FATİH UNIVERSITY

The Graduate School of Sciences and Engineering

Master of Science in
Environmental Engineering

APPLICABILITY OF ADVANCED OXIDATION PROCESSES FOR THE DECOLORIZATION OF TEXTILE WASTEWATER

by

Yüsra TANRISEVEN ALTUN

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M.S.
2013

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A thesis submitted to

the Graduate School of Sciences and Engineering

of

Fatih University

in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

January 2013
Istanbul, Turkey

APPROVAL PAGE

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APPLICABILITY OF ADVANCED OXIDATION PROCESSES FOR THE DECOLORIZATION OF TEXTILE WASTEWATER

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M.S Thesis – Environmental Engineering
January 2013

Supervisor: Assoc. Prof. Dr. Gökçe TEZCANLI GÜYER

ABSTRACT

The failure of water treatment processes of industrial complexes and factories to an environmentally friend level always brings up severe ecological problems. This pollution does not affect only the hydrological resources but has complex effects on the food chain at its all levels. Because many of the industrial waste waters contain highly toxic contaminants that become very active and lethal when dissolved in water. To bring this contamination to an end it is very important for the factories to have their own water treatment facilities that use modern technologies. Advanced oxidation processes hold great promise to provide alternative for better treatment and protection of environment. In the present study, the treatment efficiency of selected, well-known advanced oxidation processes (Photo-Fenton, Ozone, Ultrasound, UV, and H_2O_2) was examined for the decolorization and detoxification of textile wastewater. This has been based upon a study to the water treatment processes of the wastewaters both chemically and using advanced oxidizing techniques.

In this study several of advanced oxidation processes (O_3, O_3/UV, O_3/H_2O_2, O_3/H_2O_2/UV, UV/H_2O_2, UV/H_2O_2/Fe^{+2}, H_2O_2/Fe^{+2}, US, US/UV, US/O_3) used for the Post-treatment to eliminate color, remove the COD, TOC and toxicity from textile industry effluent. Kinetic analyses indicated that the decolorization rates of textile effluent could be approximated as pseudo-first-order kinetics for oxidation processes. And finally, economic analysis conducted for each studied oxidation processes. In UV/H_2O_2 process several H_2O_2 concentrations (5 mM, 10 mM, 25 mM, 50 mM, 100 mM) was applied the wastewater in the presence of 40W UV-C light.

The optimum concentration was observed in 25 mM H_2O_2 concentration at pH 7,6. This process showed 93% color removal in 30 minutes. The evaluation of treatment efficiency was made using the parameters of oxygen demand (COD), total organic carbon (TOC), color absorbances at 436 nm, 525 nm and 620 nm for RES method and 465 nm for Pt-Co method. Finally Vibrio fisheri was monitored for toxicity. For photo-Fenton experiments different Ferrous concentrations (0,05 mM, 0,1 mM, 1 mM and 2,5 mM) was used with 25 mM H_2O_2 concentration for treatment in the presence of 40W UV-C light at pH 3. The decolorization percentage of textile wastewater began to decrease when the concentration of Fe^{+2} was higher than 1 mM. This process resulted in 85% color and 87% TOC and 79% COD removal. In dark Fenton process 25 mM H_2O_2 was performed with 1 mM Fe^{+2} absence of UV light at pH 3. Dark-Fenton process showed 70% color removal. Addition of UV light to system was elevated the efficiency of treatment.

Ozonation experiments were conducted at various ozone doses (5, 15 25 mg/l). And different pH values (3, 7.6, 10) was applied to system for indicate the effect of pH on ozonation process. The result showed that 15 mg/l ozone dosage at natural pH of wastewater (7,6) is optimum for this system. As a result %99 color removal, %98 removal of the total organic carbon (TOC), and %77 COD removal had seen. Ozone-Alone treatment process showed no inhibition effect on *Vibrio fisheri* organism on toxicity. In O_3/H_2O_2 process, 15 mg/l ozone concentration and 25 mM H_2O_2 was applied to system. 98% color removal was observed. O_3/UV process was performed at 15 mg/l ozone dosage and 40W UV-C light. The application of this system resulted in 96% color removal. O_3/H_2O_2/UV process showed the best efficiency of this system with 15 mg/l ozone, 25 mM H_2O_2 and 40W UV-C light. 100% color, 99% TOC and 83% COD removal was obtained in this process after 120 min treatment.

In the case of Ultrasound oxidation, the decolorization were performed the one hour pre-aerated wastewater, at optimum conditions by using ultrasound at 860 kHz frequency. In US-Alone process the reaction was very slow and at the end of 120 min sonolysis period, no decolorization has been observed. Addition of UV had no effect on color removal. 15% and 2% color removal had seen in US-Alone and US/UV processes, respectively. The combination US and O_3 showed 98,6% color removal. The results showed that the combination of ozonation and sonolysis was a highly effective way to remove color from wastewater.

Cost evaluation for AOPs was based on electrical energy per order EE/O (that is the electrical energy required to re move a pollutant by one order of magnitude in one m_3 of wastewater) and calculated by the electrical consumption cost (Bolton, 1996).

The electrical energy requirements of the tested processes followed the increasing order O_3 < UV/H_2O_2/O_3 < O_3/H_2O_2 < O_3/UV < UV/H_2O_2/Fe^{+2} < UV/H_2O_2 < US/O_3. Estimated operational costs of O_3, UV/H_2O_2/O_3, O_3/H_2O_2, O_3/UV, UV/H_2O_2/Fe^{+2}, UV/H_2O_2 and US/O_3 processes for 0,070 €/m^3 cost of electrical consumption were 0.2 €/m^3, 0.47 €/m^3, 0.54 €/m^3, 0.58 €/m^3, 0.88 €/m^3, 1.70 €/m^3 and 1.77 €/m^3, respectively.

Keywords: Textile Industry Wastewater, Advanced Oxidation Processes, Ozonation, Decolorization, COD, TOC

TEKSTİL ATIKSULARININ RENK GİDERİMİNDE İLERİ OKSİDASYON TEKNİKLERİNİN UYGULANABİLİRLİĞİ

Yüsra TANRISEVEN ALTUN

Yüksek Lisans Tezi – Çevre Mühendisliği
Ocak 2013

Tez Danışmanı: Doç. Dr. Gökçe TEZCANLI GÜYER

ÖZ

Sanayi tesisleri ve fabrikaların çevreye uygun şekilde atık su arıtması ve deşarj başarısızlığı birçok ekolojik sorunları da beraberinde getirmektedir. Bu kirlilik sadece su kaynakları ile sınırlı kalmıyor aynı zamanda besin zincirine karışarak gıda kirliliğine giriyor. Endüstriyel atıksuların birçoğu sucul ortamda ve canlılarda birikir ve canlı dokusu üzerinde doğrudan toksik etkiler yapar. İleri oksidasyon proseslerinin daha iyi bir arıtım sağlayarak çevrenin korunması için çok iyi bir alternatif olduğu söylenebilir. Bu çalışmada ileri oksidasyon prosesleri kullanılarak tekstil atıksuyunun renk giderimi ve toksik madde içeriğindeki azalma incelenmiştir. Atıksu arıtım teknolojileri olarak ileri oksidasyon teknikleri ile beraber kimyasal analizlerin de uygulandığı bir çalışma olmuştur.

Bu çalışmanın amacı UV/H_2O_2, Foto-Fenton, sonoliz, ozonlama ve kombinasyonları kullanılarak tekstil endüstrisinin atıksuyunun renk gideriminde ileri oksidasyon proseslerinin verimliliği incelenmiştir. Renksizleştirme çalışmalarının yanında, toplam organik karbon (TOK), Kimyasal Oksijen İhtiyacı (KOİ) ve zehirlilik analizleri de yapılmıştır. Sonuç olarak giderimde uygulanan her oksidasyon tekniği için ekonomik analiz hesaplanmıştır.

Farklı konsantrasyonlarda (5 mM, 10 mM, 25 mM, 50 mM, 100 mM) H_2O_2, 40W UV ışığı varlığında atıksuya beslenmiştir. En yüksek giderim hızı 25 mM H_2O_2 varlığında olmakla beraber, deneyler atıksuyun 7,6 olan doğal pH'ında ve oda sıcaklığında yapılmıştır. 30 dakika içerisinde %93 renk giderimi gözlenmiştir. Foto-Fenton prosesleri optimum H_2O_2 konsantrasyonunda (25 mM), ve çeşitli demir konsantrasyonlarında (0,05 mM, 0,1 mM, 1 mM and 2,5 mM Fe^{+2} çözeltiler), UV ışıma varlığında pH 3'te gerçekleştirilmiştir. En yüksek renk giderme hızı sabiti ortama 1 mM Fe^{+2} ilave edildiğinde tespit edilmiştir. Arıtım sonucunda %85 renk giderimi, %87 TOK ve %KOİ giderimi gözlenmiştir. Karanlık Fenton prosesinde 25 mM H_2O_2, 1 mM Fe^{+2} ile pH 'te gerçekleşmiş olup %70 renk giderimi gözlenmiştir. Foto-Fenton prosesinde k değerleri (dk^{-1}) Karanlık Fenton prosesine göre daha büyük çıkmıştır. Karanlıkta yavaş ayrışma oranı nedeniyle, hidroksil radikal oluşumu azaltılmıştır. UV ışını, hidrojen peroksid ile tepkimeye girerek hidroksil iyon ve radikallarini üretip etkili bir biçimde Fenton reaksiyonunu desteklemiştir.

Optimum ozon dozunun tespiti amacıyla, farklı ozon konsantrasyonları (5, 15,25 mg/l), atıksuya beslenmiştir. Atıksuyun pH'I 3, 7.6 ve 10' a getirilerek pH'ın renk giderimine etkisini incelenmiştir. Giderim yüksek pH'ta (10) ve atıksuyun orjinal pH'ında (7.6) hemen hemen aynı olduğundan numunenin orjinal pH'ı ile çalışılmıştır. Optimum ozon konsantrasyou 15 mg/l olarak belirlenmiştir.İşletme maliyeti göz önünde bulundurularak 15 mg/l ozon konsantrasyonu yeterli görülmüştür. Sonuç olarak %99 renk, %98 TOK ve %77 KOİ giderimleri görülmüştür. Sadece ozonun kullanıldığı proseslerde sulardaki toksisitenin azaldığı görülmüştür. O_3/H_2O_2 prosesinde, 15 mg/l ozon dozu ve 25 mM H_2O_2 konsantrasyonu varlığında %98 renk giderimi gözlenmiştir. O_3/UV prosesinde, 40W UV ışığı varlığında 15 mg/l ozon atıksuya beslenmiştir ve %96 renk giderimi görülmüştür. O_3/H_2O_2/UV prosesi ise 15 mg/l ozon dozu, 25 mM H_2O_2 konsantrasyonu ve 40W UV ışığı varlığında %100 renk, %99 TOK ve %83 KOİ giderimi ile en iyi giderim verimlerine sahip olmuştur.

Bir saatlik havalandırılmış atıksu 860 khz ses üstü ışıma ile artılmıştır. Sadece ultrason kullanılan proseste 120 dakikalık sonikasyon süresince %20'lik renk giderimi olmuştur. Ultrason prosesine, 40W UV ışığı eklenmesi %15'lik renk giderimi ile sonuçlanmıştır. Ultrason sistemi ozon ile kombin edildiğinde ise %98,6'lık renk giderimi gözlenmiştir. Elde edilen sonuçlara göre O_3 ve sonikasyon kombinasyonunun renk giderimi için etkili bir yol olduğu görülmüştür.

İleri oksidasyon proseslerine ait enerji verimlerini karşılaştırabilmek için EE/O (elektrik enerjisi/derece) terimi kullanılmıştır. Bu terim 1 m^3 atıksuda bulunan kirletici maddenin konsantrasyonunu onda birine düşürmek için tüketilen elektrik enerjisi olarak tanımlanabilir (Bolton, 1996). İşletim maliyetleri ise elektrik enerjisi ile elektrik tüketim maliyeti kullanılarak hesaplanmıştır.

Uygulanan proseslerin elektrik enerji ihtiyaçları artış oranı sırasıyla: O_3 < $UV/H_2O_2/O_3$ < O_3/H_2O_2 < O_3/UV < $UV/H_2O_2/Fe^{+2}$ < UV/H_2O_2 < US/O_3. Uygulanan O_3, $UV/H_2O_2/O_3$, O_3/H_2O_2, O_3/UV, $UV/H_2O_2/Fe^{+2}$, UV/H_2O_2 ve US/O_3 prosesleri için 0,070 €/m^3 elektrik tüketim maliyeti ile hesaplanan işletim giderleri sırasıyla: 0.2 €/m^3, 0.47 €/m^3, 0.54 €/m^3, 0.58 €/m^3, 0.88 €/m^3, 1.70 €/m^3 and 1.77 €/m^3 olarak belirlenmiştir.

Anahtar Kelimeler: Tekstil Atıksuları, İleri oksidasyon prosesleri (İOP), Ozonlama, Renk giderimi, KOİ, TOK

I lovingly dedicate this thesis to my family, who supported me each step on the way

ACKNOWLEDGMENTS

First and foremost, I am heartily thankful to my supervisor, Assoc. Prof. Dr. Gökçe Tezcanlı Güyer, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. It has been a great pleasure for me to work under her supervision.

I am also greatful to the gratitude is extended to my committee members Prof. Dr. Mehmet Borat, Assist. Prof. Dr. Sami Gören, Assoc. Prof. Dr. Güven Kıymaz, Assist. Prof. Dr. Mustafa Petek for their contribution to this study and for their valuable recommendations.

I would also like to thank my dear friends; Abdulkadir Yıldız for his infinity assistance, Serkan Akkuş, Muhammed Karaosman, Ramazan Aydemir, Nihan Yıldız Doğan for their interest, help and encouragement during this study.

I sincerly wish to thank my dear sisters Şeyma Tanrıseven and Meysa Tanrıseven for their self-sacrifice and being near me whenever I needed. I am also thankful to their husbands Abdurrahman Tuna and Mehmet Ali Demiralp for their courteous support.

I would like to express my special thanks to my dear husband, Osman Altun, for his love, friendship, endless support to me and believing, relieving and trusting in me throughout my study and my life.

Last but not least, my greatest thanks go to my precious mother Dr. Yıldız Tanrıseven for her support and believe in me during all my life and my dear father Dr. Salah Tanrıseven for his kindness help, his guidance and sharing his limitless mind and opinions with me.

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SYMBOL/ABBREVIATION

A	Absorbance
AATCC	American Association of Textile Colorists and Chemists
AOP	Advanced Oxidation Process
atm	Atmosphere pressure
BOD	Biochemical Oxygen Demand
C°	Celsius
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
EC_{50}	Effective Concentration
EE/O	Electrical Energy per Order
EPA	Environmental Protection Agency
eV	Electron Volt
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulfuric Acid
$h\nu$	Ultraviolet irradiation
ISO	International Standards Organization
k	Kinetic Rate Constant
K°	Kelvin
kHz	Kilo Hertz
kWh	Kilo Watt Hour
mM	Millimolar
NaCl	Sodium Chloride
nM	Nanometer
O_3	Ozone
OH•	Hydroxyl radical
ppm	Parts per million

Pt-Co	Platinum-Cobalt
RES	Chromaticity Number (Renklilik Sayısı)
T	Temperature
t	Time
TOC	Total Organic Compounds
TREDAŞ	Tekirdağ Elektrik Dağıtım A.Ş.
TSS	Total Suspended Solids
TU	Toxicity Unit
TWPCR	Turkish Water Pollution Control Regulation
US	Ultrasound
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

The textile industry wastewater contains high flow rates and extreme concentrations of organic compounds and toxic chemicals. It is one of the complicated industries among manufacturing industries. Various toxic chemicals such as complexing, sizing, wetting, softening, anti-felting and finishing agents, biocides, carriers, halogenated benzenes, surfactants, phenols, pesticides, dyes and many other additives are used in wet processes which are mainly called washing, scouring, bleaching, mercerizing, dyeing, finishing processes. As a result textile factories produce highly toxic wastewaters (Dorn P.B., et al., 1993; Navarro V.A., et al., 2001).

The release of those wastewater into the environment can cause serious health and environmental problems. Furthermore, industrial wastewaters spoil the neighborhood and cause severe ecologic imbalance. It has been noticed that most of these factories have no water treatment facilities and discharge their contaminated waste waters illegally to the city waste water underground network or just drain them in open lands, or the nearest water reservoirs. This pollution affects food chain and also may cause carcinogenic effects on human health. Many of the industrial wastewaters that contain organic dyes and their breakdown products have toxic and/or mutagenic features to life (Weisburger, 2002). Therefore, advanced treatment of industrial effluents is a must for the protection of environment (Talarposhti et al., 2001; Dos Santos et al., 2006). Although there are many conventional methods for the treatment of textile industry wastewater, they are not effective for decolorization and complete treatment.

Advanced oxidation processes (AOPs) are innovative alternative for efficient treatment of industrial wastewaters containing refractory materials. These processes are basically chemical oxidation processes that use one of the most powerful oxidizing species which are hydroxyl radicals (OH•) They aggressively and unselectively attack most refractory compounds which may results in complete mineralization at the end AOPs are widely used for the treatment of textile wastewaters, as they are able to degrade strong dyes and high total organic carbon and chemical oxygen demand values (Malato et al., 2007).

In recent years, the use of hydrogen peroxide (H_2O_2), ozone (O_3), and iron (Fe^{2+}) with or without a source of UV (Ultraviolet) light has been proposed as potential alternatives for color, substantial Chemical Oxygen Demand (COD), and Total Organic Carbon (TOC) removal from textile effluents (Tezcanli, 2003). Advanced oxidation processes have significant advantages over conventional treatment methods since chemical oxidation methods. They do not produce sludge and almost complete demineralization and detoxification of organics is possible, but the main disadvantage of AOPs lies in the high cost of reagents and/or energy sources like ultraviolet light and ozone generator. (Galindo et al., 2001). AOPs are also effective alternatives for the degradation of non-biodegradable organic compounds in industrial wastewater. These processes are based on the generation oxidizing radicals which has very high oxidant power.

Decolorization of textile effluents is major environmental concern that should be focused on. Although color is an important pollution parameter for industrial wastewater discharge for many countries (ISO EN 7887, 1994) for a long time, it is a new pollution parameter for Turkey. Lately, color parameter (as Pt-Co and Chromacity number unit) and the related discharge limit value have been defined in Turkish Water Pollution Control Regulation (TWPCR, 2004). By the year 2012, colored industrial wastewater should be decolorized before discharge into aquatic media.

The purpose of this study is to determine the applicability of advanced oxidation techniques for the decolorization of biological wastewater treatment plant effluent of a textile industry, which was located in Ergene Basin, Turkey. Various AOPs, involving oxidizing agents such as H_2O_2, O_3, and/or catalyst such as iron, in the presence and absence of UV light, ultrasound or combinations thereof, were studied to investigate the most feasible AOP technique interms of decolorization and cost effectiveness.

The yield of AOP was determined by monitoring the residual dye, chemical oxygen demand (COD), total organic carbon (TOC), and toxicity. The effect of process parameters such as pH and oxidant concentrations was studied to optimize the operating conditions for maximum color and TOC removal. The color was monitored by two different methods, such as Pt-Co, and Chromacity number (RES). Rate of color degradation was estimated by first order kinetic assumption. Operational cost of each AOP was also calculated to determine the most feasible technique that sustains the Turkish Water Pollution Control Regulation discharge standards for color.

CHAPTER 2

THEORITICAL BACKGROUND

2.1 TEXTILE INDUSTRY WASTEWATER

The textile industry plays a vital role in the economy around the World. For instance, the European industry is composed of more than 110 thousands companies with an average turn-over of nearly € 200 billion a year, making it the world's leading exporter of textiles and the third largest exporter of clothing. Unfortunately, linked to great economical benefits given by the textile sector to several countries, severe environmental problems have been created due to discharge or inadequate disposal of textile wastes (Cervantes, 2009).

The textile industry is one of the most complicated industries and contains various toxic chemicals. Major pollutants in textile wastewaters are high-suspended solids, chemical oxygen demand, heat, color, acidity and other soluble substances (Dae-Hee et al., 1999). Textile wastewater includes a large variety of high color intensities and chemicals additions as organic or inorganic contents that make the environmental challenge for textile industry (Venceslau *et al.*, 1994). As a result these toxicants or pollutants are seriously harmful to natural aquatic environment when released without treatment.

The wastewater in textile industry is generated in several stages of textile manufacturing and processing, such as sizing of fibers, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing (Rodriguez et al., 2002).

Likely sources of textile process wastewater include wet processes such as scouring, dyeing, finishing, printing and coating of textile products.

Dyeing processes are one of the largest sources of wastewater. The primary source of wastewater from dyeing operations is spent dyebath and washwater. Finishing processes generally produce wastewater containing natural and synthetic polymers. Chemical handling and high pH are the primary pollution concerns associated with the bleaching process (US EPA, 2004).

Textile industry basically includes the production of fabrics from fibers such as cotton, wool and synthetics (nylon, polyester, acrylics) as mentioned with a number of processes (Cooper, 1978). These steps in the production of textiles and these processes generate highly contaminated liquid streams. The quantity and composition of these wastewaters depend on many different factors, including the processed fabric and the type of process. Type of machinery, chemicals applied and other characteristics of the processes also determine the amount and composition of the generated wastewater. In the textile sector, although processes should be considered separately, treatment of each process may not be considered individually.

Combined selected streams can lead to a better treatable wastewater. A stream could be separated from the rest to facilitate the recovery of water or chemicals, or to prevent dilution of a compound difficult to remove.

2.2 SOURCES OF TEXTILE EFFLUENT

Textile industry mostly involves wide range of raw materials, machineries and processes to engineer the required shape and properties of the final product. Waste stream generated in this industry is essentially based on water-based effluent generated in the various activities of wet processing of textiles. The main cause of generation of this effluent is the use of huge volume of water either in the actual chemical processing or during re-processing in preparatory, dyeing, printing and finishing (Das, 2000).

Actually, in a practical estimate, it has been found that 45% material in preparatory processing, 33% in dyeing and 22% are re-processed in finishing (Sivaramakrishnan, 2004). The fact is that the effluent generated in different steps is well beyond the standard and thus it is highly polluted and dangerous. This is demonstrated in Table 2.1.

Table 2.1 Properties of Wastewater from Textile Chemical Processing (Das, 2000).

Property	**Standard**	**Cotton**	**Synthetic**	**Wool**
pH	5.5-9.0	8-12	7-9	3-10
BOD, mg/L, 5 days	30-350	150-750	150-200	5000-8000
COD, mg/L, day	250	200-2400	400-650	10,000-20,000
TDS, mg/L	2100	2100-7700	1060-1080	10,000-13,000

2.3 CATEGORIZATION OF WASTE IN TEXTILE INDUSTRY

Textile waste is broadly classified into four categories, each of having characteristics that demand different pollution prevention and treatment approaches. Such categories are discussed in the following sections:

2.3.1 Generic Categorization of Wastes

This section discusses generic categories of wastes to identify the general characteristics of wastes that make them most amenable to pollution prevention.

2.3.1.1 Hard to Treat Wastes

These wastes include those that are persistent, resist treatment, or interfere with the operation of waste treatment facilities. Non-biodegradable organic or inorganic materials are the chief sources of wastes, which contain color, metals, phenols, certain surfactants, toxic organic compounds, pesticides and phosphates. The main sources are; color and metal wastes are coming from dyeing operations, phosphate is coming from preparatory processes and dyeing, non-biodegradable organic materials are coming from surfactants.

Since these types of textile wastes are difficult to treat, the identification and elimination of their sources are the best possible ways to tackle the problem. Some of the methods of prevention are chemical or process substitution, process control and optimization, recycle/reuse and better work practices (US EPA, 1996).

2.3.1.2 Hazardous or Toxic Wastes

These category of wastes are a subgroup of hard to treat wastes. But, owing to their substantial impact on the environment, they are treated as a separate class. In textiles, hazardous or toxic wastes include metals, chlorinated solvents, non-biodegradable or volatile organic materials. Some of these materials often are used for non-process applications such as machine cleaning (US EPA, 1996).

2.3.1.3 High Volume Wastes

High-volume of wastes can be a problem for the textile processing units. High-volume of wastewater, wash water from preparation and continuous dyeing processes and alkaline wastes from preparatory processes and batch dye waste which contains large amounts of salt, acid or alkali are include large volume wastes. These kind of wastes sometimes can be reduced by recycle or reuse as well as by process and equipment modification (US EPA, 1996).

2.3.1.4. Dispersible Wastes

Many wastes that are well contained when generated become highly dispersed once they are released or mixed with other wastes. It is important to segregate and capture such highly dispersible wastes at the source because removing them from a mixed waste stream requires substantially more treatment at greater cost and effort. Examples of these wastes in industry includes; waste streams from continuous operations, print paste (especially from screen, squeegee, and drum cleaning), lint, waste from coating operations, waste solvents from machine cleaning, still bottoms from solvent recovery and batch dumps of unused processing (US EPA, 1996).

2.3.2 Specific Wastes in Textile Wastewater

This section presents specific examples for these wastes that are often found in textile processes and typical pollution prevention strategies applicable for each. The main pollution problems are as known as; color, salts, air toxics, h-proved treatability of wastes, metals, aquatic toxicity and water conservation.

2.3.2.1 Color Value

Color in effluent from textile dyeing and printing operations is being increasingly regulated and is widely recognized as a compliance problem that must be addressed through pollution prevention (Smith, 1994; Wagner 1993). Effluent from most textile dyeing operations generally has a dark reddish-brown hue that is aesthetically disturbing when discharged to receiving waters. Although only an aesthetic pollutant,’ color might be easy to detect (depending on the flow of the receiving stream), and even trace quantities of commercial textile colorants in wastewater are readily evident to the naked eye.

Even though many methods of color removal exist, none works in every case (Koonce, 1993). Because of the difficulties and expense in treating color, the best approach for minimizing color discharges is pollution prevention (Cooper, 1989).

Measuring color in textile wastewater is inherently difficult (Koonce, 1993). If the wastewater sample is not filtered, suspended solids can interfere with transmission measurement, rendering the measurement meaningless.

2.3.2.1.1 Sources of Color in Wastewater

Dyes and pigments from printing and dyeing operations are the principal sources of color in textile effluent. 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 (AATCC, 1981).

2.3.2.1.2 Common Textile Dyes

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 (Tezcanli, 1998). List of the major dye classes and the types of fibers for which dyes has affinity is shown in Table 2.2.

Dyes have a complex aromatic and polymeric structure, constituting high solubility in water, and at the same time are often toxic and non-biodegradable, becoming extremely dangerous for ecosystems. Some problems which may arise due to dye pollution include the absorbing of sunlight by dyes, affecting the photosynthesis of aquatic plants, and the possibility of production of aromatic amines by the degradation of azo dyes, which are considered highly carcinogenic (Bali et al., 2004; Torrades et al., 2004).

Table 2.2 Dye classes and their associated fibers (US EPA, 1996).

Dye Class	**Fibers**
Acid	Wool and nylon (polyamide)
Basic	Acrylic, certain polyesters
Direct	Cotton, rayon and other cellulosief
Disperse	Polyester, acetate, and other synthesis
Fiber reactive	Cotton and other cellulosic, wool
Mordant	Natural fibers
Vat	Cotton and other cellulosic

There are many types of colorants varying according to end use requirements for wash, light, resin, chlorine, heat, gas and crock fastness. Variations in dyeing charges are dependent upon many factors, including course, fastness, brilliance, depth and intensity.

Acid Dyes

Acid dyes are used for dyeing wool, nylon, certain acrylics such as Types 24 and 28 Orlon, and other chemical fibers. These powdered dyes are intended for tub dying yardage, yarns or clothing. These type of dyes exhibit little affinity for cellulosic or polyester fiber. Their 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.

These 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 (US EPA, 1996).

Basic Dyes

Basic dyes were the first synthetically manufactured dye class. Basic dyes are applied mainly to acrylic fibers such as Types 42 and 75 Orlon and Type 61 Creslan, to produce bright and deep shades with good light and wash fastness. They also applied on modified nylons and polyester too (US EPA, 1996).

These dyes have limited water solubility and applied in weakly acidic dyebaths. They have unlimited color range and good fastness properties (Tezcanli, 1998).

Direct Dyes

Direct dyes are perhaps the most widely used and most economical of all classes. Some of the pastels and light shades possess good wash and light fastness but medium and heavy colors, particularly the latter, are not recommended. The application of direct dyes is the least complicated; chemically they are salts of complex sulfonic acids. They are soluble in water and have an affinity for a wide variety of fibers.

They have been used extensively for dyeing cotton, nylon, linen, hemp and silk. The term of “direct dye” refers to the fact that these dyes can be applied directly to cellulosic without mordents. The dyes are absorbed into hydrophilic fibers expand in the water (US EPA, 1996).

Disperse Dyes

Disperse dyes are used mainly on acetate, nylon, polyesters and acrylics. Their fastness properties vary with the dye, color and fiber on which they are used; on acrylics their fastness properties are generally inferior to Basic or Acid dyes.

Disperse dyes are applied by a procedure similar to Direct dyes but with different controls depending on the fiber to which they are applied.

Fiber Reactive Dyes

Very bright shades of pink, green, blue and turquoise can be produced with Reactive dyes. Fastness properties are generally good except to chlorine. These dyes are edluble in water and are salted out of solution onto the fiber where they are make to react chemically within the fibers such as cotton and rayon.

During dyeing with reactive dyes, 50 % of the dye cannot be reacted with the fibers and stay put hydrolyzed in water phase. If it is released into the environment, it can cause some environmental problems (O’Neill et al., 1990).

Vat Dyes

Vat dyes are best for all-around fastness and are generally the most expensive. They may be selected for fastness to overbleaching and are the best class for chlorine fastness. Reasonably bright shades can be produced except for brilliant red.

Vat dyes are insoluble compounds and have no amnity for the fibers until reduced with caustic soda and hydro. These dyes are applied in a solution in reduced state and oxidized to the insoluble dye again within the fiber.

2.3.2.2 Metals

The presence of metals in textile mill effluents is of concern primarily because of their toxicity to aquatic and mammalian species (Wagner, 1993; Smith, 1989; Richardson, 1991). Metals also inhibit waste treatment operations and are difficult to remove or treat using pollution control technologies (Smith, 1989; Richardson, 1991).

The sources of metals can be difficult to identify in textile operations; locating metals sources requires careful examination of all aspects of plant operations (Richardson, 1991). Many textile mills have little or no metals in their effluent but, whenever metals are present, they often include those shown in Table 2.3. The table indicates only harmful metals. Materials such as iron are not listed.

Table 2.3 Typical Sources of Metals in Effluent (US EPA, 1996).

Metal	**Typical Sources**
Arsenic	Fibers, incoming water, fugitive, treated timber
Cadmium	Impurity in salt
Chrome	Dyes, laboratory
Cobalt	Dyes
Copper	Dyes, incoming water, fiber
Lead	Dyes, plumbing, shop
Manganese	Permanganate strip (repair mildew)
Mercury	Dye/commodity chemical impurity
Nickel	Dyes
Silver	Photo operations
Tin	Finishing chemicals, plumbing
Titanium	Fiber
Zinc	Dyes, impurity in commodity chemicals, incoming water, plumbing

Dye manufacturers now are considering the environmental impact of the dyes that they produce, in addition to traditional concerns such as economy, higher wet fastness, and high tinctorial value. Many anthraquinone dyes are derived by sulfonation in the presence of mercury catalysts. The metals most commonly found in dyes as part of the dye structure are shown in Table 2.4.

Table 2.4 Typical Metals Found in Dyes by Dye Class (Wagner, 1993).

Dye Class	**Typical Metals in Structure**[a]
Direct	Copper
Fiber Reactive	Copper and nickel
Vat	None
Disperse	None
Acid	Copper, chrome, cobalt
Premets	Copper, chrome, cobalt
Mordants	Chrome

[a] Does not imply that all dyes contain these metals.

2.4 WASTE PROBLEMS IN TEXTILE INDUSTRY

2.4.1 Discharge of Electrolytes

Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile wet processes (see Table 2.5) Several authors have identified salt in textile-dyeing wastewater as a significant future problem area (Wagner, 1993). Typical cotton batch dyeing operations use quantities of salt that range from 20 percent to 80 percent of the weight of goods dyed, and the usual salt concentration in such wastewater is 2,000 ppm to 3,000 ppm (Smith, 1986).

Table 2.5 Types of Salt Used in Textile Operations and Toxicity Characteristics*

Salt Type	**Typical Use**	**Aquatic Tlm_{96} (ppm)**	**Typical Mammalian Oral Toxicity LD_{50} (mg/kg)[8]**
Calcium chloride	Formed	>1,000[a]	3,500
Common salt	Dyeing	2,000[b]	3,000
Epsom salt	Fixing	NA	3,000
Glaubers salt	Dyeing	NA	6,000
Magnesium chloride	Catalyst	NA	8,100
Potassium chloride	Formed	1,000-100[8]	7,000

*(Sax, 1984; Herlant, 1991).

The removal of salt from mixed textile wastewater to reduce chloride concentration from 3,000 ppm to 250 ppm is extremely difficult and expensive by any known treatment method. Therefore, reducing salt concentrations through pollution prevention measures is the only practical alternative to solve the dilemma presented by this hard-to-treat, toxic, high-volume waste (US EPA, 1996).

2.4.2 Toxic Air Emissions

Textile operations involve numerous sources of air emissions, and these sources give rise to a variety of air quality issues. Unit operations that present the greatest concern are coating, finishing, and dyeing (Mohr, 1993). The textile industry is a relatively minor source of air pollutants compared with other industries, but the industry emits a great variety of materials, making sampling, analysis, treatment, and prevention more complex (Zeller, 1975).

2.4.3 Improving Treatability

Properly designed waste treatment systems can remove or destroy many of the harmful contaminants in raw textile wastewater and produce an effluent that can be discharged safely to receiving waters. Certain wastes or contaminants, however, can interfere with the ability of treatment systems to operate to design specifications, resulting in system upsets and exceedances of permit limitations. Other contaminants are removed from the treatment system and partition into sludges, disposal of which can be difficult. Where possible, steps should be taken to avoid these wastes or to improve their treatability so that wastewater treatment systems can manage them more easily (US EPA, 1996).

2.4.4 Aqua Toxicity

Compounds that contribute to aquatic toxicity are a particular environmental concern for all industry. EPA has identified toxic compounds under the general heading “Priority Pollutants,” numbering approximately 126 compounds (Dichlorobenzene, phenol, toluene, pyrene, isophorone, etc.) in 65 classes. Categorical discharge standards regulate these compounds. EPA identified priority pollutants on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity (US EPA, 1996).

The aquatic toxicity of textile industry wastewater varies considerably among production facilities. Data are available that show that some facilities have fairly high aquatic toxicity, while others show little or no toxicity (US EPA, 1996).

The source of aquatic toxicity in textile wastewater can be hard to identify. Many textile dyes and auxiliary chemicals, many generally known groups of chemical agents contribute to aquatic toxicity of textile wastewater. And these agents are salts, surfactants, metals, toxic organic chemicals, biocides, toxic anions. Examples of compounds in each of these classes and their sources are shown in Table 2.6.

Table 2.6 Typical Causes of Aquatic Toxicity (US EPA, 1996).

Agent	**Chemical Example**	**Typical Source**
Salt	NaCl, Na_2SO_4	Dyeing
Surfactants	Ethoxylated phenols	Multiple sources
Metals	Copper, zinc, etc.	Dyes
Organic	Chlorinated slovents	Scour, machine cleaning
Biocides	Pentachlorophenol	Wool fiber contaminant
Toxic anions	Sulfide	Sulfur dyeing

2.4.5 Water Conservation

Water is used extensively throughout textile processing operations. Almost all dyes, specialty chemicals, and finishing chemicals are applied to textile substrates from water baths. In addition, most fabric preparation steps, including desizing, scouring, bleaching, and mercerizing, use aqueous systems.

The amount of water used varies widely in the industry, depending on the specific processes operated at the mill, the equipment used, and the prevailing management philosophy concerning water use. Reducing water consumption in textile processing is important for furthering pollution prevention efforts, in part because excess water use dilutes pollutants and adds to effluent load (US EPA, 1996).

2.5. POLLUTION PARAMETERS FOR TEXTILE INDUSTRY

The characteristics and the effects of control parameters in the Textile Industry are listed below:

2.5.1 Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) is a standard and very common method for indirect measurement of amount pollutant organic material in water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water.

This test serves an important function in stream pollution-control activities. It is a bioassay procedure that measures the amount of oxygen consumed by living organisms while they are utilizing the organic matter present in waste, under conditions similar in nature.

For the result of a BOD test to be accurate, indicates the amount of water-dissolved oxygen consumed by microbes incubated in darkness for five days environmental monitoring at an ambient temperature of 20°C. This test is utilized as a means of stating what level of contamination from pollutants is entering a body of water (Shelton 1991; Wallace 2000).

2.5.2 Chemical Oxygen Demand (COD)

These method can be used for indirect measurement of the amount of pollution (that cannot be oxidized biologically) in a sample of water. The chemical oxygen demand test procedure is based on the chemical decomposition of organic and inorganic contaminants, dissolved or suspended in water.

The result of a chemical oxygen demand test indicates the amount of water-dissolved oxygen (expressed as parts per million or milligrams per liter of water) consumed by the contaminants, during two hours of decomposition from a solution of boiling potassium dichromate. The higher value of the chemical oxygen demand means, the high amount of pollution in the test sample. For the contaminants that can be oxidized biologically, the biochemical oxygen demand (BOD) method can be used.

Chemical oxygen demand (COD) does not differentiate between biologically available and inert organic matter and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water (Brown and Caldwell, 2001).

2.5.3 Total Suspended Solids

Total solids are dissolved solids plus suspended and settleable solids in water. In stream water, dissolved solids consist of calcium, chlorides, nitrate, phosphorus, iron, sulfur, and other ions particles that will pass through a filter with pores of around 2 microns (0.002 cm) in size. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulate matter. These are particles that will not pass through a 2-micron filter.

Higher concentrations of suspended solids can serve as carriers of toxics, which readily cling to suspended particles. This is particularly a concern where pesticides are being used on irrigated crops. Where solids are high, pesticide concentrations may increase well beyond those of the original application as the irrigation water travels down irrigation ditches. Higher levels of solids can also clog irrigation devices and might become so high that irrigated plant roots will lose water rather than gain it.

At the same time, total solids also affect water clarity. Higher solids decrease the passage of light through water, thereby slowing photosynthesis by aquatic plants. Water will heat up more rapidly and hold more heat; this, in turn, might adversely affect aquatic life that has adapted to a lower temperature regime (US EPA, 1997).

2.5.4 Oil and Grease

The Environmental Protection Agency Administrator designated ``oil and grease'' as a conventional pollutant under the Clean Water Act (see 40 CFR 401.16). U.S EPA Method 1664 is used to extract oil and grease from water. Oil and grease consists of those chemical substances extracted from water or wastes using a solvent. The natures of the substances extracted are determined by the extracting solvent and the extraction technique.

Both CFC-113 and n-hexane extract many pure materials at nearly 100 percent efficiency. When mixtures of substances that typically occur in complex wastewater discharges and in complex solid and semi-solid wastes are present, the two solvents may extract different amounts of material.

For most of the wastes and wastewaters, materials commonly extracted are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. Because the nature and amount of material extracted is defined by the solvent and, to a lesser degree, by the details of the procedure used for extraction, EPA uses the term ``method-defined analytes" to identify oil and grease (US EPA, 1999a).

2.5.5 Sulfide

Dissolved sulfide ions can decrease the pH of the water and they are transformed into a black precipitate with reaction iron or the other metal ions. Therefore they can cause odor problems and have toxic effect on aquatic life. The toxicity effect of sulfides on fishes, increases when pH decreases. And sulfides react chemically with dissolved oxygen in the water and decrease the level of dissolved oxygen.

2.5.6 Ammonium Nitrogen (NH_4-N)

Ammonium is a nitrogen compound which is usually colorless and readily soluble in water. Ammonium compounds are most often produced by direct reaction between dissolved or gaseous ammonia and an acid. They are of great technical and economic significance as they are used in commercial fertilizers, explosives and baking powder and also as fire-preventing additives in textiles (Swedish EPA, 2010).

The discharge of wastewater containing high concentration of ammonia nitrogen is one of the most important factors. Biological denitrification is the most common process in the treatment of ammonia nitrogen wastewater. But the process is only suitable for the removal of relatively low ammonia concentration due to the requirement of appropriate C/N ratio (Yang et al., 1999). Ammonia stripping makes use of stripping tower and consumes much energy (Kim et al., 2006).

Chemical precipitation needs additional reagents, which may introduce new pollutants to water body. As the ammonium ion is a weak acid, nitrogen fertilization with ammonium compounds has an acidifying effect (Swedish EPA, 2010). For this reason, it is necessary to develop cost-effective method for the removal of ammonia nitrogen from wastewater.

2.5.7 Chromium

Chromium salts are used extensively in several industrial processes, and enter water supplies through the discharge of effluents from industries that employ Cr^{6+} compounds as corrosion inhibitors and water-cooled heat exchange systems, and also from electroplating, metal finishing, chromate preparation, tannery and fertilizer industries, tanning, dyeing, textile, cement, and chemical industries (Gao et al., 2004; Balasubramanian and Pugalenthi, 1999).

They are reported to have a toxic effect on the biological systems. Presently, Cr(VI) has been recognized as a probable agent of lung cancer, and it also produces gastrointestinal disorders, dermatitis and ulceration of skin in man (Pretty et al., 1994).

2.5.8 Phenolic Compounds

Wastewater containing phenolic pollutants has been found in many industries, such as oil refineries, chemical and plastic plants. As is well known, those compounds are toxic even at low concentration (Verschueren, 1977), and they are the representatives of aromatic compounds. Especially for chlorinated phenols (CPs), which are widely found in the environment and are significant contaminants at many sites selected for cleanup on the US EPA priorities list of the superfund program (Lin and Tseng, 1999). Therefore it is very important to treat such contaminants (Wu et al., 2002).The common sources of phenolic compounds present in industrial effluents are: petroleum refineries, plastic manufacturing plants, pharmaceutical industries, coal carbonization and tar distillation units, wood charcoal production units, coke ovens and phenolformaldehyde plants (Meikap and Rot, 1997).

2.5.9 pH

pH is a term used to indicate the alkalinity or acidity of a substance as ranked on a scale from 1.0 to 14.0. Acidity increases as the pH gets lower.

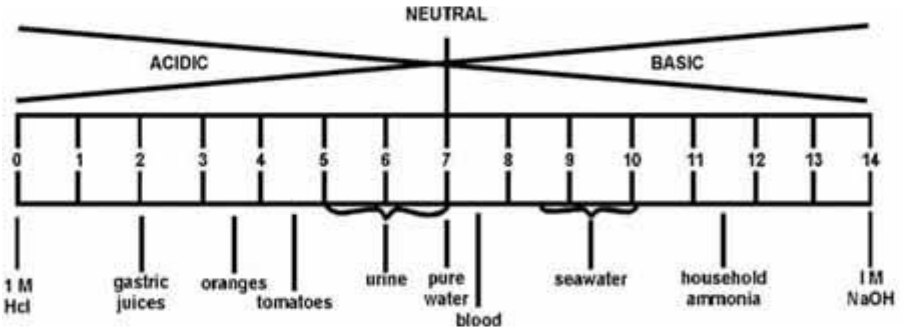

Figure 2.1 The pH of some common liquids (US EPA, 1997).

pH affects many chemical and biological processes in the water. For example, different organisms flourish within different ranges of pH. The largest variety of aquatic animals prefers a range of 6.5-8.0. pH outside this range reduces the diversity in the stream because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds to become mobile and "available" for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life, particularly to sensitive species like rainbow trout. Changes in acidity can be caused by atmospheric deposition (acid rain), surrounding rock, and certain wastewater discharges (US EPA, 1997).

2.6 TREATMENT METHODS FOR TEXTILE WASTEWATER

Wide range of techniques has been developed for the removal of synthetic dyes from wastewater to decrease their pollution effect on the environment. These techniques are divided into three major categories: chemical, physical and biological treatment techniques (Robinson et al., 2001; Pearce et al., 2003).

Biological techniques include bacterial, fungal biosorption and biodegradation in aerobic, anaerobic or combined treatment processes.

Physical techniques include adsorption, ion exchange, irradiation, membrane filtration, electrolysis, coagulation/flocculation and ultrasonic mineralization.

Chemical techniques include advanced oxidation (ozonation, Fenton oxidation, wet air oxidation, catalytic wet air oxidation, catalytic wet peroxide oxidation and photocatalytic oxidation) and chemical reduction (Chang and Lin, 2000; Robinson et al., 2011; Pearce et al., 2003).

These treatment methods and their efficiencies are expounded in following sections.

2.6.1 Biological Treatment

In this treatment, color removal is achieved by the use of living organisms. Biological method mainly involves the use of microorganisms through the release of biocatalyst such as enzymes which acts on the dyes that are present in the effluent. Biological method offers for being cheap and environmental friendly (Knackmuss, 1996). Biological treatment can be applied to textile wastewaters as aerobic, anaerobic and combined aerobic-anaerobic.

Due to insufficiency of biological treatment in the removal of the dyes from textile and dyestuff manufacturing, this process requires the involvement of other physical, chemical, and physicochemical operations" (Rai, 2005; Banat et al., 1997).

"Physical and chemical treatment techniques are effective for color removal but use more energy and chemicals than biological processes. They also concentrate the pollution into solid or liquid side streams requiring additional treatment or disposal" (Shaw et al., 2001).

2.6.2 Physical Treatment

The common physical treatment methods used for the treatment of colored textile effluents include membrane filtration, ion exchange, adsorption with activated carbon, irradiation and coagulation and flocculation (Doble and Kumar, 2005).

General main disadvantages include the generation of hazardous sludge that demand safe dispose or treatment by some other process (Mattioli et al., 2002; Van der Zee, 2002), high investment cost and replacement of equipment such as filters after a certain period (Mishra and Tripathy, 1993).

However the color of wastewater from today's new dyes is much more difficult to treat by physical techniques such as adsorption and chemical coagulation to achieve complete decolorization, especially for highly soluble dyes (Oğuz and Keskinler, 2008).

2.6.3 Chemical Treatment

The most commonly used method of decolorization in textile dyes by chemical methods is oxidative processes. They are known to be much more effective than the others in breaking down unsaturated bonds in the dye molecules (Ciardelli *et al*., 2001).

This kind of treatment typically involves the use of an oxidizing agent such as ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's reagent etc. to change the chemical composition of a compound or a group of compounds, e.g. dyes (Metcalf and Eddy, 2003). Among these oxidants, ozone is the most widely used oxidant because of its reactivity with many dyes, usually providing good color removal efficiencies (Alaton et al., 2002).

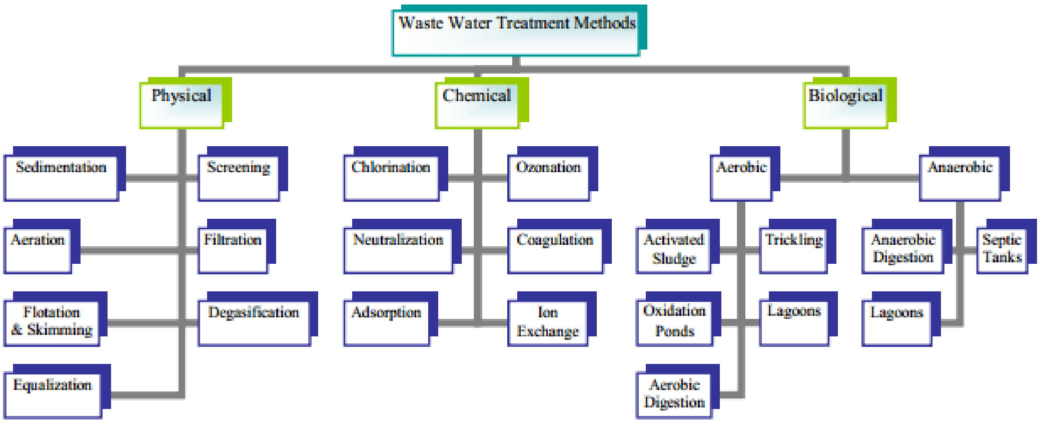

Figure 2.2 Wastewater Treatment Methods.

2.6.4 Advanced Treatment (Advanced Oxidation Processes)

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods

(Ledakowicz et al., 2001). However, being water-intensive in nature and because of the extensive consumption of dyes along with auxiliary chemicals, dye effluent is typically associated with high chemical oxygen demand (COD) and color levels (Yasar et al., 2006).

Textile wastewater, being mostly non-degradable under both natural and sewage treatment plant conditions, is a potential nuisance to the environment. Therefore, it is necessary to find an effective method of wastewater treatment capable of removing color and toxic organic compounds from textile effluents. These less or non-biodegradable compounds, called xenobiotics, can not be completely removed by biological treatment (Ledakowicz et al., 2001).

Their recalcitrant character and complex nature, textile wastewater is not generally amenable to conventional other treatment methods (Correia et al., 1994). Therefore it should be selected appropriate method for treatment. Some of the common methods for this purpose include: adsorption on activated carbon, coagulation/flocculation followed by sedimentation or dissolved air flotation and reverse osmosis (Vilar et al., 2011). However these methods are mostly ineffective as they simply transfer the contaminant from water to a solid phase or sludge (Torrades, 2004; Pekakis et al., 2006).

As a result, the use of alternative technologies, aiming to remove color and toxicity and mineralize or transform refractory molecules into others which could be further biodegraded, is pleased for environment. Among them, advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes (Stasinakis, 2008).

Advanced oxidation processes are chemical oxidation processes based on the use of the hydroxyl radicals (OH·), which are one of the powerful oxidizing species. These hydroxyl radicals have a high oxidation potential (2.8 eV) and attacks organic molecules by either abstracting a hydrogen atom or by adding to double bonds resulting in mineralization of these complex organic molecules to non-toxic compounds, such as carbon dioxide or water (Mourand et al., 1995; Gulyas et al., 1995).

Table 2.7 shows the relative oxidation potentials of several chemical oxidizers. Hydroxyl radicals attack is not selective, which is a useful attribute for use in the treatment of textile wastewaters, as they are able to degrade different recalcitrant compounds effectively, including dyes (Vilar et al., 2011). Thus, AOPs applied after biological treatment are much more effective for the breakdown of refractory organic compounds and for color removal as a result of the reduction of suspended matter and decrease in the contaminant concentrations.

Table 2.7 Oxidizing potential for conventional oxidizing agents*.

Oxidizing agent	**Electrochemical Oxidation (EOP), V**	**EOP relative to potential chlorine**
Fluorine	3.06	2.25
Hydroxyl Radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

(Carey, 1992; Techcommentary, 1996; Zhou and Smith, 2002; Metcalf and Eddy, 2003)

2.6.5 Photochemical and Non-Photochemical AOPs

Advanced oxidation processes are produced highly oxidative radicals to degrade refractory organic compounds. These techniques are divided in two methods; photochemical processes and non-photochemical processes. Photochemical advanced oxidation processes refers both, to AOPs that need photons to initiate the oxidation process, and non-photochemical AOPs that increase their efficiency when working with natural radiation.

2.6.5.1 Photo-Chemical AOPs

Photochemical advanced oxidation means, the degradation of compounds by the assist of a light irradiation; most times it is UV light irradiation. UV is not always enough to complete degradation of compounds. The additive chemicals as H_2O_2 are needed to increase systems efficiency.

Many organic contaminants absorb UV energy in the range of 200-400 nm and decompose due to direct photolysis or become excited and more reactive with chemical oxidants. Among the AOPs, photochemical processes including the UV photolysis of H_2O_2 and the photo-Fenton reaction (UV photolysis of H_2O_2 catalyzed by Fe^{+2} ions under acidic pH conditions) are known as the most efficient, feasible and kinetically favorable types (Alaton and Hanci, 2011).

2.6.5.1.1 UV/H_2O_2

This process includes H_2O_2 injection and mixing followed by a reactor that is equipped with UV light (200-280 nm). Hydrogen peroxide is an efficient and easy to use chemical oxidant suitable for a wide usage. It was first used to reduce odor in wastewater treatment plants, and from then on, it became widely used in the field of the wastewater technologies (US EPA, 2002). However, hydrogen peroxide itself is not an efficient oxidant for many organic pollutants; it must be combined with UV light, US (Ultrasound) or ozone to produce the desired degradation results. The describing UV/ H_2O_2 process are presented below (Buxton et al., 1988).

$$H_2O_2 + h\nu \rightarrow 2\ HO \tag{2.1}$$

$$H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O_2 \tag{2.2}$$

$$H_2O_2 + HO_2\cdot \rightarrow HO\cdot + H_2O + O_2 \tag{2.3}$$

$$2\ HO\cdot \rightarrow H_2O_2 \tag{2.4}$$

$$2\ HO_2\cdot \rightarrow H_2O_2 + O_2 \tag{2.5}$$

$$HO\cdot + HO_2\cdot \rightarrow H_2O + O_2 \tag{2.6}$$

As seen above in Eq. 2.1 is the rate limiting reaction because the rates of the other reactions are much higher than that of Eq. 2.1. Theoretically in UV/ H_2O_2 process, the higher initial hydrogen peroxide concentration produces higher hydroxyl radical concentration (Eq. 2.1), which decomposes more target compound. However, an optimal hydrogen peroxide concentration exists because overdosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of hydroperoxyl radical $HO_2\cdot$ (Eq. 2.2) (Stasinakis, 2008).

2.6.5.1.2 O_3/UV

Ozone is a powerful oxidant agent for water and wastewater. Ozone application can be generalized into two; a powerful disinfection and a strong oxidant to remove color and odor, eliminating trace toxic synthetic organic compounds (Langlais et al., 1991). According to Rein (2001), conventional ozonation of organic compounds does not completely oxidize organics to CO_2 and H_2O in many cases. Remaining intermediate products in some solution after oxidation may be as toxic as or even more toxic than initial compound and UV radiation could complete the oxidation reaction by supplement the reaction with it. UV lamp must have a maximum radiation output 254 nm for an efficient ozone photolysis. The O_3/UV process is more effective when the compounds of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with hydroxyl radicals (Rein, 2001; Metcalf and Eddy, 2003). The O_3/UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals.

$$O_3 + hv \longrightarrow O_2 + O\ (^1D) \tag{2.7}$$

$$O\ (^1D) + H_2O \longrightarrow OH\bullet + OH\bullet \tag{2.8}$$

$$O_3 + H_2O + hv \longrightarrow H_2O_2 + O_2 \tag{2.9}$$

Hung-Yee and Ching-Rong (1995) documented O_3/UV as the most effective method for decolorizing of dyes comparing with UV oxidation by UV or ozonation alone. While, Perkowski and Kos (2003) reported no significant difference between ozonation and O_3/UV in terms of color removal.

Even though ozone can be photo decomposed into hydroxyl radicals to improve the degradation of organics, UV light is highly absorbed by dyes and very limited amount of free radical (HO·) can be produced to decompose dyes. Thus same color removal efficiencies using O_3 and O_3/UV could be expected (Al-Kdasi et al., 2004).

2.6.5.1.3 *O_3/H_2O_2/UV*

The addition of H_2O_2 to the O_3/UV process accelerates the decomposition of ozone, which results in an increased rate of OH• generation (Teccommentary, 1996). Among all AOPs for, dye house wastewater and acetate, polyester fiber dying process effluent combination of H_2O_2/O_3/UV appeared to be the most efficient in terms of decoloration (Azbar *et al*., 2004; Perkowski and Kos, 2003).

$$H_2O_2 + 2\,O_3 + hv \rightarrow 2\,OH\cdot + 3\,O_2 \qquad (2.10)$$

2.6.5.1.4 *Photo-Fenton (H_2O_2/Fe^{+2}/UV)*

This process involves the OH formation through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/ Fe^{+2}).

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + HO\cdot \qquad (2.11)$$

In the presence of UV irradiation, the ferric ions (Fe^{+3}) produced in Eq 2.11 are photocatalytically converted to ferrous ions (Fe^{+2}), with formation of an additional equivalent of hydroxyl radical (Eq 2.13) (Moraes et al., 2004).

$$Fe^{+2} + OH\cdot \rightarrow Fe^{+3} + OH^- \qquad (2.12)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ + HO_2 \qquad (2.13)$$

$Fe^{+2} + HO\cdot \rightarrow Fe^{+3} + HO^{-}$ (2.14)

$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2$ (2.15)

$Fe^{+3} + HO_2\cdot \rightarrow Fe^{+2} + H^{+} + O_2^{-}$ (2.16)

$Fe^{+3} + O_2^{-} \longrightarrow Fe^{+2} + O_2$ (2.17)

$Fe^{+2} + HO_2^{-} \rightarrow Fe^{+3} + HO^{-}_2$ (2.18)

In the dark, the reaction retarded is after complete conversion of Fe^{+2} to Fe^{+3}. After H_2O_2 addition, ferrous ion concentration decreases rapidly and ferric ion is occurs. Thereafter 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) as shown in Eq. (2.12). The primary step is photooxidation of ferrous ions to ferric ones Eq. (2.13). In the presence of light feedback reaction takes place, Eq. (2.13). In the presence of light following reaction takes place:

$Fe^{+3} + H_2O_2 + h\nu \rightarrow Fe^{+2} + H^{+} + OH\cdot$ (λ<300 nm) (2.19)

Also, H_2O_2 photolysis occurs directly under UV light irradiation, Eq (2.20).

$H_2O_2 + h\nu \rightarrow 2HO\cdot$ (λ<300 nm) (2.20)

Walling and Weil (1974) reported that the Fe^{+3} formed in Eq. (2.12) can react with the H_2O_2 present in the medium and be reduced to Fe^{+2} again, then forming to the hydroperoxyl radical, according to Eq. (2.13). This reaction, referred to by Neyens and Baeyens (2003) as Fenton-like, occurs more slowly than reaction in Eq. (2.12), as reported by Pignatello (1992). The Fe^{+3} ions also react with the $HO_2\bullet$ and are reduced to Fe^{+2}, as shown by Eq. (2.17)

2.6.5.2 Non-Photochemical AOPs

These process generally involve the generation and use of powerful but relatively nonselective transient oxiziding species, primarily the hydroxyl radical (OH·) and in some cases the single oxygen atom. The OH· can be generated by both photochemical and non-photochemical means to oxidizing environmental contaminants.

Non-photochemical oxidation processes have been demonstrated to be effective for treatment of contaminated water. Water matrices to which non-photochemical processes have been applied include contaminated groundwater, industrial wastewater, municipal wastewater, contaminated drinking water, landfill leachate and contaminated surface water. (US EPA, 2001)

2.6.5.2.1 Ozonation

Ozone is a powerful oxidant agent for wastewater treatment. Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical (Baig and Liechti, 2001). Indirect ozonation that produces •OH radicals makes ozonation process as an advanced oxidation method. The rate constants of •OH radicals are 10^4-10^8 times faster than ozone.

It has known that ozone is a very powerful disinfection and very strong oxidant to remove odor and color, also degrade organic compounds. Results presented by a few researchers revealed that ozone decolorize all dyes, expect non-soluble disperse and vat dyes which react slowly and take longer time (Namboodri et al., 1994; Marmargne and Coste, 1996; Rajeswari, 2000).

Furthermore, it has been documented that color removal using ozonation from textile wastewater is depended on dye concentration (Sheng and Chi, 1993; Mehmet and Hasan, 2002). Higher initial dye concentration of textile wastewater causes more ozone consumption.

Increasing ozone concentration enhances mass transfer that causes an increase in ozone concentration in liquid phase, which increase color removal. The other possible explanation is that more intermediates, which consume more ozone are generated when the initial dye concentration is high. According to Ahmet et al., (2003) and Arslan and Işıl (2002), 40-60 min ozonation of biotreated textile wastewater yielded 99% of decolorization efficiency.

2.6.5.2.2 O_3/H_2O_2 (Peroxone)

The addition of both hydrogen peroxide and ozone to wastewater accelerates the decomposition of ozone and enhances production of the hydroxyl radical. Hydroxyl radicals are produced during the spontaneous decomposition of ozone. By accelerating the ozone decomposition rate, the hydroxyl radical concentration is elevated, which increases the oxidation rate. (US EPA, 1999b).

The peroxone process utilizes oxidation by hydroxyl radicals. The oxidation potential of the hydroxyl radical and ozone are as follows:

$$OH\cdot + e^- \rightarrow OH^- \qquad (2.21)$$

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad (2.22)$$

$$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^- \qquad (2.23)$$

Hoigne and Bader (1976) reported that having an oxidation potential of hydroxyl radical higher than ozone, the hydroxyl radical is also much more reactive approaching the diffusion control rates for solutes such as aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols, and formic acid. Peroxone is used to remove taste and odor causing compounds because many of these compounds are very resistant to oxidation, even ozone-oxidation (US EPA, 1999b).

2.6.5.2.3 Ultrasound

Ultrasound processes have been used for treatment of contaminated water. This process refers to formation, growth, and implosive collapse of gas or vapor-filled bubbles in a liquid matrix. The most commonly used frequencies for industrial cleaning are those between 20 and 50 kHz. Ultrasound has wavelengths between successive compression waves measuring roughly 10 to 10-3 cm. These are not comparable to molecular dimensions (Figure 2.3)

Collapse of the bubbles produces localized high-temperature (about 5000 ˚C) and high pressure (about 50 megapascals) hot spots. The extreme conditions generated during cavitation result in OH· formation. Methods for inducing cavitation include ultrasonic irradiation of water (acoustic cavitation or sonolysis), high-voltage discharge in water (electrohydraulic cavitation), and creating a pressure differential (from below vapor pressure to above vapor pressure conditions) in a flowing water stream (hydrodynamic cavitation). (US EPA, 2001).

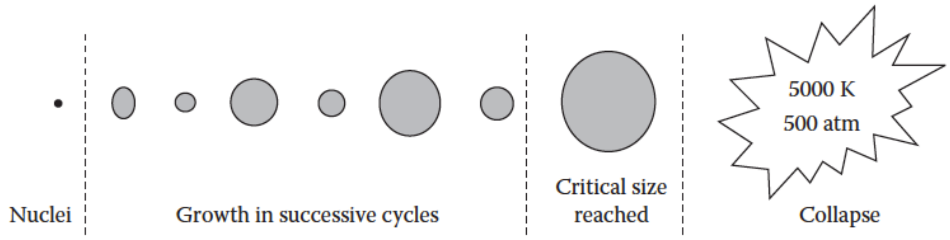

Figure 2.3 Bubble formation, growth and collapse (Chowdhury, P. and Viraraghavan, 2009).

Ultrasound waves consist of expansion (rarefaction) and compression cycles (Figure 2.4). Compression cycles exert a positive pressure on the liquid and push molecules together, while expansion cycles exert a negative pressure and pull molecules apart. Cavities can be generated during the expansion of a sound wave cycle with sufficient intensity, that the distance between the molecules exceeds the critical molecular distance necessary.

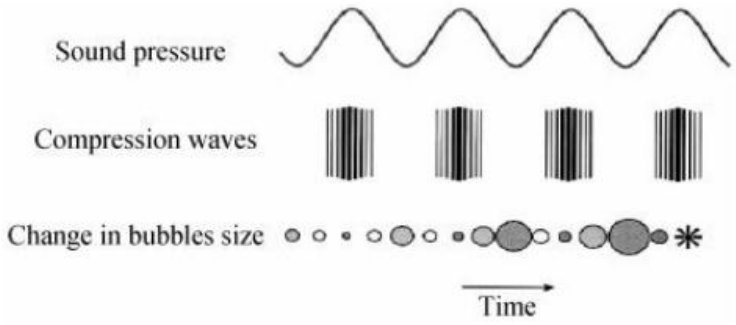

Figure 2.4 Compressions and expansions of ultrasound cycle (Suslick, 1994).

Bubble Cavitation

Ultrasound reactor technology (USRT) in a liquid leads to the acoustic cavitation phenomenon such as formation, growth, and collapse of bubbles (cavitation), accompanied by generation of local high temperature, pressure, and reactive radical species (°OH , °OOH) via thermal dissociation of water and oxygen. These radicals penetrate into water and oxidize dissolved organic compounds. Hydrogen peroxide (H_2O_2) is formed as a consequence of °OH and °OOH radical recombination in the outside of the cavitation bubble (Jiang et al., 2002; Visscher and Langenhove, 1998). Concentration of HO° at a bubble interface can be as high as $4\text{x}10^{-3}$ M, which is 10^8-10^9 times higher than that in the other advanced oxidation processes.

Bubbles form, grow and subsequently collapse through compression-rarefaction cycles. Temperature in collapsing bubbles can reach to 3000-5000 °K and pressure to 500-10,000 atm. Under such extreme conditions, water molecules undergo homolysis to yield hydroxyl radicals and hydrogen atoms. Since oxidation by hydroxyl radical is an important degradation pathway, amount of the hydroxyl radicals present in the sonolysis system is directly related to the degradation efficiency (Zheng et al., 2005).

2.7 DEGRADATION OF TEXTILE WASTEWATER by AOPs: LITERATURE SURVEY

A variety of AOPs have been proposed for treatment of textile wastewaters or degradation of dyes: UV/H_2O_2 (Bali et al., 2004), UV/Fe^{+2}/H_2O_2 (Rodriguez et al., 2002; Bali et al., 2004; Torrades et al., 2004).

Commonly applied treatment methods for color removal from dye contaminated effluents consist of integrated processes involving various combinations of biological, physical and chemical decolorization methods (Galindo et al., 2001; Robinson et al., 2001). These integrated treatment methods are efficient but not cost effective.

Traditional physical–chemical techniques such as ultrafiltration, reverse osmosis, ion exchange and adsorption on various adsorbents (activated carbon, peat, flyash and coal, wood chips, silica gel, corncob, barley etc.) have efficiently been used for the purpose of color removal from textile effluents.

Activated carbon is the most commonly applied method for color removal especially for cationic, mordant, and acid dyes and a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes (Raghavacharya, 1997). Carbon adsorption of dyes is only successful in some classes of dye (ionic type and hydrophobicity) for a given type of carbon in a certain pH range (Hao et al., 2000). Nevertheless, these techniques are non-destructive, since they just transfer the pollutant from water to solid matrix. Consequently, expensive operations such as regeneration of the adsorbent materials and post-treatment of solid wastes are needed.

Coagulation may not remove highly soluble dyes and it may be good for disperse dyes, but it produces a large quantity of sludge. Some processes are effective within a narrow pH range, for example pH<3.5 for Fenton’s reagent. Ozonation alone is not effective for disperse dyes (Solozhenko et al., 1995). A combination of these processes is necessary to achieve the desirable goal. For example, the degree of the inhibition for a synthetic dye in a biological-activated sludge system has been reduced from 47% to 10% after a pretreatment with O_3/UV or O_3/H_2O_2/UV (Ledakowicz and Gonera, 1999).

Advanced oxidation processes for the degradation of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods. AOPs based on the generation of very reactive and oxidizing free radicals have been used with an increasing interest due to their high oxidant power. Production of those radicals is achieved either using single oxidants or combination of ozone-hydrogen peroxide and UV radiation (Glaze and Kang, 1989) and also, with the combination of hydrogen peroxide and UV with ferrous ions in the so-called Photo-Fenton's reagent (Walling, 1975).

Although AOPs have a significant advantage over conventional treatment methods since chemical oxidation do not result in high amount of either chemical or biological sludge and almost complete demineralization of organics is possible, the main handicap with AOPs lies in the high cost of reagents or energy sources like ultraviolet light (Galindo et al., 2001). Decolorization of textile effluents is of major environmental concern that remains to be solved.

AOPs have been thoroughly and comparatively evaluated for a variety of organic compounds and wastewaters in the past but with several limitations. Also many investigations have demonstrated that AOPs are effectively removing color and partially organic content of dyestuffs (Legrini et al., 1983; Marechal et al., 1997).

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Sampling

The industrial textile wastewater was collected from one of the textile industry that located in Ergene Basin, Tekirdag/Turkey. This industrial facility is operating on dyeing, finishing and printing processes and has a biological treatment plant. The textile industry has 2500 m^3/day flow rate. AOP experiments were conducted with biological treatment plant effluent wastewater.

The company should permit to the discharge limits presented Table 10.1 of Turkish Water Pollution Control Regulation (TWPCR). The characterization of the wastewater before and after biological treatment is given in Table 3.1 with the related TWPCR limit values. The samples have studied immediately after taken to avoid degradation and oxidation.

Table 3.1 Physical-chemical characterization of the textile industry wastewater.

Parameters	**Influent**	**Effluent**	**WCQA limit values (Table 10.1)**
Temperature (˚C)	35,4	29,6	-
pH	10,04	7,65	6-9
Conductivity (µS/cm)	9200	9000	-
COD (mg/L)	595	156	350
Ammonium Nitrogen (NH_4-N) (mg/L)	0,84	0,16	5
Free Chlorine (mg/L)	0,02	0,04	0,3
T. Chrome (mg/L)	0,12	0,03	2
Sulfide (mg/L)	0,33	0,14	0,1
Sulfite (mg/L)	6,30	3,44	1
Oil and Grease (mg/L)	8,89	2,45	10
Color (Pt-Co)	1500	1300	280

3.1.2 Laboratory Equipment

3.1.2.1 UV Reactor

A 40 W low-pressure mercury vapor sterilization lamp was immersed in a quartz jacket and cooled with air during experiments. UV lamp was emitting short wave ultraviolet radiation at 253.7 nm. During a typical run, 800 ml sample solution was introduced to the glass reactor and the wastewater was mixed with magnetic stirrer throughout the experiments. The picture of UV reactor is presented in Figure 3.1.

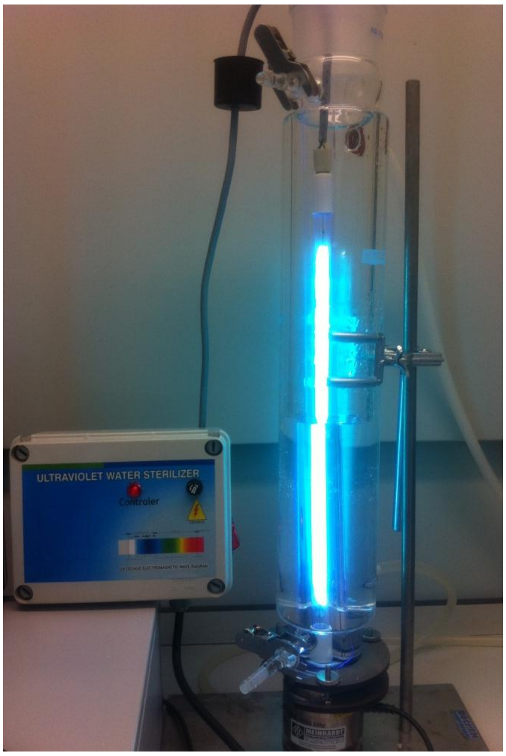

Figure 3.1 The picture of the UV reactor

3.1.2.2 Ozone Generator

During the ozonation and ozone-combined experiments, the ozone has supplied to the system with Ozone Generator LAB2B model. This model is a 105 W system which feeds 10 gr/hr ozone to water. It also has oxygen flow rate 2-5 ltr/min.

Figure 3.2 The picture of the Ozone Generator.

3.1.2.3 Ultrasonic Reactor

The system consists of 1500 ml glass reactor surrounding by cooling jacket to keep the temperature constant at 20±0.5˚C. Piezoelectric transducer is emitting at three frequencies, 582, 860 and 1136 kHz. 250-Watt generator converts the electrical power input into mechanical energy. The active acoustical vibration area is 22cm^2 (Figure 3.3).

An ultrasonic system transforms electrical power input vibrational energy, i.e. mechanical energy, which is then transmitted into the sonicated reaction medium. The power supplied from the generator to into the reactor has measured by calorimetry, which involves a measurement of the initial rate of heating produced when a system is irradiated by ultrasound (Mason, 1999).

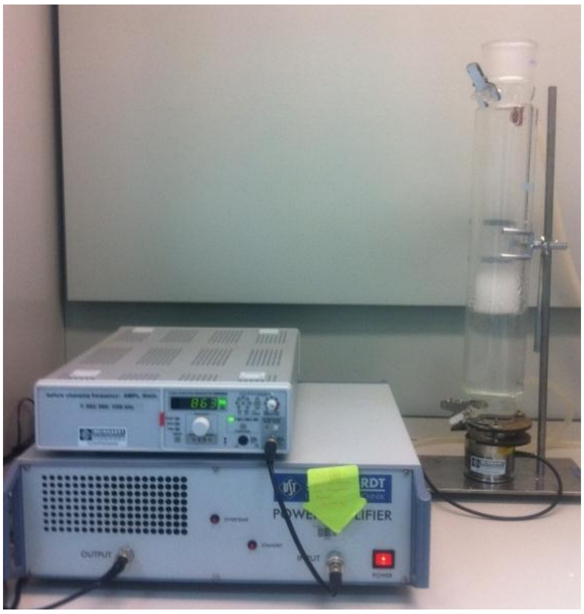

Figure 3.3 The picture of the Ultrasound Reactor.

3.1.2.4 TOC Analyzer

The total carbon analyses of the samples generated during the degradation experiments gave us the mineralization rate of the processes in a simple and quick analysis. Total organic carbon of samples was determined with a Shimadzu TOC-VCPn analyzer seen in Figure 3.4.

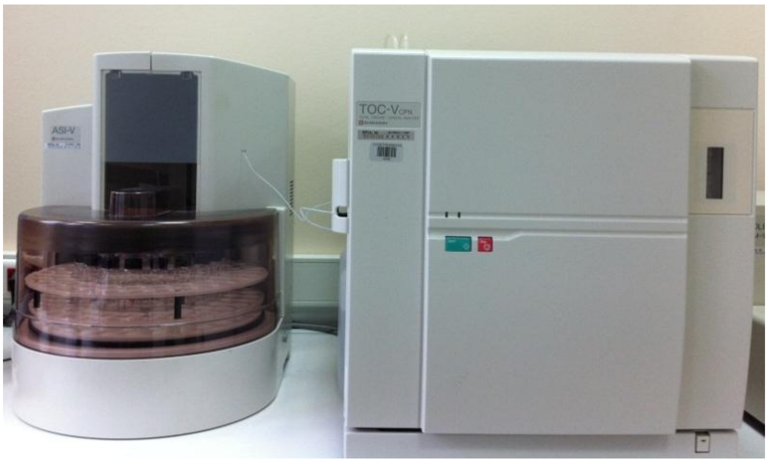

Figure 3.4 The picture of the TOC Analyzer.

3.1.2.5 Spectrophotometer

HACH DR5000 UV-Visible spectrophotometer was used to determine the absorption spectra of the samples at 436, 525, 620 nm and Pt-Co scale. The degradation of color was monitored by measuring the reduction in wavelengths, 436, 525 and 620nm, respectively. For Pt-Co scale color measurement, the color at 465 nm absorbance was monitored. Hydrogen peroxide was measured spectrophotometrically and ozone determination has done spectrophotometrically at 600nm.

Figure 3.5 The picture of the Spectrophotometer.

3.1.2.6 Microtox Analyzer

Toxicity of the samples was determined using a Microtox Model 500 Analyzer (Figure 3.6), which utilizes freeze-dried luminescent bacteria (*V. fisheri*) as test organisms.

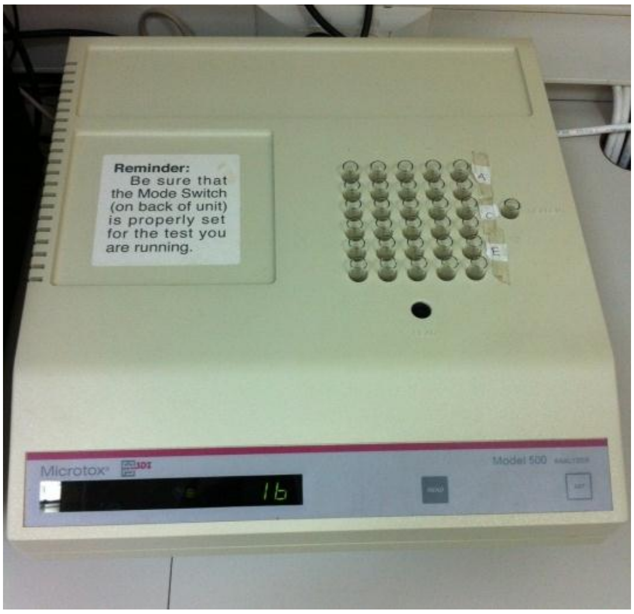

Figure 3.6 The picture of the Microtox Analyzer.

3.1.3 Reagents

Hydrogen Peroxide, H_2O_2 (35%, Merck) was provided fromMerck. Ferrous sulfate heptahydrate, FeSO4.7H2O, (99.5%, Fluka) was used for preparing Fenton reagent. Sodium Hydroxide (97.5%, Fluka) and sulfuric Acid (95-98%, Fluka) was used for pH adjustments.

3.1.4 Analytical Methods

Chemical Oxygen Demand (COD): The COD (Chemical Oxygen Demand) test represents the amount of chemically digestible organics (food). COD measures all organics that were biochemically digestible as well as all the organics that can be digested by heat and sulfuric acid. It is used in the same applications as BOD.

COD has the advantage over BOD in that the analysis can be completed within a few hours whereas BOD requires 5 days. The major drawback of the COD test is the presence of hazardous chemicals and toxic waste disposal.

In the case of COD analyze, 2,5mL sample of waste water containing organic material is placed in contact with a very strong inorganic oxidant, a mixture of potassium dichromate $K_2Cr_2O_7$ (1.5 mL of digestion solution) and sulphuric acid (3.5 mL catalyst solution, (Ag_2SO_4/H_2SO_4) with silver sulphate as a catalyst. The temperature is increased to the point of ebullition of the mixture, resulting in an increase of the oxidation rate. After two hours (the standard duration of the test) heating to the temperature (148 ºC) of the organic compounds is virtually complete. The resulting COD value can be determined by means of titration by reading the concentration of formed chromium (Cr^{+3}) concentration.

Color Analyses: Wastewater from industries does not show sharp and distinguished absorption maxima. Characterization of the intensity of color of a water sample can be defined by measuring the absorption of light. Different colors cause maximum absorption at different wavelengths of the incident radiation. Although there are several color determination methods, in this study two most pronounced color determination methods are used. They are i) Chromacity number (RES), and ii) Pt-Co methods.

i) According to International Standard, the color of the water is determined by using photometer or spectrometer at least three different wavelengths distributed over the range of the visible spectrum:

$\lambda(1)=436$ nm $\lambda(2)=525$nm $\lambda(3)=620$nm

Absorbance of filtrated samples measured in their true color with a spectrophotometer according to ISO EN 7887. Measurements have performed at 436, 525 and 620 nm against optically pure water. Then, Chromaticity Number of the specified wavelength (α) calculated with the aid of Eq. (3.1):

$$(\lambda) = \frac{A}{d} \text{ x } f \tag{3.1}$$

where:

A is the absorbance of the water sample at the wavelength λ;
d is the optical path length, in millimeters, of the cell;
f is a factor used to give the spectral coefficient, in reciprocal meters (*f*=1000)

As defined in ISO EN 7887, the limit discharge values for are 7, 5, 3 m_{-1}, for the wavelengths 436 nm, 525 nm, and 620 nm, respectively.

ii) Pt-Co is a color standard, made from dilutions of a Pt-Co solution by A.Hazen in American Chemical Journal, in 1892, adopted in Standard Methods For the Examination of Water and Waste Water, made by APHA. HACH DR 5000 UV-Vis spectrophotometer was used for the examination of color in terms of Pt-Co color unit. The stored program in spectrophotometer is calibrated in color units based on the APHA-recommended standard of 1 color unit being equal to 1 mg/l platinum as chloroplatinate ion. Test results (Programs 125) are measured at 465 nm. Prior to measurements, all samples are filtrated (0.45μm filter paper) to avoid interferences by undissolved matters.

According to the current Turkish Water Pollution Control Regulation, color discharge limit for the related textile industry (Table 10.1) was given as 280 Pt-Co. In the near future, The Ministry of Environment is planning to define new standard, which is RES, for color examination (9 m^{-1}, 7 m^{-1}, 5 m^{-1} are the limit values for RES color unit for the wavelengths 436nm, 525nm, 620nm respectively).

TOC Analyses: The key point about a TOC analyzer is whether it can efficiently oxidize hard-to-decompose insoluble and macromolecular organic compounds, not just the easily decomposed, low molecular weight organic compounds. The 680°C combustion catalytic oxidation method that efficiently analyze all organic compounds. The technique has been recognized for its ability to analyze samples with particulates, refractory compounds, and high salt matrices in wastewater and other difficult matrices.

For this study, both the total organic carbon (TOC) method, as well as the chemical oxygen demand (COD) method have been used for determine the organic charge present.

Toxicity Analysis: Toxicity is the ability or property of a chemical, substance or sample to disrupt or inhibit a biochemical process within a living thing. Toxicity of the samples was determined using a Microtox Model 500 Analyzer, which utilizes freeze-dried luminescent bacteria (*V. fisheri*) as test organisms. The test system is based on the principle that bacterial luminescence is tied directly to cell respiration, so that any inhibition of cellular activity (due to toxicity) results in a reduction in the degree of luminescence. The Microtox analyzer is made of an array of sample wells for holding dilutions of bacterial suspensions, and a photometer to measure the light output of *V. fisheri* at 5 and 15 min after contact with the toxicant.

Light readings are compared to those of control bacteria (healthy) to determine the inhibition of light emission, and to estimate the EC50 of the sample. (EC50 is defined as the effective concentration of the toxicant- expressed as percentage relative to the original sample strength- that causes a 50 per cent reduction in the light output of the test organisms during the designated time interval.) Sample preparation, osmotic adjustment and serial dilution procedures were carried out by reference to the Basic Protocol of the Microtox assay (Microtox Manual, 1992). Toxicity Unit (TU) value was calculated by using EC50 (100/EC50, expressed as volume percentage). The higher the TU, the higher the toxicity of the sample.

3.1.5 Kinetic Studies

The degradation of color in all test samples was pseudo-first order with respect to the absorbance of the dye in the visible band. The analysis of absorbance versus time data by non-linear regression showed that absorbance decays exponentially:

$$\frac{A}{Ao} = e^{-kt} \tag{3.2}$$

where; A and A_0 are the maximum absorbance of the effluent at time t and zero, respectively, and k is the decay constant (min^{-1}).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 UV/H_2O_2 PROCESS

4.1.1 Optimum H_2O_2 Concentration

Different concentrations of (5, 10, 25, 50 ve 100 mM) H_2O_2 were studied by feeding 800 ml sample with in the presence of UV light (40W). During a 30-minute experiment, with combine of H_2O_2 and UV the color removal was investigated. In order to determinate the optimum dosage, kinetic rate constant were calculated by monitoring the absorbance decays. The RES absorbance wavelengths were 436 nm, 525 nm and 620 nm, respectively. The experiments were conducted at wastewaters natural pH 7,6 and at room temperature. The results of the experiments are given below as A/A_o versus time.

The color degradation increases in 25 mM and 50 mM concentration of H_2O_2 but on the other hand when H_2O_z concentration increases (100 mM) color removal declines. The reason behind the decline of high concentration of H_2O_2 can be based on the reaction of excessive hydrogen peroxide with hydroxyl radicals.

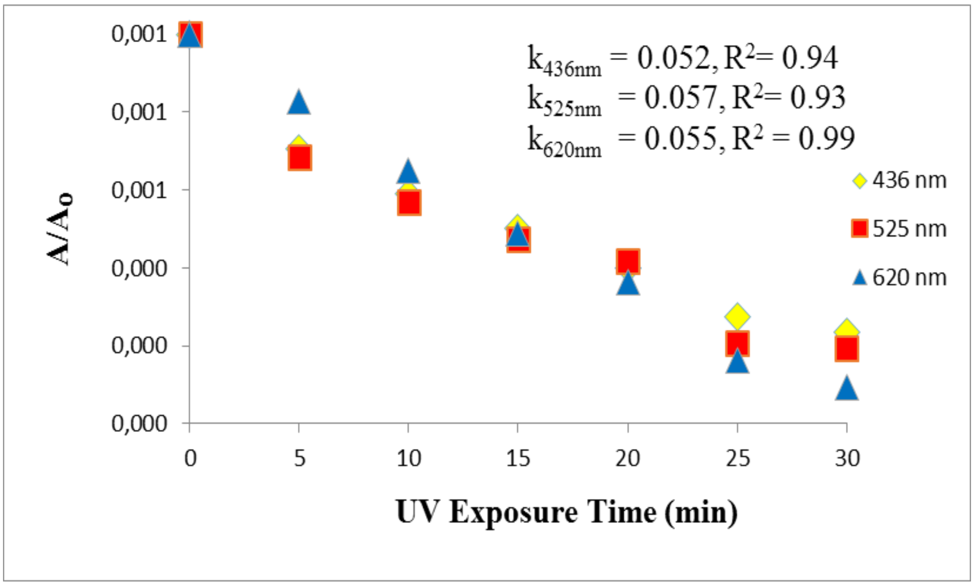

Figure 4.1 Rate of color removal for 5 mM H_2O_2, 40W UV-C light at pH 7,6.

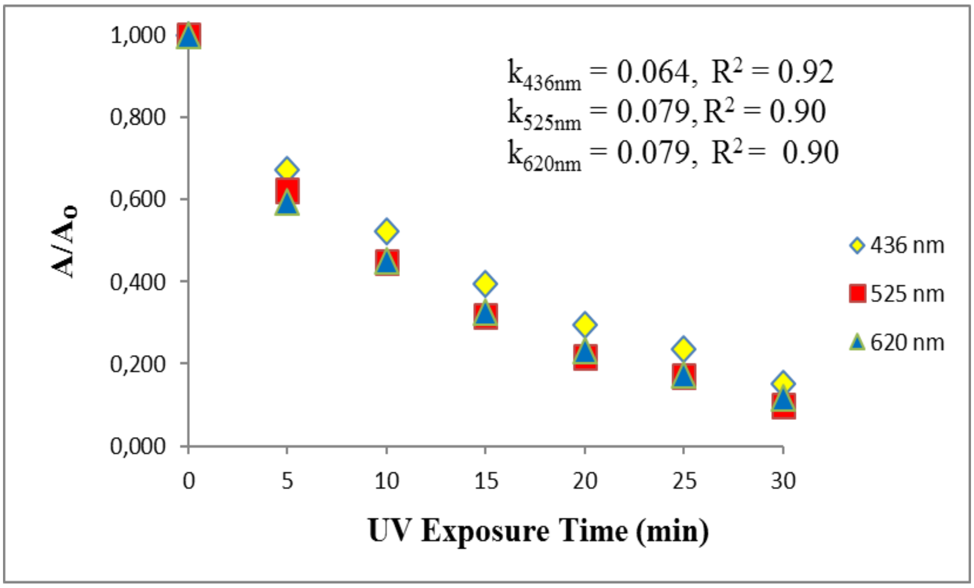

Figure 4.2 Rate of color removal for 10 mM H_2O_2, 40W UV-C light at pH 7,6.

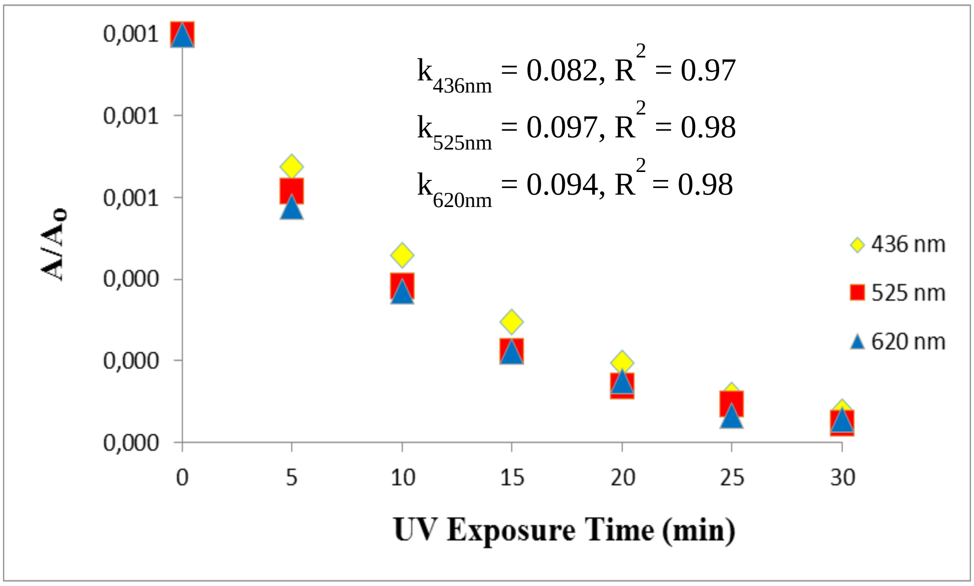

Figure 4.3 Rate of color removal for 25 mM H_2O_2, 40W UV-C light at pH 7,6.

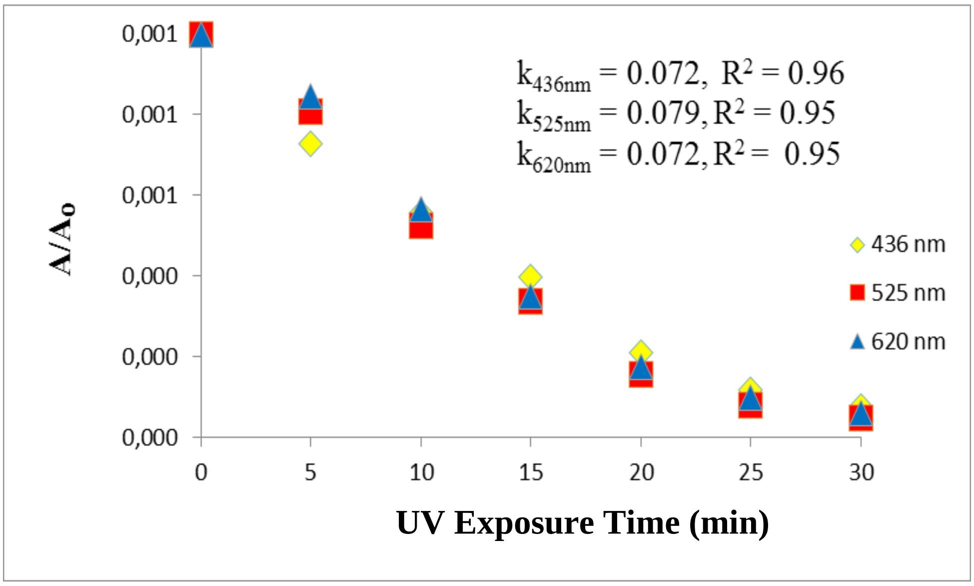

Figure 4.4 Rate of color removal for 50 mM H_2O_2, 40W UV-C light at pH 7,6.

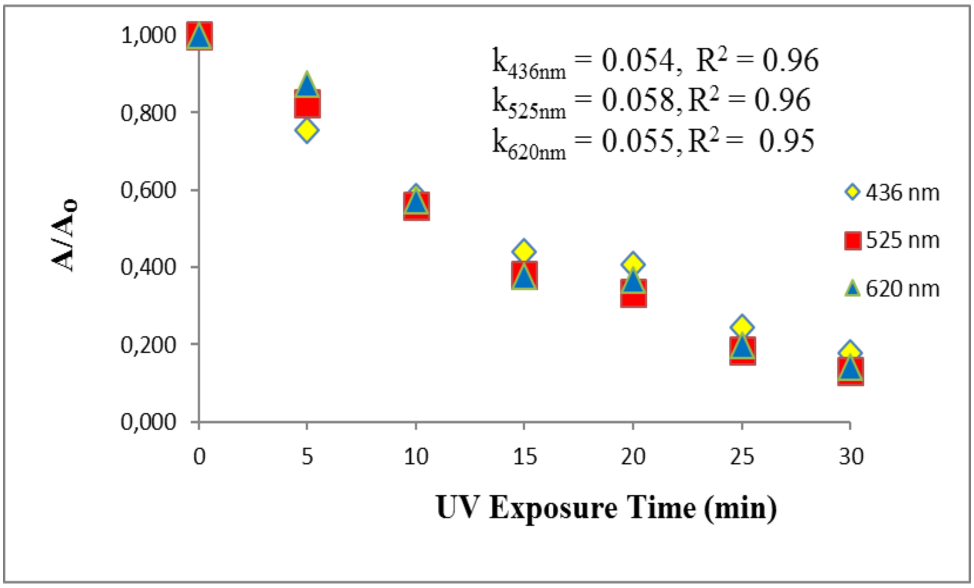

Figure 4.5 Rate of color removal for 100 mM H_2O_2, 40W UV-C light at pH 7,6.

Optimum concentration was observed in 25 mM H_2O_2. Normally 25 and 50 mM H_2O_2 supplement has similar efficiency. In order to reduce operating cost, 25 mM H_2O_2 supplement is considered as sufficient (Figure 4.3). The reaction rates at various H_2O_2 concentrations for UV/ H_2O_2 process are given in Table 4.1.

Table 4.1 Kinetic Rate Constants of H_2O_2 Concentrations, k (min^{-1}) values.

H_2O_2 Conc (mM)	**Kinetic Rate Constants (k min^{-1})**		
	436 nm	**525 nm**	**620 nm**
5	0,0524	0,0572	0,0551
10	0,0645	0,0795	0,0789
25	**0,0821**	**0,0979**	**0,0945**
50	0,0722	0,0791	0,0724
100	0,0539	0,0584	0,0546

4.2 PHOTO-FENTON PROCESS

This process involves the hydroxyl radical (HO•) formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/Fe^{+2}). (Fenton, 1894; Baxendale and Wilson, 1956). The HO• with oxidation potential of 2.80 V can oxidize a broad range of organic compounds indiscriminately.

4.2.1 Optimum Fe^{+2} Concentrations

Photo-Fenton processes carried out in the optimum H_2O_2 concentration (25 mM), and in the various ferrous concentrations (0.05, 0.1, 1 and 2.5 mM Fe^{+2} solutions) and in the UV (40W) presence of radiation, at pH 3. At the end of the experiments, pH of samples raised about up to 8 with 1 N NaOH after the iron separated from water by centrifugation. Same procedure was applied for dark Fenton process.

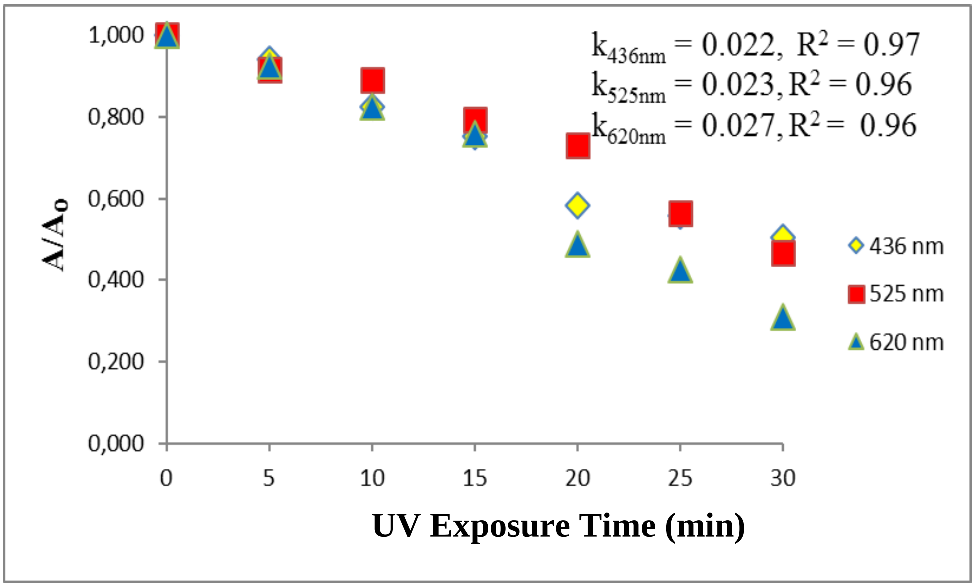

Figure 4.6 Rate of color removal for 0.05mM Fe(II), 25mM H_2O_2, 40W UV-C light at pH:3.

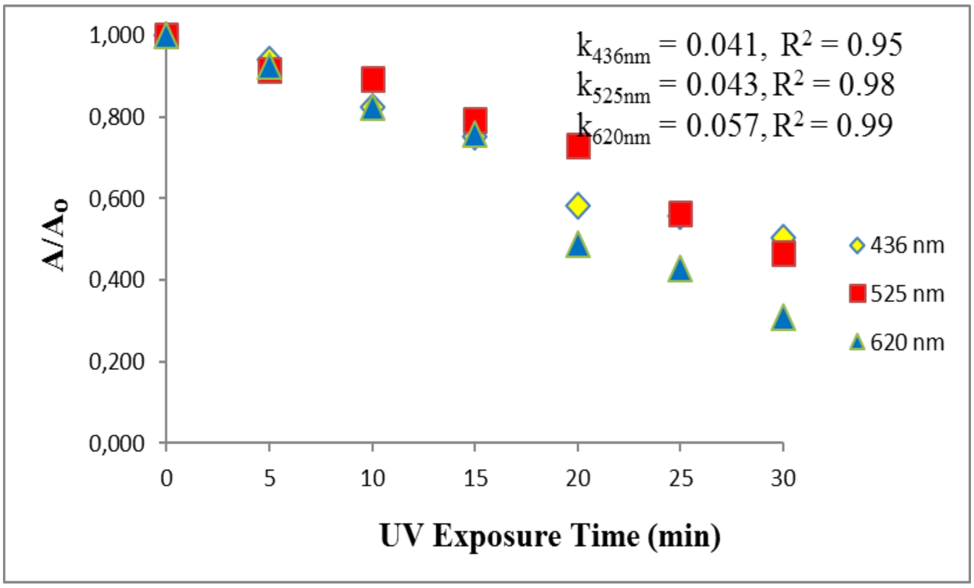

Figure 4.7 Rate of color removal for 0.1mM Fe(II), 25mM H_2O_2, 40W UV-C light at pH:3.

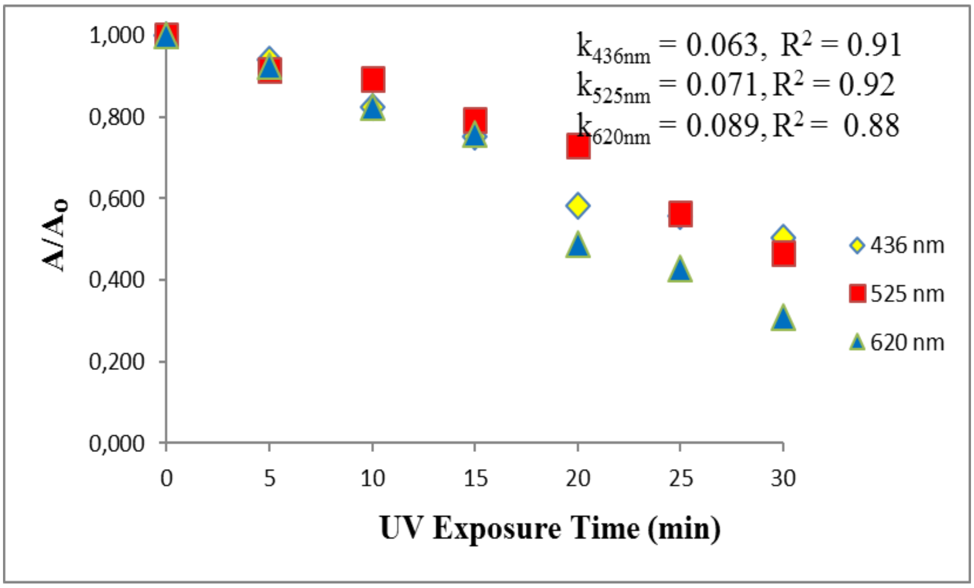

Figure 4.8 Rate of color removal for 1mM Fe(II), 25mM H_2O_2, 40W UV-C light at pH:3.

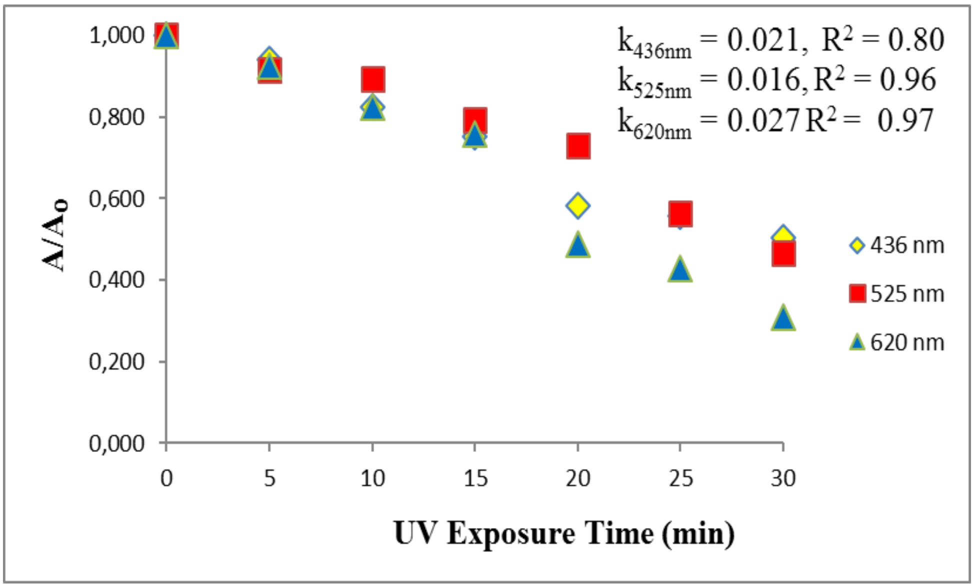

Figure 4.9 Rate of color removal for 2,5mM Fe(II), 25mM H_2O_2, 40W UV-C light at pH:3.

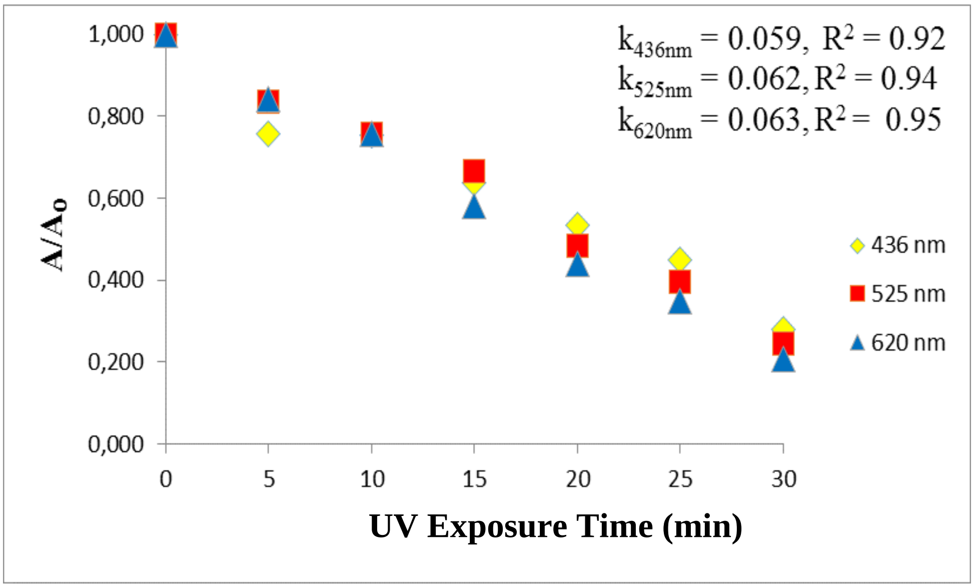

Figure 4.10 Rate of color removal for 1mM Fe(II), 25mM H_2O_2 at pH:3.

Iron in its ferrous and ferric forms acts as a photo-catalyst and requires a working pH below 4.0 (Xu *et al.*, 2003). Amount of ferrous ion is one of the main parameters to influence the Fenton and photo-Fenton processes. From the experimental results shown in Figure 4.11, that decolorization rate of the textile wastewater distinctly increased with the increasing amount of Fe^{+2}.

Addition of Fe^{+2} above 1 mM in this process did not affect the decolorization rate. The decolorization percentage of textile wastewater began to decrease when the concentration of Fe^{+2} was higher than 1 mM. It is known that Fe^{+2} had a catalytic decomposition effect on H_2O_2. When Fe^{+2} concentration is increased, the catalytic effect also accordingly increases and when its concentration was higher, a great amount of Fe^{+3} was produced.

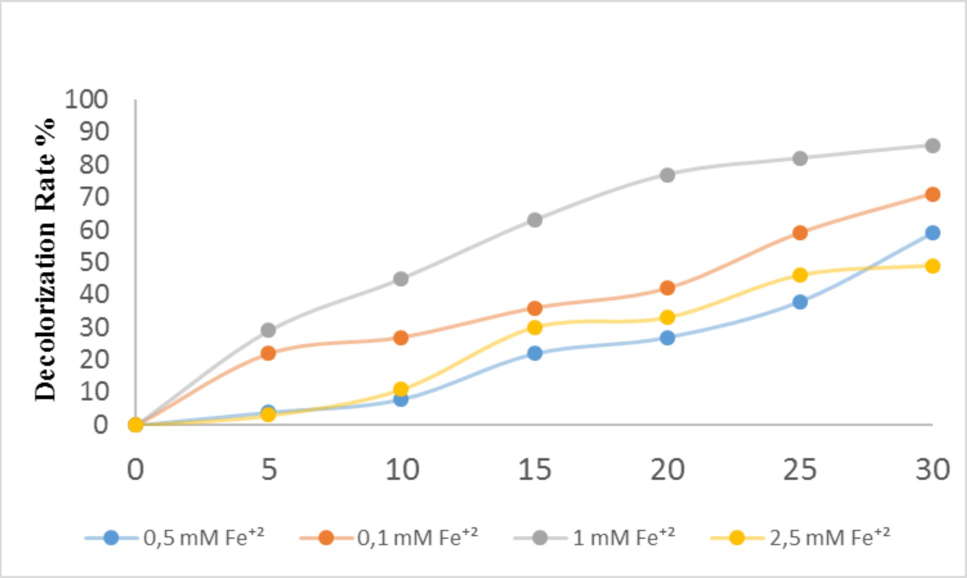

Figure 4.11 Effect of the initial concentration of Fe^{+2} in photo-Fenton process.

4.2.2 Effect of pH

The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency.

4.2.3 Effect of UV light

The effect of UV light intensity on the decolorization of the textile wastewater in comparing photo-Fenton and Fenton process was investigated by 40W-254 nm UV light intensity is depicted in Figure 4.12. The UV effect also shown as between Figure 4.8 and 4.10.

The degradation rates decreased with absence of UV. Figure 4.10 showed that photo-Fenton process produces more hydroxyl radicals than dark Fenton process. For this reason photon addition in oxidation process has effective color removal rates than dark Fenton process.

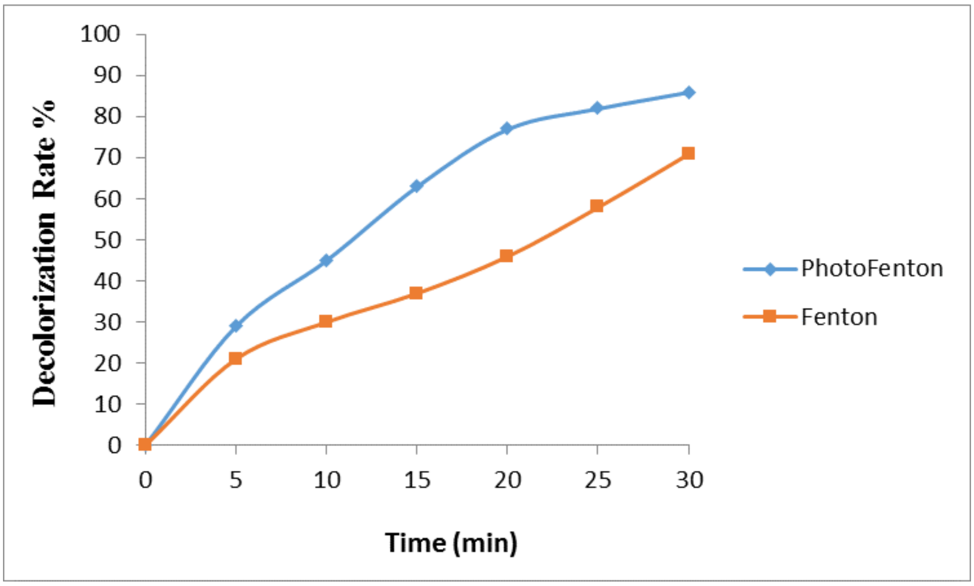

Figure 4.12 Effect of UV light intensity in photo-Fenton and Fenton process.

Within 30 min of UV light presence 85% decolorization rate had seen. In dark Fenton process, 71% decolorization rate had reached in 30 min. In this process UV light intensity is mainly used for photolysis of H_2O_2 and photo reduction of ferric ion to ferrous ion (Muruganandham and Swaminathan, 2004). The enhancement of removal is due to the increase in hydroxyl radical formation. The rate of photolysis of H_2O_2 depends directly on the incident light intensity. At absence of UV light intensity the photolysis of H_2O_2 is limited, but at presence of UV light intensity more hydroxyl radicals are produced upon photodissociation of H_2O_2, hence removal rate increases (Modirshahla et al., 2006).

4.3 OZONATION PROCESS

4.3.1 Ozone Alone

Ozone reacts with aqueous organic pollutants found in water and wastewater via two different pathways, namely direct molecular and indirect radical chain-type reactions (Gottschalk et al., 2000). The ozonation reaction pathway strongly depends on the characteristics of the wastewater to be treated, i.e., pH, concentration of ozone decomposition initiators, promoters and scavengers in the reacting medium (Glaze et al., 1987).

Ozonation experiments were conducted at different ozone doses (5, 15, 25 mg/lt) for up to 120 min at pH 7,65 the natural pH of textile biocide effluents, as well as at pH 3 and 10 to explore the effect of enhanced ozone decomposition at elevated pH on biocide oxidation efficiency.

4.3.1.1 Effect of pH

Solution pH plays a major role in the formation of OH radicals during ozonation. The experiments were carried out at various pH values at the optimum ozone dose of 15 mg /l and the data are presented in Figure 4.13.

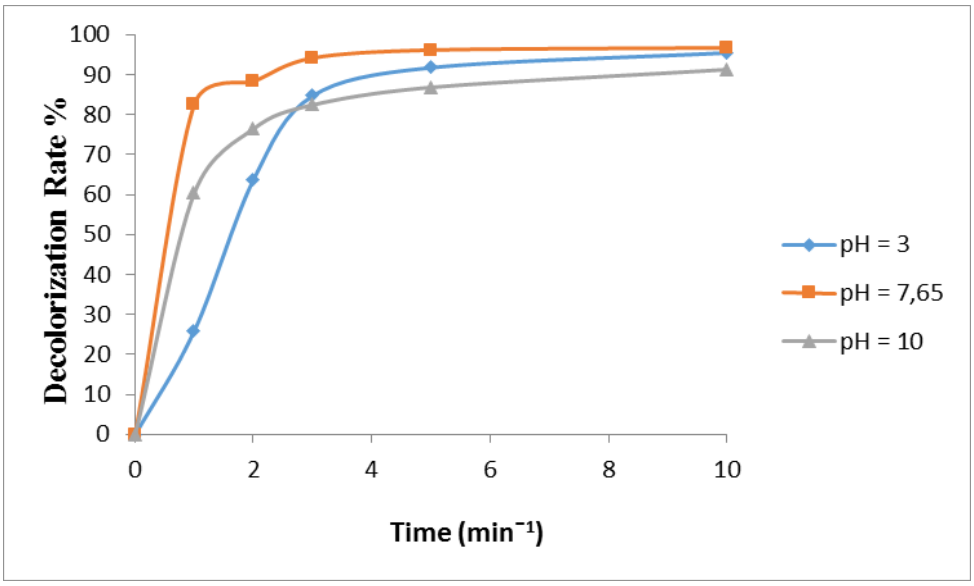

Figure 4.13 Decolorization rates of the wastewater at various pHs.

It could be seen from the Figure 4.13, that as the pH was increased from 3 to 7, color removal increased, this indicate that the alkaline pH is favorable for decomposition by ozonation which is initiated by the formation of hydroxyl radicals at higher pH values (Dore at al., 1988; Selcuk, 2005). The applied ozone dose was able to decolorize dyes within 2 min of ozonation turning the solution colorless. Color removal is 91% at pH 10, while 97% at pH 7. This is shown that better removal was observed t at pH 7. The solution also turned from brown-yellow to colorless.

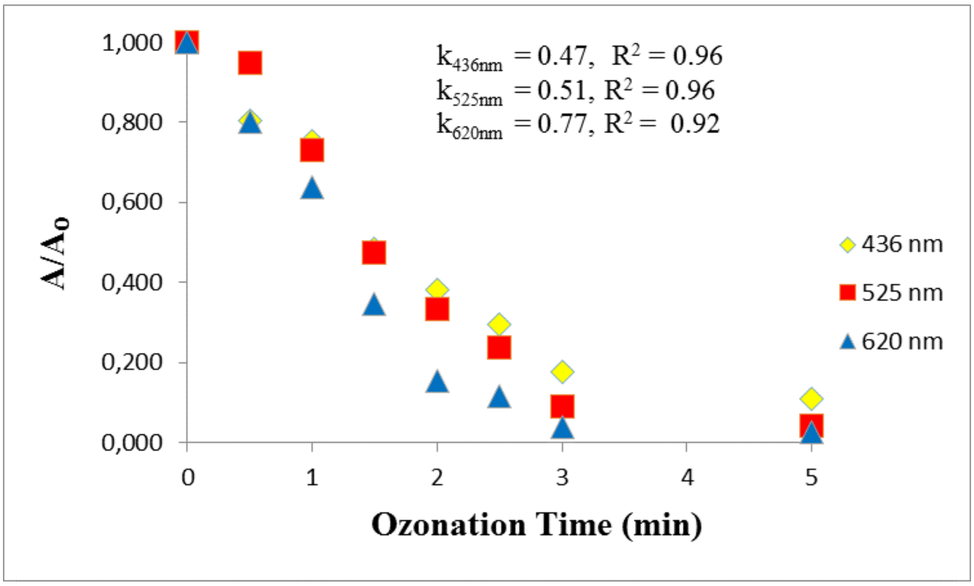

Figure 4.14 Rate of color removal at pH: 3 (15 mg/l ozone dosage).

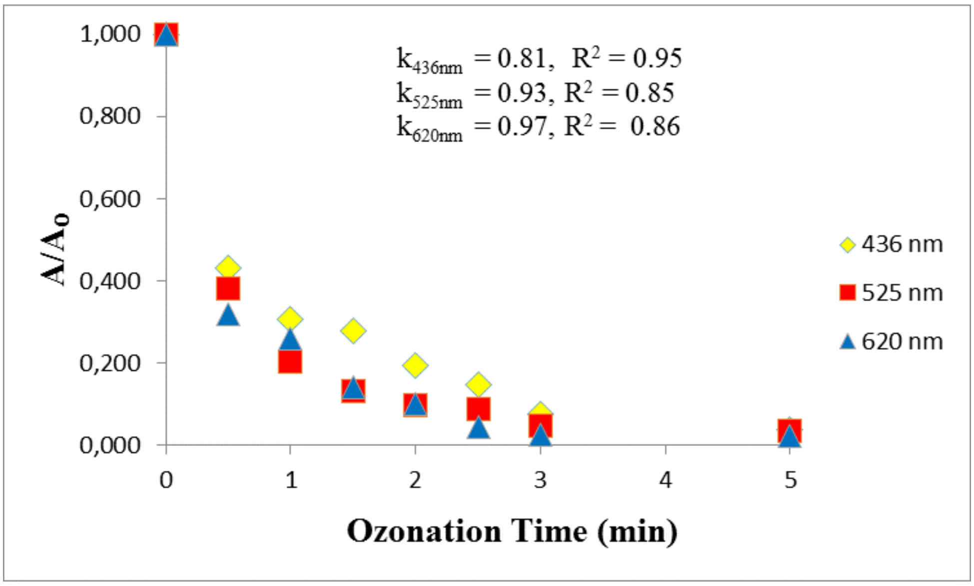

Figure 4.15 Rate of color removal at natural pH: 7,65 (15 mg/l ozone dosage).

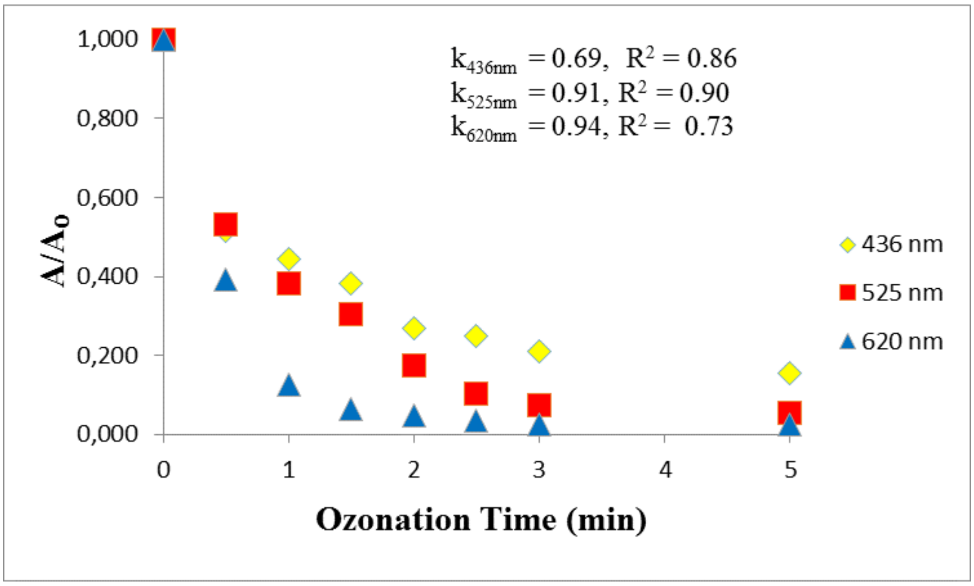

Figure 4.16 Rate of color removal at pH: 10 (15 mg/l ozone dosage).

The ozonation of textile wastewater at various pH values (3, 7 and 10) were examined and the results are shown in Figure 4.14, 4.15 and 4.16. For the results, it is shown that textile effluent reduction is greatly influenced by the pH of the wastewater.

The highest ozonation rate and the efficient degradation is observed at the highest pH (10); and the oxidation rate declines with decreasing pH value to 3. As you can see there is not much more difference between pH 7,6 and pH 10. In the experiments of pH natural (7,65) decolorization occurs less than one minute.

4.3.1.2 Effect of Ozone concentration

Initial ozone concentration plays an important role not only for direct reactions of ozone with organics in the liquid phase but also for the production of OH• radicals. Experiments were performed at different doses (5, 15, 25 mg/lt ozone) of ozone at pH 7,65.

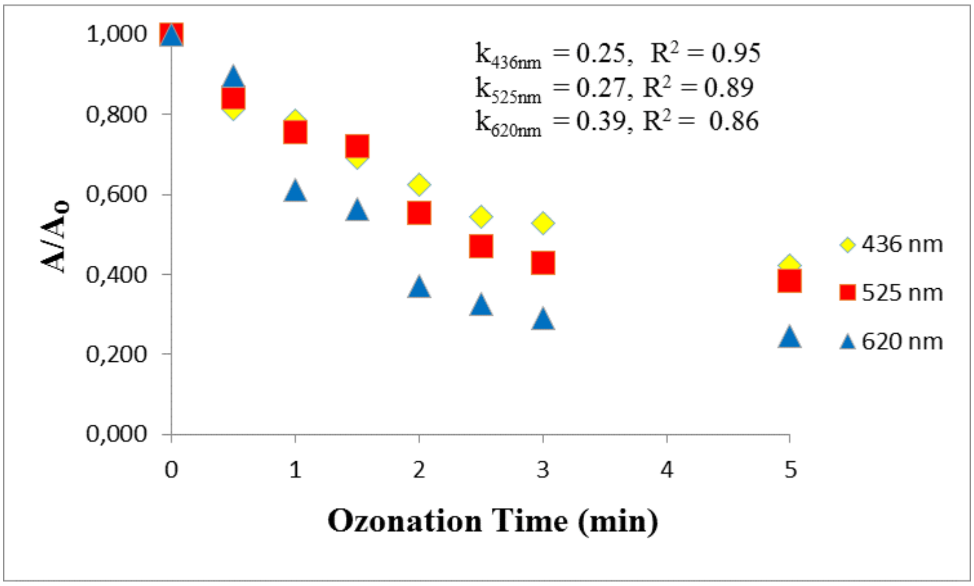

Figure 4.17 Rate of color removal at 5 mg/l ozone concentration (pH:7,65).

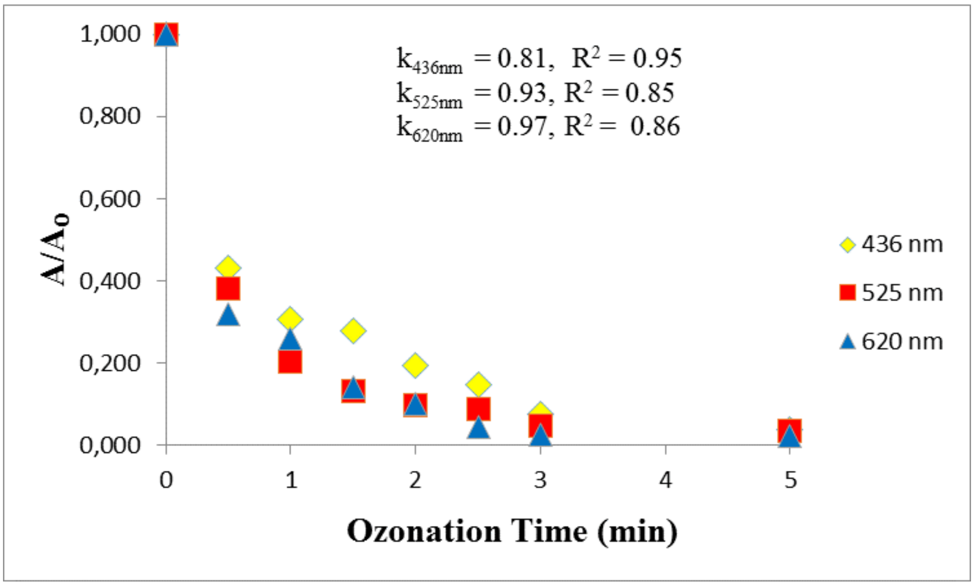

Figure 4.18 Rate of color removal at 15 mg/l ozone concentration (pH:7,65).

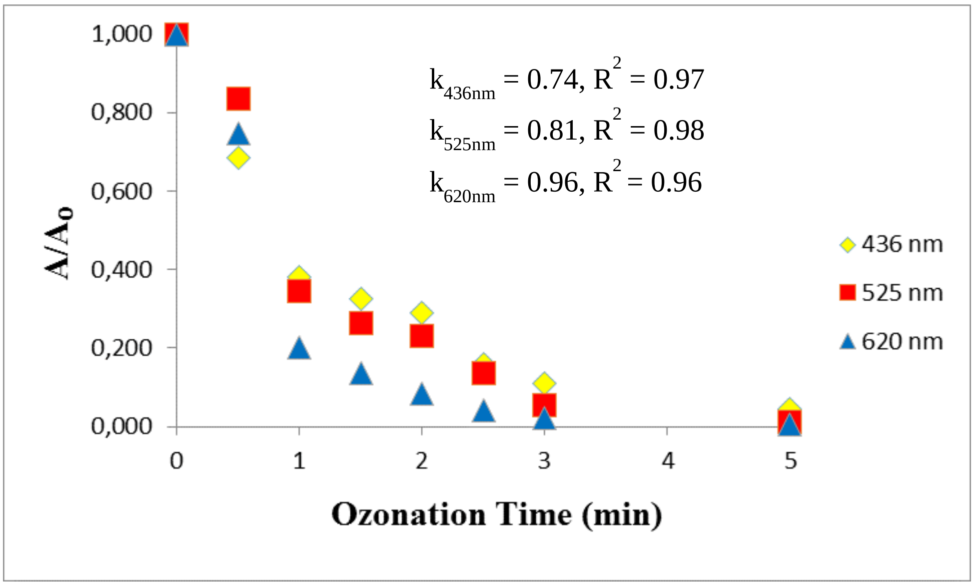

Figure 4.19 Rate of color removal at 25 mg/l ozone concentration (pH:7,65).

Efficiency of ozone treatment of textile wastewater depends on operating parameters, such as the applied ozone dose (Wu *et al.*, 2008) and pH. As seen below, the best degradation observed in 15 mg/l ozone concentration.

4.3.2 Ozone/H_2O_2 Process

H_2O_2 addition is usually known to increase the rate of ozone oxidation by allowing an enhancement in the quantum yield of formation of hydroxyl radical (Khadhraoui *et al.*, 2009). The effect of hydrogen peroxide to addition of ozonation process was examined in 25 mM hydrogen peroxide used in optimum ozone dose which is 15 mg/l. Experiments were performed at natural pH of wastewater (7,65).

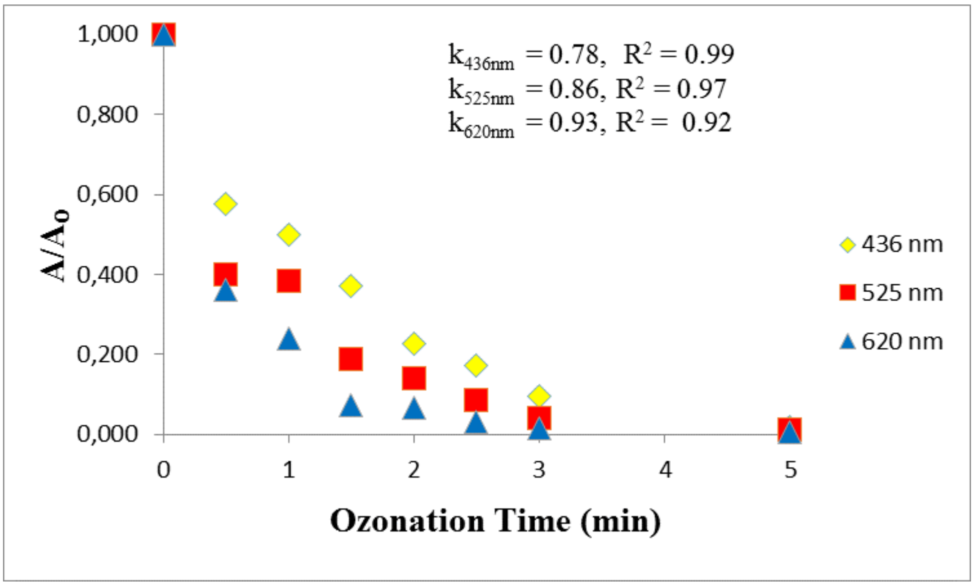

Figure 4.20 Rate of color removal at 15 mg/l O_3 concentration and 25 mM H_2O_2 (pH:7,65).

4.3.3 Ozone/UV Process

In contrast to UV and ozone treatments alone, O_3-UV AOP was effective at decolorization the wastewater. The optimum ozone dosage (15 mg/l ozone) fed up the system in 800 ml wastewater and supplied with 40W 254 nm UV light.

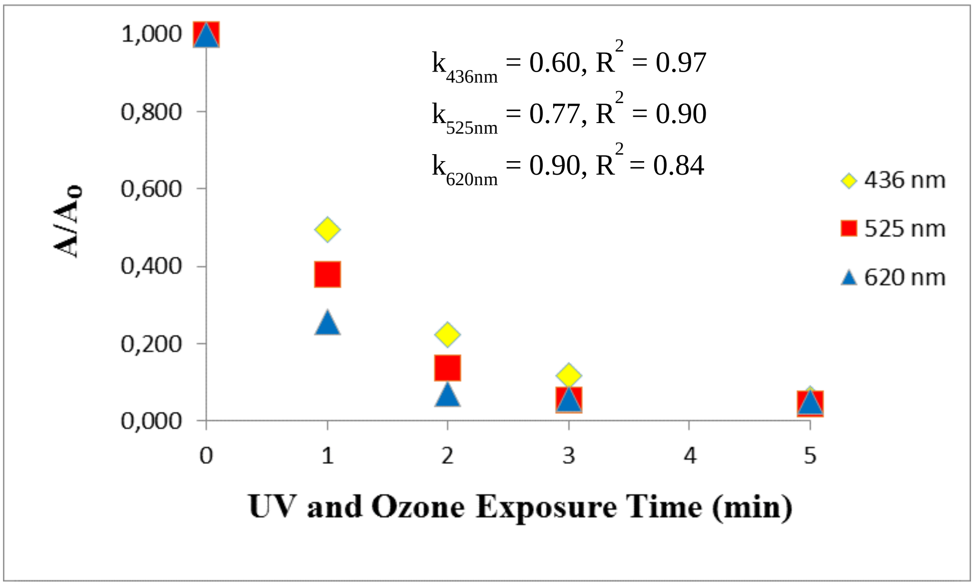

Figure 4.21 Rate of color removal at 15 mg/l O_3 concentration and 40W UV (pH:7,65)

4.3.4 Ozone/H_2O_2/UV Process

Addition of hydrogen peroxide shows a net enhancement due to the dominant production of OH• radicals. This combine process was performed with optimum H_2O_2 concentration (25 mM), and the optimum ozone dosage (15 mg/l) in 800ml sample with presence 40W 254 nm UV light. Color removal has seen in 2 minutes.

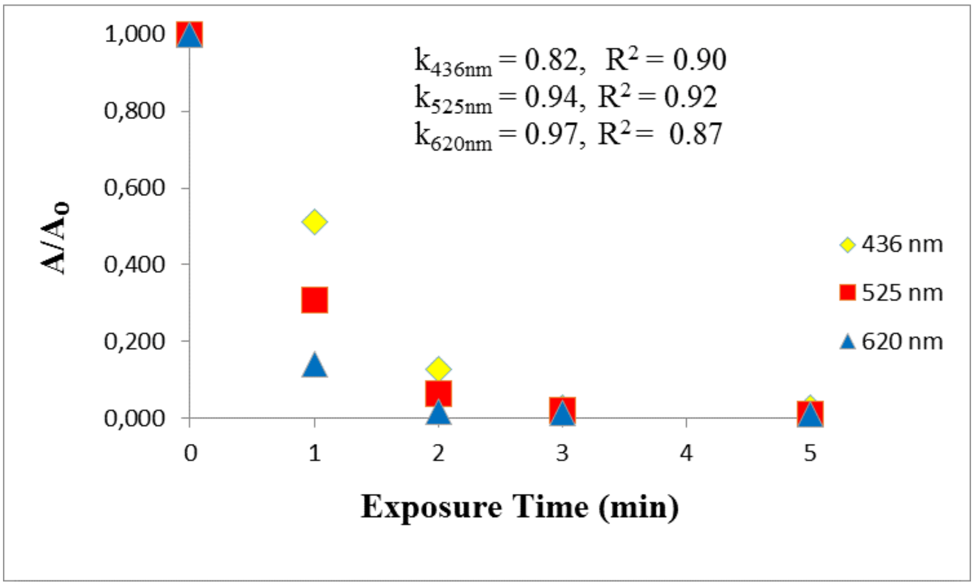

Figure 4.22 Rate of color removal at 15 mg/l O_3 concentration, 25 mM concentration of H_2O_2 and 40W UV-C light (pH:7,65).

4.4 ULTRASOUND PROCESS

This method involves the measurement of the temperature rise T against time t for about 30 seconds, using a thermocouple placed in the reaction vessel. From T versus t data, the temperature rise at zero time, dT/dt, can be estimated either by curve-fitting the data to a polynomial in t, or by constructing a tangent to the curve at time zero. The ultrasonic power (P) actually entering the system can then be calculated by substituting the value of dT/dt into equation 4.1. (Mason, 1999; Mason and Cordemans, 1998; Mason *et al.*, 1992):

$$\text{Power} = (dT/dt).C_p.M \qquad (4.1)$$

where:

C_p= heat capacity of water (~4.1840-4.1790 J g^{-1}.ºC^{-1}),

(dT/dt)= the temperature rise at zero time,

M= total mass of water in the reaction vessel (g).

After calculating the power in the reaction medium, the efficiency of the system can be determined either by calculating the ultrasonic intensity which is equal to total (determined) power per unit emitting area (W cm^{-2}), or by ultrasonic density (W mL^{-1}), i.e. total power per total mass of the solvent (water) in the reactor (Doğan, 2011). Optimization of system conditions are 800 ml at 7 degree amplitude and 860 kHz.

4.4.1 US-Alone Process

The one hour pre-aerated 800 ml sample were irradiated at 860 kHz in the presence of aeration about 120 min at natural pH (7,65).The reactor was cooled with water circulation to keep the temperature constant. Absorbance measurements were done with filtrated samples. The results are shown in Figure 4.23.

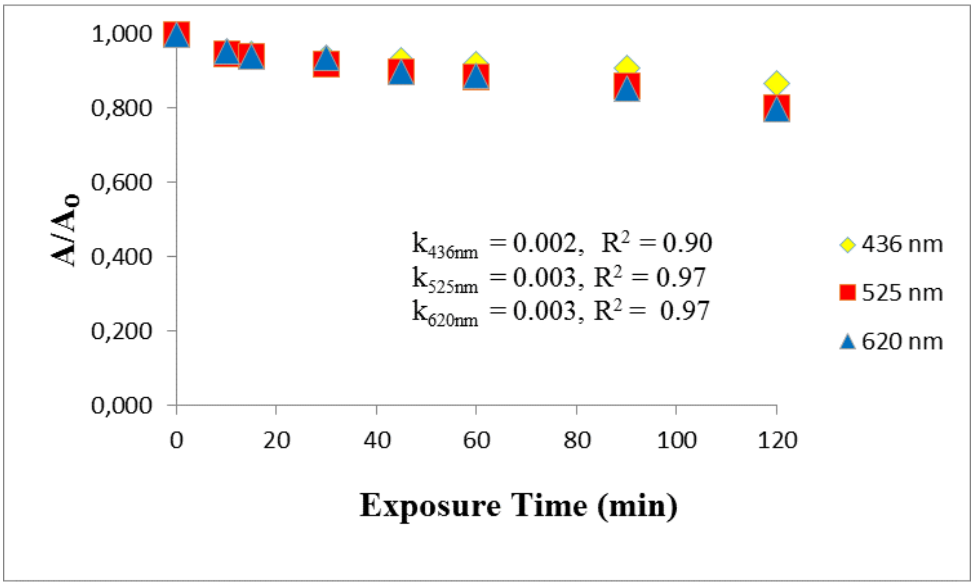

Figure 4.23 Color Removal Rate for US-Alone Process (860 kHz).

4.4.2 US/UV Process

In this process one hour pre-aerated 800 ml sample were irradiated at 860 kHz in the presence of 40W 254 nm UV light about 120 min at natural pH (7,65).

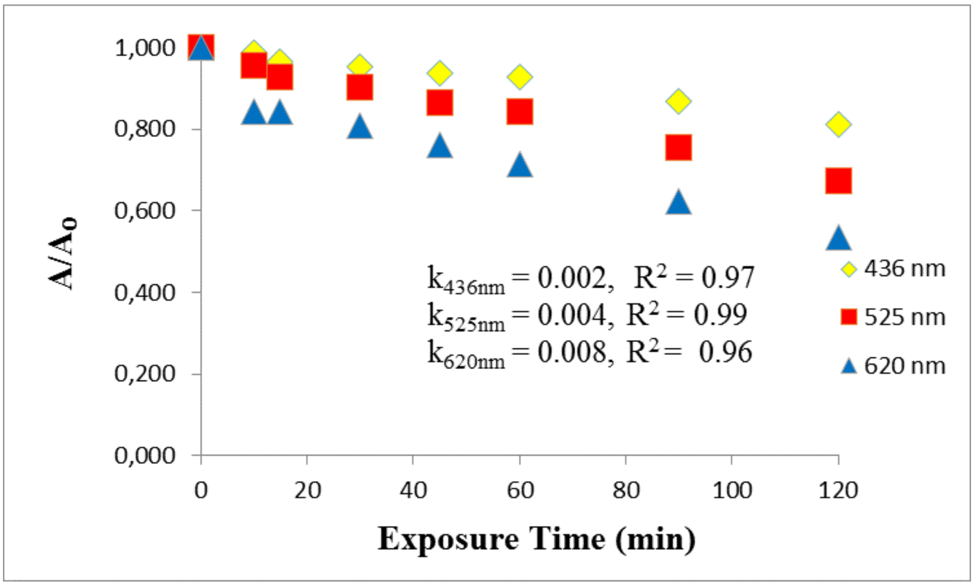

Figure 4.24 Color Removal Rate for 860 kHz US and 40W UV-C light (pH:7,65).

4.4.3 US/Ozone Process

At least one hour pre-aerated 800ml of sample were used for US/Ozone. The experiments were carried out at original pH of the samples. Ozone dosage was 15 mg/l. Ultrasound frequency was 860 kHz.

This process is more effective than US-Alone and US/UV process. As shown in below, in US/Ozone process color removal occurs less than 2 minutes. The other processes are too slow than US/Ozone process. Ozone exceedingly induce decolorization and decomposition of organic compounds.

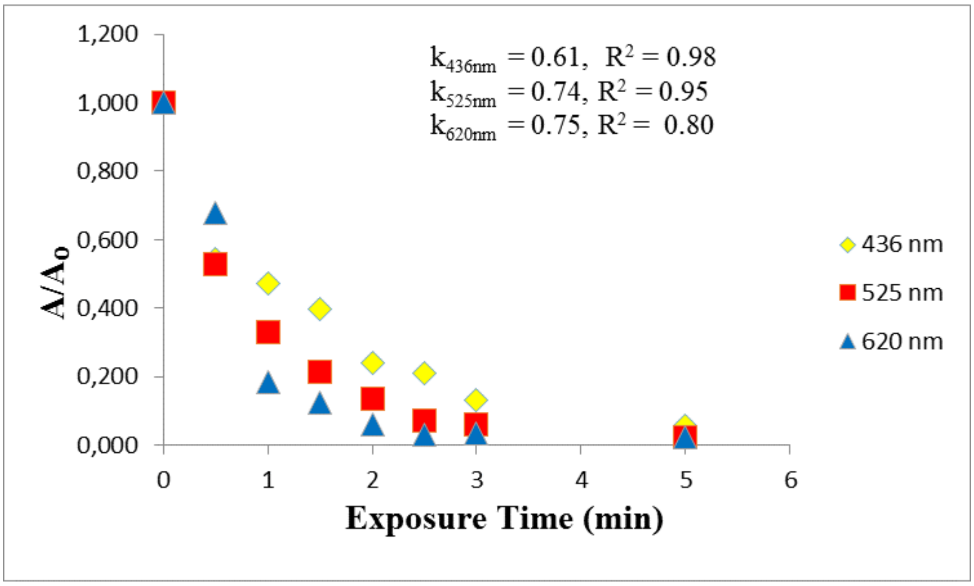

Figure 4.25 Color Removal Rate for 860 kHz US and 15 mg/l ozone concentration (pH:7,65)

4.5 COMPARISON of the OPTIMUM AOPs

4.5.1 Comparison by Color Removal

Color removal kinetic constant rates were determined by using the pseudo-first kinetic model. The decolorization rates were determined at 436, 525 and 620 nm in Figure 4.25. Pt-Co measurements for all studied AOPs have given in Figure 4.26.

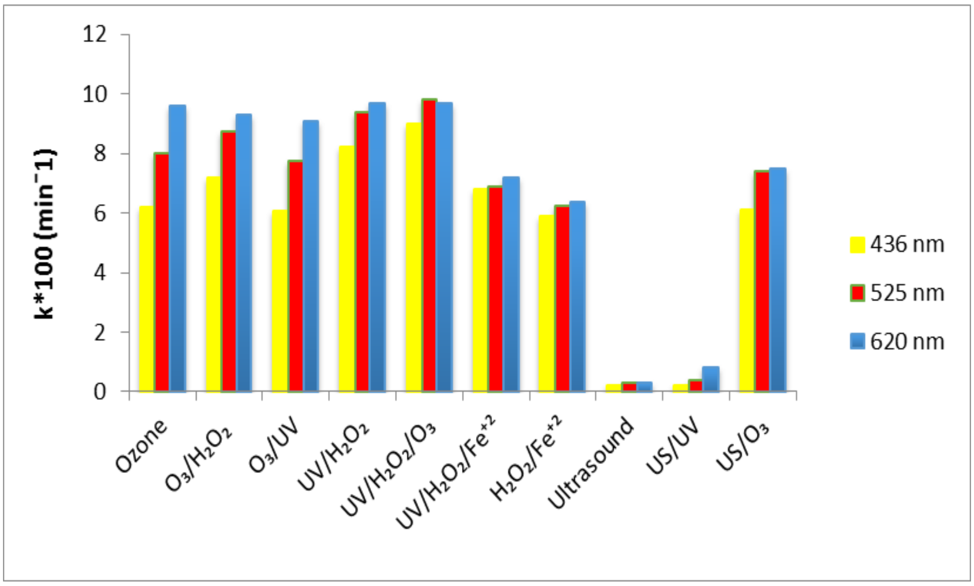

Figure 4.26 Kinetic rate constants, k*100 (min-1) for studied optimum AOPs.

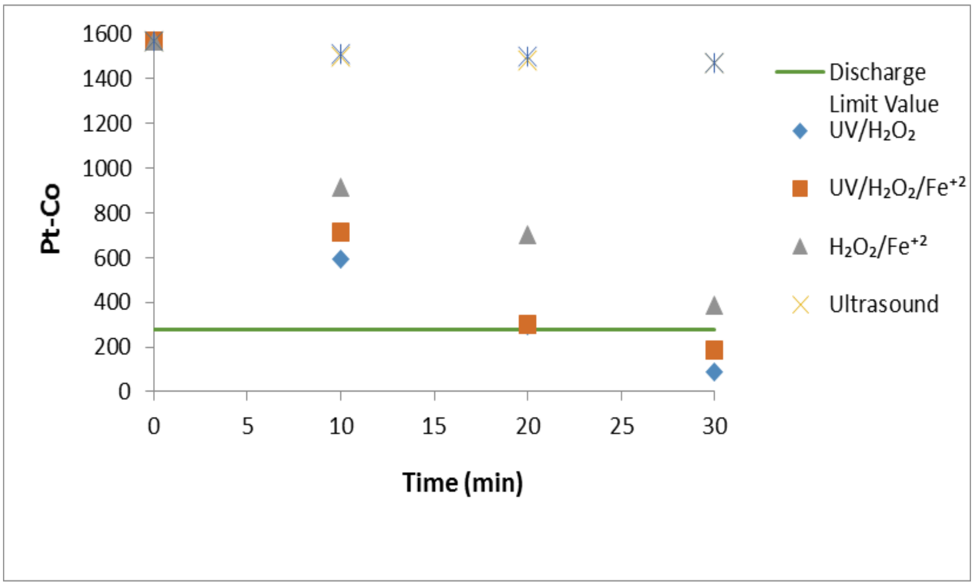

Figure 4.27 Pt-Co values for studied AOPs.

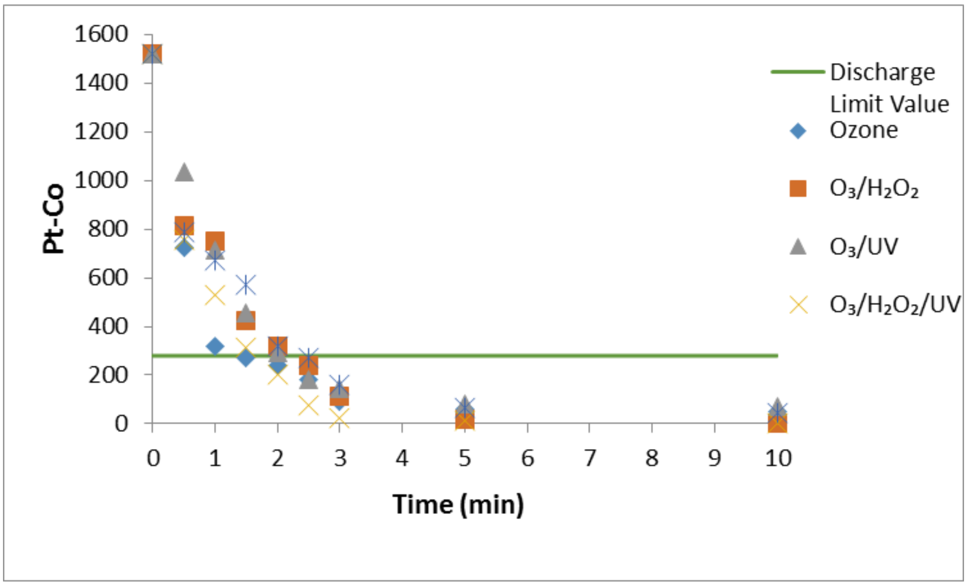

Figure 4.28 Pt-Co values for Ozone based oxidation processes.

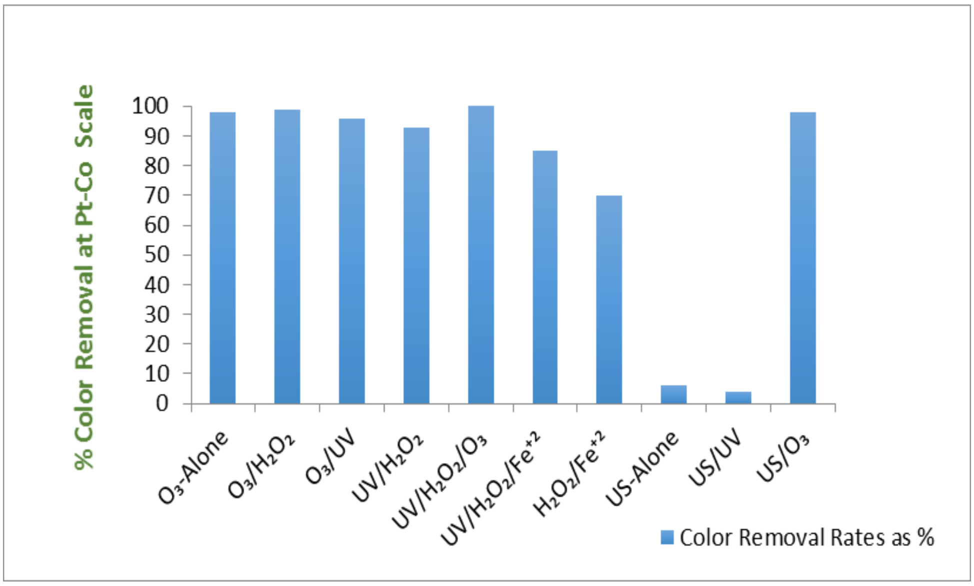

Figure 4.29 Color removal of selected AOPs at their optimum conditions.

As seen at Figure 4.27 most of the Advanced Oxidation Processes are suitable for color removal, however Ozone based processes gives best efficiency (Figure 4.28). At three different RES wavelengths gives the different kinetic rate constants.

Ozonation, UV/H_2O_2 and photo-Fenton processes are showed effective performance on the color removal as seen the above figures. After all US-Alone and US/UV processes are not good enough for color treatment. Ozone-Alone process showed 98%, O_3/H_2O_2 99%, O_3/UV 96%, UV/H_2O_2 93%, UV/H_2O_2/O_3 100%, Photo-Fenton 85%, H_2O_2/Fe^{+2} 70%, US/O_3 98%, color efficiency while US-Alone 15% and US/UV 20% had not very effective treatment rates in Pt-Co color unit (Fig 4.29). Based on the average 1300 Pt-Co influent color value of the biologically treated wastewater and the 280 Pt-Co discharge limit value, about 85 % color removal efficiency was accepted for AOP experiments.

4.5.2 Comparison by TOC Removal

The oxidation processes produces very strong oxidants, hydroxyl radicals, to non-selectively attack the hydrocarbons resulting bond cleavage into some smaller molecules till further mineralization to carbon dioxide while total organic carbon (TOC) was employed to indicate mineralization effectiveness of textile wastewater as shown in Figure 4.30.

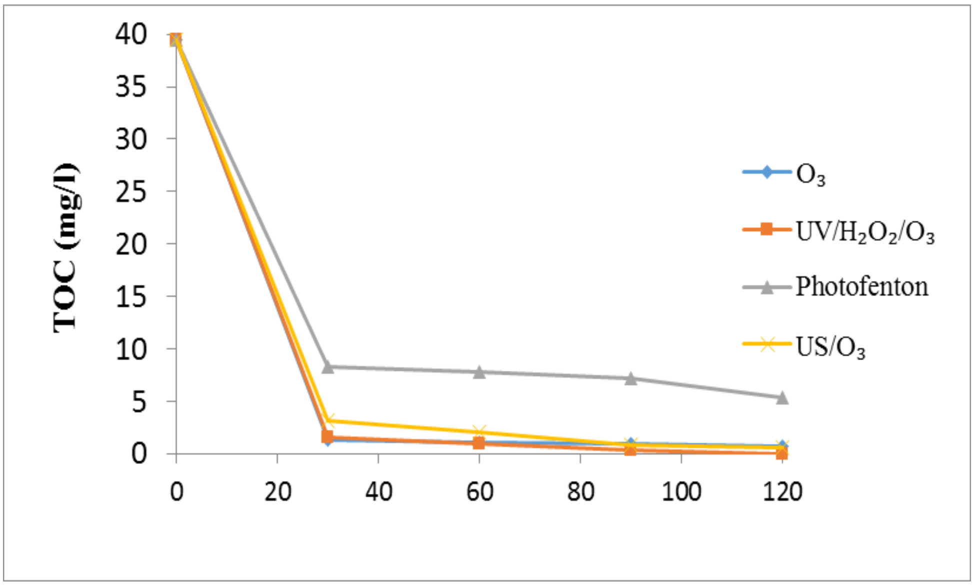

Figure 4.30 TOC values for most efficient AOPs after 120 min irradiation.

Utilizing the oxidation processes about 120 min, the initial TOC of textile wastewater, for Ozone-Alone process 98%, $UV/H_2O_2/O_3$ 99%, photo-Fenton 87%, US/O_3 98% mineralization showed the best TOC removal.

4.5.3 Comparison by COD Removal

The impact of oxidation on degradability can be characterized by the relative also COD degradation after AOPs. The COD seems relatively insensitive to the presence of OH•. This indicates that the OH• attacks both COD and color in the beginning, however, the OH• oxidation is effective only for color removal, but not for the COD removal in the end (Kang et al., 1999). Figure 4.31 shows that almost same removal efficiencies were observed at Ozonation and photo-Fenton processes. Ultrasound processes had no improvement in COD removal.

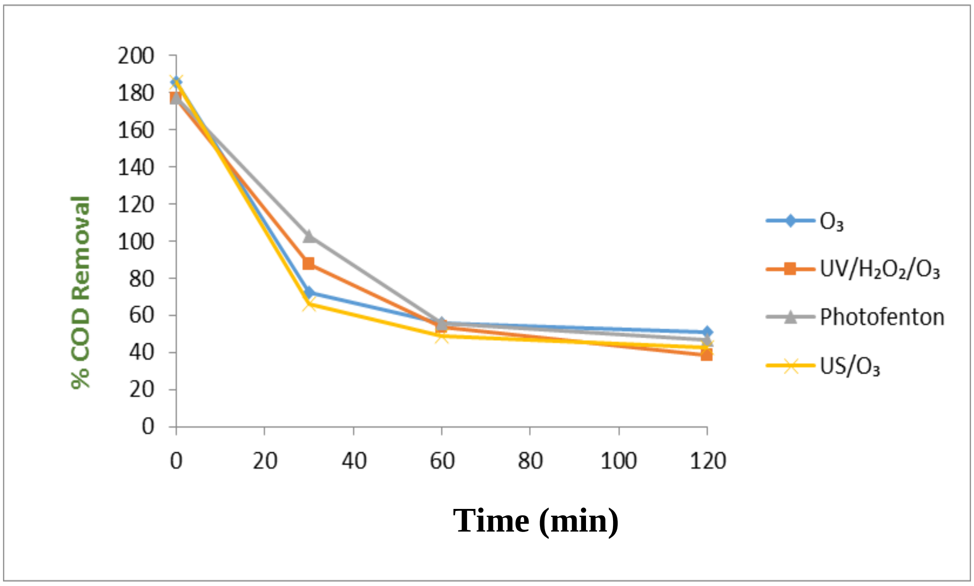

Figure 4.31 COD concentrations for most efficient AOPs after 120 min irradiation.

Ozonation process and UV/H_2O_2/O_3 are the best efficient systems for mineralization as well the color removal, they reached the 77 and 78 % COD removal rates at end of 2 hours. COD removal rates are 77% for photo-Fenton and 71% for US/O_3 process. But this study showed that color removal is faster than COD removal.

4.5.4 Comparison by Toxicity

The toxicity of untreated and treated textile wastewater was determined using luminescence inhibition in Vibrio fischeri test. AOPs was observed compared to the untreated tannery wastewater. As can be seen in Table 4.2, the ozonation significantly reduced toxicity in the wastewater and the ozonized wastewater. It is concluded that ozonation decreases toxicity level in the wastewater.

Table 4.2 Toxicity analysis of optimum AOPs after 30 minutes irradiation.

Process	**Toxicity Unit (5 min)**	**Toxicity Unit (15 min)**
Untreated	5,19	4,05
Ozone	0,25	0,21
Photo-Fenton	3,52	3,82
UV/H_2O_2/O_3	3,86	3,23
US/ O_3	2,47	3,37

As seen the results, optimum systems; photo-Fenton and UV/ H_2O_2/O_3 decreased the toxicity of the untreated samples. Ozone-Alone system almost has no toxicity effect, which is already used as disinfection.

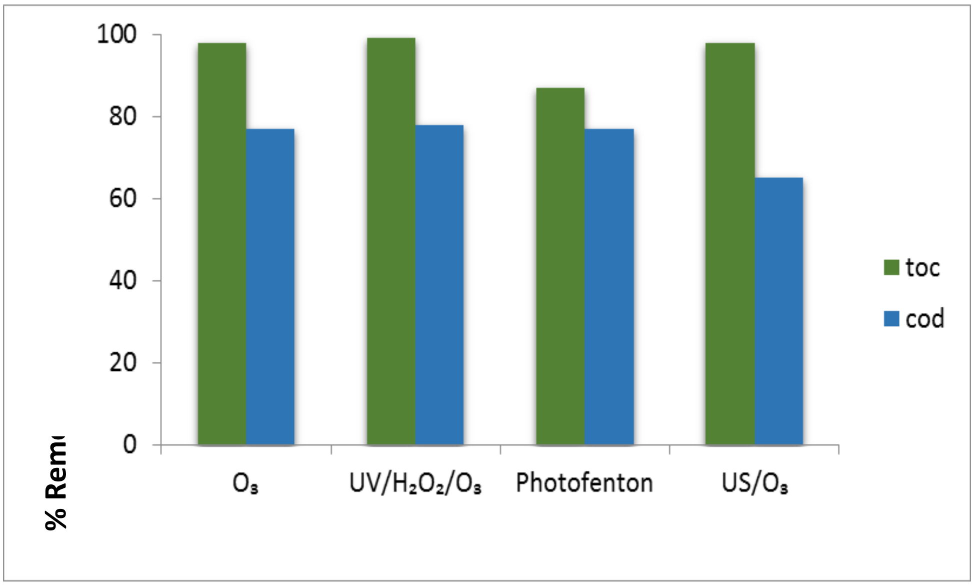

Figure 4.32 Comparison of the most efficient oxidation processes after 120 min irradiation

Mineralization by Ozone based process has higher removal rates in TOC and COD after 120 minutes irradiation. (Figure 4.32).

CHAPTER 5

ECONOMIC ANALYSIS

The overall costs are represented by the sum of the capital costs, the operating costs and maintenance. For a full-scale system these costs highly depend on the flow rate of the effluent. Cost evaluation for AOPs was based on electrical energy per order EE/O (that is the electrical energy required to re move a pollutant by one order of magnitude in one m3 of wastewater) using the following formula:

$$\text{EE/O}\ \left(\frac{kWh}{ma}\right) = \frac{P\ t\ 1000}{V\ 60\ \log\left(\frac{Cinf}{Ceff}\right)} \qquad (5.1)$$

where; P (kW) is the power input,

t is the oxidation time (in min),

V is the volume of the effluent sample (in liter) and

Cinf and Ceff are the initial and final concentrations of the contaminant (Bolton et al., 1996).

The rate constants (Table 5.1) were used to calculate the oxidation time for color degradation of the pollutant for achieve the effluent discharge limit value of 280 Pt-Co which was given by Turkish Water Pollution Control Regulation. The initial biologic treatment effluent water Pt-Co color value is 1300 with the color degradation, it was reached the 280-limit value.

Table 5.1 Color degradation kinetic rate constants.

Process	**k (min $^{-1}$)**
Ozonation	0,047
O_3/H_2O_2	0,066
O_3/UV	0,055
UV/H_2O_2	0,085
UV/H_2O_2/O_3	0,096
UV/H_2O_2/Fe^{+2}	0,067
H_2O_2/Fe^{+2}	0,036
Ultrasound	0,002
US/UV	0,001
US/O_3	0,137

It is important to achieve the desired effluent limits within the shortest detention times for lower operational costs. EE/O parameter calculated by the equation (5.1) and the results are presented below:

Table 5.2 Energy requirement for one m³ wastewater treatment.

Processes	**Power Input (W)**	**Volume of Sample (V)**	**Oxidation Time (t, min)**	**EE/O (kWh/m³)**
Ozonation	105	800	1	2,92
O_3/H_2O_2	105	800	2,5	7,54
O_3/UV	145	800	2	8,33
UV/H_2O_2	40	800	17	21,2
UV/H_2O_2/O_3	145	800	1,5	6,25
UV/H_2O_2/Fe^{+2}	40	800	10	12,4
H_2O_2/Fe^{+2}	-	800	36	-
Ultrasound	250	800	-	-
US/UV	290	800	-	-
US/O_3	355	800	2,5	25,07

Table 5.3 Summary of economic analysis of the textile wastewater treatment with studied AOPs.

Advanced Oxidation Processes	Power Input (W)	O_3 (mg/l)	H_2O_2 (mM)	Fe^{+2} (mM)	UV	US	pH	Color (Pt-Co)	Time (min)	Electrical Cost*** €/m³	Chemical Cost €/m³	Total Cost €/m³
Ozonation	105	+(15)	-	-	-	-	7,6	<280	1	0,2	-	0,2
O_3/H_2O_2	105	+(15)	+(25)	-	-	-	7,6	<280	2,5	0,52	0,022	0,54
UV/O_3	145	+(15)	-	-	+	-	7,6	<280	2	0,58	-	0,58
UV/H_2O_2	40	-	+(25)	-	+	-	7,6	<280	17	1,68	0,022	1,70
$UV/H_2O_2/O_3$	145	+(15)	+(25)	-	+	-	7,6	<280	1,5	0,45	0,022	0,47
$UV/H_2O_2/Fe^{+2}$	40	-	+(25)	+(1)	+	-	3	<280	10	0,86	0,025	0,88
H_2O_2/Fe^{+2}	-	-	+(25)	+(1)	-	-	3	<280	36	-	0,022	-
Ultrasound	250	-	-	-	-	+	7,6	~15%	120	**	-	**
US/UV	290	-	-	-	+	+	7,6	~20%	120	**	-	**
US/O_3	355	+(15)	-	-	-	+	7,6	<280	2,5	1,77	-	1,77

** Thence there was no decolorization, value was not able to be evaluated.

***The samples have taken from the wastewater treatment unit in Tekirdag. Electrical consumption cost in Tekirdag for the industries have taken from the TREDAS (Tekirdag Elektrik Dagitim A.S) data. The cost of the electricity consumption is approximately 0.17lira/kWh= 0.070Euro/kWh

EE/O parameter calculated by the equation (5.1) and the cost of the electricity was calculated by the electrical consumption of the studied area.

And the chemical requirements were calculated by the cost of the consumables. The price of hydrogen peroxide (30%) was considered to be 6.8 euro per liter. And the price of Fe(II)Sulphate was considered as 1.42 Euro per kg. The chemicals were used in UV/ H_2O_2, photo-Fenton, dark-Fenton, Ozone/ H_2O_2 and UV/ H_2O_2/Ozone processes. H_2O_2 consumption is 3.19 ml/L for all H_2O_2 based processes. Ferrous salt consumption is 17 ml/L for photo-Fenton and dark Fenton process.

Finally total operating cost is the sum of consumed energy and chemical costs (Table 5.3).

As can be seen from the above table (5.3), the lowest oxidation time to achieve the required color limit value (280 Pt-Co) was observed in Ozonation process. Besides achieving the required discharge limits, low operational costs are desirable for industrial application of the system in large scale. Therefore, it is important to achieve the desired effluent limits within the shortest oxidation times for lower operational costs.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In this study, different oxidation technologies (O_3, O_3/H_2O_2, O_3/UV, UV/H_2O_2, UV/H_2O_2/O_3, UV/H_2O_2/Fe^{+2} (photo-Fenton), H_2O_2/Fe^{+2} (Dark Fenton), Ultrasound, US/UV and US/O_3) were applied to the biological treatment plant wastewater of a textile industry. The effectiveness of AOPs were determined by monitoring the decay in color, TOC, COD and the toxicity of the residuals. The effect of process parameters such as pH and oxidant concentrations was studied to optimize the operating conditions for maximum color and TOC removal.

In UV/H_2O_2 experiments, H_2O_2 concentration up to 25mM increase the color degradation then it begins to decline with increasing oxidant concentration (100 mM) due to the scavenging effect of excess H_2O_2 with hydroxyl radicals. The highest decolorization was observed at the natural pH of the wastewater (pH 7,65) and the presence of 40W UV light.

In UV/H_2O_2/Fe^{+2} (photo-Fenton) and H_2O_2/Fe^{+2} (dark Fenton) processes, 1 mM Fe^{+2} was coupled with H_2O_2 (25mM) in the presence and absence of UV light at pH 3. UV catalyzed system was found more efficient for color degradation.

The highest decolorization rate was observed for 15 mg/l ozone concentration. Different pH values were examined in ozone treatment and the original pH value of textile wastewater (7,65) was selected as optimum pH value. When ozone is coupled with H_2O_2 or UV, the increase in decolorization rate was neglicable. Among O_3 based processes, UV/H_2O_2/O_3 process had the best efficiency.

US-Alone and US/UV processes did not decolorize the wastewater in test time (120 min) and 15%, 20% decolorization were observed. US was coupled with other AOP techniques to enhance the decolorization efficiency. However in US/Ozone process, decolorization rate was higher than the single systems, which was attributed to the enhanced mass transfer of ozone with ultrasonic irradiation.

Considering the obtained experimental results, the following conclusions could given:

- Ozone based treatment system appeared to be an effective method for decolorizing color, and removing TOC, COD and toxicity. This process achieved 280 Pt-Co discharge limit value at 15 mg/l ozone concentration within 2 minutes. Among all studied AOPs, the minimum electrical cost was calculated for ozone based systems. Also it should be considered that this process is very clean and alternative process for decolorizing textile wastewater due to not to produce sludge.

- In UV (40 W) radiation and H_2O_2 combined process, 25 mM H_2O_2 was coupled with UV light at pH 7,6. The limit value of 280 Pt-Co was reached in about 17 minutes.

- Working with UV/H_2O_2/Fe^{+2} (photo-Fenton) oxidation process, in the presence of 40W UV light, with the addition of 25 mM H_2O_2 and 1 mM Fe^{+2}, the discharge limit value of 280 Pt-Co was reached in 10 minutes at pH 3. But in H_2O_2/Fe^{+2} (Dark Fenton) process, 36 minutes is required to achieve 280 Pt-Co color value.

- When 861 kHz ultrasonic frequency was applied, no appreciacable color removal was obtained in 120 min. When US was coupled with UV light, again no color degradation was observed. When US was coupled with ozone (15 mg/l), a synergistic effect was determined due the enhanced mass transfer of ozone. High operating costs of US system makes it inefficient in the industry.

The 30 min color removal efficiency (%) of the studied AOPs are in the order: UV/H_2O_2/O_3 > Ozone-Alone process > US/O_3 > O_3/H_2O_2 > O_3/UV > UV/H_2O_2 > UV/H_2O_2/Fe^{+2} photo-Fenton process > H_2O_2/Fe^{+2} dark Fenton > US/UV > US-Alone and the corresponding % color removal are as 100%, 99%, 98,6%, 98%, 96%, 93%, 85%, 70% 20% and 15% respectively.

High TOC removal efficiency achieved after 2 hours of AOP treatment. UV/H_2O_2/O_3 had 99% TOC and 83% COD removal, while ozonation process had 98% TOC and 77% COD removal.

As a result AOPs are effective alternatives for the decolorization and degradation of non-biodegradable organic compounds in industrial wastewater. These processes hold great promise to provide alternative for better treatment and protection of environment.

It was observed that the biological treatment plant of the studied textile industry did not achieve decolorization. Therefore, AOPs can be applied as a post treatment to the textile industry wastewater for efficient decolorization.

The following suggestions may be considered for higher decolorization yields with AOPs:

- AOP can be applied as a post treatment after a well operated classical biological treatment. Enhanced removal of COD, nitrate, sulfide, etc. during biological treatment will also increase the AOP treatment yield.
- Color removal with ozone will accelerate ozon conversion to at high temperatures and high pH, therefore T < 35 ° C temperatures and pH < 7 provide a better color removal efficiency.
- If insoluble dyes, such as disperse dyes are predominant in textile industry, decolorization efficiency with ozonation will be slow.

- Besides additional operating cost due to sludge production, photo-Fenton systems are effective in color removal. The system efficiency can be increased at pH 3 or at T > 65 ° C.

APPENDIX A

OZONE DETERMINATION

For the determination of ozone concentrations in water, the indigo-trisulfonate method (Bader and Hoigné, 1981, 1982; Standard Methods 4500-O3 B, 1985; Masschelein et al., 1998) has been used. It is based on the principle that in acidic solution potassium indigo-trisulfonate ($C_{16}H_7N_2O_{11}S_3K_3$) is discolored by aqueous ozone and the degree of discoloration is compared to a blank solution of the dye. The decrease in absorbance is linear with increasing ozone concentration. The proportionality constant at 600 nm, maximum absorbance of the indigo solution, is 0.42 ± 0.01 $L.cm^{-1}.mg^{-1}$. The range of application of this method is 0.05 to 0.6 mg $O_3.L^{-1}$. This method is quantitative, selective, and simple.

Preparation of the reagents was done as follows:

- Indigo stock solution: Add about 500 mL distilled water and 1 mL conc. phosphoric acid to a 1-L volumetric flask. With stirring, add 770 mg potassium indigo trisulfonate. Fill to mark with distilled water. A 1:100 dilution exhibits an absorbance of 0.20 ± 0.010 cm -1 at 600 nm. This stock solution is stable for about 4 months when stored in the dark. Discard when absorbance of a 1:100 dilution falls below 0.16 cm^{-1}.
- Working solution: 100 mL indigo stock solution, 10 g sodium dihydrogen phosphate (NaH_2PO_4), and 7 mL conc. phosphoric acid were added to a volumetric flask and filled to 1 L with deionized water. Then 10 ml indigo reagent and 5 mL sample were mixed and diluted to 100 mL with deionized water. Blank sample was prepared in the absence of sample. The difference in absorption of light at 600 nm between blank and sample is measured.

The measurement is to be done as soon as possible but in all instances within 4 hours when stored in the dark. The concentration is dissolved ozone is determined as following equation:

$$C_{O_3}\ (\mathrm{mg/L}) = \frac{100\ \mathrm{x}\ \Delta A}{0.42\ x\ b\ x\ V} \qquad \text{(A.1)}$$

where; ΔA is the difference in absorbance between sample and blank, VT is the total volume (50 mL), b is the path length of cell (1 cm), V is the volume of sample added (10 mL) and f is the proportionality constant (0.42 cm-1).

The absorbance values at 600 nm were recorded and samples taken within time intervals, and given in Figure A.1. The fed ozone concentration to deionized water was calculated by substituting the absorbance value at 600 nm into the above equation. The reagents diluted at rate of 1:100 for preparing indigo stock solution. Next, the solutions were observed 0,114 absorbance in 600 nm.

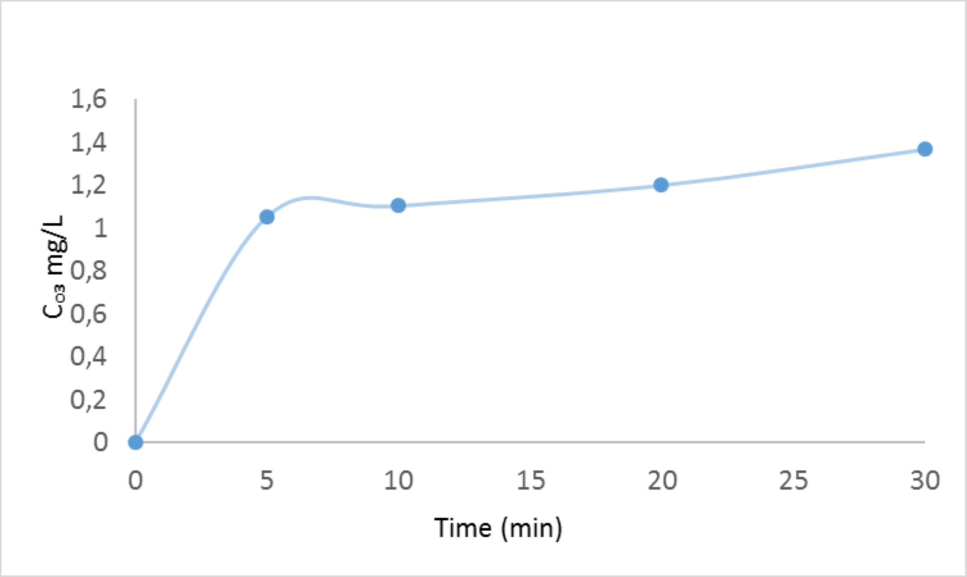

Figure A.1 Indigo calibration: The concentration of Ozone with time.

APPENDIX B

H_2O_2 DETERMINATION BY THE I^{-3} METHOD

H_2O_2 determination was carried out according to the procedure described by Klassen *et al*., (1994). This method is based on the reaction of (I^-) with H_2O_2 to form the triiodide ion (I^{-3}), which has a strong absorbance 351 nm. The analysis of H_2O_2 at concentrations as low as 1 μM is conveniently done by determining the yield of I^{-3} formed when H_2O_2 reacts with KI in a buffered solution containing ammonium molybdate tetrahydrate as a catalyst. Solutions A and B for the I^{-3} method were prepared according to the recipe given by Kalssen *et al*., (1994).

Solution A consisted of 33 g of KI, 1 g of NaOH, and 0.1 g of ammonium molybdate tetrahydrate diluted to 500 ml with deionized water. The solution was stirred for ∼1 h to dissolve the molybdate. Solution A was kept in dark to inhibit the oxidation of I-. Solution B, an aqueous buffer, contained 10 g of KHP per 500 ml. Various concentrations of H_2O_2 was prepared from reagent grade H_2O_2 (35%), Merck. 2.5 mL of solution A, 2.5 mL of solution B, 1 mL of sample were mixed and diluted to 10 mL by deionized water, and the absorbance at 351 nm was recorded. Blank sample was prepared in the absence of sample.

Various concentrations of H_2O_2 (3, 5 mg/L) and the corresponding absorbance values at 351 nm are recorded for calibration curve. Plot of H_2O_2 concentration versus the corresponding absorbance of the solution, and the calibration curve for H_2O_2 analysis is given in Figure B.1.

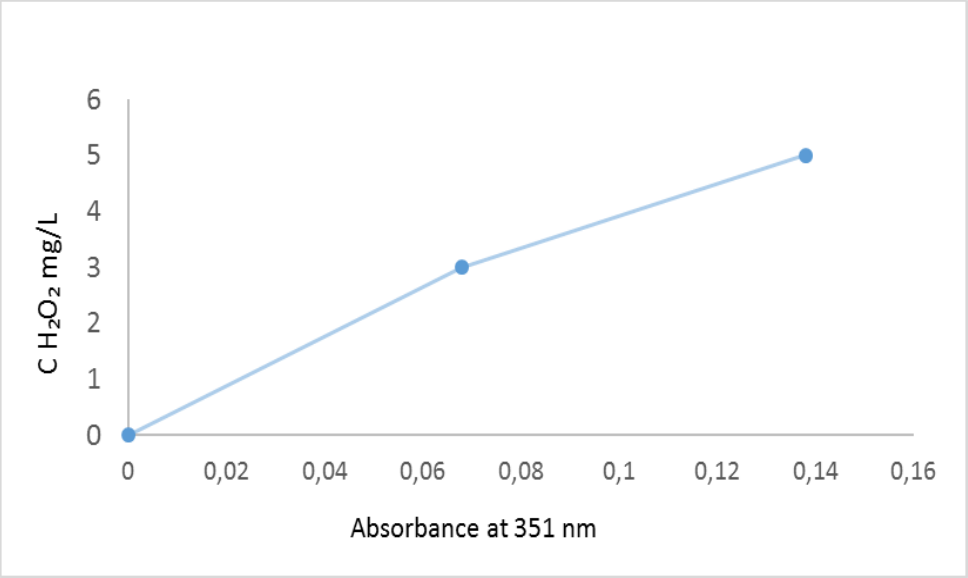

Figure B.1 H_2O_2 Calibration Curve.

1 mL of sample was taken at time intervals during sonication of deionized water, and mixed with 2.5 mL solution A and solution B, and then diluted to 10 mL with deionized water. The absorbance at 351 nm was recorded for each sample, and then substituted into H_2O_2 calibration curve equation given in above.

REFERENCES

AATCC (American Association of Textile Colorists and Chemists).Dyeing primer: A series of short papers on the fundamentals of dyeing. *Textile Chem. and Colorist,* 1981.

Ahmet, B., Ayfer, Y., Doris, L., Nese, N. and Antonius, K., Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, *Dyes and Pigments*, Vol. 58, pp. 93-98, 2003.

Alaton, I.A., Balcioğlu, I.A and Bahnemenn, D., Advanced oxidation of a reactive dyebath effluent: Comparison of O_3, H_2O_2 /UV-C and TiO/UV-A processes, *Water Research* Vol. 36, pp. 1143-1154, 2002.

Alaton, I.A., Hanci, T.O., *"Effect of Photochemical Advanced Oxidation Processes on the Bioamenability and Acute Toxicity of an Anionic Textile Surfactant and a Textile Dye Precursor in Advances in Treating Textile Effluent"*, Prof. Peter Hauser (Ed.), 154 pages, ISBN: 978-953-307-704-8, InTech Publishing, İstanbul, 2011.

Al-Kdasi A., Idris A., Saed K., Guan C.T., Treatment of Textile Wastewater by Advanced Oxidation Processes – A Rewiev, *Global Nest J*., Vol. 6, pp, 222-230, 2004.

Arslan, I.A. and Isil, A.B., The effect of pre-ozonation on the H_2O_2 / UV –C treatment of raw and biologically pre-treated textile industry wastewater, *Water Science and Tech.*,Vol. 45, pp, 297- 304, 2002.

Azbar, N., Yonar, T. and Kestioglu K., Comparison of various advanced oxidation processes and chemical treatment methods for COD and colour removal from a polyester and acetate fiber dying effluent, *Chemosphere,* Vol. 55, pp. 35-43, 2004.

Bader, H. and Hoigne, J., "Determination of ozone in water by the Indigo method: a submitted standard method", *Ozone Sci. & Eng*.,Vol. 4 (4), pp, 169-176, 1981.

Bader, H. and Hoigne, J., "Determination of ozone in water by the Indigo method", *Wat. Res*., Vol. 15, pp. 449-456, 1982.

Baig, S. and Liechti, P.A., Ozone treatment for biorefractory COD removal, *Water Sci and Tech*., Vol. 43, pp. 197-204, 1981.

Balasubramanian S. and Pugalenthi V., Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV–visible spectrophotometric methods. *Talanta*. Vol. 50, pp. 457-467, 1999.

Bali, U., Çatalkaya, E., Sengül, F., Photodegradation of Reactive Black 5, Direct Red 28 and Direct Yellow 12 using UV, UV/H_2O_2 and UV/ H_2O_2/Fe^{+2} : a comparative study. *J Hazard. Mater.* Vol. 146, pp. 447-452, 2004.

Banat, İ.M., Nigam, P., Singh, D., Marchant R., Microbial decolorization of textile dyecontaining effluents. A review, *Bioresource Tech*. Vol. 58, pp. 217-277, 1997.

Baxendale, J.H., Wilson, J.A., The photolysis of hydrogen peroxide at high light intensities. *Trans. Faraday Soc*. Vol. 53, pp. 344-356, 1956.

Brown and Caldwell, "*Watershed Protection Plan Development Guidebook*" *Description of commonly considered water quality constituents,* Northeast Georgia Regional Dev. Center, 2001.

Bolton, J.R., Figures of merit for the technical development and application of advanced oxidation processes. *J. Adv. Oxid. Technol.*, Vol. 1 (1), pp. 13, 1996.

Buxton, G.R., Greenstock, W., Helman, P., and Ross, A.B., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, *Appl. Catal*., Vol. B 74, pp. 63-72, 1988.

Carey, J.H., An Introduction to AOP for Destruction of Organics in Wastewater. *Water Pollution Res. J. Canadian*, Vol. 27, pp. 1-21, 1992.

Cervantes, J.F., *Environmental Technologies to Treat Nitrogen Pollution*, IWA Publishing, 2009

Chen, K.C., Wu, J.Y., Liou, D.J and Hwang, C.J., Decolorization of textile dyes by newly isolated bacterial strains, *Biotechnology* Vol. 10, pp. 57-68, 2003.

Chowdhury, P., Viraraghavan, T., Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes - a review. *Sci Total Environ.*, Vol. 407 (8), pp, 2474-2492, 2009.

Ciardelli, G., Capanelli, G., Bottino, A., Ozone treatment of textile wastewaters for reuse, *Water Science and Technology* Vol 44 No 5 pp 61–67, IWA Publishing, 2001.

Cooper-Sydney, G., *The textile industry: environmental control and energy conservation*. Park Ridge, N.J.: Noyes Data Corp, 1978.

Cooper, P., "*Are textiles finishing the environment?" International Wool Secretariat (IWS)* Development Center Monograph. IWS, West Yorkshire, England, 1989.

Correia, V.M., Stephenson, T. and Judd, S.J., Characterization of textile wastewater a review. *Environ. Technol*. Vol 15, pp 917-929, 1994.

Dae-Hee A., Won-Seok C., Green S.A., Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process, *Process Biochem*, Vol. 34, pp. 329-439, 1999.

Das., S., Textile Effluent Treatment – A Solution to the Environmental Pollution, http://www.fibre2fashion.com/industry-article/pdffiles/textile-effluent-treatment.pdf.

Doble, M., Kumar, *A., Biotreatment of Industrial Effluents*, Elsevier Inc., Oxford, United Kingdom, 2005.

Dogan, F.N., *Degradation of Colored Industrial Wastewaters by Advanced Oxidation Processes*, M.S Thesis, Fatih University, İstanbul, 2011.

Dorn, P.B., Salanitro, J.P., Evans, S.H., Kravetz, L., Assessing the Aquatic Hazard of Some Branched and Linear Nonionic Surfactants by Biodegradation and Toxicity. *Environ Toxico and Chemistry*. Vol. 12, pp. 1751-62, 1993.

Dore, M, Merlet, N, Legubeand, B, Croue, J.P., Interaction between ozone, halogens and organic compounds. *Ozone Sci Eng*, Vol.10, pp. 153e72, 1988.

Dos Santos, Andre B., Cervantes Francisco, J., Van Lier, Jules, B., Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology, *Biosource Technology* Vol. 98, pp. 2369-2385, 2001.

Fogler, S., *Elements of Chemical Reaction Engineering*, fourth ed. NJ: Prentice Hall Publications, 2004.

Galindo, C., Jacques, P., Kalt, A., Photochemical and Photocatalytic Degradation of an Indigolid Dye; A Case Study of Acid Blue 74 (AB74). *J. Photochem. Photobiol. A: Chem.* Vol. 141, pp. 47-56, 2001.

Gao, P., Chen, X., Shen, F., Chen, G., Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter. *Separation and Purification Tech*. Vol. 43, pp. 117-123, 2004.

Glaze, W.H., Kang, J.W., Chapin, D.H., The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet irradiation. *Ozone Science Engineering* Vol. 9, pp. 335–352, 1987.

Glaze, W.H., Kang, J.W., Advanced oxidation processes. Description of a Kinetic Model for the Oxidation of Hazardous Materials in Aqueaous Media with Ozone and Hydrogen Peroxide in a Semibatch Reactor. *Ind. Eng. Chem. Res*. Vol. 28, pp. 1573-1587, 1989.

Gottschalk, C., Libra, J.A., Saupe, A., Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and its Application. Wiley-VCH, Weinheim, Vol. 2, pp.23, 2000.

Gulyas, H., Von Bismarck, R., and Hemmerling, L., Treatment of industrial wastewaters with ozone/hydrogen peroxide. *Water Sci. Technol.*, Vol. 32 (7), pp. 127–134, 1995.

Hao, O.J., Kim, H., Chiang, P.C., Decolorization of wastewater. *Crit. Rev. Environ. Sci. Technol*. Vol. 30 (4), pp. 449–505, 2000.

Herlant, M.A., Low salt dyeing of cellulosics with direct and fiber reactive dyes. American Association of Textile Colorists and Chemists (AATCC)-ITC Proceedings. pp. 287-293, 1991.

Hoigné, J. and Bader, "The Role of Hydroxyl Radical Reacting in Ozonation Processes in Aqueous Solutions." *Water Resources*. Vol. 10, pp, 377, 1976.

Hung-Yee, S. and Ching-Rong, H., Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process, *Chemosphere*, Vol. 31, pp, 3813-3825, 1995.

ISO EN 7887, European Norm of Water Quality – Examination and determination of colour, 1997.

Jiang, Y., Petrier, C.H., Waite, T.D., Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueos solution. *Ultrason Sonochem*, Vol. 9, pp. 163-68, 2002.

Kang, S.H., Liao, H.C., Po, S.T., Decolorization of textile wastewater by photo-Fenton oxidation technology. *Chemosphere*, Vol. 41, pp.,1287-1294, 1999.

Kim, K.W., Kim, Y.J, Kim, I.T., Park G.I. and Lee E.H., Electrochemical conversion characteristics of ammonia to nitrogen. *Water Res.*,Vol. 40, pp. 1431–1441, 2006.

Khadhraoui, M., Trabelsi, H., Ksibi, M., Bouguerra, S., Elleuch, B., Discoloration and detoxicification of a Congo red dye solution by means of ozone treatment for a possible water reuse, *Journal of Hazardous Materials* Vol.,161,pp. 974-981, 2009.

Koonce, A.S., *Color reduction in textile wastewater via chitin adsorbent*.,M.S Thesis, Department of Textile Chemistry, North Carolina State University, Raleigh, NC, 1993.

Langlais, B., Reckhow, D.A, and Brink, D.R., *Ozone in water treatment: Application and Engineering*, Lewis Publishers, Inc., Chelsea, Mich, 1991.

Ledakowicz, S., Gonera, M., Optimisation of oxidant dose for combined chemical and biological treatment of textile wastewater. *Water Res*. Vol. 33 (1), pp. 2511–2516, 1999.

Ledakowicz, S., Solecka M., Zylla R., Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation process. *J Biotech* Vol. 89, pp 175-184, 2001.

Legrini, O., Oliveros, E., Braun, A.M., Photochemical processes for water treatment. *Chem. Rev.* Vol. 93, pp. 671–698, 1983.

Lin, C. H. and Tseng, S. K., “Electrochemically Reductive Dechlorination of Pentachlorophenol Using a High Overpotential Zinc Cathode,” *Chemosphere,* Vol. 39, pp. 2375, 1999.

Malato S., Blanco J., Alarcon D.C., Maldonado M.I., Fernandez-Ibanez P., Gernjak, W., Photocatalytic Decontamination and Disinfection of Water with Solar Collectors. *Catal. Today* Vol. 122, pp. 137-149, 2007.

Marechal, M.L., Slokar, Y.M., Taufer, T., Decolorization of chlorotriazine reactive azo dyes with H_2O_2/UV. *Dyes Pigments* Vol. 33, pp. 281, 1997.

Marmagne, O. and Coste C., Color removal from textile plant effluents, *American Dyestuff Reports*, Vol. 85, pp. 15-21, 1996.

Mason, T. J., Sonochemistry: current uses and future prospects in the chemical and processing industries. *Phil. Trans. R. Soc. Lond.* A, Vol. 357 No.(1751), pp. 355-369, 1999.

Masschelein, W., Langlais, B., Thielsen, E., Blaich, L., Bell, J. and Reading, A., “Colorimetric method for manual determination of ozone concentrations in water”, *Ozone Sci. & Eng,*.Vol. 20 (6),pp. 443-445, 1998.

Mattioli, D., Malpei, F., Bortone, G. and Rozzi, A., *Water minimization and reuse in textile industry: Analysis, technologies and implementation*. IWA Publishing, Cornwall, UK. p. 677, 2002.

Mehmet, F.S. and Hasan Z.S., Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration, *Journal of Chemical Technology and Biotechnology,* Vol. 77, pp. 842-850, 2002.

Meikap, B. C. And Rot, G. K., Removal of Phenolic Compounds From Industrial Waste Water by Semifluidized Bed Bio-Reactor, *J. of the IPHE,* Vol. 1997, No 3,pp. 54-61, 1997.

Metcalf, Eddy, Inc., *Wastewater engineering treatment and reuse*, Fourth Edition, McGraw-Hill, New York, 2003.

Mishra, G and Tripathy, M., A critical review of the Treatment for decolorisation of textile effluent, *Colourage,* Vol.40, pp. 35-38, 1993.

Modirshahla. N., Behnajady. M.A., Ghanbary. F., Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes, *Dyes and Pigments*, Vol. 73, pp. 305-310, 2006.

Mohr, U., Ecology must be dealt with. Australasian Textiles (Jan/Febr.) pp. 45, 1993.

Moraes J.E.F., Quina F.H., Nascimento C.A.O., Silva D.N., and Chiavona-Filho O., Treatment of Saline Wastewater contaminated with Hydrocarbons by the photo-Fenton process, *Environ Sci. Tech.*, 38, 1183-1187, 2004.

Mourand, J.T., Crittenden, J.C., Hand, D.W., Perram, D.L. and Notthakun, S., Regeneration of Spent Adsorbents Using Advanced Oxidation. *Water Environ. Res.*, 67, 355, 1995.

Muruganandham M, Swaminathan M., Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. *Dyes Pigments*. ;63:315e21, 2004.

Namboodri C.G., Perkins W.S. and Walsh W.K., Decolorizing dyes with chlorine and ozone: part II, Am. *Dyestuff Report*, Vol. 83, pp. 17-26, 1994.

Navarro V.A., Ramirez M.Y., Salvador M.S.S.B., Gallardo J.M., Determination of Wastewater LC_{50} of the Different Process Stages of the Textile Industry. *Ecotoxicol Environ Safety*; Vol. 48, pp.51-61, 2001.

Neyens, E. and Baeyens, J., A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, Vol. 98 (1-3). pp. 22-50, 2003.

Oğuz E., Keskinler B., Removal of color and COD from synthetic textile wastewaters using O_3, PAC, H_2O_2 and HCO_3^-, *Journal of Hazardous Material.*, Vol. 151, pp. 753–760, 2008.

O'Neill, C., Hawkes, F.R., Hawkes, D.L., Lourenço, N.D., Pinheiro, H.M., Delee, W., Colour in textile effluents-sources, measurement, discharge consents and simulation: a review, *J. Chem. Technol. Biotechnol.* Vol. 74, pp. 10009-10018, 1999.

Pearce, C.I., Lloyd, J.R., Guthrie, J.T., The removal of colour from textile wastewater using whole bacterial cells: a review, *Dyes Pigments* Vol. 58, pp. 179-196, 2003.

Pekakis, P.A., Xekoukoulotakis, N.P., Mantzavinos D., Treatment of textile dyehouse wastewater by TiO_2 photocatalysis. *Water Res.* Vol. 40, pp. 1276-1286, 2006.

Perkowski, J. and Kos L., Decolouration of model dye house wastewater with advanced oxidation processes, *Fibres and Textiles in Eastern Europe*,Vol. 11,pp. 67-71, 2003.

Pignatello, J.J., Dark and photoassisted Fe^+3 -catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* Vol. 26, pp. 944-951, 1992.

Pretty, J.R., Blubagh, A.E., Caruso, A.J. and Davidson, M.I., Determination of Chromium(VI) and Vanadium(V) Using an Online Anodic Stripping Voltammetry Flow Cell with Detection by Inductively Coupled Plasma Mass Spectrometry.. *Anal. Chem.*, Vol. 66 (1994), pp. 1540-1547, 1994.

Raghavacharya, C., Colour removal from industrial effluents—a comparative review of available technologies. *Chem. Eng. World*. Vol. 32, pp. 53–54, 1997.

Rai, H.S., Removal of dyes from the effluent of textile and dyestuff manufacturing industry: A review of emerging techniques with reference to biological treatment, *Critical Reviews in Environmental Science and Technology*, Vol. 35, No. 3, pp.219–238, 2005.

Rajeswari, K.R., *Ozonation treatment of textile dyes wastewater using plasma ozonizer*, Ph.D thesis, University Malaysia. Malaysia, 2000.

Rein, M., Advanced oxidation processes – current status and prospects, Proc. Estonian Acad, *Science Chemistry*, Vol. 50, pp. 59–80, 2001.

Richardson, S., *"Multimedia environmental concerns in warp sizing: Low tech approaches to waste reduction". North Carolina Pollution Prevention Program*, Raleigh, NC (February), 1991.

Robinson, T., McMullan, G., Marchant, R., Nigam, P., Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Biores. Technology* Vol. 77, pp. 247-255, 2001.

Rodriguez M., Sarria, V., Esplugas, S., Pulgarin, C., Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution. *J. Photochem. Photobiol.*, Vol. A 151, pp. 129–135, 2002.

Sax, I., *Dangerous properties of industrial materials*, NY: Van Nostrand Reinhold 6th ed., 1984.

Selcuk, H., Decolorization and detoxification of textile wastewater by ozonation and coagulation process. *Dyes and Pigments*; Vol. 64, pp. 217-222, 2005.

Shaw, C.B., Carliell, C.M., Wheatley, A.D., Anaerobic/aerobic treatment of colored textile effluents using sequencingbatch reactors, *Water Research* Vol. 36, pp. 1993 – 2001., 2002.

Shelton, T., *Interpreting Drinking Water Quality Analysishat Do the Numbers Mean?,* New Brunswick, NJ: Rutgers Cooperative Extension, 1991.

Sheng, H.L. and Chi, M.L., Treatment of textile waste effluents by ozonation and chemical coagulation, *Water Research,* Vol. 27, pp. 1743 – 1748, 1993.

Sivaramakrishnan, C.N., Colourage, LI, Kazmi, Shabbir. "*Leather Industry in Pakistan" Pakistan & Gulf Economist."* 28 January - 3 February 1995, pg 6, 2004.

Smith, B., *"Identification and reduction of pollution sources in textile wet processing*". *North Carolina Department of Natural Resources and Community Development, Pollution Prevention Pays Program*, Raleigh, NC, 1986.

Smith, B., *A workbook for pollution prevention by source reduction in textile wet processing. Office of Waste Reduction*, North Carolina Department of Environment, Health, and Natural Resources, Raleigh, NC, 1989.

Smith, B., *Future pollution prevention opportunities and needs in the textile industry. In: Pojasek, B., ed. Pollution prevention needs and opportunities*. Center for Hazardous Materials Research (May), 1994.

Solozhenko, E.G., Soboleva, N.M., Goncharuk, V.V., Decolourization of azodye solutions by Fenton's oxidation. *Water Res*. Vol. 29 No.(9), pp. 2206–2210, 1995.

STANDARD METHODS for the examination of water and wastewater, American Public Health Association, 1985.

Stasinakis, A.S., Use of Selected Advanced Oxidation Processes (AOPs) for Wastewater Treatment – A Mini Review. *Global Nest Journal*. Vol. 10, pp. 3766-385, 2008.

Suslick, K.S., The chemistry of ultrasound. Chicago: *Encyclopedia Britannica*, pp.: 138-55, 1994.

Swedish EPA, Bertills U., Näsholm T., *Effects of Nitrogen Deposition on Forest Ecosystems*, 2010.

Talarposhti, A.M., Donnely, T., Anderson, G.K., Colour removal from a simulated dye wastewater using a two-phase anaerobic packed bed reactor, *Water Res.* Vol. 35: pp. 425-432, 2001.

Tchobanoglous, G., and Burton, F., *Wastewater Engineering: Treatment, Disposal and Reuse,* McGraw-Hill Publishing Company, New York, 1991.

Techcommentary, *Advanced oxidation processes for treatment of industrial wastewater*. An EPRI community environmental centre publ. No 1, 1996.

Tezcanli-Güyer G., *Degradability of Synthetic Dyestuff With Acoustic Caviation: Impacts of System Conditions and Physical/Chemical Agents,* Ph.D Thesis, Istanbul: Bogazici University, 2003.

Torrades, F., Garcia-Montano, J., Antonio Garcia-Hortal J., Domenech, X., Peral, J., Decolorization and Mineralization of Commercial Recative Dyes Under Solar Light Assisted Photo-Fenton Conditions. *Sol. Energy* Vol. 77, pp. 573-581, 2004.

Turkish Water Pollution Control Regulation (TWPCR) Official Gazette dated 31.12.2004 and numbered 25687, 2004.

U.S. EPA, Best Management Practices for Pollution Prevention in the Textile Industry. Cincinnatio, Ohio USA, 1996.

U.S. EPA, Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003. November. Office of Water, Washington, DC. 211 pp, 1997.

U.S. EPA., Guidelines Establishing Test Procedures for the Analysis of Oil and Grease and Non-Polar Material Under the Clean Water Act and Resource Conservation and Recovery Act; Final Rule. Federal Register, Rules and Registrations. Vol 64, No 93, pp. 26315-26327, 1999b.

U.S. EPA, Guidance Manuel, Alternative Disinfection and Oxidants, 1999b

U.S. EPA., Handbokk on Advanced Nonphotochemical Oxidation Processes, EPA, 625/R-01/004, Cincinnati, Ohio, 2001.

U.S. EPA., National Recommenden Water Quality Criteria; 2002 Office of Water, Office of Science and Technology, EPA-822-R-02-047, 2002.

U.S. EPA, *Technical Support Document for the Effluent Guidelines Program Plan*, 2004.

Van der Zee, F.P., Azo dye decolorization by anaerobic granular sludge, *Chemosphere* Vol. 44, pp. 1169-1176, 2002.

Venceslau, M.C., Tom S. and Simon J.J., Characterization of textile wastewaters- a review, *Environmental Technology*, Vol. 15, pp. 917-929, 1994.

Verschueren, K., *"Handbook of Environmental Data on Organic Chemicals,"* Van Nostrand Reinhold Co., New York, 1977.

Vilar, J.P., Pinho, L.X., Pintor, A.M.A., Boaventura, R.A.R., Treatment of textile wastewaters by solar-driven advanced oxidation processes. *Solar Energy*. Vol. 85, pp. 1927-1934, 2011.

Visscher, A.D., Langenhove, H.V., Sonochemistry of organic compounds in homogeneous aqueous oxidizing system. *Ultrason Sonochem*, Vol. 5, pp. 87-92, 1998.

Wagner, S., *"Improvements in products and processing to diminish environmental impact." COTTECH Conference*, Raleigh, NC (November 11-12), 1993.

Wallace, R., Maxcy-Rosenau- *Last Public Health and Preventive Medicine.* Stamford, CT: Appleton & Lange, 2000.

Walling, C. and Weil, T., The ferric ion catalyzed decomposition of hydrogen peroxide in perchloric acid solution. *Int. J. Chem. Kinet*. Vol. 6, pp. 507-516, 1974.

Walling, C., Fenton's Reagent Revisited. *Acc. Chem. Res*. Vol. 8, pp. 125-131, 1975.

Weisburger, J.H., Comments on the history and importance of aromatic and heterocyclic amines in public health, *Mutation Research* Vol. 506, pp. 9-20, 2002.

Wu, Z., Cong, Y., Zhou, M., Ye, Q. and Tan, T., Removal of Phenolic Compounds by Electro-assisted Advanced Process for Wastewater Purification, *J. Chem Eng*, Vol. 19, pp. 866-870, 2002.

Wu, J., Doan, H., Upreti, S., Decolorization of aqueous textile reactive dye by ozone, *Chemical Engineering Journal* Vol. 142, pp. 156–160, 2008.

Xu, X, Zhao, W, Huang, Y, Wang, D., 2-Chlorophenol oxidation kinetic by photo-assisted Fenton process. *J Environ Sci.,* Vol. 15, pp. 475-481, 2003.

Yang, M., Uesugi, K., and Myoga, H., Ammonia removal in bubble column by ozonation in the presence of bromide. *Water Res*., Vol. 33, pp. 1911–1917, 1999.

Yasar, A., Ahmad, N., Khan, A.A.A., Energy Requirement of Ultraviolet and AOPs for the Post-treatment of treated combined industrial effluent. *Coloration Tech,* Vol. 122, pp. 201-206, 2006.

Zeller, M.V., Instrumental techniques for analyzing air pollutants generated in textile processing. *Textile Horizons* (January), 1975.

Zheng, W., Maurin, M., Tarr, M.A., Enhancement of sonochemical degradation of phenol using hydrogen atom scavengers. *Ultrason Sonochem*, Vol. 12, pp. 313-317, 2005.

Zhou H. And Smith, D.W., Advanced technologies in water and wastewater treatment, *Journal Environ. Eng Science*, Vol. 1, pp. 247-264, 2002.