlı su kaynaklarının korunması, yeniden kullanılması ve geri çevrimdeki acil ihtiyacı, insanoğlunu endüstriyel proseslerin atık sularının arıtılması ve yönetimi için yeni metotlar araştırmaya ve keşfetmeye zorlamıştır. Bu özellikle boyama, yıkama ve durulama proseslerinde büyük miktarda su kullanan tekstil boyama endüstrileri için önemlidir.

Bu çalışmanın amacı tekstil boya kazanı atıksularının UV ışığının varlığında ve yokluğunda, H₂O₂ ve demir sülfat içeren homojen ileri oksidasyon sistemi ile tekstil doldur-boşalt boyama prosesinde geri kazanabilirliğinin araştırılmasıdır.

Sentetik boya kazanı çıkış suları, endüstrideki yaygın kullanımından dolayı reaktif azo boyası, Procion Kırmızı HE-7B kullanılarak hazırlanmıştır. Sistemin verimliliği renk ve toplam organik madde giderimi izlenerek tespit edilmiştir. Ayrıca kimyasal oksijen ihtiyacı ve toplam çözünmüş madde miktarı da tespit edilmiştir. Arıtılmış suyun geri kullanılabilirliği boya kazanında değişik azo boyalar kullanılarak test edilmiştir.

Belirlenen deneysel koşullar ve 20 dakika UV ışığı altında tam renk giderimi ve %71 toplam organik karbon giderimi bulunmuştur. Arıtılmış çıkış suyunun kumaş üzerinde istenilen boya kalitesini sağladığı belirlendiğinden doldur-boşalt pamuklu boyamada geri kullanılabilirliğine karar verilmiştir.

Geri kullanılan boyama kazanı çıkış suyunun önerilen teknik ile arıtılmasının tahmini maliyeti 1.54 USD/m³ bulunmuştur. Buna karşılık ticari su kullanımı tahmini maliyeti 2.42 USD/m³ olarak hesaplanmıştır.

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1. INTRODUCTION

The growing understanding of the urgent need to conserve, recycle, and reuse the limited water resources has forced mankind to research and develop new methods and technologies for treating and managing used waters from process, cooling and/or rinse facilities of industrial applications. This is especially important in textile finishing and dyeing industries, where huge amounts of water are consumed in dyeing and washing/rinsing of the fabrics. Water reuse is very important for those industries suffering from increasing water supply costs and constraints in environmental standards. Holme [1] pointed out that cotton accounted for 44.9 per cent of the world's fiber production in 1995 and that the demand for reactive dyes will grow stronger. This trend, it was said, will require more effective systems for treating and recycling effluents.

The total volume of wastewater originating from textile dyeing and finishing processes in Turkey is around 150 million metric tons/year, 2/3 which is wasted in dye and rinse baths. In the conventional batch dyeing process, which is widely used in the region, water is pumped into a dyeing machine, where the fabric is placed and allowed to be saturated. The bath is heated to dyeing temperature (above 60 °C) after the addition of auxiliaries (e. g. wetting, pH control, leveling and chelating agents) and maintained there until dyeing is completed. The fabrics are then washed in the same tank to free their surfaces from residual dye-bath constituents. When the dye-bath is emptied, the machine is refilled with fresh water to begin the process for the next load. After each dye-bath discharge (dyeing solution and wash water), large quantities of energy, water and useful chemicals are lost [2]. Furthermore, effluents of dyeing mills are known to contain considerable color, dissolved solids, temperature, pH, salinity, total organic carbon (TOC), toxicity and high chemical oxidation demand(COD), in addition to carcinogenic products such as aromatic amines, owing to large consumption of azo-dyes in the dyeing process [3,4]. Conventional treatment methods (biological, physical and chemical processes, or combinations thereof) are not effective for complete color removal and total destruction of refractory chemicals in the effluent to enable to reuse of the effluents in the dye/rinse processes [4]. Although

dilution can reduce the intensity of the colored effluents, it is no longer considered an alternative for handling textile effluents. Furthermore, most of these methods require high investment and/or running costs, while producing large amounts of hazardous sludge which must be disposed of [5]. The most current research for such technologies is focused on integrated systems, combining dissolved air floatation, advanced oxidation processes (AOPs) and membrane systems, where the function of the AOP is complete destruction of dyestuffs and other organic matter [6].

Dyestuffs are highly structured polymers with low biodegradability. Their concentration in dye-baths range from 10 to 10000 mg/l, depending on the dyeing process in operation [7]. There are about 3000 different dyes available in the commercial market, and more than half of them are azo compounds, which are a class of organic dyes characterized by the presence of at least one azo linkage (-N=N-), and one or more alkyl sulfonate reactive groups.

While chemical oxidation reactions are very common in industrial processes, the use of conventional oxidants for the treatment of water contaminated with organic compounds is not always feasible because of kinetic limitations, which are now handled by AOPs in which the overall rate of oxidation of a contaminant is greatly increased over that obtained by the simple additions of oxidizing agents [8]. The use of AOP, involving oxidizing agents such as (H_2O_2), ozone (O_3), and/or catalysts such as iron or titanium dioxide, with or without a source of UV light has been proposed in recent years as potential alternatives for color, substantial COD and TOC removal from textile effluents.

The purpose of this study was to investigate the reusability of dyebath effluents after treatment by an advanced oxidation process involving H_2O_2 and ferrous sulfate, in the presence and absence of UV-light. Dyebaths were simulated by using a reactive azo dye, Procion Red HE-7B, and typical cotton dye-bath constituents. The effectiveness of the AOP was determined by monitoring the residual dye, and TOC concentrations, in addition to total dissolved solids (TDS). The effect of process parameters such as temperature, pH, chemical concentrations, and alkalinity were investigated to optimize the operating conditions for maximum color and TOC removal. Rates of color degradation and

mineralization were estimated by first order kinetic assumption. The optimized parameters were applied in real textile dyebath effluents to investigate the efficiency of the proposed technique. The treated effluents were finally reused in a textile dyeing/finishing plant in a batch dyeing process.

2. THEORITICAL BACKGROUND

2.1. The Textile Industry

Textile manufacturing begins with the harvest of raw fiber. Fiber used in textile can be harvested from natural sources (e. g. wool, cotton) or manufactured from regenerative cellulosic materials (e.g., rayon, acetate), or it can be entirely synthetic (e.g., polyester, nylon). After the raw natural or manufactured fibers are shipped from the farm or the chemical plant, they pass through four main stages of processing [9]:

-Yarn Production, where the natural fibers, predominantly cotton and wool, are cleaned, carded, and/or combed, and then spun into yarn.

-Fabric Production, the second step, involves either weaving or knitting.

-Finishing, represents the third step. Most broadwoven fabrics retain the natural color of the fibers from which they are made.

-Fabrication, final step, the finished cloth is fabricated into a variety of apparel and household and industrial products [9].

Textile manufacturing is one of the largest industrial producers of wastewater. On average, approximately 160 pounds of water (20 gallons) are required to produce 1 pound of textile product [9]. Textile is a chemically intensive industry, and therefore, the wastewater from textile processing contains processing bath residues from preparation, dyeing, finishing, slashing, and other operations. These residues can cause damage if not properly treated before discharge to the environment.

Dye-bath water and wash basins are hard-to-treat wastes. They are persistent and resist treatment, or interfere with the operation of waste treatment facilities. These wastewaters often contain nonbiodegradable or inorganic materials, and biologic processes

can not remove or break down these wastes. Dye-bath wastewaters are also high volume wastes and reuse of these processes' effluents must assume the primary role in terms of life cycle [9].

Figure 2.1.1. shows the typical diagram of textile dyeing.

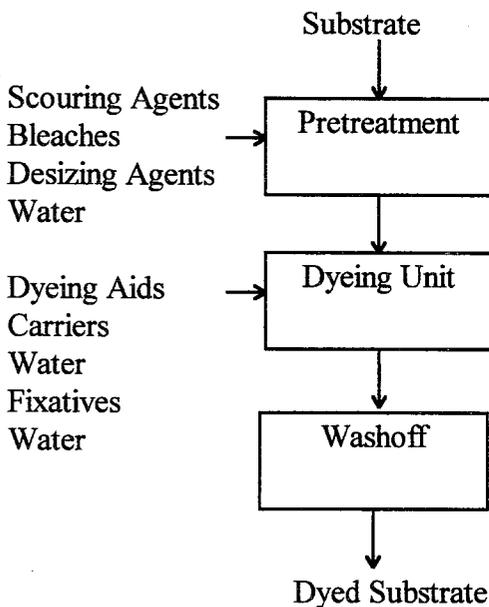


Figure 2.1.1. Flow Diagram of Bath Process.[10]

Residual size must always be removed from woven goods because of the risk of dye wastage by reaction with hydroxy groups in size components. Owing to the brilliant hues of reactive dye, sufficient brightness may be attainable without prebleaching. Precipitation with hardness causing constituents may occur at the alkali fixation stage and thus soft water should be used for all dissolving and dye bath operations. Sources of water with variable bicarbonate content can adversely affect reproducibility of fixation conditions.

2.2. Overview of Dye-Baths

2.2.1. Sources of Color in Textile Wastewater

Dyes and pigments from printing and dyeing operations are the principal sources of color in textile effluents. 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 per cent of the color is fixed on the fiber as can be in Table 2.2.1.1., and the remainder is discarded in the form of spent dyebaths or in wastewater from subsequent textile-washing operations [9].

Table 2.2.1.1.. Typical Exhaustion/Fixation Rates for Dyes of Various Classes [9]

Dye Classes	Typical Fixation (%)	Fibers Typically Applied to
Acid	80 to 93	wool, nylon
Azoic	90 to 95	Cellulose
Basic	97 to 98	Arcylic
Direct	70 to 95	Cellulose
Disperse	80 to 92	Synthetic
Reactive	50 to 80	Cellulose
Sulfur	60 to 70	Cellulose
Vat	80 to 95	Cellulose

Reactive dyes are widely used and fall in the lower range of the fixation scale. As such, they require special attention to maximize fixation and therefore minimize waste color discharge. Important factors for exhaustion are bath ratio, optimized salt use, and adequate time.

2.2.2. Sources of Salt in Textile Wastewater

Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile wet processes as shown in Table 2.2.2.1.

Salts such as common salt (sodium chloride) and Glaubert salt (sodium sulfate), are used to assist the exhaustion of ionic dyes, particularly anionic dyes direct and fiber reactive dyes on cotton. Salt addition enhances dyebath exhaustion by increasing dye affinity for cellulose fibers. It is added to the dye solution to displace the dye to the fibre.

Table 2.2.2.1. Types of Salt Used in Textile Operations [9]

Salt Type	Typical Use
Calcium chloride	Formed
Common salt	Dyeing
Epsom salt	Fixing
Glaubert salt	Dyeing
Magnesium chloride	Catalyst
Potassium chloride	Formed

Each dye class requires characteristic amounts of salt. Salt requirements for batch dyeing of cotton for different dye classes are shown in Figure 2.2.2.1.

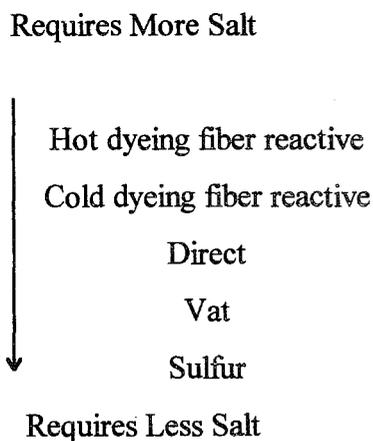


Figure 2.2.2.1. Salt Requirements for Various Dye Classes-Batch Dyeing of Cotton

Fiber reactive dyeing of cotton can not achieve the high fixation levels of other fibers such as wool and synthetics which are in the range of 90 per cent or higher. Large quantities, up to 100 grams per liter, of salt are required for fiber reactives to maximize dye fixation. As a result of low fixation, large amounts of color is discharged to the wastewater [9].

2.2.3. Types of Chemical Specialities

Wrap Sizes: Size is a chemical mixture applied to warp yarns to improve the strength and bending behavior of the yarn's fibers, thereby preventing breakage during weaving operations.

-Permanent Press Finishes: Cotton, rayon, and other forms of cellulose blends that contain these fibers usually require finishing with a reactive agent to cross-link adjacent cellulose chains. This step immobilizes the fibers, reducing shrinkage and improving bending properties (e.g., crease recovery).

-Softeners: The main types of softeners are fat, petrochemical, and silicon based. Reactive silicone softeners are very well fixed and do not wash off of the fiber, whereas most other types wash off during home laundering of the textile products.

Builders: Functional materials applied to textiles to improve their softness or feel are known as builders or handbuilders.

-Surfactants: Surfactants are used in wet processing to ensure complete wetting and penetration of processing solutions. In addition, surfactants can serve as dispersing agents, emulsifier, bath detergents, foaming agents, and levelers. Essentially all chemical specialties thus contain surfactants to improve their solubility and dispersibility and to suspend water-insoluble materials in processing baths. This is important to prevent the precipitation of insoluble materials [9].

2.3. Dyes and Dyeing Processes

Dyes used in the textile industry are largely synthetic and derived from coal tar and petroleum-based intermediates. The use of naturally occurring dyes from animal and plant sources has little commercial applications. Dyes are sold as powders, granules, pastes, and liquid dispersions and solutions, with concentrations of active ingredients ranging typically from 20 to 80 per cent. Different auxiliary chemicals are used during dyeing to assist in dye absorption and fixation into the fibers [9].

Dyeing of textile goods is carried out by batch or continuous processes. In batch dyeing, a certain amounts of textile substrate, usually 100 to 1000 kilograms, is loaded into a dyeing machine and brought to equilibrium, with a solution containing dye. Because the dyes have an affinity for the fibers, the dye molecules leave the dye solution and enter the fibers in minutes to hours. Auxiliary chemicals and controlled dyebath conditions (temperature) accelerate and optimize the action. The dye is fixed in the fiber using heat and/or chemicals and the colored textile substrate is washed to remove unfixed dyes and chemicals.

In continuous dyeing process, textiles are fed continuously. It consists of dye application, dye fixation with chemicals or heat, and washing [9].

The environmental problems arising from dye consumption can be summarized as:

- Wastage of large amounts of water
- Use of massive amounts of salt in cellulose dyeing
- treatment difficulties for some metals which can be constituents of some dyes
- Interference of color (unfixed dye) with the transmission of light in receiving body, interrupting photosynthesis and aquatic life.
- wastage of numerous auxiliary chemicals, such as salt in dye rinse water and spent dyebaths

2.3.1. Pollutants Associated with Dyeing

Pollutants associated with dyeing may originate from the dyes themselves (e.g., toxicity, metals, color) or derive from auxiliary chemicals used during the dyeing process (e.g., salt, surfactants, levellers, lubricants, alkalinity). Pollutants are also associated with chemicals used during dyeing equipment maintenance and cleaning. Dyeing contributes essentially all of the salt and color in effluent from textiles operations [9].

Alkalinity of dyeing effluents is a further environmental concern. Preparation process generally are carried out in a range of neutral pH conditions to highly alkaline conditions. Alkali is introduced to cause the reaction between the dye and the fibre. The reactivity with hydroxyl groups of cotton which made the new dyes so successful brought with a huge problem water and alkalinity. Therefore any reaction between the dye and water before or during the dyeing process results in loss of dye due to the hydrolysis. On the other hand, the commercial success of the dyes was dependent on their high reactivity and their water-solubility [11]. Some common aquatic pollutants in dyeing processes are presented in Table 2.3.1.1.

Table 2.3.1.1. Types of Pollutants Associated with Various Dyes [9]

Class	Fiber	Type of Pollution
Direct dyes	Cotton	Salt Unfixed dye Copper salts Cationic fixing agents
Reactive dyes	Cotton	Salt Alkali Unfixed dye
Vat dyes	Cotton	Alkali Oxidizing agents Reducing agents
Sulphur dyes	Cotton	Alkali Oxidizing agents Reducing agents Unfixed dye
Chrome dyes	Wool	Organic acids Unfixed dye Metals Sulfide
Acid dyes	Wool	Organic acids Unfixed dyes
Disperse dyes	Polyester	Reducing agents Organic acids Carriers

2.3.2. Dye Classes

Textiles are dyed using many different colorants, which may be classified in several ways (e.g. according to chemical constitutions, dyeing property, solubility). The primary classification of dyes is based on the fibers to which they can be applied, and the chemical nature of each dye determines the fibers for which the dye has affinity. Table 2.3.2.1. lists the major dye classes and the types of fibers for which they have an affinity [9].

Table 2.3.2.1. Dye Classes and Fibers for Which They Have Affinity [9]

Dye Class	Fibers
Acid	Wool and nylon(polyamide)
Azoic	Cotton and cellulose
Basic	Acrylic, certain polyesters
Direct	Cotton, rayon and other cellulosic
Disperse	Polyester, acetate, and other synthetics
Fiber reactive	Cotton and other cellulosic, wool
Mordant	Natural fibers
Pigment	All
Sulfur	Cotton and other cellulosic
Vat	Cotton and other cellulosic

- **Acid Dyes**

Acid dyes are water soluble anionic compounds applied to nylon, wool, silk, and some modified acrylic textiles in an acidic medium. They exhibit little affinity for cellulosic or polyester fiber. Colors are generally bright, and the material exhibits good to excellent fastness properties. Fastness of dyes is a term referring to its relative resistance to chemical and physical breakdown or removal when in use. Acid dyes have one or more sulfonic or carboxylic acid groups in their molecular structure. The dye-fiber affinity is the result of ionic bonds between the sulfonic acid part of the dye and the basic amino groups in wool, silk, and nylon fibers [9].

- **Azoic Dyes**

Azoic dyes, also known as naphthol dyes, are used on cellulosic fibers (particularly cotton) but may also be applied to rayon, cellulose acetate, linen, jute, hemp, and sometimes polyester. Azoic dyes are made up of two chemically reactive compounds, which are applied to the fabric in a two-stage process. The reaction of the two compounds in the fiber produce the colored azo chromophore. During dyeing, the azoic dye forms inside the fiber.

The color index (CI) refers to the components used in azoic dyeing as CI Azoic Coupling Components and CI Azoic Diazo Components [9].

Azo dyes produce bright and dark shades of yellow, orange, red, maroon, navy blue, brown, and black. The dyes exhibit good light fastness and fastness to peroxide and other bleaches.

- **Basic (Cationic) Dyes**

Basic dyes were the first synthetically manufactured dye class. Modified basic dyes are used exclusively to color synthetic fibers such as acrylic, modified nylons and polyesters, in which their fastness is acceptable. Basic dyes are rarely used on natural fibers, both because of their poor light and wash fastness and because of the need for mordants to improve wetfastness [9].

They have limited water solubility and are applied in weakly acidic dyebaths. Ionic bonds are formed between the cation in the dye and the anionic site on the fiber. They have unlimited color range and good fastness properties.

- **Direct Dyes**

Direct dyes are water-soluble, anionic compounds used extensively for dyeing cotton, nylon, linen, hemp, and silk. The term “direct dye” refers to the fact that these dyes can be applied directly to cellulose without mordants. The dyes are absorbed into hydrophilic fibers as the fibers expand in the water [9].

- **Disperse Dyes**

Disperse dyes have a very low water solubility, so they are applied as a dispersion of finely ground powders in the dye bath. The particles dissolve at low concentrations in the aqueous dyeing medium but transfer into the synthetic fiber polymer because of their higher solubility in the substrate [9].

• Fiber Reactive Dyes

Fiber reactive dyes are water soluble, anionic dyes that provide high wetfastness and require relatively simple dyeing methods. They are mainly used for dyeing cellulosic fibers such as cotton and rayon. Fiber reactive dyes have largely replaced direct, azoic, and vat dyes and are the largest dye class in commercial value. They have bright shades, particularly orange, scarlet, and turquoise.

Fiber reactive dyes form covalent chemical bonds with the fiber and become part of the fiber, giving excellent fastness properties. Because of their solubility, leveling takes place rapidly before fixation, which provides flexibility in the dye application methods. To exhaust the dyes, however large amounts of salt are generally necessary, and substantial amounts of dye can remain unfixated at the end of the process. After dyeing, the fabric is washed with an anionic surfactant to remove unreacted dye [9].

The characteristic structural features of a reactive dye are shown in Figure 2.3.2.1. [12].

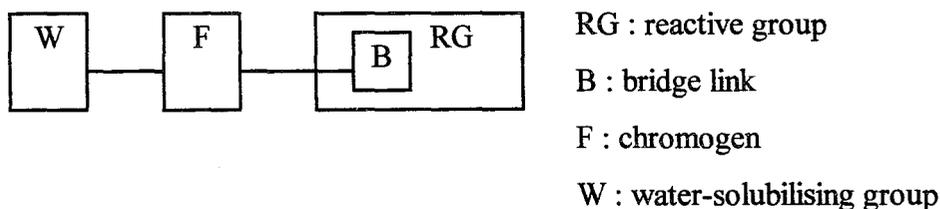


Figure 2.3.2.1. Characteristic Structural Features of a Reactive Dye

Reactive Groups: All reactive groups are based on the fact that cellulose, protein and nylon fibres contain groups that are able to react as nucleophilic substrates, i.e. hydroxyl, amino groups.

Bridge Link: Generally the reactive system is attached to the chromogen by a bridging group. The reactivity and other dyeing characteristics of a reactive dye are influenced by the bridging group, and still more, by other substituents attached to the reactive system. It influences a) the reactivity of the reactive system since dissociation of reactive groups can lead to lower fixation, b) the degree of fixation; some isomeric forms of the dyes have lower selectivity towards cellulose, c) the stability of reactive dyeing.

Chromogen: The colored part of a reactive dye, usually an azo, metal-complex azo, or anthraquinone residue. Fastness to light and to chemical treatments are largely determined by the stability of the chromogen.

Water-Solubilising Groups. Water solubility is generally conferred by sulphonic acid groups attached to the chromogen and/or, occasionally to the reactive system.

Hydrolysis of a reactive dyes is very important process [12]:

- (1) aqueous solutions of reactive dyes become unreactive towards textile substrates through hydrolysis
- (2) hydrolysis is the same type of reaction as fixation to the functional groups of fibres, in particular to cellulose hydroxyl groups ($R-OH$: cellulose, $R=cell$, water, $R=H$)

From (1) it would be suitable to make reactive dyes very stable against hydrolysis, but (2) indicated that this would be undesirable. What is required is that the ratio of the reactivity towards functional groups of the fibre to that of hydrolysis should be as high as possible.

Environmental Concern about Fiber Reactive Dyes:

Environmental concern about fiber reactive dyes are focused on two pollutants which are most important, such as color and salt. The relatively low fixation efficiency of the dyes results in effluent color, which was mentioned before, and is not easily removed in the treatment system. Decolorization of the effluent is difficult because of the low level of the aerobic biodegradation and/or adsorption onto activated carbon. Large amounts of salts are required to exhaust the dyes, and some are tightening salt limits to levels that may be difficult to meet since the conventional treatment systems are not effective for the removal of salt. Some improvements in fixation of fiber reactive dyes have been made with the introduction of bifunctional reactive dyes. Bifunctional dyes have two reactive groups, which increases the efficiency of dye fixation [9].

- **Sulfur Dyes**

Sulfur dyes are mainly used for dyeing cotton and rayon substrates. Sulfur dyes are reduced with sodium sulfide to a water soluble form before application to the fiber. In reduced form, sulfur dyes are soluble and have an affinity for cellulose. They color by absorption, like direct dyes but with exposure to air they oxidize to re-form the original insoluble dye inside the fiber. This makes them resistant to removal by washing [9].

- **Vat dyes**

They are often most used to dye cotton and cellulosic fibers. They are either supplied in water soluble reduced "leuco" form or reduced with a reducing agent such as sodium hydrosulfite. Then they are allowed to migrate into the fiber by an exhaustion process. When this is complete, the substrate is rinsed to remove surface dye, then the dye is oxidized back to its water insoluble form within the fiber. The result is a dyeing of very high fastness to washing [9].

2.3.3. A Plant Specific Batch Cotton Dyeing Process Scheme*

The procedure of cotton dyeing with Procion dyes in the selected textile company is given in Figure 2.3.3.1. [7].

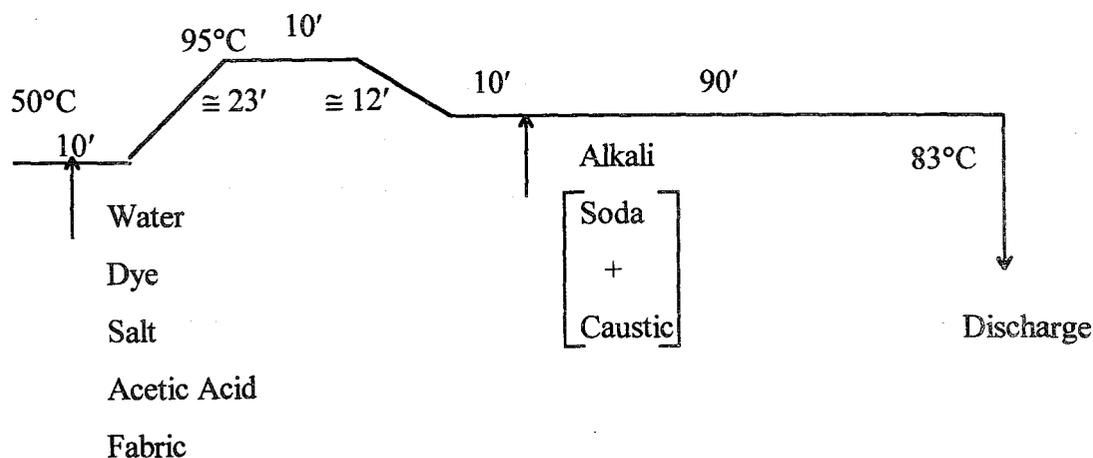


Figure 2.3.3.1. Schematic Diagram of Cotton Dyeing with Procion Dyes

* specific to a textile mill in İstanbul

The dyeing procedure used in the referred plant is as follows:

The dyeing tank is filled with water and the temperature is raised to 50 °C. The Glaubert's salt (NaCl), dye and a sufficient amount of acetic acid are added to achieve a pH of 4.5-5, followed by addition of the fabric into the bath. The temperature of the bath is then raised to 95 °C within 23 min and maintained at that temperature for 10 min. Then the temperature is slowly lowered from 95°C to 83 °C in 12 minutes, and soda and caustic are added. The temperature is maintained at 83 °C for 90 min. At the end of 90 min, the water is discharged and the fabric is rinsed up to 10 times in the same tank depending on the color intensity. The Glaubert's may crystallize in the fibre and be very difficult to re-dissolve at temperatures below 45 °C, so the temperature of rinsing water is preferred to be above 45 °C. The amount of chemicals to be added, depends on dye concentration, i.e., shade depth (1 per cent, 2 per cent, 3 per cent, etc.). The shade depth was considered as 5 per cent (to obtain dark color as discussed above). The concentration of chemicals to be added for five per cent dyeing intensity are given in Table 2.3.3.1.

Table 2.3.3.1. The Concentration of Chemicals for 5 (%) Shade for Procion Dyeing [7]

Chemical Name	5 (%) Shade
NaCl	90 g/L
Na ₂ CO ₃	10 g/L
NaOH	1.65 g/L (48 Be °)
CH ₃ COOH	0.5 g/L

2.4. Advanced Oxidation Processes

Although chemical oxidation is a common technique in treating industrial process effluents, remediation of such wastewaters with conventional oxidants is sometimes non-feasible due to kinetic limitations[6]. These limitations have been overcome by the development of advanced oxidation processes (AOP), which use strong oxidants (O_3 , H_2O_2) and/or catalysts (Fe^{2+} , TiO_2) in the presence and absence of an irradiation source. Advanced oxidation technologies (AOTs) involve the generation of powerful hydroxyl radicals ($\bullet OH$) for the destruction of organic compounds in contaminated water. The success of the system is based on the fact that the rate constants for the reaction of hydroxyl radicals with most organic pollutants are very high as shown in Table 2.4.1. The hydroxyl radical typically reacts one million to one billion times faster than chemical oxidants like ozone and hydrogen peroxide [13].

Table 2.4.1. Reaction Rate Constants (k, in L/moles) of Ozone vs. Hydroxyl radical

Compounds	O_3	$\bullet OH$
Chlorinated Alkenes	10^{-1} to 10^3	10^9 to 10^{11}
Phenols	10^3	10^9 to 10^{10}
N-containing Organics	10 to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	10^8 to 10^{10}
Ketones	1	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9
Alkanes	10^{-2}	10^6 to 10^9

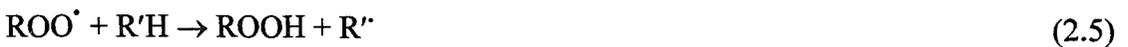
Many organic and inorganic chemicals in the environment absorb sunlight and undergo transformation to new molecular species[14]. Thus, much of photochemical processes initiates the breakdown of organic molecules into simpler molecules and ultimately to carbon dioxide and other mineral products.

AOTs involving ultraviolet irradiation in conjunction with hydrogen peroxide or ozone are known as UV/Oxidation processes. In these processes, an oxidizing agent,

generally hydrogen peroxide, is added to the contaminated water and is activated by the UV light to form hydroxyl radicals.



The hydroxyl radical then reacts with the dissolved contaminants, initiating a rapid cascade of oxidation reactions that ultimately fully oxidize (mineralize) the contaminants [15].



There are a number of advanced oxidation processes generating hydroxyl radicals. Light induced AOPs are given in Table 2.4.2.

Table 2.4.2. AOPs Initiated by Hydroxyl Radicals [16]

Process	Efficiency*	Spectral Domain
$\text{H}_2\text{O}_2/h\nu$	h	UV-C
$\text{H}_2\text{O}_2/\text{Catalyst}/h\nu$	h	UV-C to A
$\text{O}_3/h\nu$	m	UV-C
$\text{H}_2\text{O}_2/\text{O}_3/h\nu$	h	UV-C
$\text{TiO}_2/h\nu$	l/m	UV-C to A
VUV Photolysis	m	VUV

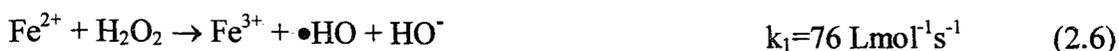
*h : high; m : medium; l : low

2.4.1. Non - Photochemical Oxidation [17]

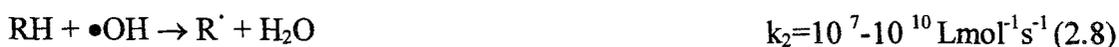
Generation of hydroxyl radical can also be achieved in the absence of UV light by a number of AOPs. Reaction pathways are as the following:

- Fenton's Reaction

If H_2O_2 is added to an aqueous medium containing organic compounds and excess ferrous ions at acidic conditions, the following complex redox reaction will occur [18];



The generated $\bullet\text{OH}$ Radicals attacks the organic substrate RH resulting in the formation of new organic radicals;



Then, three reaction alternatives are possible:



or



or



The main advantage of this system to the more popular homogenous AOP $\text{UV}/\text{H}_2\text{O}_2$ oxidation is that the process and reactor configuration is not limited to by UV -irradiation. However, the main disadvantage is the formation of ferric ion precipitation after pH adjustment as well as acidic conditions ($\text{pH}<4$) necessary for this treatment process [19].

- Ozone at high pH



- Ozone and Hydrogen Peroxide



2.4.2. Photochemical Processes

AOPs involving ultraviolet irradiation in conjunction with an oxidant and/or catalyst are known as UV/Oxidation processes.

2.4.2.1. UV Photolysis

Photooxidation reactions upon electronic excitation of the organic substrate imply in most cases an electron transfer from the excited state (C^*) to ground state molecular oxygen. Rates of such photooxidation depends on the adsorption cross section of the medium, the quantum yield of the process, the photon rate at the wavelength of excitation, and the concentration of dissolved molecular oxygen [13]. Direct photolysis procedures are generally of low efficiency when compared to procedures involving hydroxyl radical generation. However, photolysis of pollutants may be important in cases where hydroxyl radical reactions are known to be very slow.

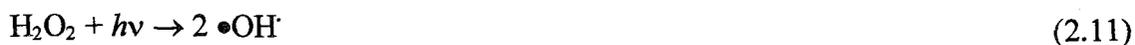
2.4.2.2. Vacuum Ultraviolet (VUV) Process

The vacuum ultraviolet (VUV) consists of UV-C spectral domain, at 190 nm, where air strongly absorbs radiation, and excitation in this spectral domain leads to the homolysis of chemical bonds.

This technique may provide a potentially clean process for treatment as these oxidation reactions require only air, water, and UV irradiation.

2.4.2.3. H₂O₂/UV Process

The mechanism most commonly accepted for the photolysis of H₂O₂ is the cleavage of the molecule into hydroxyl radicals and other reactive species that attack the organic molecules :



If an excess of H₂O₂ is used, $\bullet\text{OH}$ radicals will produce hydroperoxyl radicals, $\text{HOO}\bullet$, which are much less reactive.

The use of H₂O₂ as an oxidant brings a number of *advantages* in comparison to other methods of photochemical treatment, such as, commercial availability of the oxidant, thermal stability, storage on-site, infinite solubility in water, costs that are less sensitive to scale of operation than ozone [14].

A catalyst is needed for the formation of hydroxyl radicals, which are much more powerful than hydrogen peroxide as an oxidizing agent. This is particularly due to the stability of H₂O₂ at normal condition which makes it quite selective in oxidation.

UV irradiation catalyses the chemical oxidation of organic compounds in two ways:

- 1) the toxic substances absorb the energy of the UV irradiation, and then changes their chemical structure and increases their reactivity with oxidants, [but it is important that most organics have the same absorbance range with hydrogen peroxide , so they may compete with hydrogen peroxide for light, decreasing the fraction normally it absorbs. This slows down the rate of hydroxyl ion generation [3].
- 2) formation of hydroxyl radicals which have high oxidation potential [19].

2.4.2.4. Ozone / UV Process

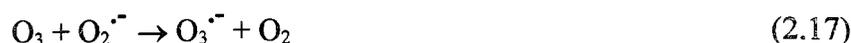
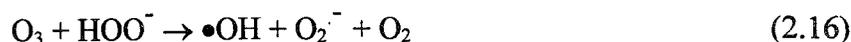
The O₃ / UV process seems at present to be the most frequently applied AOP for a wide range of compounds. This is due to the fact that ozonation is a well-known procedure for water and wastewater technology. For the photolytic oxidation by ultraviolet light combined with ozone, hydroxyl radicals are generated as active species.



Hydrogen peroxide is produced after photolysis of ozone, and that is photolyzed to $\bullet OH$ radical.

2.4.2.5. O₃ / H₂O₂ / UV Process

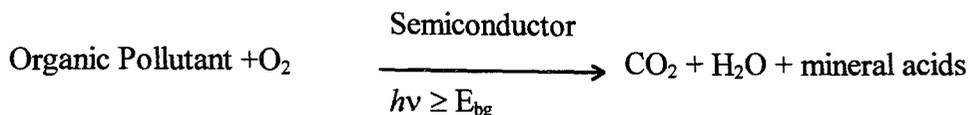
For the O₃ / H₂O₂ / UV process the reaction pathways to the generation of HO[•] radicals can be summarized as follows :



Again hydroxyl radicals are considered to be the most important intermediate, initiating oxidative degradation of organic compounds. Addition of hydrogen peroxide results in a net enhancement due to the dominant production of HO[•] radicals.

2.4.2.6. H₂O₂/TiO₂/UV Process

Overall process can be summarized by the following reaction :



Most of the semiconductors photocatalysts studied to date are metal oxides (e.g. TiO₂, ZnO, SnO₂) and chalcogenides (CdS, ZnS, CdSe, ZnSe). Among the different semiconductor photocatalysts, TiO₂ appears the most reactive. In addition, although TiO₂ is only a UV absorber ($E_{\text{bg}} = 3.2 \text{ eV}$), it is cheap, insoluble under most conditions, photostable, and non-toxic.

When TiO₂ particles are irradiated by UV photons, photon energy matching or exceeding the bandgap energy excites an electron on the TiO₂ surface from the valence band to the conduction band, leaving a positive hole in the valence band. If electron donors such as OH and H₂O are available, hydroxyl radicals can be generated by electron transfer from the electron donors to positive holes. Organic compounds then be destroyed either by hydroxyl radicals or by positive holes directly.

2.4.2.7. H₂O₂/Fe(II)/UV Process

Since hydrogen peroxide weakly absorbs between 200-300 nm and does not absorb beyond 300 nm, the UV/H₂O₂ process is often not suitable for the treatment of polluted water with a high UV absorbance; another homogenous reaction, the Fenton reaction, produces hydroxyl radicals by interaction of H₂O₂ with ferrous salt, is an alternative process [20] for the treatment of wastewater.

Iron is the second most abundant metal in the Earth's crust where it is found as ferrous (Fe²⁺) or ferric (Fe³⁺) ions. It is introduced into the atmosphere by wind and is found in aerosols, fogs, rain drops, ground waters and lakes. It plays a significant role in atmospheric photochemistry and its importance has been discussed [21,22,23,24,25].

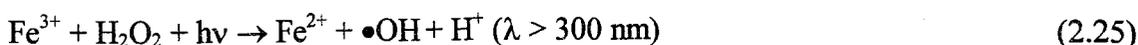
The reactivity of the system was first observed in 1894 by the inventor H.J.H. Fenton, and today Fenton's reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (complex wastes derived from dyestuff, phenol, pesticides, etc.). The process may be applied to wastewaters with the effects being:

- Organic pollutant destruction
- Biodegradability improvement
- BOD/COD removal
- Color removal
- TOC removal
- Toxicity reduction

The reaction is based on the catalytic effect of the ferrous ions on the decomposition of H_2O_2 . The main dark reactions are [26]:



In the dark, the reaction is retarded after complete conversion of Fe^{2+} to Fe^{3+} . After H_2O_2 addition, ferrous ion concentration decreases rapidly and ferric ion is formed. After the complete disappearance of the oxidant, no more Fe(II) can be consumed. The concentration of Fe(II) increases rapidly, in contrast with the dark reaction where Fe(III) can not be photoreduced to Fe(II) [27] as shown in eqn. (2.24). The primary step is photo oxidation of ferrous ions to ferric ones (eqn. (2.19)). In the presence of light feedback reaction takes place (eqn. (2.25)).



The additional effect of direct H_2O_2 photolysis of acidic solutions give OH^\bullet as primary photoproducts (eqn. (2.26)).



The utilization of Fenton's reagent for the oxidation of organics is only effective under acidic conditions, especially at pH 3-5 [18,26, 28,29,30], and in the presence of UV-visible light [27, 28,31,32,33].

The initial rate of mineralization (transformation of organic pollutants) is faster with $\text{Fe(II)/H}_2\text{O}_2$ (Fenton reagent), than $\text{Fe(III)/H}_2\text{O}_2$ (Fenton like reaction), due to the force of hydroxyl radicals which is produced by Fenton's reagent. [20] Fenton like reagent is needed, because the regeneration of ferrous ion by organic radicals increases the chain length which may result in a more complete destruction of the organic compound [26]. If only the transformation of parent pollutants is desired, the use of Fenton's reagent is favorable. In photoassisted Fenton reaction, hydroxyl radicals can be formed following three pathways: free radicals from hydrogen peroxide can be obtained either by the catalytic reaction of iron salt (ferrous and ferric) or by UV light. Figure 2.4.2.7.1. shows schematically the chemical reactions for the formation of $\bullet\text{OH}$ radicals and the oxidation of organic compound in the photoassisted Fenton reaction.

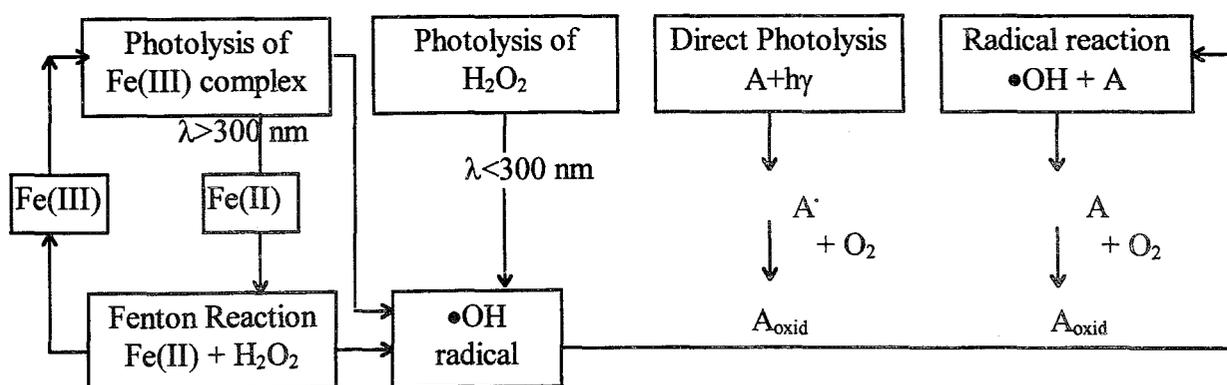


Figure 2.4.2.7.1. Scheme of Chemical Reactions in the Photoassisted Fenton Reaction
[31]

The increased efficiency of Fenton/Fenton like reaction with UV-visible irradiation is attributed to [20]:

Photoreduction of ferric ion: Irradiation of ferric ion produces ferrous ion, and the produced ferrous ion reacts with hydrogen peroxide to generate a second hydroxyl ion and ferric ion, and the cycle continues.

Efficient Use of Quanta: The absorption spectrum of H_2O_2 is low beyond 250 nm. On the other hand, the absorption spectrum of the ferric ion is high in the UV-visible region, and even in visible light.

Photolysis of Fe(III)-organic intermediates chelates: Complexes formed with the reaction of Fe^{3+} and oxygenated intermediates, that are generated by the initial oxidation of organic pollutants, are also photoactive and produce CO_2 , organic radicals and ferrous ions on irradiation.

2.4.2.7.1. Parameters Effecting the Photo-Fenton Process

- **Effect of Iron Concentration**

As the concentration of iron is increased, organic pollutant removal accelerates until a point and further addition of iron becomes inefficient. An optimal dose range for iron catalyst range varies between wastewaters. Iron dose may be expressed as a ratio of H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt).

- **Effect of Iron Type (Ferrous or Ferric):**

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction. The catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. It is also possible to recycle the iron. This can be done by raising the pH, separating the iron floc, and re-acidifying the iron sludge.

- **Effect of Light:**

The absorption spectrum of hydrogen peroxide does not extend beyond 300 nm and has a low molar absorption coefficient beyond 250 nm. The absorption spectrum of ferric ion extends to the near UV-visible region and has a relatively large molar absorption coefficient, thus making more efficient use of the lamp output when polychromatic light is employed.

- **Effect of H₂O₂ Concentration:**

In the absence of H₂O₂, there is no evidence of hydroxyl radical formation. Typical Fe:H₂O₂ ratios are 1:5-10 wt/wt.

- **Effect of Temperature:**

The rate of Fenton reaction increases with increasing temperature. As a practical matter, most commercial applications of Fenton's reagent occur at temperatures between 20-40 °C.

- **Effect of pH:**

The Fe(II)/Fe(III)-H₂O₂ system has its maximum catalytic activity at a pH of about 2.8-3.0. An increase or decrease in the pH sharply reduces the catalytic activity of the metal ion. At high pH, the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of Fe(III) with H₂O₂ (eqn. (2.24)) is inhibited. The pH of the solution decreases rapidly by the addition of FeSO₄ catalyst which typically contains residual H₂SO₄. Second, more pronounced drop in pH occurs as the H₂O₂ is added, and continues gradually at a rate which is largely dependent on catalyst concentration. The drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned. The absence of such a pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of H₂O₂ is occurring within the reaction mixture.

- **Effect of Reaction Time:**

The time needed to complete a Fenton reaction will depend on many variables such as catalyst dose, wastewater strength, light intensity.

- **Effect of Post Treatment:**

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more responsive to conventional treatment, e.g., flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation.

The use of Fe(II)/H₂O₂ for wastewater treatment is attractive due to the fact that :

1. iron is a highly abundant and non-toxic element
2. hydrogen peroxide is easy to handle and is environmentally benign
3. low capital cost
4. toxicity reduction for biological treatment
5. instantaneous startup time

Also there are some liabilities:

1. Additional chemical cost
2. sludge disposal cost
3. salt formation
4. maintaining proper chemical reaction conditions

2.4.3. Degradation of Azo Dyes by AOPs

Azo dyes are synthetic organic colorants that exhibit great structural diversity. They are characterized by the presence of nitrogen double bonds (-N=N-). Treatment of textile wastewater containing azo-dye by conventional methods have recently found to be inadequate [5]. Due to the resistance of azo dyes, these wastewaters can be treated chemically to improve biodegradability or simply to reduce their organic and inorganic

content. Advanced oxidation treatments AOTs are currently being studied as a practical way of achieving these objectives.

2.4.3.1. H₂O₂/UV Process

Initial studies show that the azo dyes using typical spent dyebath concentration levels are resistant to decolorization with peroxide alone, but Nambodri, et al. [34], conducted a study for decolorizing spent dyebaths using small amount of hydrogen peroxide in the absence of ultraviolet light, at neutral pH, and a temperature close to the boiling point of water. Small amounts of ferrous or ferric ions (ferric ion gave a higher rate of decolorization) as catalyst with peroxide at pH 7, and at 95-98 °C decolorized the resistant azo direct dye. There are many studies for the treatment of azo-dyes with UV/H₂O₂. Neither UV (without H₂O₂) nor H₂O₂ (without UV) treatments were found to be efficient to decompose azo dyes significantly [35]. The two non-biodegradable azo-dyes acid red 1 and acid yellow 23 were degraded efficiently under UV/H₂O₂, using a low pressure mercury lamp. The high reaction was due to the generation of radicals from the UV irradiation of hydrogen peroxide at acidic pH. Total organic carbon removal was found to be slow at the beginning of reaction as the OH[•] was used for decolorization reaction and after the color was removed, the OH[•] was then spent on the degradation of TOC compounds. Another research was focused on a UV/H₂O₂ oxidation, to achieve the destruction of Reactive Black 5 [3]. It was found that UV/H₂O₂ treatment was a suitable degradation method for the azo dye. It was reported that, additives, non-ionic detergents that were present in dyebath wastewater would interfere and scavenging effects would slow down the degradation. In the same study, inhibition of low pH on carbonate scavenging was discussed but not suggested because of increasing operational costs, especially for textile dyeing effluents where pH is much greater than neutral. Also addition of excess H₂O₂ increased TOC removal efficiency but did not recommended because of its inhibitory and cost-raising influence. Ince et al. studied the remazol degradation and toxicity reduction of an azo dye, Black-B under UV/H₂O₂, using a medium pressure mercury lamp [4]. Complete color degradation was accompanied with 44 per cent mineralization and 68 per cent toxicity reduction under their experimental conditions. Majcen et al., [19] studied the decoloration of chlorotriazinyl reactive azo dyes with hydrogen peroxide activated with UV irradiation and observed a

decrease both in color and ecological parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD_5) and total carbon (TC). The COD reduction was observed higher than TOC reduction as a result of compounds formed through oxidation that was easily broken down into forms that do not harm the environment, and C compounds in the form of carbonates which were present and they were not transformed to CO_2 to be tracked in terms of TOC. Morison et al., [36] determined an initial rate of degradation and decoloration for Orange II in the presence of H_2O_2 in the dark and by using simulated and natural sunlight.

2.4.3.2. UV/ H_2O_2 /TiO₂ Process

Heterogeneous photocatalysis with TiO_2 suspensions were seem to accelerate the photodegradation rate by Tang et al.[37]. The degradation kinetics of azo dyes seemed to be significantly induced by their electrical nature, the number of azo bonds present in the dye molecule and pH. Triazo dye found to be the most refractory, diazo dyes were the most readily degradable and the diazo dye were in the middle range. Since pH affected the degradation rate by affecting the electrical forces between azo dyes and TiO_2 surface, electrical reduction of azo bonds seemed to be the most reasonable reaction pathway at pH 3, however OH^\bullet oxidation appeared to be the dominant reaction mechanism at pH 7 and 11 due to the similar rate constants.

2.4.3.3. Fenton-PhotoFenton Process

Rupert et al., [38] conducted a study for the mineralization of dyebath wastewater. Under laboratory conditions, photo-Fenton reaction was found to be most effective while the Fenton reaction was found to be inefficient for mineralization of 4-CP. Natural sunlight with $Fe(III)$ -hydroxy[$Fe(OH)^{2+}$] for the photodegradation of five different dyes were studied by Nansheng et al. [39]. The photodegradation of those five different dyes were pseudo-first order reactions and the efficiency of the solar photodegradation was a little lower than that of UV-light photodegradation. The initial rates of degradation and decoloration was determined for Orange (II) in the presence of Fenton reagent applying simulated and natural sunlight [32]. Light and dark processes involving Fenton reagent were effective for the

degradation of Orange II solutions at pH lower than 5 [40] and complete mineralization was attained in less than one hour. The reaction of an azo-dye with Fenton reaction caused a drop in color at an acidic medium and additional aeration had no effect upon the process rate [41]. Decolourization in the system azodye- H_2O_2 - Fe^{2+} was accelerated by raising the temperature or under the sunlight influence. Kuo [42] studied the decolorization of simulated dye house wastewater prepared with disperse, direct, reactive, acid and basic dyes with Fenton's reagent. Rate of decolourization was mainly influenced by temperature and pH, and the best results were obtained at a pH below 3.5. 90 per cent COD and 97 per cent color removal were achieved. Lin and Peng [43] proposed that Fenton's reagent is effective in color and COD degradation of wastewater from a large dyeing and finishing mill combined with chemical coagulation and activated sludge. Economic evaluation of continuous Fenton treatment showed that the tested treatment method is highly competitive with the conventional treatment systems practiced in the industry.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Dye

Procion Red HE-7B, Reactive Red (MW=1781 g mol^{-1}) was obtained from BASF-Istanbul, in 75 per cent purity. The chemical structure of the dye is represented in Figure 3.1.1.1. The characteristics of the dye are as follows:

Type : Reactive azo dye (Reactive Red 141)

Formula: $\text{C}_{52}\text{H}_{34}\text{O}_{26}\text{S}_8\text{N}_{14}\text{Cl}_2$ (as sodium salt)

Color content: approximately 75 %

λ_{max} : 543.5 nm

MW : 1781 g mol^{-1}

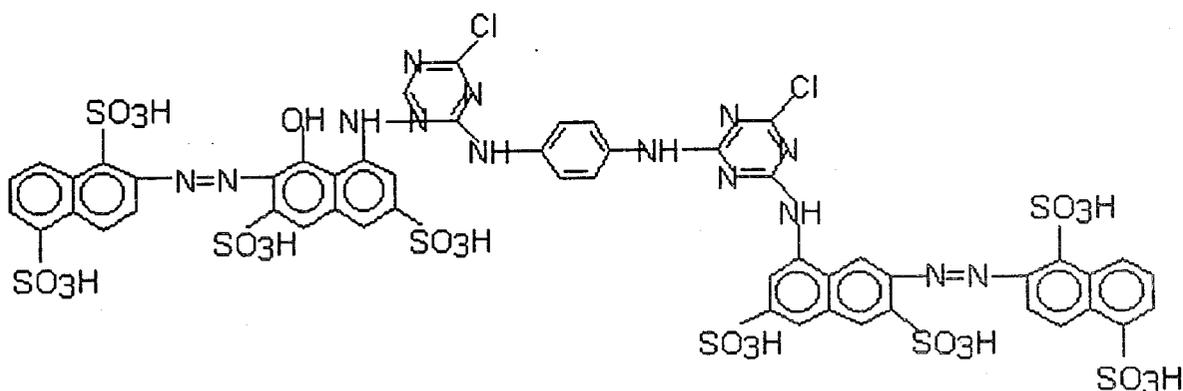


Figure 3.1.1.1. The Chemical Structure of Reactive Red HE-7B

3.1.2. Hydrogen Peroxide

Reagent grade hydrogen peroxide, H_2O_2 , (30 %) was obtained from Merck.

3.1.3. Ferrous Sulfate Heptahydrate

Ferrous sulfate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (99.5 %, Merck) was used for preparing Fenton reagent.

3.1.4. Sodium Hydroxide and Sulfuric Acid

Reagent grade NaOH (Merck) and H_2SO_4 (96 %, Merck) at various concentrations were used for pH adjustment.

3.1.5. Hydrogen Peroxide Killer

The enzyme solution Perizym red was obtained from Textilchemie Dr. Petry GMGH, and used for removing H_2O_2 from effluent samples.

3.1.6. Laboratory Equipment and Analytical Procedures

Shimadzu UV-160 Double Beam Spectrophotometer was used to determine the absorption spectra of the dye solution between 200-600 nm. The degradation of color and aromatic structures were monitored by measuring the reduction in the absorption at each maxima observed in the 200-600 nm band. These were in the UV-B and visible bands, 289 nm and 543.5 nm, respectively. Organic matter degradation was periodically monitored at 289 nm by the Shimadzu UV-160 Double Beam Spectrophotometer. In the second part of the study, the destruction of the dye was monitored only by the reduction in the 543.5 nm absorption using a Shimadzu UV-120-01 Spectrophotometer. Dye concentrations in effluent samples were estimated from the absorbance of effluent samples at the visible band, using the molar extinction coefficient of the tested dye solution. These coefficients were calculated for each test pH. Hydrogen peroxide was monitored spectrophotometrically based on the reaction of hydrogen peroxide with iodide catalyzed by molybdate [44].

The reduction in total organic carbon (TOC) was monitored using a Fisons TCM 480 analyzer. The instrument was calibrated by standard solutions of phenol (1-30 ppm), and calibration curves were established by linear regression.

Concentrations of total dissolved solid (TDS) of influent and effluent samples were determined in accordance with the procedure described in the Standard Methods of Water and Wastewater Analysis (APHA/AWWA/WPCH, 1989) [45].

The chemical oxygen demand (COD) of influent and effluent samples were determined in accordance with the procedure described in the Standard Methods of Water and Wastewater Analysis (APHA/AWWA/WPCH, 1989) [45]. The enzyme, Perizym Red was used to remove residual hydrogen peroxide to prevent its interference with COD analysis. The amount of excess COD exerted by Perizym was measured as well, and subtracted from the measured COD of the sample. In the second part of the study, where COD of 20 min treated samples were determined, no enzyme/Perizym was used, because H_2O_2 was completely consumed during the process.

Ferrous sulfate was removed from solution after AOP treatment, via coagulation/flocculation, followed by one hour of settling. The supernatant was separated and reused in dyeing in a cotton batch dyeing process in a dye house.

All glassware were rinsed with distilled water before use.

3.2 Methods

3.2.1 Experimental Set-up

A. Irradiation Experiments

The experiments were carried out in a four liter plexy-glass reactor at constant temperature, and mixed at constant speed using an IKAMAG RCT Basic temperature controlled stirrer. The reactor was equipped with four 15 W low pressure monochromatic mercury lamps emitting short wave ultraviolet radiation at 253.7 nm. The lamps were located on the top of the reactor with a perpendicular distance of 7 cm from the surface of the solution. The reactor contents were mixed with three magnetic stirrers, (one of which was temperature controlled) and no additional oxygen was supplied to the system. The schematic diagram of the reactor from side and top views is given in Figure 3.2.1.1.

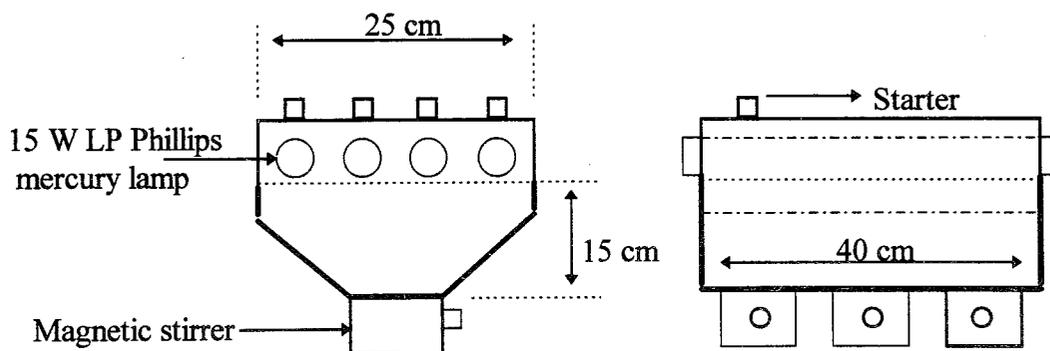


Figure 3.2.1.1. Schematic Diagram of the Reactor

B. Dark Experiments

All light free experiments were carried out in the same reactor and under the same conditions as the UV experiments. Color and aromatic fragment degradations were

monitored by measuring the reduction in the absorption at 543.5 nm and 289 nm, respectively.

3.2.2. Experimental Procedure

Procion Red HE-7B was chosen as a model compound for its dyestuff properties. Test concentrations were selected considering typical dyebath effluent concentrations in textile dyeing/finishing plants according to the information obtained through personal communication with a textile company [7]. Procion dyeing procedure followed in the selected textile dyeing mill was given in Section 2.3.3. The dye concentration in typical dyebath effluents at the end of the rinse process was estimated by using the information given in Table 3.2.2.1.

Table 3.2.2.1. Cotton Dyeing Process Parameters

Parameter	Value
Initial ratio of fabric/water in tank	1 : 8 mass/volume (1 g fabric/8 ml water)
Color intensity	5% (0.05 g dye/ g fabric)
Fixation rate	70 %
Adsorption of water by fabric	1 : 2 mass/volume (1 g fabric absorbs 2 ml water)
Dilution rate at each rinse	1 : 6

Dye concentration in the tank before rinse is calculated as :

$$\frac{1g\text{fabric}}{8ml} \times \frac{5g\text{dye}}{100g\text{fabric}} \times \frac{10^3 mg / g}{10^{-3} L / ml} \times (1-0.70) = 1875 \text{ mg/L}$$

The fabric is rinsed after dyeing to remove unfixed dyes and chemicals. The amount of water absorbed by fabric should be considered when dealing with the dye concentration in the final effluent. The dye-bath water absorbed by the fabric is assumed to be diluted by 1/6 at each rinsing step and the dye fabric is known to absorb the bath solution in 1:2 ratio.

Therefore, 125 g fabric ($\frac{1g\text{fabric}}{8ml} \times \frac{1000ml}{1L}$) absorbs 250 ml water. The changing dye concentrations from first to sixth rinse are calculated as, [dye concentration in water which is absorbed by the fabric / (volume of water absorbed by the fabric + volume of the rinsing water)] :

$$[1875 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 469 \text{ mg/l}$$

$$[469 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 118 \text{ mg/l}$$

$$[118 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 30 \text{ mg/l}$$

$$[30 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 7.5 \text{ mg/l}$$

$$[7.5 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 1.9 \text{ mg/l}$$

$$[1.9 \text{ mg/L} \times 250\text{ml}] / [250\text{ml} + (125 \times 6)\text{ml}] = 0.5 \text{ mg/l}$$

The first rinse is wasted with the dyebath wastewaters due to its high dye content. For reusing the rest of the dyebath, it is necessary that tall rinse effluents are collected in a sort of equalization tank. Assuming all except the first rinse bath are collected in such an equalization tank, the average dyestuff concentration in the tank must be 31.5 mg/L. If the total amount of water loss at the operating temperature during the washing process is about five per cent, then the remaining 95per cent of the volume will contain 30 mg dye/L. Therefore, the concentration of the dye in the equalization tank must be 30 mg/L.

In accordance with the estimation above, 33.3 mg/L Procion Red HE-7B was weighed out and dissolved in 4 liters of distilled water to simulate effluent dye concentrations, typical of Reactive Red dyebaths after rinse [2]. The dye was transformed to its hydrolyzed form by adjusting the pH to 10.6 using sodium hydroxide, followed by heating to 80 °C. The solution was kept at that temperature for 6 hours to simulate typical batch-dyeing conditions. The hydrolyzed dye solution was then cooled to the test temperature and emptied into the reactor. The initial hydrogen peroxide concentration to be added was selected with respect to the chemical oxygen demand (COD) of the solution, which was determined analytically according to the Standard Methods of Water and Wastewater Analysis (APHA/AWWA/WPCH, 1989) [45]. The COD of the solution was determined as 28 mg/L by using low COD method. Hydrogen peroxide was added in

stoichiometric requirement, and twice or four times the stoichiometric requirements, using the oxygen equivalent of its COD as represented in Equation (3.1).

$$1 \text{ g COD} = 0.03125 \text{ mol O}_2 = 0.0625 \text{ mol H}_2\text{O}_2 = 2.125 \text{ g H}_2\text{O}_2 \quad (3.1)$$

(the COD of 33 mg/L dye was determined as 28 mg/L).

Hence, the stoichiometric H_2O_2 requirement was found as:

$$28 \times 10^{-3} \text{ g/L COD} \times 2.125 \text{ g/L H}_2\text{O}_2 \times 1 \text{ mol/34 g H}_2\text{O}_2 = 1.75 \times 10^{-3} \text{ M H}_2\text{O}_2$$

The ferrous sulfate dose was selected by testing molar ratios of 10:1, 20:1, and 40:1 as $\text{H}_2\text{O}_2/\text{FeSO}_4$.

A 5 g/L ferrous sulfate stock solution was made acidic by adding concentrated H_2SO_4 to prevent the oxidation of Fe^{2+} to Fe^{3+} .

The flow diagram of the experimental scheme is given in Figure 3.2.2.1.

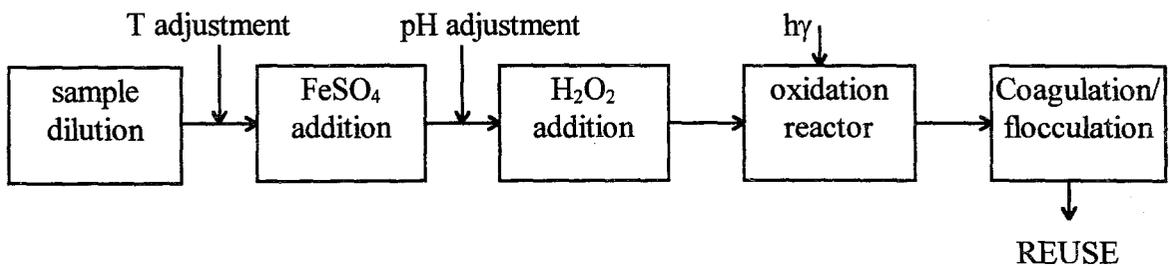


Figure 3.2.2.1. Experimental Scheme

The experimental procedure given in Figure 3.2.2.1. involves:

- adjusting the solution temperature
- addition of the catalyst (as a solution of FeSO_4),
- adjusting the solution pH (after catalyst addition, the pH of the solution dropped to values below 3 because of residual H_2SO_4 in 5 g/L stock ferrous sulfate solution)
- addition of H_2O_2 .
- turning on/off the lamps.

The amount of ferrous sulfate to be added was selected by testing molar $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratios of 10:1, 20:1 and 40:1 (for the real effluent), using 1.80×10^{-3} M H_2O_2 .

Samples were withdrawn from the reactor at time zero (before reagent addition, and before turning on the lights in irradiation experiments), and within short intervals thereafter to monitor dye degradation and total organic carbon reduction. The effluents of test solutions were also monitored for total dissolved solids, and chemical oxygen demand.

UV experiments were run also for real dyebath effluent samples collected from cotton dyeing process/rinse effluents of a textile dyeing mill in Istanbul by diluting the actual dye-bath effluent to obtain typical dyebath effluent concentrations.

The residual iron was removed from the treated effluent by coagulation/flocculation, where the existing ferrous sulfate quantity (0.18×10^{-3} M) was sufficient as the coagulant, so that no additional chemical coagulant was added. The optimum pH was found to be 9 by the jar test [45]. After the concentration of ferrous sulfate was increased, an increase in the TDS concentration was observed. After 1 min of rapid and 20 min of slow mixing at 160 rpm and 30 rpm, respectively, the solids were allowed to settle for one hour. The supernatant phase was separated by centrifuging, tested for color, COD, and TDS contents, and sent to a textile company for reuse.

3.2.3. Estimation of First Order Rate Constants

The reaction rate constants were determined analytically assuming first order degradation kinetics as represented by Equation (3.2) :

$$\frac{dc}{dt} = -k_{\text{obs}} C \quad (3.2)$$

The integration of Equation (3.2) yields a linear equation, the slope of which is the pseudo first order reaction rate constant:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{\text{obs}} t \quad (3.3)$$

where: k_{obs} is the observed first order rate constant (min^{-1}), C_0 and C_t are the initial and the residual dye concentrations (mg/l) at time 0 and t, respectively [3].

The dye concentrations were calculated from the absorbance of each effluent sample using Beers Law as represented by Equation (3.4). It is a fundamental law governing the absorption of all types of electromagnetic radiation. It is known variously as the *Lambert-Beer*, *Bouguer Beer*, or most commonly, as *Beer's law* [47].

$$A = \varepsilon C b \quad (3.4)$$

where: *A* is the *absorbance*, ε is the *molar absorptivity* when the concentration of *C* is expressed in terms of moles of absorber per liter, and *b* is *the path length* given in centimeters.

The extinction coefficient of the dye at each absorption wavelength (543.5 and 289 nm) was calculated by using the optical density of the dye solution at the wavelength concerned, and a pathlength of 1 cm.

4. RESULTS AND DISCUSSION

4.1. Evaluation of the Applied AOP System for Synthetically Prepared Rinse Water

The operating pH, temperature, H₂O₂/Fe(II) molar ratio, and the contact time were selected in accordance with the maximum color and TOC removal rates in 20 min exposure to light conditions, and with maximum color removal rate in 90 min exposure to dark conditions. Degradation rate constants were estimated by assuming first order kinetics.

4.1.1. UV-Visible Spectra

The absorption spectra of the dye (33.3 mg/l Procion Red HE-7B at acidic pH), H₂O₂ (1.75x10⁻³ M), FeSO₄ (0.18x10⁻³ M) and dye + H₂O₂ + FeSO₄ mixture is presented in Figure 4.1.1.1. The dye spectra has two main bands, one in the visible range ($\lambda_{\max}=543.5$ nm, $\epsilon_{\max}=4.73 \times 10^4$ M⁻¹ cm⁻¹), and another in the UV region ($\lambda_{\max}=289$ nm, $\epsilon_{\max}=6.17 \times 10^4$ M⁻¹ cm⁻¹). The calculation of ϵ_{\max} , the molar absorptivity coefficient by Equation (3.4) is given below for $\lambda = 543.5$ nm :

$$A_o = 0.663 \text{ (average of 16 experiments, 33 mg/l dye at } T=40^\circ\text{C, and pH=3)}$$

$$C_o = (33.3 \text{ mg/l} \times 10^{-3} \text{ g/mg}) \times (1 / 1781 \text{ g/mol} \times 0.75 \text{ purity})$$

$$= 33.3 \frac{\text{mg}}{\text{L}} \times 10^{-3} \frac{\text{g}}{\text{mg}} \times 1781 \frac{\text{mol}}{\text{g}} \times 0.75 = 1.4 \times 10^{-5} \text{ M}$$

$$b = 1 \text{ cm}$$

$$\epsilon_{\max} = (A_o / (C_o \times d)) = 4.73 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$$

The visible band at 543.5 nm is due to the long conjugated π system of aromatic rings connected by the azo groups, whereas the UV band at 289 nm is characteristic of individual rings, particularly the naphthalene groups [46].

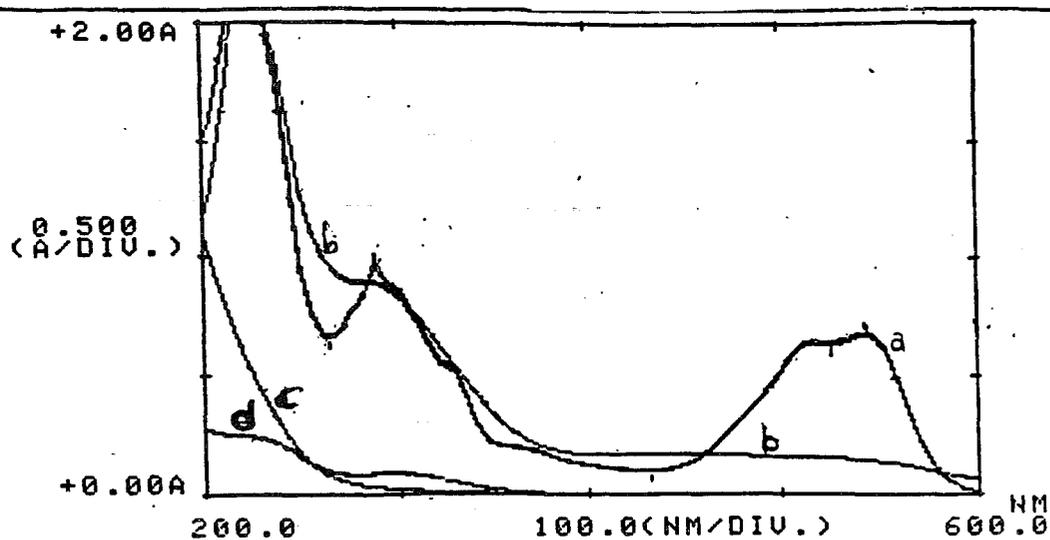


Figure 4.1.1.1. Optical Absorption Spectra of Pure Dye, Pure H_2O_2 , pure $\text{Fe}(\text{II})$ and Mixture at $t=0$ Initial conditions were 33.3 mg/L pure dye, 1.75×10^{-3} M H_2O_2 and 0.18×10^{-3} M $\text{Fe}(\text{II})$, pH=3, $T=40^\circ\text{C}$. (a: 33.3 mg/L dye, b: 33.3 mg/L dye with 1.75×10^{-3} M H_2O_2 and 1.8×10^{-3} M $\text{Fe}(\text{II})$, c: 1.75×10^{-3} M H_2O_2 , d: 0.18×10^{-3} M $\text{Fe}(\text{II})$).

As it can be seen from Figure 4.1.1.1., the color of the dye solution ($\lambda = 543.5$ nm), immediately disappeared (from a to b) as hydrogen peroxide and ferrous sulfate were added, while no reduction was observed in the UV band, upon their addition. The decrease in the UV band was detected only after 5 min exposure to treatment (Figure 4.1.1.2.). It is also important that H_2O_2 and $\text{Fe}(\text{II})$ do not have any significant absorption that would interfere with that of the dye.

The UV-visible spectra of a 33.3 mg/L dye solution before and after treatment with $\text{H}_2\text{O}_2/\text{Fe(II)}$ under 20 min irradiation is shown in Figure 4.1.1.2. A rapid disappearance of the visible part (color) was observed during the first 3 minutes which slowed down thereafter, and remained nearly constant at values close to zero after 20 min of irradiation. The treated effluent had a pale yellow color at the end, which was due to the residual iron. This was removed by coagulation/flocculation before reusing the effluent in the dye process. The removal procedure was discussed in Section 3.2.2. The UV band at 289 nm was also observed to vanish, as obvious in Figure 4.1.1.2., but at a rate which was nearly 4 times slower than that of the visible band. The relative degradation rates of color and aromatic fragments, represented by the absorption of the solution at 543.5 nm and 289 nm, respectively is shown in Figure 4.1.1.3.

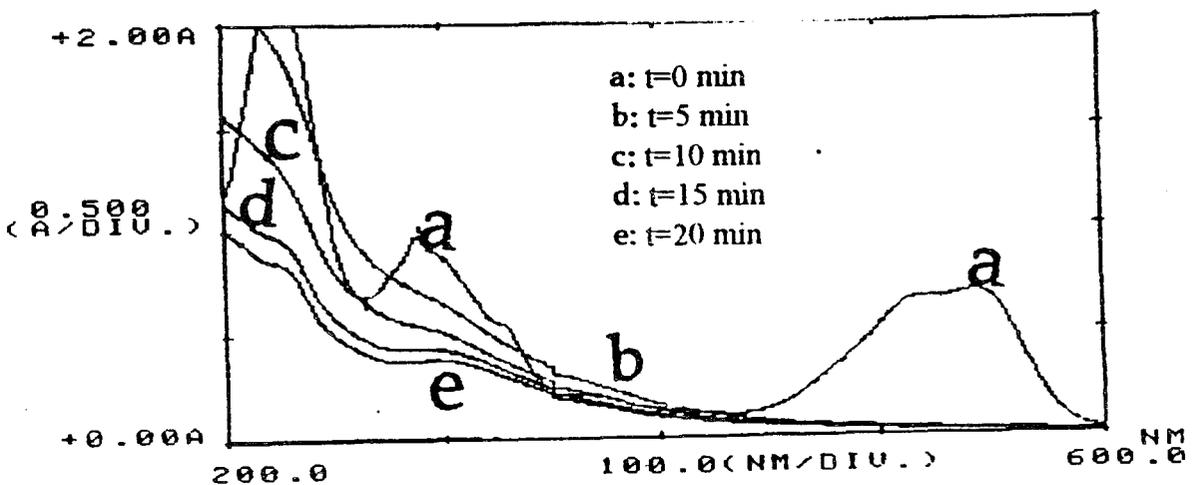


Figure 4.1.1.2. Optical Absorption of the Dye Solution During Treatment with UV/ $\text{H}_2\text{O}_2/\text{Fe(II)}$ for 20 min. Initial conditions were 33.3 mg/L pure dye, $\text{H}_2\text{O}_2/\text{Fe(II)}=20:1(\text{M})$, $3.5 \times 10^{-3} \text{ M H}_2\text{O}_2$, $1.75 \times 10^{-4} \text{ M}$, $\text{pH}=3$, $T=40^\circ\text{C}$.

From the data in Figure 4.1.1.3., it was found that the selected AOP at the conditions employed is capable of ultimate color removal, while destroying 58 per cent of the aromatic fragments in the dye molecule. Treatment at the same conditions, but without light resulted in 43 per cent reduction in the 289 nm band. The relative effect of light and dark conditions on the destruction of aromatic fragments is represented in Figure 4.1.1.4.

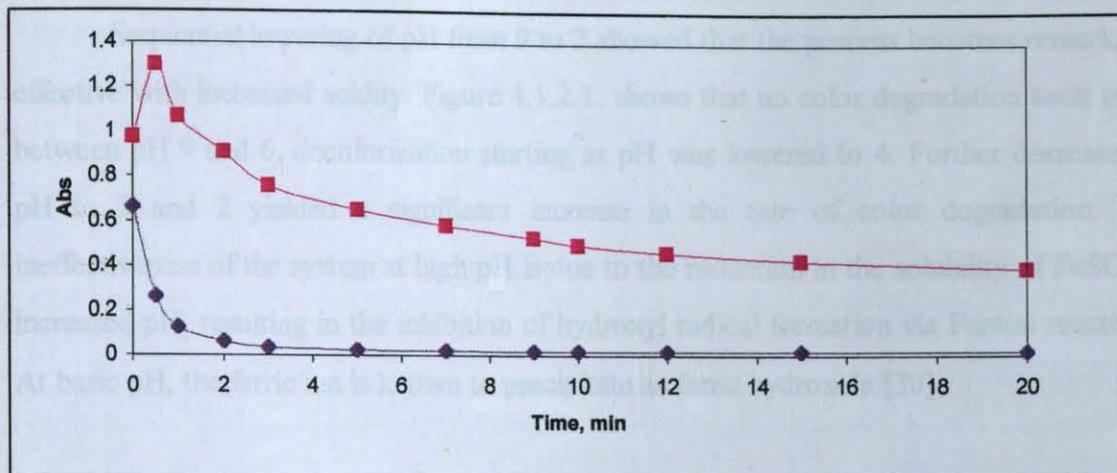


Figure 4.1.1.3. Comparison of Color and Aromatic Fragment Degradation under Treatment with UV/H₂O₂/Fe(II) for 20 min. Initial conditions were 33.3 mg/L pure dye, spiked with 0.0035 M H₂O₂, 0.00018 M Fe(II) at pH=3 and T=40°C.

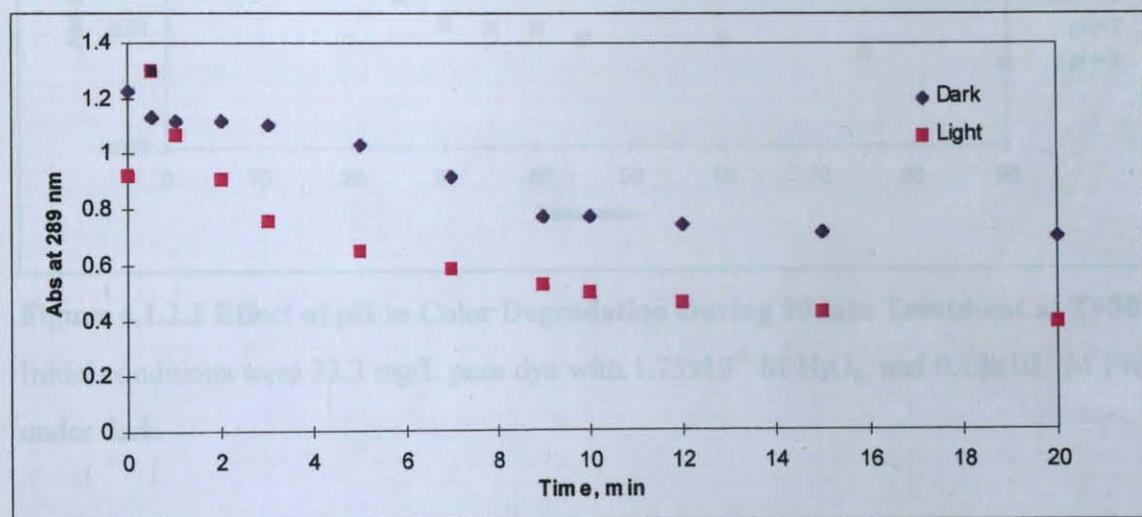


Figure 4.1.1.4. Comparison of Aromatic Fragment Degradation under Light and Dark Initial conditions were 33.3 mg/L pure dye spiked with 0.0035 M H₂O₂, 0.00018 M Fe(II) at pH=3 and T=40°C.

4.1.2. Selection of Optimum pH

The operating pH was selected with respect to the rate of color degradation, as determined by spectrophotometric analysis at 543.5 nm. It was found that the system when operated under alkali conditions and with H₂O₂/Fe(II) molar ratio of 10:1 was ineffective for color removal, both in the presence and absence of UV light.

Sequential lowering of pH from 9 to 2 showed that the process becomes remarkably effective with increased acidity. Figure 4.1.2.1. shows that no color degradation took place between pH 9 and 6, decolorization starting as pH was lowered to 4. Further decreases in pH to 3 and 2 yielded a significant increase in the rate of color degradation. The ineffectiveness of the system at high pH is due to the reduction in the solubility of FeSO_4 at increased pH, resulting in the inhibition of hydroxyl radical formation via Fenton reactions. At basic pH, the ferric ion is known to precipitate as ferric hydroxide [30].

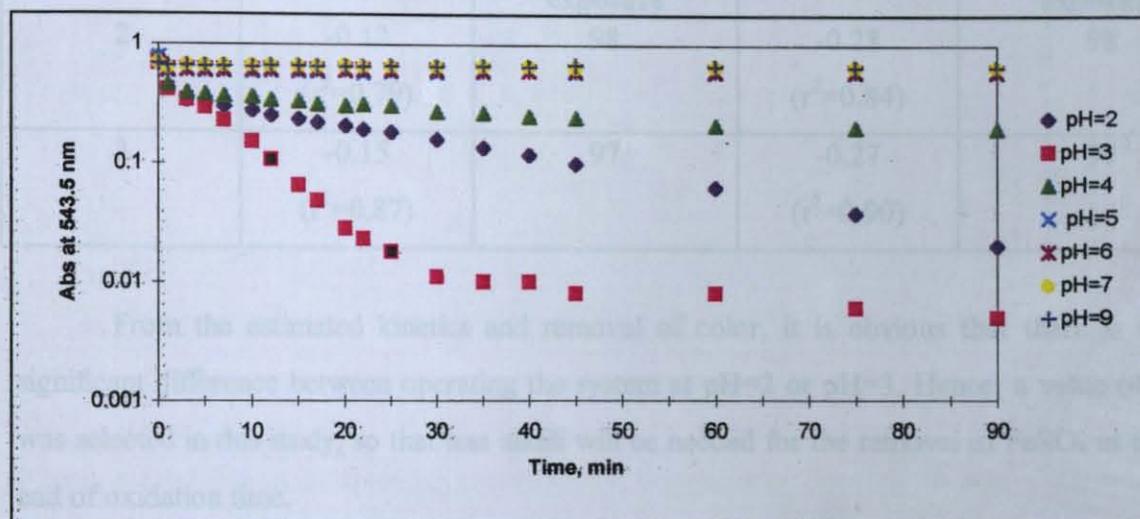


Figure 4.1.2.1 Effect of pH in Color Degradation During 90 min Treatment at $T=30^\circ\text{C}$ Initial conditions were 33.3 mg/L pure dye with 1.75×10^{-3} M H_2O_2 , and 0.18×10^{-3} M $\text{Fe}(\text{II})$ under dark.

In accordance with Figure 4.1.2.1., the operating pH range should lie between 2 and 3 for the treatment of dyebath effluents by FeSO_4 added chemical oxidation. To set a precise value, the relative effectiveness of pH 2 and 3 was investigated by monitoring color degradation at two different temperatures as shown in Figure 4.1.2.2. At a temperature of 30°C , pH=3 was more effective in color degradation than pH=2, but when the temperature was raised to 40°C , it was observed that a value of 2 for pH was more effective (Figure 4.1.2.2.).

Estimated first order color degradation rate constants, and total amount of color removed at the employed conditions are summarized in Table 4.1.2.1. The reported results

were obtained by regression analyses using the first 10 min data of treatment where degradation kinetics was linear.

Table 4.1.2.1. Comparison of First order Decolorization Rate Constants and Total Color Removal at Different Temperatures and pH

pH	T= 30 °C		T= 40 °C	
	k_{obs}, min^{-1}	% color removal after 90 min exposure	k_{obs}, min^{-1}	% color removal after 90 min exposure
2	-0.12 ($r^2=0.79$)	98	-0.28 ($r^2=0.84$)	98
3	-0.15 ($r^2=0.87$)	97	-0.27 ($r^2=0.90$)	97

From the estimated kinetics and removal of color, it is obvious that there is no significant difference between operating the system at pH=2 or pH=3. Hence, a value of 3 was selected in this study, so that less alkali will be needed for the removal of FeSO_4 at the end of oxidation time.

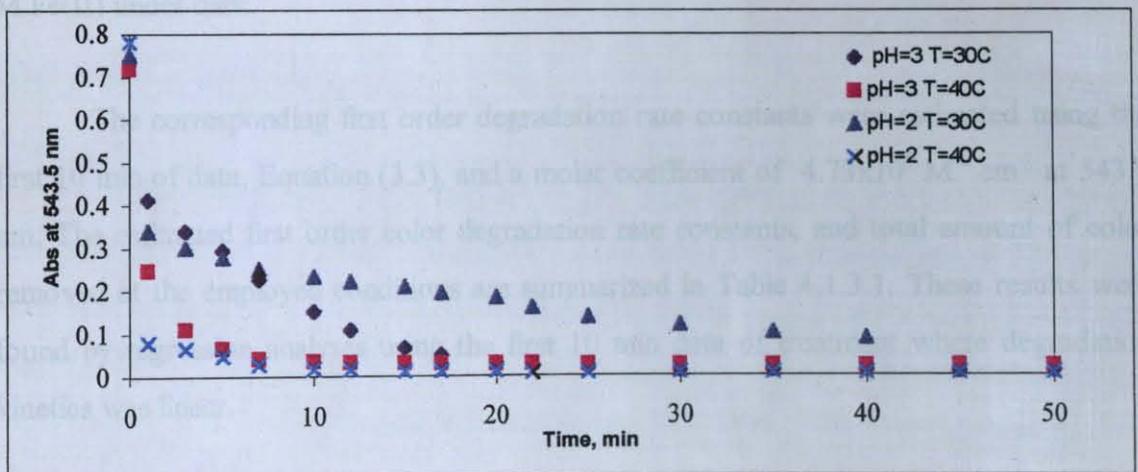


Figure 4.1.2.2. Effect of pH and Temperature in Color Degradation During 50 min Treatment Initial conditions were 33.3 mg/L pure dye with 1.75×10^{-3} M H_2O_2 , and 0.18×10^{-3} M Fe(II) under dark

4.1.3. Selection of Optimum Temperature

The selection of the operating temperature was based on the kinetics of the decolorization at the temperatures tested, namely 20 °C, 30 °C, and 40 °C. The results of this study are shown in Figure 4.1.3.1, where the temperature effect is as follows:

$$40\text{ }^{\circ}\text{C} > 30\text{ }^{\circ}\text{C} > 20\text{ }^{\circ}\text{C}$$

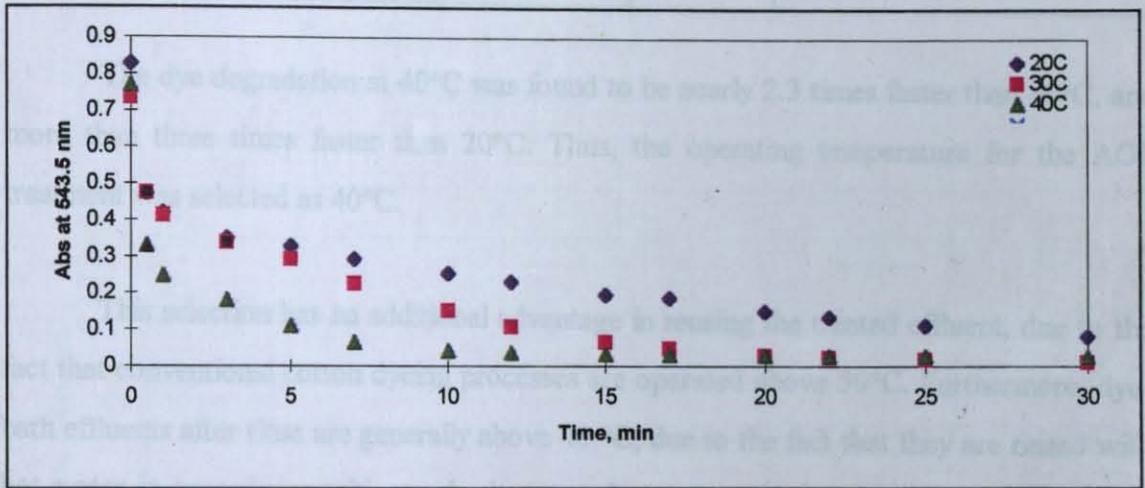


Figure 4.1.3.1 Effect of Temperature in Color Degradation During 30 min Treatment at pH=3 Initial conditions were 33.3 mg/L pure dye with 1.75×10^{-3} M H_2O_2 , and 0.18×10^{-3} M Fe(II) under dark.

4.1.4. Effect of UV Light

The corresponding first order degradation rate constants were estimated using the first 10 min of data, Equation (3.3), and a molar coefficient of $4.73 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 543.5 nm. The estimated first order color degradation rate constants, and total amount of color removed at the employed conditions are summarized in Table 4.1.3.1. These results were found by regression analyses using the first 10 min data of treatment where degradation kinetics was linear.

and (2.26).

Furthermore, the dye itself is expected to be degraded by direct photolysis in accordance with the mechanism previously proposed by Ince et al. [4]. H_2O_2 photolysis generates very reactive $\cdot\text{OH}$, which attack the dye molecules initiating their fast oxidation.

Table 4.1.3.1. Comparison of First order Decolorization Rate Constants and Total Color Removal at Different Temperatures

Temperature, °C	k_{obs} , min^{-1}	% color removal after 90 min exposure
20	-0.07 ($r^2=0.69$)	90
30	-0.15 ($r^2=0.87$)	97
40	-0.27 ($r^2=0.90$)	97

The dye degradation at 40°C was found to be nearly 2.3 times faster than 30°C, and more than three times faster than 20°C. Thus, the operating temperature for the AOP treatment was selected as 40°C.

This selection has an additional advantage in reusing the treated effluent, due to the fact that conventional cotton dyeing processes are operated above 50°C. Furthermore, dye-bath effluents after rinse are generally above 45 °C, due to the fact that they are rinsed with hot water in accordance with standard cotton dyeing procedure with reactive dyes. This means that heating is not required for treating these effluents by the AOP technique in this study.

4.1.4. Effect of UV Light

The Fenton process when catalyzed by UV light significantly enhanced the rate of color degradation. It was found that complete removal of color was possible in 20 min of irradiation, while same results were obtained after 90 min of dark reaction, other conditions being the same. This can be attributed to the fact that the photo-Fenton process is much more effective in terms of free radical formation reactions as was shown in Equation (2.25) and (2.26).

Furthermore, the dye itself is expected to be degraded by direct photolysis in accordance with the mechanism previously proposed by İnce et al [4]. H_2O_2 photolysis generates very reactive $\bullet\text{OH}$, which attack the dye molecules initiating their fast oxidation

to various intermediates, which eventually are mineralized. The direct photolysis of the dye also takes place, but the constant associated with this photochemical processes is very low ($k=0.023 \text{ min}^{-1}$). A simplified reaction scheme is the following [4] :

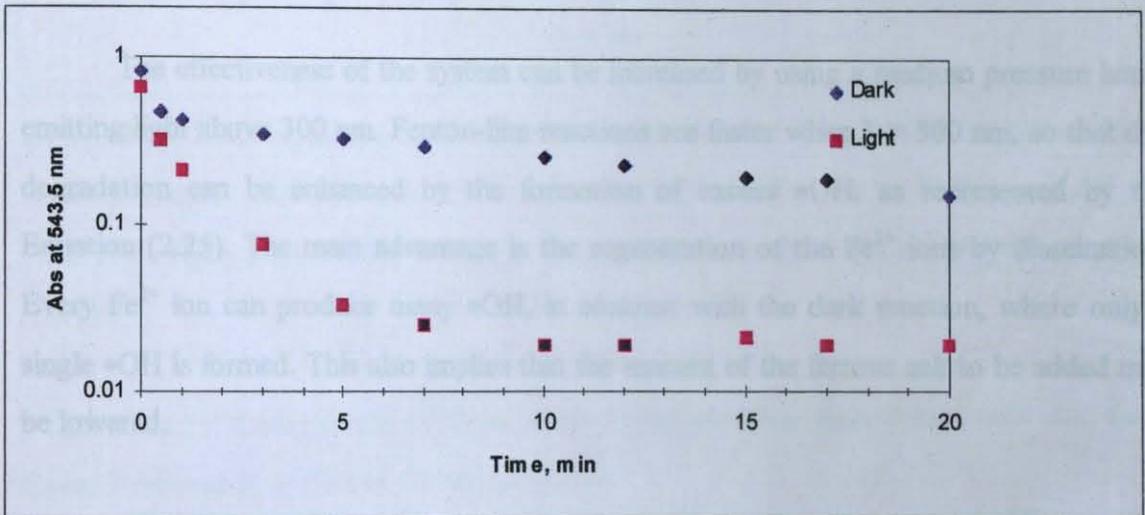


Figure 4.1.4.1 Effect of Light in Color Degradation During 20 min Treatment at pH=3, T=40 C Initial conditions were 33.3 mg/L pure dye spiked with $1.75 \times 10^{-3} \text{ M H}_2\text{O}_2$, and $0.18 \times 10^{-3} \text{ M Fe(II)}$ (10:1).

Comparison of decolorization rates with and without light is shown in Figure 4.1.4.1. The estimated first order color degradation rate constants, and total amount of color removed with or without UV light are summarized in Table 4.1.4.1. The results were found by regression analyses using the first 5 min data of treatment where degradation kinetics was linear.

Table 4.1.4.1. Comparison of First order Decolorization Rate Constants and Total Color Removal under Dark and Light Conditions

Condition	k_{obs} , min^{-1}	% color removal after 20 min exposure
Dark	-0.14 ($r^2=0.63$)	80
Light	-0.56 ($r^2=0.97$)	97

Decolorization under light conditions was found to be four times faster than the dark conditions. Thus, the UV catalyzed system was selected for treating the dye-bath effluents.

The effectiveness of the system can be increased by using a medium pressure lamp, emitting light above 300 nm. Fenton-like reactions are faster when $\lambda > 300$ nm, so that dye degradation can be enhanced by the formation of excess $\bullet\text{OH}$, as represented by the Equation (2.25). The main advantage is the regeneration of the Fe^{2+} ions by illumination. Every Fe^{2+} ion can produce many $\bullet\text{OH}$, in contrast with the dark reaction, where only a single $\bullet\text{OH}$ is formed. This also implies that the amount of the ferrous salt to be added may be lowered.

4.1.5. Effect of Reagent Dose

The selection of optimum reagent dose and ratio was based on the rate of color degradation at various H_2O_2 and FeSO_4 doses. These doses were set by increasing the concentration of H_2O_2 from its stoichiometric to twice the stoichiometric, and four times the stoichiometric requirements. The FeSO_4 dosage was kept constant at all times, because no significant advantage was obtained by its increase. Furthermore, the low level of FeSO_4 provided an advantage of lower dissolved solids in the effluent as TDS.

In accordance, the operating parameter for reagent dosing was selected as the molar ratio of H_2O_2 to FeSO_4 . The effect of three test ratios is shown in Figure 4.1.5.1. Estimated reaction rate constants at each of the tested ratios are presented in Table 4.1.5.1. These

results were found by regression analyses using the first 2.5 min data where degradation kinetics was linear.

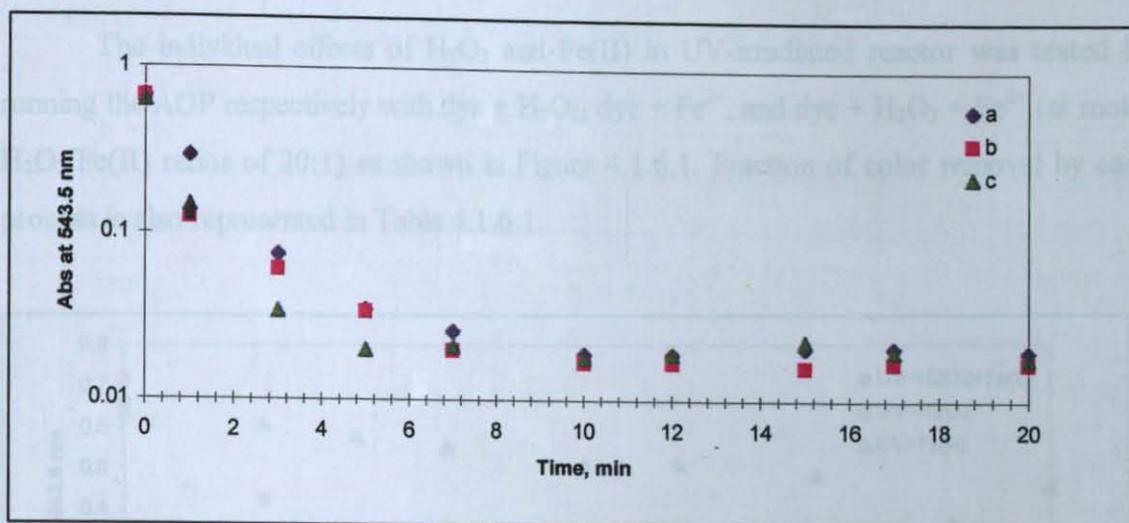


Figure 4.1.5.1. Comparison of Reagent Doses Under UV Irradiation Initial conditions were 33.3 mg/L pure dye spiked with a: 1.75×10^{-3} M H_2O_2 and 0.18×10^{-3} M Fe(II), b: 3.5×10^{-3} M H_2O_2 and 0.18×10^{-3} M Fe(II), c: 7×10^{-3} M H_2O_2 and 0.18×10^{-3} M Fe(II) at 40°C and $\text{pH}=3$.

Table 4.1.5.1. Comparison of First order Decolorization Rate Constants and Total Color Removal at Different Chemical Ratios

Molar Ratio of H_2O_2 to FeSO_4	$k_{\text{obs}}, \text{min}^{-1}$	% color removal after 20 min exposure
10:1	-0.71 ($r^2=0.91$)	97
20:1	-0.74 ($r^2=0.88$)	98
40:1	-1.06 ($r^2=0.84$)	97.1

Although the 40:1 molar ratio provides nearly 25% higher rate of dye degradation than the 20:1 ratio, the nearly complete color removal was observed both by 20:1 and 40:1 molar ratios. Hence, a 20:1 molar ratio was found sufficient as the operating reagent parameter. Further, this provided an economic advantage due to lower H_2O_2 consumption.

4.1.6. Comparison of the Photo-Fenton (UV+H₂O₂+Fe²⁺), UV/H₂O₂, and UV/Fe²⁺ Processes

The individual effects of H₂O₂ and Fe(II) in UV-irradiated reactor was tested by running the AOP respectively with dye + H₂O₂, dye + Fe²⁺, and dye + H₂O₂ + Fe²⁺ (at molar H₂O₂/Fe(II) ratios of 20:1) as shown in Figure 4.1.6.1. Fraction of color removal by each process is also represented in Table 4.1.6.1.

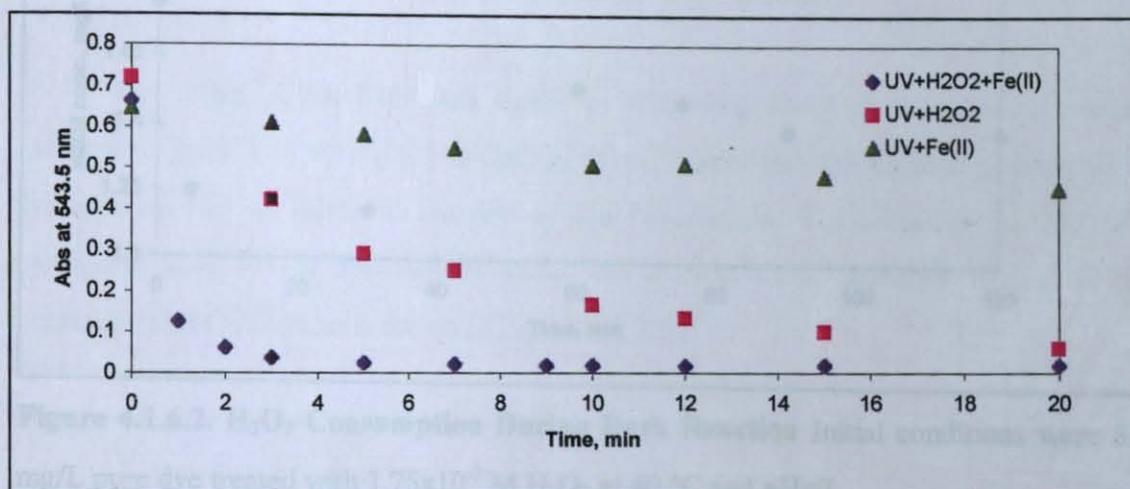


Figure 4.1.6.1. Color Degradation of Dye Solution with Fe(II), H₂O₂ and Both. Initial conditions were 33.3 mg/L pure dye spiked with 3.5×10^{-3} M H₂O₂, and 0.18×10^{-3} M Fe(II) at 40 °C and pH=3, under UV irradiation.

4.1.6. Table 4.1.6.1. Comparison of Color Removal Rates with Photo-Fenton, UV/H₂O₂, and UV/Fe²⁺ Processes

Process	% color removal after 20 min exposure
UV/Fe ²⁺	30
UV/H ₂ O ₂	90
Photo-Fenton	97

It is obvious from Figure 4.1.6.1. and Table 4.1.6.1. that the most effective AOP for treating dye-bath effluents is a UV-enhanced H₂O₂/Fe(II) process.

Hydrogen peroxide alone was not even half as effective, when the reaction was run in the absence of light, due to its slow rate of dissociation in the dark to generate hydroxyl radicals [2]. Total hydrogen depletion during 75 min exposure to the dark conditions at 40 °C and at pH 3 was about 5 per cent as presented in Figure 4.1.6.2.

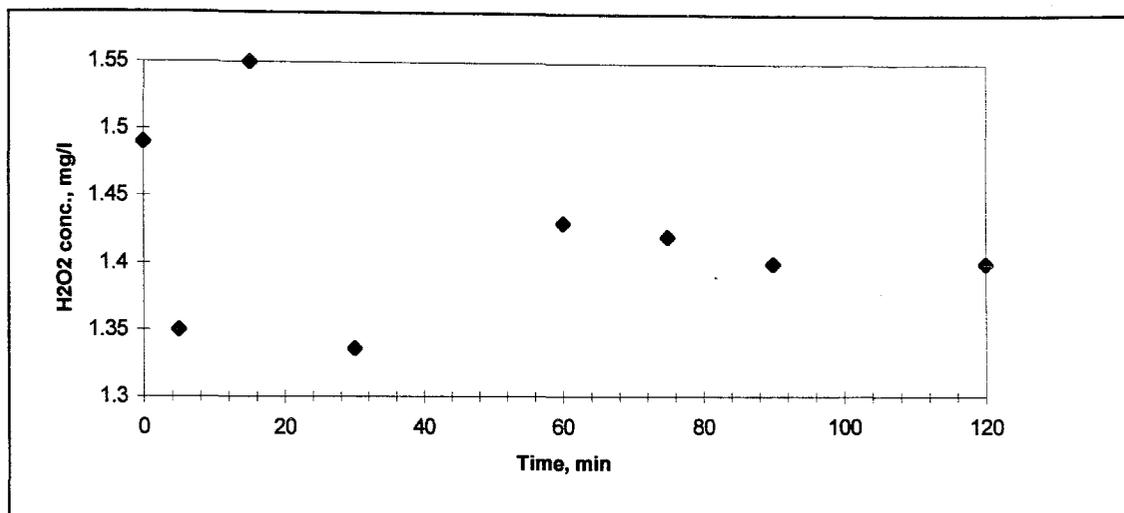


Figure 4.1.6.2. H₂O₂ Consumption During Dark Reaction Initial conditions were 33.3 mg/L pure dye treated with 1.75×10^{-3} M H₂O₂ at 40 °C and pH=3.

The difference between the added and observed H₂O₂ concentration at time zero might be due to experimental errors during pipetting or immediate conversion of H₂O₂ to water in the absence of irradiation. The increase in H₂O₂ concentration between 30 min and 60 min may be due to H₂O₂ formation during the reaction represented by Equation(2.22). Total hydrogen depletion during 20 min exposure to the light enhanced oxidation at 40 °C and at pH 3 was about 96 per cent, and 90 per cent for the 20:1(M) and 40:1(M), H₂O₂/Fe(II) ratios, respectively.

4.1.7. Effect of Alkalinity

The carbonate species HCO₃⁻ and CO₃²⁻, are expected to affect the photolysis of H₂O₂ in aqueous solution through various pathways [48]. Both species are known as •OH scavengers, and hence their presence may cause a significant reduction in the oxidation rate of the target contaminants by lowering the amount of available radicals as [13] :

Table 4.1.7.1. Effect of Carbonate Alkalinity on First order Decomposition Rate Constants and Total Color Removal

Dye Solution	$\bullet\text{OH} + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \bullet\text{CO}_3^-$	(4.6)
in distilled water	$\bullet\text{OH} + \text{CO}_3^{2-} \rightarrow \text{HO}^- + \bullet\text{CO}_3^-$	(4.7)

Although, the generated carbonate radical anion has been shown to be an oxidant itself, its oxidation potential is much lower than that of the $\bullet\text{OH}$ radicals. Hence, in large scale treatment operations, the presence of carbonate alkalinity (due to use of ground water or municipal supply) can lower the efficiency of the AOP system.

The effect of alkalinity was tested by dissolving the dye in tap water, with a carbonate alkalinity of 90 mg L^{-1} as CaCO_3 . It was found that the alkaline quantity of the dye solution had no effect on the rate of dye degradation. The reduction in the visible absorption band of the dye-distilled water and dye-tap water solutions during 20 min treatment with UV/Fenton is shown in Figure 4.1.7.1.

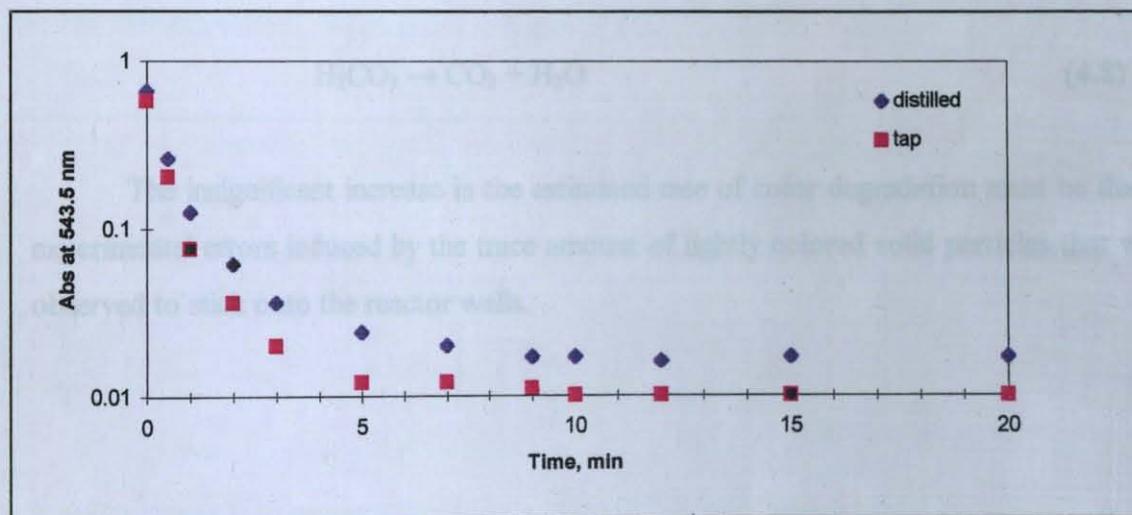


Figure 4.1.7.1. Effect of Alkalinity in Color Degradation Initial conditions were 33.3 mg/L pure dye spiked with $3.5 \times 10^{-3} \text{ M H}_2\text{O}_2$, and $0.18 \times 10^{-3} \text{ M Fe(II)}$ (20:1 molar ratio) at 40°C and $\text{pH}=3$, under UV irradiation.

First order color degradation rate constants, and total amount of color removed at the employed conditions were estimated and summarized in Table 4.1.7.1. (Reported values were found by regression analyses using the first 5 min data where degradation kinetics was linear).

Table 4.1.7.1. Effect of Carbonate Alkalinity on First order Decolorization Rate Constants and Total Color Removal

Dye Solution	k_{obs} , min^{-1}	% color removal after 20 min exposure
in distilled water	-0.62 ($r^2=0.85$)	97.5
in tap water	-0.72 ($r^2=0.85$)	98.0

The total amount of color removed in both dye solutions were nearly the same, 98 per cent and 97.5 per cent, respectively as shown in Table 4.1.7.1. Degradation was found to be only 1.1 times faster in the dye-tap water solution than the dye-distilled water solution. The unaffected performance of the system in a dye-tap water containing carbonate alkalinity is due to the low operating pH (pH=3), at which carbonates are destroyed so that hydroxyl radical scavenging reactions are prevented. This is due to the fact that at low pH, all carbonates are in the form of carbonic acids, and at elevated temperatures, they are liberated as CO_2 :



The insignificant increase in the estimated rate of color degradation must be due to experimental errors induced by the trace amount of lightly colored solid particles that were observed to stick onto the reactor walls.

4.2. System Evaluation for a Real Dye-Bath Effluent from a Dyeing/Finishing Textile Plant

After the selection of operating parameters, the AOP system with UV irradiation was applied on a real dyebath effluent, obtained from a cotton batch dyeing process before rinse. Sample preparation involved proper dilution to simulate rinsing conditions and pH adjustment, as previously described in Section 3.2.2. Temperature of the diluted effluent was raised to 40 °C by an electrical heater. This is required only under laboratory condition, because dilution was made with tap water at 23 °C. On site treatment in the dye house will receive influents at approximately 45 °C due to warm rinsing at $T > 50$ °C, a the requirements of the standard cotton-dyeing procedures.

The effect of chemical ratio and pH in color degradation during 20 min treatment of the real dyebath effluent is presented in Figure 4.2.1.

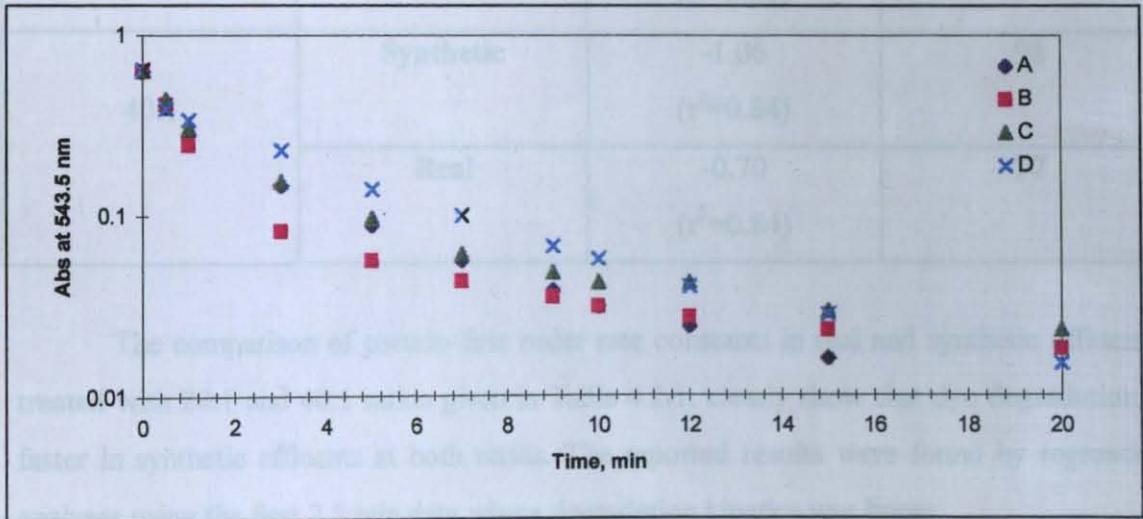


Figure 4.2.1. Effect of Chemical Ratio and pH in Color Degradation of Real Dyebath Effluents under UV irradiation. Initial conditions were: A= 33.3 mg/L dye, $T=40^{\circ}\text{C}$, $\text{pH}=2$, 40:1(M/M), B= 33.3 mg/L dye, $T=40^{\circ}\text{C}$, $\text{pH}=3$, 40:1(M/M), C= 33.3 mg/L dye., $T=40^{\circ}\text{C}$, $\text{pH}=3$, 20:1(M/M), D= 33.3 mg/L dye., $T=40^{\circ}\text{C}$, $\text{pH}=2$, 20:1(M/M)

Total color removal at the 40:1 ratio was 98.7 per cent and 97 per cent at $\text{pH} = 2$ and $\text{pH} = 3$, respectively. Fraction of color removal was slightly decreased when the H_2O_2

dosage was lowered, or the chemical ratio was reduced to 20:1 ratio, ending in 96 per cent and 97.6 per cent removal for pH = 2 and 3, respectively. These observations made it clear that any value of pH between 2 and 3 would be used, while the selection of a 40:1 chemical ratio might be more appropriate for treating real dyebath effluents. The investigation of pseudo-first order rate constants revealed also that the degradation is much faster when the H₂O₂ dosage is doubled as given in Table 4.2.1. Reported results in Table 4.2.1. were found by regression analyses using the first 2.5 min data of treatment where degradation kinetics was linear.

Table 4.2.1. Comparison of First Order Decolorization Rate Constants and Total Color Removal for Real and Synthetic Effluents, Treated with 20:1 and 40:1 H₂O₂/FeSO₄

Molar ratio of H ₂ O ₂ to FeSO ₄	Type of Effluent	k _{obs} , min ⁻¹	% color removal after 20 min exposure
20:1	Synthetic	-0.74 (r ² =0.88)	97
	Real	-0.48 (r ² =0.89)	94
40:1	Synthetic	-1.06 (r ² =0.84)	98
	Real	-0.70 (r ² =0.84)	97

The comparison of pseudo-first order rate constants in real and synthetic effluents, treated with 20:1 and 40:1 ratios given in Table 4.2.1. clearly show that dye degradation is faster in synthetic effluents at both ratios. The reported results were found by regression analyses using the first 2.5 min data where degradation kinetics was linear.

This implies that there are hydroxyl radical scavengers in real effluents, or mechanisms that interfere or inhibit radical formation reactions. Furthermore, the slower rate of dye degradation might be due to sources of H₂O₂ consumption that lower its photodissociation rate.

The very high concentration of carbonate alkalinity in the effluent is an obvious source of $\bullet\text{OH}$ scavengers. Further, the extended use of acetic acid in the dye-house for pH adjustment is a clear indication of scavenging reactions, for acetic acid is reported to reduce quantum yields in photoreactions by extinguishing the chain reactions of H_2O_2 photolysis [48].

As a result, a higher H_2O_2 dosage should be used for treating real dye-bath effluents, so that the previously selected 20:1 molar $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio was replaced by the 40:1 ratio.

4.3. Total Organic Carbon Removal

For the development of effective wastewater treatment methods, complete degradation of the contaminants to harmless end products (CO_2) and inorganic salts (Cl^-) is important in most cases. Therefore, monitoring of total organic carbon, during the reaction is essential to determine the degree of completeness of mineralization of the organic carbon. It was observed that when any of the reagents is omitted from the oxidation scheme, the system becomes ineffective for TOC removal. (This was also true for color removal, as discussed in Section 4.1.6.)

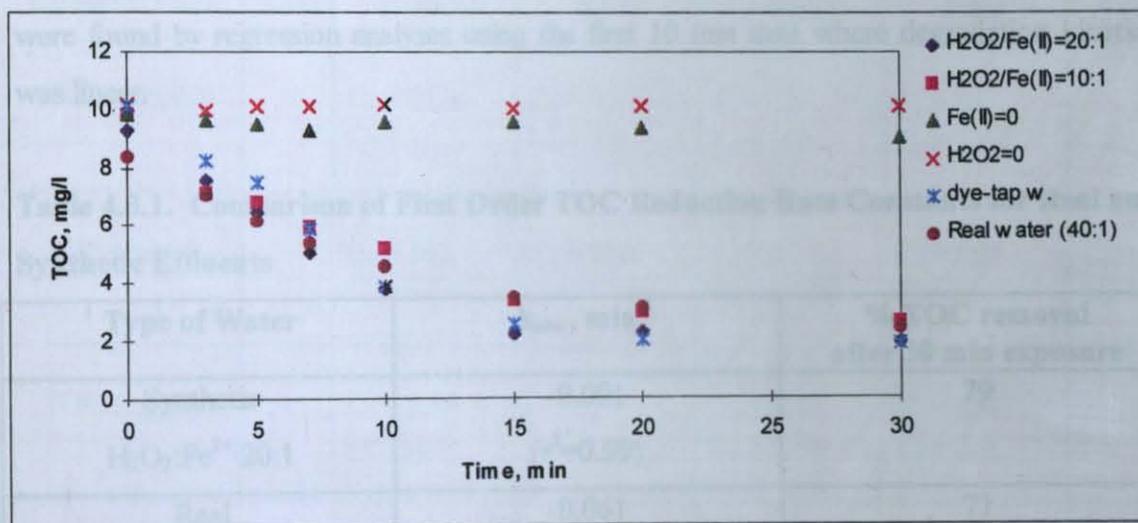


Figure 4.3.1. Rate of Organic Carbon Mineralization During 30 min Irradiation at Various Options of the AOP System Initial conditions were 33.3 mg/L pure dye spiked with 1.75×10^{-3} M, H_2O_2 3.50×10^{-3} M H_2O_2 , 7.0×10^{-3} M H_2O_2 (10:1, 20:1 and 40:1) and 0.18×10^{-3} M Fe(II) at 40C and pH=3

The rate of dye mineralization was monitored along with operating parameter selection as shown in Figure 4.3.1. Two different molar ratios, 20:1 and 10:1 $\text{H}_2\text{O}_2/\text{Fe(II)}$, were carried out and the 20:1 $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio was found to be more effective than the 10:1 ratio. After 30 min treatment under UV irradiation, 79 per cent, and 72 per cent TOC degradation were determined for 20:1 and 10:1 $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratios, respectively. The 20:1

ratio which was previously stated as the optimal chemical ratio for decolorization, was also found as the optimum chemical ratio for TOC degradation.

Total organic carbon removal was 79 per cent and 71 per cent for synthetic and real dyebath effluents, respectively. Although the optimum chemical ratio for the treatment of real dyebath effluent was twice the synthetic dyebath effluent's chemical ratio (40:1 and 20:1 $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$), the fraction of TOC removal was lower.

The comparison of pseudo-first order rate constants for TOC degradation in real and synthetic effluents, treated with 20:1 and 40:1 ratios, respectively are given in Table 4.3.1. It is obvious from the table that TOC removal for synthetic effluents is about 1.5 times faster than that in the real effluents. This again must be the result of the more complex character of the real effluents, inducing radical scavenging reactions. The reported results were found by regression analyses using the first 10 min data where degradation kinetics was linear.

Table 4.3.1. Comparison of First Order TOC Reduction Rate Constants for Real and Synthetic Effluents

Type of Water	k_{obs} , min^{-1}	% TOC removal after 30 min exposure
Synthetic $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ 20:1	-0.091 ($r^2=0.99$)	79
Real $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ 40:1	-0.061 ($r^2=0.99$)	71

4.4. Total Dissolved Solids and Chemical Oxygen Demand

The dissolved solids content of the effluent samples during the course of treatment were observed to increase (both in synthetic and real effluents). The changes in TDS and COD along with dye concentration upon 20 min treatment with various H_2O_2 dosages are reported in Table 4.4.1.

Table 4.4.1. COD, Dye, TOC and TDS Reduction During UV/ H_2O_2 /Fe²⁺ Treatment of Synthetic and Real Rinse Water

Contaminant Concentration	10: 1		20: 1		40: 1	
	Real	Synthetic	Real	Synthetic	Real	Synthetic
COD (mg/L)	-	$C_o = 29.9$ $C_f = 19.2$	$C_o = 22$ $C_f = 9.6$	$C_o = 26$ $C_f = 9.2$	$C_o = 21$ $C_f = 13.7$	-
TDS (mg/L)	-	$C_o = 162$ $C_f = 672$	$C_o = 930$ $C_f = 1255$	$C_o = 177$ $C_f = 787$	$C_o = 921$ $C_f = 1265$	$C_o = 183$ $C_f = 917$
TOC (mg/L)	-	$C_o = 9.86$ $C_f = 2.66$	-	$C_o = 9.31$ $C_f = 1.94$	$C_o = 8.4$ $C_f = 2.4$	-
DYE (mol/L)	-	$C_o = 1.4E^{-5}$ $C_f = 4.01E^{-7}$	$C_o = 1.36E^{-5}$ $C_f = 6.97E^{-7}$	$C_o = 1.44E^{-5}$ $C_f = 2.53E^{-7}$	$C_o = 1.35E^{-5}$ $C_f = 3.17E^{-7}$	$C_o = 1.32E^{-5}$ $C_f = 4.01E^{-7}$

In terms of color removal, almost all the tested H_2O_2 /Fe(II) ratios provided nearly the same reduction, differing however in their rates.

The amount of COD removal showed variations with respect to H_2O_2 dosage. The total COD removal with the 20:1 ratio was twice that of the 10:1 ratio in synthetic effluent. However, in real effluents, COD reduction was observed to decrease as H_2O_2 dosage was doubled from twice the stoichiometric requirement to 4 times the stoichiometric

requirement (from 20:1 to 40:1 as $\text{H}_2\text{O}_2/\text{FeSO}_4$). This can be attributed to the residual H_2O_2 at the end (in 40:1 ratio), which is known to exert a COD itself [49].

In terms of TDS, with all chemical test dosages, the concentration was observed to increase at the end of the 20 min exposure, which might be due to the formation of intermediate oxidation products and the presence of Fenton and Fenton-like residuals in solution.

4.5. Reuse of Treated Effluent in the Dye House

4.5.1. Cost of Reusing Dye-bath Effluents

The UV-Fenton treated real and synthetic effluents (by the 40:1 and 20:1 $H_2O_2/Fe(II)$ ratios) were used in a dye-house for coloring cotton fabrics, in four different shades. The shades were made by using three different azo dyes and a proper combination of all. The result of this process in terms of the color intensity and fixation of the dye is summarized in Table 4.5.1, and also given in Appendix .

A control was used with the operating process of the dye-house to compare with the performance of the reused water. The parameter ΔE in Table 4.5.1. refers to the color difference of the fabric from the control. Values of $\Delta E \leq 1$ are accepted when dyeing is operated by altering several of the standardized condition. When only one of such conditions is changed, such as the quality of the process water as in our case, $\Delta E \leq 0.5$ is acceptable [7]. All values in the table are below 0.5, implying that the quality of the treated effluent was satisfactory. Note also that ΔE is much smaller with the reused water treated by the 40:1 ratio.

Table 4.5.1. Reuse of Treated Effluent in the Dye-house

Process	Water	Reused Water								
		I			II			III		
Azo-dye	fabric	fabric	ΔE^*	result	fabric	ΔE	result	fabric	ΔE	result
Cr.HEXL 2%			0.376	Pass		0.408	Pass		0.311	Pass
HE4R 2%			0.135	Pass		0.366	Pass		0.215	Pass
N.HEXL 2%			0.127	Pass		0.162	Pass		0.140	Pass
Mixture of three dyes			0.492	Pass		0.498	Pass		0.411	Pass

I : UV/ $H_2O_2/Fe(II)$ treated real dyebath effluent ($H_2O_2/ Fe(II)=40:1(M/M)$)

II : UV/ $H_2O_2/Fe(II)$ treated real dyebath effluent ($H_2O_2/ Fe(II)=20:1(M/M)$)

III : UV/ $H_2O_2/Fe(II)$ treated synthetic dyebath effluent ($H_2O_2/ Fe(II)=20:1(M/M)$)

4.6. Economic Evaluation

4.6.1. Cost of Reusing Dye-bath Effluents

Cost analysis is carried out for the real dye-bath effluent obtained from a textile company. Cost analysis of the AOP system is based on operating costs only. Unit costs for chemical reagents are based on technical grade prices, as paid by companies in İstanbul. Costs of electrical power and commercial water supply are obtained from the related institutions, and companies. Cost of heating the operating water in the dye house is obtained from their records as 0.66 USD/m³. All fixed unit costs used for the estimation are given below:

- 1) Electrical Energy = 0.055 USD/kWh
- 2) H₂O₂ = 0.20 USD/L
- 3) FeSO₄·7H₂O = 0.21 USD/L
- 4) NaOH = 0.15 USD/kg
- 5) H₂SO₄ = 0.18 USD/L
- 6) UV Lamps = 6 USD/60Wlamp (Lamp life = 1000 h radiation/60W lamp)

It was found that 97% of influent dye was removed in 20 min during batch operation with the UV/H₂O₂/Fe(II) molar ratio of 40:1 (Initial dye concentration = 1.79×10^{-5} M, V = 4 L, H₂O₂ = 7×10^{-3} M, Fe(II) = 0.18×10^{-3} M). The electrical power consumption during the 20 min irradiation of the tank with four 15 W lamps (60 W) was estimated to be 0.02 kWh.

Operating costs are calculated on the basis of 1 batch of treated dye-bath effluent using the above parameters, and total cost is found by summing up all individual cost items and converting them to USD per cubic meter of dye-bath.

NET OPEARTING COST = cost of consumables + cost of electricity

cost of consumables/batch:

- Cost of H_2O_2 /batch = $2.85 \text{ ml/batch} \times 0.20 \text{ USD/L} \times \text{L}/10^3 \text{ ml} = 0.57 \times 10^{-3} \text{ USD/batch}$
- Cost of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /batch = $0.195 \text{ g/batch} \times 0.21 \text{ USD/kg} \times \text{kg}/10^3 \text{ g} = 4 \times 10^{-5} \text{ USD/batch}$
- Cost of NaOH /batch = $2.4 \text{ g/batch} \times 0.15 \text{ USD/kg} \times \text{kg}/10^3 \text{ g} = 0.36 \times 10^{-3} \text{ USD/batch}$
(for pH adjustment during treatment)
- Cost of NaOH /batch = $3.1 \text{ g/batch} \times 0.15 \text{ USD/kg} \times \text{kg}/10^3 \text{ g} = 0.46 \times 10^{-3} \text{ USD/batch}$
(for pH adjustment during coagulation/flocculation)
- Cost of H_2SO_4 /batch = $1.6 \text{ ml/batch} \times 0.18 \text{ USD/kg} \times \text{kg}/10^3 \text{ g} = 0.29 \times 10^{-3} \text{ USD/batch}$
- Cost of 60W UV irradiation/batch = $(6 \text{ USD/lamp}) / (3 \text{ batch/1h} \times 1000 \text{ h}) = 0.002 \text{ USD/batch}$

cost of electricity:

- Cost of electrical energy/batch (due to light)
= $(60\text{W} \times 10^{-3} \text{ kW/W} \times 20 \text{ min/batch} \times 1\text{h}/60 \text{ min}) \times 0.055 \text{ USD/kWh} = 1.1 \times 10^{-3} \text{ USD/batch}$
- Cost of electrical energy /batch (due to heating)

Cost of heating is based on the fact that 1 cal/ml is required for raising the temperature of a solution 1 °C. Raising the temperature from 25 °C to 40 °C in the 4 L tank requires : 15 cal/ml \times 4000 ml/L = 60 kcal/batch. This is equivalent to 0.063 kWh of energy.

- Cost of electrical energy /batch (due to heating)
= $0.055 \text{ USD/kWh} \times 0.063 \text{ kWh/batch} = 3.8 \times 10^{-3} \text{ USD/batch}$

$$\begin{aligned} \text{Net Operating Cost} &= 0.57 \times 10^{-3} \text{ USD/batch} + 4 \times 10^{-5} \text{ USD/batch} + 0.36 \times 10^{-3} \text{ USD/batch} + \\ &0.002 \text{ USD/batch} + 1.1 \times 10^{-3} \text{ USD/batch} + 3.8 \times 10^{-3} \text{ USD/batch} + 0.46 \times 10^{-3} \text{ USD/batch} + \\ &0.29 \times 10^{-3} \text{ USD/batch} = 8.62 \times 10^{-3} \text{ USD/batch} \times \text{batch}/4\text{L} \times \text{L}/10^{-3} \text{ m}^3 \\ &= 2.15 \text{ USD/m}^3 \end{aligned}$$

The above value is valid only in laboratory conditions, where the effluent was electrically heated. In on site treatment, there will be no such cost item, for the fact that, the treatment system will receive the dye-bath effluents at above 40 °C. In that case, total cost may be accepted as that without electrical heating costs, that is:

Net Operating Cost = 1.21 USD/m³.

Cost of heating should also be considered for the reuse of treated effluents. Cost of heating is based on the fact that 1 cal/ml is required for raising the temperature of a solution 1 °C. Raising the temperature from 40 °C (treated effluent's temperature) to 60 °C requires: 20 kcal/L. Cost of heating the operating water in the dye house is obtained from the industry's records as:

$$\frac{20000 \text{ kcal / L}}{600 \text{ kcal / kgsteam}} \times 0.01 \text{ USD / kgsteam} = 0.33 \text{ USD/m}^3$$

Net Operating Cost = 1.21 USD/m³ + 0.33 USD/m³ = **1.54 USD/m³**

4.6.2. Cost of Using Commercial Water Supply

The dye house purchases its water from a commercial supply sources, but has to use the ISKI discharge rates, because it discharges its wastewater to the sewage system.

Cost of water consumption in a dye-house where a commercial water supply is used, is calculated as follows:

$$\begin{aligned} \text{Cost of Process Water} &= \text{Raw Water Cost} + \text{Water Softening Cost} + \text{Heating Cost} + \\ &\text{Wastewater Treatment Cost} + \text{ISKI Discharge Water Cost} = 0.73 \text{ USD/m}^3 + 0.11 \text{ USD/m}^3 \\ &+ 0.66 \text{ USD/m}^3 + 0.19 \text{ USD/m}^3 + 0.73 \text{ USD/m}^3 = \mathbf{2.42 \text{ USD/m}^3} \end{aligned}$$

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of the study was to investigate the reusability of cotton dye-bath effluents, exposed to an AOP system involving hydrogen peroxide and ferrous sulfate ($\text{H}_2\text{O}_2/\text{FeSO}_4$), in the presence and absence of UV-light. System performance was investigated by monitoring the reduction in color, total organic carbon, and total dissolved solids.

The results of the study are summarized below:

1. Decolorization and TOC reduction for the Fenton and photo-Fenton reactions were greatly affected by pH and took place only in acidic medium. The operating pH of the treatment processes was selected as 3.

2. It was observed that increasing the reaction temperature to 40 °C accelerated the color removal rate. The operating temperature was selected as 40 °C. This selection has an additional advantage in reusing, onsite treated effluents due to the fact that conventional cotton dyeing processes are operated above 50 °C.

3. Experiments showed that UV-C light irradiation improved the effectiveness of the $\text{H}_2\text{O}_2/\text{Fe(II)}$ system significantly for color degradation. It was found that nearly complete color removal was possible in 20 min irradiation while same results were obtained after 90 min dark reaction, other conditions being the same. Decolorization under light conditions was found to be four times faster than the dark conditions.

4. The $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio was selected as 20:1 (M/M) for synthetic effluents, but a ratio of 40:1 for real dyebath effluents provided faster degradation and more satisfactory reuse quality.

5. The ferrous sulfate was removed from the solution by coagulation/flocculation followed by 1 hour of settling and the supernatant phase was separated as a final effluent for reuse purposes. The optimum pH for coagulation/flocculation was selected as 9.

6. Alkaline quantity (90 mg CaCO_3/L) of synthetically prepared dye-bath effluent had no adverse effect on the rate of dye degradation due to the low operating pH, at which carbonates are destroyed to a level where $\bullet\text{OH}$ scavenging is prevented.

7. It was found that 98 per cent color degradation and 79 per cent TOC reduction was possible under treatment with UV/ $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ at 20:1 (M/M), pH=3 and T=40 °C, for synthetic dye-bath effluent. 97 per cent color degradation and 71 per cent TOC reduction was possible under treatment with UV/ $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ at 40:1 (M/M), pH=3 and T=40 °C, for real dye- bath effluents.

8. Total dissolved solids contents of the synthetic and industrial dye-bath effluents were observed to increase upon treatment.

9. COD removal was two-fold enhanced in synthetic effluents with doubling the amount of H_2O_2 . This is not true for real effluents, as the $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio was increased to 20:1 to 40:1. This can be attributed to the residual H_2O_2 at the end (in 40:1 molar ratio), which is known to exert a COD itself.

10. The final effluent after removal of FeSO_4 , was reused in a cotton dyeing process in a dye house. The dyed fabric was well above the internationally acceptable color quality standards in terms of intensity and fixation.

11. Operational cost estimation of the proposed system for reusing real dye-bath effluents resulted in 1.54 USD/m³ when the cost of heating to 40 °C is excluded. The corresponding cost of using commercial water supply and discharging the waste to municipal sewage system was estimated to be 2.42 USD/m³.

5.2. Recommendations

1. The efficiency of the photo-Fenton process for treating dye-bath effluents can be increased by using a medium pressure halogen lamp which emits a wider spectrum of light, and a peak at around 300 nm. The expected efficiency increase at such irradiation is due to the discussion made earlier in Section 4.1.4., that in photo-Fenton processes at $\lambda \geq 300$ nm, the production of hydroxyl radicals is higher.

2. Although reuse of textile process effluents is known to require advanced solids removal technologies (such as membrane), it was shown in this study that this is not essential, when the treated water is used for cotton dyeing.

3. Alternatives of reducing the estimated operating cost of the UV-enhanced AOP system must be investigated by reusing the effluents of dark reaction, as well as the effluent of 5, 10, and 15 min treated samples by the UV-enhanced system.

APPENDIX

d: KALITE/~CR.HEXL İŞLETME SUYU
 KALITE/~CR.HEXL ARITILMIŞ SU (20/1)
 : CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

obs.	ΔL	ΔC	ΔH	ΔE	
	0.144	-0.106	-0.367	0.408	PASS Lighter Wr Br (Gr)
	0.124	-0.077	-0.404	0.429	PASS Lighter Wr Rr (Br)

d: KALITE/~CR.HEXL İŞLETME SUYU
 KALITE/~CR.HEXL ARITILMIŞ SU (40/1)
 : CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

obs.	ΔL	ΔC	ΔH	ΔE	
	-0.035	-0.209	-0.311	0.376	PASS Darker Wr Br (Gr)
	0.008	-0.092	-0.260	0.276	PASS Lighter Wr Rr (Br)

d: KALITE/~CR.HEXL İŞLETME SUYU
 KALITE/~CR.HEXL ARITILMIŞ SU (LAB 20/1)
 : CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

obs.	ΔL	ΔC	ΔH	ΔE	
	0.003	-0.104	-0.293	0.311	PASS Lighter Wr Br (Gr)
	-0.032	-0.120	-0.348	0.370	PASS Darker Wr Rr (Br)

: KALITE/~İŞLETME SUYU
 KALITE/~ARITILMIŞ SU (20/1)
 CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

bs.	ΔL	ΔC	ΔH	ΔE
	0.071	-0.255	0.253	0.366
	0.064	-0.268	0.350	0.445

PASS Lighter Wr Yr (Gr)
 PASS Lighter Wr Yr (Gr)

: KALITE/~İŞLETME SUYU
 KALITE/~ARITILMIŞ SU (40/1)
 CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

bs.	ΔL	ΔC	ΔH	ΔE
	0.079	-0.106	0.028	0.135
	0.073	-0.120	0.086	0.165

PASS Lighter Wr Yr (Gr)
 PASS Lighter Wr Yr (Gr)

: KALITE/~İŞLETME SUYU
 KALITE/~ARITILMIŞ SU (LAB 20/1)
 CMC(2.0:1)

LAV::SCI::UVC 100 %
 LAV::SCI::UVC 100 %

bs.	ΔL	ΔC	ΔH	ΔE
	0.059	-0.121	0.168	0.215
	0.050	-0.114	0.172	0.212

PASS Lighter Wr Yr (Gr)
 PASS Lighter Wr Yr (Gr)

rd: KALITE/~N.HEXL İŞLETME SUYU LAV::SCI::UVC 100 %
 KALITE/~N.HEXL ARITILMIŞ SU (20/1) LAV::SCI::UVC 100 %
 a: CMC(2.0:1)
 /obs. ΔL ΔC ΔH ΔE
 0.103 0.029 -0.121 0.162 PASS Lighter Sr Gr (Yr)
 0.103 0.034 -0.107 0.152 PASS Lighter Sr Gr (Yr)

rd: KALITE/~N.HEXL İŞLETME SUYU LAV::SCI::UVC 100 %
 KALITE/~N.HEXL ARITILMIŞ SU (40/1) LAV::SCI::UVC 100 %
 a: CMC(2.0:1)
 /obs. ΔL ΔC ΔH ΔE
 0.114 0.008 -0.056 0.127 PASS Lighter Sr Gr (Yr)
 0.125 -0.002 -0.063 0.140 PASS Lighter Wr Gr (Yr)

rd: KALITE/~N.HEXL İŞLETME SUYU LAV::SCI::UVC 100 %
 KALITE/~N.HEXL ARITILMIŞ SU (LAB 20/1) LAV::SCI::UVC 100 %
 a: CMC(2.0:1)
 /obs. ΔL ΔC ΔH ΔE
 -0.094 -0.009 -0.104 0.140 PASS Darker Wr Gr (Yr)
 -0.101 -0.019 -0.064 0.121 PASS Darker Wr Gr (Yr)

ard: KALITE/~YEŞİL İŞLETME SUYU					LAV::SCI::UVC 100 %
: KALITE/~YEŞİL ARITILMIŞ SU (20/1)					LAV::SCI::UVC 100 %
la: CMC(2.0:1)					
s/obs.	ΔL	ΔC	ΔH	ΔE	
0	0.218	0.084	0.440	0.498	PASS Lighter Sr Gr (Br)
0	0.209	0.078	0.398	0.456	PASS Lighter Sr Gr (Br)

ard: KALITE/~YEŞİL İŞLETME SUYU					LAV::SCI::UVC 100 %
: KALITE/~YEŞİL ARITILMIŞ SU (40/1)					LAV::SCI::UVC 100 %
la: CMC(2.0:1)					
s/obs.	ΔL	ΔC	ΔH	ΔE	
0	0.043	0.155	0.466	0.492	PASS Lighter Sr Gr (Br)
0	0.039	0.151	0.448	0.475	PASS Lighter Sr Gr (Br)

ard: KALITE/~YEŞİL İŞLETME SUYU					LAV::SCI::UVC 100 %
: KALITE/~YEŞİL ARITILMIŞ SU (LAB 20/1)					LAV::SCI::UVC 100 %
la: CMC(2.0:1)					
s/obs.	ΔL	ΔC	ΔH	ΔE	
0	0.287	0.055	0.289	0.411	PASS Lighter Sr Gr (Br)
0	0.277	0.032	0.194	0.339	PASS Lighter Sr Gr (Br)

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