OZONATION OF A DENIM PRODUCING TEXTILE INDUSTRY WASTEWATER – PROCESS OPTIMIZATION

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OZONATION OF A DENIM PRODUCING TEXTILE INDUSTRY WASTEWATER – PROCESS OPTIMIZATION

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ABSTRACT

OZONATION OF A DENIM PRODUCING TEXTILE INDUSTRY WASTEWATER – PROCESS OPTIMIZATION

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Denim production is one of the leading sub-sectors of textile industry which basically generates highly colored indigo-dyeing effluents. In the present study, ozonation was applied to the indigo-dyeing effluent(COD=820 mg/L;color=5500 Pt-Co), and to the whole effluent from a denim-producing plant before(COD=2750 mg/L;color=3950 Pt-Co) and after(COD=800 mg/L,color=3700 Pt-Co) biological treatment for degradation/detoxification purposes. Ozonation was also tried in the wastewater of the plant(COD=3100 mg/L;color=4500 Pt-Co) that would be produced after some foreseen cleaner production measures; caustic recovery and reusing of dyeing process wastewater.

When applied to indigo-dyeing wastewater; ozonation provided 95% color and 61% COD removals at 1320 mg/h ozone dose within 60 minutes The optimum pH was evaluated as 4 when indigo-dyeing wastewater exposed to ozonation at different pHs(1.6-12.3). On the other side, ozonation applied as pre-treatment to the plant effluent provided 86% color and 46% COD removals with 3240 mg/h ozone dose in

70 minutes. Less satisfactory results were obtained when ozonation was tried in the wastewater after measures, with 86% color and 31% COD removals at 3960 mg/h ozone dose in 80 minutes. When applied to the biologically-treated effluent; at 420 mg/h ozone dose and within 40 minutes, ozonation removed 47% of influent COD and 96% of influent color indicating better performance of ozonation in post-oxidation. In order to assess possible improvements on ozonation with the addition of H_2O_2, different concentrations were tried, but no significant improvement was obtained. The improvement in BOD_5/COD index was also determined for the ozone-treated plant effluent to measure the effects of ozonation on biodegradability and found out that BOD_5/COD ratio has improved to 0.39 from 0.22.

Keywords: Ozonation, color removal, textile wastewater, indigo, hydrogen peroxide

ÖZ

KOT KUMAŞI ÜRETEN BİR TEKSTİL ENDÜSTRİSİNİN ATIK SUYUNUN OZONLANMASI – YÖNTEM OPTİMİZASYONU

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Kot üretimi renkli indigo boyama atıksuyu ortaya çıkaran tekstil endüstrisinin önde gelen alt sektörlerinden biridir. Mevcut çalışmada ozonlama işlemi indigo boyama atıksuyuna(KOİ=820 mg/L; Renk=5500 Pt-Co) ve kot kumaşı üreten tesisin bütün atıksuyuna hem biyolojik arıtmadan önce (KOİ=2750 mg/L; Renk=3950 Pt-Co) hem de biyolojik arıtmadan sonra (KOİ=800 mg/L; Renk=3700 Pt-Co) parçalama ve toksisiteyi azaltma amacıyla uygulanmıştır. Ozonlama ayrıca tesis içinde alınması öngörülen kostik geri kazanımı ve boyama prosesi atıksuyunun yeniden kullanımı tedbirlerinden sonraya ortaya çıkacak atıksuyun (KOİ=3100 mg/L; Renk=4500 Pt-Co) arıtılmasında denenmiştir.

Ozonlama indigo boyama atıksuyuna uygulandığında, 1320 mg/saat ozon dozunda ve 60 dakikalık arıtma süresi neticesinde %61 KOİ ve %95 renk giderimi sağlanmıştır. 1.6-12.3 pH değerleri arasında indigo boyama atıksuyunda yapılan çalışmalarda ise optimum pH değeri 4 olarak bulunmuştur. Diğer taraftan, ön-arıtma olarak tesis atıksuyuna uygulanan ozonlama işleminde 3240 mg/saat ozon dozunda 70 dakikalık arıtma neticesinde %86 renk ve %46 KOİ giderimi sağlanmıştır.

Ozonlama işlemi tesiste önlemler alındıktan sonra ortaya çıkması öngörülen atıksuya uygulandığında 3960 mg/saat dozunda 80 dakikalık arıtma neticesinde %31 KOİ ve %86 renk giderimi ile daha düşük verimli arıtım sağlanmıştır. Ozon, biyolojik olarak arıtılmış atıksuya uygulandığında ise çok daha düşük ozon dozu olan 420 mg/saat dozunda 40 dakikalık bir arıtım neticesinde, son-arıtmanın ön-arıtmadan daha verimli olduğunu gösteren %47 KOİ ve %96 renk giderimi değerleri elde edilmiştir. H_2O_2 ilavesi ile arıtım değerlerinde olası bir artışı gözlemlemek için yapılan çalışmalarda ise değişik H_2O_2 konsantrasyonları denenmiş olup; herhangi bir değişiklik gözlemlenememiştir. Renk ve KOİ gideriminin yanı sıra, ozon ile arıtılmış tesis atıksuyunda ozonlamanın biyoçözünürlük üzerinde etkisini değerlendirebilmek için $BOİ_5$/KOİ değerleri hesaplanmıştır ve $BOİ_5$/KOİ oranının 0.22'den 0.39'a yükseldiği saptanmıştır.

Anahtar kelimeler: Ozonlama, renk giderimi, tekstil atıksuyu, indigo, hidrojen peroksit

To My Family

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ABBREVIATIONS

AOP : Advanced Oxidation Processes

BOD : Biochemical Oxygen Demand

BTTG : British Textile Technology Group

COD : Chemical Oxygen Demand

EC : European Commission

EOP : Electrochemical Oxidation Potential

EPA : Environmental Protection Agency

F/M : Food to Microorganism Ratio

METU : Middle East Technical University

MLSS : Mixed Liquor Suspended Solids

Pt- Co : Platinum - Cobalt

SS : Suspended Solids

T/C : Textile and Clothing

TDS : Total Dissolved Solids

TUBITAK : The Scientific and Technological Research Council of Turkey

V : Volt

CHAPTER 1

INTRODUCTION

“The textiles and clothing sector (or "T/C sector") is a diverse and heterogeneous industry which covers a wide variety of products from hi-tech synthetic yarns to wool fabrics, cotton bed linen to industrial filters, or nappies to high fashion. This diversity of end products corresponds to a multitude of industrial processes, enterprises or market structures” (EC, 2010).

“Turkey’s textile industry has shown a stable growth over the years. The textile sector is the Turkey’s largest manufacturing industry and its largest export sector and a relatively important position in the world. Turkey’s textile industry remains important to the economy. Turkey ranks sixth in world exports of clothing with 3.5% of the total global apparel trade, and the second largest supplier to the European Union, after China” (Öztürk, 2005).

“Textile industries consume large amounts of water and their effluents contain a wide range of contaminants. Environmentally, these contaminants mean suspended solids, COD, BOD, as well as high pH and strong color. The removal of dye color in the treatment of textile dyeing and dye manufacture wastewaters is one of the main problems of textile industry” (Turhan and Turgut, 2008). In addition, there are many different types of dyes and different dyeing manufacture processes, making difficult that only a single treatment process answers satisfactorily to the treatment requirements in all situations (Soares et al., 2006).

“For the removal of the recalcitrant organic fraction of textile wastewater coming from dye carriers, dyestuffs, surfactants and sequestering agents, conventional treatment methods are inappropriate and advanced chemical oxidation Technologies such as ozonation or advanced oxidation processes (AOPs) have to be employed” (Arslan Alaton, 2006).

Ozonation application began in the early 1990s with drinking water treatment, has spread worldwide and today grows in the industrial wastewater treatment field. In this area, full-scale plants use ozone treatment to recycle marina aquaria waters, to eliminate cyanides in the metal finishing industry, to reuse washwaters in electronics manufacture, to lower color and surfactant concentrations in wastewaters from textile dyeing plants, to destroy phenols or hydrocarbons in petroleum refinery wastewaters, to remove COD in landfill leachates and chemical industry wastewaters (Baig and Liechti, 2001).

“The use of ozone in textile effluent treatment appears to be a very attractive alternative with considerable application potential. Ozone is a powerful oxidizing agent (E^0 2.08 V), when compared with other well-known oxidizing agents such as H_2O_2 (E^0 1.78 V), and can react with several classes of compounds through direct or indirect reactions. Ozone is capable of causing the degradation of dyes. Chromophore groups, generally organic compounds with conjugated double bonds can be broken by ozone (directly or indirectly) into smaller forms, decreasing the color of the effluent” (Oguz and Keskinler, 2006).

The addition of both hydrogen peroxide and ozone to wastewater accelerates the decomposition of ozone and enhances production of the hydroxyl radical (Al-Kdasi et al., 2005). Ozone and hydroxyl radical (OH) species generated in aqueous solution are able to open aromatic rings. “The advantage is that ozone can be applied directly in its gaseous state and therefore does not increase the volume of wastewater and sludge” (Sundrararjan et al., 2006).

In a TUBITAK financed-project carried out in the Department of Environmental Engineering at METU; a study was undertaken as the first application and evaluation

of Best Available Techniques (BAT) within the context of the EU's IPPC (Integrated Pollution Prevention and Control) Directive to a textile mill in Turkey. The objective of the project was to develop a "best practice example" for the textile sector (TUBITAK, 2008). In the project; for a denim manufacturing textile mill in Kayseri, Turkey, BAT requirements were determined, several better-water management alternatives were identified and applied targeting at the minimization, and where applicable, reuse of both water and raw materials inevitable. In this context; several alternatives were developed for the treatment and reuse of overall plant wastewater and also segregated dyeing wastewater. The alternatives that can be categorized under two headings were:

1. Treatment of the overall plant wastewater by,
    a. biological treatment followed by MF and NF,
    b. membrane bioreactor,
    c. ozonation followed by aerobic biological treatment,
    d. ozonation with hydrogen peroxide followed by aerobic biological treatment,
    e. biological treatment followed by ozonation,
    f. Fenton oxidation followed by aerobic biological treatment,
    g. biological treatment followed by Fenton oxidation,
    h. biological treatment followed by Fenton oxidation and then MF.
2. Treatment of the dyeing wastewater for water reuse by,
    a. coagulation,
    b. membrane filtration,

c. ozonation,

d. Fenton oxidation processes.

In the present study which is a part of the above mentioned investigation; ozonation and ozonation + H_2O_2 application alternatives were considered. The effectiveness of the ozonation and ozonation + H_2O_2 application processes for their potential to remove of color and COD from wastewater of a textile mill including indigo dyeing process was assessed. The specific research objectives are to investigate;

1. the use of only ozonation and ozonation/H_2O_2 application as a pre-treatment method before aerobic oxidation of the overall plant effluent,
2. the use of ozonation as post-treatment after aerobic biological oxidation of the overall plant effluent,
3. the use of ozonation in the treatment of segregated indigo dyeing wastewater.

The research for pre-treatment of the overall plant effluents is carried out in two parts; of which the first is with the already existing overall plant wastewater and the second is with the wastewater expected (simulated wastewater) after the application of a number of cleaner production measures such as the reuse of caustic in the alkaline finishing process wastewater and the reuse of indigo dyeing wastewater following membrane filtration. During the tests with the overall plant wastewater, wastewater samples collected from the entrance of the wastewater treatment facility of the textile mill were utilized. These wastewater samples corresponded to the already existing situation of the water and wastewater management in the mill. In running the tests with the wastewater expected, the wastewater samples were synthetically prepared based on the expected performances of the cleaner production measures using real wastewater samples taken from the mill. In all the ozonation and ozonation + H_2O_2 application tests; color, COD, BOD_5, pH, conductivity, ozone utilization ratio and BOD_5/COD parameters were measured to determine the treatment efficiency.

The overall motivation for the present study is to explore the possibility of using ozonation in the treatment of highly colored wastewater from a denim textile producing plant and, eventually, to evaluate the best treatment technology for this specific industrial sector. Better water and wastewater management is of great importance to textile industry. The results of this study should contribute to the evaluation of the best method of treatment of denim textile wastes and eventual water reuse.

CHAPTER 2

THEORETICAL BACKGROUND

The textile industry is a major economical sector 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. The most important contaminants released by the textile industry are dyes, which enter the environment mainly via discharge of wastewaters (Cervantes, 2009).

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 (EPA, 2004).

It is broadcasted that more than 60 % of the world dyestuff production is consumed by textiles industries. Designated as water soluble, it was estimated that 10 – 20 % of dye was lost during the dyeing process and released as effluent. "The reagents used in textile industry are very diverse in chemical composition. The non-biodegradability of textile wastewater is due to the high content of dyestuffs, surfactants and other additives, which are generally organic compounds of complex

structure" (Gharbani *et al.*, 2008). Textile mill effluents are known to have extremes of pH (either alkaline or acidic) and temperature, high BOD, high COD and high concentrations of suspended solids (SS). Textile mill effluents are also characterized by high levels of color caused by residual dyes that were not fixed to fibers in the dyeing process. Dye molecules are highly structured polymers that are toxic to organisms (Sevimli and Kınacı, 2002).

2.1 Textile Wastewaters

There are several different 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.

"Some processes in a textile mill hardly generate wastewater, such as yarn manufacture, weaving (some machines use water), and singeing (just some lightly polluted cooling water). The amount of wastewater produced in a process like sizing is small, but very concentrated. On the other hand, processes like scouring, bleaching and dyeing generate large amounts of wastewater, varying much in composition" (Cervantes, 2009).

Although effluent characteristics differ greatly even within the same process, some general values for major processes in a textile mill is given in Table 2.1. Mixed textile wastewater generally contains high levels of COD and color, and usually has a high pH (Dos Santos *et al.*, 2007).

Table 2. 1. Average and peak values for some quality parameters in wastewaters from main processes

Parameter	Desizing	Scouring	Bleaching	Dyeing
COD (mg/L)	3580-5900	3200-40000	250-6000	550-8000
COD peak	11000	90000	13500	40000
BOD (mg/L)	200-5200	300-8000	80-400	11-2000
BOD peak		60000	2800	27000
TS (mg/L)	7600-42000	1100-30000	900-14000	200-2000
TS peak		65000		14000
SS (mg/L)	400-800	200-20000	35-900	25-200
SS peak	6000	40000	25000	
TDS (mg/L)	1600-6900	-	40-5000	-
TDS peak			20000	
Lipids (mg/L)	190-750	100-9000	-	-
Lipids peak				
pH	6-9	7-14	6-13	3.5-12

2.2 Treatment Methods for Textile Wastewater

Common treatment methods for textile wastewaters are: biological treatment, physical treatment and chemical treatment. These treatment methods and their efficiencies are reviewed in following sections.

2.2.1 Biological Treatment

Biological treatment can be applied to textile wastewaters as aerobic, anaerobic and combined aerobic-anaerobic. In most cases, activated sludge systems (aerobic treatment) are applied. In all activated sludge systems, easily biodegradable compounds are mineralized whereas heavily biodegradable compounds need certain conditions, such as low food-to-mass-ratios (F/M) (<0.15 kg BOD_5/kg MLSS.d),

adaptation (which is there if the concerned compounds are discharged very regularly) and temperature higher than 15^{o}C (normally the case for textile wastewater) (Lacasse and Baumann, 2004).

Ineffectiveness of aerobic biological treatment in reducing color caused by heavily biodegradable organics causes aesthetic problems in the receiving waters and encourages researchers to investigate alternatives. Dyes themselves are generally resistant to oxidative biodegradation, and a difficulty occurs in acclimation the organisms to this substrate. Acclimation presents a problem with textile wastewater due to constant product changes and batch dyeing operations (Reife and Freeman, 1996).

“Depending on the dyeing process; many chemicals like metals, salts, surfactants, organic processing assistants, sulphide and formaldehyde may be added to improve dye adsorption onto the fibers” (Dos Santos, 2007). These chemicals are mainly in toxic nature and decrease the efficiency of biological treatment in color removal regarding textile wastewater.

“The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfill the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment.

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).

Therefore, the tendency in recent years is towards using alternative technologies, especially advanced oxidation processes for the removal of color caused by hardly biodegradable organics (Baban *et al.,* 2003*;* Sevimli and Sarıkaya, 2002; Birgül and Solmaz, 2007).

2.2.2 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).

Membrane based separation processes have gradually become an alternative method in the treatment of textile wastewaters. Application of membrane processes allows reuse of water besides high removal efficiencies. "Ultrafiltration has been successfully applied for recycling high molecular weight and insoluble dyes (e.g. indigo, disperse), auxiliary chemicals (polyvinyl alcohol) and water. However, ultrafiltration does not remove low molecular weight and soluble dyes (acid, reactive, basic, etc.), but efficient color removal has been achieved by nanofiltration and reverse osmosis" (Fersi *et al.,* 2005).

Related to ion exchange, Mock and Hamodua (1998) reported that an ion exchange system would decolorize a dilute mixture of a colored wastewater sample. However, because the colorant was irreversibly adsorbed onto the resin and regeneration was not possible this technology does not seem effective. They claimed that, further testing with ion exchange-macroreticular polymer systems might have been successful but initial cost estimates, requirement for off-site resin regeneration, and secondary waste disposal requirements resulted in removal of this technology from consideration for color destruction. Robinson et al. (2001) also documented that ion exchange can not be used for the treatment of dye-containing effluents mainly due to cost disadvantage and its ineffectiveness in disperse dyes.

“The coagulation and flocculation process is a versatile method used either alone or combined with biological treatment, in order to remove suspended solids and organic matter as well as providing high color removal in textile industry wastewater” (Meriç *et al*, 2004). “Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulphate, sulphate and ferric chloride” (Anouzla, 2009).

The adsorption is one of the effective methods and the main adsorbent used in dye removal is activated carbon. Activated carbon has been generally used to remove composite reactive dye from dyeing unit effluent. The main disadvantage of activated carbon adsorption method is its high regeneration cost (Demirbaş, 2009).

Moreover, 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). “On the other hand, methods such as coagulation/flocculation and activated carbon adsorption can only transfer the contaminants from one phase to another leaving the problem of color in dyehouse effluent essentially unsolved. Therefore, much attention has been paid to the development of water treatment techniques that lead to complete destruction of the dye molecules” (Solmaz *et al.,* 2006).

2.2.3 Chemical Treatment

In treatment of textile wastewaters, chemical treatment methods are known to be much more effective than others in breaking down the straight, unsaturated bonds in the dye molecules (Ciardelli *et al*., 2001).

Chemical oxidation typically involves the use of an oxidizing agent such as ozone(O_3), hydrogen peroxide(H_2O_2), Fenton’s reagent, permanganate (MnO_4) etc. to change the chemical composition of a compound or a group of compounds, e.g. dyes (Metcalf and Eddy, 2003). Fenton oxidation operates at acidic pH in the presence of H_2O_2 and excess ferrous ions yielding hydroxyl radicals which oxidize organic matter. Fenton’s reagent is effective in reducing COD, color and toxicity of

textile wastewaters, but has the disadvantage shifting problems from water into the solid phase. Therefore a further removal mechanism is required for the Fenton sludge (Meriç *et al.*, 2004; Eckenfelder *et al*., 1994).

Recently, a growing interest is observed in combined methods of chemical oxidation by means of H_20_2 and O_3 as well as O_3 and UV radiation, and of the three agents simultaneously (Perkowski *et al.*, 1999). "Advanced technologies based on chemical oxidation seem to be viable options for decontaminating a biologically recalcitrant wastewater. Such oxidation technologies are broadly classified as follows:

(i) advanced oxidation processes (AOPs) including wastewater remediation based on ozone, hydrogen peroxide, hydrogen peroxide/ferrous iron catalyst (the so called Fenton's reagent), UV irradiation, photocatalysis and electrochemical oxidation;

(ii) wet air oxidation processes (WAO)" (Mantzavinos and Psillakis, 2004).

2.3 Advanced Oxidation Processes

"Advanced oxidation is one of the potential alternatives to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents. This process implies generation and subsequent reaction of hydroxyl radicals, which are the most powerful oxidizing species after fluorine. Among AOPs, treatment with ozone (often combined with H_2O_2, UV, or both), an UV/H_2O_2 system, or Fenton and photo-Fenton type processes have proven to yield very good results either for complete mineralization of reactive dyes or for their transformation into less complex structures that are more easily biodegradable" (Neamtu et al.,2004). The goal of any AOPs design is to generate and use hydroxyl free radical (OH·) as strong oxidant to destroy compound that cannot be oxidized by conventional oxidizing agent. In the Table 2.2, some oxidation potentials of several chemical oxidizers are given. Advanced oxidation processes are characterized by production of OH• radicals and selectivity of attack which is a useful attribute for an oxidant (Al-Kdasi *et al,* 2004).

Table 2. 2. Oxidizing potential for conventional oxidizing agents

Oxidizing agent	**Electrochemical oxidation potential (EOP),V**	**EOP relative to 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

Hydroxyl radicals are extraordinarily reactive species; they attack the most part of organic molecules easily and also characterized by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOPs is also enhanced due to their different possible ways for hydroxyl radical production thus allowing a better compliance with specific treatment requirements.

There are four well-known methods for generating hydroxyl radicals without using light energy. Two of the methods involve the reaction of ozone while the fourth uses the Fe^{+2} ions.

- O_3 / OH^-
- O_3 / H_2O_2
- O_3 / Catalyst

- Fenton's Reaction (Fe^{+2} / H_2O_2)

There are many different UV light enhanced treatment processes available. The following are the five most common.

- O_3 / UV-C
- H_2O_2 / UV-C
- O_3 / H_2O_2 / UV-C
- Photocatalytic (TiO_2 / UV-A)
- Photo Fenton (Fe^{+2} / H_2O_2 / UV-A)

2.3.1 Treatment of Textile Wastewaters with Ozone

It is well known that ozone is a strong oxidant (E^0 = 2.08 V), and is able to form the more powerful, nonselective oxidant of the hydroxyl radical (E^0 = 3.06 V) at high pH values. "Due to this high oxidation potential, ozone can effectively break down the complex aromatic rings of dyestuffs, resulting in the decolorization and transformation of the dye compounds .Actually, ozone can react with reactive dyes more effectively than with other types, such as disperse, acid and sulfur dyes" (Fanchiang and Tseng, 2008).

Because ozone is an unstable molecule, it should be generated at the point of application for use in treatment purposes. It is generally formed by, combining an oxygen atom with an oxygen molecule. Reaction, given in 1.1, is endothermic and requires a considerable input of energy.

$$3O_2 \Leftrightarrow 2O_3 \qquad (1.1)$$

Ozone can be produced several ways, although one method, corona discharge, predominates in the ozone generation industry (Rice, 1998). "Corona discharge, also

known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and a discharge gap. Voltage is applied to the electrodes, causing an electron flow through across the discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone" (EPA, 1999).

"Ozone alone and in combination with UV light, catalyst, ultrasound or activated carbon has been successfully applied to textile industrial effluents. The advantage is that ozone can be applied directly in its gaseous state and therefore doesn't increase the volume of wastewater and sludge. Typically, ozonation doesn't yield complete mineralization to CO_2 and H_2O but leads to formation of partial oxidation products such as organic acids, aldehydes and ketones" (Sundrarajan *et al*., 2007).

"Although some treatment processes (adsorption, coagulation etc.) achieve reduction in COD, substantial amounts of residual color remain. Several different methods have been developed for treatment of textile effluents. The ozone method is known to be effective for decomposing organic chemicals containing carbon–carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon–nitrogen double bonds, carbon–hydrogen bonds, silicon-hydrogen and carbon-metal bonds. Most of the dyestuffs are composed of aromatic organic compounds, so the ozone method is getting more attention with the prediction that it could decompose various kinds of dyestuffs. It is reported that ozone is an effective agent for reducing the color of dyestuff wastewater" (Turhan and Turgut, 2009).

As shown in Figure 2.1, ozone can react by either or both modes in aqueous solutions:

- Direct oxidation of compounds by molecular ozone (O_3(aq)),
- Oxidation of compounds by hydroxyl free radicals produced during the decomposition of ozone (EPA, 1999).

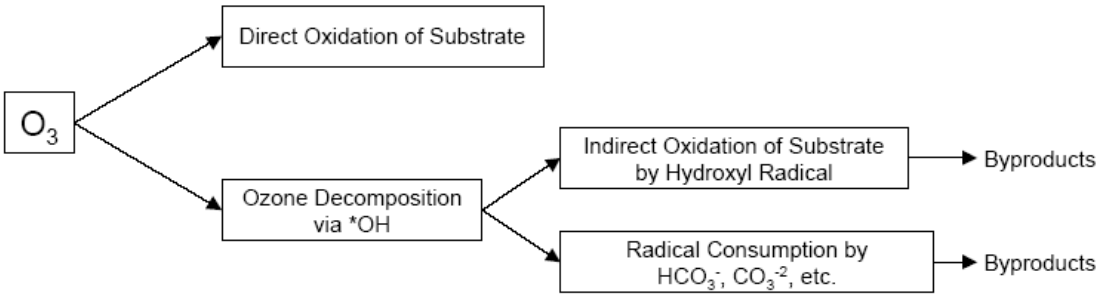


Figure 2. 1.Oxidation reactions of compounds during ozonation

"The two oxidation pathways compete for substrate (i.e., compounds to oxidize). The direct oxidation with aqueous ozone is relatively slow (compared to hydroxyl free radical oxidation) but the concentration of aqueous ozone is relatively high. On the other hand, the hydroxyl radical reaction is fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively small" (EPA, 1999). Hoigné and Bader (1976) found that:

· Under acidic conditions, the direct oxidation with molecular ozone is of primary importance;

and

· Under conditions favoring hydroxyl free radical production, such as high pH, exposure to UV, or addition of hydrogen peroxide, the hydroxyl oxidation starts to dominate.

Thanks to its capacity of color removal, ozone oxidation has been studied as textile wastewater treatment. In fact, elimination of color from textile wastewater is of both immediate and long term interest to textile manufactures, because they either currently or will in the future have to limit the discharge of color from their plants. Furthermore, elimination of color from dyebath water after dyeing may make the

water suitable for reuse in the dyeing process or in some other process in the manufacturing plant.

Many investigations have shown that ozonation was highly effective in breaking down the straight, unsaturated bonds in the dye molecules, causing rapid decoloration of textile wastewater, but concerning COD removal, ozone is considerably less efficient (Ciardelli *et al.*, 2001). “The capability of ozone in oxidizing various pollutants by direct attack on the different bonds (C=C) bond, aromatic rings are further enhanced in the presence of hydrogen peroxide due to the generation of highly reactive OH• radicals. The dissociation of hydrogen peroxide results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals” (Gogate and Pandit, 2004). Application of ozone for color removal and partial oxidation to improve biodegradability seems to be more promising. It is stated that an increase in the ratio of BOD_5/COD after ozonation results from an improved biodegradability of toxic substances. “Ozonation reportedly produces compounds that may elicit toxicity or mutagenicity, but most researchers found less toxicity in ozonated wastewater samples and considerable biodegradability improvement particularly in the case of textile dyes. Important is to optimize the applied ozone dose (ozonation time) to achieve a maximum biodegradability of the specific pollutant that might diminish with extended ozone exposure and higher COD reduction” (Arslan Alaton, 2003; Selçuk, 2004).

2.3.1.1 Effects of Ozonation on COD and Color Removal

“Chemical oxidation with ozone is one of the most suitable chemical oxidation processes for effective color removal from textile effluents, with simultaneous interaction and breakdown of refractory organic matter resistant to biodegradation, without leading to sludge production” (Doğruel *et al*., 2002). However, the ozonation has proven to be rather inefficient for the reduction in COD, whereas, its application in one step for color removal and partial oxidation to improve biodegradability seems to be more promising (Torregrosa *et al.* , 2008).

Sarikaya and Sevimli (2002) and Konsowa (2003) stated that color removal using ozonation from textile wastewater is depended on initial dye concentration and also initial COD. In parallel; Gianluca and Nicola (2001) also stated that COD removal from a textile wastewater, which has been pre-treated, was depended on the initial COD of the wastewater. In their study, 67% and 39% COD removal were realized when the initial COD was 160 and 203 mg/L, respectively.

Koch *et al.* (2002) achieved 50% COD removal after 60 min. with 18.5 mg/L ozone concentration and 40% COD removal after 90 min with an ozone concentration of 9.1 mg/L, Ciardelli *et al.* (2001) also conducted a study on pre-treated wastewater coming from a fulling and dyeing plant used to dye fabrics, hanks, skeins, tops and flocks of different natural and synthetic fibres and mixture of both. They achieved 67% COD removal and 99% color removal in the effluents with 40 g/m^3 ozone concentration when initial COD concentration was 160 mg/L and stated that higher doses do not give further benefits in terms of water discoloration.

In a similar way, Doğruel *et al.* (2002) tested ozonation efficiency both in terms of ozone flow-rate and contact time; a level of around 60 mg/min was determined as the optimum ozone flow-rate, providing almost complete color removal. Total COD reduction, however, could not be improved beyond 32%, even for extended contact times.

Several researchers have reported high color removal efficiencies by ozonation for different dye types. For example, Kabdaşlı et al.(2002) realized 99% color removal with 63 mg/min ozone dose within 45 minutes on reactive dyes (Procion); Sundrarajan *et al.* (2007) achieved complete color removal after ozonation for 40 min at an ozone consumption of 76.5 mg/L. However, COD removal efficiency (22%) was not as high as color removal efficiency in the study. In the research of Solmaz *et al.* (2006), ozonation resulted in 97% color removal and 43% COD removal, with 20 mg/min ozone dose.

On the other hand, some researchers stated that ozone can decolorize all dyes, except nonsoluble disperse and vat dyes whose reactions with ozone are slower and take

longer time (Namboodri *et al.*, 1994; Rajeswari, 2000). However, in general case, treatment with ozone on textile wastewaters gives satisfactory results on color removal, however, for COD; removal efficiencies are not so satisfactory. The low COD reduction is attributable to the fact that the structured polymer dye molecules are oxidized by ozonation to small molecules, such as acetic acids, aldehyde, ketones, etc., instead of CO_2 and water. These small molecules still possess a considerable amount of COD (Lin and Lin, 1993).

2.3.1.2 Effects of Ozonation on Biodegradability

Ozone can be applied either before or after the biological treatment process. As indicated before, the best results concerning color removal are achieved if the wastewater has been previously pretreated in order to remove other constituents so that the ozone oxidizing power is "consumed" only or at least at a maximum proportion in color removal (Ozone Solutions, 2010). But still, in some cases, preozonation may be expected to ease biological treatment by converting the more slowly biodegradable COD into simpler compounds or by reducing the amount of inert organic matter. Post-ozonation, on the other hand, may have a polishing effect on the effluent quality (Orhon, 2002).

The BOD_5/COD ratio is usually used to measure the biodegradability of the wastewater. A larger BOD_5-to-COD ratio indicates a higher biodegradability of the wastewater (Wu *et al.,* 2008). The improved biodegradability is associated with the partial oxidation of organic matter to give smaller oxygenated compounds rather than complete oxidation to carbon dioxide (Beltran, 2004).

In the studies of Lackey *et al's* (2006), the initial BOD_5/COD ratio was 0.0083 and over time increased by an order of magnitude to a maximum ratio of 0.126 at 30 minutes. Such results indicate that the wastewater biodegradability increased with an increase in ozonation time. Similarly, Somensi *et al.* (2010) studied on a raw wastewater of a textile mill in Brazil showing a low BOD_5/COD ratio (0.06), that is, raw wastewater have a low biodegradability, which could be attributed to the toxicity

and/or low solubility of compounds present in this sample. After 240 minutes of ozonation, this ratio reached an acceptable value (0.41), which could ensure good biodegradability.

Wu *et al.* (2008) also observed an increase on biodegradability about 18.7-68.5 times with different operating parameters. In their studies changes in BOD_5 and COD is negligible after a certain time.

Sevimli and Kınacı (2002) achieved an improvement in biodegradability by increasing BOD_5/COD ratio from 0.58 to 0.62 and 0.75 with 30 minutes of ozonation at the ozone dose of 12 and 111 mg/L.min, respectively. In a similar case, Liakou *et al.* (1997) presented an increase in biodegradability in their studies with Orange II.

The examples above demonstrate that the general trend in biodegradability when ozone treatment was used is an increase in BOD_5/COD ratio. Therefore, because ozone can convert biorefractory dyes into biodegradable species, it can be used before any biological treatment (Wu and Wang, 2001)

2.3.1.3 Effects of Ozone Dose on Treatment Efficiency

Efficiency of ozone treatment of textile wastewater depends on operating parameters, such as the applied ozone dose (Wu *et al.*, 2008) and pH . Determination of the required ozone dose in the treatment of effluents is essential for the economical evaluation of the process (Soares *et al.*, 2006).

Increase in ozone doses has a positive effect on treatment efficiency with regard to color and COD removal (Kabdaşlı *et al.*, 2002; Ciardelli *et al.*, 2001; Baig and Liechti, 2001; Arslan Alaton, 2007; Koyunluoğlu *et al.*, 2006; Ölmez *et al.*, 2003) However, higher doses do not give further benefits in terms of water discolorization (Ciardelli and Ranieri, 2000).

Shu and Huang (1995) made a study on acid orange 10 dye in order to observe effect of ozone dose on treatment efficiency, and they stated that after a certain ozone dose,

no improvement was observed on treatment efficiencies. They realized 99% color removal in 10 minutes with 6.0, 7.5 and 9.0 dm^3/min ozone doses. Similarly, Jiangning *et al*. (2008) presented an equilibrium dose for ozone and after that value no change was observed in removal efficiency with respect to color parameter. Therefore, an optimum dose for ozone should be determined in the studies related to ozone treatment of textile wastewaters. In addition, it is necessary to make another assessment from viewpoint of the ozone utilization ratio for the removal of parameters like color and COD (Sevimli and Sarıkaya, 2002).

2.3.1.4 Effects of pH on Treatment Efficiency

Ozone chemistry is related with pH of the medium. As described in Section 2.2.1, under acidic conditions ozone can mainly react directly with organic compounds. However under alkaline conditions, ozone can mainly decompose to OH radicals ($OH^{\cdot}$), which react with the target pollutant (Wang *et al*., 2008).

Arslan Alaton (2007) stated that an increase in reaction pH has a profound, positive effect on COD removal rates under ozone-saturated reaction conditions (800 mg O_3/h), particularly when the ozonation pH is 12. In a similar case, Somensi *et al.* (2010) stated that ozonation treatment was more effective at degrading wastewater dyes under basic pH than acidic pH. The average efficiencies for color removal were 40.6% for pH 3.0 and 67.5% for pH 9.1.

When the pH value changed from 2 to 12, Konsowa (2003) documented 32% reduction in the dye decolorization time; whereas Turhan and Turgut (2009) documented this value as 55.71%.

In the study of Soares *et al.*'s (2006), ozonation experiments were conducted on different pH values for two kinds of textile effluents including reactive dyes; one is a raw textile effluent and the other one is an equal mixture of the raw textile wastewater and biologically pre-treated wastewater. For the raw textile effluent, the highest decolorisation efficiency is obtained at pH 3, on the contrary; for the other effluent, the lowest removal efficiency is achieved at this pH. In another study,

highest color removal rates were obtained when pH value is 7 and pH value is 12 in the ozonation studies on Cibacron F reactive dyestuff; on the other hand lowest removal rate was obtained at pH 2 (Arslan Alaton *et al.*, 2002). Pirgalioğlu and Özbelge (2009) documented that the dye removal rate decreases with the increasing solution pH from 3 to 7, increasing again between pH values of 7 and 10. The reason for this difference was explained by them as the decreasing ozone concentration at pH 7, while the contribution of hydroxyl radicals was low with respect to the case at pH 10. Higher dye removal rate was observed at pH 10 where the contribution of hydroxyl radicals was higher with respect to that at pH 7.

On the other hand, in some studies it is stated that there is no effect of pH on treatment efficiency of ozonation. For example, Souza *et al.* (2010) conducted a study by using the textile dye Ramazol Black B dye, and observed that the reduction in the dye concentration was independent of the initial pH value in the range of 3–11. Similarly, Shu and Chang (2005) presented almost same removal rates in acidic, neutral and basic conditions.

2.3.1.5 Effects of Reaction Time on Treatment Efficiency

In the oxidation of dyestuff by ozonation; colour and COD removals generally increase with the ozonation time (reaction time). However, in the ozonation process, increase in color and COD removal rates slowdowns when time passes and after a certain time color and COD values remain constant at their lowest value (Birgül and Akal Solmaz, 2007; Konsowa, 2003; Wu *et al.*, 2008).

Meriç *et al.* (2005) conducted a study on an intense textile wastewater whose COD is 910 mg/L and color is 1570 Pt-Co, and obtained 90% color removal in 15 minutes. In this study, color removal was 60% after 5 minutes, 80% after 10 minutes, 85% after 12.5 minutes and 90% after 20 minutes.

Colindres *et al. (*2010) conducted a study on Reactive Black 5 (RB5), as an industrial sample without any further purification, and found that relatively short ozonation times, 10 minutes, are sufficient to remove the color. After 10 minutes, no significant

color removal was observed in this study, parallel to the findings from other studies like the cases stated in the first paragraph. Therefore, in the treatment of textile wastewaters with ozone, the color removal seems to be rapid and not differ at all considerably after a certain time. Fanchiang and Tseng (2009) presented a linear relationship between the ozone feed rate and various removal efficiencies. In other words, with an increase in ozone feed rate the rate constants or removal efficiencies are increasing linearly.

Although in most of the cases the treatment efficiency increases with increasing ozonation time; in some studies, there is a tendency toward an increase in COD with increasing ozonation time. Souza *et al.* (2010) observed this case in their studies especially for times of 100 and 105 min. The increase in COD may be due to dye molecules being oxidized by ozonation, resulting in small organic molecular fragments, such as acetic acid, aldehydes, ketones, which are not completely mineralized under the oxidative conditions described, contributing to an increase in COD with ozonation time.

From the foregoing discussions, it can be concluded that the effect of ozonation time on treatment efficiency with ozone with regard to color and COD removal is almost always positive up to a certain time after which no significant removal is observed (Doğruel *et al.*, 2002; Baban *et al.*, 2003; Chu *et al.*, 2008; Oğuz and Keskinler, 2008; Gharbani *et al.,* 2008; Santana *et al.,* 2009; Turhan and Turgut, 2009). According to a recent study the reaction order may not be constant throughout the ozonation process, since it can change with the variation of the ozone to dye ratio during the progress of the ozonation process (Peng and Fan, 2005). Another general finding from the literature is that the oxidation of color causing organics from textile effluents is rapid and almost complete color removal is achieved within 20-60 minutes, except some exceptional cases(Selçuk, 2005; Koyuncu et al., 2001; Orhon et al., 2002).

2.3.1.6 Effects of H_2O_2 Addition on Treatment Efficiency

The combination of ozone and hydrogen peroxide is generally used essentially for the oxidation of contaminants, which are difficult to oxidize and therefore requires large amounts of oxidant, in order to decrease high cost of ozone generation (Alsheyab and Munoz, 2005). 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).

In the treatment of the wastewater, whose COD is 820 mg/L, of a textile mill located in Bursa, Turkey, Solmaz *et al.* (2006) achieved 20% of the increase in COD removal and very little increase in color removal by the addition of 5 mg/L hydrogen peroxide to ozone application. In another study, much better performance was achieved with H_2O_2 addition; Perkowski *et al.* (1999) reported 98.8 % and 100% color removal in one hour and two hours reaction times, respectively, with the addition of hydrogen peroxide, on a dyebath including Acid Blue 62, Direct Yellow 44, Direct Brown 2; whereas color removal rate was 98.3 % with ozonation alone.

On the contrary, in some studies, addition of hydrogen peroxide did not provide any additional benefits on color removal from textile mill effluents. For example, Arslan and Balcıoğlu (2001) have shown that no degradation was observed on COD removal efficiency and decolorization rate compared to ozonation alone after the addition of 60 – 120 mg/L H_2O_2 to the dyehouse effluent. Similarly, performance of ozonation was not influenced by the hydrogen peroxide addition in the study of Ko *et al. (*2009). Wang *et al*. (2008) and Swaminathan *et al*. (2005) also presented ineffectiveness of hydrogen peroxide addition in their studies. All tried different H_2O_2 concentrations between 1.1 – 100 mg/L and in most cases O_3/H_2O_2 process negatively affected the COD removal efficiency for the removal of color and COD as compared to the ozonation process alone.

Moreover, Khadhraoui et al. (2009) concluded that color removal efficiency was lower in case of H_2O_2 and O_3 combination as compared to ozone alone and this lower performance was due to the scavenging effect of high H_2O_2 dose applied. In a recent

study, similar findings have been reported; Oğuz and Keskinler (2007) stated that H_2O_2 used in the O_3/H_2O_2 process negatively affected the removal of COD from synthetic wastewater including Bomaplex Red CR-L dye. In this study, it was thought that OH^- radicals in the O_3/H_2O_2 process transformed dye molecules into smaller intermediate products, and these intermediate products caused an increase in COD values. In addition to these studies, Lopez et al. (2004) observed that the discolorization is inhibited by high hydrogen peroxide concentrations in their studies with in which Orange Red and Acid Red 27 Azo Dyes are chosen as a representative model

From all above discussions, it can be concluded that dependent on dye type and characteristics of the medium, the effect of hydrogen peroxide addition on ozone treatment can differ as positive or negative; or hydrogen peroxide may be ineffective.

CHAPTER 3

EXPERIMENTAL

3.1 Experimental Materials

Wastewaters used in the study were obtained from a denim textile producing mill in Turkey, which is located in Kayseri. The textile mill was established in 1953 as a spinning and weaving factory with 100 % Turkish capital. In 1986, it was restructured and started to manufacture denim. The factory has a manufacture capacity of 45 million meters fabric per year and operates in an area of 156.000 m^2 with 1170 employees.

The textile mill is one of the major innovation leaders of jeans and sportswear in Europe. The cotton having high strength and fibre length both from internal and external sources is used by the company in order to produce denim fabrics.

Textile production starts with fiber manufacturing continues with sizing, dyeing, weaving and ends up with finishing. Among these, dyeing, sizing and finishing are the wet processes; fiber manufacturing and weaving are the dry processes. The plant provides its water from wells, softens through the processes of an ion exchange and a reverse osmosis, and discharges its treated wastewaters into the sewer line that ends up with a municipal wastewater treatment plant. More than 70% of the total water extracted, which is 3500-5000 tons/day, is used for dyeing and finishing processes; and the rest being used for other purposes such as steam generation, sizing, good housekeeping etc. (Ünlü, 2008).

As indicated in Introduction Part, ozonation experiments were conducted on four types of wastewater from the textile mill: indigo dyeing wastewater, wastewater before cleaner production measures are taken (overall plant wastewater), wastewater after cleaner production measures are taken and biologically treated wastewater.

Mentioned cleaner production measures are caustic recovery from alkaline finishing wastewaters and water reuse after the application of membrane filtration to indigo dyeing wastewater in the mill. After these measures are taken in the mill, it is expected that there will be reduction in the volume of wastewater from dyeing and finishing operations.

Moreover, there will be an increase in the strength of the wastewater from indigo dyeing, as the reject stream from membrane filtration will be going to the wastewater treatment plant.

On the other side, caustic recovery from finishing wastewaters will yield a finishing wastewater with a lower caustic content which is again the reject stream from the membrane filtration of caustic finishing wastewater. It is expected that these reject streams and the wastewaters from other units will come together to form the overall wastewater coming to the wastewater treatment plant. Thus, as stated in Introduction Part wastewater so called " before measures" was taken from the entrance of the existing treatment plant of the textile mill, however, in order to prepare wastewater so called "after measures" for cleaner production, wastewater samples coming from dyeing, finishing and other lines were mixed at ratios indicated in Table 3.1. Table 3.2 presents the characteristics of the overall wastewater before and after cleaner production measures and also those of indigo dyeing wastewater and also overall plant wastewater after biological treatment.

Table 3.1. Wastewater streams forming the overall plant wastewater before and after the cleaner production measures

Process	Before Measures	After Measures
Dyeing	35%	24%
Finishing	45%	31%
Other	20%	45%

The characteristic of the wastewaters used in the experiments are given in Table 3.2**.**

Table 3.2. Characteristics of wastewaters

Parameter	Indigo dyeing wastewater	Overall Plant Wastewater (before measures)	Wastewater (after measures)	Biologically treated wastewater
Color, Pt-Co	4560-6120	3920-4200	4230-4820	3300-4100
COD, mg O_2/L	715-942	2680-2840	3057-3162	743-865
Conductivity, mS/cm	6.91-7.02	19.75-19.85	13.54-14.01	14.26-14.60
pH	9.06-9.28	12.4-12.6	12.09-12.24	7.08-7.15

Indigo dyeing wastewater samples used throughout the study is the mixture of the most common three dyeing recipes of the textile mill in one-to-one ratio. Such a mixture was utilized as the textile plant applies hundreds of different indigo dyeing recipes. In cooperation with the plant, the dyeing recipes applied in the last three years and their application intensities were assessed and the most common three were determined. Wastewater samples taken on the days, at which these three recipes were applied, were brought to the laboratory and mixed in order to prepare the sample to be used in the tests with indigo dyeing wastewater.

Biologically treated wastewater was obtained from the outlet of bench-scale biological reactor (10 L) which was fed with whole wastewater of the textile mill and was operated at eight days of hydraulic retention time as part of the project conducted at METU (TUBITAK, 2008). The effluent from the reactor was kept at 4 ^{o}C and used in ozonation experiments within 2 days in order to obtain reliable results.

The values given for all wastewater types in Table 3.2 show fluctuations because characteristics of the recipes may differ due to the operating conditions of the textile mill such as flow rate of the rinsing water in dyeing process, change in the concentration of auxiliary chemicals in the processes, production capacity etc. Moreover, the wastewater samples were dispatched by the textile mill at different times which also cause fluctuation on measured parameter values.

The wastewater samples used in the study were taken from the mill as grab samples and transferred to the laboratory in ice-boxes. Then, all the samples were passed through a metal filter with 0.8 mm pore size in order to remove coarse fiber and similar large particles. Samples were kept at 4^{o}C in 25 L plastic containers.

3.2 Experimental Apparatus

3.2.1 Ozone Generator

WEDECO Modular 4 HC with 4 g/h ozone production capacity was used in the experiments. The width, depth and height of the ozone generator, a photograph of which is given in Figure 3.1, are 600 mm, 210 mm and 600 mm, respectively. All experiments with the ozone generator were conducted in Unit Operations Laboratory in the Department of Environmental Engineering at METU.

Figure 3. 1. Ozone generator

Ozone is produced from pure oxygen, which is generated from AirSep AS 12 oxygen generator placed as a part in WEDECO Modular 4 HC ozone generator. The oxygen gas to ozonated crosses the ozonizer through the annular thin spaces of the plate ozone generator. A part of the electric energy necessary for this ozone generation is transformed into heat. This heat is removed by the air cooling. Ozone concentrations can be adjusted by means of potentiometer installed on the panel of the ozone generator. Fluorinated plastic (PTFE) was used in all connections from which ozone gas passes.

In order to set a specific ozone production quantity and concentration the performance curve, which is given in Appendix and supplied by the manufacturer, of the ozone generator is needed. Ozone production quantity was calculated from the following equation.

$$m_{O3} = C_{O3} * V_{gas} \quad (3.1)$$

where;

$\mathbf{m_{O3}}$: Ozone dose (g/h)

$\mathbf{C_{O3}}$: Ozone concentration (g/m^3)

$\mathbf{V_{gas}}$: Gas volume flow (m^3/h)

The operating pressure in the ozonation experiments was 0.5 bar. This value is also advisable in the Manual of WEDECO Ozone Generator Modular HC Series. Although it can be adjusted in the range from 6 L/h to 60 L/h, experiments were conducted at constant flow rate (60 L/h) for elimination of effects of gas flow rate on removal efficiencies.

3.2.2 Reactor

Ozonation experiments were carried out in a batch reactor with 6 cm diameter and 78 cm height made of glass (Figure 3.2). The reactor has ports for inlet ozone gas coming from ozone generator, outlet ozone gas and sampling. Ozone gas was given from the bottom of the reactor through a sintered glass plate diffuser.

Figure 3. 2. Ozone reactor

Unused ozone was collected from the top of the reactor and transmitted to gas washing bottle with 400 mL volume and containing 2% potassium iodide solution in order to determine the dose of the output ozone gas passing through the reactor.

3.2.3 Measurement Apparatus

Color and COD measurements were done by using HACH DR-2000 Model Spectrophotometer (Model No 45600-02, Cole Parmer Instrument Co., USA). Conductivity and pH measurements were done by means of portable Hach Sension 378 pH/conductivity/dissolved oxygen meter.

Color measurements were done at 455 nm wavelength, whereas, COD measurements were done at 420 nm for COD values up to 150 mg/L and at 620 nm for COD values up to 1500 mg/L.

3.3 Experimental Methods

All experiments were performed at room temperature ($23^{o}C \pm 2^{o}C$) using 1.5 L wastewater samples. During the experiments for each wastewater type examined in the scope of the study, samples were withdrawn between ten minutes interval by the means of sampling port placed at 38^{th} cm of the reactor from the bottom. The samples with 25 mL volume were withdrawn periodically from the reactor in order to monitor the change in the parameters like COD, color, pH and conductivity.

Gas washing bottle including 2% KI solution was placed after the reactor in order to calculate the unused ozone dose in the experiments. All experiments were conducted at two times in order to eliminate the possible mistakes. Experiments with wastewater before and after measures were considered as pre-treatment, those with biologically treated wastewater were considered as post-treatment. On the other hand, the studies with indigo dyeing wastewater were conducted

Different ozone doses were applied for the wastewaters at different durations. In the studies with indigo dyeing wastewater; 960 mg/h, 1320 mg/h, 2100 mg/h, 2580 mg/h and 3240 mg/h ozone doses were applied during 80 minutes. Then, optimum ozonation time and optimum ozone dose for indigo dyeing wastewater were determined. Effect of pH was also studied in the experiments with indigo dyeing wastewater after an optimum ozone dose was determined.

2340 mg/h, 3240 mg/h and 3960 mg/h ozone doses were applied during 70 minutes to the overall plant wastewater. Effect of H_2O_2 and change in biodegradability were also studied in the experiments with this wastewater. 180 mg/L, 600 mg/L and 1800 mg/L H_2O_2 concentrations were tried in the study and which concentration is effective was investigated.

Because of the strength of the wastewater (after measures), higher ozone doses, which are 2760 mg/h, 3240 mg/h and 3960 mg/h, were applied to this wastewater during 80 minutes. 1500 mg/L H_2O_2 concentration was also tried in order to observe the possible effects of H_2O_2 addition.

Lower ozone doses compared to other types of wastewater studied were tried in biologically treated wastewater. 216 mg/h, 420 mg/h, 960 mg/h and 1320 mg/h ozone doses were applied during 50 minutes and determination of the optimum ozone dose were aimed in the scope of the study.

Moreover, in order to see the effect of pH on treatment efficiency for indigo dyeing wastewater, ozonation experiments were conducted at different pH values, which are 1.6, 4, 7, 10 and 12.3. These pH values were chosen in order to observe the treatment efficiency changes in acidic, neutral and basic mediums and pH was adjusted by using sulphuric acid and sodium hydroxide whose properties given in the following chapter. pH of the samples were kept constant during the experiments by using phosphate buffers.

The reactor was washed with distilled water after each experiment in order to eliminate the possible contamination from the previous experiment.

3.4 Chemicals Used in the Experiments

35 % (w/w) H_2O_2 chemical purchased from Merck was used in the experiments. H_2O_2 addition was not implemented to indigo dyeing wastewater and biologically treated wastewater.

Sulphuric acid (H_2SO_4) with 1 N and sodium hydroxide (NaOH) with 0.5 N was used in order to adjust pH of the wastewater to the desired value. Effect of pH has been studied only in the experiments with indigo dyeing wastewater. Phosphate buffers were used in order to keep pH of the wastewater constant during experiments.

In order to calculate the unused ozone dose, potassium iodide (KI) solutions were prepared for each set of the experiments. The solution (2 per cent) was hold in 400 mL gas washing bottles. Distilled water was used for the preparation of the solutions.

Sodium thiosulfate ($Na_2S_2O_3$) with 0.2 N, purchased from Merck, was used in the titration procedure for the determination of unused ozone dose. Starch solution and sulphuric acid were also used during titration stage of the experiments.

3.5 Analytical Methods

The analytical procedures implemented in the study for each parameter are described below.

Color Measurements: HACH DR-2000 Model Spectrophotometer (Model No 45600-02, Cole Parmer Instrument Co., USA) was used for the color measurements in Pt-Co unit. USEPA approved HACH Method No.8025 was implemented for the measurement and the wavelength of 455 nm was selected. Samples were not diluted if the normal range is expected, and diluted to 1:10 - 1:20 if darker colors are expected.

COD Measurements: Chemical oxygen demand measurements were carried out according to USEPA-approved HACH's reactor digestion COD Method (No. 8000).

The wavelength 620 nm was used for COD values expected up to 1500 mg/l and 420 nm was used for COD values up to 150 mg/l for the measurements as required by the HACH Method No.8000. Samples were diluted in a certain ratio, in order to remain in the measurement interval of the spectrophotometer.

BOD_5 Measurements: Dilution BOD test method was carried out for the BOD_5 measurements. The Winkler method was used for the dissolved oxygen measurements (APHA, 1989).

Consumed Ozone Measurements: Ozone dose in the outlet of the reactor was determined according to the iodometric method. The gas washing bottle including 2% KI solution was hold unused ozone during experiments. When ozone gas enters the bottle iodine appears and yellow color was observed in the bottle. This yellow color solution was titrated with $Na_2S_2O_3$ and unused ozone dose was calculated. The formula numbered 3.2 was used in order to calculate unused ozone dose.

$$O_3\ (mg/\min) = \frac{V_{S_2O_3^{2-}}\ x\ N_{S_2O_3^{2-}}\ (eqg.L^{1-})\ x\ 24\ (g.eqg^{-1})}{t\ (\min)} \qquad (3.2)$$

From the characteristic curves, exact ozone dose given to the system was calculated according to Formula, 3.1. The difference between Formula 3.1 and 3.2 gave us the consumed ozone dose.

Ozone Utilization Ratio: In order to evaluate whether the ozone dose given to the reactor was used efficiently or not, ozone utilization ratios were calculated in the scope of the study by dividing consumed ozone concentration to given ozone concentration to the system.

pH Measurements: HACH Sension 378 pH meter was used in the scope of the pH measurements.

Conductivity Measurements: HACH Sension 378 conductivity meter was used in the scope of the conductivity measurements.

CHAPTER 4

RESULTS AND DISCUSSIONS

In this chapter; the results of experiments that were carried out and discussion of the results that were obtained are presented. As stated in Chapter 3, the experiments were conducted with four different wastewaters in order to evaluate the effect of ozonation time and ozone dose on mainly color and COD removal efficiency.

In indigo dyeing wastewater, effect of pH and in the wastewaters, before and after measures were taken in the textile mill, effect of H_2O_2 addition on treatment efficiency and effect of ozonation on biodegradability were also studied.

The cleaner production measures to be taken in the mill are the reusing of wastewater from dyeing process, and recovery of sodium hydroxide (NaOH, caustic) from mercerization wastewaters within finishing process as explained in previous chapters. In this study, the main aim of the ozonation experiments on the wastewaters, both before and after measures, was to test the ozonation method as pre-treatment, whereas, as post-treatment on biologically treated wastewater. On the other hand, the objective of the studies on indigo dyeing wastewater was the reusing of dyeing wastewater after ozonation.

In this chapter, the results of the ozonation studies are given and discussed for each wastewater, differently. In the results of the studies on indigo dyeing wastewater, the wastewater before measures, the wastewaters after measures and biologically treated wastewater are given in Sections 4.1, 4.2, 4.3 and 4.4, respectively.

4.1 Ozonation of Indigo Dyeing Wastewater

As indicated in Section 3.1, the wastewater sample used in this part of the research was a mixture of wastewater samples belonging to the three most commonly indigo dyeing recipes. The change in color and COD parameters was mainly investigated in this set of experiments. Apart from these parameters, pH and conductivity was measured in the experiments.

Optimum treatment time and optimum ozone dose were determined first of all. When these were determined, in order to determine in which pH value more effective treatment is achieved, experiments were done at different pH values.

4.1.1 Ozonation Kinetics of Indigo Dyeing Wastewater

As is known, ozone is a powerful oxidant and the use of it in textile effluent treatment is a very attractive alternative technology for other treatment types like chemical coagulation and biological treatment (Oğuz and Keskinler, 2006). Ozone attacks double bonds that are often associated with color (Li *et al*., 2008) and therefore provides satisfactory discolorization. However, ozone is known to be not very effective in the mineralization of organic substances. Ozonation can only provide partial oxidation of organic substances leading to the formation of compounds such as aldehydes, organic acids and ketones (Li *et al*., 2008). Accordingly, the ozonation of a colored textile effluent has to be assessed not only in terms of color removal efficiency but also COD removal efficiency.

In this part of the present study, in order to assess the effectiveness of ozonation in the removal of color and COD from indigo dyeing wastewater and also to determine ozone requirement, different ozone doses were applied and time-dependent variation in the removal of color and COD were followed. The ozone application rates or ozone doses tested in these experiments were 960 mg/h, 1320 mg/h, 2100 mg/h, 2580 mg/h and 3240 mg/h for a wastewater sample of 1.5 L having a COD and colour values given in Table 3.2 in Chapter 3. At all doses; ozonation reaction was

followed for a period of 80 minutes and the samples taken from the reactor at predetermined time intervals (10 min) were analyzed for their color and COD content. The ozone utilization ratio and ozone consumption per COD removal ratio were calculated in order to take them into consideration when determining optimum ozone dose and treatment time.

As explained above, five different doses were applied to indigo dyeing wastewater during 80 minutes and the timely color removals presented in Figure 4.1 were obtained.

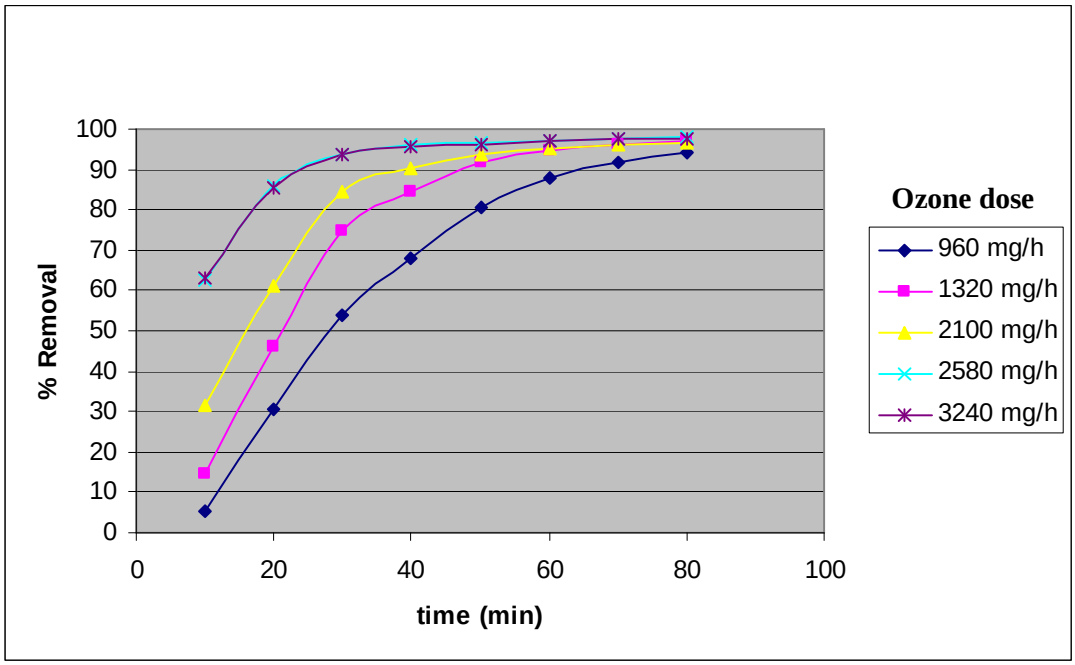


Figure 4. 1. Color removal with ozonation in indigo dyeing wastewater

As can be seen from Figure 4.1, at all ozone doses tested, color removal was quite rapid during the first 30 min and the initial discolorization rate has not considerably changed with an increase in ozone dose. At the time of 10 min; % color removal was 5 % for the ozone application rate of 960 mg/h, and over 60% for the ozone rate of 3240 mg/h. This result was an expected result when compared to other studies

conducted in recent years with different type of dyes (Ciardelli *et al*., 2001; Kabdaşlı *et al.*, 2002; Sundrarajan, 2007; Meriç *et al.*, 2005; Sevimli and Sarikaya, 2002). In all these studies, higher color removals were reported with increasing ozone doses. The same removal ratios with 2580 mg/h and 3240 mg/h ozone doses may be explained with the solubility of ozone in the sample. After a certain ozone doses, almost same color removal ratios may be obtained.

Color removal in indigo dyeing wastewater may be considered in three different phases. Within the first thirty minutes, removal rate of color is rapid; whereas, between 30^{th} and 60^{th} minutes these rate slowdowns and after 60^{th} minutes no important change in color removal ratios was observed.

Color removal ratios between 94 – 98% with various doses were achieved after 80-minute treatment time. However, Figure 4.1 shows that for most doses, except 960 mg/h, there is not any improvement in color removal after 60-minute treatment time.

In the same manner, after 60^{th} minute of the treatment, no distinct color removal was observed when ozone dose increases. At this point, consumed ozone values for each treatment dose should be taken into consideration. In Table 4.1, consumed ozone amounts are given during 80-minute treatment time. The values given in the table are cumulative values.

Table 4. 1. Consumed ozone amounts in indigo dyeing wastewater

Time (min)	Consumed Ozone(mg)				
	960 mg/h	**1320 mg/h**	**2100 mg/h**	**2580 mg/h**	**3240 mg/h**
10	156.64	213.28	309.68	356.08	443.04
20	298.40	368.96	500.80	570.08	779.52
30	399.36	477.60	639.60	729.84	1054.08
40	490.72	587.20	785.60	886.24	1345.92
50	562.88	672.32	937.36	1032.56	1629.12
60	624.00	775.20	1081.44	1127.04	1912.80
70	690.88	858.88	1150.64	1216.24	2101.44
80	749.60	935.36	1196.80	1270.40	2285.76

From Table 4.1, it can be seen that consumed ozone amount increases with applied ozone dose, which is an expected result. By considering color removal ratios given in Figure 4.1, it can be concluded that for ozone doses higher than 1320 mg/h, 1.5-2.5 times higher ozone doses were consumed when compared to 1320 mg/h ozone dose, although the same removal efficiencies were obtained. Besides ozone utilization ratio at 60^{th} minute is 58.73 % in the experiments with 1320 mg/h ozone doses; on the other hand this ratio is 51.50 %, 43.68 % and 59.04 % in the experiments with ozone dose 2100 mg/h, 2580 mg/h and 3240 mg/h, respectively.

When both ozone dose and ozone utilization ratio is considered 1320 mg/h ozone dose is the optimum ozone dose for 60 minutes treatment time for color removal. However, in order to be certain whether this dose and treatment time is optimum or not, results of COD removals in indigo dyeing wastewater should be taken into consideration.

For color removal only, it can be concluded that high removal efficiencies were obtained in indigo dyeing wastewater and observed that after 60^{th} minutes there is no any remarkable changes in the removal ratios.

The result of the experiments with regard to COD removal is given in Figure 4.2.

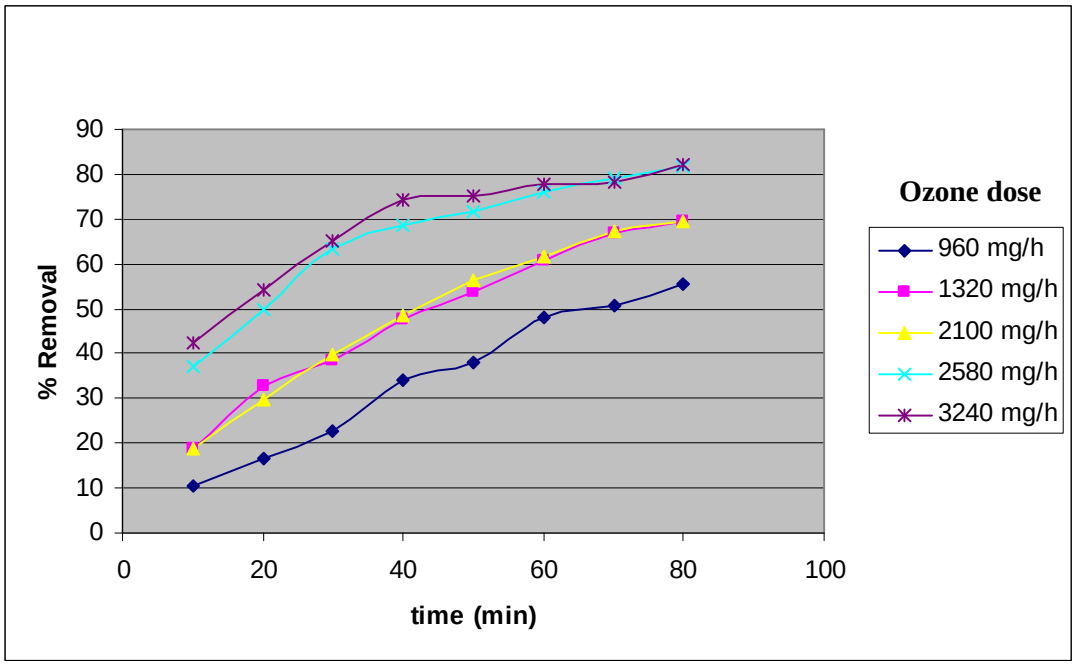


Figure 4. 2. COD removal with ozonation in indigo dyeing wastewater

The main marked point in the figure is that ozonation is less effective in COD removal when compared to color removal. The main reason for this result may be explained by stating that ozonation can not completely oxidize organic substances into carbon dioxide, leading to partial oxidation products, such as aldehydes, organic acids and ketones (Chu *et al.*, 2008). This result is consistent with the other studies in the literature (Doğruel *et al.*, 2002; Koch *et al.*, 2002; Baban *et al.*, 2003; Arslan Alaton, 2007).

Lower COD removal ratios are observed at low ozone doses, whereas at high ozone doses COD removal efficiency increases. The highest COD removal ratio was achieved when the applied ozone dose is 3240 mg/h. In the same manner, removal ratios are high when ozone dose is 2580 mg/h. The lowest removal ratio was obtained at 960 mg/h ozone dose. On the other hand, the COD removal ratios when ozone dose is 1320 mg/h and 2100 mg/h are in acceptable level. COD removal ratios demonstrate that almost the same removal ratios were obtained at 1320 mg/h and

2100 mg/h ozone doses. The reason for this condition may be related with the different dispatching time of indigo dyeing wastewater by the textile mill management. The experiments with 1320 mg/h and 2100 mg/h ozone doses were conducted at different times but with the same dyeing process wastewater. However, there were small fluctuations in initial COD concentrations of indigo dyeing wastewaters, which were dispatched at different times, as indicated in the Table 3.2 in Chapter 3.

Although high COD removal ratios are observed, unused ozone amounts at 3240 mg/h and 2580 mg/h are higher than those at other ozone doses. At this point, consumed ozone per removed COD ratio should be calculated in order to learn how much ozone consumed (mg) for 1 mg/L COD removal. In Table 4.2, this ratio for five different doses is given.

Table 4. 2. Consumed ozone/Removed COD ratio in indigo dyeing wastewater

Time	**Consumed Ozone/Removed COD**(mg O_3/ mg/L COD)				
(min)	**960 mg/h**	**1320 mg/h**	**2100 mg/h**	**2580 mg/h**	**3240 mg/h**
10	2.21	1.49	2.31	1.34	1.37
20	2.64	1.47	2.35	1.59	1.89
30	2.58	1.62	2.24	1.60	2.11
40	2.12	1.62	2.26	1.80	2.37
50	2.16	1.64	2.32	2.00	2.84
60	1.90	1.67	2.46	2.07	3.22
70	2.00	1.69	2.39	2.14	3.53
80	1.97	1.76	2.41	2.17	3.64

As it can be observed form Table 4.2, at 1320 mg/h ozone dose less ozone was consumed in order to remove 1 mg/L COD. In addition, it is known that optimum ozone dose for the color removal is 1320 mg/h for 60-minutes treatment time.

When we consider both color and COD removal, and consumed ozone for 1 mg/L COD removal, it can be concluded for indigo dyeing wastewater, optimum ozone dose is 1320 mg/h and optimum treatment time is 60 minutes.

The numeric values related to COD and color removal ratios in indigo dyeing wastewater with different ozone doses are given in Table 4.3.

Table 4. 3. % Color and COD removals from indigo dyeing wastewater at different ozone doses

Time (min)	**Ozone Dose (mg/h)**									
	960		**1320**		**2100**		**2580**		**3240**	
	Color	**COD**	**Color**	**COD**	**Color**	**COD**	**Color**	**COD**	**Color**	**COD**
10	5.56	10.36	14.62	18.72	31.36	18.74	62.55	37.07	63.05	42.28
20	30.59	16.50	46.19	32.85	61.07	29.79	85.75	49.83	85.39	53.99
30	53.74	22.63	74.79	38.48	84.34	39.86	93.92	63.41	93.86	65.25
40	68.16	33.87	84.41	47.51	90.34	48.53	95.91	68.43	95.81	74.35
50	80.52	37.96	91.72	53.80	93.85	56.50	96.37	71.85	96.01	75.13
60	87.89	47.88	94.66	60.93	95.37	61.47	97.26	75.82	97.26	77.81
70	91.57	50.51	95.96	66.69	96.05	67.27	97.66	79.23	97.46	78.01
80	94.08	55.47	97.11	69.57	96.75	69.51	97.88	81.60	97.79	82.20

The conductivity and pH values were also measured in the scope of the studies on indigo dyeing wastewater. Very little changes were observed in the conductivity of the wastewater. For example; conductivity values after 60-minute treatment time are 6.93, 7.01, 7.03, 7.05 and 6.93 in mS/cm for 960 mg/h, 1320 mg/h, 2100 mg/h, 2580 mg/h and 3240 mg/h ozone doses, respectively. When we consider initial conductivity values of the wastewater, which is between 6.91-7.02 mS/cm, ozonation did not make any changes on conductivity. This condition is compatible with the past studies in the literature (Ciardelli *et al*., 2001; Anouzla *et al.*, 2009)

There is a decreasing trend in pH values during the experiments; however, this decrease was too low. The pH values, which are between 9.06 and 9.28 at the beginning, dropped to the interval between 8.31 and 8.53.

Experimental results of indigo dyeing wastewater shows that high color removal ratios can be obtained by ozonation, whereas the same ratios cannot be obtained for COD removal.

Regarding to reuse of indigo dyeing wastewater in the process of the textile mill, it is obvious that only with ozonation it cannot be achieved. Because, the obtained water quality is not satisfactory according to the common standards stated by British Textile Technology Group especially in terms of conductivity and COD. These standarts indicates that conductivity value should be less than 1 ms/cm, COD value should be less than 80 mg/L, color value should be less than 20 Pt-Co and pH values should be between 6 and 8 for water reusing in the process (BTTG, 1999).

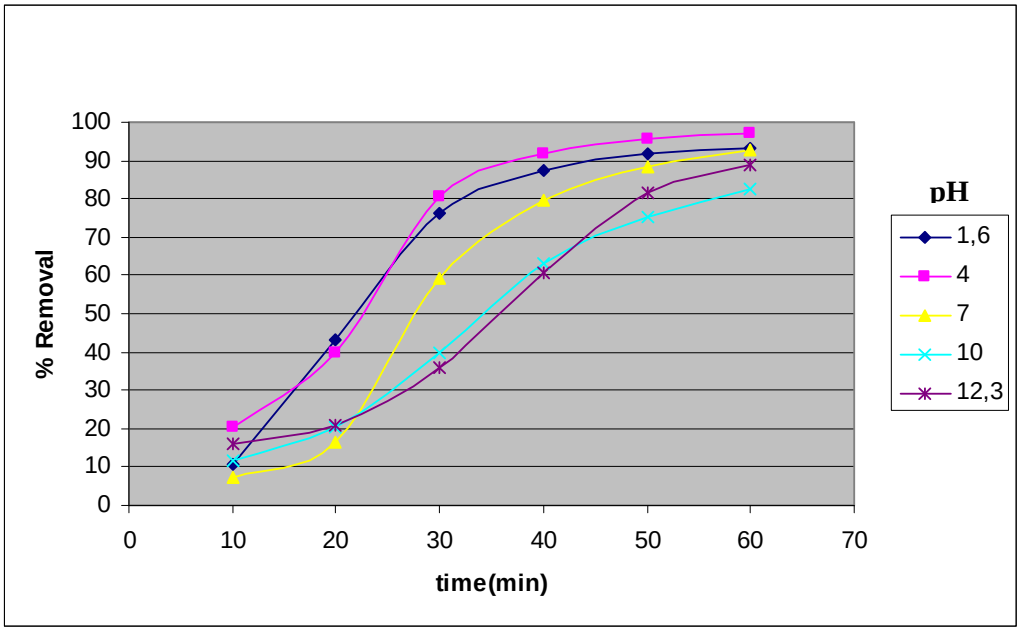
4.1.2 Effect of Initial pH on Ozonation Kinetics of Indigo Dyeing Wastewater

Wastewater pH is an important factor influencing treatment efficiency in ozonation studies. In this study, in order to investigate the effects of pH on ozonation of indigo dyeing wastewater, the experiments were conducted at five different pH values: 1.6, 4, 7, 10 and 12.3 and the kinetics of ozonation were followed. These experiments were conducted at 1320 mg/h ozone dose, and the color and COD parameters were followed during a 60 minutes of reaction time.

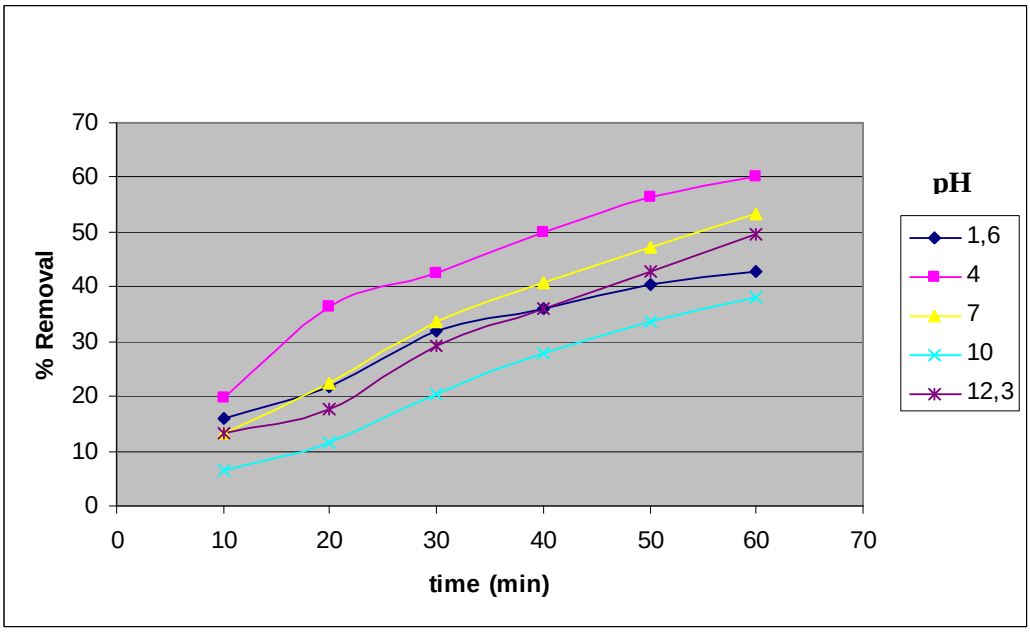
The obtained results related to color and COD removal ratios are demonstrated in Figure 4.3. As expected, wastewater pH influences both COD and color removals andthe highest color and COD removal ratios were observed when pH value was 4. On the other side, at basic pH values of 10 and 12.3, lower COD and color removal efficiencies were achieved. It could also be seen from Figure 4.3 that there is a difference between the rates of discolorization as the pH was increased, although there is no difference or negligible difference in the rate of COD removal. Initial discolorization rate, corresponding to first thirty minutes, was slightly faster at low

pHs. This may be an indicator for a predominant direct oxidation pathway over radical reactions during ozonation.

Like the discussion in Section 4.1.1, color removal mechanism with ozone may be considered in three different phase with different rates, such as rapid discolorization in the first phase, then slower discolorization in the second phase, and no significant color removal in the third phase.



(a)



(b)

Figure 4. 3. (a) Color and (b) COD removal curves at different pH values (at 1320 mg/h ozone dose)

As can be seen from Table 4.4, discolorization is very rapid at the acidic pH values 1.6 and 4 and approximately 80 % color removal appears after 30 min of ozonation when pH value is 4. The reason for this case is most probably as a result of the dominancy of direct oxidation with molecular ozone. Arslan Alaton et al. (2002) and Pirgalioğlu and Özbelge (2009) also documented higher removal rates at low pH values in their studies realized with different dyestuffs.

Table 4. 4. Color removals at different pH values

Time (min)	**pH**				
	1.6	**4**	**7**	**10**	**12.3**
10	10.89	20.54	7.23	11.44	16.23
20	43.14	39.89	16.67	20.26	21.05
30	76.25	80.40	59.40	39.87	35.96
40	87.47	91.86	79.82	63.15	60.64
50	91.72	95.51	88.21	75.33	81.69
60	93.36	97.03	92.56	82.60	88.71

If we compare the experimental results obtained by making pH adjustment to those obtained when no pH modifications were made (Section 4.1.1), we can say that highest discolorization and COD removal was obtained at pH = 4. For other pH values, there is a decrease in removal efficiencies. At unconditioned pH of indigo dyeing wastewater, color and COD removal efficiencies are 94.66 % and 60.93 %, respectively (Table 4.3). These ratios are 97.03 % for color and 60.21 % for COD when pH value is 4 (Table 4.4).

No positive changes were noted also in the conductivity values. On the contrary, in acidic and basic pH values high conductivity was measured due to acid and base addition. Conductivity values were 15.78 when pH = 1.6; 10.55 when pH = 4; 9.61 when pH = 7; 8.47 when pH = 10 and 13.51 when pH = 12.3.

4.2 Ozonation Experiments on the Wastewater before Measures

4.2.1 Color and COD Removal on the Wastewater before Measures

As mentioned at the beginning of this chapter, there are some measures that are to be taken in the textile mill, which were also described in Section 3.1 , mainly in order to reuse of indigo dyeing wastewater by filtration and recovery of caustic during finishing processes. The wastewater before measures represents the wastewater when no measures are taken in the mill.

The ozonation experiments were conducted both before and after measures are taken so as to observe the changes in the treatment of the overall plant wastewater, in terms of color and COD removal ratio, increasing of biodegradability etc.

The characteristic of the wastewater before measures are given in Table 4.5. This table indicates that it contains high amounts of COD and conductivity, and its biodegradability is low.

Table 4. 5. Characteristic of the wastewater before measures

Parameter	Value
Color, Pt-Co	3920-4200
COD, mg/L	2680-2840
Conductivity, mS/cm	19.75-19.85
pH	12.4-12.6
BOD_5/COD	0.23

Ozonation process on this wastewater was considered as a pre-treatment technique, because only with ozonation to decrease high COD levels to desired levels (400 mg/L according to Water Pollution Control Directive) does not seem possible. With ozonation, decreasing the toxicity of the wastewater and increasing the biodegradability of it is aimed. For this reason, BOD_5/COD ratio was also taken into

consideration during the experiments, in addition to COD, color, pH and conductivity.

In the experiments with indigo dyeing wastewater, there were no obvious changes in color and COD removal ratios after 60th minutes. In the wastewater before measures are taken, COD and color removal ratio's curves have become fixed after 70th minute of the treatment. In other words, after 70-minute treatment time, major percentage of the applied ozone dose to the reactor exits from the system without being used by the system, and this causes the decreasing of the ozone utilization ratio. Thus, ozonation experiments were conducted to the wastewater before measures during seventy minutes.

Three different ozone doses were applied in the scope of the experiments, which are 2340 mg/h, 3240 mg/h and 3960 mg/h. The graph demonstrating color removal ratios from the wastewater before measures at different ozone doses applied is given in Figure 4.4.

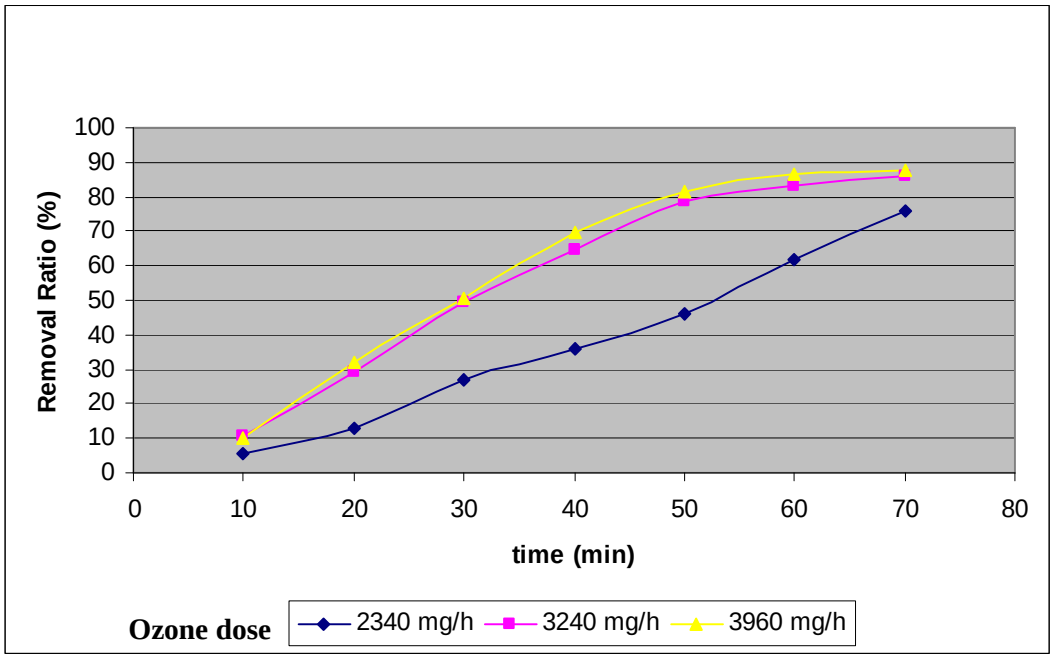


Figure 4. 4. Color removal ratios in the wastewater before measures

It can be observed from Figure 4.4 that the lowest ozone dose tested, i.e. 2340 mg/h, is not sufficient for the wastewater, because after treatment with this dose, the effluent still contains noticeable amounts of color which may not be treated biologically. An effluent whose color is approximately 1000 Pt-Co appears with 2340 mg/h ozone dose after the experiments. Moreover, Wu and Wang (2001) reported that subsequent biological treatment has almost no effect on the color of textile effluents. At this ozone dose, color removal achieved is about 75 % after 70 min of ozone application.

Although the other two doses give almost same and more satisfactory results than 2340 mg/h ozone dose in color removal, we should check their efficiency in COD removal and increasing in biodegradability.

Figure 4.5 shows COD removal ratios in the wastewater before measures with three different ozone doses.

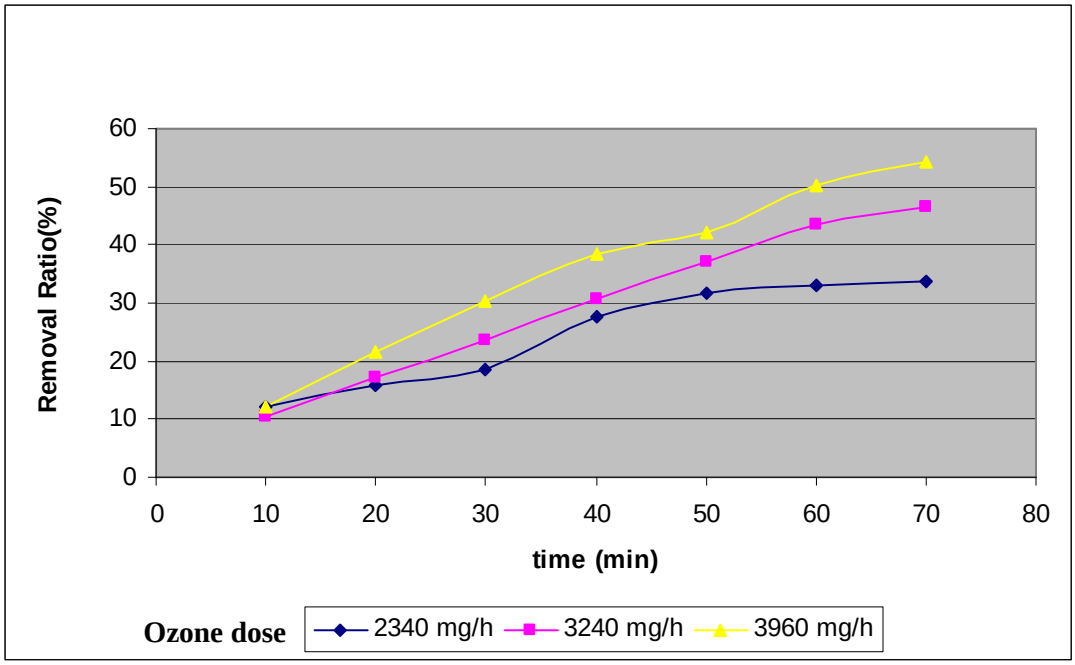


Figure 4. 5. COD removal from the wastewater before measures at different ozone doses

Like the case in color removal, the COD removal efficiency is also too low when 2340 mg/H ozone doses are applied. 3960 mg/h ozone doses give the best result with respect to COD removal among other doses. In Table 4.6, numeric values regarding to removal ratios are given.

Table 4. 6. COD and Color removals from the wastewater before measures

Ozone Dose (mg/h)	Color Removal (%)	COD Removal (%)
2340	75.64	33.66
3240	85.94	46.43
3960	87.40	54.19

At higher ozone doses, higher COD and color removal was obtained, as it was expected. However, cost of ozone, accordingly consumed ozone amount, should be taken into consideration before determination of the optimum dose. In Figure 4.6, consumed ozone amounts for each ozone doses are given. Although high COD removal ratios are obtained at the highest ozone dose, applied and consumed ozone is the highest at that dose, which is a drawback when consider cost effectiveness of the system.

Consumed ozone per removed COD ratios for the doses studied in the wastewater before measures are 2.75 mg ozone/ mg COD for 2340 mg/h ozone dose; 2.31 mg ozone/ mg COD for 3240 mg/h ozone dose and 2.26 mg ozone/ mg COD for 3960 mg/h ozone dose, respectively.

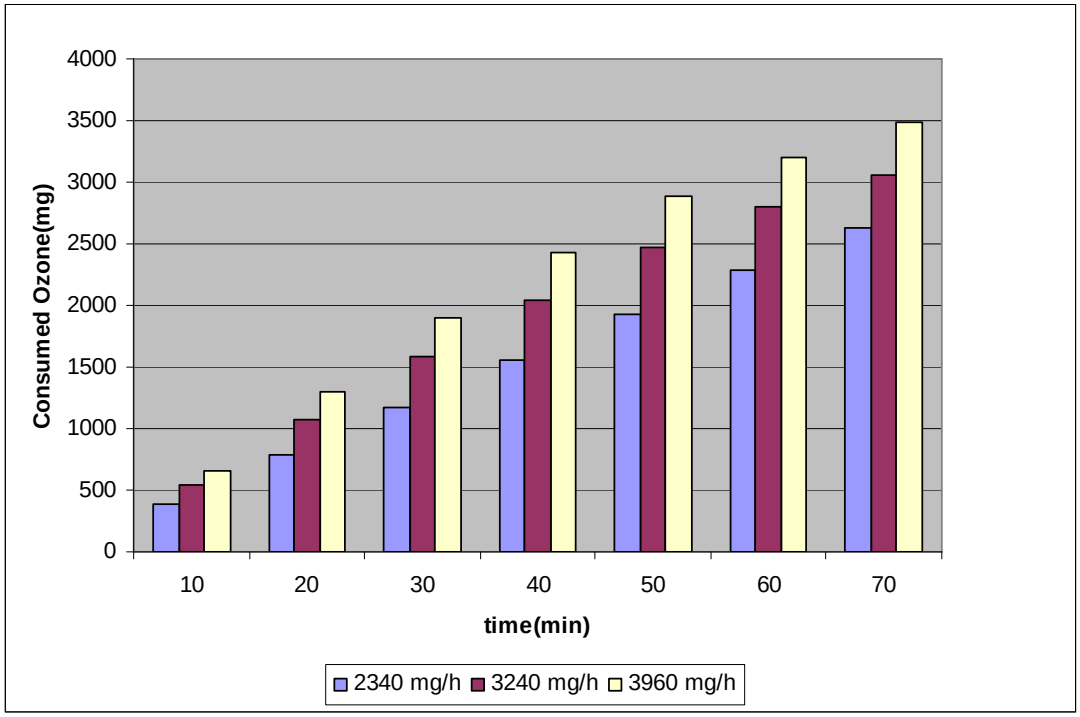


Figure 4. 6. Consumed ozone amounts in the wastewater before measures

4.2.2 Change in Biodegradability in the Wastewater before Measures

While we consider ozonation as pre-treatment in this wastewater, we should check whether ozonation ensure sufficient chemical changes of biorefractory compounds to enhance the wastewater biodegradability or not. Ozone treatments may cause high costs when performed to achieve important oxidation yields of organic pollutants. To provide considerable cost advantage, ozonation can then be applied prior to a possible biological treatment (Baig and Liechti, 2001). From the point of view of wastewater treatment, it is very important that ozone can increase the *biodegradability of* wastewater, i.e. increase the ratio BOD_5/COD before the activated sludge process (Munter, 1999).

The changes in the biodegradability with respect to different ozone doses are given in Figure 4.7. As it can be seen from this figure, with ozonation noticeable

improvements are obtained at higher ozone doses. Therefore, usage of ozonation as pre-treatment technique in the wastewater before measures are taken is favorable at 3960 mg/h ozone dose.

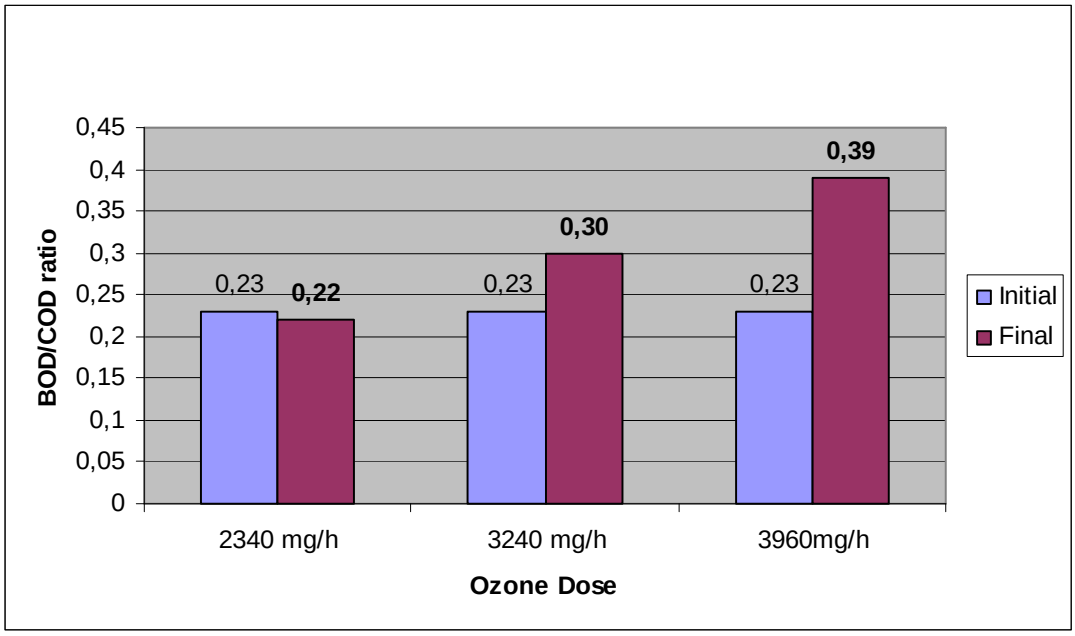


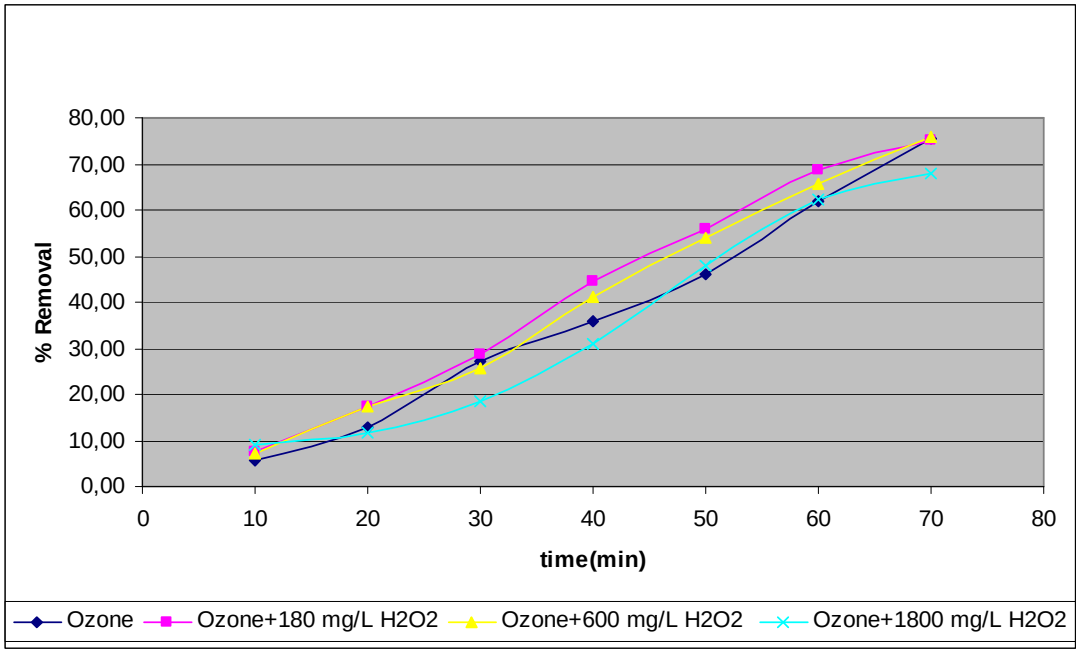
Figure 4. 7. Change in the BOD_5/COD ratio of the wastewater before measures at various ozone doses

By considering color removal ratios, COD removal ratios and improvement in biodegradability, it can be concluded that if our primary objective were only color removal, 3240 mg/h would be preferable; however, our objective is not only removing of color, but also increasing the biodegradability of the wastewater. Therefore, 3960 mg/h ozone dose seems optimum dose for the wastewater before measures.

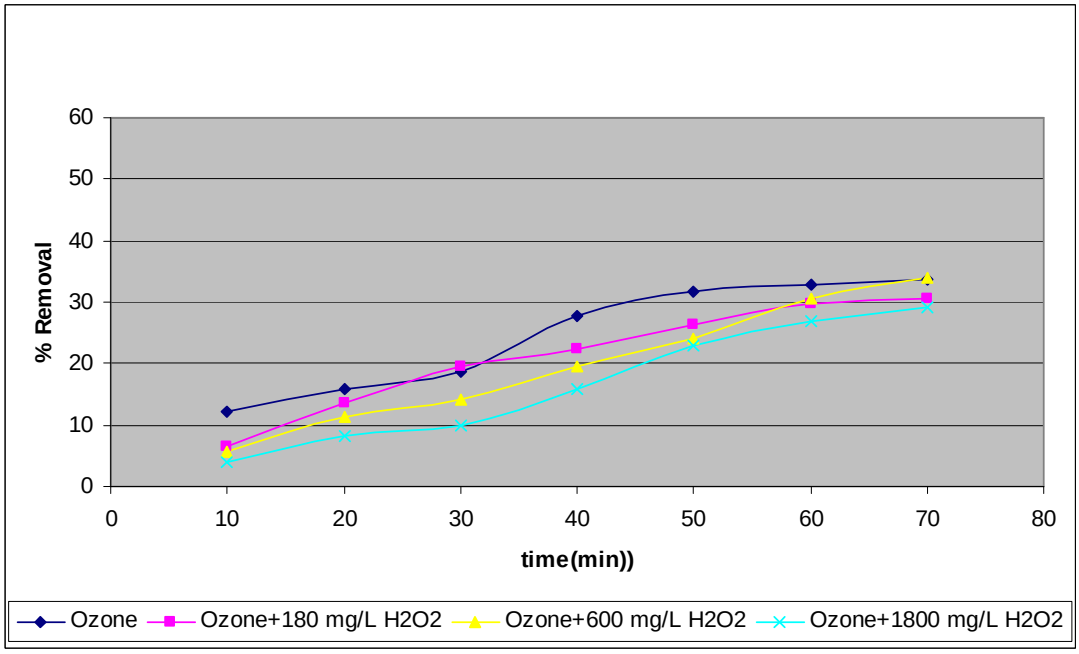
Conductivity values during the ozonation experiments have dropped a little as expected. After 70 minutes, conductivity is 14.97 for 2340 mg/h ozone dose; 13.59 for 3240 mg/h ozone dose and 12.92 for 3960 mg/h ozone dose.

4.2.3 Addition of Hydrogen Peroxide

Although operation of ozonation process is easy, its operation cost is very expensive (Doğruel *et al.*,2002, Torregrasa *et al.,* 2009). For this reason, by using hydrogen peroxide, consumption of less ozone was aimed in the scope of the study. Therefore, with three different hydrogen peroxide doses, 180 mg/L, 600 mg/L and 1800 mg/L, ozonation experiments were done at 2340 mg/h ozone dose. The main purpose was to obtain same treatment efficiency at lower ozone doses by the addition of hydrogen peroxide. The curves related to color and COD removal are given in Figure 4.8.



(a)



(b)

Figure 4. 8. (a) **%** Color and (b) COD removal when H_2O_2 added at various doses at the 2340 mg/h ozone dose

The removal curves show us addition of hydrogen peroxide did not make positive effect on treatment efficiency, on the contrary, addition of more hydrogen peroxide affected color and COD removals in a negative manner. This result is consistent with the studies of Khadhraoui *et al.* (2009), Oğuz and Keskinler (2007) and Lopez *et al.* (2004). Oğuz and Keskinler (2007) stated that H_2O_2 used in the O_3/H_2O_2 process negatively affected the removal of COD from the wastewater. Khadhraoui et al. (2009) strengthened this idea by indicating that color removal efficiency was lower in case of H_2O_2 and O_3 combination as compared to ozone alone and this lower performance was due to the scavenging effect of high H_2O_2 dose applied. In addition to these studies, in the past Lopez et al. (2004) observed that the discolorization is inhibited by high hydrogen peroxide concentrations in their studies.

As the main objective is to use ozonation as a pre-treatment technique, improvement in BOD_5/COD ratios was also evaluated in the experiments with the addition of hydrogen peroxide. The calculated BOD_5/COD ratios for the H_2O_2 concentrations tested are given in Table 4.7.

Table 4. 7. Changes in BOD_5/COD ratio in the wastewater before measures(O_3+H_2O_2)

H_2O_2 Concentration, mg/L	**BOD_5/COD Ratio**
0	0.23
180	0.25
600	0.27
1800	0.27

As it can be seen from Table 4.7, addition of hydrogen peroxide does not also give satisfactory result in the improvement of biodegradability. The BOD_5/COD ratio has increased from its earlier value of 0.23 in the experiments without using hydrogen peroxide, to 0.25-0.27 when H_2O_2 is used with 2340 mg/h ozone dose.

In addition to biodegradability, by the addition of hydrogen peroxide no improvement was observed in conductivity values of the wastewater before measures with respect to the case in which hydrogen peroxide was not used. Conductivity value was 14.97 in the effluent wastewater when only ozonation was applied at 2340 mg/h ozone dose. With the use of hydrogen peroxide the conductivity values were measured as 14.51, 14.02 and 14.69 at 180 mg/L, 600 mg/L and 1800 mg/L concentrations, respectively.

4.3 Ozonation Experiments on the Wastewater after Measures

In the textile mill, as stated in Section 3.1, some measures are planned to be taken in order to reuse of indigo dyeing wastewater and caustic recovery from finishing process. After these measures are taken, flow rate distribution from each process in the textile mill would become different; therefore, characteristic of the wastewater will change. Within the scope of this study, the question of how ozonation treatment would be affected when measures are taken in the plant was also answered by running ozonation experiment with the simulated wastewater, so called "wastewater after measures". The characteristic of the wastewater used in this set of experiments were measured in the scope of the study and are given in Table 4.8.

Table 4. 8. Characteristic of the wastewater after measures

Parameter	Value
Color, Pt-Co	4230 - 4820
COD, mg/L	3057-3162
Conductivity, mS/cm	13.54-14.01
pH	12.09-12.24
BOD_5/COD	0.40

When compared to the wastewater before measures were taken, this wastewater is stronger with respect to color and COD parameters. This situation arises due to producing of more intense wastewater after measures are taken in the plant.

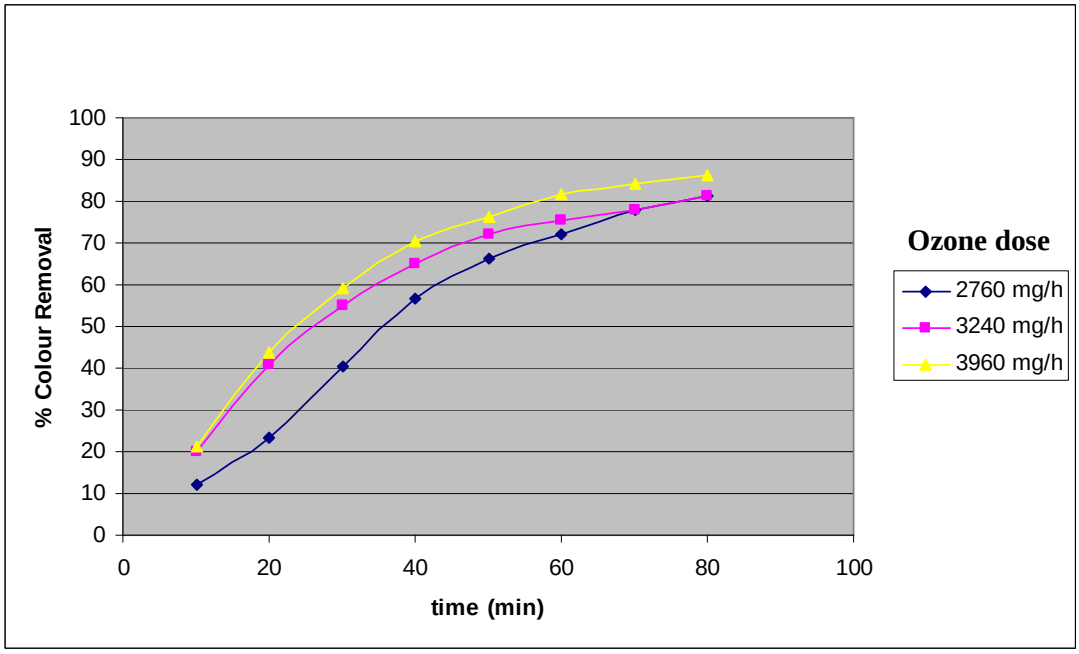
Membrane filtration to be applied to indigo dyeing wastewaters provides water reuse but also it results in a reject or concentrate stream. On the other hand, calculated BOD_5/COD value increases when measures are taken in the plant, this condition may be explained with non-existence of caustic in this wastewater, in other words, there is no toxic effects of caustic soda in this wastewater.

Ozonation in this wastewater is considered as a pre-treatment technique like the case in the wastewater before measures. Therefore, changes in BOD_5/COD ratio were followed in the study, beside color and COD removal ratios, conductivity and pH.

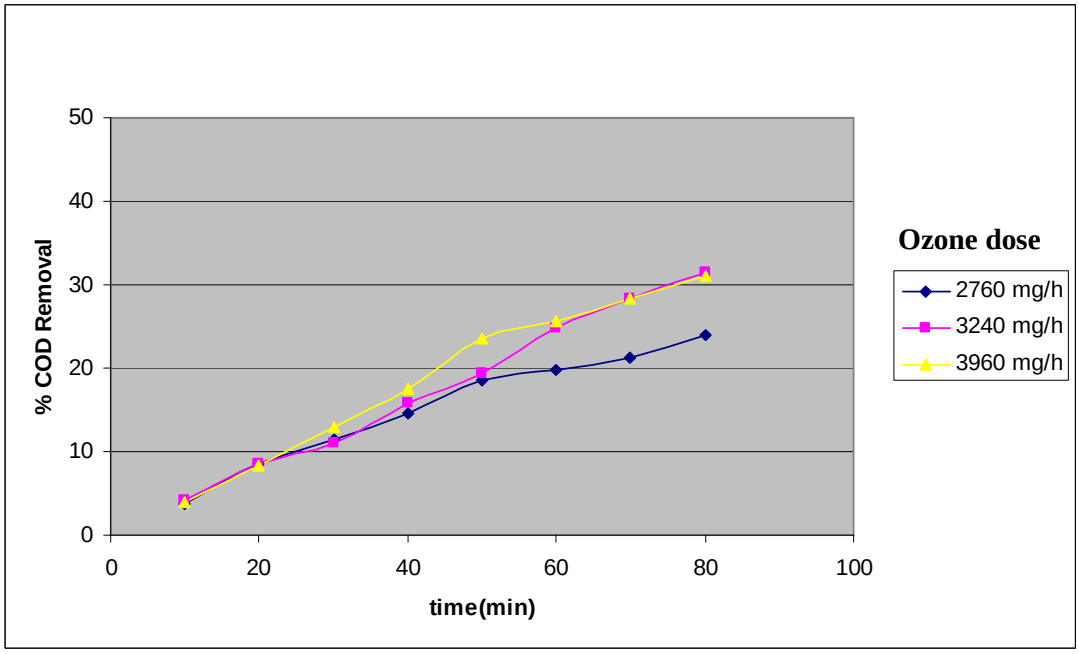
4.3.1 Color and COD Removal on the Wastewater after Measures

Three different ozone doses were applied to the wastewater after measures: 2760 mg/h, 3240 mg/h and 3960 mg/h. After 80th minutes, no improvement was observed in color removal and COD removal ratios. This means applying of more ozone to the system does not affect the effluent wastewater quality, in other words, dye molecules in the wastewater are only oxidized to their derivatives and after that point ozone treatment does not give satisfactory results.

The curves demonstrating the color and COD removal ratios are given in Figure 4.9. The figure shows that the removal ratios are not as high as those obtained in the wastewater before measures. This condition strength the idea that after measures are taken in the plant, more strength wastewater will be produced and its treatment with ozone will be difficult and not be efficient.



(a)



(b)

Figure 4. 9. (a) Color and (b) COD removal ratios in the wastewater after measures

Figure 4.9 also shows that almost same removal efficiencies were observed at ozone doses 3240 mg/h and 3960 mg/h. 2760 mg/h ozone dose did not give satisfactory results especially in COD removal. Color removal ratios change between 85-88 % and COD removal ratios are around 31-32 % in the ozonation experiments with the wastewater after measures.

Consumed ozone per removed COD ratios for the doses studied in the wastewater after measures are 4.46 mg ozone/ mg COD for 2760 mg/h ozone dose; 4.00 mg ozone/ mg COD for 3240 mg/h ozone dose and 4.75 mg ozone/ mg COD for 3960 mg/h ozone dose, respectively.

Lower removal ratios in this wastewater may create a discussion about ozonation. When both color and COD values are high in a wastewater stream, its treatability with ozone does not seem effective due to high consumption of ozone and long treatment durations. These two increases the cost of operation in ozonation.

4.3.2 Change in Biodegradability in the Wastewater after Measures

As is known, ozonation is a common treatment technology for color containing wastewater to decrease color and COD, and increase the biodegradability (BOD_5/COD) (Lackey *et al.*, 2006). In the wastewater after measures, biodegradability is 0.4 and is not as low as that in the wastewater before measures. Decreasing of the toxic effect of the plant wastewater after cleaner production measures, reusing of indigo dyeing wastewater and recovery of caustic from finishing process, may be the reason for an increase in BOD_5/COD ratio. This ratio has been counted as a threshold value for biodegradability in some studies and values less than 0.4 suggest that the wastewater is difficult for biodegradation (Gilbert, 1988; Kuo, 1999; Mehrvar et al., 2005; de Morais and Zamora, 2005).

Obtained results in biodegradability after application of three different ozone doses to the wastewater after measures are given in the Table 4.9.

Table 4. 9. BOD_5/COD ratio in the wastewater after measures

Dose, mg/h	BOD_5/COD Ratio
0	0.40
2760	0.43
3240	0.42
3960	0.47

The table depicts us that ozonation in the wastewater after measures do not give further improvement in biodegradability except for higher doses when compared to the wastewater before measures. This result is acceptable by considering the initial BOD_5/COD ratio of the wastewater, which is 0.4 and stays in a biodegradable range.

Therefore, by considering small COD removal ratios and little increase in biodegradability, we may state that ozonation in the wastewater after measures can be used for color removal purposes in spite of its initial objective that is pre-treatment.

4.3.3 Addition of Hydrogen Peroxide

Like the case in the wastewater before measures, by using hydrogen peroxide, consumption of less ozone was aimed in the scope of the study. Addition of hydrogen peroxide did not give satisfactory results in the wastewater before measures, therefore, in the experiments with wastewater after measures, hydrogen peroxide with high concentration was added and its efficacy was observed in the study.

Ozonation experiments after addition of 1500 mg/L hydrogen peroxide were conducted at 2760 mg/h during 80 minutes. Figure 4.10 demonstrates the changes regarding the color removal ratios when hydrogen peroxide is added to the wastewater.

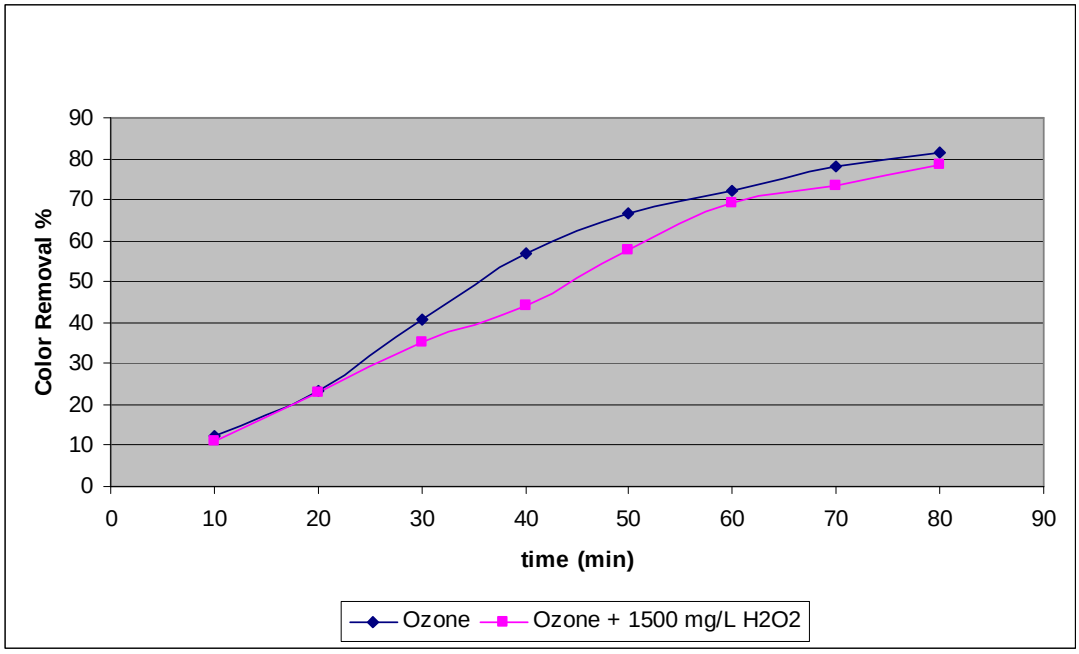


Figure 4. 10. Color removal after addition of H_2O_2 (at 2760 mg/h ozone dose)

Figure 4.10 depicts inefficiency of the addition of hydrogen peroxide to the wastewater after measures. Moreover, we can say that with respect to color removal the ozonation process is a little frustrated by the hydrogen peroxide.

The COD removal ratios when hydrogen peroxide is used are depicted in the Figure 4.11, below. With respect to color removal, there is a very minor increase in COD removal ratios by the addition of hydrogen peroxide.

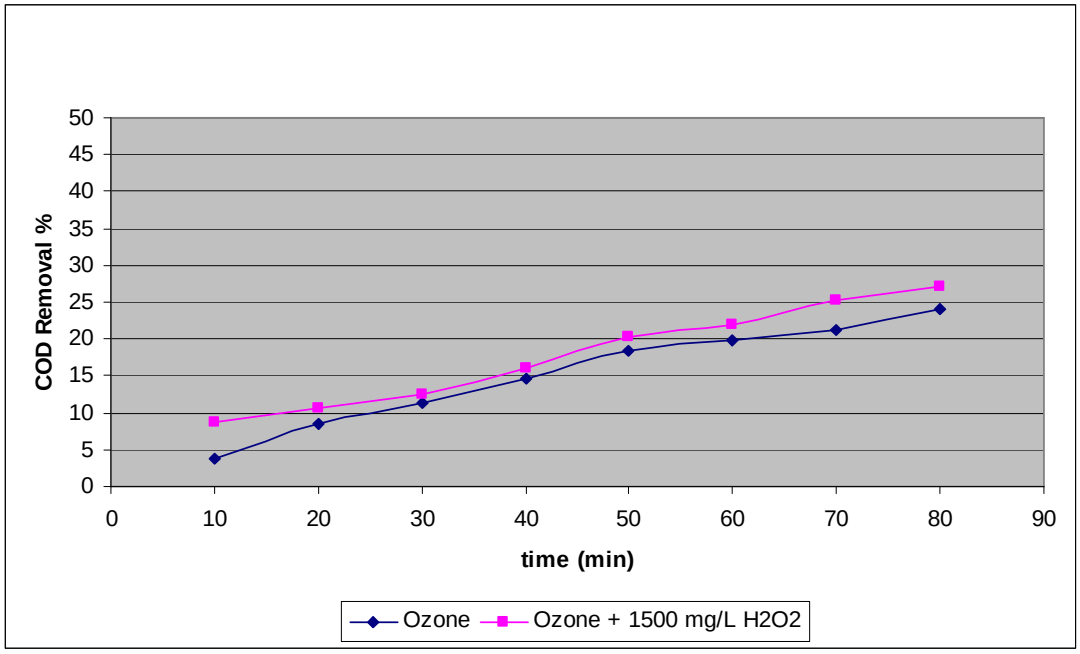


Figure 4. 11. COD removal after addition of H_2O_2 (at 2760 mg/h ozone dose)

If we consider biodegradability of the wastewater, the BOD_5/COD ratio has not increased. Only with ozone the ratio was 0.43, and with ozone plus H_2O_2 the ratio was 0.42.

The cases regarding to conductivity and pH is not different from the case in biodegradability. Addition of hydrogen peroxide did not give further improvements especially in conductivity amounts.

4.4 Ozonation Experiments on Biologically Treated Wastewater

In this part of the study ozonation process is considered as a post-treatment technique, and ozone was applied to the biologically treated wastewater in different doses. With ozonation removal of color and COD, which was reduced a certain value in biological treatment, in high efficiency was the main objective of the studies. Post-treatment with ozonation may have a polishing effect on effluent quality; therefore, it

is important to set the basis for the selection of the appropriate location for ozone application (Yasar *et al.*, 2007).

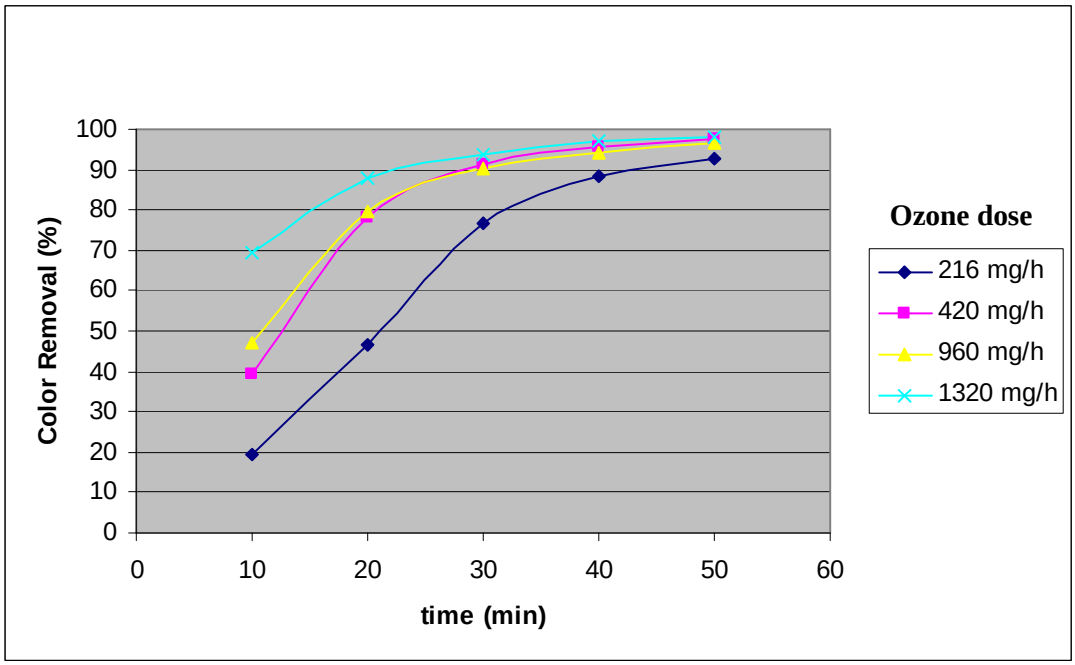
The characteristics of the wastewater used in these experiments are given in Table 4.10.

Table 4. 10. Characteristics of biologically treated wastewater

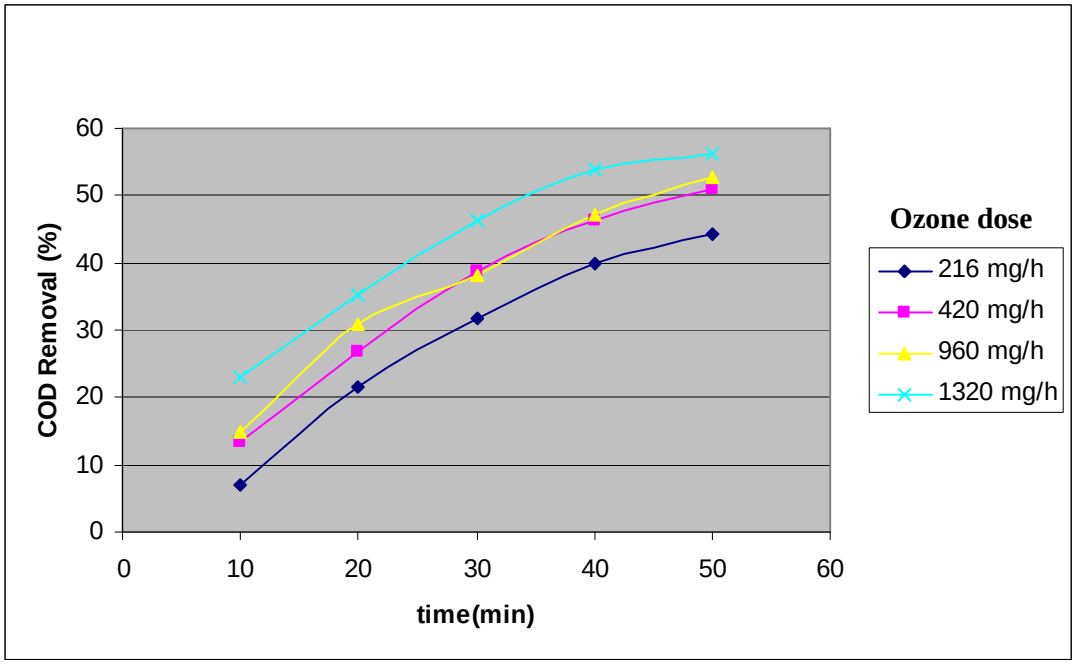
Parameter	Value
Color, Pt-Co	3300-4100
COD, mg/L	743-865
Conductivity, mS/cm	14.26-14.6
pH	7.08-7.15

Table 4.10 depicts that the COD values of the textile mill has been dropped up to 743 mg/L levels by biological treatment. However, the color values did not differ too much, this may be due to the nature of color causing compounds which are totally dissolved and resistant to biodegradation (Koyunlu *et al.*, 2001).

In the scope of the study, four different ozone doses were applied to the biologically treated wastewater and observed results regarding to color and COD removal is given in Figure 4.12.



(a)



(b)

Figure 4. 12. (a) Color and (b) COD removal in the biologically treated wastewater

Curves demonstrated in Fig 4.12 reflecting color removal ratios in color and COD reveal that ozonation gives satisfactory result in the biologically treated wastewater. Regarding to COD treatment, the removal ratios between 44 -56 %; and regarding to color treatment, 93 -98 % removal ratios were obtained in the study.

With respect to other wastewaters studied in the scope of the thesis, in a very short time high color removal ratios were observed. The inexistence of high COD content and utilization of ozone molecules by the color causing substances mainly may be an explanation of this situation.

As it is understood from the Figure 4.12.(a), showing color removal ratios, on 20^{th} minutes nearly 90 % color removal was obtained at 1320 mg/h ozone dose. In the experiments with lower ozone doses, also such a condition prevails, but as not sharp as the case at 1320 mg/h. At 420 mg/h and 960 mg/h ozone doses almost same color removal ratios have been observed.

From the Figure 4.12 (b), it can be extracted that 216 mg/h ozone dose gives lowest removal ratios compared other ozone doses tried in the study. Like the case in color removal, 420 mg/h and 960 mg/h ozone doses yield almost same efficiencies in COD removal.

When we consider both COD and color removal ratios in the biologically treated wastewater, there is no substantial changes in the curves after 40 minutes. Additionally, the consumed ozone amounts were measured as 135 mg, 150 mg, 516 mg and 544 mg for the ozone doses 216 mg/h, 420 mg/h, 960 mg/h and 1320 mg/h, respectively.

Corresponding consumed ozone per removed COD ratios for the doses studied in the biologically treated wastewater are 0.41 mg ozone/ mg COD for 216 mg/h ozone dose; 0.36 mg ozone/ mg COD for 420 mg/h ozone dose; 1.46 mg ozone/ mg COD for 960 mg/h ozone dose and 1.13 mg ozone/ mg COD for 1320 mg/h ozone dose, respectively.

By considering above discussion, we can say that optimum ozone dose for the biologically treated wastewater is 420 mg/h and optimum treatment time is 40 minutes.

The conductivity and pH values of this wastewater did not differ too much like the case in other three wastewater types investigated in this study. pH value was between 7.08-7.15 at initial case, and between 6.78-6.96 after the experiments were made. Similarly, conductivity values were measured between 14.40-14.58, which were between 14.26-14.60 initially.

The overall results demonstrate that the usage of ozonation as a post-treatment procedure provides good results in a shorter treatment time and at lower ozone doses when compared to the results of the ozonation experiments conducted on the wastewater before and after measures as a pre-treatment procedure. In the literature, post-treatment with ozonation also has given better results in some studies (Assalin et al., 2009; Blonskaja and Zub, 2009; Aben and Kurnitski, 2006).

CHAPTER 5

CONCLUSIONS

The main objective of ozone treatment in textile sector is the removal of color almost completely and reducing the COD values to an acceptable level for further treatment steps or obeying the discharge limits determined by the related directives. In this study, four types of wastewater (indigo dyeing wastewater, wastewater before measures were taken, wastewater after measures were taken, biologically treated wastewater) from a denim producing textile mill were studied and removal efficiencies with respect to color and COD were investigated mainly. Optimum ozone dose and optimum ozonation time have also been determined for all types of wastewater. The study demonstrated that, in all cases, COD and color can be rapidly removed from indigo dyeing wastewater using ozonation and the removal efficiency and rate are not affected by the addition of H_2O_2. For all types of wastewaters, satisfactory color removal ratios have been obtained at around 86 % to 96 %. Whereas, COD removal ratios were not as high as color removal ratios and remain at around 31% to 62% when optimum cases are considered. Color removal ratio was the highest in the biologically treated wastewater and the least in the wastewater after measures were taken.

Regarding the COD removal, most satisfactory results were observed in indigo dyeing wastewater as 80%, approximately. Experiments with biologically treated wastewater also yielded respectable COD removal ratios. However, removal ratios in the wastewaters both before and after measures taken in the mill was not in desired level in COD removal ratios on the contrary to color removal ratios.

By considering only color and COD removals, it can be concluded that implementation of ozonation as post-treatment in biologically treatment wastewater seems the most effective method in the textile mill. When ozonation has been considered as pre-treatment, like the case in the wastewaters before and after measures taken, especially COD parameters obtained in the effluent was not low. Therefore, application of ozonation after biological treatment seems more effective in the wastewaters of the textile mill.

As explained in previous chapters, some measures were planned to be taken in the textile mill as caustic recovery in finishing process and water reuse after dyeing process in the mill. The characteristics of the wastewater of the textile mill after measures are taken had changed and a much stronger wastewater was obtained with respect to the wastewater when no measures exist in the mill. This condition effected the treatment of wastewater with ozonation and in the experiments with wastewater after measures the lowest removal ratios were obtained. From this point it can be concluded that ozonation is not an efficient method for wastewater after measures because of high ozone consumption and waiting longer times for achieving good color removal ratios.

BOD_5/COD ratio is an important indicator demonstrating the biodegradability of the wastewater. In this study, for the wastewaters whose treatment was considered as post-treatment, improvements in the BOD_5/COD ratio was also investigated and the question whether the ozonation would be effective for further biological treatment or not was answered. The results of the experiments showed that an increase in this ratio was obtained only in wastewater before measures. The initial BOD_5/COD ratio, which is 0.23, was increased up to 0.39 in the study. On the other hand, no considerable improvement was observed in the wastewater after measures. BOD_5/COD ratio was increased from 0.40 to 0.47 for the wastewater after cleaner production measures have been taken in the mill.

In this study, effects of hydrogen peroxide addition were investigated in the wastewaters before and after measures and no improvement was observed in both wastewaters. Moreover, at some doses of H_2O_2, lower removal ratios were seen with

respect to the treatment only with ozonation. Therefore, it is obvious that addition of H_2O_2 is not an effective method for the wastewaters of the textile mill.

For indigo dyeing wastewater, effects of pH on treatment efficiency were also investigated in the scope of this study. Optimum color removal and COD removal ratios were obtained when pH is 4, and lowest removal ratios were obtained when pH is 10. Therefore, it can be said that in acidic conditions treatment with ozonation gives better results in indigo dyeing wastewater.

Conductivity values were measured in the experiments with all types of wastewater and no drastic changes were observed. The conductivity value is important in indigo dyeing wastewater because it is one of the indicative parameter in the determination of reusing of wastewater in the process. The results show that reusing of indigo dyeing wastewater does not seem possible only with ozonation (BTTG, 1999).

Ozonation time and applied ozone dose are important operation parameters in ozone treatment. In this study, optimum treatment time was determined as 60 minutes for indigo dyeing wastewater; 40 minutes for biologically treated wastewater; 70 minutes for the wastewater before measures and 80 minutes for the wastewater after measures. This shows that when the strength of the wastewater increases treatment time also increases, like the case in ozone dose.

Optimum applied ozone doses were found as 1320 mg/h in the experiments with indigo dyeing wastewater during 60 minutes; 420 mg/h for biologically treated wastewater during 40 minutes; 3960 mg/h for the wastewaters before and after measures, during 70 minutes and 80 minutes, respectively. 3240 mg/h ozone dose may be chosen for the wastewater before measures whenever only color removal from the wastewater is the concern.

In conclusion, with the optimum ozone doses and optimum ozonation time for each wastewater, 95% color removal and 61% COD removal were obtained for indigo dyeing wastewater; 86% color removal and 46% COD removal were obtained for overall textile wastewater (before measures); 86% color removal and 31% COD

removal were obtained for indigo dyeing wastewater and 96% color removal and 47% COD removal were obtained for biologically treated wastewater.

CHAPTER 6

RECOMMENDATIONS

In this study, ozonation has been investigated for the effectiveness in COD and color removal, increase in biodegradability and result of the experiments has shown that except from biologically treated wastewater long ozonation times are required past in order to reach expected values in the wastewaters. Therefore, implementation of ozonation method as post-treatment after biological treatment should be favored in textile mills using indigo dyes.

Measures taken in the textile mill created a wastewater which can be treated more difficultly. Therefore, an analysis explaining whether taking of some measures is a logical decision or not should be done. This analysis should include cost effects of planned measures in the mill and treatment of wastewater after measures and comparison of these costs.

In the study, both optimum ozonation time and ozone dose have been determined at high levels for the wastewaters containing high COD and color content. Therefore, detailed cost estimation for the wastewaters studied in the thesis should be conducted in the future, and a comparison of this cost should be done with alternative technologies, such as coagulation, Fenton oxidation, membrane filtration etc., for the removal of color and COD.

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APPENDIX A

PERFORMANCE CURVE

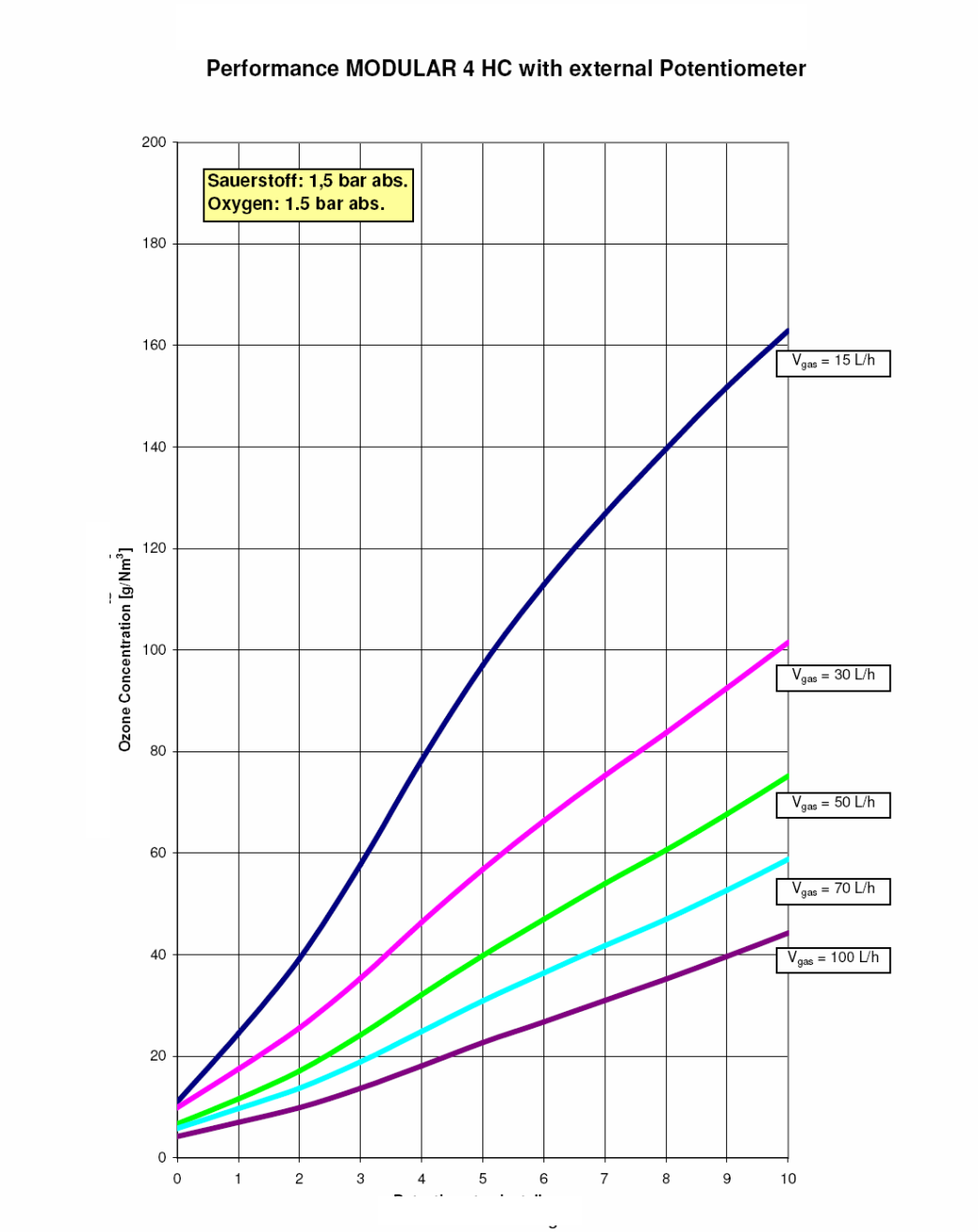

Figure A. 1. Performance curve