INTEGRATED OZONE AND BIOTREATMENT OF PULP MILL EFFLUENT

by

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ABSTRACT

In this study, the effluents from the biggest pulp and paper plant in Turkey that having a multistage chlorine bleaching process were treated by an integrated process consisted of ozonation and activated sludge processes to enhance the biodegradability and increase the quality of effluent.

In the first part of the study, ozonation process was applied to CEHDED and CEH stage bleaching effluents. The effects of fibre type, pH, H_2O_2, and ozone dose were investigated on treatment performance of ozonation process. Significant COD and color removals were achieved by increasing ozonation pH of combined bleaching effluents to a value of 12. The highest treatment efficiency was achieved by the O_3/H_2O_2/pH=7 process with 1632 mg/L ozone dose for CEHDED effluent. While 41 per cent COD removal was obtained by applying O_3/pH=7 process to CEHDED effluent, COD removal was increased to 57 per cent by the addition of 15 mM H_2O_2. Although ozonation of CEHDED effluent at pH=7 resulted in only a moderate alteration in BOD_5/COD ratio, O_3/H_2O_2 /pH=7 treatment increased the BOD_5/COD ratio from 0.2 to 0.4. Almost complete color removal was also achieved by O_3/H_2O_2 /pH=7 treatment.

In the second part of the study, activated sludge process was applied to pulp mill effluent. While for the raw effluent overall COD_s removal efficiency of biological process was 61 per cent, it was 77 per cent for the pulp mill effluent, which contained the pretreated (O_3/H_2O_2/pH=7) CEHDED effluent. Furthermore, AOX removal rate was increased from 39 to 70 per cent by the pretreatment of combined bleaching effluent.

ÖZET

Bu çalışmada, altı basamaklı klorla ağartmanın yapıldığı Türkiye'nin en büyük kağıt üretim tesisinin atıksuları biyolojik parçalanabilirliği arttırmak ve atıksuyun kalitesini yükseltmek amacıyla ozonlama ve biyolojik arıtmayı içeren bir entegre arıtma yöntemi ile arıtılmıştır.

Çalışmanın ilk kısmında, ozonlama prosesi CEHDED ve CEH ağartma atıksularına uygulanmıştır. Değişik ağaç türlerinin işlenmesinden kaynaklanan ağartma atıksularının arıtımında pH, H_2O_2, ve ozon dozunun etkileri incelenmiştir. CEHDED ağartma atıksuyunun ozon ile ön arıtımında KOİ ve renk giderimleri, pH'ın 12'ye yükseltilmesi ile arttırılmıştır. CEHDED atıksuyu için en yüksek arıtma verimi 1632 mg/L.h ozon dozunun kullanıldığı O_3/H_2O_2/pH=7 prosesi sağlanmıştır. CEHDED atıksuyunun pH=7'de bir saat ozonlanması sonucunda yüzde 41 olan KOİ giderimi, O_3/H_2O_2 15 mM/pH=7 prosesi ile yüzde 57'ye yükseltilmiştir. CEHDED atıksuyunun O_3/pH=7 prosesi ile arıtımı sonucunda $BOİ_5$/KOİ oranında küçük bir değişim elde edilirken, CEHDED atıksuyunun O_3/H_2O_2/pH=7 ön arıtımı ile $BOİ_5$/KOİ oranı 0.2'den 0.4'e arttırılmıştır. O_3/H_2O_2/pH=7 ön arıtımı ile aynı zamanda atıksuyun renginin neredeyse tamamının giderilmesini sağlamıştır.

Çalışmanın ikinci kısmında, kağıt fabrikası atıksularına biyolojik arıtma uygulanmıştır. Ön arıtım uygulanmamış kağıt atıksuyunun biyolojik arıtımı sonucunda yüzde 61 KOİ giderimi sağlanırken, O_3/H_2O_2/pH=7 ile ön arıtılmış CEHDED atıksuyunu içeren karışımının biyolojik arıtımı sonunda KOİ giderimi yüzde 77'ye yükseltilmiştir. Ayrıca AOX giderimi CEHDED atıksuyunun ön arıtımı ile yüzde 39'dan yüzde 70'e yükseltilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Depending upon the type of the pulping process, various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, and chlorinated resin acids are generated in the pulp and paper making process (Pokhrel and Viraraghavan, 2004) and reach into wastewater. However, the most serious pollution problems arise from the use of chlorine in bleaching of pulp. The spent liquors from the chlorine bleaching process contain a variety of chlorinated organic compounds, which are of high molecular weight, colored, non-biodegradable, and toxic.

The growing concerns about environment force the pulp industry to adopt cleaner production technologies and use of advanced waste treatment methods in developed countries. In Turkey however, AOX and color as important wastewater quality parameters are not part of the water pollution control regulations, so unidentified and untreated toxics spread out to the land, air and water environments. Therefore pollution limitations should be reconsidered in accordance with the European Union standards to eliminate specific pollutants from pulp mill, in Turkey.

Biological treatment processes including activated sludge and aerated lagoons are the conventional treatment processes for pulp mill effluents. Biologically treated pulp mill effluents are still far from attaining stringent limits. Advanced oxidation processes including ozone (Heinzle et al., 1992; Kallas and Munter, 1994; Oeller et al., 1997; Helble et al., 1999; Balcıoğlu et al., 2003), ozone/hydrogen peroxide (Gulyas et al., 1995), photocatalytic oxidation (Balcıoğlu and Arslan, 1998) have been proposed as post or pretreatment to reduce recalcitrant compounds and color in the effluent. Integration of advanced oxidation and biological treatment for pulp mill effluent was also investigated (Heinzle et al., 1992; Helble et al., 1999; Balcıoğlu and Çeçen, 1999). In these studies the interest was focused on the treatment of bleaching effluent however the effect of fibre types on effluent characteristic and stream segregation on ozonation process were not taken into consideration.

The aim of the present work is to treat pulp and paper industry wastewater more efficiently. The specific objectives of this investigation are to (1) characterize each effluent originated from different processes of pulp manufacturing, (2) study the effect of used fibre type on the effluent characteristics, (3) pretreat the segregated bleaching streams which are not amenable to biological treatment, (4) investigate the effect of pH on ozonation performance, (5) evaluate the effects of H_2O_2 addition to the ozonation process, and (6) evaluate the effects of pre-ozonation of bleaching effluents on the subsequent activated sludge process of pulp mill effluent, in order to evaluate the beneficial effects of integrated process. While ozonation performance was evaluated by COD, BOD, AOX, pH, UV_{254}, UV_{280}, and A_{436}, biological treatment performance was evaluated by COD_s, OUR, and AOX parameters.

2. THEORETICAL BACKGROUND

2.1. Pulp and Paper Industry

The pulp and paper industry converts fibrous raw materials into pulp, paper, and paperboard. The processes involved in papermaking include raw materials preparation, pulping (chemical, semichemical, and mechanical), bleaching, chemical recovery, pulp drying, and stock preparation.

2.1.1. Raw Materials for Pulp

Pulp and paper are manufactured from raw materials containing cellulose fibres. Although wood is the chief raw material of pulp and paper industry, non-wood raw materials such as bagasse, cereal straw, bamboo, reeds, grasses, jute, kenaf, flax, and sisal (Pokhrel and Viraraghavan, 2004) are used in pulp and paper industry.

Softwood and hardwood are used in pulp production as raw material. Softwood trees are conifers e.g., pine and spruce. Hardwood trees are birch, aspen, and red gum. Softwood fibres with their length and coarseness are generally used to provide strength to a sheet of paper. Hardwood fibres, being finer and more conformable, give a sheet of paper its smooth printing surface and opacity. Hardwood fibres have less lignin content and require less bleaching chemicals for high brightness.

Dry weight of wood consists of approximately 45 per cent cellulose, 25-30 per cent hemicellulose, and lignin that is present in the cell wall, conferring structural support, impermeability, resistance against microbial attack and oxidative stress (Perez et al., 2002). Lignin has a very complicated structure (Figure 2.1) and is responsible for the brown color of pulp effluent. Wood also includes fats, esters, terpenes, resin acids, phenolic materials, and tannins as extractives.

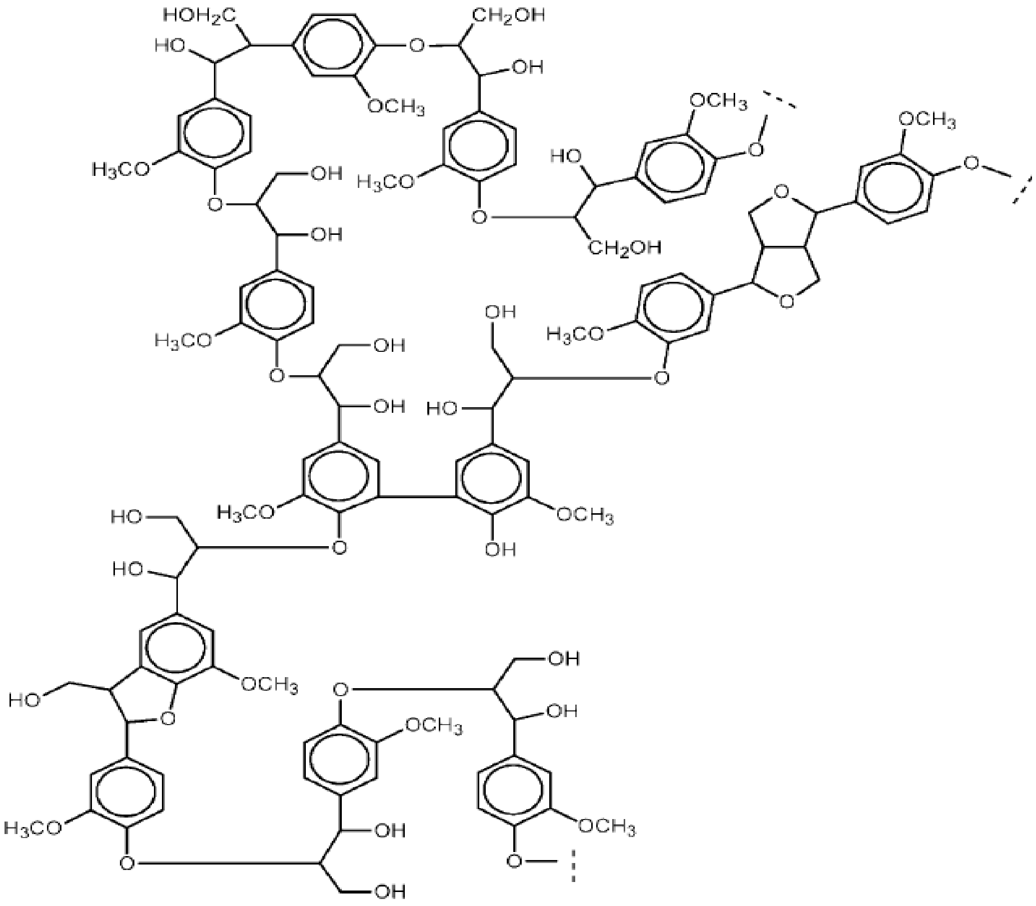

Figure 2.1. Structure of lignin (Perez et al., 2002).

2.1.2. Processing of Wood

The main raw material preparation operations typically include debarking, chipping, and conveying. Processing of wood begins by debarking in a debarking drum where the bark of wood is torn. Removed barks are used for fuel. Subsequently the debarked wood is cut into manageable sizes by chipping machines. The chips are then screened to remove too large or small chips. Large chips are sent to be recut, while the smaller chips are burned with bark.

2.1.3. Pulping Processes

In order to obtain cellulose in usable form for paper manufacture, the wood must be pulped to separate the fibres and remove impurities. Manufacturing methods for pulp are basically classified into the mechanical pulp manufacturing methods (stone groundwood, refiner mechanical, and thermomechanical pulping) in which physical force is applied to wood to mill it, the semichemical pulp manufacturing methods in which both physical force and chemical agents are employed, and the chemical pulp manufacturing methods (Kraft and sulfite pulping) in which extract fibres with chemical agents.

Stone groundwood pulp is produced by forcing logs against a grindstone by mechanical pressure. Nearly the entire log is converted into a low-grade pulp used primarily for newsprint. Groundwood pulp is usually not bleached; if it is bleached, it is not bleached to a high degree of brightness (EPA, 1997). The advantage of this method is its high yield.

In refiner mechanical pulping, wood chips are passed through double-disc steel refiners, where the fibres are mechanically separated. Refiner mechanical pulp is stronger than stone groundwood pulp and is more suitable for certain uses where strength is an important factor (EPA, 1997).

Thermomechanical pulp is produced by preheating wood chips with steam before refining. The heat acts to soften the lignin, which binds the wood fibres together, and promotes fibre separation. This process results in the highest grade of pulp from mechanical pulping (EPA, 1997).

In semichemical pulping process, primarily hardwood chips are chemically pretreated before they are mechanically pulped. The chemical solution most often consists of sodium sulfite/sodium carbonate liquor, which acts to soften the lignin and promote fibre separation (EPA, 1997). Other pulping liquors and chemical solutions may also be used to produce semichemical pulp. Most semichemical pulp is not bleached and is used for corrugated board, newsprint, and specialty boards. Bleached pulp can be used to manufacture writing and bond papers, offset papers, tissues, and towels.

The most widely used chemical pulping in paper making is the Kraft (sulfate) process (Figure 2.2). Kraft pulping is carried out in a digester by batch or continuous process. White liquor, which contains the mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), and woodchips are cooked at a high temperature and pressure (about 160°C and 10 atmospheric pressures). In the cooking process, lignin is removed from wood matrix and wood fibres are released. While some of the cellulose is hydrolyzed to methanol, acetone, and other volatile and water-soluble organics, the rest reacts with the sulfide ion to produce sulfonated organics such as methanethiol, which can cause odor problems. Cooked wood chips (brownstock) are discharged from the digester under pressure into a blow tank. The discharge from the blow tank consists of separated wood fibres and a solution, known as black liquor. Composition of black liquor depending upon the type of processed wood type is presented in Table 2.1.

Table 2.1. Composition of Kraft black liquor (Harms, 1998).

Components	Softwood (% of dry weight)	Hardwood (% of dry weight)
Kraft lignin	45	38
Hydroxycarboxylic acids	22	24
Acetic and formic acids	10	20
Resins and fatty acids	7	6
Turpentine	1	-
Others (including ashes)	15	12

Black liquor is a mixture of sodium hydroxide, sodium sulfide, sodium sulfate, sodium carbonate, lignin, resins, fatty acids, and turpentine (a mixture of branched aromatic hydrocarbons). After digestion, the black liquor is separated from the brownstock pulp usually by counter current drum washing. The black liquor upon dilution in the brownstock washing system is known as weak black liquor and is recycled within the process. The majority of the weak black liquor is sent to a chemical recovery section to recover the pulping chemicals, while the remaining small fraction is recycled to the digester directly (EPA, 1995). Kraft pulping is the dominant method of pulp production because this process produces the high strength, long fibre, and very low lignin content pulp. This high quality pulp is mainly used for higher quality paper production. One drawback of chemical pulping is high water consumption.

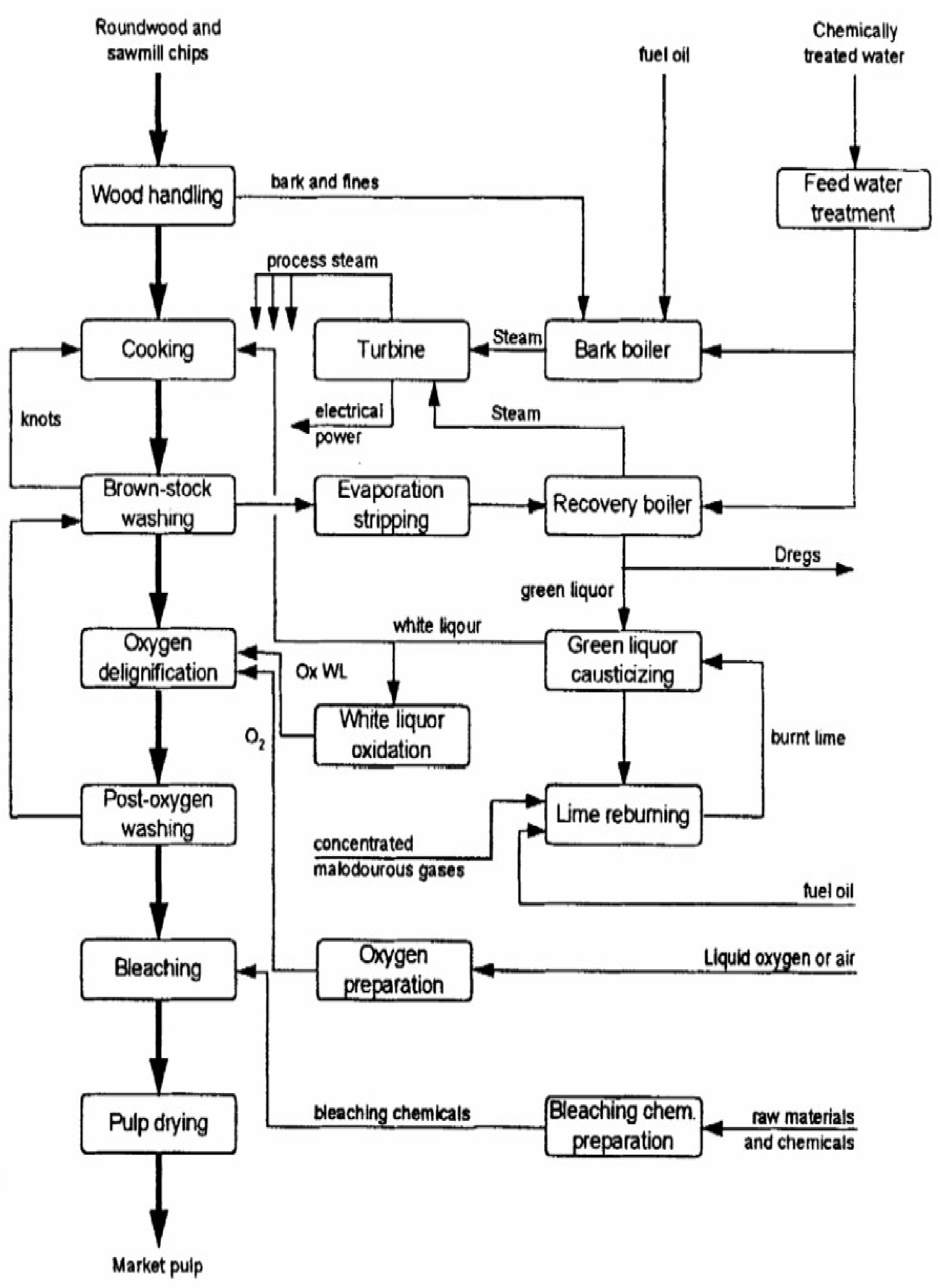

Figure 2.2. Kraft pulping and recovery process (EIPPCB, 2001).

The manufacture of sulphite chemical pulps includes the acidic sulphite process, bisulphite process, multistage sulphite process, neutral sulphite process, and alkaline sulphite process (Fengel and Wegener, 1989; Minor, 1982). All are described in terms of the composition of the cooking liquor which in turn defines the process pH and the choice of basic chemicals used. The gas sulphur dioxide is used to generate the sulphite chemicals in digestion process. Pulping conditions vary widely according to the mill furnish and the different processes produce pulps of differing chemical composition and papermaking application. Similar to the Kraft process, the sulfite process allows for burning of the used liquor, allowing the pulping chemicals to be reused in the majority of mills. Sulphite pulps are relatively small components of the pulps produced globally in relation to Kraft, semichemical, and mechanical pulps.

Organosolvent pulping has been receiving increased attention in recent years. Aqueous organic solvents such as methanol and ethanol are used for delignification to produce a pulp, which can be bleached with non-chlorine chemicals. Solvent pulping offers a number of potential advantages over conventional pulping techniques such as relatively low chemical and energy consumption coupled with low capital costs and low environmental impact.

2.1.4. Chemical Recovery

The chemical recovery process has important environmental and financial benefits for pulp and paper mills. Environmental benefits include the recycle of process chemicals and lack of resultant discharges to the environment. Regeneration rates of process chemicals, and energy generation from pulp residue burned in a recovery furnace provide economic benefits that include savings on chemical purchase costs (Smook, 1992).

The brownstock washing wastewater was recirculated to a recovery boiler where the pulping chemicals were recovered for reuse. In the recovery boiler, the used pulping chemicals are separated from the wood waste. The pulping chemicals form a smelt at the base of the recovery boiler; the wood waste is burned at the top of the recovery boiler. This heat is used to generate high pressure steam, which can be used to meet the mill's steam and electricity requirements. The smelt is poured into a large tank of water to form green liquor, a mixture of sodium sulfide and sodium carbonate. In the next step, lime is added to the green liquor to convert the sodium carbonate into sodium hydroxide, and thus remake the white liquor. The resulting calcium carbonate is converted back to lime in a lime kiln. Some other operations are frequently carried out in the chemical recovery section. These include soap skimming and tall oil recovery, black liquor oxidation, and waste gas incineration (Grace et al., 1989).

Chemical pulping recovery systems are also used in sulfite pulping. Heat and sulfur can be recovered from all liquors generated; however the base chemical can only be recovered from magnesium and sodium base processes.

2.1.5. Pulp Bleaching Methods

The amount of material (lignin and non-lignin compounds) remaining in pulp after cooking is measured as Kappa number. Pulps entering the bleached plant with low Kappa numbers require less bleaching chemicals. Kappa numbers of conventional cooking were 14-22 for hardwood, 30-35 for softwood. Kraft pulp is generally dark brown in color, while sulphite pulps are light yellow-brown after cooking process, as they still contain some amount of lignin.

Because of the different reaction mechanisms, different types of bleaching chemicals are employed in the bleaching process (Table 2.2).

Table 2.2. Bleaching chemicals.

Stage	**Chemicals Used**	**Symbol**
Chlorination	Cl_2	C
Alkaline extraction	NaOH	E
Hypochlorite	NaOCl	H
Chlorine dioxide	ClO_2	D
Peroxide	H_2O_2	P
Oxygen	O_2	O
Ozone	O_3	Z

In the oxygen delignification bleaching stage, the pulp is treated with oxygen in a pressurized vessel at elevated temperature in an alkaline environment to remove lignin and modify other coloring components. Ozone is an effective delignifying agent. It brightens the pulp as well. However, ozone attacks the cellulose fiber as well as the lignin. Hydrogen peroxide is used mainly to brighten pulps. Peroxide is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time and preferred for mechanical and recycled fiber. Elemental chlorine is also an effective delignifying agent. As it breaks lignin bonds, it adds chlorine atoms to the lignin degradation products, thus produces significant amounts of chlorinated organic material. Despite handling difficulties, chlorine dioxide is largely replacing elemental chlorine in the initial bleaching stages. Its perceived advantages are: higher pulp brightness, improved fibre strength properties, lower chemical consumption, and considerable reduction in the AOX of discharged effluents.

Various combinations of chemicals are employed in bleaching processes. Chemical reactions with lignin during the acid stage of the bleaching process increase the whiteness of the pulp. The alkaline extraction stages dissolve the lignin/acid reaction products. If the delignification process is going towards the end kappa number, the most detrimental bleaching chemicals (chlorine and hypochlorite) are used for bleaching. Typically, the pulp is treated with each bleaching chemical in a separate stage. Each stage includes a tower, where the bleaching occurs; a washer, which removes bleaching chemicals and dissolved lignin from the pulp prior to entering the next stage; and a seal tank, which collects the washer effluent to be used as wash water in other stages.

There is a considerable variation in bleaching processes. Different sequences are used to obtain the required quality of product (Table 2.3).

Table 2.3. Common industrial bleaching sequences (Fengel and Wegener, 1989).

Pulp Type	**Sequence**
Sulphite and Bisulphite Pulp	
3- Stage	C-E-H
4- Stage	C-E-H-H
	C-E-H-D
	C-E-D-H
	C-C-E-H
	C-H-E-H
	H-C-E-H
	C-E-D-D/H
	C+D-E-H-D
	E-C-H-D
5- Stage	C-E-H-D-H
	C-C-E-H-H
Kraft Pulp	
3- Stage semi-bleached	C-E-H
	D/C-O-D
4- Stage part semi-bleached	C-E-H-D
	C-E-H-P
	C-E-H-H
	C-H-E-H
	C-D-E-D
	O-C-E-H
	O-C-E-D
	O-D-E-D
	O-D-O-D
5- Stage	C-E-H-P-D
	C-E-H-D-P
	C-E-H-E-H
	C-E-D-E-D
	C-E-D-P-D
	C-E-H-E-D
	C-H-D-E-D
	D-E-D-E-D
	C-C/H-E-H-H
6- Stage	C-H-E-D-E-D
	C-E-H-D-E-D
	C-E-H-E-H-D
	C-E-H-D-P-D
	C-E-H-E-D-P
	C+D-E-H-D-E-D
	O-C-E-D-E-D
	O-C+D-E-D-E-D
	O-D-E-D-E-D
	O-C-D-E-H-D
7- Stage	C-H-H-D-D-D-P

The preferred sequence to produce high-brightness pulps was the application of chlorine gas (C stage) followed by aqueous caustic soda and/or sodium hypochlorite extraction (E) followed by aqueous chlorine dioxide application (D) followed by another E stage or another D stage. Primary function of C stage is to further delignify the pulp. Chlorine reacts with lignin to form compounds that are water soluble or soluble in an alkaline medium, which aids in delignifying the pulp before it proceeds to the next bleaching stage. The E stage and the remaining stages serve to bleach and whiten the delignified pulp. The extraction stage removes the chlorinated and oxidized lignin by solubilization in a caustic solution. H stage is the actual bleaching stage. Hypochlorite is a true bleaching agent that destroys certain chromophobic groups of lignin. It also attacks the pulp, resulting in high cellulose degradation in Kraft pulp. Application of hypochlorite to Kraft pulp is usually used only as an intermediate stage of the sequence or to produce semi-bleached pulps. Using more stages means more effective use of chemicals because there would be huge demand on bleaching chemicals in one stage bleaching to attain the desired properties.

Increasingly stringent effluent limitations have meant growing interest in Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) bleaching processes during the 1980s. The ECF method, which has neither chlorination nor hypochlorite processes that generate chloroform, can reduce the chloroform release to wastewater and air to almost negligible. After bleaching, pure chemical pulps must be briefly refined. ECF bleaching uses chlorine dioxide, alkali for the extraction of dissolved lignin, peroxide and oxygen for the reinforcement of the extraction stages. TCF bleaching uses oxygen, ozone, and peroxide with alkali for lignin extraction. TCF pulps tend to have lower Kappa and reduced strength properties compared with ECF pulps. TCF processes allow the bleaching effluents to be fed to the recovery boiler for steam generation; the steam is then used to generate electricity, thereby reducing the amount of pollutants discharged. Zero Discharge (ZD) process is the most reliable solution for pulp mill effluent which still includes high amount of organic material, chlorinated or not. In ZD process everything is recycled and no pollutants are being discharged into the environment. The use of ECF bleaching results in reduced levels of chlorinated pollutants in the wastewater stream. TCF bleaching almost eliminates chlorinated pollutants in the wastewater stream. The solution of the bleach plant problems has proven to be the most difficult without substitution of chlorine bleaching to elemental chlorine free, totally chlorine free or zero discharge process.

2.2. Environmental Problems Associated with Pulp and Paper Industry

2.2.1. Liquid Effluent Discharges

By 1988 average water usage had been reduced to 72 m^3 per air dried ton of pulp, whereas in 1959 around 240 m^3 of water were used in the production of one ton of air dried pulp (Greenpeace, 1996). Although water consumption was decreased in pulp and paper industry, still considerable amount of wastewater is still released to the environment. The pulp and paper industry is the sixth largest polluter (after oil, cement, leather, textile, and steel industries) discharging a variety of solid, liquid, and gaseous waste into the environment (Ali and Sreekrishnan, 2001).

Especially Kraft pulping and bleaching of pulp produces additional water discharge. The wastewater from pulping that result from washing process contains lignin as well as the chemicals used to separate the lignin from the cellulose. When chlorine enters the bleaching process it reacts mainly with lignin, its breakdown products, and other organic plant components. As a result numerous chlorinated organic contaminants such as dioxins, furans, chloroform, and chlorophenolics are formed (Peck and Daley, 1994). Among these pollutants dioxin and furan are classified as the ‘dirty dozen’ group of persistent organic pollutants. The bulk of the chlorinated organics (75-90 per cent) are high molecular weight compounds (> 1,000), which are difficult to characterize due to their large size and varying structures (Commoner et al., 1996). The remaining chlorinated organics can be classified as: relatively water soluble (~19 per cent); potentially bioaccumulative, relatively fat soluble (~0.09 per cent); and bioaccumulative, highly fat soluble (~0.1 per cent).

Chlorinated organic compounds, which include dioxin and furans, have the ability to induce genetic changes in exposed organisms (Nestmann, 1985). Since the pulp mill effluents mostly end up in the aqueous environment, the effect of the wastewater on fish species was investigated by many authors. Experiments have been demonstrated that when fishes were exposed to pulp and paper mill wastewater, respiratory stress, mixed function oxygenase activity, toxicity, mutagenecity, liver damage, genotoxic, and lethal effects were occurred (Owens et al., 1994; Vass et al., 1996; Lindstrom-Seppa et al., 1998; Johnsen et al., 1998; Leppanen and Oikari, 1999; Schnell et al., 2000).

Fatty acids, tannins, and resin acids, which are caused by processing of wood, are the other well known pollutants and sources of toxicity to fish, especially salmonoids (Leach and Thakore, 1973; Voss and Rapsomatiotis, 1985).

Natural resin acids, which occur in high concentrations in softwood pulp, are most concentrated in mechanical and chemotermomechanical pulp effluents. They can be chlorinated in bleached Kraft pulp effluent. Resin acids are the most toxic compounds of wood extractives to aquatic life (Walden and Howard, 1981) and they are toxic to fish at concentration of 200-800 µg/L in wood processing wastewater (McFarlane and Clark, 1988). The half life of the total resin acid concentration from sediment cores was estimated to be 30 years (Stuthridge and Tavendale, 1996). Physiological effects of resin acids have been found to include inhibition of a conjugation enzyme UDP-glucuronosyltransferanse (Tana, 1988), intestinal inhibition of bile uptake, perturbation of the potassium transport tested with isolated rainbow trout hepatocytes (Rabergh et al., 1992).

Color in pulp and paper mill effluents is largely due to lignin, lignin derivatives, and polymerized tannins (Goring, 1971; Sankaran and Vand Lundwig, 1971; Sundman et al., 1981; Reeve, 1991). Color in the pulp mill effluent reduces penetration of solar radiation in the receiving water and causes changes in the algal and aquatic plant productivity (Ali and Sreekrishnan, 2001).

2.2.2. Air Emissions

Pulp and paper mill power boilers and chip digesters are generic sources of air pollutants such as particulates and nitrogen oxides. Chip digesters and chemical recovery evaporators are the most concentrated sources of volatile organic compounds. The chemical recovery furnace is a source of fine particulate emissions and sulfur oxides. In the Kraft process, sulfur oxides are a minor issue in comparison to the odor problems created by four reduced sulfur gasses, called together total reduced sulfur (TRS): hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The TRS emissions are primarily released from wood chip digestion, black liquor evaporation, and chemical recovery boiler processes.

Liquid effluent discharges and the levels of emissions are highly dependent upon the type of process technology employed and individual mill practice. Another important factor is the fuel type and quality. Whilst older mills caused severe air pollution, mitigating technology now exists to eliminate most harmful gas and particulate emissions. Utilizing this technology depends on local factors such as legislation, company and mill policy and proximity to populated areas. The major gaseous pollutants and their effects are summarized in Table 2.4.

Table 2.4. Air emissions from the pulp and paper industry (Stanley, 1996).

Pollutant	**Effect**	**Source**
Carbon dioxide	greenhouse gas	fuel combustion
Hydrogen sulphide	rotten egg smell	Kraft process
Sulphur dioxide	acid rain	fuel combustion and pulping process
Volatile organics	some toxic effects and precursors to the formation of ozone	various
Chloroform	toxic, possible carcinogen	chlorine bleaching
Other organo-chlorines	some highly toxic	chlorine bleaching

The contribution of the paper industry to global warming has been an ongoing debate for several years, with some suggesting that the absorption of carbon dioxide by plantation forestry more than offsets the emissions of greenhouse gases caused during the production, transportation, and disposal of pulp and paper products.

2.2.3. Solid Waste

Solid waste is generated in various forms. They include inorganic sludge (dregs and lime mud) from the chemical recovery section, bark and wood residues and rejects (mainly sand) from the wood handling section, sludge from wastewater treatment, ashes from boilers and furnaces. Organic waste such as bark and wood residues can be burned for energy recovery.

Disposal is usually to landfill, although incineration is becoming increasingly widespread. However incineration is an unsatisfactory solution as burning sludge produces a relatively high proportion of ash and gaseous emissions. Other experimental disposal techniques include using the waste as a soil improver. However, as with all disposal options; there is some concern about possible dioxin and heavy metal contamination.

2.3. Conventional Treatment Methods for Pulp and Paper Industry Wastewater

Wastewater treatment systems are used to control the quality of wastewater discharged to receiving waters. Besides COD, BOD, SS, and toxicity, recently AOX and color have been used to evaluate the quality of pulp mill effluent in developed countries. However in Turkey wastewater of this industry is still evaluated with conventional parameters which are presented in Table 2.5.

Table 2.5. Pulp and paper industry discharge limits in receiving water for Turkey (http:// www.bcm.org.tr/pdf/su_kir_kont_yon.pdf).

Parameter		Composite sample
Flow rate	(m^3/t)	200
COD	(mg/L)	1000
SS	(mg/L)	50
Fish test	-	8

Typically, conventional effluent treatment processes of modern pulp and paper mill include aerobic (stabilization basins, aerated lagoons, and activated sludge processes) and anaerobic biological processes. These processes effectively remove oxygen consuming substances and suspended solids however pulp mill effluents contain high molecular weight chlorinated compounds, which are relatively resistant to biological treatment.

Aerobic systems were utilized for pulp and paper wastewater treatment. It was observed that low molecular weight AOX was effectively removed (43–63 per cent) as compared to high molecular weight AOX (4–31 per cent) in aerated stabilization basins (Bryant et al., 1992).

Aerated lagoon treatment system was utilized for treatment of a bleaching pulp and paper mill wastewater (Zender et al., 1994; Welander et al., 1997). 96 per cent influent resin acid removal was achieved by lagoon treatment system (Zender et al., 1994). On the other hand it was found that COD removal efficiency of full-scale lagoon (30-40 per cent) was less than that of the pilot-scale plant (60-70 per cent) (Welander et al., 1997).

Çeçen et al. (1992) and Altınbaş et al. (1999) studied the activated sludge treatment of chlorine bleaching and alkali extraction step of Kraft softwood effluent. The results of these studies indicated that high pollution load of wastewater could be reduced by activated sludge process. 17-50 per cent COD and 10-33 per cent AOX abatements were obtained by biological treatment (Çeçen et al., 1992).

In order to increase the efficiency of biological systems aerobic and anaerobic systems were sequentially applied to Kraft pulp effluent (Ferguson, 1994; Tezel et al., 2001). Biological AOX removal of Kraft pulp bleaching effluent was investigated, 30-35 per cent removal for aerobic, 40-45 per cent for anaerobic, and 50-55 per cent removal for anaerobic-aerobic sequential treatment was achieved by Ferguson (1994). Application of sequential biological systems to Kraft pulp mill effluent resulted in 91 per cent COD removal (Tezel et al., 2001). Significant color removal (90 per cent) was also achieved by anaerobic process. Similar to the findings in the study of Ferguson (1994), 58 per cent AOX removal was obtained.

2.4. Advanced Oxidation Methods for Pulp and Paper Industry Wastewater

High molecular weight chlorinated lignin derivatives of bleached Kraft mill effluent are resistant to microbial degradation. Although different biological treatment methods; such as activated sludge, lagoons or anaerobic processes are being used to reduce the organic content before wastewater is discharged into receiving water, the color from lignin derived products remains almost unaltered by the depurative process (Livernoche et al., 1983; Martin and Manzanares, 1994). Moreover recalcitrant compounds remain in the treated effluent. Consequently, advanced oxidation systems are getting widespread attention for the treatment of effluents containing high amount of non-biodegradable compounds. During the last decade, advanced oxidation processes have been performed in treatment of pulp and paper industry wastewater.

Advanced oxidation processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in water and wastewater. The common oxidation processes for the production of hydroxyl radicals at ambient conditions are cavitation, photocatalytic oxidation, Fenton's chemistry, ozonation, and use of hydrogen peroxide. Hybrid methods (e.g. O_3/H_2O_2, $O_3/$ UV, O_3/ultrasound, O_3, H_2O_2/UV, photo-Fenton, photochemical oxidation) have been also used to produce hydroxyl radicals. Hydroxyl radicals react with most organic and many inorganic solutes with high rate constants (Glaze et al., 1992; von Sonntag, 1996; Hoigne, 1997). Many researchers studied the effectiveness of heterogeneous and photocatalytic advanced oxidation process on the treatment of various pulp and paper mill effluents (Mansilla et al., 1997; Balcıoğlu and Arslan, 1998; Balcıoğlu and Çeçen, 1999; Torrades et al., 2001).

Ozonation (Tuhkanen et al., 1997; Baig and Liechti, 2001; Sevimli, 2005) and catalytic ozonation processes (Balcıoğlu et al., 2003; Kıvılcımdan, 2003) were applied to enhance biodegradability of raw and biologically pretreated bleaching effluents.

Integrated chemical and biological processes were investigated to enhance the quality of treated pulp industry wastewater. Heinzle et al. (1992) treated chlorine bleaching and alkaline extraction step of sulfite pulp mill effluent (COD_0=1400-1800 mg/L) by the sequential application of aerobic biological and ozonation processes. While only 20-30 per cent AOX removal was obtained by biological treatment of effluent, by integration of biological process with ozonation AOX removal performance was increased to 70 per cent.

Ozonation process was also used as post treatment for pulp mill effluent (Roy-Arcand and Archibald, 1996; Oeller et al., 1997). Effluents yielded a substantial decrease in the biologically recalcitrant residual AOX, COD, and color by ozonation.

Nakamura et al. (1997) investigated the effect of sequential application of ozonation and activated sludge processes on the removal of lignin in the Kraft pulp wastewater from a pulp manufacturing plant. The obtained results indicated that the consecutive treatments of ozone and then activated sludge treatment degrade the lignin, maleic and oxalic acids efficiently.

In order to increase biodegradability, woodfree and newsprint paper mill effluents were treated by ozonation (Helble et al., 1999). BOD/COD ratios of both effluents were increased from < 0.1 to 0.3 by ozonation.

Ozonation was also used for the removal of specific compounds from pulp mill effluent (Korhonen et al., 2000; Korhonen and Tuhkanen, 2000). 65 per cent COD, 90 per cent ethylenediaminetetraacetic acid (EDTA) and resin acids removals were obtained by ozonation.

CEH stage of Kraft bleaching process effluent was treated by ozonation, homogeneous catalytic ozonation (O_3/Fe^{2+}, O_3/Mn^{2+}), and heterogeneous ozonation (O_3/GAC-granulated active carbon) by Kıvılcımdan (2003). COD removal efficiency of ozonation was increased from 25 to 63 per cent by the use of granulated active carbon as heterogeneous catalyst in ozonation process. The BOD_5/COD value of effluent was increased from 0.11 to 0.29 by the O_3/GAC process.

Bijan and Mohseni (2004) improved the biodegradability of alkaline bleach plant effluent at ozone dosage of 600-800 mg O_3/L. More than 30 per cent high molecular weight constituents and more than 70 per cent color removals were achieved by the ozonation process.

Sevimli (2005) investigated the effectiveness of chemical oxidation by applying ozonation, combination of ozone/hydrogen peroxide, and Fenton’s processes for decolorization and residual COD removal of biologically pretreated corrugated board production factory wastewater which has 470 mg/L COD and 680 Pt-Co color. COD removal efficiency of ozonation was increased from 43 to 83 per cent by the Fenton’s oxidation. Almost complete color removal was achieved by ozonation and Fenton’s oxidation processes.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Kraft Pulp Mill Effluent

The effluents used for the experiments were obtained from the biggest integrated pulp and paper mill in Turkey. The mill produces about 140 t/d of pulp from soft and hardwoods. The main steps of pulp and paper manufacturing in the plant are:

(a) raw material preparation (debarking of wood and chip making),
(b) pulp manufacturing,
(c) pulp bleaching,
(d) paper and cardboard manufacturing.

Cellulose pulp is manufactured from the raw materials using Kraft process in which woods chips are cooked with caustic soda to produce brown stock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy. Kraft mill operates a closed looped system whereby 95-98 per cent of the chemicals used in the process are recovered and reused. After the pulping, a multistage bleaching process is applied to pulp. Cardboard is prepared from unbleached pulp. The objective of bleaching is to remove the small fraction of the lignin and to produce brightness. Chlorine, calcium hypochlorite, and chlorine dioxide are used as bleaching agents, to transform lignin into an alkali soluble form in six stages-CEHDED (chlorination, alkaline extraction, hypochlorite, chlorine dioxide, alkaline extraction, chlorine dioxide) bleaching sequence (Figure 3.1). Sodium hydroxide is used in the two stages of bleaching process to extract the alkali soluble form of lignin. 28 million m^3/year of fresh water is consumed in Kraft pulp mill. Especially pulping and bleaching processes consume huge amount of water since after each stage of bleaching pulp is washed with water.

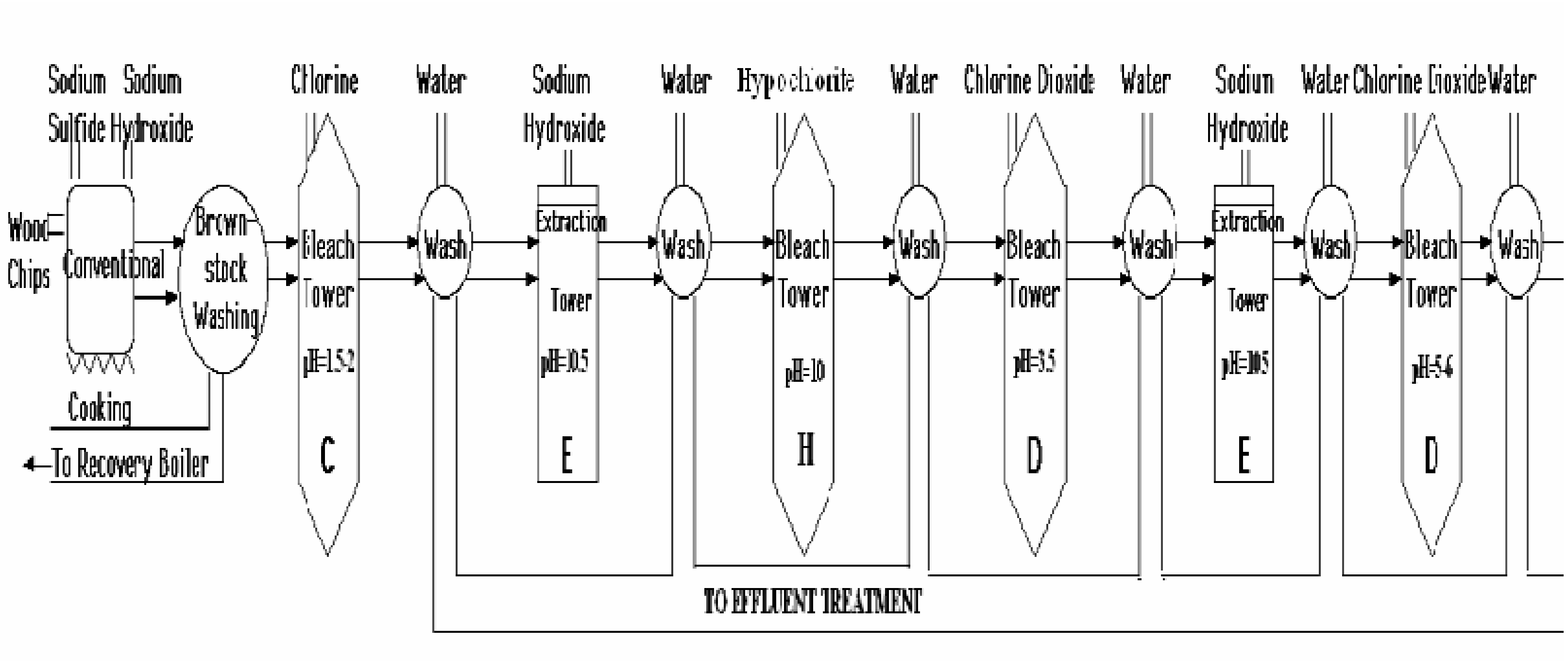

Figure 3.1. Bleaching sequence and reagents.

In the plant, effluents are collected into four different streams. Wastewater originated from the preparation of pulp and bleaching operation is collected into cellulose stream. Effluents from soda and caustification tanks are combined in another stream which is named as chemical recovery stream. Preparations of cardboard and chlorine-alkaline constitute the other two waste streams. Flow rate of each waste stream is presented in Table 3.1.

Table 3.1. Flow rate of waste streams.

Wastewater	Flow rate (m^3/h)
(1) Cellulose stream	950
Pulp production	200
Bleaching	750
Each bleaching stage	125
(2) Chemical recovery stream	200
(3) Cardboard stream	450
(4) Chlorine-alkaline stream	10
Total effluent	1,610

Contribution of each wet process to the combined effluent is as follows: cellulose 59 per cent (including 47 per cent bleaching effluent), cardboard 28 per cent, chemical recovery 12 per cent, and chlorine-alkali 0.6 per cent. Cellulose stream includes both cooking and bleaching wastewater. Each stage of bleaching process has the same flow rate. Combined bleaching effluent and effluents from each stage of CEH bleaching sequence as well as effluents from cellulose, cardboard, chemical recovery, and chlorine-alkaline streams were stored at 4°C prior to use in the experiments.

3.1.2. Oxidant

Hydrogen peroxide, which was obtained from Merck, was used in homogeneous catalytic ozonation experiments.

3.1.3. Catalase

In order to eliminate the interferences of remaining hydrogen peroxide on the measurement of absorbance and COD catalase with an enzyme activity of 17600 A.U. from bovine liver (Sigma) was used. 1 A.U. of the catalase destroys 1 µmoles of H_2O_2 per minute at pH=7 at 25°C.

3.1.4. Synthetic Domestic Wastewater

Pulp mill effluent was diluted with synthetic domestic wastewater to acclimate the sludge to pulp mill effluent. Activated sludge was first acclimated to the synthetic domestic wastewater with a loading rate of 500 mg COD/L.d. The composition of stock synthetic domestic wastewater was as follows: $CaCl_2$ (0.45 g/L), CH_3COONa (6 g/L), $FeCl_3.6H_2O$ (0.2 g/L), glucose (5.6 g/L), KH_2PO_4 (2.0 g/L), K_2HPO_4 (2.0 g/L), $MgSO_4$ (1 g/L), $NaHCO_3$ (3.0 g/L), $(NH_4)_2SO_4$ (5.0 g/L), peptone (2 g/L). The COD, TKN, and phosphorus content of stock synthetic domestic wastewater were 10,000 mg/L, 1,060 mg/L, and 810 mg/L, respectively.

3.1.5. Activated Sludge

An eight liter glass mother reactor was inoculated with the sludge taken from the aeration tank of an activated sludge treatment unit of a plant. Suspended solid and volatile suspended solid content of mother activated sludge tank were around 5,000 and 3,700 mg/L, respectively, at a sludge age of 20 days. A mixture of synthetic domestic wastewater and composite paper mill effluent including pretreated combined bleaching effluent was used as feed during acclimatization period and proportion of paper mill effluent in mixture was increased gradually. Since the wastewater did not contain enough phosphorus and nitrogen, appropriate amount of $(NH_4)_3PO_4$ was added to reach the ratio of COD:N:P=100:5:1. After achieving steady state operating conditions in mother activated sludge reactor, six batch activated sludge reactors including one control reactor for untreated integrated Kraft mill effluent and five reactors for mill wastewater comprised pre-ozonated different stages of bleaching effluents were inoculated from mother reactor and operated simultaneously at room temperature. The activated sludge reactors were allowed to operate for 24 hours and samples were taken and analyzed regularly for COD_s

and OUR. Aeration and mixing within the reactors were achieved by feeding of air through diffusers. The dissolved oxygen was available in excess and was measured as 7-8 mg/L.

3.2. Methods

3.2.1. Experiments in Ozone Bubble Reactor

Ozone was generated from pure oxygen by electrical discharge using an ozone generator (Fisher OZ 500 model). Ozonation experiments were carried out in a laboratory semi-batch bubble reactor consist of a glass column with a working volume of 1,500 mL (78 cm height and 6 cm diameter) and the experimental setup is shown in Figure 3.2. All experiments were conducted at room temperature and in semi-batch mode by sparging the ozone containing gas continuously into the solution. Ozone/oxygen gas was supplied at the bottom of the reactor through a gas diffuser. The inlet gas flow rate was 100 L/h, which provided appropriate mixing conditions. The volumetric mass transfer coefficient (k_{La}) of ozone at bubble reactor was 0.029 L/sec (Ötker, 2002). Circulation of the wastewater with a peristaltic pump (Cole-Parmer, Illinois, USA) provided additional mixing in the reactor. Two ozone traps containing 10 per cent potassium iodide solution were connected in series with the reactor in order to collect ozone which did not react.

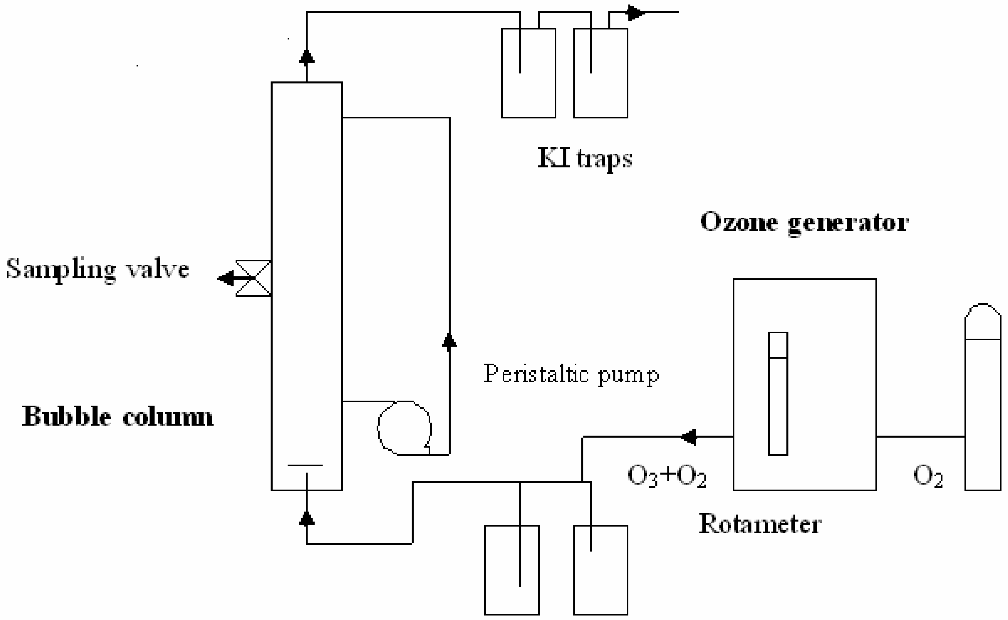

Figure 3.2. Experimental setup for ozonation experiments.

3.2.2. Analytical Procedure

3.2.2.1. COD Measurements. COD measurements were conducted in accordance with Standard Methods (APHA/AWWA/WPCF, 1995) by closed reflux colorimetric method. For soluble COD analysis (COD_s) samples were filtered through 0.45 μm Millipore filter and filtrate was used whereas total COD analysis (COD_t) was performed without filtration.

3.2.2.2. BOD_5 Measurements. BOD_5 measurements were performed by the dilution method (APHA/AWWA/WPCF, 1995). Dissolved oxygen concentrations were measured by Hach Portable DO apparatus with membrane electrode.

3.2.2.3. TKN Analysis. TKN (Total Kjeldahl Nitrogen) was measured by Gerhardt Digesdahl by digestion and distillation method (APHA/AWWA/WPCF, 1995).

3.2.2.4. AOX Measurements. Euroglas ECS Analyzer was used to measure Absorbable organic halogen (AOX) (ISO, 1989).

3.2.2.5. MLSS Measurements. The MLSS was measured by filtering 10 mL sample through 0.45 μm filter paper and drying residue on paper for one hour at 103±5°C (APHA/AWWA/WPCF, 1995).

3.2.2.6. MLVSS Measurements. The MLVSS was measured by igniting residue from MLSS analysis for one hour at ±550°C (APHA/AWWA/WPCF, 1995).

3.2.2.7. pH Measurements. Orion SAS20 pH meter was used for pH measurements.

3.2.2.8. Oxygen Uptake Rate Measurements. OUR was measured by WTW Microprocessor Oximeter Oxi 3000.

3.2.2.9. Spectrophotometric Measurements. Quantitative analyses of aromatic compounds, lignin derived compounds, and color compounds were determined by measuring the absorbance of wastewater samples in 1 cm path-length cell. UV–visible parameters were described in terms of the absorbance values measured at the selected wavelengths as follows: absorbance values at 436 nm as A_{436}, 280 nm as UV_{280}, and 254 nm as UV_{254}. Specific absorbance ($UV_{254,280}$/COD, A_{436}/COD, L/mg) values were also used to evaluate the results. Schimadzu UV-160 model spectrophotometer was used for absorbance measurement. Most of the samples were diluted so that absorbencies were within the range of measurements of the equipment.

3.2.2.10. Measurement of Gas Ozone Concentration. The ozone concentrations in the feed gas stream and outlet gas stream were determined by an iodometric method (IOA, 1987). 110 mL KI solution was used to absorb ozone in gas washing bottle. 10 ml H_2SO_4 (25 per cent) solution was added to the solution and then titrated with sodium thiosulfate. Gas ozone concentration was calculated by the following formula:

$$O_3(mg/\min) = \frac{V_{S_2O_3^{2-}}(mL)\,x\,N_{S_2O_3^{2-}}(eqg/L)\,x\,24\,g/eqg}{t\,(\min)} \tag{3.1}$$

where

O_3= ozone gas concentration (mg/min)

V= Volume of consumed $S_2O_3^{2-}$

N= Normality of $S_2O_3^{2-}$

24= equivalent weight of ozone

t= reaction time

The ozone adsorption was determined with a mass balance between the inlet and outlet gas stream.

4. RESULTS AND DISCUSSION

4.1. Characterization of Kraft Pulp Mill Effluents

In order to differentiate the characteristics of hardwood and softwood pulp mill effluents and select stream that has to be pretreated by ozone, different effluents (chlorine-alkali, cardboard, cellulose, chemical recovery, and each bleaching stage) originated from hardwood and softwood processing were characterized by using COD, BOD_5, AOX, pH, and alkalinity parameters (Table 4.1). Since nutrient control is of critical importance in the biological treatment of industrial wastewaters (Saunamaki, 1997), nitrogen and phosphate measurements were also conducted.

As can be seen from the Table 4.1 the wastewater from the first three stages of bleaching process had significantly higher COD values. Effluents from extraction and hypochlorite stages had alkaline pH value whereas other streams were acidic. Considering the AOX content and flow rate of each stream, it is obvious that the major source of AOX was the bleaching operation. Parallel to high AOX values, biodegradabilities of first three stages of bleaching effluents as expressed BOD_5/COD ratio were low and the lowest BOD_5/COD ratio was for E_1 stream, which had comparable high alkalinity value. Although pollution loads of D_1, E_2, and D_2 stage effluents were not high, their biodegradabilities were low.

By taking into account the low biodegradability and high AOX content, the study was focused on bleaching effluents. CEH, E_1, and H stages as well as combined bleaching (CEHDED) effluents were separately treated by ozonation. Cardboard and chemical recovery effluents were added to pretreated effluents for the biological treatment. Since the biodegradability of chemical recovery stream was relatively high it was added to the biological treatment without ozonation. Cardboard stream was subjected to direct biological treatment since it did not contain chlorinated toxic substances.

Table 4.1. Physicochemical properties of the hardwood and softwood waste streams.

Effluent	Fibre type	COD (mg/L)	BOD_5 (mg/L)	AOX (mg/L)	TKN (mg/L)	PO_4^{3-} (mg/L)	Alkalinity (mg $CaCO_3$/L)	pH
Chlorine-alkaline	Hardwood	97	ND	ND	4	3.4	372	10.7
	Softwood	ND	ND	ND	ND	ND	ND	ND
Cardboard	Hardwood	90	47	ND	6	0.9	270	7.2
	Softwood	390	31	1	ND	ND	ND	8.2
Cellulose	Hardwood	599	143	13.4	5	0.52	197	6.9
	Softwood	662	140	8.2	ND	ND	ND	7.42
Chemical Recovery	Hardwood	1,046	368	ND	20	1.1	53	9.0
	Softwood	970	493	9.3	ND	ND	ND	11.1
Bleaching C_1 stage	Hardwood	414	173	17.9	8	10.1	<1	1.6
	Softwood	707	29	27.2	ND	ND	ND	2.0
Bleaching E_1 stage	Hardwood	967	228	22.8	7	3.8	1,207	10.9
	Softwood	1,705	205	33.1	ND	ND	ND	11.3
Bleaching H stage	Hardwood	768	154	10.3	8	1.7	757	9.3
	Softwood	1,550	213	38.9	ND	ND	ND	9.0
Bleaching D_1 stage	Hardwood	269	72	3.0	5	1.8	92	2.6
	Softwood	259	38	5.5	ND	ND	ND	3.9
Bleaching E_2 stage	Hardwood	117	33	2.4	6	0.8	260	11.0
	Softwood	224	40	2.5	ND	ND	ND	10.4
Bleaching D_2 stage	Hardwood	86	<1	2.4	5	1	28	3.6
	Softwood	90	<1	1.9	ND	ND	ND	5.5

ND=not determined

Table 4.2 displays characteristics of combined and CEH stages of bleaching effluents. Since softwood pulp mill effluent contains high amount of resin and fatty acids (Gonzales and Zaror, 2000) it requires higher bleaching chemicals, compared to hardwood pulp. Therefore the softwood bleaching effluents contain higher amount of COD and AOX as shown in Table 4.2.

Table 4.2. Characteristics of bleaching effluents.

Parameters	Combined Bleaching (Softwood)	Combined Bleaching (Hardwood)	CEH Stage Bleaching (Softwood)
COD (mg/L)	649	455	1,145
BOD_5/COD	0.2	0.24	0.17
UV_{254}	7.4	5.3	12.4
UV_{280}	5.86	4.2	10.16
A_{436}	0.51	0.45	1.045
AOX (mg/L)	11.6	ND	25.2
pH	7.8	9.3	9.2

ND: not determined

4.2. Ozonation of Hardwood Combined Bleaching Effluents

It is known that bleaching process is the major source of recalcitrant pollutants in Kraft pulp wastewater. After conventional biological treatment processes noticeable amount of organic pollutants still remained in effluent. Ozonation was applied to the selected Kraft pulp bleaching streams in order to reduce the amount of recalcitrant organic contaminants.

4.2.1. Effect of Ozone Dose on the Treatment Performance

In order to elucidate the effect of ozone dose combined hardwood bleaching effluent was treated by using three different ozone input doses for one hour reaction period at natural pH of effluent. The effect of ozone dose on ozonation performance was evaluated by COD abatement and Figure 4.1 presents the variation of normalized COD value (COD_t/COD_o) as a function of treatment time.

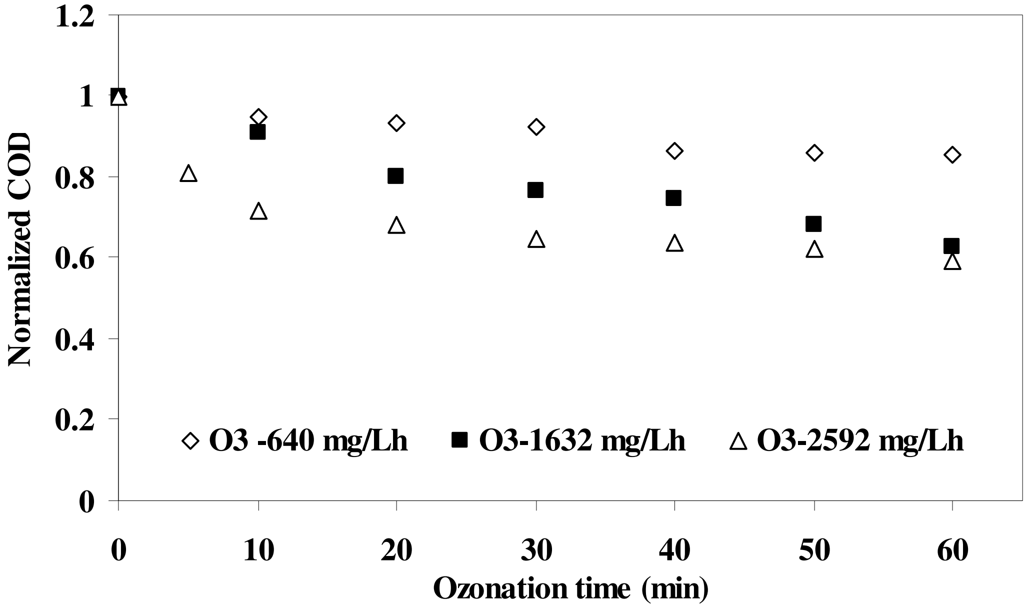

Figure 4.1. Effect of applied ozone dosage on the treatment efficiency of hardwood combined bleaching effluent at pH=9.

In general an increase in the ozone concentration in the liquid bulk causes an increase in the oxidation rate of the substrate (Adams et al., 1990; Duguet et al., 1990; Bellamy et al., 1991). By increasing the applied ozone dose from 640 mg/L.h to 2592 mg/L.h, COD removal rate was increased from 5 per cent to 28 per cent within 10 minutes (Figure 4.1.). Although a linear correlation between the oxidation rate and liquid ozone concentration was found by Adams and Randtke (1992) for the oxidation of atrazine in drinking water by ozonation, such correlation was not observed for the treatment of complex hardwood combined bleaching effluent in this study. Overall COD abatements obtained in one hour ozonation period were 14, 37, and 41 per cent with applied ozone doses of 640 mg/L.h, 1632 mg/L.h, and 2592 mg/L.h, respectively. Ozonation efficiency was not improved by applying excess amount of ozone because of the limited solubility of ozone in water.

4.2.2. Effect of pH on the Treatment Performance of Hardwood Combined Bleaching Effluent

It was known that the performance of ozonation process can be improved by increasing pH due to the reason that ozone undergoes self-decomposition to generate hydroxyl free radical, which can oxidize the organic and inorganic compounds unselectively (Hsu et al., 2004). Hardwood combined bleaching effluent was ozonated at pH values of 7, 9, and 12, in order to elucidate the effect of pH on the ozonation performance. Figure 4.2 depicts COD change as a function of ozonation time.

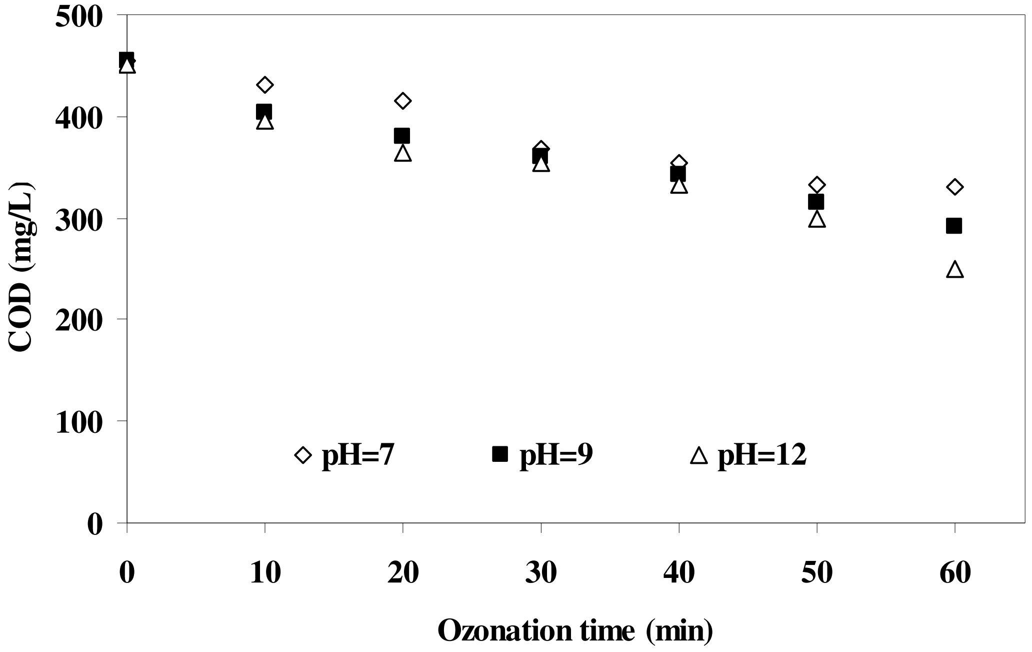

Figure 4.2. Effect of pH on ozonation performance of hardwood combined bleaching effluent.

By elevating the pH value from 7 to 12, COD abatement was increased from 27 per cent to 44 per cent, in one hour ozonation period. During the course of ozonation treatment pH values of samples were also measured and it was found that by the progress of ozonation process pH of wastewater dropped gradually due to the formation of acidic products. At the end of the treatment 0.25, 2.18, and 2.35 unit decreases were determined in pH of 7, 9, and 12, respectively. Accordingly in other study oxalic, glyoxylic, formic, acetic, propionic, and maleic acids were determined as easily biodegradable oxidation products of pulp bleaching effluents (Heinzle et al., 1992). Ozone decomposition occurs in a chain process that can be presented by the following fundamental reactions (Langlais et al., 1991).

Initiation step

$O_3 + OH^- \rightarrow HO_2^{\cdot} + O_2^-$ $\quad k= 70\ M^{-1}\ s^{-1}$ (4.1)

$HO_2^{\cdot} \leftrightarrow O_2^- + H^+$ $\quad k= 10^{-4.8}\ M^{-1}\ s^{-1}$ (4.2)

Propagation step

$$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2 \qquad k=1.6 \times 10^{9}\ M^{-1}\ s^{-1} \qquad (4.3)$$

$$O_3^{\cdot -} + H^{+} \rightarrow HO_3^{\cdot} \qquad k=5.2 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (4.4)$$

$$HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2 \qquad k=1.1 \times 10^{5}\ M^{-1}\ s^{-1} \qquad (4.5)$$

$$OH^{\cdot} + O_3 \rightarrow HO_4 \qquad k=2.0 \times 10^{9}\ M^{-1}\ s^{-} \qquad (4.6)$$

$$HO_4 \rightarrow HO_2^{\cdot} + O_2 \qquad k=2.8 \times 10^{4}\ M^{-1}\ s^{-1} \qquad (4.7)$$

Termination step

$$HO_4 + HO_4 \rightarrow H_2O_2 + 2\ O_3 \qquad (4.8)$$

$$HO_4 + HO_3 \rightarrow H_2O_2 + O_3 + O_2 \qquad (4.9)$$

However presence of radical scavengers in reaction medium such as HCO_3^- ions decreases the extent of degradation by reacting with the free radicals (Staehelin and Hoigne, 1985). Although hardwood combined bleaching effluent has alkalinity constituents, it was possible to observe the effect of pH on ozonation performance due to the lower value of it compare to that of CEH and E_1 stage effluents.

$$OH^{\cdot} + CO_3^{2-} \rightarrow OH^{-} + CO_3^{\cdot -} \qquad k=4.2 \times 10^{8}\ M^{-1}\ s^{-1} \qquad (4.10)$$

$$OH^{\cdot} + HCO_3^{-} \rightarrow OH^{-} + HCO_3^{\cdot} \qquad k=1.5 \times 10^{7}\ M^{-1}\ s^{-1} \qquad (4.11)$$

During the ozonation period BOD_5 was also determined in samples taken from the reactor in order to evaluate biodegradability of products formed by ozonation. While Figure 4.3 displays changes in the BOD_5 values, Figure 4.4 depicts BOD_5/COD ratio of combined hardwood bleaching effluent as a function of ozonation time at three different pHs. Throughout the ozonation period BOD_5 value of wastewater first exhibited a slight increase and than it decreased. The BOD_5/COD ratio indicates biodegradable fraction of organics in wastewater. Since BOD_5 values did not change significantly throughout the ozonation period, BOD_5/COD ratio was increased considerably especially for the effluent treated at pH=12. By the application of 1632 mg/L ozone dose, BOD_5/COD ratio was enhanced from 0.24 to 0.41 at alkaline pH. On the other hand ozonation conducted at pH 7 and 9 resulted in BOD_5/COD of 0.3 at the end of the treatment period. Similar to current study, biodegradability of alkaline bleached plant effluent was increased from 0.18 to 0.25 by ozonation at alkaline pH (Bijan and Mohseni, 2004).

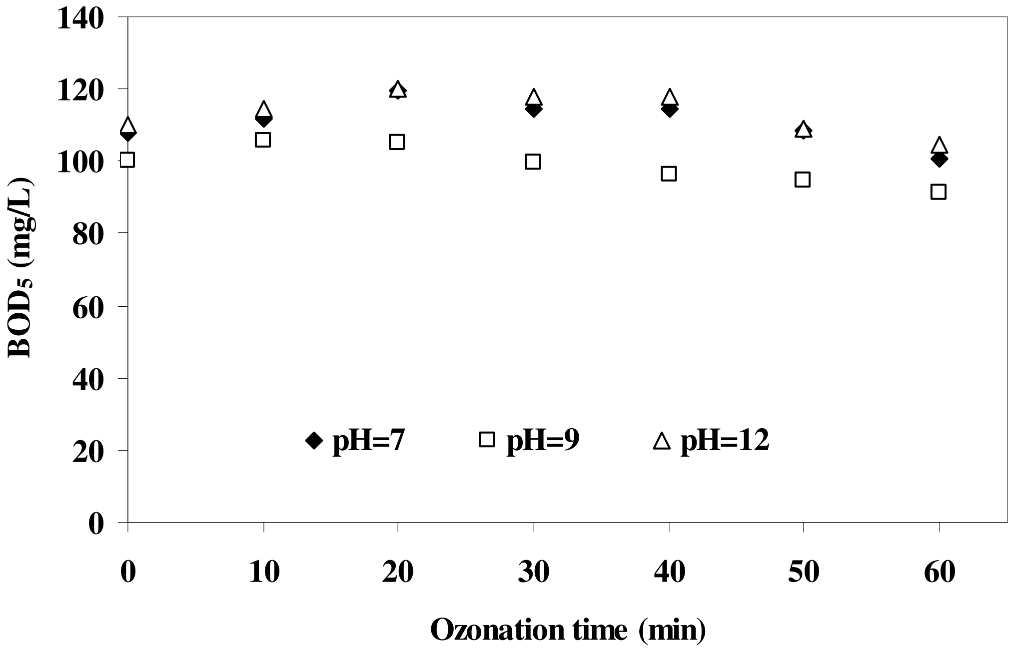

Figure 4.3. Changes in BOD_5 values of hardwood combined bleaching effluent by ozonation.

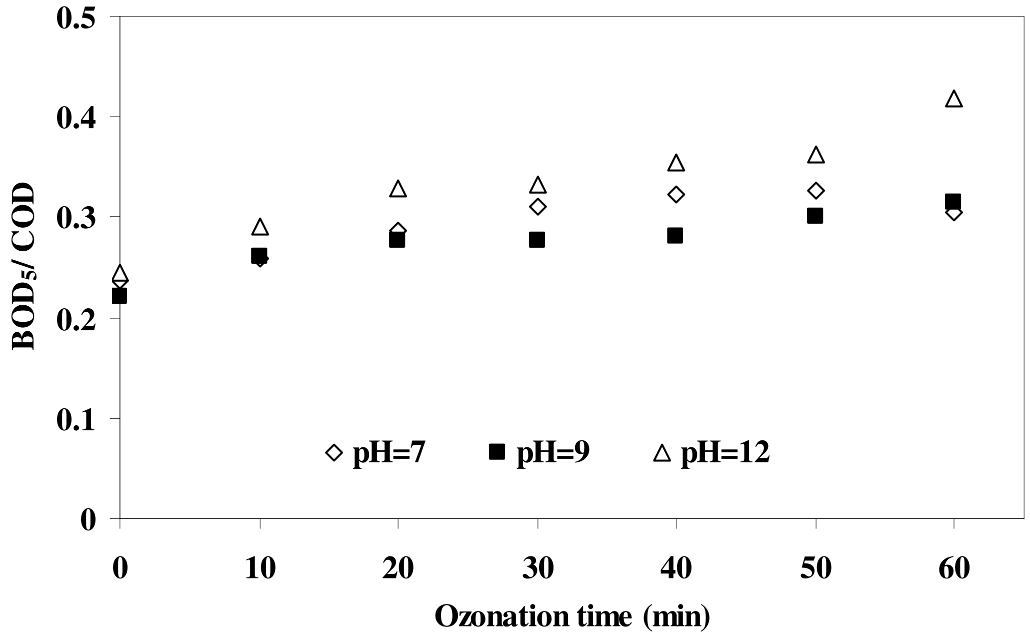

Figure 4.4. Changes in the biodegradability of hardwood combined bleaching effluent by ozonation.

Spectrophotometric measurements were also conducted to determine the removal of the specific compounds that contribute to the effluent COD. Aromatic and lignosulfonate contents of bleaching pulp mill effluent were detected by absorbencies at 254 and 280 nm, respectively. Parallel to the results for COD removal, the highest UV_{254} abatement was obtained at pH=12 (Figure 4.5). Reduction in absorbance values was more pronounced in the initial period of process. 54 per cent UV_{254} abatement was achieved within ten minutes of ozonation at alkaline pH. Although continuous removal was obtained for UV_{254} at pH=9 and pH=12, UV_{254} reduction at pH=7 leveled off within 40 minutes of ozonation. By increasing the pH value from 7 to 12 UV_{280} removal rate was enhanced from 48 to 55 within ten minutes of ozonation (Figure 4.6).

Ozone is typically being employed to decolorize bleaching effluents in the pulp mill industry. By increasing the applied ozone dose from 48 to 300 mg/L color removal efficiency was increased from 29 to 65 per cent for different pulp mill effluents (Ng et al., 1978; Boyden, 1991; Roy-Arcand et al., 1991). In this study the absorbance value at 436 nm was used to evaluate the color content of wastewater. Figure 4.7 depicts A_{436} removal kinetics of hardwood combined bleaching effluent.

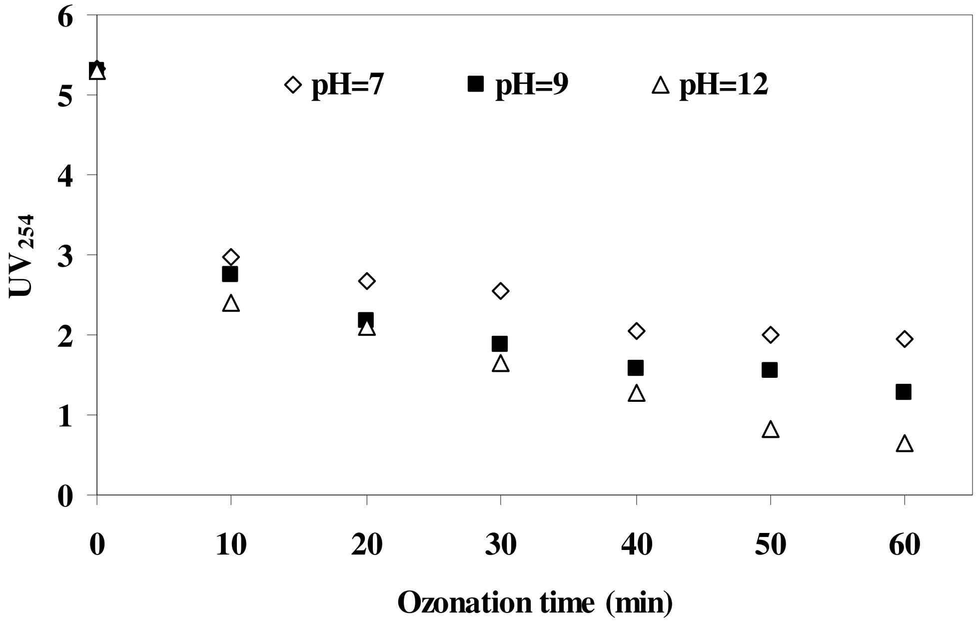

Figure 4.5. Effect of pH on UV_{254} removal kinetics of hardwood combined bleaching effluent.

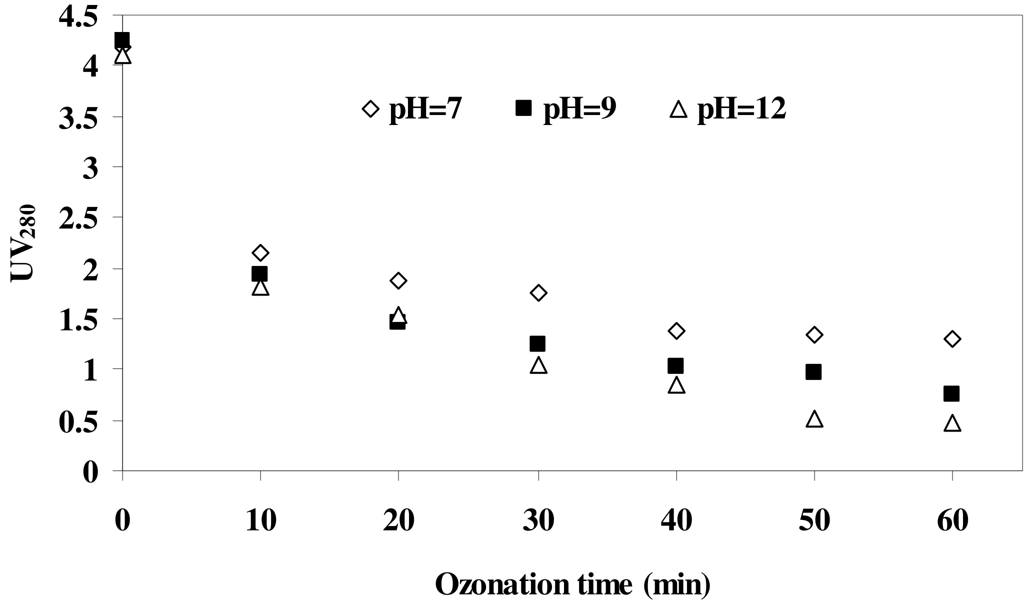

Figure 4.6. Effect of pH on UV_{280} removal kinetics of hardwood combined bleaching effluent.

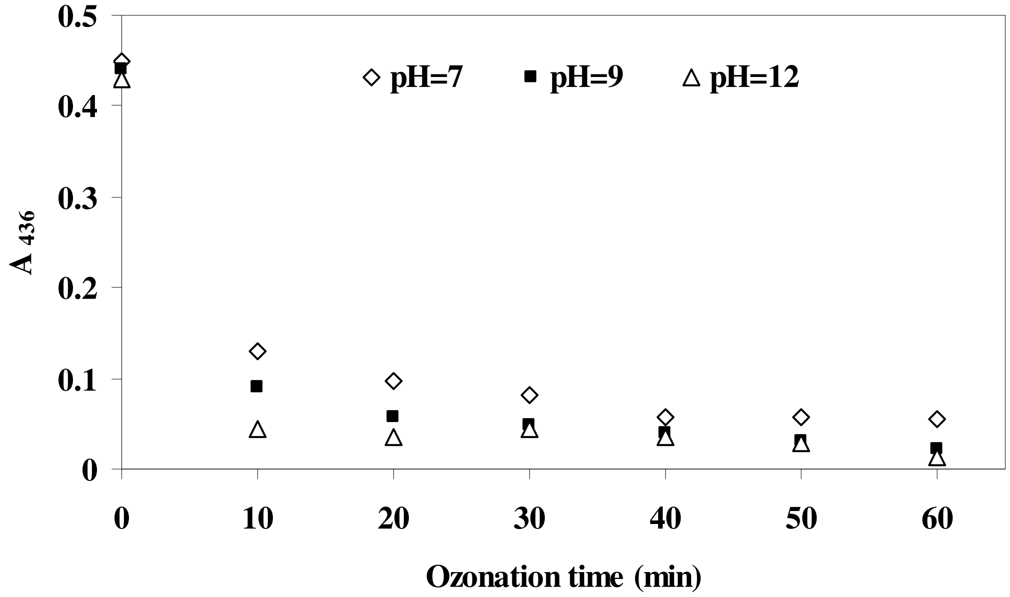

Figure 4.7. Effect of pH on color removal kinetics of hardwood combined bleaching effluent.

In agreement with literature obtained results indicated that application of ozone was very effective on the removal of colored compounds. 71, 79, and 89 per cent A_{436} removals were achieved with 272 mg/L ozone dose within 10 minutes at pH values of 7, 9, and 12, respectively. Almost complete color removal was achieved by one hour ozonation at pH=9 and pH=12.

COD comprise all organic substances that can be oxidized chemically. However, absorption values are specific for some chemical groups. Relationship between COD and absorbance value was expressed by specific absorbance ratio of absorbance value to the COD.

As previously mentioned, removal rates of COD and absorbencies were high at alkaline pH, so variation of specific absorbance ratios became more pronounced by increasing pH from 7 to 12. As can be seen from the Figure 4.8, specific absorption ratio of wastewater samples exhibited decreasing trend by ozonation time since the removal rate of other compounds was lower than the removal of aromatic acid, lignosulfonic acid, and colored compounds. Similar to the ozonation results photocatalytic treatment of softwood Kraft bleaching effluent led to decrease in UV_{254}/COD and A_{436}/COD ratios depending on their initial values (Balcıoğlu and Çeçen, 1999).

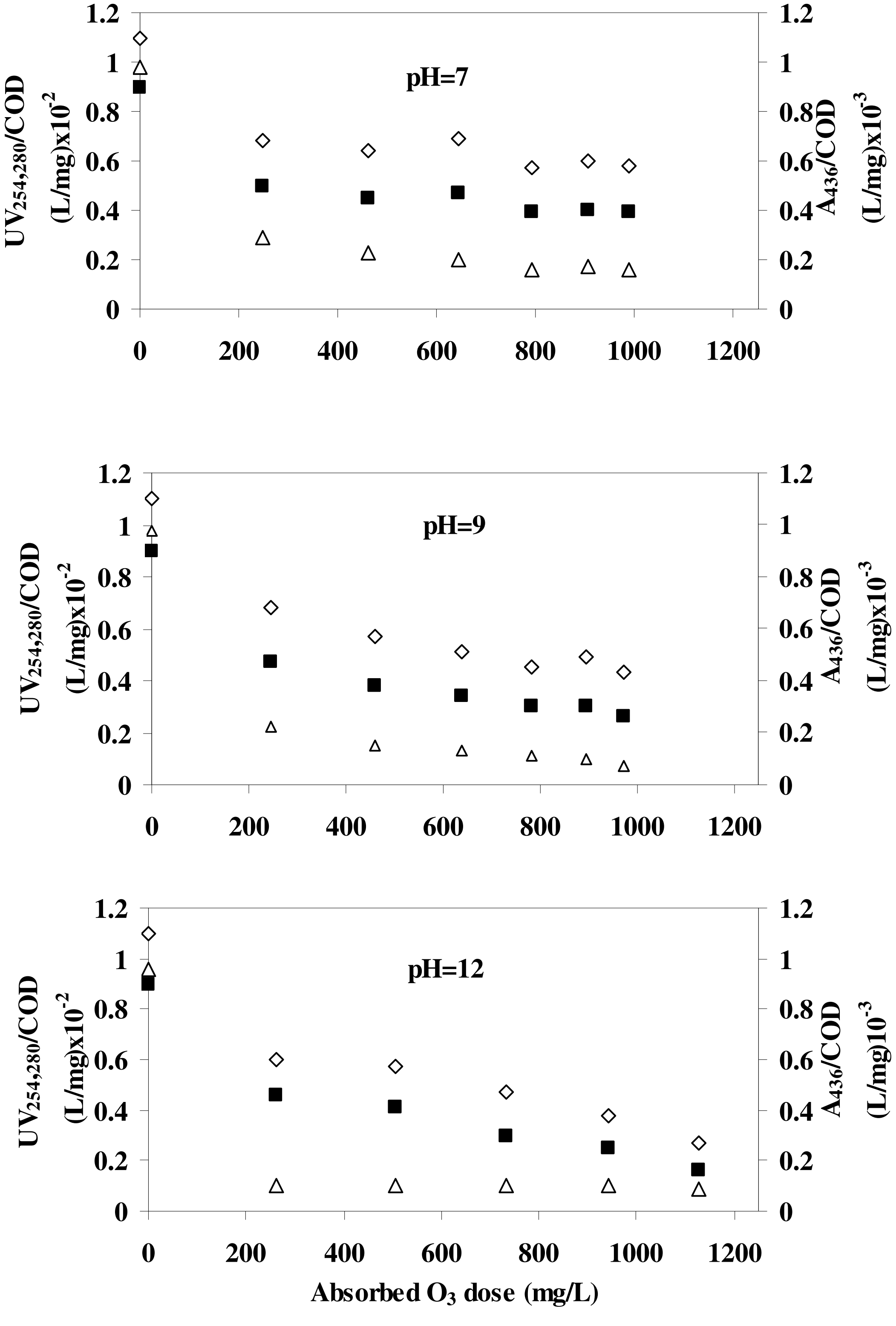

Figure 4.8. Specific absorption ratios of combined hardwood bleaching effluent ozonated at different pHs as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

Table 4.3 summarizes the overall BOD_5/COD ratios, COD, and absorbance removal rates of pretreated hardwood combined bleaching effluent at three different pH values. COD and absorbance removals were dependent upon the pH of ozonation process and treatment efficiency of ozonation process was higher at alkaline pH. By increasing the pH from 7 to 12 BOD_5/COD ratio was increased to a value of 0.42.

Table 4.3. The effect of pH on overall ozonation treatment performance of hardwood combined bleaching effluents.

Treatment	Removal (%)				BOD_5/COD
	COD	UV_{254}	UV_{280}	A_{436}	
O_3/pH=7	27	64	69	88	0.30
O_3/pH=9	36	76	82	95	0.31
O_3/pH=12	45	88	88	97	0.42

4.3. Ozonation of Combined Softwood Bleaching Effluents

4.3.1. Effect of pH on the Treatment Performance of Softwood Combined Bleaching Effluent

Since the load of chlorinated phenols and acids in softwood Kraft mill wastewater is three to eight times of what is found in the hardwood Kraft mill effluent (Mohamed et al., 1989), initial COD value of softwood wastewater was higher than that of hardwood wastewater. The effect of pH on ozonation performance was also investigated for softwood combined bleaching effluent and obtained results are presented in Figure 4.9 - 4.15.

While COD value of hardwood combined bleaching effluent was 455 mg/L, COD value of softwood combined bleaching effluent was 645 mg/L. Similar to the results obtained for hardwood combined bleaching effluent, the highest COD removal was achieved at pH=12. COD removal efficiency of softwood bleaching effluent was higher than that of the hardwood in spite of softwood pulp bleaching effluent having more pollution load. Parallel to higher COD removal rate, variation in pH value was higher at alkaline pH by the progress of ozonation process. At the end of one hour ozonation period 0.85, 1.3, and 2.47 unit changes in pHs were observed at pH values of 7, 9, and 12, respectively. Same COD removal efficiency was obtained at pH 7 and 9.

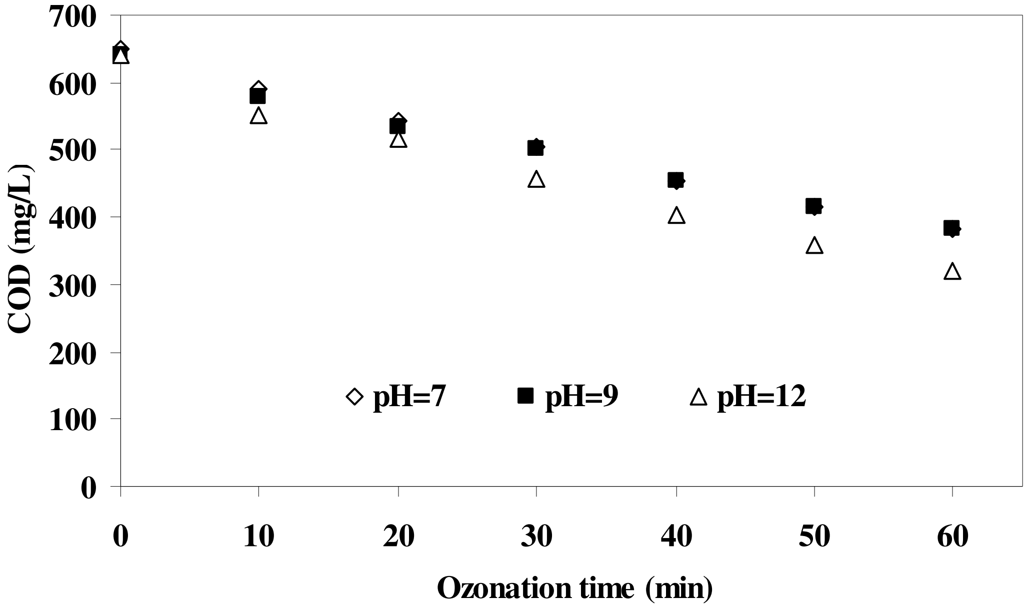

Figure 4.9. Effect of pH on COD removal of softwood combined bleaching effluent.

As opposed to the results obtained by hardwood effluent BOD_5 values were decreased slightly throughout ozonation process for all pH values (Fig. 4.10). BOD_5 value of wastewater ozonated at pH=7 was lower than that of ozonated at alkaline pH.

Ozonation was more effective in reducing of AOX content of effluent. 62 and 64 per cent AOX abatements were obtained at pH=7 and pH=12, respectively, in one hour ozonation period. Together with COD and AOX reductions, BOD_5/COD ratio was increased from 0.17 to 0.2 at pH=7 with absorbed ozone dose of 1519 mg/L.h whereas this ratio was 0.3 at pH=12 (Figure 4.11). Although COD removal was lower in hardwood combined bleaching effluent, biodegradability of effluent after one hour ozonation was higher in hardwood combined bleaching effluent. BOD_5/COD ratio of treated hardwood combined bleaching effluent was 0.4 at pH=12.

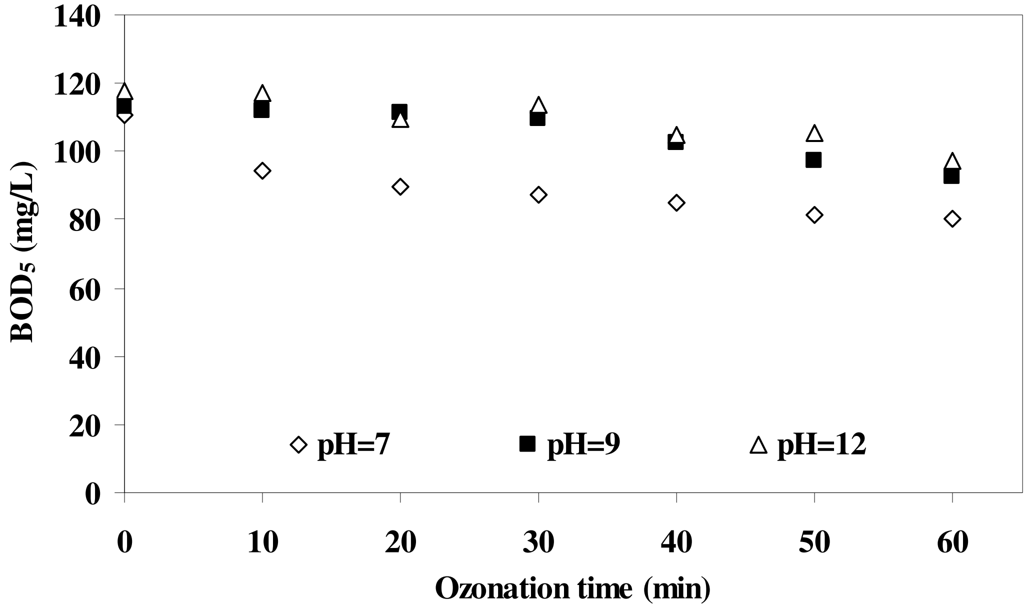

Figure 4.10. Changes in BOD_5 values of softwood combined bleaching effluent by ozonation.

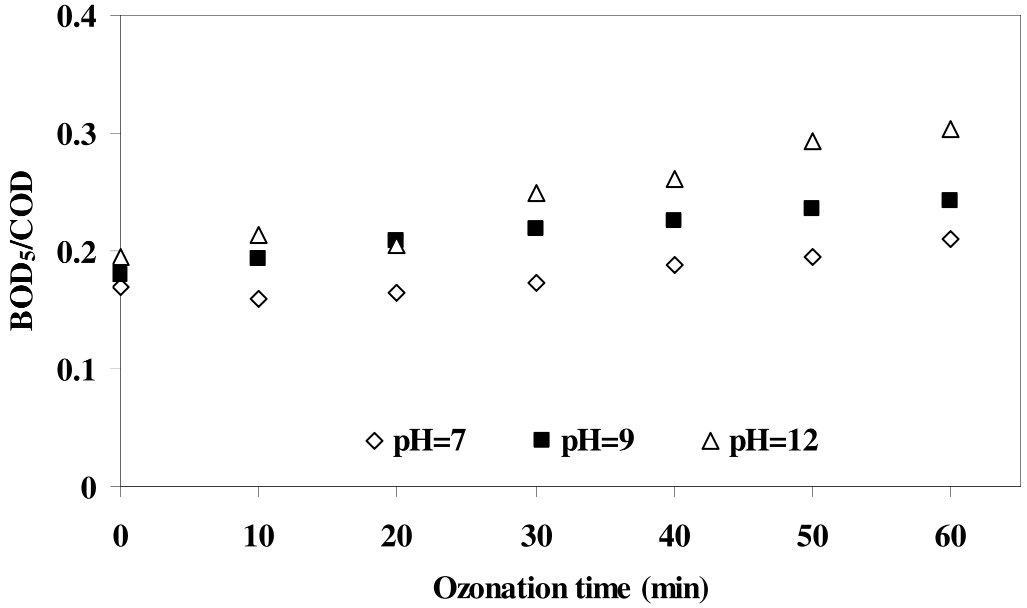

Figure 4.11. Changes in the biodegradabilities of softwood combined bleaching effluent by ozonation.

Similar to the high COD values of softwood combined bleaching effluent, initial absorbance values of softwood combined bleaching effluent (UV_{254}=7.3 cm^{-1}) were higher than that of combined hardwood bleaching effluent (UV_{254}=5.3 cm^{-1}). By increasing the ozonation pH from 7 to 12, UV_{254} abatement ratio of combined softwood bleaching effluent was increased from 30 to 50 per cent within 10 minutes ozonation period (Figure 4.12). Like in the case of UV_{254}, abatement rate of UV_{280} was improved from 40 to 56 per cent by increasing the initial pH value of wastewater from 7 to 12 (Figure 4.13). These results are in agreement with the previous results obtained by Namakura et al. (1997) who found that higher UV_{280} removal was obtained at alkaline pH. The highest degradation rate of pollutants at pH=12 can be explained by the fact that the radical-type oxidation reaction was enhanced because of the numerous hydroxide ions in the strong alkaline solution (Hoigne and Bader, 1983).

The results indicated that ozonation was very effective in decolorization and provided 90 per cent overall color removal for both hardwood and softwood combined bleaching effluents (Figure 4.14).

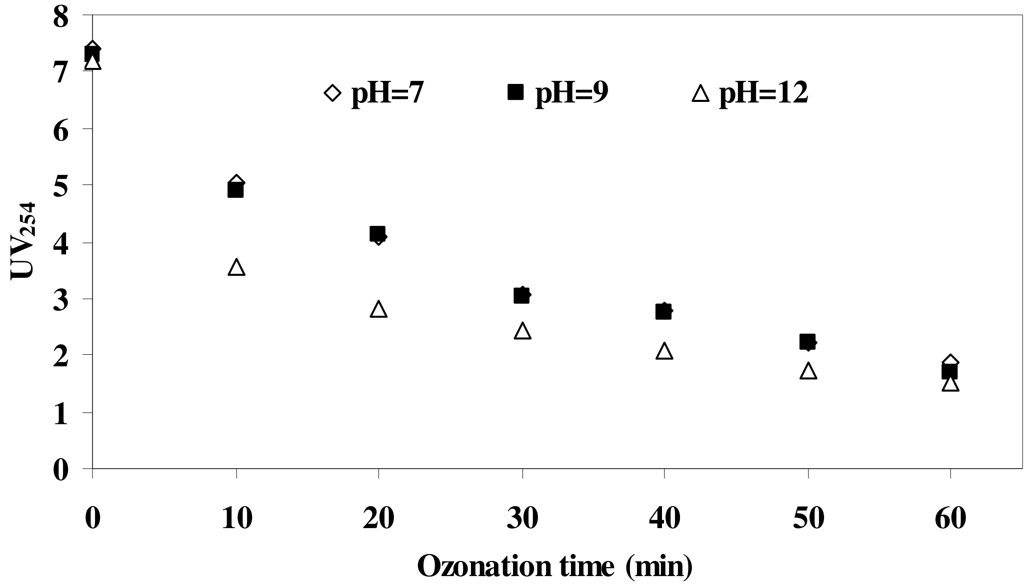

Figure 4.12. Effect of pH on UV_{254} removal kinetics of softwood combined bleaching effluent.

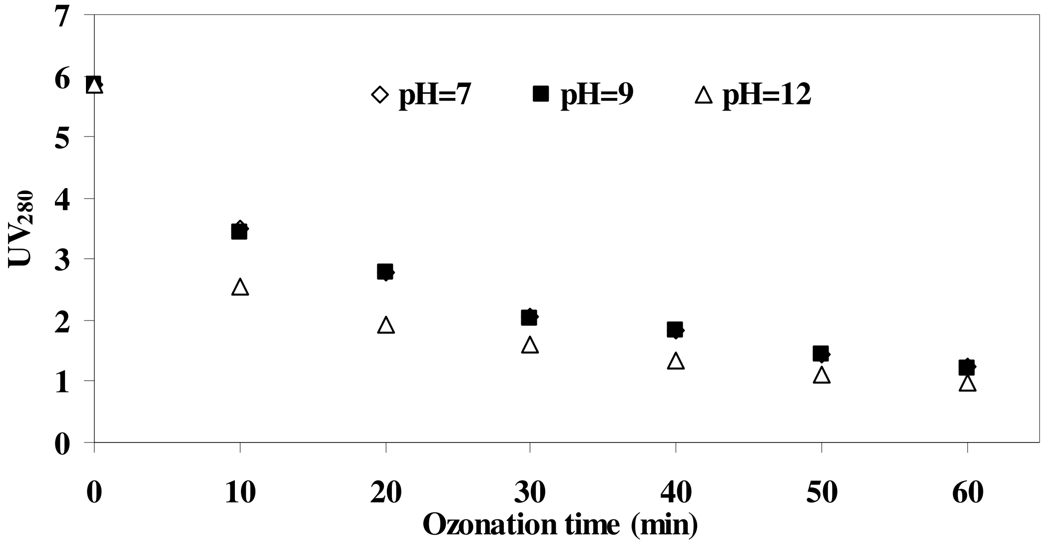

Figure 4.13. Effect of pH on UV_{280} removal kinetics of softwood combined bleaching effluent.

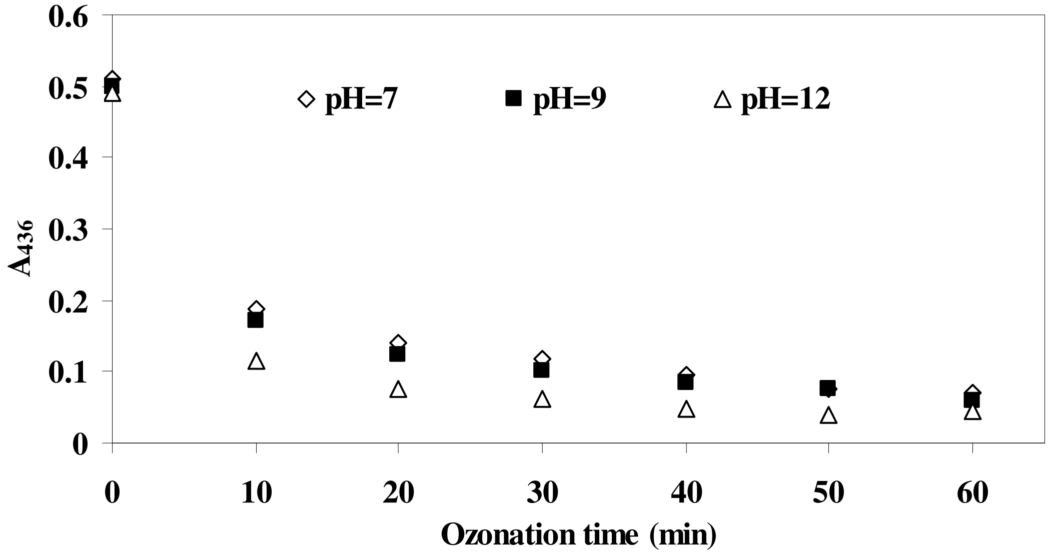

Figure 4.14. Effect of pH on color removal kinetics of softwood combined bleaching effluent.

As can be seen from the Figures 4.15, the specific absorption ratios of softwood bleaching effluent exhibited decreasing trend during the ozonation process. UV_{254}/COD and UV_{280}/COD had similar trends since the removal rate of lignosulfonic acids were almost parallel to removal of other organics. However ozone reacted more selectively with the colored compounds.

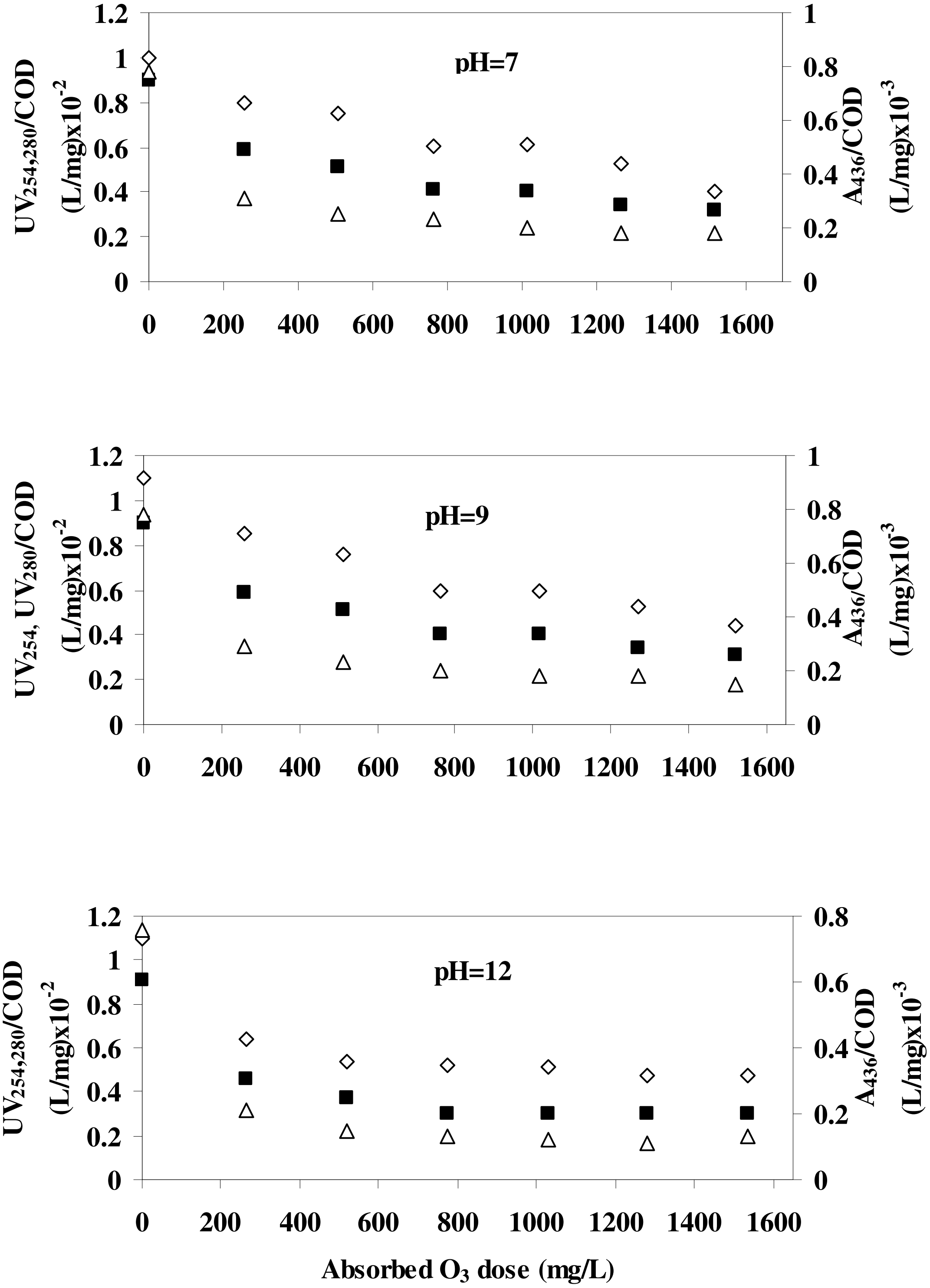

Figure 4.15. Specific absorption ratios of softwood combined bleaching effluent ozonated at different pHs as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

The overall results for the ozonation of softwood combined bleaching effluents were summarized in Table 4.4. Although COD removal rate of softwood combined bleaching effluent was higher than that of the hardwood combined bleaching effluent, higher BOD_5/COD ratio was obtained in hardwood combined bleaching effluent. Reduction of pH value of effluent due to the formation of acidic reaction products reduced the importance of radical type of reactions. Hence, the effect of pH on ozonation of softwood combined bleaching effluent could not clearly be determined. However, similar to previous results obtained for the treatment of hardwood combined bleaching effluent, the highest BOD_5/COD ratio, overall COD, and absorbance removals were achieved at alkaline pH.

Table 4.4. The effect of pH on overall ozonation treatment performance of softwood combined bleaching effluents.

pH	Removal (%)				BOD_5/COD
	COD	UV_{254}	UV_{280}	A_{436}	
O_3/pH=7	41	74	79	86	0.21
O_3/pH=9	40	77	79	88	0.24
O_3/pH=12	50	78	83	91	0.30

4.3.2. Effect of H_2O_2 Addition on Ozonation Performance of Softwood Combined Bleaching Effluent

Combination of ozone and H_2O_2, which results in a more efficient generation of hydroxyl radicals, is often used to improve the rate of organic degradation (Mokrini et al., 1997). The initiation, propagation and overall reactions of hydrogen peroxide with ozone are the followings:

Initiation step

$$H_2O_2 + H_2O \leftrightarrow HO_2^- + H_3O^+ \qquad pK=11.6 \qquad (4.12)$$

$HO_2^- + O_3 \rightarrow O_3^- + HO_2^\cdot$ k=2.8 x 10^6 M^{-1} s^{-1} (4.13)

$HO_2^\cdot \leftrightarrow H^+ + O_2^-$ k=1.6 x 10^{-5} M^{-1} s^{-1} (4.14)

Propagation step

$O_2^{\cdot -} + O_3 \rightarrow O_3^{\cdot -} + O_2$ k=1.6 x 10^9 M^{-1} s^{-1} (4.15)

$O_3^{\cdot -} + H^+ \rightarrow HO_3^\cdot$ k=5.2 x 10^{10} M^{-1} s^{-1} (4.16)

$HO_3^\cdot \rightarrow OH^\cdot + O_2$ k=1.1 x 10^5 M^{-1} s^{-1} (4.17)

Overall reaction is

$2O_3 + H_2O_2 \rightarrow 2OH^\cdot + 3O_2$ (4.18)

Reaction rate of ozone decomposition depends on the concentration of H_2O_2 (Staehelin and Hoigne, 1982). Although the stoichiometric ratio of H_2O_2/O_3 is 1:2 (equation 4.18) the dose ratio resulting in the fastest reaction rate has often been found to lie between 0.5 and 1.4 moles H_2O_2/mol O_3 (Glaze et al., 1987; Aieta et al., 1988; Duguet et al., 1990; Gottschalk and Jekel, 1997). However, addition of H_2O_2 to some industrial wastewater may not enhance the treatment performance of ozonation process because of the presence of radical scavengers (Masten and Davies, 1993; Gulyas et al., 1995) and the high concentration of H_2O_2 (Glaze et al., 1987; Ollis et al., 1991).

$H_2O_2 + OH^\cdot \rightarrow O_2^- + H_2O + H^+$ k=2.7 x 10^7 M^{-1} s^{-1} (4.19)

$HO_2^- + OH^\cdot \rightarrow OH^- + HO_2^\cdot$ k=7.5 x 10^9 M^{-1} s^{-1} (4.20)

In this study in order to enhance the treatment efficiency of ozone for combined softwood pulp bleaching effluents H_2O_2 was used. Preliminary experiments were conducted to determine optimum H_2O_2 dose for the ozonation of softwood combined bleaching effluent at pH=7. The results obtained in 30 minutes ozonation period were assessed in terms of COD removal (Figure 4.16). By the addition of 15 mM H_2O_2, COD removal rate was enhanced from 27 to 35 per cent. 38 per cent COD removal was achieved when H_2O_2 was further increased to 80 mM. COD removal efficiency of ozonation slightly decreased with 100 mM H_2O_2 for hydroxyl radicals.

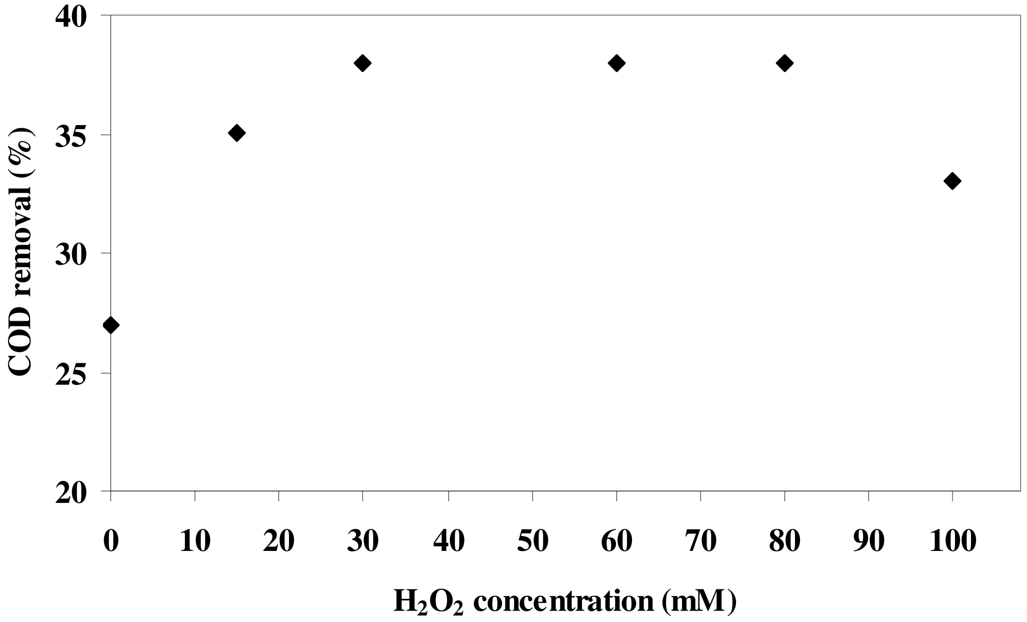

Figure 4.16. Effect of H_2O_2 dose on percent overall COD removal achieved in 30 min for the O_3 treatment of softwood combined bleaching effluent at pH=7.

Figure 4.17 depicts the changes in COD value of combined bleaching effluent by O_3/H_2O_2/pH=7 treatment process. 41 per cent COD abatement was obtained for the ozonation of combined softwood bleaching effluent at pH=7 whereas addition of H_2O_2 improved the overall COD abatement to 57 per cent. The effect of H_2O_2 addition to ozonation process was also investigated in the other study in which biologically pretreated corrugated board production factory wastewater was treated by ozonation (Sevimli, 2005). H_2O_2 enhanced the treatment performance in both cases, although wastewater characteristic was not the same. H_2O_2 promotes the generation of hydroxyl radicals, which are more powerful than molecular ozone and they react unselectively with pollutants found in wastewater. Therefore higher COD abatements were obtained by the addition of H_2O_2. While 0.85 unit pH change was observed for O_3/pH=7 process, 0.33 unit change in pH was observed for O_3/H_2O_2/pH=7 process at the end of one hour treatment period.

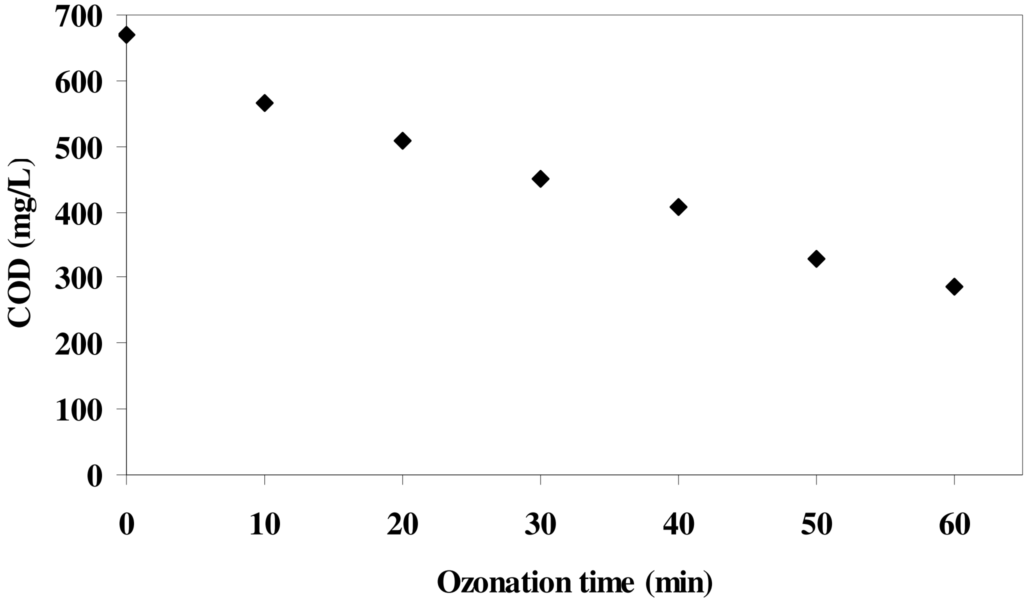

Figure 4.17. Changes in COD values of softwood combined bleaching effluent by O_3/H_2O_2 treatment at pH=7.

Noticeable improvement was achieved in BOD_5/COD ratio of combined bleaching effluent by the application of O_3/H_2O_2 treatment (Figure 4.18). Biodegradability of O_3/H_2O_2 treated effluent was two folds higher than that treated by mere ozonation.

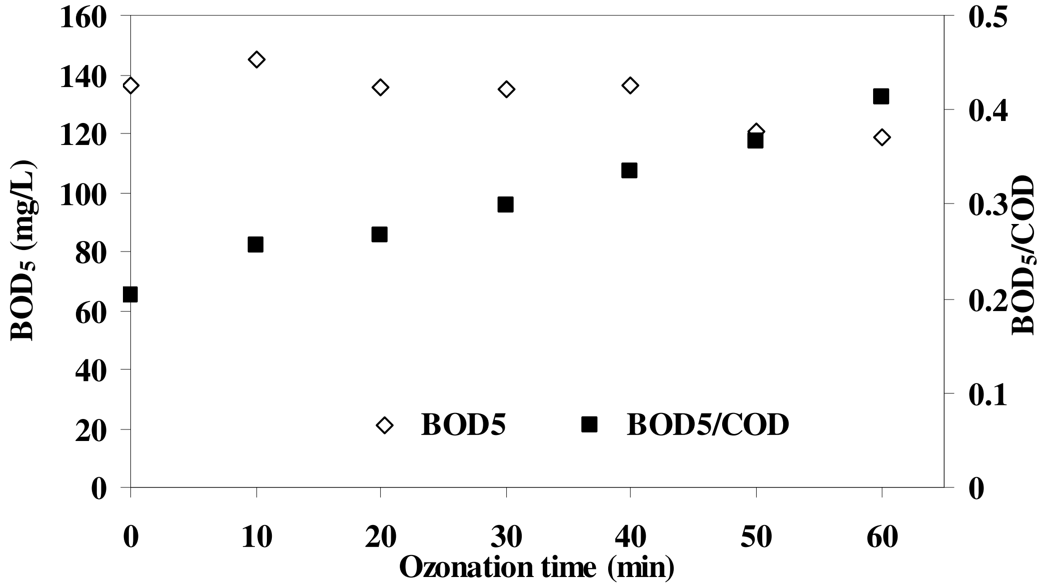

Figure 4.18. Changes in the BOD_5 values and BOD_5/COD ratios of softwood combined bleaching effluent in the presence of 15 mM H_2O_2 at pH=7.

The addition of 15 mM H_2O_2 enhanced the overall UV_{254}, UV_{280}, and A_{436} removal rates (Figure 4.19) especially in the initial period of ozonation. This effect was more pronounced for color removal. Continuous removals of absorbencies were obtained during one hour ozonation period. Similar positive effect of hydrogen peroxide addition on the absorbance removal was achieved in the previous study conducted by Sevimli (2005). However inhibition effect of high hydrogen peroxide concentration was not observed in his study.

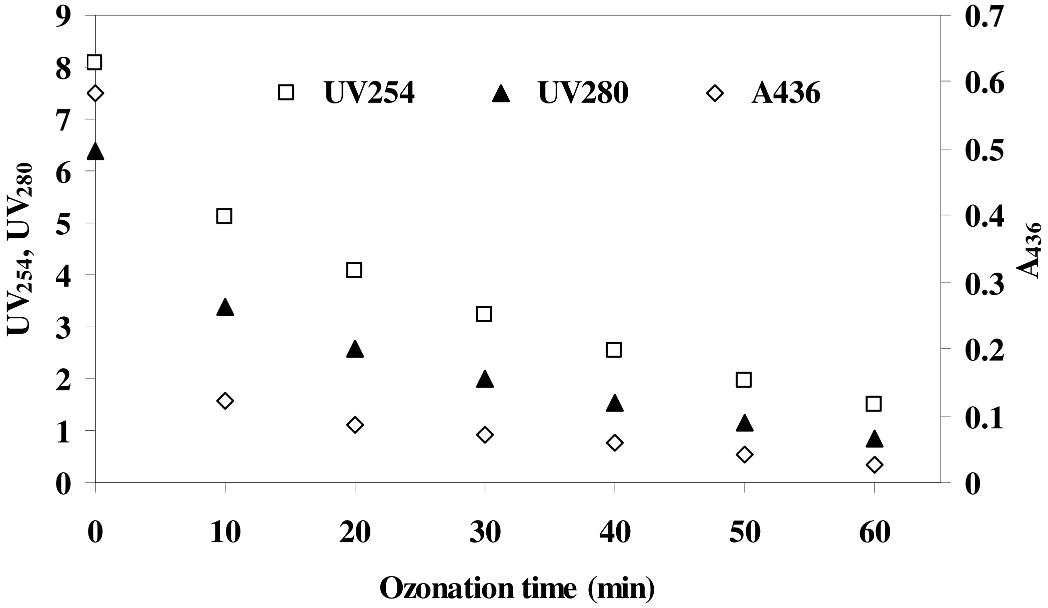

Figure 4.19. Changes in UV_{254}, UV_{280}, and A_{436} values of softwood combined bleaching effluent by O_3/ H_2O_2 (15 mM) process at pH=7.

Figure 4.20 depicts the variation of specific absorption ratios of softwood combined bleaching effluent by $O_3/H_2O_2$15 mM/pH=7 process. Significant absorbance removal was obtained by consuming 97 per cent (263 mg/L) of applied ozone dose within 10 minutes of ozonation. $O_3/H_2O_2$15 mM/pH=7 treatment produced more hydroxyl radicals in medium that was resulted in low values of UV_{254}/COD and UV_{280}/COD.

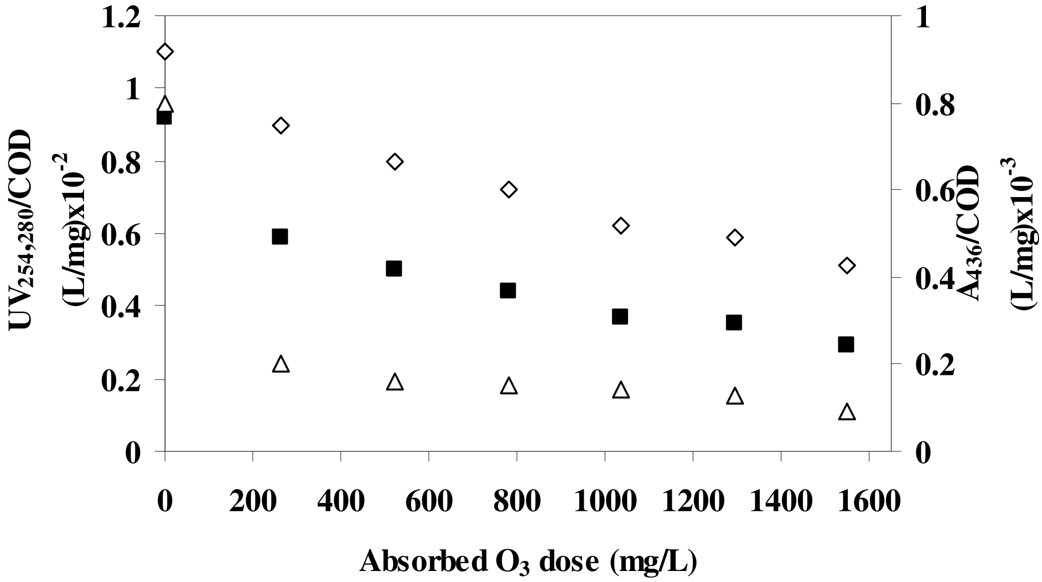

Figure 4.20. Specific absorption ratios of softwood combined bleaching effluent ozonated in the presence of 15 mM H_2O_2 at pH=7 as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

The results of O_3/H_2O_2 15 mM/pH=7 process for softwood combined bleaching effluent were summarized in Table 4.5 and compared with the results obtained by mere ozonation. Addition of 15 mM H_2O_2 to the ozonation was enhanced the BOD_5/COD ratio of combined softwood bleaching effluent to a value of 0.41. Besides 57 per cent removal of COD, 81, 86, and 95 per cent UV_{254}, UV_{280}, and A_{436} overall abatements were achieved, respectively, by O_3/H_2O_2 treatment of effluent. Incomplete oxidation of organics caused the lower COD removal compared to the UV_{254}, UV_{280}, and A_{436} abatements.

Table 4.5. The effect of H_2O_2 addition on overall ozonation treatment performance of combined softwood bleaching effluent.

pH	Removal (%)				BOD_5/COD
	COD	UV_{254}	UV_{280}	A_{436}	
O_3/pH=7	41	74	79	86	0.21
O_3/H_2O_2 pH=7	57	81	86	95	0.41

4.4. Ozonation of Separated Softwood Bleaching Effluents

It was known that in pulp and paper industry the bleach plant effluent comprises a highly significant proportion of the total process effluent. The organochlorine content of effluent originated from chlorination, extraction, and hypochlorite step of multistage bleaching process is higher than that of other streams. Taking this fact into account, CEH, E_1, and H stage effluents were separately ozonated in order to enhance their biodegradability and reduce the total cost of treatment.

4.4.1. Ozonation of Softwood CEH Stage Effluent

In order to elucidate the pH effect on the ozonation performance of CEH stage bleaching effluent experiments were conducted at pH=7 and pH=12. COD, BOD_5, absorbance, and pH values were determined to evaluate the treatment performance of ozonation (Figure 4.21-4.26). CEH stage effluent was more alkaline (pH=9) than combined bleaching effluent (pH=7.8). Since the residual lignin and other wood components which contribute to the COD of wastewater were extracted from the pulp and remained in the CEH stage bleaching effluent, the COD value of this effluent was almost two times that of combined bleaching effluent (Table 4.2).

As a result of ozonation of CEH stage bleaching effluent, almost same overall COD removal rates were obtained at pH=7 and pH=12 (Figure 4.21). pH did not affect the COD removal efficiency of ozonation process. The presence of radical scavengers such as HCO_3^- ions may decrease the extent of degradation by reacting with the free radicals (Beltran et al., 1994).

At the end of one hour ozonation of CEH 1.71 unit drops in pH was observed at alkaline pH whereas 2.47 unit drops in pH was observed by ozonation of combined bleaching effluent at alkaline pH. This indicates that the accumulated reaction products of CEH stage bleaching effluent were less acidic.

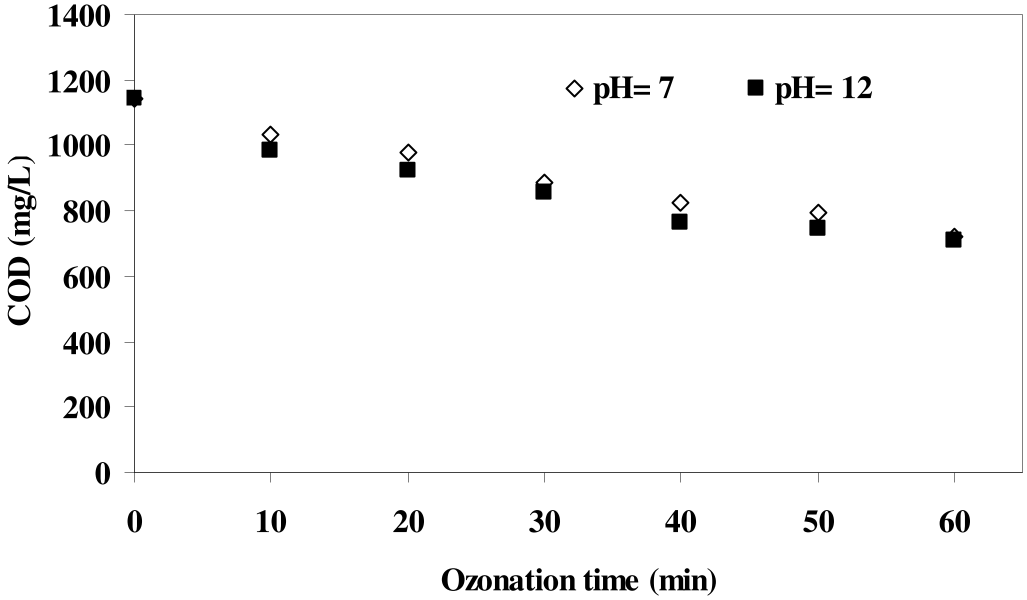

Figure 4.21. Effect of pH on COD removal kinetics of softwood CEH stage bleaching effluent for ozonation process.

Although COD values of one-hour ozonated CEH at pH=7 and pH=12 were almost same, BOD_5 value was slightly higher at pH=12 (Figure 4.22). The results reveal that during the ozonation period, some biodegradable reaction products were formed.

Figure 4.23 depicts changes in biodegradabilities of CEH stage bleaching effluent. CEH stage bleaching effluent showed low initial biodegradability (BOD_5/COD=0.17), indicating non-biodegradable characteristics of the effluent. Similar to previous study performed by Kıvılcımdan (2003), only slight improvement was achieved in biodegradability of CEH stage effluent by ozonation. The removal of AOX enhanced the BOD_5/COD ratio to a value of 0.29 at alkaline pH. 57 and 61 per cent overall AOX abatements were obtained by increasing the pH from 7 to 12.

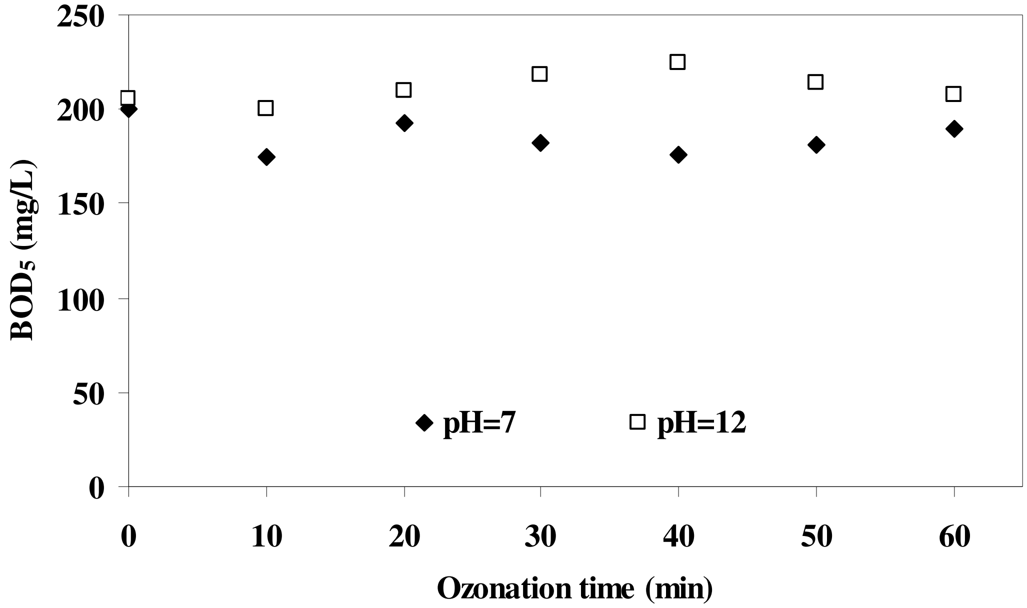

Figure 4.22. Changes in BOD_5 values of softwood CEH stage bleaching effluent by ozonation.

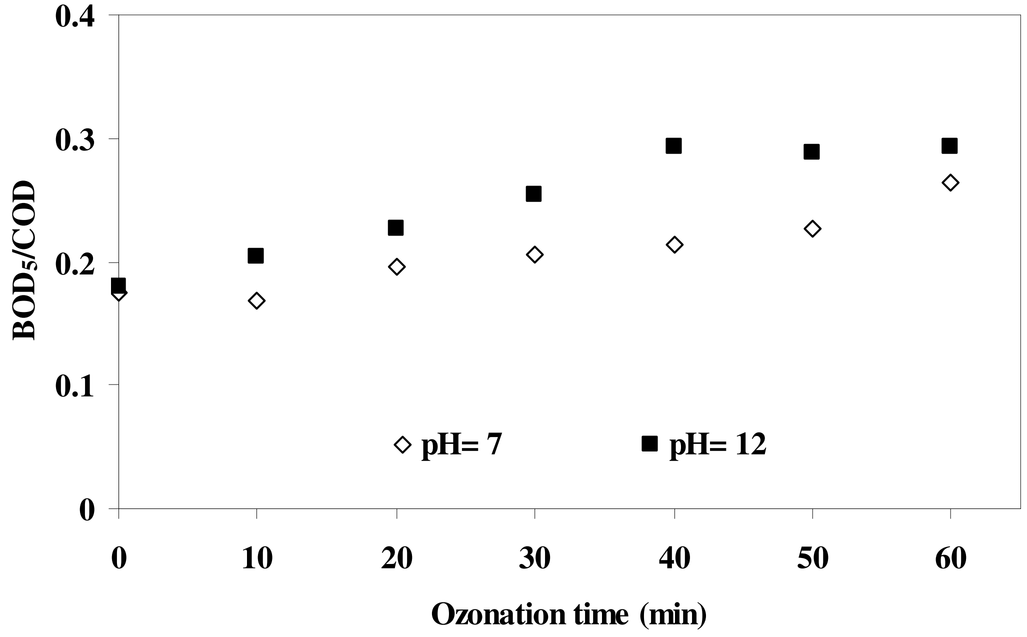

Figure 4.23. Changes in the biodegradabilities of softwood CEH stage bleaching effluent by ozonation.

Parallel to the high initial COD value, initial absorbance values of the CEH stage bleaching effluent were very high it was about two folds of combined softwood bleaching effluent. Within the first 10 minutes of ozonation period 24 and 35 per cent UV_{254}, 33 and 37 per cent UV_{280} abatements were obtained at pH=7 and pH=12, respectively (Figure 4.24 and 4.25).

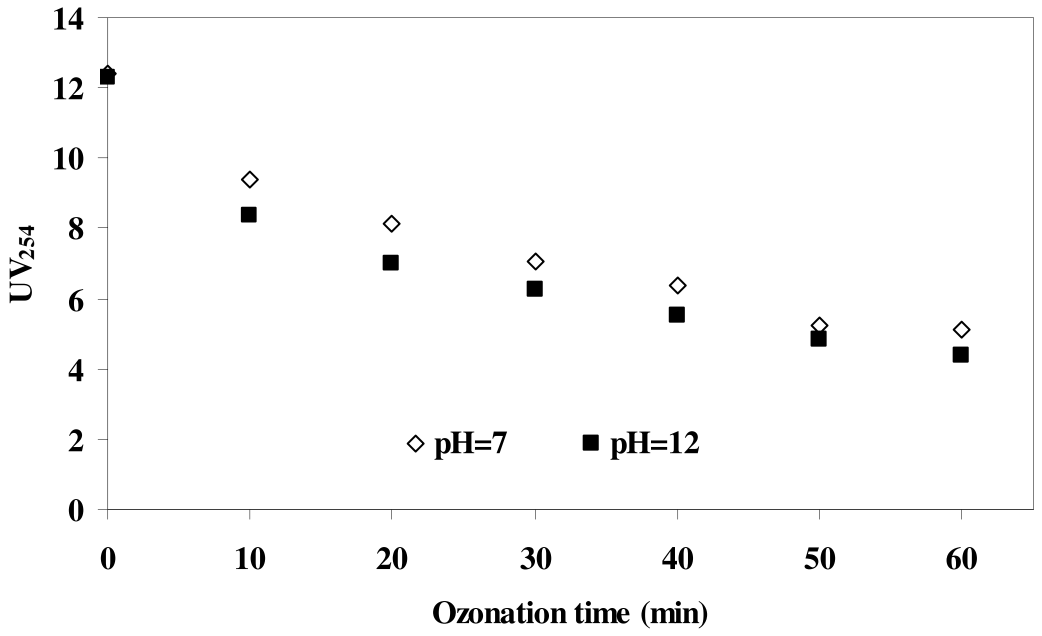

Figure 4.24. Effect of pH on UV_{254} removal kinetics of softwood CEH stage bleaching effluent.

More than 60 per cent A_{436} abatements were obtained within first 10 minutes of ozonation period. At the end of one hour ozonation period, 90 per cent color removal was achieved by the application of 1632 mg/L ozone dose (Figure 4.26).

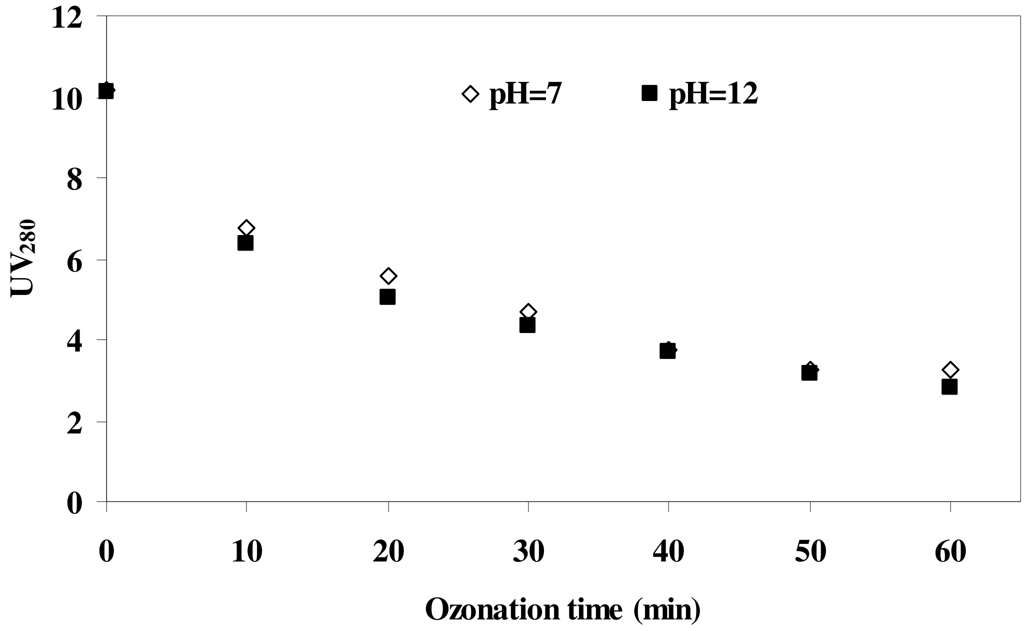

Figure 4.25. Effect of pH on UV_{280} removal kinetics of softwood CEH stage bleaching effluent.

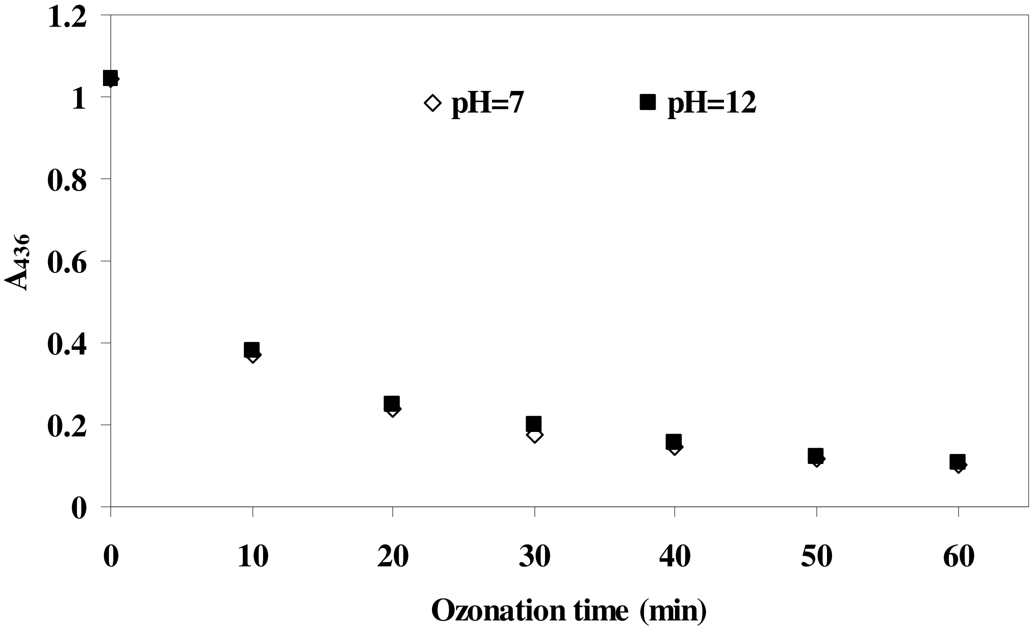

Figure 4.26. Effect of pH on color removal kinetics of softwood CEH stage bleaching effluent.

Figure 4.27 depicts the specific absorbance ratios of CEH stage effluent as a function of absorbed ozone dose. Similar specific absorbance removals were obtained by ozonation of combined and CEH stage bleaching effluents. All specific absorbance ratios were reduced during ozonation. More pronounced variation in specific absorbance values were obtained at the initial period of ozonation. Since absorbance removal of CEH stage effluent were less, UV_{254}/COD ratio of CEH stage bleaching effluent was slightly higher than UV_{254}/COD ratio of combined bleaching effluent at the end of one hour ozonation at pH=7.

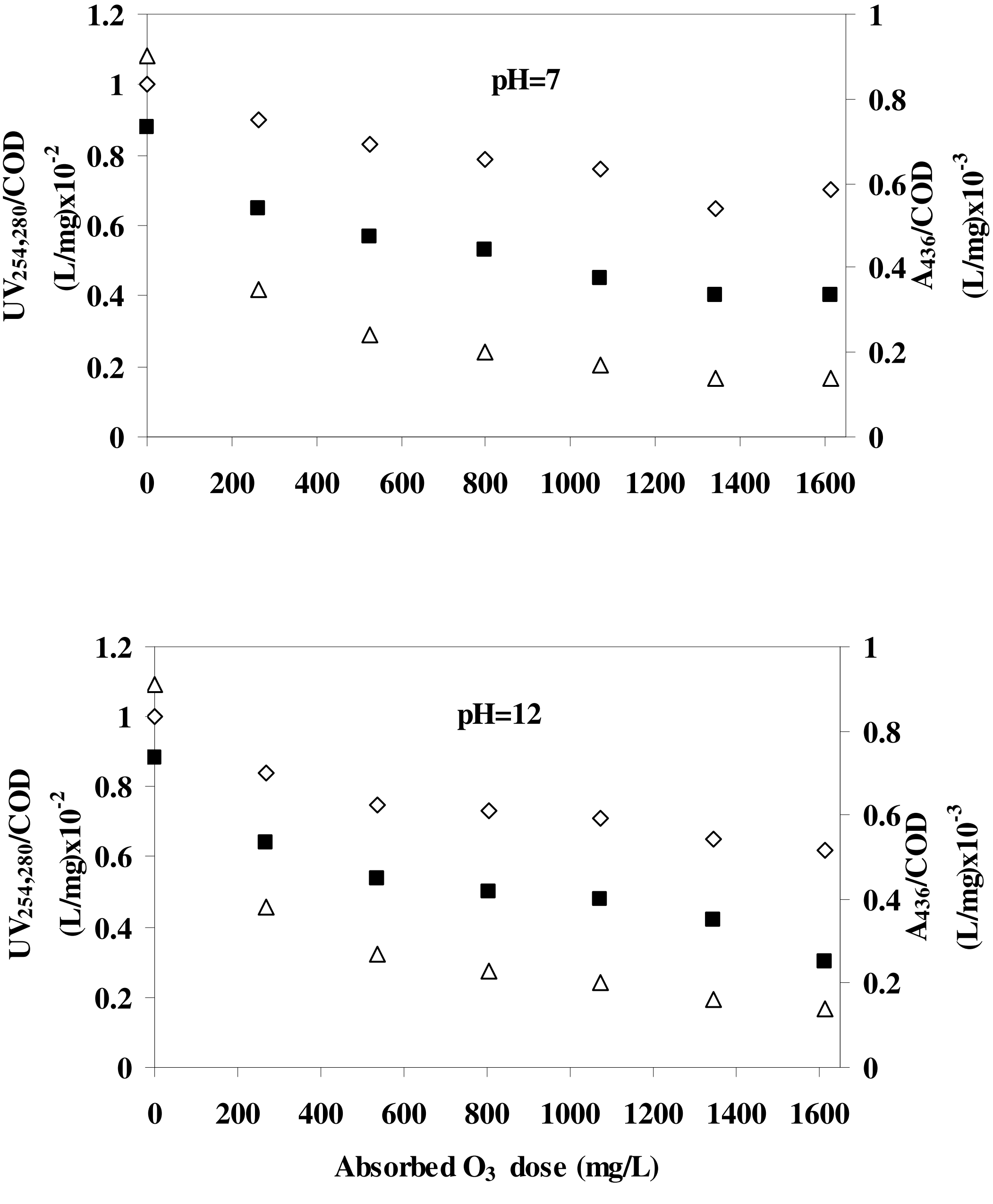

Figure 4.27. Specific absorption ratios of softwood CEH stage bleaching effluent ozonated at different pHs as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

Table 4.6 summarizes overall abatements of parameters for softwood CEH stage bleaching effluent by ozonation. pH did not influence the COD removal rate. It might be the fact that radical scavengers in the reaction medium decrease the available hydroxyl radical concentration in reaction medium. In the previous study (Kıvılcımdan, 2003) application of higher ozone dose (2960 mg/L.h) to the CEH stage bleaching effluent at pH=12, resulted in 52 per COD removal rate. This indicated that application of higher ozone dose was necessary in the presence of high concentration of radical scavengers to increase the treatment efficiency of ozonation. Although pH did not affect the COD removal of CEH stage bleaching effluent, overall removal rate of absorbencies were higher at alkaline pH. Similar to previous results ozonation had more pronounced effect on color removal in this study because of the selective reaction of ozone towards specific functional groups found in the structure of pollutants in the wastewater. BOD_5/COD ratio of effluent was increased from 0.17 to 0.29 by O_3/pH=12 process.

Table 4.6. The effect of pH on overall ozonation treatment performance of CEH stage softwood bleaching effluents.

pH	Removal (%)				BOD_5/COD
	COD	UV_{254}	UV_{280}	A_{436}	
O_3/pH=7	37	59	68	90	0.26
O_3/pH=12	38	64	72	90	0.29

4.4.2. Ozonation of E_1 Stage Effluent

Ozonation was conducted at original pH of E_1 stream (pH=11.3). After one hour treatment pH dropped 2.85 units. Among the bleaching steps, the highest COD was determined for E_1 stage effluent. COD removal rate of E_1 stream was as high as 21 per cent within first ten minutes of ozonation. Overall COD removal rate of E_1 stream was only 37 per cent (Figure 4.28) whereas ozonation efficiency for combined bleaching effluent it was 50 per cent at alkaline pH. Higher ozone dose or extended treatment time may be applied to increase the biodegradability and to remove residual COD of E_1 stream.

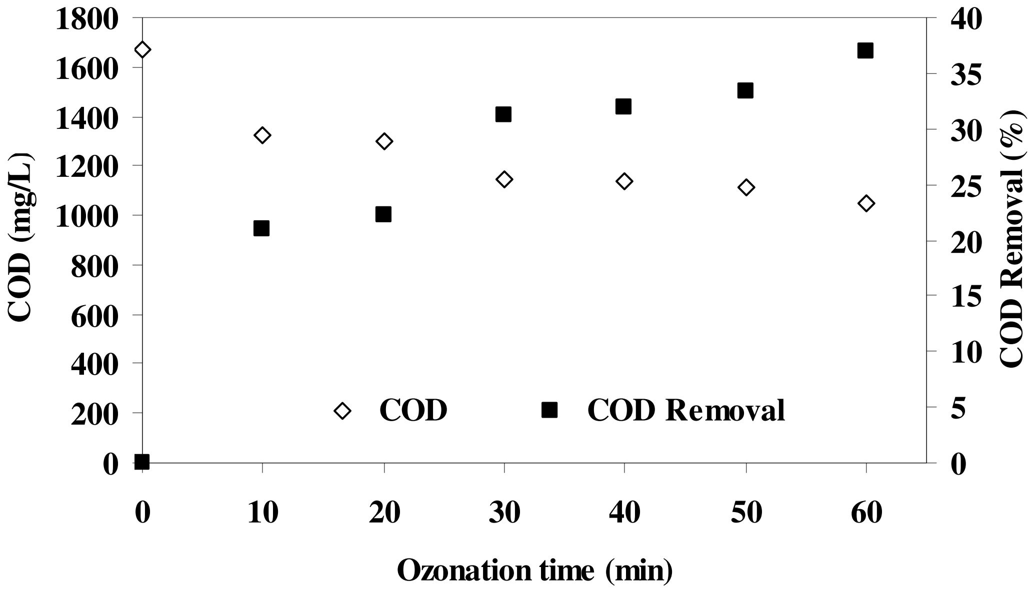

Figure 4.28. COD values and COD removal rates of E_1 stage effluent as a function of ozonation time.

BOD_5 value of E_1 stage effluent has been fluctuated between 218 and 273 mg/L during the ozonation period (Figure 4.29). Biodegradability of raw E_1 stage effluent was very low ($BOD_5/COD_i=0.14$) and this ratio was increased to 0.21 by the application of 1632 mg/L ozone dose.

While 64 per cent AOX abatement was achieved by one hour ozonation of combined bleaching effluent at pH=12, 40 per cent AOX abatement was obtained by one hour ozonation of E_1 stage effluent at pH=11. It was found that enhancement of effluent biodegradability is parallel to AOX removal.

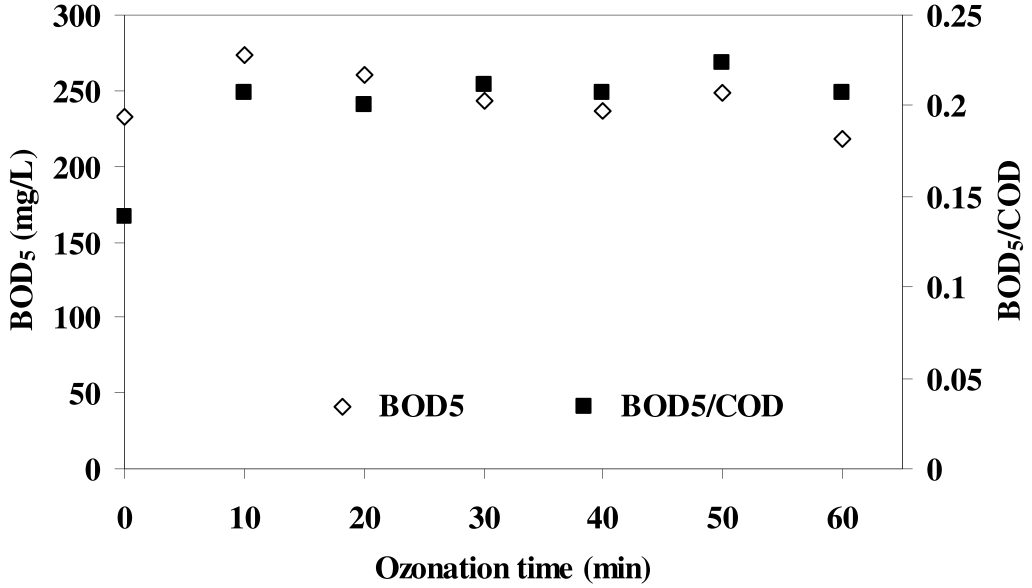

Figure 4.29. BOD_5 values and changes in the biodegradability of E_1 stage effluent by ozonation.

The absorbance values of E_1 stage effluent at 254 and 280 nm were 3.2 and 3.6 times higher than that of combined bleaching effluent, respectively. As residual color causing lignin was extracted from the pulp in E_1 stage, the A_{436} value was 4.8 times higher than the combined bleaching effluent. Absorbance removals at 254, 280, and 436 nm were very fast within first 30 minute of ozonation period (Figure 4.30). Overall removal rates of UV_{254} and UV_{280} were 70 and 77 per cent for E_1 stage effluent, respectively.

Ozonation had significant contribution for the removal of highly colored compounds from pulp mill effluent. Although E_1 stream was the most colored stream among all bleaching streams, 93 per cent color abatement was achieved after one hour ozonation. On the other hand 91 per cent color removal was obtained by ozonation of combined bleaching effluent at pH=12. Compared to the results of previous studies (Bijan and Mohseni, 2004; Wang et al., 2004) done with the lower ozone dose, higher color removal performance was achieved in this study.

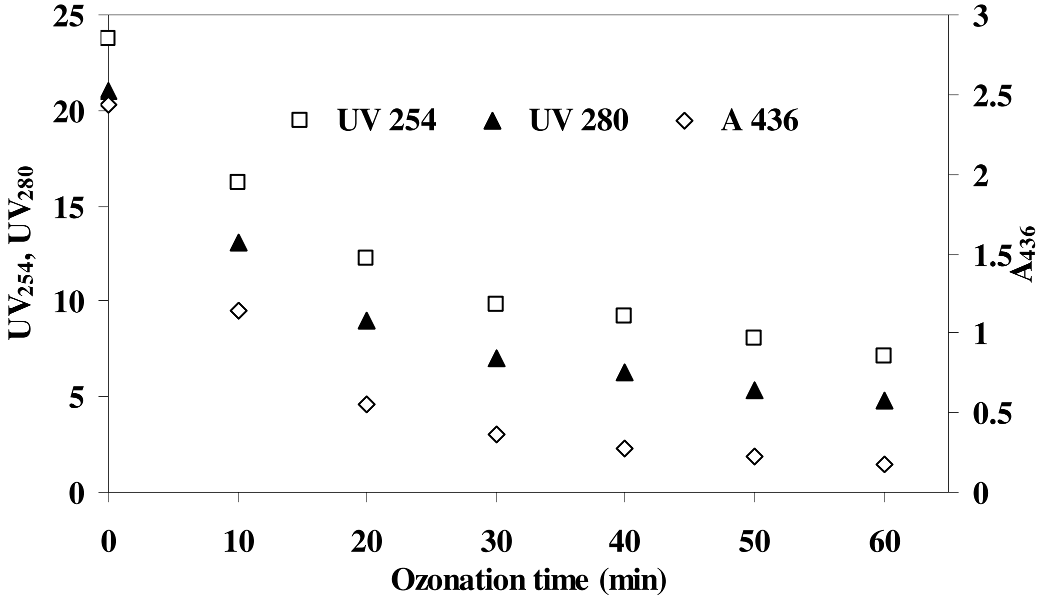

Figure 4.30. Changes in UV_{254}, UV_{280}, and A_{436} values of ozonated E_1 stage effluent by ozonation.

Figure 4.31 depicts the specific absorption ratios of E_1 stage effluent as a function of absorbed ozone dose. UV_{280}/COD and UV_{436}/COD ratios of ozonated E_1 stream were higher than that of ozonated combined bleaching effluent.

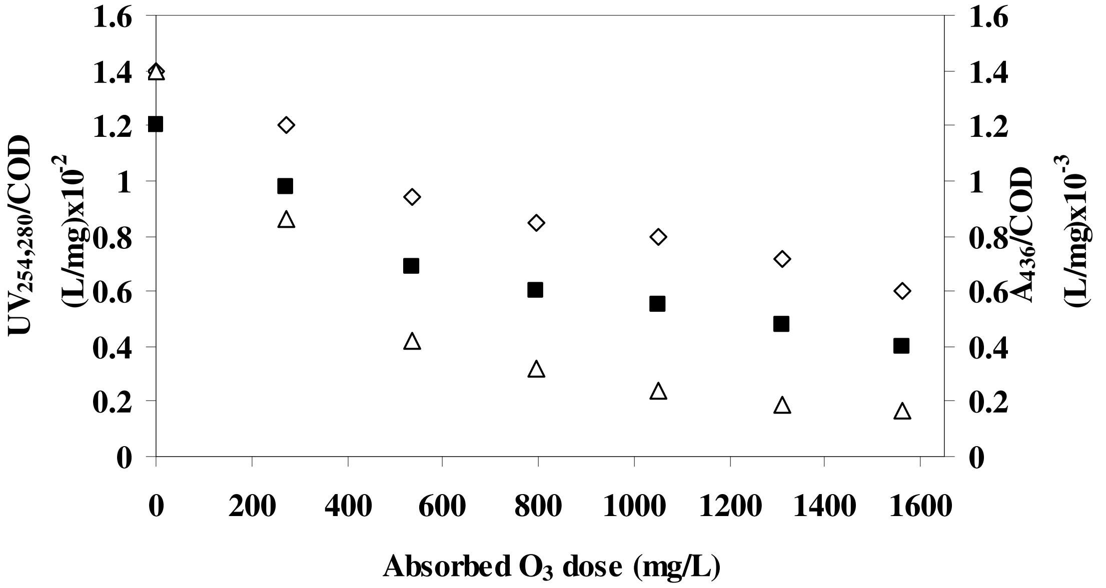

Figure 4.31. Specific absorption ratios of softwood E_1 stage effluent as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

4.4.3. Ozonation of H Stage Effluent

Since softwood H stream had the highest AOX content among the multistage bleaching streams it was segregated and subjected to ozonation at its original pH (pH=9). Figure 4.32 depicts COD reduction rate of H stage effluent as a function of treatment time. Although slow initial COD abetment rate of H stage effluent was obtained by ozonation, overall reduction rate was not different from the values of E_1 and CEH stage effluents. At the end of ozonation process 1.4 unit drops in pH was observed for H stream, whereas 2.47 unit drops in pH was observed for combined bleaching effluent by ozonation at alkaline pH.

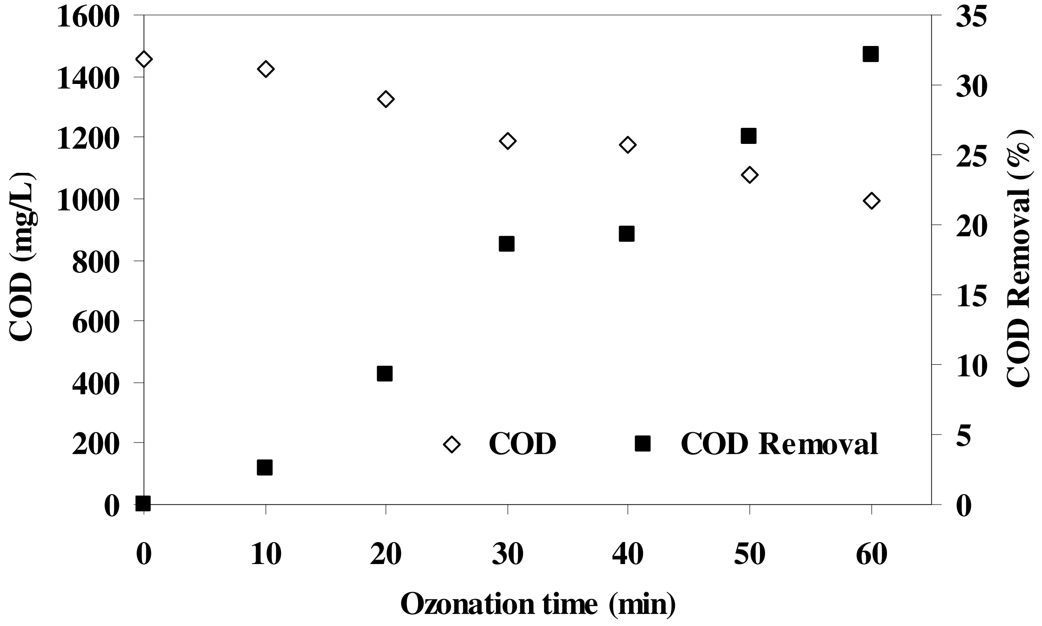

Figure 4.32. COD values and COD removal rates of ozonated softwood H stage effluent.

BOD_5 value of H stage effluent was remained almost constant through ozonation period. Similar to ozonation of the E_1 stage effluent BOD_5/COD ratio of H stage effluent was not improved considerably (Fig. 4.33). Treated H stream effluent still contained high amount of AOX which reduced the biodegradability of wastewater.

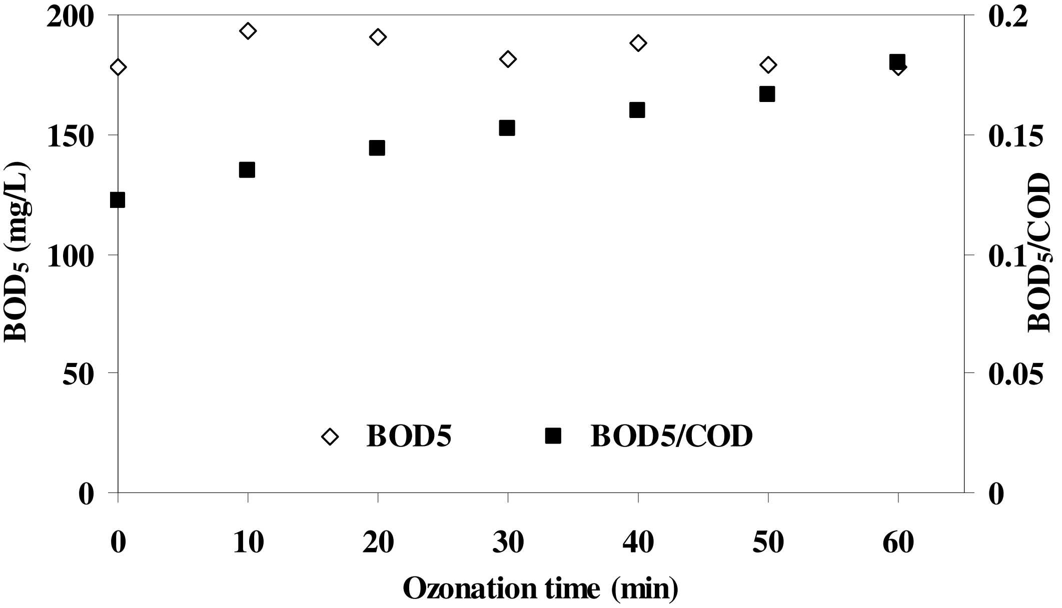

Figure 4.33. BOD$_5$ values and changes in the biodegradability of softwood H stage effluent by ozonation.

The absorbance values of H stage effluent at 254 and 280 nm were more than two folds higher than that of the combined bleaching effluent. By application of one hour ozonation process to H stage effluent 58, 63, and 76 per cent abatements were achieved for UV$_{254}$, UV$_{280}$, and A$_{436}$, respectively (Figure 4.34).

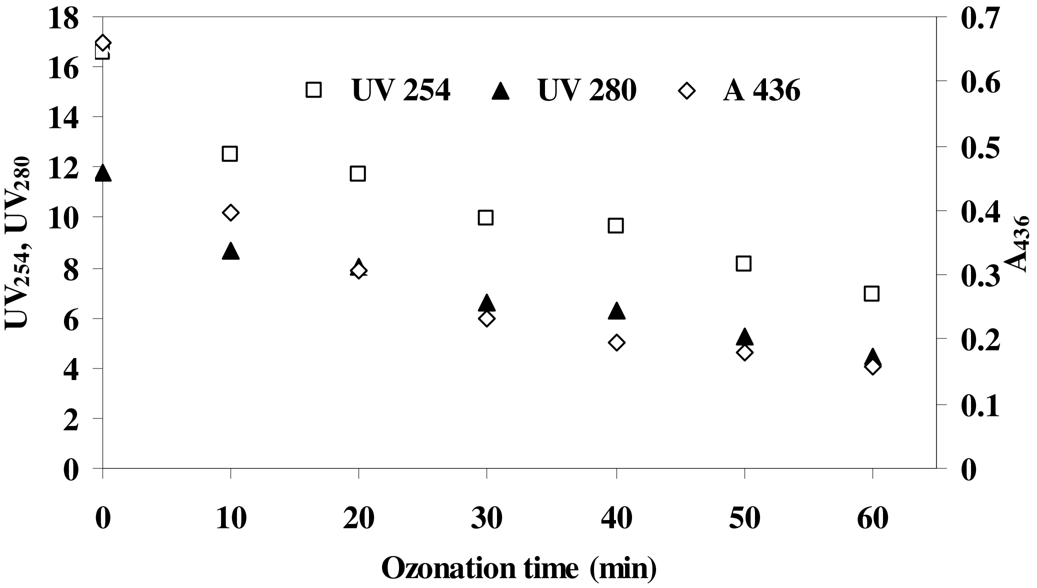

Figure 4.34. Changes in UV$_{254}$, UV$_{280}$, and A$_{436}$ values of softwood H stage effluent by ozonation.

Figure 4.35 depicts the specific absorption ratios of H stream effluent as a function of absorbed ozone dose. The UV_{436}/COD ratio of H stage effluent was less than the E_1 stage effluent. Similar to the previous results obtained by ozonation of E_1 stage effluent, specific absorbance ratios were reduced significantly in initial period of ozonation. For H stage effluent higher ozone absorption was observed in the treatment period. Contrary to higher ozone absorption (1586 mg/L.h) lower treatment efficiency was achieved for H stage compared to the absorbed ozone dose (1562 mg/L.h) and treatment efficiency of E_1 stage effluent.

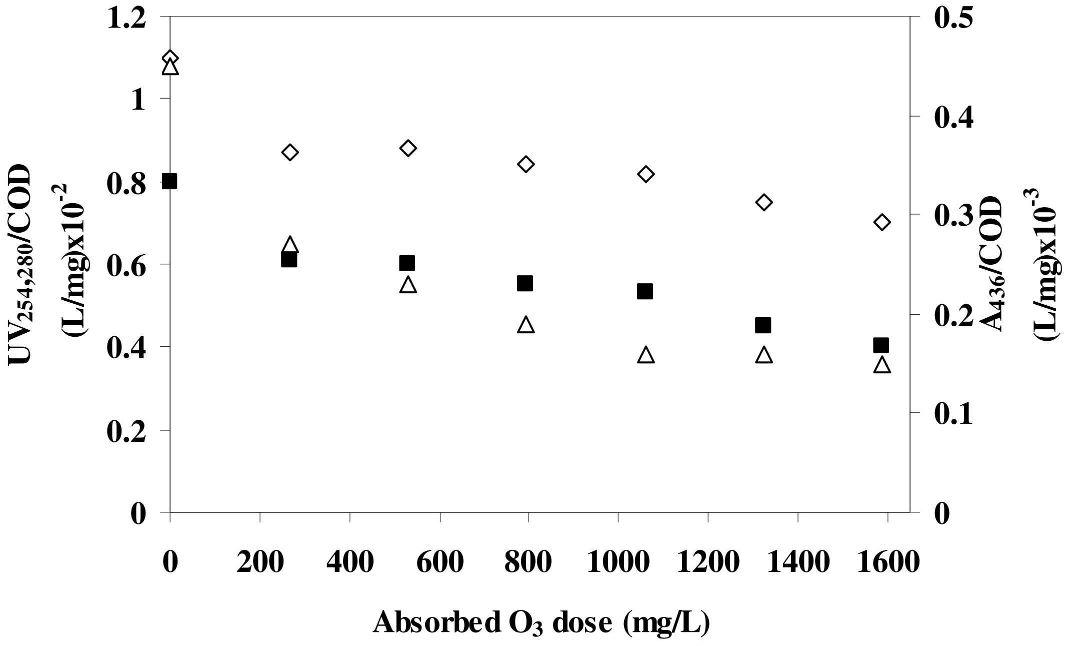

Figure 4.35. Specific absorption ratios of softwood H stage effluent as a function of absorbed ozone dose (UV_{254}/COD; ◊, UV_{280}/COD; ■, A_{436}/COD; Δ).

Table 4.7 summarizes the results of overall ozonation treatment performance for different streams of softwood bleaching effluent. Treatment efficiency was enhanced by increasing the pH of effluent for combined and CEH stage bleaching effluents. Combined and CEH stage bleaching effluents were selected for subsequent activated sludge treatment since they have relatively high BOD_5/COD ratios and higher flow rates compared to the E_1 and H stages effluents.

Table 4.7. The effect of stream segregation on overall ozonation treatment performance of softwood bleaching effluents.

pH	Removal (%)					BOD_5/COD
	COD	AOX	UV_{254}	UV_{280}	A_{436}	
CEHDED-O_3/pH=7	41	62	74	79	86	0.21
CEHDED-O_3/pH=9	40	ND	77	79	88	0.24
CEHDED-O_3/pH=12	50	64	78	83	91	0.30
CEH O_3/pH=7	37	57	59	68	90	0.26
CEH O_3/pH=12	38	61	64	72	90	0.29
E_1-O_3/pH=11	37	40	70	77	93	0.21
H-O_3/pH=9	32	66	58	63	76	0.18

ND: not determined

4.5. Biological Treatment of Pretreated Bleaching Effluent

Biological treatment is a less expensive and more effective process for eliminating organic pollutants in wastewater. Unfortunately, not all compounds are biodegradable in pulp mill effluent. Therefore, a chemical pretreatment is necessary in order to increase the biodegradability of wastewater, although chemical treatment is expensive. The aim of combining an unavoidable chemical oxidation with a biological process is to minimize the amount of oxidants needed and thus to reduce the operating costs.

In this study ozonated CEH and combined bleaching effluents were mixed with the cardboard and chemical recovery streams of Kraft mill. Combined pulp mill effluent was subsequently fed to biological reactor containing activated sludge, which was previously acclimated to Kraft pulp mill effluent. Raw integrated Kraft pulp mill effluent was also treated by activated sludge process in order to compare the obtained results. Depending upon the results of a previous study (Boyden et al., 1994) F/M ratio was selected as 0.3 in activated sludge process. Oxygen uptake rate of sludge was determined to estimate biological activity of activated sludge. Biomass change in activated sludge reactor was negligible during experiment due to the relatively low substrate to biomass ratio. pH of wastewater was also constant during the activated sludge treatment period. Treatment performance of activated sludge was evaluated by changes in COD_s and OUR. Four parallel experiments were performed for effluents containing pretreated streams and presented as run 1-4 in Figure 4.36 - 4.40.

Pre-ozonated CEHDED/pH=7 effluent together with other effluents (cardboard and chemical recovery stream) and raw effluent were biologically treated by activated sludge for 24 hour treatment period. Although COD_s removals for pre-ozonated combined and raw effluents were almost same in the second (44 per cent) and the sixth hours (55 per cent) of activated sludge treatment, at the end of the 24 hour treatment period, COD_s removals were 71 and 61 per cent, respectively. Since low molecular weight biodegradable compounds, which are derived from degradation of lignin in the bleaching process, constitute the small portion of pulp effluent (Colberg, 1988; Field et al., 1988), treatment efficiency of raw pulp mill effluent was lower than the pre-ozonated sample. Similar COD_s abatement was achieved for raw hardwood Kraft bleaching effluent with the F/M ratio of 0.85-2.86 (Boyden et al., 1994).

It is important to point out that, 67 per cent AOX removal was achieved for pre-ozonated combined effluent, together with a significant decrease in COD_s at the end of 24 hour activated sludge process. Pre-ozonated bleaching streams constituted half of the feeding mixture and AOX removal rate of raw effluent was 1.7 times lower than that of the pretreated effluent. It can be concluded that AOX removal was enhanced by pre-ozonation of bleaching effluent.

Since activity of sludge is directly proportional to its O_2 consumption rate, OUR measurement was conducted during the treatment period. As expected, initial OUR of pre-ozonated effluent was higher than that of raw effluent. OUR of pretreated sample rapidly dropped from 52 mg/L.h to 1 mg/L.h at the end of 24 hour treatment process (Figure 4.36).

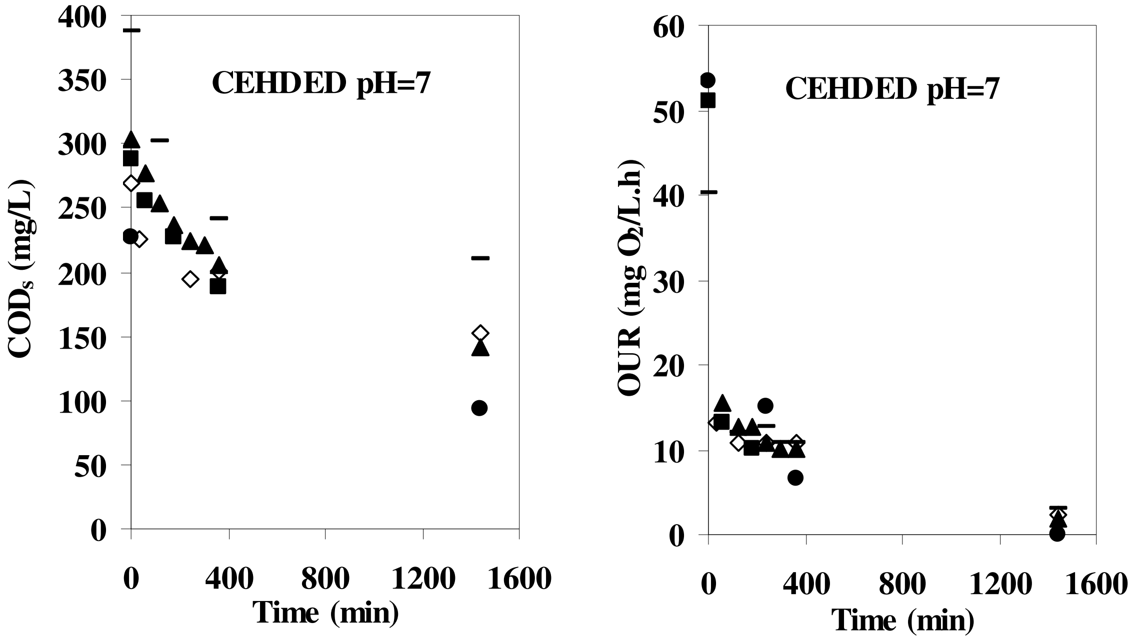

Figure 4.36. Treatment of pulp mill effluent containing pre-ozonated combined bleaching effluent at pH=7 by activated sludge process (run 1◊; run 2 ■; run 3 ▲; run 4●; raw▬).

Pre-ozonated CEHDED/pH=12 effluent together with other effluents of mill was treated by activated sludge. Performance of activated sludge treatment was slightly higher at alkaline pH as expected since BOD_5/COD ratio of effluent at alkaline pH was higher for the effluent pre-ozonated and 72 per cent overall COD_s removal was obtained at the end of 24 hour treatment period.

OUR rapidly dropped from 48 mg/L.h to 2.4 mg/L.h at the end of the biological treatment period of pretreated combined bleaching effluent (Figure 4.37). Activated sludge was also very effective for AOX removal for pretreated wastewater and 70 percent AOX reduction was achieved in 24 hour activated sludge treatment period.

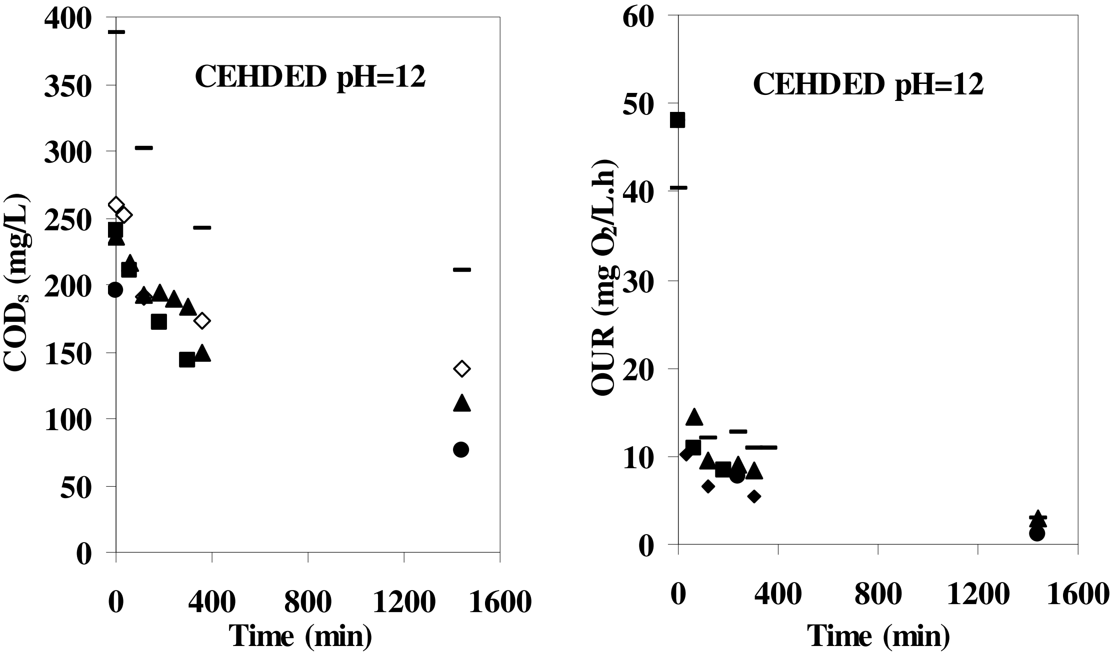

Figure 4.37. Treatment of pulp mill effluent containing pre-ozonated combined bleaching effluent at pH=12 by activated sludge process (run 1◊; run 2 ■; run 3▲; run 4●; raw▬).

The mixture of pre-ozonated CEH stage bleaching effluent and other effluents were subsequently treated by activated sludge to evaluate the effect of stream segregation on biological treatment efficiency. Figure 4.38 depicts variation of COD_s and OUR as a function of treatment time for the mixture of pre-ozonated CEH at pH=7 and other effluents. For pretreated effluent 68 per cent overall COD_s removal was obtained in the biological treatment together with the 60 per cent AOX removal, whereas 61 and 39 per cent COD_s and AOX abatements were achieved for raw effluent. Although ozonated bleaching effluent constituted only 25 per cent of feeding mixture in activated sludge process, treatment efficiency of pretreated effluent was higher than treatment performance of raw effluent.

Initial OUR of CEH stage bleaching effluent was lower than the combined bleaching effluent as expected because, BOD_5/COD ratio was lower for pretreated CEH stage bleaching effluent. By progress of activated sludge process OUR of pre-ozonated CEH stage bleaching effluent decreased and reached to a value of 1.2 mg O_2/L.h at the end of the 24 hour.

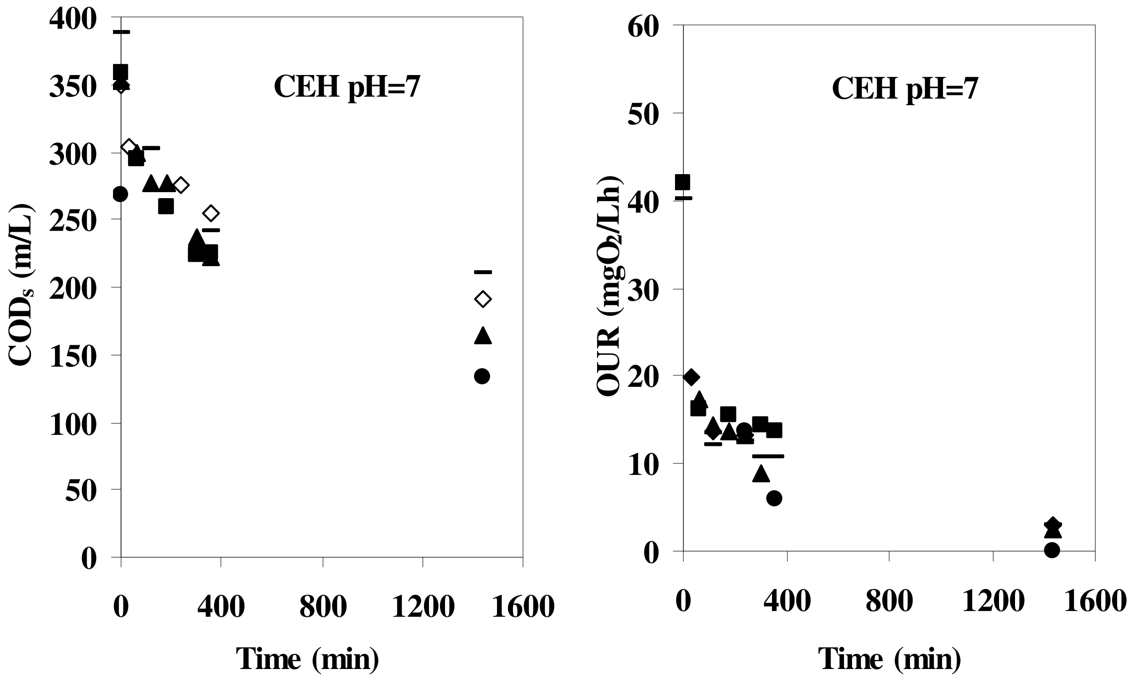

Figure 4.38. Treatment of pulp mill effluent containing pre-ozonated CEH stage bleaching effluent at pH=7 by activated sludge process (run 1◊; run 2 ■; run 3▲; run 4●; raw▬).

Application of activated sludge treatment to the mixture of pre-ozonated bleaching effluent (CEH) at pH=12 and other effluents resulted in 68 per cent COD_s and 63 per cent AOX abatements (Figure 4.39). Since the pre-ozonation efficiencies at pH=7 and pH=12 were almost the same, subsequent biological treatment performance was also the same. Fergusson (1994) found similar results for the AOX removal performance of activated sludge process for the treatment of raw chlorination and extraction stages of Kraft pulp mill effluent. OUR of pre-ozonated CEH stage bleaching effluent at pH=7 had the similar trend to the pre-ozonated CEH stage effluent at pH=12.

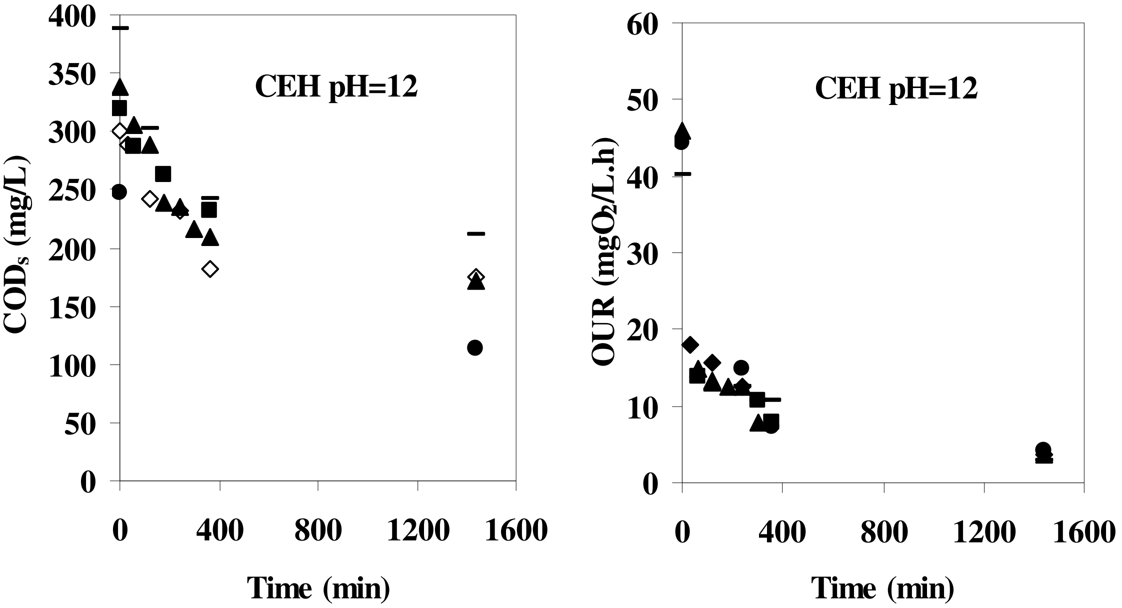

Figure 4.39. Treatment of pulp mill effluent containing pre-ozonated CEH stage bleaching effluent at pH=12 by activated sludge process (run 1◊; run 2 ■; run 3▲; run 4●; raw▬).

Activated sludge process was also applied to the mixture of pretreated CEHDED by O_3/ $H_2O_2$15 mM /pH=7 and other effluents of plant. Initial COD value of this mixture was less than the other mixture and the highest (77 per cent) COD$_s$ removal was obtained with this mixture in activated sludge process (Figure 4.40).

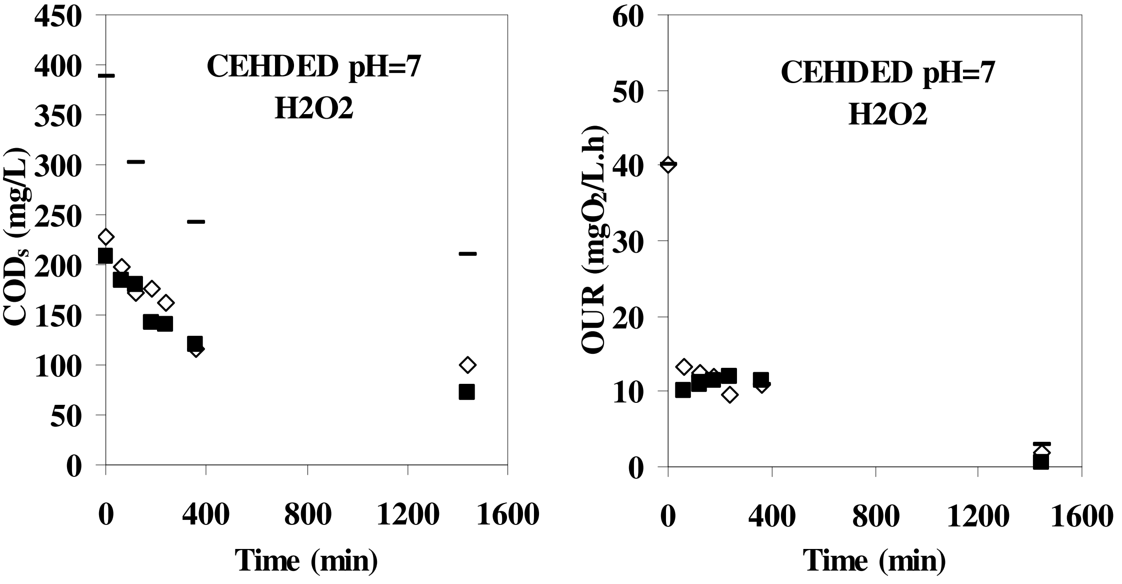

Figure 4.40. Treatment of pulp mill effluent containing O_3/H_2O_2 pretreated combined bleaching effluent at pH=7 by activated sludge process (run 1◊; run 2 ■; raw▬).

Figure 4.41 depicts the average COD$_s$ changes in activated sludge treatment of raw and pre-ozonated effluents as a function of time. Depending upon the initial COD value of wastewater in 370 to 540 mg/L range, performance of activated sludge process changed. COD$_s$ depletion rate was decreased when activated sludge was fed with effluent which had the higher COD. Since the presence of high amount of biorefractory substances COD$_s$ reduction was less in raw effluent (Chudoba, 1985). Removal efficiency of activated sludge process achieved in 24 hours treatment period was 61 per cent for raw wastewater and independent of the ozonation pH, this value ranged from 68 to 77 per cent for wastewater contained CEH stage bleaching effluent and combined bleaching effluent.

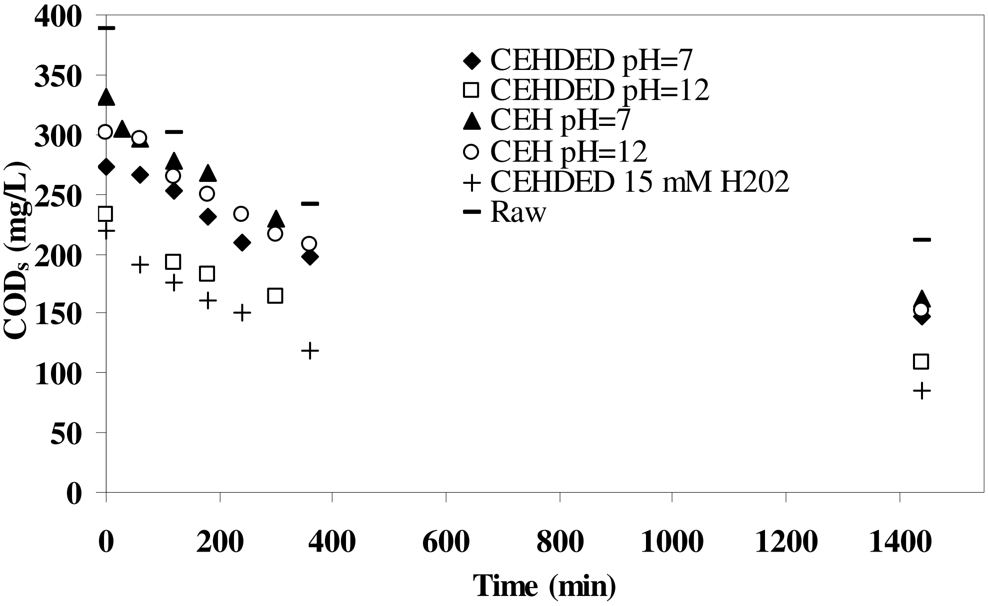

Figure 4.41. Changes in COD$_s$ values of raw and pre-ozonated effluents as a function of time in activated sludge treatment.

Figure 4.42 depicts the OUR profile of raw and pretreated effluents as a function of time in activated sludge treatment. Quite similar rates were obtained in OUR of pretreated effluent. However the lowest OUR was obtained in raw effluent.

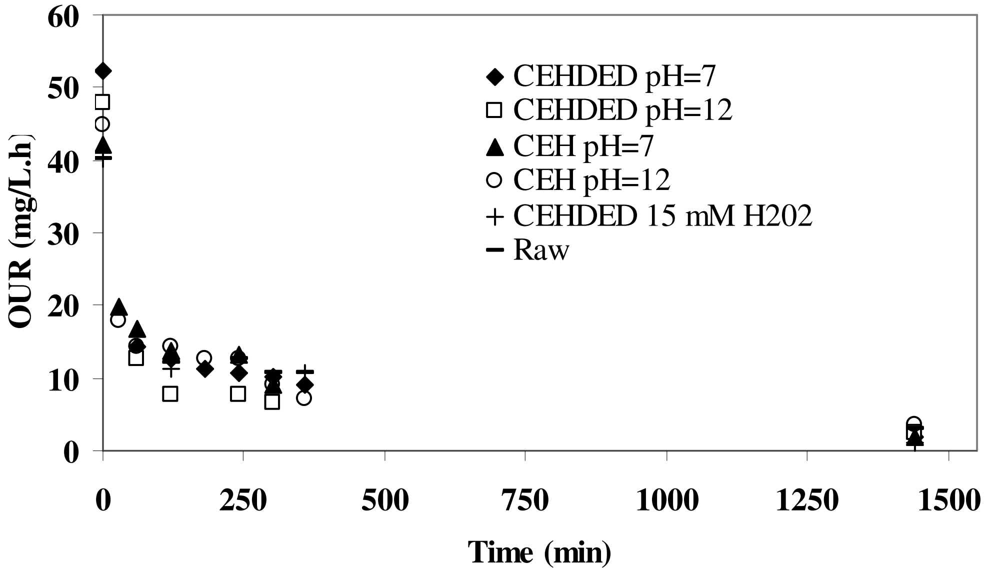

Figure 4.42. Changes in OUR values of raw and pretreated effluents as a function of time in activated sludge treatment.

Ozonation of bleaching effluents led to enhancement in the treatment efficiency of activated sludge process. This effect more pronounced for AOX removal. Treatment efficiencies of activated sludge process are presented in Table 4.8.

Table 4.8. Treatment efficiency of Kraft pulp mill effluent by activated sludge process.

Type of effluent/Treatment	COD_s (%)	AOX Removal (%)
Raw combined effluent	61	39
Combined effluent/CEH -O_3 pH=7	68	60
Combined effluent/CEH- O_3 pH=12	68	63
Combined effluent/CEHDED-O_3 pH=7	71	67
Combined effluent/CEHDED-O_3 pH=12	72	70
Combined effluent/CEHDED-O_3-H_2O_2 pH=7	77	N.D.

5. CONCLUSION

A combined process consisted of ozonation and activated sludge process was applied to integrated pulp mill effluent in order to increase the quality of wastewater. As a result of the characterization of different streams of pulp and paper mill by determining AOX, COD, and BOD_5, the combined and segregated streams of bleaching process, which contained mainly non-biodegradable compounds were pretreated by ozonation with 1632 mg/L.h ozone dose. Subsequently, a mixture of pretreated bleaching effluent and other streams of pulp and paper mill were subjected to activated sludge treatment.

When the softwood was used as raw material, COD and AOX load of pulp mill effluent was found considerably high. Major source of AOX in pulp mill effluent was found as bleaching process. AOX and color are very important parameters to evaluate the detrimental effects of pulp and paper mill effluent to the environment. However, in Turkey, these parameters are not part of the environmental regulations. Considering adverse effects of AOX and color to the environment and the possible future membership of Turkey in the European Union, it is essential for the country to adapt the environmental regulations in accordance with the European Union Regulations.

Elevation of ozonation pH from 7 to 12 resulted in higher COD removal rate together with a moderate alteration in BOD_5/COD for both hardwood and softwood combined bleaching effluents. COD and absorbance abatements of combined bleaching effluent were higher than that of CEH effluent, which had higher pollution load. pH effect on COD removal was not observed for the ozonation of CEH stage bleaching effluent. Applied ozone dose may not be sufficient for CEH stream to remove residual COD of oxidation intermediates at the same rate and efficiency, as in the case of combined bleaching effluent. Therefore different ozone doses might be applied to each effluent. pH controlled ozonation may also enhance the treatment performance, since pH of each effluent decreased by the progress of ozonation and radical type oxidation reaction became less important under this condition.

Since the initial AOX value (11.6 mg/L) of combined bleaching effluent was lower than that of CEH effluent (25 mg/L), remaining AOX was still high in CEH effluent after ozonation. Considering the remaining COD, AOX, and absorbance values of ozonated effluents, pretreatment of combined bleaching effluent can be suggested to improve the quality of treated effluent, instead of treatment of segregated bleaching streams.

Addition of 15 mM H_2O_2 to ozonation process at pH=7 enhanced the treatment efficiency for combined bleaching effluent. While COD removal was increased to 57 per cent, BOD_5/COD reached to a value of 0.41 with 1632 mg/L.h ozone dose. For all ozonated effluents, absorbance values exhibited rapid decrease within 10 minutes of ozonation and almost complete color removal was achieved by one hour ozonation.

Ozonation of E_1 effluent which has high in AOX, COD, and color resulted in 40 per cent AOX, 37 per cent COD, and 93 per cent color removals. Although two fold increases in BOD_5/COD was achieved with 1632 mg/L.h ozone dose for E_1 stream, significant amount of AOX remained after pretreatment. E_1 stream effluent consisted of 8 per cent of total effluent flow and 26 per cent of total AOX of pulp mill effluent. Other streams of bleaching process contained considerable amounts of AOX and non-biodegradable compounds, therefore activated sludge treatment for pre-ozonated E_1 stream effluent did not perform.

Pretreatment of bleaching effluent by ozonation either at pH=7 or pH=12 did not significantly affect the overall treatment performance of activated sludge process. Application of activated sludge process to raw pulp mill effluent resulted in 61 per cent COD_s and 39 per cent AOX removals. COD_s removal was enhanced to 77 per cent by pretreatment of combined bleaching effluent (O_3/H_2O_2/pH=7). However, the effluent still contained some recalcitrant compounds which can cause the detrimental effect as a result of continuous release to the environment, so cleaner production technologies should be applied in the pulp and paper production processes to reduce pollutants at the source.

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