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May 2005 Şebnem KOYUNLUOĞLU

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ABBREVIATIONS

NT	**: Natural Tannin**
ST	**: Synthetic Tannin**
BI	**: Biocide I**
BII	**: Biocide II**
GDP	**: Gross Domestic Product**
PVA	**: Polyvinyl Alcohol**
CMC	**: Carboxy Methyl Cellulose**
EPA	**: Environmental Protection Agency**
$OH^{\bullet}$	**: Hydroxyl Radical**
AOPs	**: Advaced Oxidation Processes**
$HO_2^{\bullet}$	**: Hydroperoxide Radical**
$O_2^{\bullet-}$	**: Superoxide Radical Ion**
$O_3^{\bullet-}$	**: Ozonide Radical Ion**
CEFIC	**: Conseil Européen de l'Industrie Chimique**
THMFP	**: Trihalomethane Formation Potential**
TOXFP	**: Total Organic Halide Potential**
OUR	**: Oxygen Uptake Rate**
SWW	**: Synthetic Wastewater**

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LIST OF SYMBOLS

COD : Chemical Oxygen Demand ($mg.L^{-1}$)
COD_o : Initial Chemical Oxygen Demand ($mg.L^{-1}$)
TOC : Total Organic Carbon ($mg.L^{-1}$)
TOC_o : Initial Total Organic Carbon ($mg.L^{-1}$)
UV_{254} : UV Absorbance at 254 nm (cm^{-1})
$UV_{254,o}$: Initial UV Absorbance at 254 nm (cm^{-1})
UV_{280} : UV Absorbance at 280 nm (cm^{-1})
$UV_{280,o}$: Initial UV Absorbance at 280 nm (cm^{-1})
AOX : Adsorbable Organic Halogens ($mg.L^{-1}$)
AOX_o : Initial Adsorbable Organic Halogens ($mg.L^{-1}$)
BOD_5 : 5-day Biochemical Oxygen Demand ($mg.L^{-1}$)
$k_{O3,B}$: Bimolecular Rate Constant for the Reaction Between Ozone and Compound B ($M^{-1}s^{-1}$)
D_A : Molecular Diffusivity of Ozone, (m^2s^{-1})
$C_{B,b}$: Concentration of Compound B in Bulk Phase ($mol.L^{-1}$)
k_L : Liquid Phase Individual Mass Transfer Coefficient (ms^{-1})
N_{Ao} : Absorption Rate of Ozone ($mol.s^{-1}.m^{-2}$)
M_1 : Maximum Physical Absorption Rate at the Interface ($mol.s^{-1}.m^{-2}$)
Ha_2 : Hatta Number for the Irreversible Second-order Gas-liquid Reaction
E : Reaction Factor
LD_{50} : Lethal Dose causing 50% Death in Test Organisms ($mg.L^{-1}$)
LC_{50} : Lethal Concentration causing 50% Death in Test Organisms ($mg.L^{-1}$)
C_{NT} : Concentration of NT ($g.L^{-1}$)
C_{ST} : Concentration of ST ($g.L^{-1}$)
O_{3A} : Amount of Ozone Absorbed (mg)
Y_{O3} : Specific Ozone Absorption Yield (mgO_{3A}/COD_o)
Y_{COD} : COD Removal Yield ($mgCOD/mgO_{3A}$)
D_{O3} : Specific Ozone Dose (mgO_{3o}/COD_o)
k_{COD} : 1st Order COD Abatement Rate Constant (min^{-1})
k_{UV280} : 1st Order UV_{280} Abatement Rate Constant (min^{-1})
OUR : Oxygen Uptake Rate of Heterotrophic Biomass ($mg.L^{-1}.h^{-1}$)
MLVSS : Mixed Liquor Volatile Suspended Solids (mg)
I_{OUR} : The percent Inhibition of Oxygen Uptake Rate (%)
R_B : Oxygen Uptake Rate for Blank ($mg.L^{-1}.h^{-1}$)
R_S : Oxygen Uptake Rate for Test Samples ($mg.L^{-1}.h^{-1}$)
k_La : Volumetric Mass Transfer Coefficient (min^{-1})
$C_{O3,b}$* : Gas-liquid Equilibrium Concentration of Ozone in Bulk Liquid ($mol.L^{-1}$)
$C_{O3,b}$: Concentration of Ozone in Bulk Liquid ($mol.L^{-1}$)
$C_{BI,b}$: Concentration of BI in Bulk Liquid ($mol.L^{-1}$)
r_{BI} : Ozonation Rate of BI ($M.s^{-1}$)

OXIDATION OF REFRACTORY POLLUTANTS WITH OZONE: A CASE STUDY WITH BIOCIDES AND TANNINS USED IN THE TEXTILE INDUSTRY

SUMMARY

The textile dyeing and finishing industry is characterized by its huge water requirement and the variety and complexity of process chemicals employed. The recalcitrance of the final effluent usually originates from the considerable amounts of dyestuffs and auxiliaries all of which are known for their potential toxicity and poor biodegradability although they are not mentioned in the list of priority pollutants. Despite the numerous studies that have already addressed the degradability of dyestuffs present in dyehouse effluent, only few of them pertained the treatability of dye auxiliaries and finishing agents.

In the present study, ozonation of natural and synthetic tannin (NT and ST) which are being frequently applied for the attachment of acid or metal complex dyestuffs onto polyamide (nylon) fibers, as well as two biocides (Biocide I, BI and Biocide II, BII) that are commonly used in the textile fabric finishing process, was investigated. For this purpose, synthetic wastewaters that contained these pollutants were prepared and oxidized by ozone under different reaction conditions. In the first part of the experimental work, ozonation conditions were optimized for the efficient oxidation of all selected textile chemicals. The effects of ozone dose and reaction pH on the process efficiency and pollutant abatement kinetics were evaluated. For NT and ST, the ozone feed rate ranged between 450-1100 mg/h and the reaction pH's were 3.5 (the actual application pH of tannins) and 7.0. In the case of the two textile biocides, the ozone feed rate varied between 500-900 mg/h and the reaction pH's were selected as 7.0 (the natural application pH of the studied biocides) and pH 12.0. The ozonation efficiency was assessed in terms of the collective environmental parameters COD (Chemical Oxygen Demand), TOC (Total Organic Carbon), UV_{254} (absorbance at 254 nm; presenting unsaturated bonds and ring moieties) and UV_{280} (absorbance at 280 nm; presenting aromaticity and characteristic UV absorbance). In addition to the above indicated parameters, AOX (Adsorbable Organic Halogens) was followed during ozonation of BI at varying pH. Biotreatability changes of the selected textile industry pollutants were evaluated in terms of the BOD_5 (5-day Biochemical Oxygen Demand) parameter by conducting measurements before and after ozonation under preliminary optimized reaction conditions. In addition, in order to evaluate the acute toxicity of the studied chemicals, activated sludge inhibition experiments were carried out for raw and ozonated samples. In the final part of the experimental work, a kinetic study was conducted for the textile finishing agent Biocide I of which the exact molecular structure was known. The second-order bimolecular rate constant of the direct reaction between molecular ozone and Biocide I was determined.

As a result of the experiments conducted, only 28 % COD and 16 % TOC removal were achieved after ozonation of NT for 60 min at pH = 7.0 at an ozone feed rate of 900 mg/h. Under the same reaction conditions, 64 % COD and 47 % TOC removal was achieved for ST. UV_{280} removal rate constant was approximately 10 fold higher for NT and 3 fold higher for ST compared to the COD removal rate constants, indicating the faster removal of the polyaromatic tannin structure. In parallel to the final, decreased BOD_5 value obtained for NT after 40 min ozonation at pH = 3.5 at a dose of 900 mg/h, its inhibitory effect towards activated sludge showed no change when subjected to ozonation. On the other hand, the BOD_5 value found for ST increased from 6 mg/L to 135 mg/L under the same reaction conditions, which was in agreement with the complete elimination of heterotrophic biomass inhibition after exposure to 600 mg ozone.

According to the above indicated experimental findings, due to its lower COD and TOC content as well as considerable improvement in biodegradability after pre-treatment with ozone, ST can be recommended as an auxiliary chemical for the nylon dyeing process instead of NT.

In the case of textile biocides BI and BII, the COD removal efficencies increased from 61 % and 54 % to 85 % and 87 %, respectively, when ozonation pH was elevated from 7.0 to 12.0 after 120 min ozonation at a rate of 900 mg/h. In the same manner, the TOC removal rates obtained for BI and BII increased from around 10 % at pH = 7.0 to 38 % for BI and to 56 % for BII at pH = 12.0 after 120 min ozonation (1800 mg ozone). As expected, UV_{254} and UV_{280} removals were almost the same for both pH values for BI and BII showing that ozone decomposition to $OH^{\bullet}$ at high pH did not improve the destruction of the structure of the biocides. AOX removal (BI) appeared to be even faster than dearomatization, according to the obtained abatement rate constants (k_{AOX} = 0.250 min^{-1} > k_{UV280} = 0.056 min^{-1} > k_{UV254} = 0.028 min^{-1}) at pH = 7.0. Dehalogenation was complete after application of 300 mg ozone at pH = 7.0. After 60 min ozonation at pH = 7.0 at a feed rate of 600 mg/h the activated sludge inhibitory effect of the tested biocides was significantly reduced indicating that ozonation appeared to be an efficient treatment method for the partial oxidation of both textile biocides.

In addition, the bimolecular reaction rate constant for ozonation of BI was found as 43 $M^{-1}s^{-1}$, which lies within the range of rate constants for direct reactions of ozone with aromatic compounds.

REFRAKTER KİRLETİCİLERİN OZON İLE OKSİDASYONU: TEKSTİL ENDÜSTRİSİNDE KULLANILAN TANNİN VE BİYOSİTLER İLE ARITILABİLİRLİK ÇALIŞMASI

ÖZET

Türkiye'deki başlıca endüstrilerden biri olan tekstil endüstrisi, enerji, su ve kimyasal tüketiminin yoğun olduğu bir sektördür. Elde edilmek istenen ürün ve kullanılan tekstil hazırlama, boyama ve apreleme işlemlerine bağlı olarak birçok yardımcı kimyasal kullanılmaktadır. Kullanılan yardımcı kimyasalların çoğu, kompleks yapıya sahip, biyolojik arıtmaya dirençli, refrakter kimyasallardır. Bu sebeple, ozon ile oksidasyon, bu kirleticilerin arıtılması için alternatif bir yöntemdir. Tekstil endüstrisinde kullanılan boyaların arıtılabilirliği ile ilgili birçok çalışma yapılmış olmasına rağmen, kullanılan yardımcı kimyasallar ile ilgili çalışma çok azdır.

Bu çalışmada, tekstil endüstrisinde yaygın olarak asit ve metal kompleks boyama işleminde kullanılan, boyaların naylon kumaşta tutulabilmesi için uygulanan doğal ve sentetik tanninlerin (DT ve ST) ve ayrıca apreleme prosesinde kullanılan biyositlerin (Biyosit I, BI, ve Biyosit II, BII) ozonlama prosesi ile oksidasyonu incelenmiştir. Bunun için söz konusu kimyasalları içeren sentetik boya ve apreleme atıksuları hazırlanmış ve farklı proses koşullarında ozonlamaya tabi tutulmuştur. Bu şekilde ozonlama prosesi için en uygun reaksiyon koşulları belirlenmiştir. Doğal Tannin ve Sentetik Tannin için optimum reaksiyon koşullarının belirlenmesi için 450, 750, 900, ve 1100 mg/h ozon dozlarında ve pH = 3.5'da (tanninlerin uygulama pH'ı) ozonlama reaksiyonları gerçekleştirildikten sonra ozonlama kinetiğine pH'ın etkisini inceleyebilmek için 900 mg/h ozon dozunda pH = 3.5 ve pH = 7.0'de ozonlama reaksiyonları karşılaştırılmıştır. Biyosit I ve Biyosit II için de ozon dozunun (500, 750, ve 900 mg/h) ve reaksiyon pH'ının (7.0 ve 12.0) ozonlama proses verimine ve kinetiğine etkileri belirlenmiştir. Bu çalışmalar sırasında, kollektif çevre parametrelerinden KOİ (Kimaysal Oksijen İhtiyacı), TOK (Toplam Organik Karbon), UV_{254} ve UV_{280} (254 nm ve 280 nm dalga boylarında UV absorbans değerleri) ve Biyosit I için bu parametrelere ek olarak ozonlama süresi boyunca AOX (Adsorplanabilir Organik Halojen) takip edilmiştir. Kirleticilerin biyolojik olarak arıtılabilirlikleri, ozonlamadan önce ve sonra yapılan $BOİ_5$ (5. gün Biyokimyasal Oksijen İhtiyacı) ölçümleri ile değerlendirilmiştir. Bunun yanında kirleticilerin toksik etkilerini değerlendirmek için ham ve ozonlanmış kimyasallar ile aktif çamur inhibisyon deneyleri yapılmıştır. Çalışmanın son aşamasında, ise moleküler yapısı tam olarak bilindiğinden Biyosit I için kinetik çalışmalar yapılmış ve Biyosit I'in ozon ile doğrudan reaksiyonuna ait 2. dereceden hız sabiti belirlenmiştir.

Yapılan deneyler sonucunda, DT için pH = 7.0'de 900 mg/saat ozon dozu ile 60 dakika ozonlama sonucunda ancak %28 KOİ ve %16 TOK giderimi elde edilmiştir. ST için ise aynı koşullarda %64 KOİ ve %47 TOK giderimi sağlanmıştır. Birinci dereceden UV_{280} giderim hız sabiti KOİ giderim hız sabiti ile karşılaştırıldığında, DT için 10 kat ST için ise 3 kat hızlıdır. Bu, poliaromatik tannin yapısının daha hızlı giderildiğini göstermektedir. DT için, $BOİ_5$ değerinin ozonlama sonrası (600 mg

ozon) az miktarda azalmasına paralel olarak aktif çamur inhibisyon etkisinde de bir değişiklik olmamıştır. DT'nin aksine, ST'nin ozonlama sonrası $BOİ_5$ değeri 6 mg/L'den 135 mg/L değerine artarken, aynı zamanda aktif çamur inhibisyonu da tamamen elimine edilmiştir.

Belirtilen deneysel sonuçlara bağlı olarak, daha düşük KOİ-TOK içeriği ve biyolojik arıtılabilirliğindeki önemli artış göz önüne alınırsa, naylon boyama prosesinde yardımcı kimyasal olarak NT yerine ST'nin kullanımı ve ST'nin ön arıtımı için de ozon ile oksidasyon yöntemi önerilebilir.

BI ve BII için ise, 900 mg/saat ozon dozu ile 120 dakika ozonlama sonuçları karşılaştırıldığında, pH 7.0'den 12.0'ye yükseltildiğinde, KOİ giderimleri %61 ve %54'ten %85 ve %87'ye artmıştır. KOİ giderimlerine ek olarak, 900 mg/saat ozon dozu ile 120 dakika ozonlama (1800 mg ozon) sonucu pH = 7.0'de BI ve BII için yaklaşık %10 olan TOK giderimi, pH =12.0'ye çıkarıldığında, sırası ile %38 ve %56 olmuştur. BI ve BII için UV_{280} ve UV_{254} giderimlerinde pH 7.0'den 12.0'ye çıkarıldığında bir iyileşme gözlenmemiştir. Bu, yüksek pH'ta ozonun bozunması sonucu oluşan $OH^{\bullet}$ radikallerinin biyosit yapılarının parçalanmasını iyileştirmediğini göstermektedir. Giderim hızlarına bakıldığında ($k_{AOX} = 0.250\ dk^{-1} > k_{UV280} = 0.056\ dk^{-1} > k_{UV254} = 0.028\ dk^{-1}$), BI için AOX gideriminin aromatik yapının bozunmasından daha önce gerçekleştiği söylenebilir. Dehalojenizasyonun pH = 7.0'de 300 mg ozon uygulanmasından sonra tamamlandığı gözlenmiştir. Aktif çamur inhibisyon deneylerine göre, BI ve BII'nin 600 mg/saat ozon dozunda pH = 7.0'de 60 dakika ozonlanması sonucu toksisiteleri tamamen giderilmiştir. Ozon ile arıtma sonucu elde edilen KOİ giderimleri ve toksisite sonuçları ile BI için AOX giderimine bağlı olarak, ozon ile oksidasyonun, BI ve BII arıtımı için uygun bir arıtma prosesi olduğu sonucuna varılabilir.

Bunların yanında, BI için yapılan kinetik çalışma sonucunda, BI'in ozon ile doğrudan reaksiyonuna ait 2. dereceden hız sabiti 43 $M^{-1}s^{-1}$ olarak belirlenmiştir. Bu değer, ozonun aromatik yapıdaki bileşikler ile direk reaksiyonlarına ait 2. dereceden hız sabiti aralığında bulunmaktadır.

1. INTRODUCTION

Textile industry is one of the most important industrial sectors playing an integral role in the Turkish economy. Turkey has become the EU's number three clothing supplier (behind China/Hong Kong, and Italy) along with Mexico and the number one textile supplier. The textile industry has a great contribution to the Turkish economy, providing about 10% of GDP (Gross Domestic Product), 18% of industrial production, 20% of manufacturing labour force, and 32% of total Turkish export earnings according to 2003 figures (ITKIB, 2003).

As one of the most water intensive and energy demanding industries, the textile sector is confronted with serious environmental pollution concerns. The main sources of pollution originating from the textile industry are the so-called wet processing stages (mainly featuring desizing, scouring, bleaching, mercerizing, dyeing, rinsing and finishing). Because of the great variety of fibres, dyestuffs, process aids (dye carriers, replacement tannins, surfactants, sequestering, wetting and decreasing agents) and finishing chemicals (flame retardants, antipilling, antimyte, antifungal, antimicrobial preparations) currently in use, huge wastewater volumes of immense complexity and diversity are being generated (EPA, 1997; Muthukumar et al., 2004). Most of these auxiliaries involved are classified under the name "xenobiotics", a group of synthetic chemicals that resist conventional aerobic biodegradation and may cause chronic problems at textile wastewater treatment plants, in publicly owned sewage treatment works and discharged effluent receiving water bodies (Rieger et al., 2002). Interestingly, although numerous papers have already been published covering the chemistry, fate and treatability of dyestuffs in wastewater, only very few pertain the environmental chemistry and toxicity of textile auxiliaries.

Among the refractory pollutants originating from the textile preparation, dyeing and finishing processes, textile tannins have attracted great interest due to their frequent use and extremely refractory nature. Synthetic tannins and tannic acids are high-molecular-weight; oligomeric compounds with multiple structured, poliphenolic moities. They are frequently used during polyamide dyeing with acid, metal-complex or direct dyes at the after-rinsing stage to increase the fixation rates and wet

fastness onto the dyed fabric (O'Neill and Bahojb-Allafan, 1999; Burkinshaw et al., 2004). Biocides are inorganic or organo-synthetic chemicals applied to disinfect, sanitize or sterilize objects and surfaces, or to preserve materials or processes from microbiological degradation. They are frequently used in a wide variety of processes and matrices, i.e. in the cosmetics, food and textile industries, in marine antifouling paints, personal care products, industrial process water and swimming pools, and in plastics or wood products (Chapman, 2003).

For industrial chemicals exhibiting a highly xenobiotic character (i.e. high microbial persistence and toxicity) biotreatment technologies often turned out to be rather ineffective (Rieger et al., 2002). On the other hand, chemical treatment processes can be quite effective for the elimination of toxic and/or refractory pollutants (Marco et al., 1997; Contreras et al., 2002). For over three decades now, ozone has been used for the destructive treatment of biologically difficult-to-degrade pollutants, pre-oxidation of industrial wastewater, post-treatment and disinfection of secondary treated domestic or industrial effluents (Libra and Sosath, 2003; Masten and Davies, 1993, 213-256).

Ozone is a relatively powerful oxidant, ranging only second after the hydroxyl radical ($OH^{\bullet}$), among oxidizing chemicals being typically used for water pollution control (EPA, 1999). It is because of its selectivity that most water and wastewater treatment processes can be performed with relatively low ozone doses (< 1-2 mg O_3/mg COD_o) (Hoigné, 1988). Ozone chemistry is already well established; under acidic pH conditions, ozone is mainly available as molecular ozone and takes part in direct molecular oxidation reactions. At alkaline pH ozone decomposes to secondary, more reactive and hence less selective oxidants such as $OH^{\bullet}$, $HO_2^{\bullet}$, $HO_3^{\bullet}$, and $HO_4^{\bullet}$ that initiate free radical chain reactions which play a major role in the oxidation of xenobiotic chemicals (Staehelin and Hoigné, 1985; Glaze and Kang, 1989).

Considering the above indicated facts, in the present study, the treatability by ozonation of two tanning agents (Natural Tannin, NT, and Synthetic Tannin, ST) and two textile biocides (Biocide I, BI, and Biocide II, BII) that are selected as representative refractory pollutants, at varying ozone feed rates (450, 750, 900, and 1100 mg/h for NT and ST; 500, 750, and 900 mg/h for BI and BII) and pH values (pH = 3.5 and 7.0 for NT and ST; pH = 7.0 and 12.0 for BI and BII) was investigated. Ozonation kinetics were comparatively assessed in terms of COD, TOC, and UV absorbance at 254 nm (representing double bonds) and 280 nm (representing

aromaticity). In addition to the above mentioned collective environmental parameters, BOD_5 was measured in order to evaluate the changes in biodegradability of the selected pollutants before and after treatment with ozone in terms of the BOD_5/COD ratio. In addition, activated sludge inhibition experiments were conducted for an ongoing EU COST Action (COST Action 628: Life Cycle Assessment of Textile Products, Eco-efficiency and Definition of Best Available Technology (BAT) of Textile Processing), to evaluate the toxicity of the studied pollutants. An important parameter which is a measure of total halogenated organic matter in water samples, namely AOX, was also determined for BI effluent. At the last stage of the experimental work, a separate kinetic study was carried out for BI of which the exact molecular structure was known, in order to determine its second order, bimolecular reaction rate constant with ozone.

While 26% COD and 4% TOC removals were observed at pH = 3.5 (698 mg ozone used), the COD and TOC removals increased to 28% and 16%, respectively at pH = 7.0 (764 mg ozone used) for NT at a rate of 900 mg/h after 60 min ozonation. For ST, when the reaction pH was increased from 3.5 (452 mg ozone used) to 7.0 (706 mg ozone used), the overall COD removal increased from 52% to 64% and the TOC removal from 21% to 47% at the same ozone feed rate. As a result, ozonation seemed to be inappropriate for NT oxidation, whereas it was fairly effective in degrading ST both in terms of COD as well as TOC, either via direct molecular ozone attack or indirect oxidation with $OH^{\bullet}$ radicals. The BOD_5/COD ratio which is used to assess biodegradability, increased appreciably for ST, but slightly decreased for NT after 40 min ozonation at a feed rate of 900 mg/h and at pH = 3.5. The activated sludge inhibition experiments gave results parallel to the BOD_5 measurements, i.e. ST showed no inhibiton towards activated sludge after ozonation for 40 min at a feed rate of 900 mg/h and pH = 3.5. The inhibitory effect of NT did not change after ozonation under the same reaction conditions. When the BOD_5 and activated sludge inhibition experiments were considered, combined ozonation and biodegradation is an appealing option for the pre-treatment of ST.

Ozonation at elevated pH (=12.0) and high doses (i.e. 900 mg/h corresponding to 2-3 mg O_3/mg COD_o) was required to achieve an acceptable reduction in the examined collective environmental parameters (i.e. COD, TOC) for the studied textile biocides. In the case of the textile BI, COD removal increased from 49% (ozone absorption rate = 478 mg) to 67% (ozone absorption rate = 730 mg) upon a pH increase from 7.0 to 12.0 at a feed rate of 900 mg/h . In the case of BII, by

applying the same ozone feed rate, the COD removal efficiency increased from 42% at pH = 7.0 (467 mg ozone absorbed) to 72% at pH = 12.0 (631 mg ozone absorbed). For the same ozonation experiments, the TOC removal rates obtained for BI and BII increased from around 10 % at pH = 7.0 to 38 % for BI and to 56 % for BII at pH = 12.0 after 120 min ozonation. Conclusively, a significant increase in oxidation rates at elevated pH as a consequence of ozone chemistry was observed for both tested biocides. On the other hand, in order to achieve complete AOX removal (for BI) and detoxification (for both studied textile biocides), partial oxidation at low doses (300 mg ozone) and pH = 7.0 (i.e. at the natural pH of the finishing process) was sufficient, emphasizing that ozonation can be a promising, economically feasible alternative for the effective control and treatment of refractory compounds originating from the textile dyeing and finishing industry. In addition, according to the kinetic study for BI, which is the last stage of the current study, the bimolecular rate constant for ozonation of BI was found to be 43 $M^{-1}s^{-1}$ which is in the range of bimolecular rate constants of direct ozonation reactions of aromatic compounds.

2. THEORETICAL BACKGROUND

2.1 The Textile Dyeing and Finishing Industry

The business of textile industry is production of value-added products from fiber (Moore and Ausley, 2004). Textile establishments receive and prepare fibers; transform fibers into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and finish these materials at various stages of production. The process of converting raw fibers into finished apparel and nonapparel textile products is complex (EPA, 1997).

Textiles and their end-products constitute the world's second largest industry, ranking only below food products. Industries including retail apparel marketing, construction, agriculture, machine tools, automobiles, petrochemical, carpet, and recreation all rely upon the textile manufacturing industry for raw materials (Moore and Ausley, 2004).

The textile industry includes four production stages:

1. Yarn formation: Textile fibers are converted into yarn by grouping and twisting operations including opening, blending, carding, combing, and drafting which are used to bind them together (EPA, 1997).

2. Fabric formation: The major methods for fabric manufacture are weaving and knitting. Weaving, or interlacing yarns, is the most common process used to produce the raw textile material from which most textile products are made. Starch and polyvinyl alcohol (PVA) are the most common size components used in weaving process. Semi-synthetic sizes, such as carboxy methyl cellulose (CMC) and modified starches, are also used. Oils, waxes, and other additives are often used in conjunction with sizing agents to increase the softness and pliability of the yarns (EPA, 1997).

3. Wet processing: Wet processing is different from yarn and fabric formation, which are dry processes that do not use water as a major processing compound (Moore and Ausley, 2004). Woven and knit fabrics cannot be

processed into apparel and other finished goods until the fabrics have passed through several water-intensive wet processing stages. Wet processing enhances the appearance, durability, and serviceability of fabrics by converting undyed and unfinished goods, known as grey or greige goods, into finished consumers' goods (EPA, 1997).

4. Fabrication: Finished cloth is fabricated into a variety of apparel and household and industrial products by processes like cutting and sewing (EPA, 1997).

These four stages include;

- generation of usable fiber from either a natural source (i.e., cotton, wool, and silk) or from a manufactured source (polyester, rayon, and nylon);
- production of yarn for knitted and woven fabrics;
- construction of product through knitting, weaving, and nonwoven or other methods;
- preparation, dyeing, printing, and finishing to produce finished fabric; and fabrication to produce final product (i.e., garment, household item, industrial, or specialty product) (Snowden-Swan, 1995).

The general process profile for a textile manufacturing plant is given in Figure 2.1 (EPA, 1997).

Among the production stages of textile industry, wet processing is of importance from environmental point of view, because of including processes such as bleaching, dyeing, printing and finishing that involve some form of wet or chemical treatment (Wynne, 1997, 220-225). Chemicals added to perform a variety of functions during wet processing are the reason for large volumes of toxic wastewater (Moore, and Ausley, 2004).

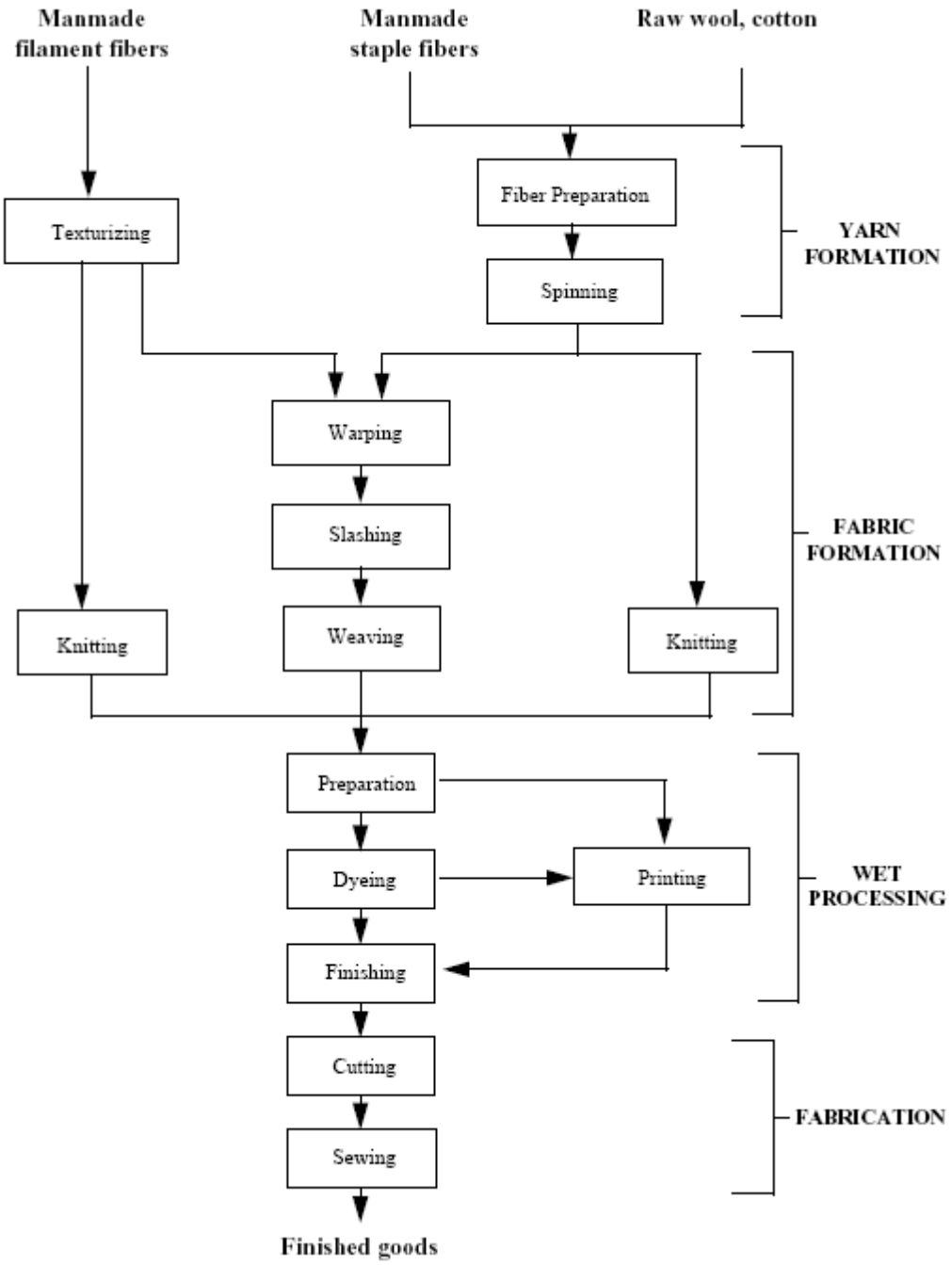

Figure 2.1. : General Process Profile for a Textile Manufacturing Plant (EPA, 1997).

As it is clear in Figure 2.1 the wet processing stages can be divided into three distinct sections, namely preparation, dyeing and finishing processes which are presented in Table 2.1 along with their functions in the corresponding process stage.

The pollutants selected for this study are two tanning agents used in the acid dyeing process and two biocides used in the finishing process.

Table 2.1. : Wet Processing Stages of the Textile Preparation, Dyeing and Finishing Industry and Its Functions (Wynne, 1997, 223).

Process	**Function**
Preparation	These processes exist to ensure that the textile has the right physical and chemical properties to enable it to be dyed or finished.
Dyeing	These processes exist to provide the textile with dye either for aesthetic reasons or for some functional purpose determined by the product.
Finishing	These processes exist to provide the textile with the properties that the end-use demands, which have been impaired or destroyed and which have not already been provided by any earlier processes.

The Fabric Preparation step consists of a series of various treatment and rinsing steps critical to obtaining good results in subsequent textile finishing processes (EPA, 1997). Preparation processes exist to ensure that the textile has the right physical and chemical properties to enable it to be dyed and finished. Textiles are often in an impure state when they arrive at the dyeing step. If the fiber used in the textile is from natural origin, for example cotton or wool, it will still contain impurities that the fiber acquired while it was growing in a field or on a sheep (Wynne, 1997, 250-260). Preparation is the step where unwanted impurities, either natural or man-made, are removed from the fabric prior to dyeing, as they would not only spoil the appearance of the textile but also would either make the dyeing process impossible or, difficult to perform (Moore and Ausley, 2004; Wynne, 1997, 250-260).

In the preparation stage, the mill removes natural impurities or processing chemicals that interfere with dyeing, printing and finishing (EPA, 1997). The fabric may be cleaned with aqueous alkaline substances and detergent, or impurities may be removed with enzymes. Many fabrics are then bleached with hydrogen peroxide or chlorine-containing compounds to whiten them. Optical brightening agents are often added if the fabrics are to be sold white rather than dyed (Moore and Ausley, 2004).

Dyeing operations are used at various stages of production to add colour and intricacy to textiles and to increase product value. Textiles are dyed using a wide range of dyestuffs, techniques, and equipment (EPA, 1997). During the dyeing process dye and auxiliary processing chemicals are introduced to the textile to obtain a uniform depth of colouration with colour fastness properties suitable to the

end use. Different fastness requirements may be applied depending on the intended end use of the textile (Moore and Ausley, 2004).

Dyeing can be performed using continuous or batch processes. In batch dyeing, a certain amount of textile substrate, usually 100 to 1,000 kilograms, is loaded into a dyeing machine and brought to equlibrium, or near equlibrium, with a solution containing the dye. Because dyes have an affinity for the fibers, the dye molecules leave the dye solution and enter the fibers over a period of minutes to hours, depending on the type of dye and fabric used. Auxiliary chemicals and controlled dyebath conditions (mainly temperature) accelerate and optimize the action. The dye is fixed on the fiber using heat and/or chemicals, and the tinted textile substrate is washed to remove unfixed dyes and chemicals (EPA, 1997).

In the continuous dyeing processes, textiles are fed continuously into a dye range at speeds usually between 50 to 250 meters per minute. Continuous dyeing processes typically consist of dye application, dye fixation with chemicals or heat, and washing. Dye fixation on the fiber occurs much more rapidly in continuous dyeing than in batch dyeing (EPA, 1997).

Different types of dyes are basic (cationic) dyes, direct dyes, sulphur dyes, azoic dyes and ingrain dyes, vat dyes, acid dyes, mordant dyes and metal-complex dyes, disperse dyes, reactive dyes, and pigments (Van der Bruggen et al., 2004).

Finishing processes involve chemical or mechanical treatments performed on fiber, yarn, or fabric to improve appearance, texture, or performance (EPA, 1997). When a textile reaches the finishing stage, previous processes may have impaired or even destroyed some of the desirable properties of the fiber, so the finishing processes carried out must attempt to reintroduce these properties or to increase them if they have been reduced. In addition, in the finishing step, properties that were not present previously may be added to the textile (Wynne, 1997, 270-280). Methods used in the wet processing step vary greatly depending on end products and applications, site-specific manufacturing practices, and fiber type. Processing methods may also differ based on the final properties desired, such as tensile strength, uniformity, and luster (EPA, 1997).

Mechanical finishes can involve brushing, ironing, or physical treatments used to increase the luster and feel of textiles. Application of chemical finishes to textiles can impart a variety of properties ranging from decreasing static cling to increasing flame resistance (EPA, 1997). Common chemical treatments to enhance the value of the

fabric are permanent press treatments, waterproofing, softening, antistatic protection, soil resistance, stain release, and microbial/fungal protection (Moore and Ausley, 2004).

Traditionally, the textile industry is very energy-, water-, and chemical-intensive. In the textile industry, approximately 60 percent of the total energy consumed is within the wet processing stages. Since most wet processing involves treatment with chemical baths, which often require washing, rinsing, and drying steps between key treatment steps, large volumes of wastewater are generated with a very diverse range of contaminants that must be treated prior to disposal; much energy is consumed to heat and cool chemical baths and wastewater and dry fabrics or yarns (Snowden-Swan, 1995). In terms of waste generation and environmental impacts, wet processing is the most significant textile operation. Much of the waste generated from the industry is produced during the wet processing stages (EPA, 1997).

2.1.1 Process and Pollution Profiles

Considering both volume discharged (typically 2000m^3/d) and effluent composition, wastewater generated by the textile industry is one of the most polluting industries among all other sectors (Vandevivere et al., 1998). The auxiliaries used in the textile industry are very diverse in chemical composition (Azbar et al., 2004). The main sources of wastewater generated by the textile industry are wet processing steps. The main source of wastewater generated in the wet processing steps are the washing (or scouring), bleaching of natural fibers and the dyeing and finishing steps. Consequently, the present study focused on the dyeing and finishing processes.

Potential releases from the textile preparation, dyeing and finishing process stages are summarized in Table 2.2.

Table 2.2. : Potential Releases Emitted during Textile Manufacturing Processes (EPA, 1997).

Process Stage	**Air Emissions**	**Wastewater**	**Residual Wastes**
Scouring	VOCs from glycol ethers and scouring solvents	Disinfectants and insecticide residues; NaOH; detergents, fats; oils; pectin; wax; knitting lubricans; spin finishes; spent solvents	Little or no residual waste generated
Bleaching	Little or no air emissions generated	Hydrogen peroxide, sodium silicate or organic stabilizer; high pH	Little or no residual waste generated
Singeing	Small amounts of exhaust gases from the burners	Little or no wastewater generated	Little or no residual waste generated
Mercerizing	Little or no air emissions generated	High pH; NaOH	Little or no residual waste generated
Heatsetting	Volatilization of spin finish agents applied during synthetic fiber manufacture	Little or no wastewater generated	Little or no residual waste generated
Dyeing	VOCs	Metals; salt; surfactants; organic processing assistants; cationic materials; colour; BOD; COD; sulfide; acidity/alkalinity; spent solvents	Little or no residual waste generated
Printing	Solvents, acetic acid from drying, and curing oven emissions; combustion gases; particulate matter	Suspended solids; urea; solvents; colour; metals; heat; BOD; foam	Little or no residual waste generated
Finishing	VOCs; contaminants in purchased chemicals; formaldehyde vapours; combustion gases; particulate matter	BOD; COD; suspended solids; toxics; spent solvents	Fabric scraps and trimmings; packaging waste
Product Fabrication	Little or no air emissions generated	Little or no wastewater generated	Fabric scraps

The use of a variety of dyes and auxiliaries in the dyeing processes causes considerable variation in the wastewater characteristics such as pH, colour and COD (Muthukumar et al., 2004). Different dyestuffs that have highly varying chemical characteristics are selected according to the material to be dyed. Therefore the chemical composition of the dyehouse effluent varies with the textile yarns or fibres being produced. Figure 2.2. schematically presents the three basic wet processing stages (preparation, dyeing and finishing) of typical textile mills together with their corresponding, individual volumetric and pollution loads.

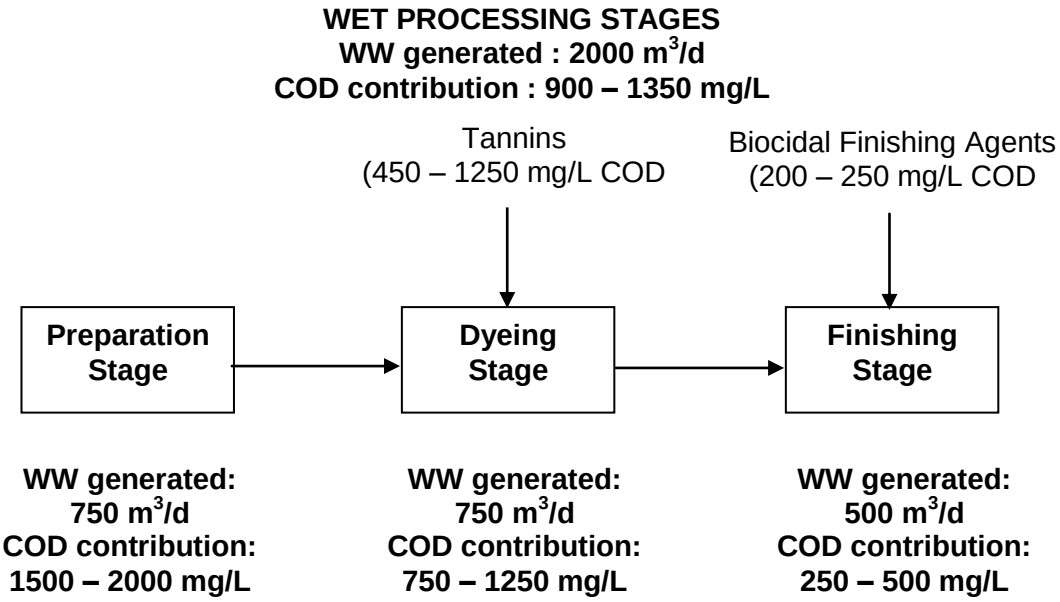

Figure 2.2. : Volume of Wastewater Generated and COD Load of Wet Processing Stages (Pisa Tekstil, 2004).

As being schematically presented in Figure 2.2, a textile mill produces 2000 m^3/d wastewater and the average COD of a typical textile dyeing and finishing effluent is 1100 mg/L. Around 750 m^3/d wastewater comes from the dyeing + rinsing (washing off) process stages, contributing to almost 35 % (900 kg/d) of the total COD load received by the treatment plant. From the finishing stage 500 m^3/d wastewater comes with around 10 % (270 kg/d) contribution, to the COD load of the wet processing stages. Although the finishing stage effluent forms a small fraction of the total wet processing COD load, its toxicity and recalcitrance cause serious problems at textile wastewater treatment plants, in publicly owned sewage treatment works and discharged efffluent receiving water bodies.

Dyes are continually being upgraded and replaced by superior compounds. There is pressure on dye manufacturers to develop dyes that can be successfully applied

using less auxiliary chemicals, especially salt, to deduce environmental problems associated with textile industry effluent. A single dyeing operation can use a number of dyes from different chemical classes resulting in a very mixed wastewater (O'Neill et al., 1999).

The textile finishing process is very water-intensive, with an average water usage of 130 m^3 per ton of fabric. Wastewater streams with varying degrees of organic and inorganic compounds are produced, depending on the finishing processes used, ranging from those with high organic loads due to sizing agents and surfactants to dye-containing streams with a relatively low organic loading, high colour and inorganic salt content (Libra and Sosath, 2003).

2.2 Refractory Compounds in the Textile Industry

Refractory or recalcitrant compounds are compounds which resist aerobic microbial wastewater treatment under conducive environmental conditions. Thus they emerge from biological treatment process unchanged, possibly to breach discharge consents and accumulate in receiving waters where they pose a potential problem for water reuse (Alvares et al., 2000).

Xenobiotic compounds resist biodegradation because of the absence of appropriate microbial degradation enzymes. The degree of recalcitrance exhibited is related to molecular complexity, for example degree of branching, degree of polymerism as well as the nature and number of substituents. Because substrate specific enzyme activity forms the basis of microbial degradation pathways, minor structural differences can cause recalcitrance (Alvares et al., 2000). As examples to xenobiotic compounds, cyanides, phenols, polycyclic aromatic compounds or long chain aliphatics may be given which are hazardous and which exhibit acute or chronic toxicity (Rieger et al., 2002).

In addition to the molecular structure, the concentation at which a compound occurs will also dictate its fate. Lower concentrations may be insufficient to support microbial growth, allowing the compound to persist. Conversely, other contaminants may persist at higher concentrations because the level of toxicity inactivates or kills the degrader organisms, which at lower concentrations would degrade it (Alvares et al., 2000).

As a result of the factors mentioned, for chemicals exhibiting high refractory character, high toxicity, and persistence, bioremedation technologies often turned out to be ineffective (Rieger et al., 2002). In addition, presence of refractory organic macromolecules such as tannin and lignin in distillery, tannery, pulp and paper wastewaters, etc., renders effective treatment of such wastewaters through biodegradation processes difficult (Saroj et al., 2005).

Cosidering the difficulties in biological treatment of wastewaters containing refractory compounds, alternative treatment methods involving ozonation or through a combination of ozonation and biodegradation appears to be feasible option (Beltran et al., 1997). Chemical oxidation processes in wastewater treatment can destroy inhibitory compounds and improve the biodegradability of originally recalcitrant organics by altering their chemical structure. Only partial oxidation to some extent is required to facilitate subsequent biodegradation of the converted organic matter. A waste constituent highly or completely resistant to conventional biological treatment can be totally mineralised using a combined chemical-biological system. Such a system for organics removal, will have economic benefits as a result of the following factors (Alvares et al., 2000):

- Less oxidant is required than that needed for complete chemical mineralisation which may not be economically feasible for the pollutant concentrations found in wastewaters,

- Biological processes, with operating costs up to a tenth of chemical ones, complete the majority of mineralisation.

Textile industries produce large volume of effluents, which are very toxic, resistant to physicochemical treatments and not easily biodegradabale. The non-biodegradability of textile wastewater is due to the high content of dyestuffs, surfactants, and dye additives which are generally organic compounds of complex structure (Muthukumar et al., 2004).

Because of the great variety of fibers, dyes, process aids and finishing products in use, these processes generate wastewaters of great chemical complexity and diversity which are not adequately treated in conventional wastewater treatment plant (Vandevivere et al., 1998).

2.2.1 The Dyeing Process

Wastewater from dyeing processes have high COD, solids, colour and recalcitrant material as a result of residuals of dyebath auxiliaries and unfixed dyestuff (Tezcanlı-Güyer et al., 2003). Effluents from dyeing process are not amenable to biological treatment due to their recalcitrant character (Arslan and Akmehmet Balcioglu, 2000).

Table 2.3. : Typical Characteristics of Dyes Used in the Textile Operations (EPA, 1997).

Dye Class	**Description**	**Applied Fabric**	**Typical Fixation, %**
Acid	water-soluble anionic compounds	Wool, nylon	80 – 93
Basic	water-soluble, applied in weakly acidic dyebaths; very bright dyes	Acrylic, some polyesters	97 – 98
Direct	water-soluble, anionic compounds; can be applied directly to cellulosics without mordants (or metals like chromium and copper)	Cotton, rayon, other cellulosics	70 – 95
Disperse	not water-soluble	Polyester, acetate other synthetics	80 – 92
Reactive	water-soluble, anionic compounds; largest dye class	Cotton, other cellulosics, wool	60 – 90
Sulfur	organic compounds containing sulfur or sodium sulfide	Cotton, other cellulosics	60 – 70
Vat	oldest dyes; more chemically complex; water-insoluble	Cotton, other cellulosics	80 – 95

The disposal of dye wastewater is an environmental concern because of the associated colour and the carcinogenic effects of some anaerobic metabolites of azo dyes (aromatic amines) (Chu and Ma, 2000).

Around 5-30% of the textile dyes remain in the exhausted dyebath (Azbar et al., 2004) depending on the efficiency of the dyeing process and the nature of the dyes applied. For instance, reactive dyes cannot be used after the dyeing process because the portion that does not react with the fabric and hence remains in the exhausted dye-bath immediately undergoes alkali hydrolysis. Practically 100% of the dye auxiliaries remain in the spent dyebath except some assisting chemicals used in nylon dyeing such as acetic acid and tannins. Acetic acid functions as a pH buffer and tannins increase the fixation rate of dyes onto the fiber.

2.2.1.1. Tannins

Tannins are naturally occuring plant polyphenols (Bhat et al., 1998). Their molecular weight ranges from 500 to 20,000 g/mol. They are soluble in water, with exception of some extremely high molecular weight structures. Gallic acid which has the molecular formula 3, 4, 5-Tryhydroxybenzoic acid, is often considered to be the building blocks of tannin and lignin macromolecules (Saroj et al., 2005).

Tannins feature the following properties:

- Strong metal complexing
- Complex formation with proteins, alkaloids and certain polysaccharides
- Strong affinity towards polyamides
- Strong anti-oxidizing nature.

Two major classes of tannins are hydrolysable and condensed tannins. Hydrolysable tannins are principally multiple esters of D-glucose with gallic acid (3,4,5,-trihydroxybenzoic acid) and its oxidative metabolites, while condensed tannins (proantocyanidins) are composed of flavan-3-ol units linked through C – C bond (Saroj at al., 2005).

The name tannic acid usually refers to natural tanner (gallotannine). Gallotannine is found in nature in sumac, tea leaves and many other plants, as well as in forest rivers and lakes, where it comes from bark and oak leaves. Tannic acid has tart waste and characteristic welting property and appears to be very toxic despite its usually low concentration in water (Perkowski et al., 2003). Due to the fact that tannic acid is a natural compound, its exact structure is not known. However, the basic structure (main building block) of tannic acid is given in Figure 2.3.

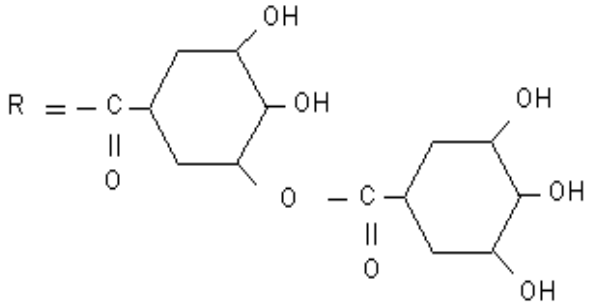

Figure 2.3. : Basic Structure of Tannic Acid

Tannins have a range of effects on various organisms from toxic effects on animals to growth inhibition of microorganisms. Tannins act as a defense mechanism in plants against pathogens, herbivores, and hostile environmental conditions. Tannin toxicity to microorganisms has been described by three mechanisms; enzyme inhibition and substrate deprivation, action on membrans, and metal ion deprivation (Reed, 1995). Tannins induce changes in morphology of several species of bacteria.

However, some microbes are resistant to tannins and have developed various mechanisms and pathways for tannin degradation in their natural milieu. The microbial degradation of condensed tannins is less than that of hydrolysable tannins in both aerobic and anaerobic environments (Bhat et al., 1998).

Bacteria are involved in the degradation and modification of lignin which is an integral plant cell wall constituent built from phenyl-propane units linked by various types of bonds (Saroj et al., 2005). Many strains are able to metabolize lignin-related compounds and some of them also mineralize and solubilize polymeric lignin. Cleavage of the different types of linkages in lignin, oxidations, demethylations and aromatic ring cleavages are catalyzed by bacterial enzymes (Zimmermann, 1990).

The use of tannins dates back to the pre-industrialised era, and some of these ancient applications are even today still in use. Today hydrolysable tannins find use in a wide variety of applications:

- Food and beverages:
    - Beer clarification and stabilization
    - Wine clarification, anti-oxidant and taste modification
- Anti-corrosion applications:
    - Anti-corrosion paints and rust converters
    - Boiler water treatment
- Ink manufacturing
- Pharmaceuticals
- Textile auxiliaries:

- Electrostatic flock activation (e.g. upholstery, automotive, gadgets)
- Wash fastness improvement (e.g. garments)
- Chlorine protection (e.g. swim- and sports-wear, carpets)
- Anti-staining (e.g. carpets)

Tannic acid becomes blue-black when reacted with iron chloride and violet-red with iodine. As a result it is used in ink production. In addition it is used in medicine as a welting agent and in treatment of burned skin. It is also used in the production of many pharmaceutics and is a basic component of alkaline dye production and used for dyeing paper, leather and textile (Perkowski et al., 2003).

2.2.1.1.1. Textile Tannins

In recent times, the fastness of dyed goods towards repeated washing, chlorine bleaching and fastness against staining has become increasingly important in response to increased consumer and retailer demands. As a result, among the refractory pollutants originating from the textile preparation, dyeing and finishing stages, textile tannins have attracted interest due to their frequent use and recalcitrant nature. Synthetic tannins and tannic acids are giant, hydrolyzable oligomeric compounds with multiple structured, poliphenolic macromolecules.

As a result of the chlorine scavenging properties of tannic acid's chemistry, it has protective action preventing oxidative degradation of the dyestuff. As a consequence, tannic acid will not only protect textile materials against the attack of bleaching water but also against other oxidizing agents (e.g. peroxides such as H_2O_2).

In spite of their rather xenobiotic and toxic character, tannins provide a more environmentally acceptable alternative to heavy metal treatment of polyamide fabrics (Burkinshaw and Bahojb-Allafan, 2004).

2.2.1.1.2. Polyamide Dyeing with Tannic Acid

Tannins are frequently used during polyamide (nylon) dyeing with acid, metal complex or direct dyes at the after-rinsing stage to increase the fixation rates and wet fastness onto the dyed fabric. Figure 2.4. displays the electrostatic repulsion between the negatively charged tannic acid and an anionic dyestuff molecule.

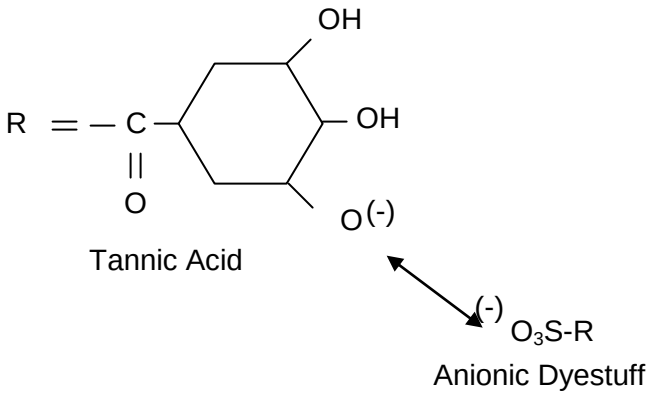

Figure 2.4. : Interaction between Tannic Acid and Anionic Dyes

In Figure 2.5., the nylon dyeing process with and without tannic acid is depicted. As it is evident from the figure, tannic acid molecules increase the fixation rates of anionic dyes, such as acid dyes onto the fabric by the help of the electrostatic repelling force between the negative charge of the hydroxyl group of tannic acid and the negative charge of the dye. When tannic acid is not used, dye molecules stay on the surface of the positively charged polyamide fabric. While the fixation rate of the dye molecules to the fabric increases, the amount of unfixed dye decreases resulting in efficient dyeing process and dyeing effluent containing less dye molecules.

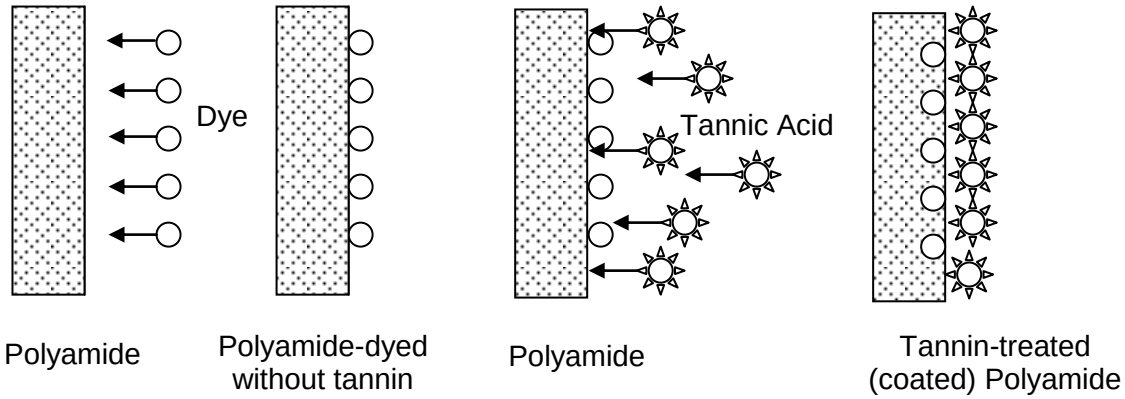

Figure 2.5.: Comparison of Polyamide Dyeing Process with and without Tannic Acid

It is believed that the improved wash fastness properties of tannic acid treated polyamide is due to the formation of a protective high molecular weight surface skin. Another belief is that dyestuff is displaced by tannin in the outer regions of the fibre and further pushed inwards, thus preventing the loss of dyestuff during washing. Prior to the addition of tannic acid, the pH should be adjusted to 3.0-3.5. In this pH-range maximum tannic acid uptake is guaranteed with a minimal risk of damaging the fabric. Higher pH values are possible but should not exceed pH = 4.5.

In many cases the tannic acid backtanning process is replaced by less effective synthetic tanning agents (syntans), owing to a number of reasons:

- The full backtan used potassium antimonyl tartrate (tartare emetic).
- A more elaborate time consuming process was required.
- Unwanted side effects are sometimes observed: e.g. harsh handle, reduced light fastness and colour changes.

2.2.2 The Finishing Process

Different properties are given to the textile by finishing processes. The scroopy-handle finish is given to the fabric in order to avoid the crackling or rustling sound produced when the fabric is rubbed or squizzed by hand. With application of softeners and lubricants, handling, cutting, sewability of the fabric can be improved. To modify certain properties the problem of static charge arises, antistatic finishing is applied to the fabric. The objectives of wrinkle free finishing are to avoid crease formation, to give the fabric improved dimensional stability, to improve tear strength, and to provide better abrasion resistance. Oil and water repellent finish makes the fabric oil- as well as water-repellent, along with imparting stain resistence, without affecting the handle of the fabric. The flameproofing finish is of importance as well. To avoid photochemical tendering caused by ultraviolet radiation, UV absorbers, usually called photostabilisers are applied to the fabric. Fragnance finishes prevent the fabric from developing bad odour, cool finishes give a cooling effect to human body, while thermal resistant finishes keep the fabric warm by producing heat retaining effect. Antimicrobial is one of the special types of finishing given to the textiles to protect the fiber from microbial attack and to protect the user against transfer of pathogenic germs (Menezes, 2003).

In the textile finishing process, biocides are used as antimicrobial finishing agents. In the present study, two representative biocides are selected to study their treatability by ozonation process. As a result, more detailed information will be given about biocidal finishing agents in the following section.

2.2.2.1. Biocides

Biocides are inorganic or synthetic organic molecules used to disinfect, sanitize, or sterilize objects and surfaces, and to preserve materials or processes from microbiological degradation. They are used in a wide variety of processes and

matrices, cosmetics, food, industrial process waters, marine antifouling paints, plastics, wood, swimming pools and textile industry (Chapman, 2003).

In U.S.A., EPA (Environmental Protection Agency) has classified more than 400 chemicals and in Europe, CEFIC (Conseil Européen de l'Industrie Chimique), has classified more than 1000 chemicals as biocides. In the directive concerning the placing of biocidal products on the market prepared by the European Parliament the Council on 16 February 1998, biocides were defined and an exhaustive list of 23 product types was prepared (67/548/EEC). According to this directive, biocidal products are defined as active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means. According to this directive biocides are classified into four main groups:

- Disinfectants and general biocidal products including human hygiene biocidal products, private area and public health area disinfectants, veterinary hygiene biocidal products, food and feed area disinfectants, drinking water disinfectants.

- Preservatives including in-can preservatives, film preservatives, wood preservatives, fibre, leather and polymerised materials preservatives, masonry preservatives, preservatives for liquid-cooling and processing systems, slimicides, metalworking-fluid preservatives.

- Pest control including rodenticides, avicides, molluscicides, piscicides, insecticides, acaricides, and products to control other arthropodes, repellents and attractants.

- Other biocidal products including preservatives for food or feedstocks, antifouling products, embalming and taxidermist fluids, control of other vertebrates.

2.2.2.1.1. Textile Biocides (Biocidal Finishing Agents)

Textiles, particularly those composed of natural organic fibers such as cotton, linen, or wool, are readily attacked by microorganisms. Most synthetic fabrics are not readily subjected to extensive biodeterioration, but some processing and finishing agents are susceptible to microbial spoilage. Microorganisms can affect all stages of

textile processing and storage. Microbial growth on a textile causes loss of strength and elognation, discolouration and changes in appearance. They follow changes in oxidation state, degree of polymerization and break down of molecular structure. There are two main ways of textile protection – control of the environmental conditions and treatment with biocides (Szostak-Kotowa, 2004). The environmental characteristics that promote microbial growth are dirt, warm temperature, moisture, and receptive surfaces. Textiles provide the entire required medium to grow microbes (Menezes, 2003).

Biocides may be added during manufacture of fabrics to protect the finished product against biodeterioration, especially where fabrics will be used under conditions that are extremely favourable for the microbiota, e.g. in tropical regions. The most important properties of biocides for use on fabrics are (Szostak-Kotowa, 2004):

- Effectiveness on low concentrations towards a wide spectrum of microorganisms;
- Low toxicity to people and mammals;
- Colourless, odourless and low cost;
- No negative effect on fabric properties;
- Affinity to fabrics and other compounds contained in them;
- Resistance to atmospheric conditions (sunlight, humidity, etc.) during use.

Biocides are also used in cases where finished fabric has already been subjected to biodeterioration and requires to be protected against further destruction, especially in the case of historically important fabrics, museum exhibits, etc. (Szostak-Kotowa, 2004).

In addition to finishes protecting the fabric against biodeterioration, hygienic finishes may also be applied. They are used for socks, stockings, shoe padding, protective clothing, shower curtains, hospital sheets, etc. Chemical compounds used for such purposes must have low toxicity to humans and should not irritate or be absorbed by skin. As well as this, they should not have a negative effect on the properties of textile products and in many cases it is required that they should be resistant to washing (Szostak-Kotowa, 2004). They inhibit the development of bacteria, occuring on human skin which results in objectionable odours, microbial stains, allergic responses, disease and infection (Menezes, 2003).

2.2.2.1.2. Treatability of Biocides

Textile biocides (pentachlorophenols, organometal complexes, insecticides, etc.) are generally classified as “recalcitrant” pollutants present in textile effluents that have a negligible BOD and are hence unsuitable for conventional biological treatment (Park and Shore, 1984).

Until now, no study conducted with the physicochemical treatability of textile biocides has been published. However, there are a few studies in the literature about the treatability of anti-fouling biocides. In general, AOPs (Advanced Oxidation Processes) are used including photodegradation by solar radiation and TiO_2/UV-A oxidation resulting in 75% to 100% COD removal (Sakkas and Albanis, 2003; Okamura, 2002). However, according to the toxicity test results conducted for treated biocides, the degradation products may be more resistant and/or may have more toxic characters compared to the biocide itself.

2.3 Ozonation

Ozone exists as a gas at room temperature. The gas is colourless with a pungent odour readily detectable at concentrations as low as 0.02 to 0.05 ppm (by volume), which is below concentrations of health concern. Ozone gas is highly corrosive and toxic. Ozone is a powerful oxidant, second only to the hydroxyl radical, among chemicals typically used in water treatment (EPA, 1999). Oxidation potentials of some common oxidants are given in Table 2.4.

Table 2.4. : Oxidation Potentials of Common Oxidants (Hao et al., 2000).

Oxidant	**E_o (eV vs NHE)**
F_2	3.10
$OH^{\bullet}$	2.80
O_3	2.08
H_2O_2	1.78
$KMnO_4^-$	1.70
$HO_2^{\bullet}$	1.70
$Cr_2O_7^{2-}$	1.60
Cl_2	1.40
O_2	1.23

2.3.1 Solubility of Ozone

Ozone is sparingly soluble in water. At 20ºC, the solubility of 100% ozone is 570 mg/L. Ozone concentrations used in water treatment are typically below 14%, which limits the mass transfer driving force of gaseous ozone into water. Consequently, typical concentrations of ozone found during water treatment range from <0.1 mg/L to 1 mg/L, although higher concentrations can be attained under optimum conditions (EPA, 1999).

The solubility of ozone is readily affected by pH, temperature, ionic strength, and presence of radical scavengers in the liquor. The infleunce of pH is the result of the relationship between oxidation potential and decomposition behaviour of ozone. The ozone stability decreases with increasing pH resulting in generation of secondary oxidants. As a result, the oxidizing power of ozone decreases from 2.08 V at acidic pH to 1.4 V in alkaline solutions (Muthukumar et al., 2004)

2.3.2 Ozone Chemistry

Due to its high reactivity, ozone has different reactions in water. These reactions can be divided into three categories (Beltran, 2004):

- Oxidation-reduction reactions: Redox reactions are characterized by the transfer of electrons from one species (reductor) to another one (oxidant). The oxidizing or reducing character of any chemical species is given by the standard redox potential. Ozone has one of the highest standard redox potentials (see Table 2.4). Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds by means of this reaction type. In most of these reactions, there is no explicit electron transfer, but rather an oxygen transfer from the ozone molecule to the other compound.

- Dipolar cycloaddition reactions: Addition reactions are those reactions resulting from the combination of two molecules to yield a third one. The ozone molecule reacts with the unsaturated bond due to its dipolar structure and leads to a splitting of the bond, which is based on the so-called Criegee mechanism.

- Electrophilic substitution reactions: In these reactions, one electrophilic reagent (such as ozone) attacks one nucleophilic

position of the organic molecule (i.e., an aromatic compound), resulting in the substitution of one part (i.e., atom, functional group, etc.) of the molecule. This type of reaction is the base of the ozonation of aromatic compounds such as phenols. Aromatic compounds are prone to undergo electrophilic substitution reactions rather than cycloaddition reactions because of the stability of the aromatic ring.

A possible fourth type of reaction could be nucleophilic addition, although this reaction has only been confirmed in nonaqueous systems.

In some cases, free radicals are formed. These free radicals propagate themselves through mechanisms of elementary steps to yield hydroxyl radicals. These free radicals are extremely reactive with any organic matter present in water. For this reason ozone reactions in water can be classified as:

a) Direct reactions of ozone with the organic compound.
b) Free radical reactions of ozone which involve an hydroxyl free radical intermediate.

The schematic of reaction pathways for ozonation of aqueous systems is summerized in Figure 2.5.

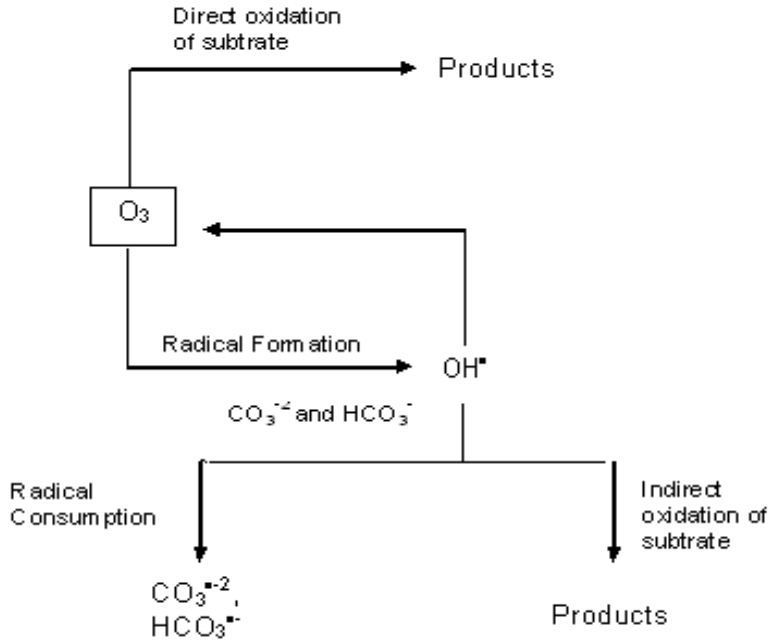

Figure 2.6. : Schematic of Reaction Pathways for Ozonation of Aqueous Systems (Beltran et al., 2001).

In the above figure, the direct oxidation of substrate and the radical formation resulting in radical consumption and indirect oxidation of substrate are depicted. These reactions lead to different oxidation products and are controlled by different types of kinetics (Gottschalk et al., 2000, 11).

Under acidic conditions (pH<4) the direct pathway and above pH = 10 the indirect pathway dominates. At pH = 7 both direct and indirect pathways can be of importance. In special wastewaters even at pH = 2 the indirect oxidation can be of importance, depending on the concentration of contaminants present (Gottschalk et al., 2000).

During ozonation, some of the added ozone reacts directly with the solute. The faster the solute is oxidized, the more it reacts by the direct reaction. However, part of the ozone decomposes to hydroxyl free radicals before reaction with the oxidizable solute. The higher the pH, the faster is the decomposition of ozone to form hydroxyl free radicals, which is initiated by hydroxyl ions. It is additionally accelerated by a chain reaction for which the formed radicals act as chain carriers. Because of this chain reaction, the lifetime of ozone in water also depends upon solutes which yield radical-types of intermediates, which additionally catalyze the decomposition of ozone, and upon solutes which scavenge the hydroxyl free radicals. Bicarbonate ions and aliphatic alcohols are examples to such scavengers. Above pH 9, bicarbonate ion dissociates significantly, forming carbonate ion. In turn, carbonate ion will cause even greater inhibition of oxidation by the free radical mechanism than will bicarbonate. Such scavengers quemch the chain reactions and stabilize ozone. At elevated pH values the hydroxyl free radical reactions dominate over the direct ozone reactions (Rice, 1981).

2.3.2.1. Direct Reaction of Ozone with Dissolved Compounds

Thermodynamically, ozone is a very strong oxidant. However, most of its reactions are so slow that its chemical effects are controlled by kinetics, and not by themodynamics (Hoigné, 1988). The direct oxiation of organic compounds with ozone is a selective reaction with slow reaction rate constants typically in the range of $k = 1.0 – 10^3\ M^{-1}s^{-1}$ (Gottschalk et al., 2000, 14).

The primary reactions of ozone with dissolved compounds can be expressed by the simple rate law, where the rate is first order with respect to both the concentration of ozone [O_3], and the concentration of the solute [M]. So the reaction of ozone with M can be expressed as:

$O_3 + M \rightarrow M_{oxid}$ (2.1)

and the rate of dissapearance of M in the presence of a given concentration of ozone [O_3] becomes:

$$-\frac{[M]}{dt} = k_M [M]^1 [O_3]^1 \quad (2.2)$$

If we consider a plug-flow or a batch-type reactor, the rate-law for the elimination of M can be written as:

$$-\ln \frac{[M]}{[M]_0} = k_M . [O_3] t \quad (2.3)$$

Thus the logarithm of the relative residual concentration of M declines linearly with the time t during which a given concentration of ozone is present. The slope increases with the concentration of ozone and the substrate-specific reaction-rate constant k_M (Hoigné, 1988).

It can be concluded that direct ozone reactions are controlled by kinetics, and not by thermodynamics. All rates of reactions are first order in ozone and substrate concentration. Ozone is a highly selective oxidant. Product formations change with ozone dose (ozone concentration multiplied by reaction time). The products mostly consist of a wide range of aldehydes, ketones, acids, and even polymers. The reaction kinetics and chemical rules for product formations are well-established but the final ozonolytic products formed from different substrates are only known approximately (Hoigné, 1988).

2.3.2.2. $OH^{\bullet}$ Radical Reactions:

While in acidic pH, ozone is available as molecular ozone, in alkaline pH it decomposes to secondary oxidants such as $OH^{\bullet}$, $HO_2^{\bullet}$, $HO_3^{\bullet}$, and $HO_4^{\bullet}$ which are more reactive but less selective oxidants. Among these, $OH^{\bullet}$ is the main secondary oxidant formed from the ozone self-decomposition cycle (Beltran at al., 2001). They are most reactive oxidants known to occur in water and has the highest oxidation potential of 2.8 V (Muthukumar et al., 2004).

Most of the $OH^{\bullet}$ radicals are produced in chain reactions where OH^- (high pH) and HO_2^- (dissociated hydrogen peroxide) act as initiators. Some organic solutes act as

promoters, but bicarbonate and some types of organic compounds act as inhibitors of this type of chain reaction (Hoigné, 1988).

In natural water, most $OH^{\bullet}$ reacts with bicarbonate and non-specified organic solutes, which both act as scavengers. But a small fraction of $OH^{\bullet}$ survives until it reacts with specified micropollutants. The reaction of $OH^{\bullet}$ with a specified micropollutant becomes faster the higher its concentration and the cleaner the water, that means the lower the concentration of the scavengers (Hoigné, 1988).

From experience, it is known that the lifetime of ozone in water is shorter the higher the pH. But in most water, decomposition also occurs in radical-type chain reactions, which can be somewhat inhibited by bicarbonate. Ozone is therefore more stable in water containing more bicarbonate and the lifetime of ozone in good groundwater can be longer than in highly distilled water of comparable pH. Even some special organic compounds can act as strong inhibitors for the ozone chain-decomposing reaction. But other types of organic impurities, e.g. carbohydrates or even methanol also promote the radical-type chain reaction, and hence acelerate the decomposition of ozone (Hoigné, 1988).

These chain reactions can be shown as below (Langlais et al., 1990):

Initiation step:

$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet-}$ $\quad k_1 = 7.0 \cdot 10^1\ M^{-1}s^{-1}$ (2.4)

$HO_2^{\bullet}$: Hydroperoxide radical

Propagation steps:

$HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^+$ $\quad k_2$ (ionization constant) $= 10^{-4,8}$ (2.4')

$O_2^{\bullet-}$: Superoxide radical ion

$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$ $\quad k_2 = 1.6 \cdot 10^9\ M^{-1}s^{-1}$ (2.5)

$O_3^{\bullet-}$: Ozonide radical ion

$O_3^{\bullet-} + H^+ \leftrightarrow HO_3^{\bullet}$ $\quad k_3 = 5.2 \cdot 10^{10}\ M^{-1}s^{-1}$ (2.6)

$k_{-3} = 2.3 \cdot 10^2\ s^{-1}$

$HO_3 \rightarrow {}^{\bullet}OH + O_2$ $\quad k_4 = 1.1 \cdot 10^5\ s^{-1}$ (2.7)

$^{\bullet}OH + O_3 \rightarrow HO_4^{\bullet}$ $k_5 = 2.0 \cdot 10^9\ M^{-1}s^{-1}$ (2.8)

$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2$ $k_6 = 2.8*10^4\ s^{-1}$ (2.9)

Termination steps:

$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3$ (2.10)

$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_3 + O_2$ (2.11)

When the chain reactions given above are evaluated, the first fundamental element in the rate constant values is that the free-radical initiating step constitutes the rate-determining step in the reaction. The second is that the regeneration of the superoxide radical ion $O_2^{\bullet -}$, or its protonic form HO_2, from the hydroxyl radical $OH^{\bullet}$ implies that 1 mole of ozone is consumed. As a result all the species capable of consuming hydroxyl radicals without regenerating the superoxide radical ion will produce a stabilizing effect on the ozone molecule in the water (Langlais et al., 1990).

In Table 2.5. the bimolecular rate constants of ozone and hydroxyl radical with organic compounds are compared. It is clear that hydroxyl radical reactions are much faster compared with the direct ozon reactions.

Table 2.5. Reaction Rate Constants (k, in $M^{-1}s^{-1}$) of Ozone and Hydroxyl Radicals with Organic Compouds (CCOT, 1993).

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

It is because of selectivity of ozone that most water treatment processes can be performed with relatively low ozone dosages. For processes requiring higher ozone doses, the cost of this oxidant, its low water solubility combined with its low mass transfer, and its tendency to decompose under certain conditions, restrict its use (Hoigné,1988). In the following section, the main application areas of ozone are explained.

2.3.3 Application Areas of Ozone

Ozone application has increased enormously both in number and diversity since the first full scale application of ozone for the disinfection of drinking water (Gottschalk et al., 2000, 21). It is used for the treatment and purification of ground and surface waters, for domestic and industrial wastewater as well as swimming pools and cooling tower systems. It has been integrated into production processes that utilize its oxidizing potential, e.g. bleaching in the pulp and paper industry, metal oxidation in the semiconductor industry. Its effectiveness is based upon the multiple effects produced by the oxidative and disinfective activity of ozone and ozone-derived species such as $OH^{\bullet}$ radicals.

Main application areas of ozone can summerized as;

- Disinfection
- Oxidation of inorganic pollutants
    - Iron and Manganese
- Oxidation of organic micropollutants
    - Taste and odour compounds
    - Phenolic pollutants
    - Pesticides
- Oxidation of organic macropollutants (nonspecific organic targets)
    - Bleaching of colour
    - Increasing the biodegradability of organics

- Destruction of trihalomethane formation potential (THMFP), total organic halide formation potential (TOXFP), and chlorine demand

- Improvement of coagulation

- Sludge processing

Ozone is used in three ways; as a disinfectant, as a classical oxidant and as a pretreatment for improving the performance of subsequent processes.

Oxidation of organic compounds is one of the most important application areas of ozone. The ozonation of organic compounds involves a step-wise process whereby oxygen atoms are progressively introduced into the compound. Smaller molecules are thus formed, containing a greater percentage of oxygen in their chemical structure in the form of hydroxyl, carboxyl or aldehyde functional groups that are more amenable to biodegradation. At low pH the predominant reaction mechanism is the direct electrophilic attack by molecular ozone (ozonolysis). This is a selective reaction as mentioned before, resulting in the formation of carboxylic acids as final end-products that cannot be oxidised further by molecular ozone. Compounds susceptible to ozonolysis are those containing C=C double bonds, specific functional groups (e.g. OH, CH_3, OCH_3) and atoms carrying a negative charge (N, P, O, S and nucleophilic carbons). Ozonolysis of aromatic compounds will cause the loss of side-chain substituent or involve cleavage of the aromatic ring structure. At high pH, organics are degraded by chain reactions involving powerful, non-selective radicals including $OH^{\bullet}$ radical produced by ozone decomposition, and total mineralisation is possible but not desirable in the interests of process efficiency (Alvares, et al., 2000).

One of the main purposes of ozone application is increasing the biodegradability of organics. Some organic compounds are readily oxidized by ozone to produce CO_2 and water, some are easily oxidized to form biodegradable reaction products, and some are not readily reactive with ozone at all. Most of the organic oxidation products of ozone are more readily biodegradable than the original compounds and therefore presumably less toxic than the starting compounds (Rice, 1981). Complete mineralization does not appear to be economical compared to partial oxidation and biodegradation. As a result, ozonation can be effectively used as a pre-treatment method for refractory and toxic pollutants in order to increase their biodegradability for further treatment.

2.3.4 Kinetic Regimes

The kinetics of heterogeneous reactions is governed by absorption theories of gases in liquids accompanied by chemical reactions. In a gas-liquid reacting system, diffusion, convection and chemical reaction proceed simultaneously and the behaviour of the system can be predicted with the use of models describing gas absorption theories. According to the film theory, in a gas-liquid system there are two films, one for each phase. In a general case, when gas and liquid phases are in contact, the components of one phase can transfer to the other to reach equilibrium. If it is assumed that one component A of a gas phase is transferred to the liquid phase, the rate of mass transfer or absorption rate of A is:

$$N_A = k_G(P_{Ab} - P_i) = k_L(C_A^* - C_{Ab}) \quad (2.12)$$

where

N_A : rate of mass transfer of A ($mol.m^{-2}.s^{-1}$)

k_G : individual mass transfer coefficient for gas phase ($mol.s^{-1}.m^{-2}.Pa^{-1}$)

k_L : individual mass transfer coefficient for liquid phase ($m.s^{-1}$)

$P_{A,b}$: partial pressure of A in the bulk gas (Pa)

P_i : partial pressure of A at the interface (Pa)

C_A^* : concentration of A at at the interface ($mol.m^{-3}$)

$C_{A,b}$: concentration of A in the bulk of the liquid ($mol.m^{-3}$)

Lewis and Whitman (1924) proposed that when two nonmiscible phases are in contact, the main resistance is located in a stationary layer of thickness δ close to the interface, called the film layer. It is also assumed that mass transfer through the film is only due to diffusion and that the concentration profiles with distance to the interface are reached instantaneously.

In most common situations the gas is continuously bubbled into the liquid phase, so the interfacial surface is due to the external surface of bubbles. Concentration profiles of the gas component being absorbed for both the gas and liquid films are shown in Figure 2.6.

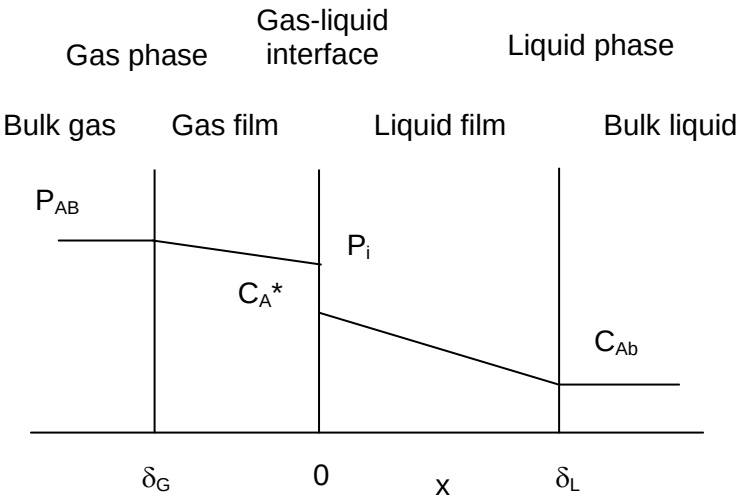

Figure 2.7. : Concentration Profile of a Gas Component A (shown as partial pressure $P_{A,b}$) with the Distance (shown as x) to the Interface During its Physical Absoption According to the Film Theory (Beltran, 2004).

The Hatta number (Ha_2) is used to represent the ratio of the maximum chemical reaction through the film layer and the maximum physical absorption rate, therefore indicating the relative importance of chemical reaction and mass transfer rates in the gas-liquid system (Beltran, 2004).

Irreversible second-order reactions are typical for most direct ozone reactions in water. The Hatta number for the irreversible second-order gas-liquid reaction is given as:

$$Ha_2 = \frac{\sqrt{k_{O3,B}\, D_A\, C_{B,b}}}{k_L} \qquad (2.13)$$

where

$k_{O3,B}$:bimolecular rate constant for the reaction between ozone and compound B ($M^{-1}.s^{-1}$)

D_A : molecular diffusivity of ozone, ($m^2.s^{-1}$)

$C_{B,b}$: concentration of compound B in the bulk phase ($mol.L^{-1}$)

k_L : liquid phase individual mass transfer coefficient ($m.s^{-1}$).

Another dimensionless number called enhancement factor E, is defined to describe the increase in mass transfer due to a simultaneous reaction.

$$E = \frac{N_{Ao}}{M_1} \qquad (2.14)$$

where

N_{Ao} : absorption rate of ozone ($mol.s^{-1}.m^{-2}$)

M_1 : maximum physical absorption rate at the interface ($mol.s^{-1}.m^{-2}$)

The degree of enhancement depends upon the relative concentration of reacting compounds in each phase, their solubility, and relative resistance of the mass transfer and reaction steps. It can be visualized by considering a reactor with a certain mass transfer rate due to physical absorption, into which various compounds are introduced (Figure 2.7).

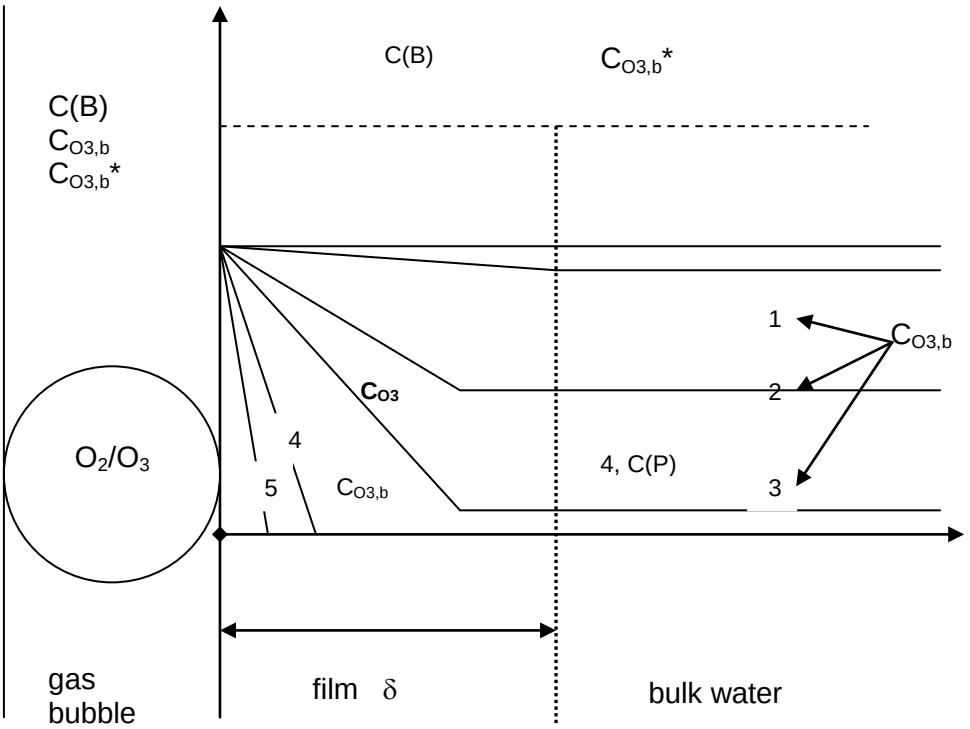

Figure 2.8. : The Different Kinetic Regimes for Mass Transfer with Simultaneous Reaction of Ozone (Gottschalk et al., 2000).

If a slow reacting compound is introduced where no mass transfer enhancement occurs, a concentration profile similar to (1) will develop in the film and bulk liquid. A compound which reacts more readily with ozone can develop a fast or instantaneous reaction causing gradient (4) or (5) to develop. Oxidation products P are formed in the film and diffuse out into the bulk (4). In between moderate regime

(2) and (3) are present. As the kinetic regime goes from slow to moderate, fast or instantaneous, the concentration gradient becomes steeper and the reaction moves further into the film. To simplify the discussion both the concentration of organic pollutants B in the liquid film and ozone in the gas phase are assumed to remain constant for all cases (Gottschalk et al., 2000).

Establishment of the kinetic regime of ozone absorption is an important aspect which should be considered in the kinetic study of a gas-liquid reaction such as ozonation, due to the variation of in the absorption rate law equation. Different kinetic regimes, conditions and parameters that are used to determine the kinetic regime of a reaction are given in Table 2.6.

Table 2.6. : Conditions and Parameters Used to Determine the Kinetic Regime of a Reaction (Beltran, 2004).

Kinetic Regime	**Conditions and Parameters of Interest**
Slow	$Ha_2<0.3$, $C_{O3,b} \neq 0$, Rate constant, $k_La>k_1$*
Moderate	$0.3<Ha_2<3$, $C_{O3,b} = 0$, Mass transfer coefficient
Fast	$Ha_2>3$, $C_{O3,b} = 0$, Rate constant or mass transfer coefficient
Fast pseudo first-order	$3<Ha_2<E_i/2$, $C_{O3,b} = 0$, Rate constant or specific interfacial area
Instantenous	$Ha_2>nE_i$, $C_{O3,b} = 0$, Mass transfer coefficient

*k_1 = pseudo-first order pollutant abatement rate constant ($time^{-1}$)

As it is evident in the above table, concentration of dissolved ozone ($C_{O3,b}$) is an important parameter to be followed. The absence of dissolved ozone is definite proof of fast or instantaneous regime while the opposite situation indicates a slow kinetic regime. In addition, the volumetric mass transfer coefficient (k_La) being greater than the pseudo-first order pollutant abatement rate constant (k_1) indicates that the reaction is kinetically limited and therefore can be categorized as occuring in a slow kinetic regime.

When both the gas and water phases are perfectly mixed, a molar balance of ozone in water leads to the following equation:

$$\frac{dC_{O3,b}}{dt} = G_{O3} \qquad (2.15)$$

where

G_{O3} : generation rate term of ozone ($mol.m^{-3}.s^{-1}$)

$C_{O3,b}$: ozone concentration in the bulk liquid ($mol.m^{-3}$)

The absorption of ozone in water is a gas-liquid reaction system because the fraction of dissolved ozone decomposes in water. The chemical reaction can be considered an irreversible first or pseudo-first order reaction, although in some works other reaction orders are reported (Roth and Sullivan, 1983). The rate constant of this reaction is very slow especially when the pH<7 and the corresponding Hatta number Ha_1 is <0.01. As a consequence, the kinetic regime of ozone absorption corresponds to a very slow reaction. Thus at pH<7 and nonstationary conditions Eq. 2.15 can be applied to a perfectly mixed reactor becomes:

$$\frac{dC_{O3,b}}{dt} = k_L a(C_{O3,b}^* - C_{O3,b}) - k_d C_{O3,b} \qquad (2.16)$$

where

$k_L a$:volumetric mass transfer coefficient (s^{-1})

k_d : rate constant of the ozone decomposition (s^{-1})

$C_{O3,b}^*$: equilibrium ozone concentration at the gas-liquid interface ($mol.m^{-3}$)

$C_{O3,b}$: concentration of dissolved ozone ($mol.m^{-3}$)

The accumulation rate of ozone in water is the sum of the ozone transfer rate from the gas minus the ozone decomposition rate ($k_d.C_{O3,b}$) that results form the chemical reaction ozone undergoes even in pure water, that is the ozone decomposition reaction.

In the kinetic study of single direct ozonation reactions, appropriate experimental conditions should first be established for the ozone – pollutant (B) reaction to be the only reaction consuming ozone. The competitive effect of ozone decomposition can be eliminated by considering the kinetic regimes of this reaction and the rate

constant of the direct reaction under study. At pH lower than 12, if both reactions (ozone decomposition and direct reaction) develop in the same kinetic regime, the former reaction can be quenched by the addition of hydroxyl radical scavengers such as t-butanol or bicarbonate/carbonate (Beltran, 2004). As a result equation 2.16 becomes:

$$\frac{dC_{O3}}{dt} = k_L a(C_{O3}^* - C_{O3}) \qquad (2.17)$$

Integrating Eq. 2.17 with boundary conditions of C = 0 at t = 0 and C = C at t = t yields:

$$\ln((C_{O3}^* - C_{O3})/C_{O3}^*) = k_L a.t \qquad (2.18)$$

the values of $k_L a$ can be obtained by plotting the left-hand side of the Eq. 2.18 against ozone-wastewater contact time and it can be compared with the first order pollutant abatement rate constant in order to evaluate the kinetic regime.

For slow kinetic regimes, the gas liquid reaction is a two series process where mass transfer through the film layer first occurs and then the chemical reaction develops in the bulk liquid (Beltran, 2004). The mass transfer rate is high and/or ozone reacts slowly with the pollutants. A small difference between the solubility level of ozone C_{O3}^* and the bulk liquid ozone concentration C_{O3} is sufficient for ozone transfer into the liquid along the linear concentration gradient. Besides the general influences of pressure and temperature, the overall rate of ozone consumption and thus, the reaction rate of the pollutant B, is exclusively influenced by chemical parameters. The reaction is controlled by chemical kinetics (Gottschalk et al., 2000).

Once direct reactions are eliminated, the rate constant of the direct reaction of ozone – B compound can be obtained directly from the mass balance of B in the batch reactor;

$$r_B = -\frac{dC_{B,b}}{dt} = k_{O3.B} \,.\, C_{O3,b} \,.\, C_{B.b} \qquad (2.19)$$

r_{BI} : Ozonation rate of BI ($M.s^{-1}$)

$C_{B,b}$: Concentration of BI in the bulk liquid ($mol.m^{-3}$)

$k_{O3,BI}$: bimolecular rate constant of direct reaction ozone-B compound ($M^{-1}s^{-1}$)

Eq. 2.19 can be used if concentrations of B and ozone are known with time, that is a typical situation for the slow kinetic regime. The recommended method is the use of an analytic procedure, that is to integrate the equation or to use differential method.

2.4 Ozonation of Industrial Pollutants

Ozone can be used to mineralize a compound or to partially oxidize it, making refractory organic compounds accessible to biodegradation (Libra and Sosath, 2003).

Chlorophenoxy herbicides have potential toxicity towards humans and animals and are considered as moderately toxic. Because of their intensive use and poor biodegradability, they have been detected as major pollutants in ground and surface waters. In the study of Brillas et al. (2004), alternative procedures involving O_3, O_3/UVA, O_3/Fe^{2+}, O_3/UVA/Fe^{2+} and O_3/Fe^{2+} + Cu^{2+}/UVA systems for degradation of 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP) at initial pH = 3.0 has been investigated. The kinetic analysis yielded a pseudo first-order rate constant k_1 = $2.4x10^{-3}$ s^{-1} for ozonation alone. The k_1 value has increased to $1.0x10^{-2}$ s^{-1} for O_3/Fe^{2+} system due to production of $OH^{\bullet}$ radicals according to the reaction mechanism of O_3/Fe^{2+} systems. The second order rate constant (k_2) of the direct reaction of 2,4-DP with molecular ozone, was found to be 260 $M^{-1}s^{-1}$ which describes the fast destruction of this herbicide by O_3 system.

The ozonation of highly condensed polycylic aromatic hydrocarbons (PAH) was studied in oil/water emulsions by Kornmüller et al. (2003). The second-order rate constant for PAH ozonation in water in a semi-batch, standard stirred reactor with a volume of 4L at pH = 2 with addition of 0.01M t-butanol was found to be $3.06x10^{1}$ $M^{-1}s^{-1}$ and in a semi-batch, stirred reactor with a volume of 1L at pH = 2 with addition of 0.01M t-butanol was found to be $4.5x10^{1}$ $M^{-1}s^{-1}$.

The study of Andreozzi et al. (2003), assessed the kinetics of chlofibric acid from aqueous solutions. The ozonation experiments were conducted in a semicontinuous stirred tank Pyrex glass reactor operated in the batch mode with respect to liquid phase. Ozonation processes of organic species in this reactor developed under slow/fast kinetic regime for Hatta number<2.0 and under a quasi-diffusive regime for Hatta number values up to 25. Ozonation of chlorofibric acid at pH = 2 and pH = 2.5 showed slow kinetic regimes and resulted in bimolecular rate constants of 29.8±1.52 and 39.7±2.30 $M^{-1}s^{-1}$, respectively. As the pH increased, the bimolecular rate

constants increased up to 2550 $M^{-1}s^{-1}$ at pH = 6.5 and the kinetic regime passed from slow to fast and from fast to quasi-diffusive regime.

Barletta et al. (2002) studied the ozonation kinetics of eight 2-chloro-4,6-dialkylamino-1,3,5-triazines which are used as persistent herbicides. The second order rate constants for the ozonation of trazines at pH = 3 were found between 1.53±0.28 $M^{-1}s^{-1}$ and 11.9±0.50 $M^{-1}s^{-1}$. It is concluded that the reaction of ozone with the triazines in water at pH = 3 occured through a rate-determining electrophilic attack of ozone.

Naphthalene and benzene sulphonic acids, widely used in azo-dyes and textile manufacturing, have been found in various surface and underground natural water bodies. Together with halogens and nitro substituents, these groups are poorly biodegradable, because of esteric effects or formation of aromatics. On the other hand, ozonation has been successfully used to destroy aromatic rings and double bonds, leading to smaller biodegradable molecules. Calderara et al. (2001) studied the ozonation kinetics of 1-naphthalene, 1,5-naphthalene, and 3-nitrobenzene sulphonic acid and found bimolecular rate constants of 252 $M^{-1}s^{-1}$, 41 $M^{-1}s^{-1}$, and 22 $M^{-1}s^{-1}$ respectively at pH = 3.

The aqueous reactivity of 2,4,6-trichlorophenol (TCP) with ozone has been studied using a bubble/liquid contacting system by Graham et al. (2003). Degradation rate constants were found to be 7.6 and 77.2 $M^{-1}s^{-1}$ at pH = 2 and 7.5, respectively. The relatively small increase in TCP degradation rate was explained by the greater reactivity of the dissociated TCP via direct molecular ozone mechanism. According to the ozone reaction scheme given, initially one chlorine in the TCP was subtituted by a hydroxyl group to produce DCQ, H^+, and Cl^-. It is noted that DCQ could be further degraded by cleavage of the aromatic ring leading to the formation of aliphatic products.

Treatment of 2-chlorophenol (2-CP), 4-chlorophenol (4-DCP), and 2,4-dichlorophenol (2,4-DCP) in aqueous solutions with direct photolysis, ozonation, and ozonation with photolysis was studied by Hautaniemi et al. (1998). Bimolecular rate constants for degradation of 2-CP, 4-DCP, and 2,4-DCP are calculated to be 460, 1810, and 1600 $M^{-1}s^{-1}$, respectively and the Hatta numbers found indicate that the kinetic regime is slow (Ha<0.3).

Benitez et al. (2000) studied the chemical decomposition of aqueous solutions of various chlorophenols by means of single oxidants and by advanced oxidation

processes. The pathways proposed by Chen and Ni (1998) to describe the complete ozonation of 2,4-dichlorophenol were hydroxylation, dechlorination, and ring-cleavage. According to this mechanism, the presence of more atoms of chlorine enhances the dechlorination step, and therefore the degradation is faster.

A quantitative estimation of direct ozonation and indirect free radical oxidation of dyes was studied through the examination of reaction kinetics in the ozonation process by Chu and Ma (1999). For all selected azo dyes, the decay rates increased as the initial pH of the solution increased, on the other hand the decay rates of anthraquinone dyes would decrease in the same situation because of their insensible structure for ozone oxidation, formation of leuco-form (less coloured), and higher solubility at lower pH.

Zenaitis et al. (2002) and Zenaitis and Duff (2002) used ozonation as a pretreatment for biological degradation of of log yard run off containing tannin and lignin. The efficiency of ozone as pre- and post-biological treatment was assessed.During ozone pretreatment, tannin and lignin concentrations and acute (Microtox) toxicity reduced by 70% and 71%, respectively. BOD and COD concentration reduced by<10%. A larger fraction of residual COD was non biodegradable after ozonation. When biologically treated effluent was subjected to ozonation, reduction in COD and tannin and lignin concentrations were observed, however no further improvement in toxicity was observed.

In the study of Perkowski et al. (1996), two-stage ozonation with intermediate biodegradation proved to be a valuable tool for obtaining high chemical oxygen demand, and elimination efficiencies in the tertiary treatment of textile effluent with high and persistent COD concentrations.

Saroj et al. (2005), studied the extent of mineralization, reduction in colour and reduction of COD of gallic acid, tannin and lignin by ozonation and a combination of aerobic biodegradation and ozonation. COD removal of greater than 80% and high removals (>90%) of specific UV absorbance at 280 nm and specific colour was observed at an ozone dose of 6 mg ozone absorbed per mg initial TOC or higher. Ozone absorption efficiency of post-aerobically biodegraded tannin is observed to be nearly identical to that of pure tannin, while that of post-aerobically biodegraded lignin is observed to be less than that of pure lignin. These results indicate that partially oxidized by-products containing higher oxidation state organic carbon, exhibit equivalent or less affinity toward ozone than pure tannin and lignin.

Rate constants of reactions between ozone and some pollutants obtained from the literature are summerized in Table 2.7 together with the experimental conditions.

Table 2.7. : Bimolecular Rate Costants of Some Pollutants Obtained from the Scientific Literature.

Pollutant	**pH**	**Bimolecular Rate Constant, $M^{-1}.s^{-1}$**
2-2,4-dichlorophenoxy propionic acid	3	260
Polycyclic hydrocarbon	2	30.6
Chlofibric acid	2	29.8
	2.5	39.7
2-chloro-4,6-dialkylamino-1,3,3-triazines	3	1.53 – 11.9
1-naphthalene sulphonic acid	3	252
1,5- naphthalene sulphonic acid	3	41
3-nitrobenzene sulphonic acid	3	22
2,4,6-trichlorophenol	2	7.6
	7.0	77.2
2,4,4'-trichloro-2'-hydroxyphenyl ether	7.0*	43

* $NaHCO_3$ is added as scavenger to stabilize ozone.

In the last raw, the bimolecular rate constant of the reaction between ozone and BI (2,4,4'-trichloro-2'-hydroxyphenyl ether) is given. The bimolecular rate constant of BI can be compared with the rate constants of some pollutants obtained from the literature data at similar experimental conditions.

3. MATERIALS AND METHODS

3.1 Materials

Tannins, one natural tannin (NT) and one synthetic tannin (ST); two finishing agents Biocide I (BI) and Biocide II (BII) that are used to simulate typical effluent from the dyeing and finishing stages have been obtained from a local textile mill in Istanbul.

3.1.1 Tannins

Among the refractory pollutants that originate form the textile preparation, dyeing and finishing process stages, textile tannins are olygomeric compounds with multiple structured, phenolic chemicals frequently used during polyamide dyeing with acidic, metal complex and direct dyes at the after-rinsing stage to increase fixation rates and wet fastness of the dyed fabric.

The physicochemical properties of the selected textile tannins are given in Table 3.1. NT is generally used at a concentration of 1.56 g/L in the acid dyebath (i.e. 4% of the fabric weight is usually applied and 25% remains unfixed in the spent dyebath) and at pH = 3.5 – 4.0; ST is used at a concentration of 1.25 g/L (i.e. 4% of fabric weight is applied to the dyebath and 25% contributes to the exhausted dyebath effluent) and at pH = 3.5 – 4.0 as well.

As it is evident from Table 3.1, although ST and NT exhibit low acute oral toxicities, SDS information obtained for their acute fish toxicity implied that in particular ST is relatively toxic toward the selected test organisms. Upon comparison of the fish toxicity data (LC_{50} values) with typical ST and NT concentrations that are most possibly encountered in dyehouse effluent (i.e. the initially applied tannin concentration in the dyebath x 0.25 for its final concentration in the exhausted dyebath x 0.375 for its concentration in the total dyehouse effluent), it might be inferred that both tannins impart potential toxicity (C_{NT},final = 0.15 g/L; C_{ST},final = 0.12 g/L) to the final wastewater.

Table 3.1. : Physicochemical Properties of the Selected Textile Tannins, ST and NT (Safety Data Sheet Information).

Property	**ST**	**NT**
Appearance	Yellow liquid with a characteristic odour	Brownish liquid With a weak odour
Ingredients	Aqueous solution of tannic acid	A methylene linked condensation product of arylsulphonic acids and hydroxyarylsulphone preparations
Density (g/cm^3)	1.15 at 25ºC	1.10 at 23ºC
pH	2.5 – 3.5	7.0 – 8.0
Viscosity (mPa.s)	10 – 100 at 25ºC	< 50 at 23ºC
Solubility	Highly water soluble	Highly water soluble
Acute oral toxicity (LD_{50}; mg/g)*	> 2000	> 2000
Fish toxicity (LC_{50}; mg/L)	>100**	1 – 10***
BOD_5 (g/kg)	55	5

*Lethal dose causing 50 % death in rats;
**Lethal concentration of pollutant (in mg/L) causing 50% death of the studied test organism, Zebra fish
***Lethal concentration of pollutant (in mg/L) causing 50% death of the studied test organism, Leuciscus idus

Due to their acutely toxic character and low biodegradability, tannins definitely require pretreatment prior to discharge into the municipal sewer or their ultimate disposal into receiving natural water bodies. Hence, ozonation might be a promising alternative for the effective treatment of textile tannins.

3.1.2 Biocides

Two commercially important biocidal finishing agents were selected for the present work in order to mimic typical textile effluents originating from the textile finishing process stage.

BI is used for antimicrobial treatment of textiles in the textile industry especially in the hosiery, underwear, apparel, bedding, carpet, rug and fibre production. It is applied with 2 – 4 % on weight of goods at a concentration of 500 mg/L at neutral pH (7±0.2).

BII is a wide spectrum textile biocide with a broad range of action against bacteria, mould and yeast fungi as well as dust mites. The formulation is also suitable for textiles worn next to the skin. They are applied to the dyes and rinsed textile fabric in a separate bath, batch wise and at a concentration of 500 mg/L at neutral pH (7±0.2) like BI.

According to the information given above, the synthetic wastewater of BI and BII are prepared by dissolving 500 mg of BI and 500 mg of BII in 1 liter distilled water in order to mimic the actual conditions.

The physicochemical properties of the studied textile biocides are summarized in Table 3.2.

Table 3.2. : Physicochemical Properties of the Selected Biocides, BI and BII.

Property	**B I**	**B II**
Appearance	Clear, colourless liquid	Clear, colourless liquid
Active Ingredients	2,4,4'-trichloro-2'-hydroxydiphenyl ether	A diphenyl alkane derivative, non-ionic
Boiling point (^{o}C)	82	130
Vapor pressure	21 mmHg (volatile organic content < 15% w/w)	Not specified
Density (g/cm^3 at 20 ^{o}C)	0.99	1.03
Acute oral toxicity* (mg/kg LD_{50} value in rats)	> 2000	Not specified
Acute toxicity** (v / v % LD_{50})	7	8
BOD_5 (g/kg)	< 12	< 4

*Lethal dose causing 50 % death in rats;
** Acute toxicity towards the water flea *Daphnia magna*; % volumetric dilution of the effluent sample causing 50 % death in the selected test organisms

The above table indicates that both biocides are practically non-biodegradable in nature. It is also important to mention here that biocide BI is a halogenated organic and seriously contributes to effluent AOX. Although BI has a low acute oral toxicity, its acute toxicity towards the water flea Daphnia magna (a commonly used specie to test potential toxicity of industrial effluents in many EU countries in accordance with OECD Guidelines and Standard Methods) implied that a 7% volumetric dilution of

the effluent sample resulting in 35 mg/L BI , may cause serious toxicity (i.e. 50% death in aquatic organisms) due to the fact that this particular concentration remains below BI concentrations found in dyehouse effluent (around 50 mg/L). The same situation exists for biocide BII, whose D. magna LD_{50} value corresponds to 40 mg/L BII that is again a lower value than typical BII concentrations in the total dyehouse effluent. It can be concluded from Table 3.2 that, BI and BII are refractory substances being resistant towards microbial degradation, and acutely toxic towards aquatic organisms.

3.2 Ozonation Experiments

3.2.1 Ozonation Set-up

Ozonation experiments were carried out in a 800 mL-capacity borosilicate glass bubble column reactor which was initially filled with synthetic wastewater and continuously ozonated in semi-batch mode with respect to ozone gas. The volumetric mass transfer coefficient of the reactor was 1.71 min^{-1} as determined by the Indigo Colourimetric Method (APHA, 1989). Ozone was generated from pure oxygen using a electrical discharge ozone generator (Sander Model S1000) with a maximum capacity of 1000 mg O_3/h. An ozone and oxygen gas mixture was introduced from the bottom of the reactor through sintered gas dispersion disc at a rate of 1.0 L min^{-1}. The unused ozone leaving from the top of the reactor was collected in two gas washing bottles connected in series and filled with 5% KI solution in order to determine the amount of off-gas ozone iodometrically (APHA, 1989). Two other gas wash bottles filled with 2% KI solution were placed in another ozonation line in order to determine ozone feed rate. For all the connections in the experimental set-up Neoprene tubing and Teflon were used. The ozonation experimental set-up is depicted in Figure 3.1.

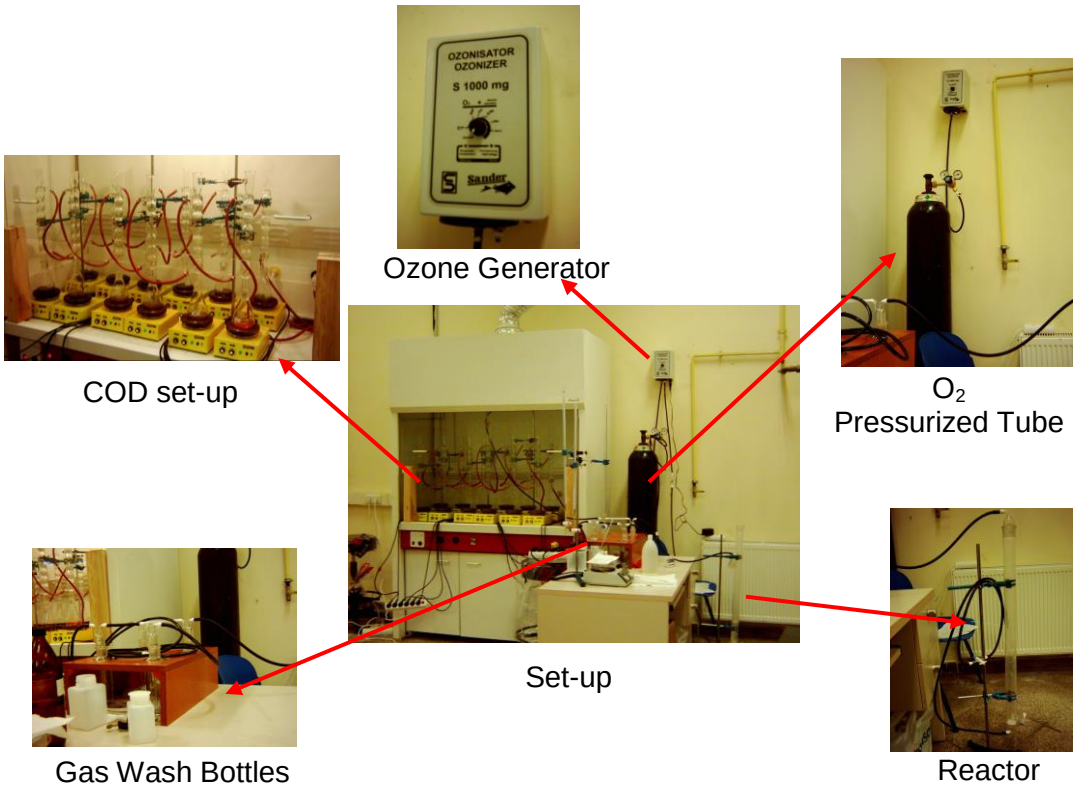

Figure 3.1. : Experimental Set-up for Ozonation Experiments

Ozonation experiments were mainly conducted for 60 min except for those to follow changes in TOC and AOX, where experiments were continued for 120 min. Samples for analyses of collective environmental parameters and determination of ozone concentrations (see 3.2.2.) were periodically withdrawn from the reactor at specific time intervals. Reaction pH of the wastewater was adjusted with phosphate buffers (Perin and Dempsey, 1974) given in Table 3.3.

Table 3.3.: Buffer Solutions Used in Ozonation Experiments (Perin and Dempsey, 1974)

Reaction pH	H_3PO_4 (0.1M)	KH_2PO_4 (0.1M)	Na_2HPO_4 (0.05M)	NaOH (0.1M)	$NaHCO_3$ (0.1M)
3.5	1*-7** mL/L	-	-	-	-
7.0	-	100 mL/L	-	60 mL/L	-
7.0***	-	-	-		50 mL/L
12.0	-	-	100 mL/L	60 mL/L	-

* for NT
** for ST
***for kinetic experiments, to eliminate the indirect, free radical reactions.

3.2.2. Determination of Ozone Concentration

3.2.2.1. Determination of Gas Phase Ozone Concentration

Ozone concentration in gas phase was determined by the iodometric titration method. The off-gas ozone collected in gas wash bottles filled with 5% KI solution, was titrated with 0.5N sodium thiosulphate solution and starch as indicator in acidic conditions attained by adding 5mL of 6M sulfuric acid solution. Iodine, which is produced from the reaction of ozone and iodide ions, is titrated with sodium thiosulphate solution according to the chemical reactions below:

$$O_3 + 2I^- 2H^+ \rightarrow I_2 + H_2O + O_2 \quad (3.1)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad (3.2)$$

The formula used for the calculation of the concentration of ozone in the off gas is given below:

$$O_3(mg/min) = \frac{V_{Na_2S_2O_3} \times N_{Na_2S_2O_3} \times 24}{t} \quad (3.3)$$

$V_{Na2S2O3}$: volume of $Na_2S_2O_3$ used (mL)

$N_{Na2S2O3}$: normality of $Na_2S_2O_3$ (eqg.L^{-1})

24 : milliequivalent mass of oxygen (g.eqg^{-1})

t : time (min)

The same procedure was used for the determination of ozone feed rate using 2% KI solution in gas wash bottles and 0.1N $Na_2S_2O_3$ solution for titration.

3.2.2.2. Determination of Liquid Phase Ozone Concentration

Aqueous phase ozone concentration was determined by the indigo colourimetric method which is based on change in the colour of indigo trisulfonate solution. Ozone concentration in liquid phase in followed by the decrease in absorbance values at 600 nm (APHA, 1989). The reaction between indigo trisulfonate and ozone is:

$$C_{16}H_7N_2S_3K_3 + O_3 \rightarrow 2C_8H_3NO_8S_2K_2 + \text{other oxidation products} \quad (3.4)$$

Ozone concentration in liquid phase (mg O_3/L) can be calculated from the formula:

$$O_3(mg/L) = \frac{\Delta Abs \, x \, V_T}{f \, x \, b \, x \, V_m} \quad (3.5)$$

where

ΔAbs : difference between absorbance values of sample and blank at 600 nm (cm^{-1})

b : optical distance of the cell (cm)

f : constant determined according to the 4500-O_3 standard method, 0.42

V_m : volume of the ozonated sample (mL)

V_T : total volume of the sample and the indigo solution (mL)

3.3. Determination of Collective Environmental Parameters

3.2.1 Determination of COD

COD measurements were performed in accordance with the open reflux method according to Standard Methods (1989). Chemical oxygen demand is the amount of dichromate ion that goes into reaction with the sample in acidic conditions. Chromate ion which is the oxidant is reduced to cromic ion, and the sample is oxidized according to the chemical reaction below:

$$C_nH_aO_b + c\ Cr_2O_7^{2-} \quad 8c\ H^+ \rightarrow n\ CO_2 + (a+8c)/2\ H_2O + 2c\ Cr^{3+} \quad (3.6)$$

After the sample which contains the pollutant is oxidized for 2 hours at 150ºC in acidic conditions, the remaining cromate ion is titrated with ferrous ammonium sulfate using ferroin as the indicator.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad (3.7)$$

$$COD = \frac{(a-b)\ x\ N\ x\ 8000}{V_{sample}} \quad (3.8)$$

where

a : volume of ferrous ammonium sulfate solution used for blank (mL)

b : volume of ferrous ammonium sulfate solution used for the sample (mL)

N : normality of ferrous ammonium sulfate solution (eqg.L^{-1})

8000 : milliequivalent mass of oxygen x 1000mL/L

3.3.2. Determination of TOC

TOC was monitored on an Apollo 9000 model TC analyzer (Tekmahr-Dohrmann Instruments, Inc.).

3.3.3. Spectrophotometric Measurements

UV absorbance measurements were carried out by using 1cm optical path length quartz cell with Shimadzu UV 1240 model spectrophotometer which has a range of 200 – 1100 nm. In addition to absorbance measurements at 280 nm indicating the aromatic structure (Nakamura et al., 2004) and 254 nm showing the unsaturated bonds (Arslan and Akmehmet Balcioglu, 2000), absorbance values at characteristic wavelengths of the tannins and biocides were followed throughout the ozonation experiments.

3.3.3.1 Absorption Spectra of Textile Tannins

The absorption spectra for 1.56 g/L NT at different pH values are given in Figure 3.2. All the samples were diluted 50 fold before measurement in order to have absorbance values lower than 1.

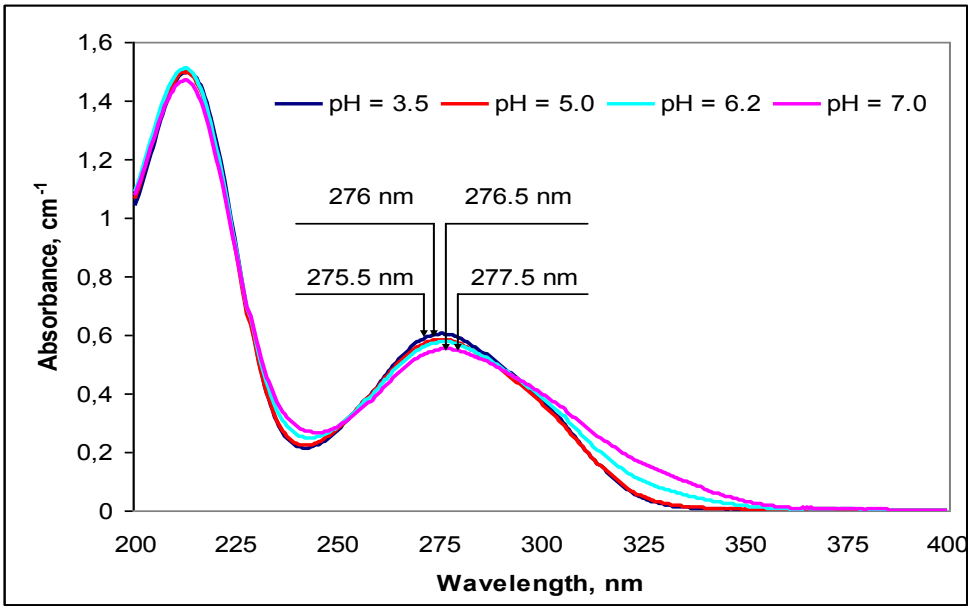

Figure 3.2. : Absorption Spectra for 1.56 g/L NT at pH = 3.5, pH = 5.0, pH = 6.2 and pH = 7.0. All samples were 50 fold diluted with deionized water (pH = 5.5).

As it can be seen from the figure, there is a characteristic absorption peak at around 276 nm wavelength. There is a slight shift in the peak value as the pH of the sample change (275.5 nm – 277.5 nm).

The absorption spectra for 1.25 g/L ST at different pH values are given in Figure 3.3. All the samples were diluted 20 fold before measurement in order to have absorbance values lower than 1.

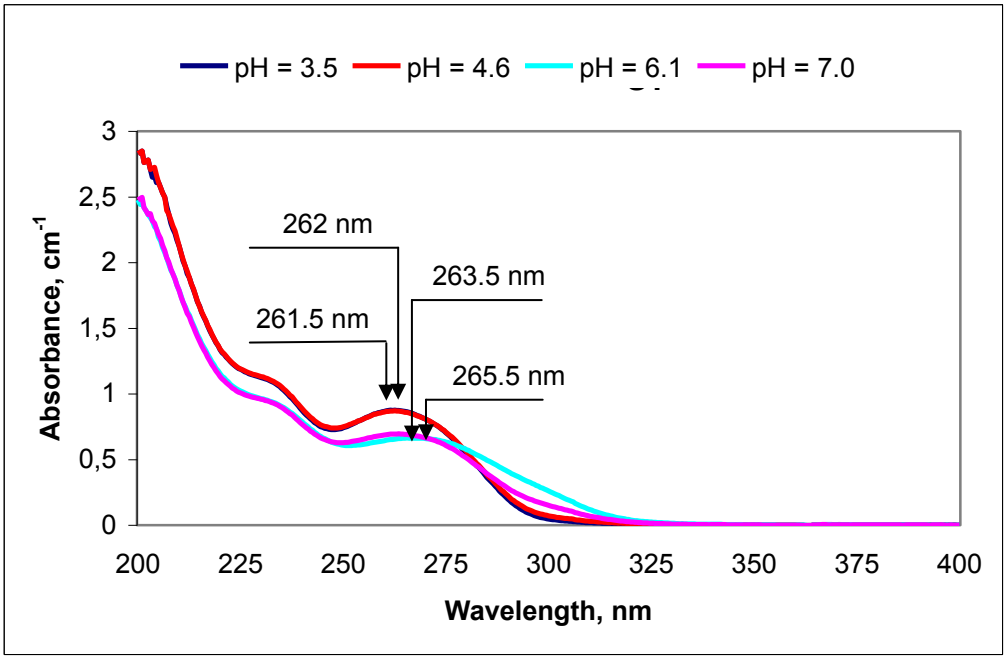

Figure 3.3. : Absorption Spectra for 1.25 g/L ST at pH = 3.5, pH = 4.6, pH = 6.1 and pH = 7.0. All samples were 20 fold diluted with deionized water (pH = 5.5).

As it can be seen from the figure, there is a characteristic absorption peak at around 263 nm wavelength. There is no difference between the absorption spectra at pH = 3.5 and 4.6. However when the pH is increased to 6.1 and 7.0 a slight shift in the spectrum, can be observed. The peak values do not change significantly ranging between 262 nm and 265.5 nm.

3.3.3.2 Absorption Spectra of Textile Biocides

The absorption spectra for 0.50 g/L BI at pH = 7.0 and 12.0 are given in Figure 3.4. As it is evident from the figure, there is a specific peak value at 279.5 nm which is very close to the wavelength, 280 nm indicating aromatic structure. Since 280 nm is the maximum wavelength for BI at pH = 7.0, UV_{280} degradation is followed in order to monitor the parent compound degradation in the kinetic studies conducted for BI.

When the pH increased to 12.0, the spectrum and as a result the peak value shifted from 279.5 nm to 292 nm.

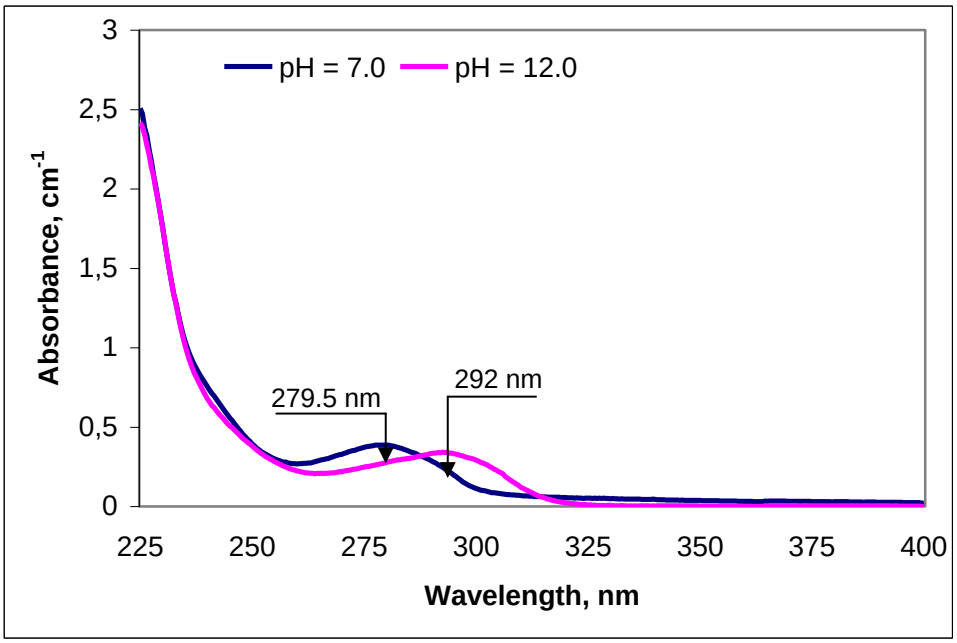

Figure 3.4.: Absorption Spectra for 0.50 g/L BI at pH = 7.0 and pH = 12.0.

The absorption spectra for 0.50 g/L BII at pH = 7.0 and 12.0 are given in Figure 3.5.

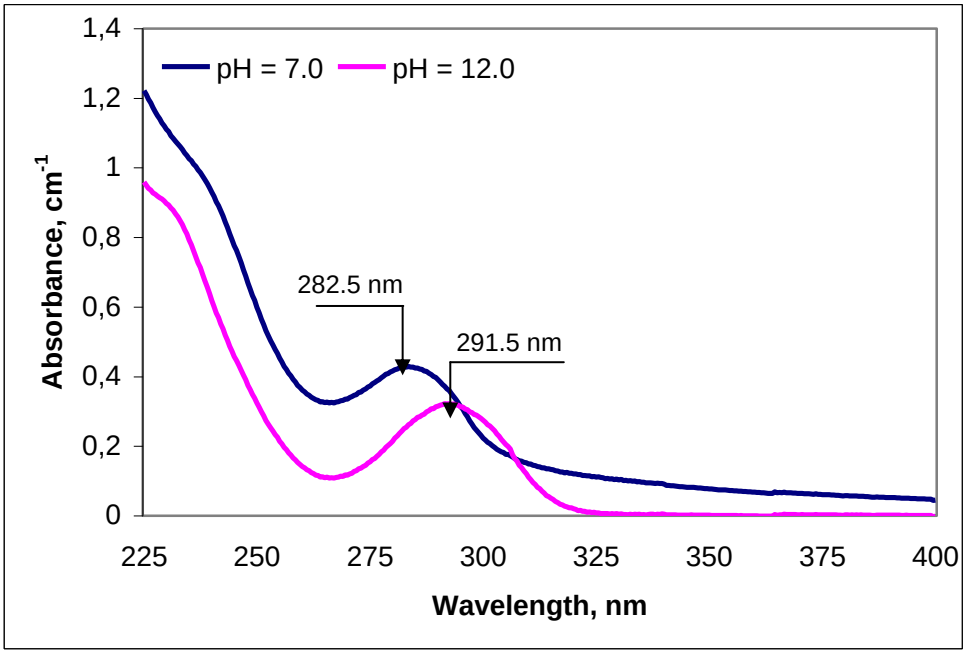

Figure 3.5. : Absorption Spectra for 0.50 g/L BII at pH = 7.0 and pH = 12.0.

As it can be seen from the figure, there is a specific peak value at 282.5 nm in the spectrum for BII at pH = 7.0. When the pH increased to 12.0, the spectrum and as a result the peak value shifted from 282.5 nm to 291.5 nm for BII.

3.3.4. Determination of BOD_5

BOD_5 measurements were performed by Alsterberg Azide Modification of the Winkler Method (AWWA, 1989). Dissolved oxygen measurements were carried out with dissolved oxygen meter. The synthetic domestic wastewater acclimated seed was used for inoculum. BOD_5 values were calculated according to the formula:

$$BOD_5 (mg/L) = \frac{(D_1 - D_2) - (B_1 - B_2) \times f}{P} \quad (3.9)$$

where

D_1 : dissolved oxygen of diluted sample before incubation (mg/L)

D_2 : dissolved oxygen of diluted sample after five day incubation (mg/L)

P : decimal volumetric fraction of sample used

B_1 : dissolved oxygen of seed control before incubation (mg/L)

B_2 : dissolved oxygen of seed control after five day incubation (mg/L)

f : ratio of seed in diluted sample to seed in seed control

3.3.5. Determination of AOX

AOX was measured by Behr Labor Technik CL 10 Model AOX analyzer. The samples were prepared according to the column method (DIN EN 1485:1996). For that purpose, the columns were rinsed with the samples + 2.5 mL 5% v/v nitric acid solution + 20 μL conc. HNO_3 all diluted to 50 mL with distilled water. The loaded, activated charcoal of the two columns was thereafter combusted separately in the 900ºC furnace for 8 min.

4. RESULTS AND DISCUSSION

The treatability of two textile tannins, Natural Tannin (NT) and Synthetic Tannin (ST); and two biocidal finishing agents, Biocide I (BI) and Biocide II (BII) by ozonation was investigated. Ozonation experiments were conducted at varying ozone feed rates and reaction pH values in a semi-batch ozone reactor by following the collective environmental parameters COD (Chemical Oxygen Demand), TOC (Total Organic Carbon), UV_{280}, and UV_{254} (representing the aromatic structure and unsatured moities of the compounds) and only for BI, AOX (Adsorbable Organic Halogens). Changes in the biodegradability of ozonated tannins were traced by measuring their BOD_5 (Biochemical Oxygen Demand) before and after oxidative pre-treatment at optimized ozonation conditions. The effect of ozonation on the acute toxicity of both textile tannins and finishing agents was evaluated by activated sludge inhibition experiments conducted within the scope of an ongoing EU COST Action (COST Action 628).

4.1 Ozonation of Textile Tannins-Process Optimization

60 min-experiments were conducted at different ozone feed rates in the range of 450 – 1100 mg/h at pH = 3.5 which is the application pH of textile tannins. After these experiments, to investigate the effect of pH on ozonation of tannins, experiments were run at pH = 3.5 and pH = 7 for 60 min and 120 min with an ozone feed rate of 900 mg/h.

4.1.1 Effect of Ozone Dose

In order to study the effect of ozone feed rate on COD, UV_{254}, and UV_{280} removal kinetics, NT and ST were subjected to 60 min ozonation at pH = 3.5 amd varying ozone feed rates. Experimental findings are given below.

4.1.1.1 COD Abatement

The effect of increasing ozone feed rate on COD removal is given in Figure 4.1 for NT and in Figure 4.2 for ST. For the interpretation of COD removal efficiency with respect to ozone utilization; the following parameters were evaluated; namely the

amount of ozone absorbed (O_{3A}), the specific ozone absorption yield (Y_{O3}), the COD removal yield (Y_{COD}), the specific ozone dose, (D_{O3}), and the pseudo-first order COD abatement rate constant (k_{COD}).

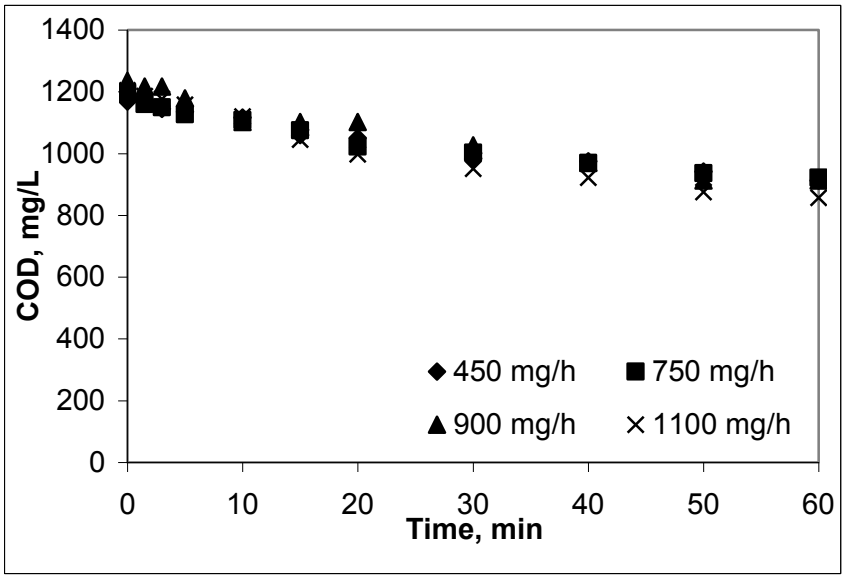

Figure 4.1.: COD Removal for NT as a Function of Treatment Time at Varying Ozone Feed Rates; COD_o = 1202 ± 34 mg/L; pH = 3.5; t = 60 min.

COD abatement (and also UV_{280} abatement) rates were found to follow first order kinetics as represented in Eq. 4.1:

$$\frac{dC}{dt} = k.C \tag{4.1}$$

where C stands for the pollutant concentration or a collective parameter, i.e. COD or UV_{280} in the present study, and k for the pseudo-first order COD or UV_{280} abatement rate constant (i.e. k_{COD} or k_{UV280}) expressed in min^{-1}.

Eq. 4.2 is obtained as a result of the integration of Eq. 4.1.

$$\ln\frac{C_t}{C_o} = -kt \tag{4.2}$$

where t is ozonation time (in min), C_o and C_t are COD or UV_{280} at time zero (initial COD and UV_{280}) and at time t, respectively.

As it is clear from Figure 4.1, increasing ozone feed rate did not affect COD removal. 22, 23, 26, and 29% COD removals were achieved after 60 min treatment time at pH = 3.5 at ozone feed rates of 450, 725, 900, and 1100 mg/h, respectively.

In the case of ST, and the same ozone feed rates, obtained COD removals were 30, 45, 52, and 58%.

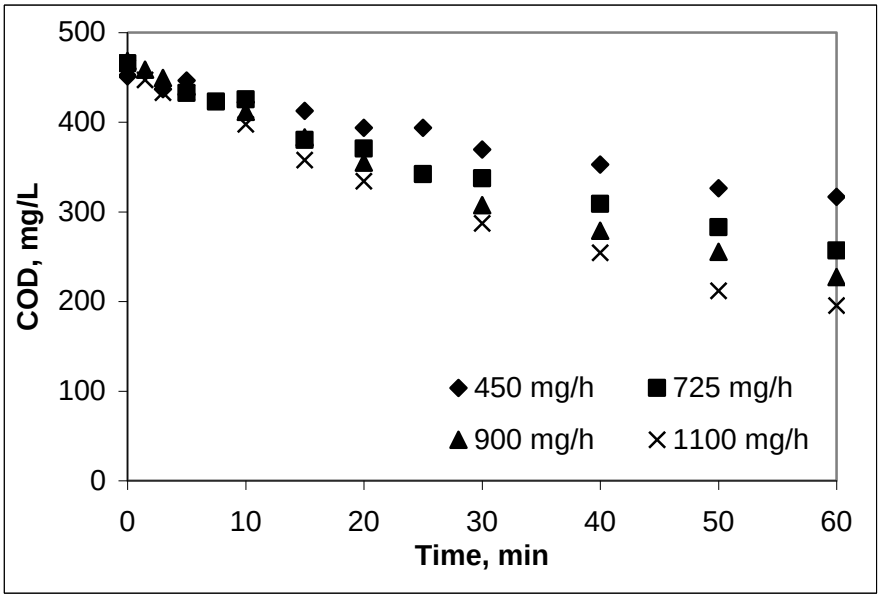

Figure 4.2. : COD Removal for ST as a Function of Treatment Time at Varying Ozone Feed Rates; COD_o = 460 ± 8 mg/L; pH = 3.5; t = 60 min.

As it can be seen from Figure 4.2., increasing the ozone feed rate appreciably affected the COD removal for ST. In order to determine the highest COD removal efficiency with respect to ozone utilization rate, it is important to evaluate O_{3A}, Y_{O3}, Y_{COD}, and k_{COD} values which are given in Tables 4.1 and 4.2 for NT and in Tables 4.3 and 4.4 for ST.

4.1.1.2 UV Absorbance Abatement

In order to evaluate the changes in the aromatic structure and unsatured moities of the textile tannins, UV_{280} and UV_{254} parameters were followed with respect to ozonation time. The decrease in the UV_{254} and UV_{280} parameters indicated the destruction of the aromatic structure and thus the parent tannin molecule.

In Figures 4.3 and 4.4, UV_{280} and UV_{254} abatement rates were displayed for NT.

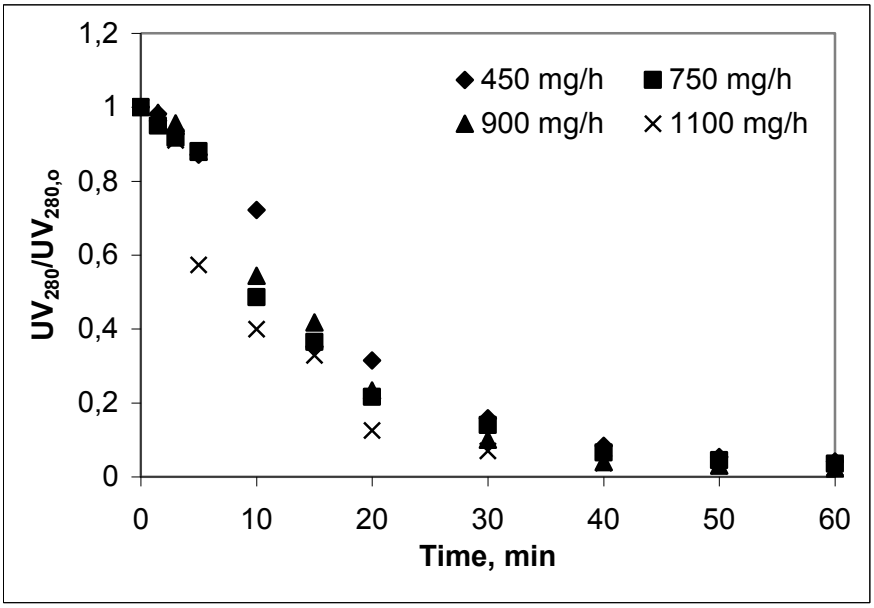

Figure 4.3. : Normalized UV_{280} Removal for NT as a Function of Treatment Time at Varying Ozone Feed Rates; $UV_{280,o}$ = 0.928 ± 0.02 cm^{-1} (after 50 fold dilution); pH = 3.5; t = 60 min.

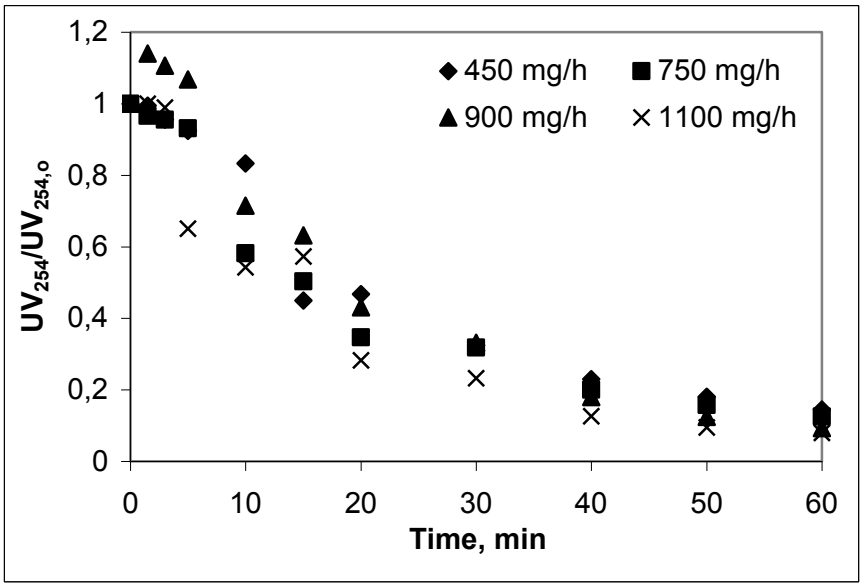

Figure 4.4. : Normalized UV_{254} Removal for NT as a Function of Treatment Time at Varying Ozone Feed Rates; $UV_{254,o}$ = 0.552 ± 0.04 cm^{-1} (after 50 fold dilution); pH = 3.5; t = 60 min.

It is evident from Figures 4.3. and 4.4 that UV_{280} and UV_{254} values did not change significantly with increasing ozone feed rate for NT. On the other hand, the UV absorbance abatement rates at 254 nm and 280 nm showed a slight increase with increasing ozone feed rates. It can be concluded that, in general NT oxidation is not affected by increasing ozone feed rate and NT oxidation is kinetically limited.

If the COD abatement rates and UV_{280} abatements are compared for NT, one may conclude that UV_{280} abatement rates were approximately 10 fold higher than for COD.

In Figures 4.5 and 4.6, UV_{280} and UV_{254} abatement rates were displayed for ST.

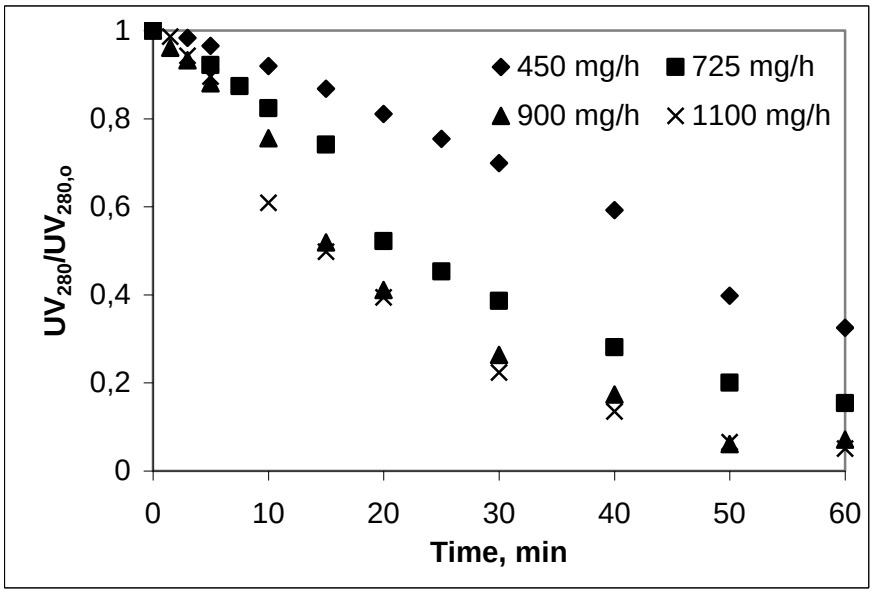

Figure 4.5. : Normalized UV_{280} Removal for ST as a Function of Treatment Time at Varying Ozone Feed Rates; $UV_{280,o}$ = 0.575 cm^{-1} (after 20 fold dilution); pH = 3.5; t = 60 min.

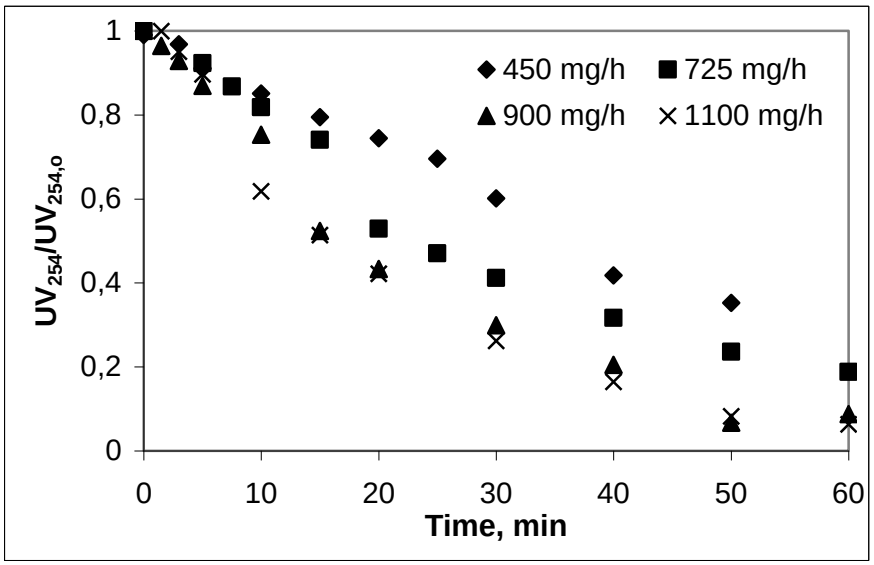

Figure 4.6. : Normalized UV_{254} Removal for ST as a Function of Treatment Time at Varying Ozone Feed Rates; $UV_{254,o}$ = 0.799 cm^{-1} (after 20 fold dilution); pH = 3.5; t = 60 min.

Figure 4.5 presents UV_{280} removal, whereas Figure 4.6 gives UV_{254} abatement. From both figures it is obvious that increasing the ozone feed rate had a profound effect on UV_{254} and UV_{280} removals in the case of ST. However, further increase of the ozone feed rate from 900 mg/h to 1100 mg/h caused no improvement for UV_{254} and UV_{280} removals for ST.

When the COD and UV_{280} removal rates are compared for ST similarly, UV_{280} abatement rates appeared to be nearly 3 fold faster than COD removal rates, that can be attributed to the fact that the fragmentation of the aromatic structure is the first and relatively faster stage of oxidation, collectively presented by the COD content of the tannins.

From the experimental data, it can be concluded that ST oxidation is definitely affected by the applied ozone dose.

O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} are summerized in Tables 4.1 and 4.2 for NT under the experimental conditions indicated.

Table 4.1. : Effect of Ozone Feed Rate on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for NT; Experimental Conditions : COD_o = 1202 ± 34 mg/L; pH = 3.5; t = 60 min.

O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} (mg COD/mg O_{3A})	Y_{O3} (mg O_{3A}/COD_o)	D_{O3} (mg O_{3o}/COD_o)
485	63	0.67	0.33	0.52
758	65	0.45	0.52	0.80
895	78	0.37	0.71	0.91
1104	69	0.37	0.79	1.15

Table 4.2. : Effect of Ozone Feed Rate onPErcent COD Removal, k_{COD}, and k_{UV280} Values for NT; Experimental Conditions : COD_o = 1202 ± 34 mg/L; pH = 3.5; t = 60 min.

O_3 Dose (mg/h)	COD_o (mg/L)	COD Removal (%)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
485	1168	22	0.006	0.065
758	1198	23	0.007	0.071
895	1236	26	0.008	0.080
1104	1205	29	0.009	0.093

From Table 4.1 it is clear that O_{3A}, Y_{O3}, and D_{O3} increased as the the ozone feed rate increased. Although the COD removal increased with increasing ozone feed

rate, Y_{COD} decreased with increasing ozone feed rate. This observation reveals that that COD removal efficiency with respect to ozone utilization decreased as the ozone feed rate was increased (Beltran et al., 2001). Accordingly, it can be concluded that an ozone feed rate of 450 mg/h provided the highest specific COD removal yield among the four ozone feed rates applied for NT. For the other three ozone feed rates, although the COD removal was higher, COD removal efficiency with respect to ozone utilization was lower. As a result, beyond a critical, "optimum" dose, increasing the ozone dose did not further improve the oxidation rate, and left the system without being used effectively.

In Tables 4.3 and 4.4, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} with changing ozone feed rate are summerized for ST under the experimental conditions indicated.

Table 4.3. : Effect of Ozone Feed Rate on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for ST; Experimental Conditions: COD_o = 460 ± 8 mg/L; pH = 3.5; t = 60 min.

O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} (mg COD/mg O_{3A})	Y_{O3} (mg O_{3A}/COD_o)	D_{O3} (mg O_{3o}/COD_o)
442	65	0.37	0.80	1.22
662	56	0.45	1.00	1.78
869	52	0.42	1.21	2.32
1065	64	0.31	1.84	2.89

Table 4.4. : Effect of Ozone Feed Rate on Percent COD Removal, k_{COD}, and k_{UV280} Values for ST; Experimental Conditions: COD_o = 460 ± 8 mg/L ; pH = 3.5; t = 60 min.

O_3 Dose (mg/h)	COD_o (mg/L)	COD Removal (%)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
442	451	30	0.007	0.012
662	466	45	0.011	0.034
869	468	52	0.014	0.045
1065	461	58	0.016	0.052

Upon closer inspection of the data given in the above tables, it can be concluded that the COD removal rate increased with increasing ozone feed rate. However, the ozone feed rate which resulted in the highest specific COD removal yield was 662 mg/h ozone feed rate. As a result, 662 mg/h was found as the optimum ozone dose for ST. It must be stated that although highest COD removal yield was observed at 662 mg/h ozone feed rate, there was almost no significant difference between the Y_{COD} values for the varied ozone feed rates.

4.1.2 Effect of pH

Ozonation of natural and synthetic tannin was performed at pH = 3.5 and pH= 7.0 to explore the effect of ozone chemistry on oxidation kinetics. The reaction pH of the tannin solutions was maintained constant using appropriate pH buffers that were already given in Table 3.3.

4.1.2.1 COD Abatement

Figure 4.7 depicts the COD removals for NT as a function of treatment time at pH = 3.5 and 7.0.

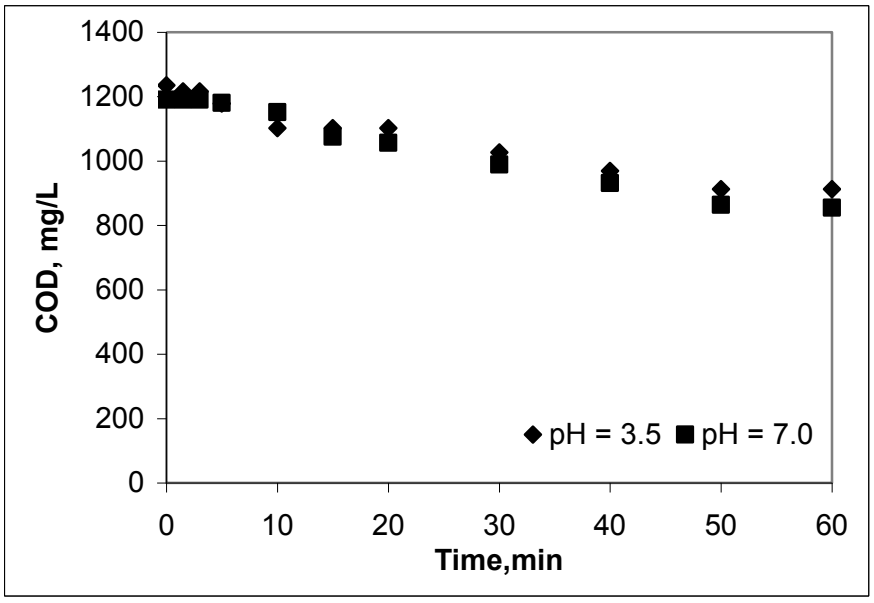

Figure 4.7.: COD Removal for NT as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 892 ± 4 mg/h; COD_o = 1213 ± 23 mg/L; t = 60 min.

As it is evident in Figure 4.7 COD removal (26% - 28% after 60 min ozonation) did not increase when the pH was raised from 3.5 to 7.0. When we look at the 120 min experiments, again a very slight increase in COD removal from 34% at pH = 3.5 to 37% at pH = 7.0 is evident.

From the above findings it can be concluded that the ozonation of NT is kinetically limited and increasing the ozone dose or pH did not affect degradation of its complex polyaromatic structure.

In the same manner, the COD removals were presented for ST as a function of ozonation time at varying pH in Figure 4.8.

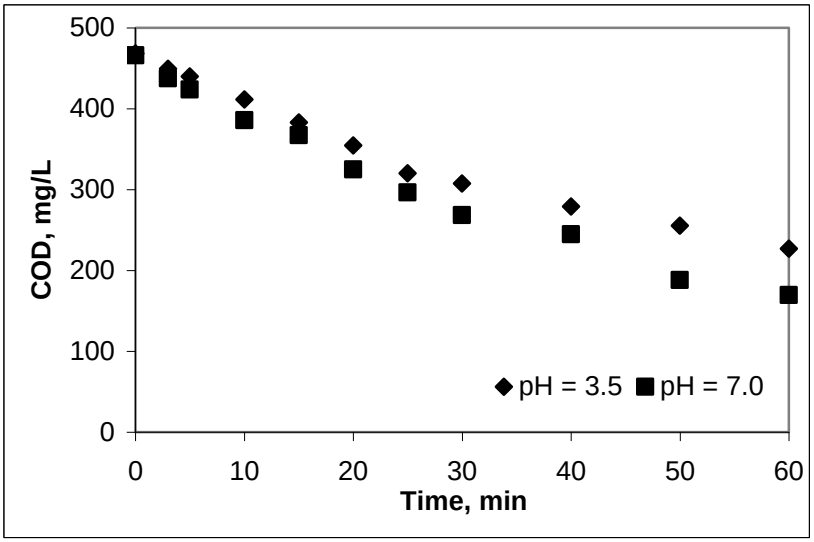

Figure 4.8. : COD Removal for ST as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 893 ± 24 mg/h; COD_o = 467 ± 1 mg/L; t = 60 min.

When the pH is increased from 3.5 to 7.0 for 60 min ozonation experiments of ST, COD removal increased from 52% to 64%, respectively, most probably as a result of the accelerated ozone decomposition to free radicals which becomes more dominant at elevated pH. In the first 30 min, there is almost no increase in COD removal showing that pH had no effect on the destruction of the tannin structure. After 30 min, COD removal increases slightly compared to the first 40 min period indicating that at elevated pH, ozonation products were oxidized more effectively compared to ozonation at acidic pH. 120 min experiments were also conducted and the COD removal increased from 60% to 78% as a result of increase in reaction pH from 3.5 to 7.0.

4.1.2.2 UV Absorbance Abatement

In addition to COD, UV_{280} and UV_{254} were monitored showing the aromatic structure and unsaturated moities, respectively. In Figures 4.9 and 4.10, UV_{280} and UV_{254} abatements with respect to ozonation time are given for the ozonation of NTat pH = 3.5 and 7.0, respectively.

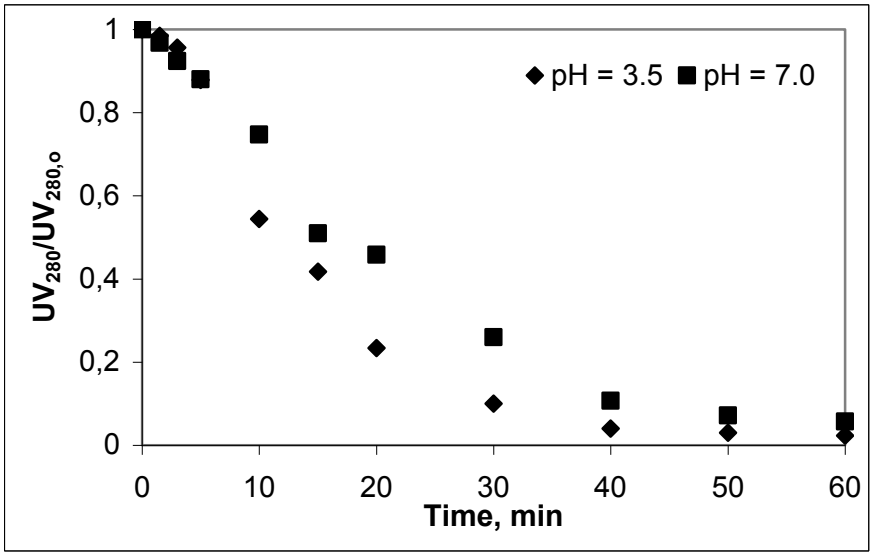

Figure 4.9. : Normalized UV_{280} Removal for NT as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 892 ± 4 mg/h, $UV_{280,o}$ = 0.780 ± 0.12 cm^{-1} (after 50 fold dilution); t = 60 min.

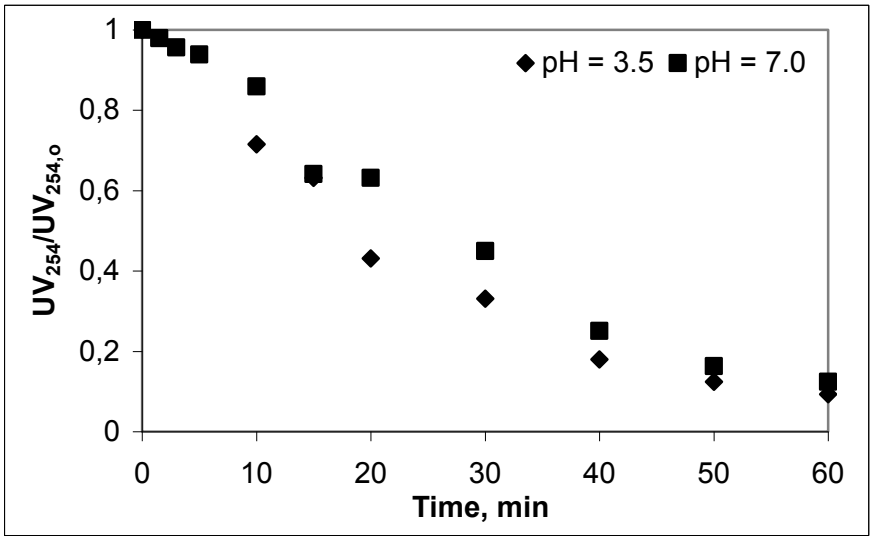

Figure 4.10. : Normalized UV_{254} Removal for NT as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 892 ± 4 mg/h; $UV_{254,o}$ = 0.430 ± 0.04 cm^{-1} (after 50 fold dilution); t = 60 min.

It is generally known that the affinity of ozone towards double bonds, aromatic structure and non-protonated amines is high (von Gunten, 2003). Abatement rates in terms of UV_{280} and UV_{254} representing aromaticity and double bonds forming the parent compound decreased with increasing pH. The decrease in UV_{280} removal at elevated pH can be explained by the ozone selectivity for aromatic structure. However, for both ozonation pH almost all UV_{280} was removed, showing the destruction of the polyaromatic structure of NT, within the first 40 min of ozonation.

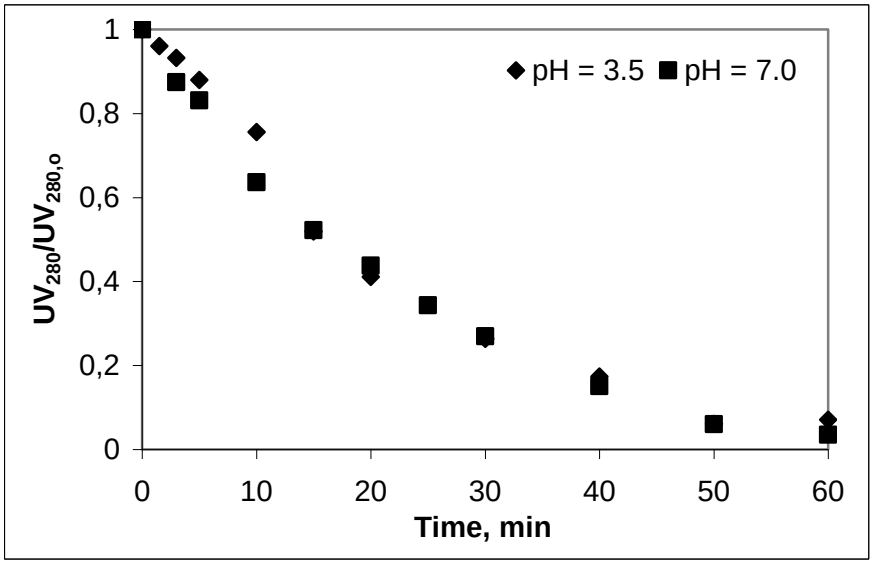

Figure 4.11. : Normalized UV_{280} Removal for ST as a Function of Treatment Time at Varying pH; Experimental Conditions; Ozone Feed Rate = 893 ± 24 mg/h; $UV_{280,o}$ = 0.575 cm^{-1} (after 20 fold dilution); t = 60 min.

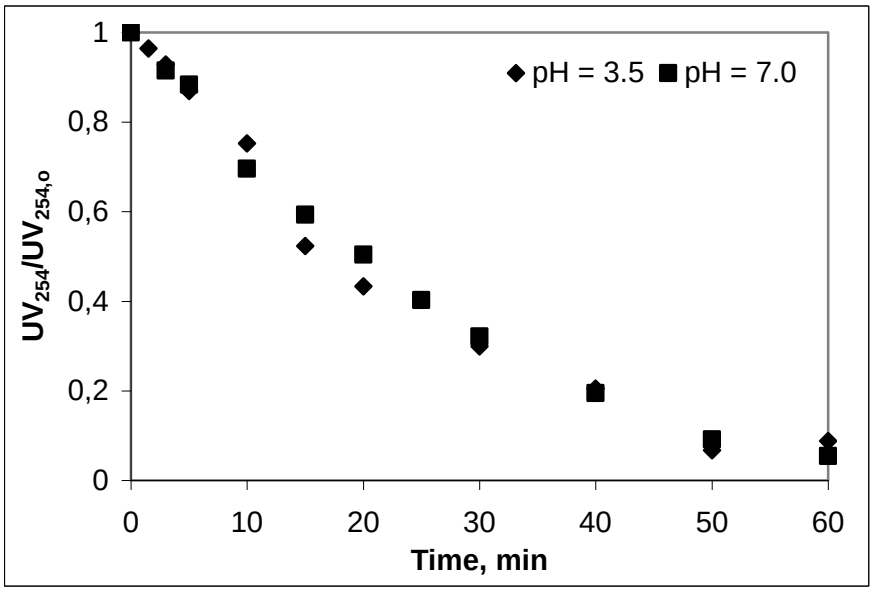

Figure 4.12. : Normalized UV_{254} Removal for ST as a Function of Treatment Time at Varying pH; Experimental Conditions; Ozone Feed Rate = 893 ± 24 mg/h; $UV_{254,o}$ = 0.799 cm^{-1} (after 20 fold dilution); t = 60 min.

In contrast to NT, for ST, UV_{254} and UV_{280} removal rates and final values were the same at both pH. UV_{280} and UV_{254} removals were practically complete after 50 min ozonation.

From the above given results it is apparent that both direct as well as free radical reactions play an important role in dearomatization of textile tannins.

In Tables 4.5 and 4.6, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} with varying reaction pH for 60 min and 120 min experiments are summerized for NT under the experimental conditions indicated.

Table 4.5. : Effect of pH on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for NT; Experimental Conditions: Ozone Feed Rate = 892 ± 4 mg/h; COD_o = 1213 ± 23 mg/L (t = 60 min) Ozone Feed Rate = 935 ± 52 mg/h; COD_o = 1222 ± 36 mg/L (t = 120 min).

Ozonation Time (min)	pH	O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} ($mgCOD/mgO_{3A}$)	Y_{O3} (mgO_{3A}/COD_o)	D_{O3} (mgO_{3o}/COD_o)
60	3.5	895	78	0.37	0.71	0.91
	7.0	888	86	0.35	0.81	0.93
120	3.5	883	69	0.28	1.22	1.76
	7.0	986	71	0.25	1.47	2.08

Table 4.6. : Effect of pH on Percent COD Removal, k_{COD}, and k_{UV280} Values for NT; Experimental Conditions: Ozone Feed Rate = 892 ± 4 mg/h; COD_o = 1213 ± 23 mg/L (t = 60 min); Ozone Feed Rate = 935 ± 52 mg/h; COD_o = 1222 ± 36 mg/L (t = 120 min).

Ozonation Time (min)	pH	COD_o (mg/L)	COD Removal (%)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
60	3.5	1236	26	0.008	0.080
	7.0	1190	28	0.007	0.045
120	3.5	1258	34	0.007	0.084
	7.0	1186	37	0.007	0.043

When the ozonation period was raised from 60 min to 120 min, no significant change in COD removals at pH = 3.5 and 7.0 was observed for NT.

When the k_{COD} and k_{UV280} values were compared at pH = 3.5 and pH = 7.0, both the k_{COD} values at both pH were the same while k_{UV280} values increased almost 2 fold as the pH decreased. Generally, when the pH increases, indirect reactions become dominant due to accelerated ozone decomposition (Staehelin and Hoigné, 1982). At acidic pH, direct oxidation by ozone molecule is the dominant reaction pathway. At pH = 7.0, both direct and indirect reactions are of almost equal importance. Inspite of the nonselective, fast reactions of $OH^{\bullet}$, the decrease in k_{UV280} values with increasing pH demonstrates the inherent ozone selectivity for NT. Even though $OH^{\bullet}$ has a higher oxidation potential than ozone, its selectivity is very poor (Muthukumar, et al., 2004). Accordingly, it can be concluded that the direct oxidation reaction of ozone with tannins is more selective and hence very fast such that ozone decomposition forming $OH^{\bullet}$ results in less selective, side reaction with other compounds (aliphatic oxidation products) so that a significant fraction of $OH^{\bullet}$ is

consumed and molecular ozone is being less available for tannin oxidation. The change in ozone chemistry hence may shift the reaction to a less desired and less effective oxidation pathway. Although the COD removal increased slightly at pH = 7.0, the rate constants showed no difference which were calculated in the first 30 min when the tannin structure was oxidized. The increase in COD removal was due to the oxidation of intermediate ozone products formed as a result of NT oxidation.

In Tables 4.7 and 4.8, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} for pH = 3.5 and 7.0 were presented for 60 min and 120 min ozonation experiments for ST under the experimental conditions indicated.

Table 4.7. : Effect of pH on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for ST; Experimental Conditions: Ozone Feed Rate = 893 ± 24 mg/h; COD_o = 467 ± 1 mg/L (t = 60 min); Ozone Feed Rate = 955 ± 29 mg/h; COD_o = 474 ± 11 mg/L (t = 120 min).

Ozonation Time (min)	pH	O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} ($mgCOD/mgO_{3A}$)	Y_{O3} (mgO_{3A}/COD_o)	D_{O3} (mgO_{3o}/COD_o)
60	3.5	869	52	0.42	1.21	2.32
	7.0	917	77	0.33	1.91	2.46
120	3.5	926	69	0.18	3.31	4.78
	7.0	984	71	0.21	3.76	5.32

Table 4.8. : Effect of pH on Percent COD Removal, k_{COD}, and k_{UV280} Values for ST; Experimental Conditions: Ozone Feed Rate = 893 ± 24 mg/h; COD_o = 467 ± 1 mg/L (t = 60 min); Ozone Feed Rate = 955 ± 29 mg/h; COD_o = 474 ± 11 mg/L (t = 120 min).

Ozonation Time (min)	pH	COD_o (mg/L)	COD Removal (min)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
60	3.5	468	52	0.014	0.040
	7.0	466	64	0.018	0.044
120	3.5	485	60	0.013	0.040
	7.0	463	78	0.017	0.050

As it is evident in Tables 4.7 and 4.8, elevated pH resulted in slight increase in ozone absorption, as well as slight increase in first order rate constants with respect to COD removal and UV_{280} removal of ST. The only significant change with increasing the pH was observed for the O_{3A} value; after 60 min ozonation percent ozone absorption improved from 50% to almost 80%, as a consequence of the enhanced mass transfer rate due to enhanced ozone decomposition. The difference in O_{3A} became insignificant after 120 min, when Y_{COD} decreased appreciably indicating that ozone was overdosed and no further benefit of increasing the reaction pH could be achieved.

4.2 Ozonation of Biocides-Process Optimization

For the optimization of ozonation conditions for the studied biocides, 60 min-experiments were conducted at different ozone feed rates, i.e. 500, 750, and 900 mg/h feed rates at pH = 7.0, which is the application pH of biocides in the finishing stage. In addition, experiments were conducted at pH = 7.0 and pH = 12.0 for 60 min and 120 min with 900 mg/h ozone feed rate to investigate the effect of pH on ozonation of biocides.

4.2.1 Effect of Ozone Dose

In order to examine the effect of ozone feed rate on ozonation of biocides, ozonation experiments were conducted for 60 min at varying ozone feed rates (= 500, 750, and 900 mg/h) at pH = 7.0 i.e. the natural application pH of biocides in the textile industry. Changes in COD, UV_{254} and UV_{280} parameters were followed throughout the ozonation experiments.

4.2.1.1 COD Abatement

Effect of increasing the applied ozone dose on the COD abatement rates of biocides were studied by conducting 60 min experiments at 500, 750, and 900 mg/h ozone feed rates at the application pH of biocides. The experimental results are given in Figures 4.13 and 4.14 for biocides BI and BII, respectively.

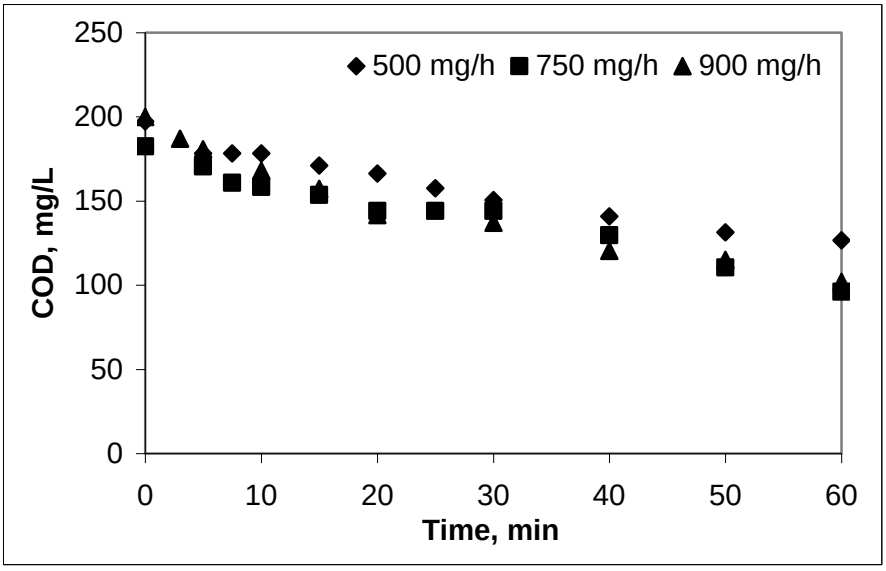

Figure 4.13. : COD Removal for BI as a Function of Treatment Time at Varying Ozone Feed Rates; Experimental Conditions: COD_o = 191 ± 9 mg/L; pH = 7.0; t = 60 min.

As can be seen from Figure 4.13 and Figure 4.14, increasing the ozone feed rate slightly increased the COD removals for both tested biocides at pH = 7.0.

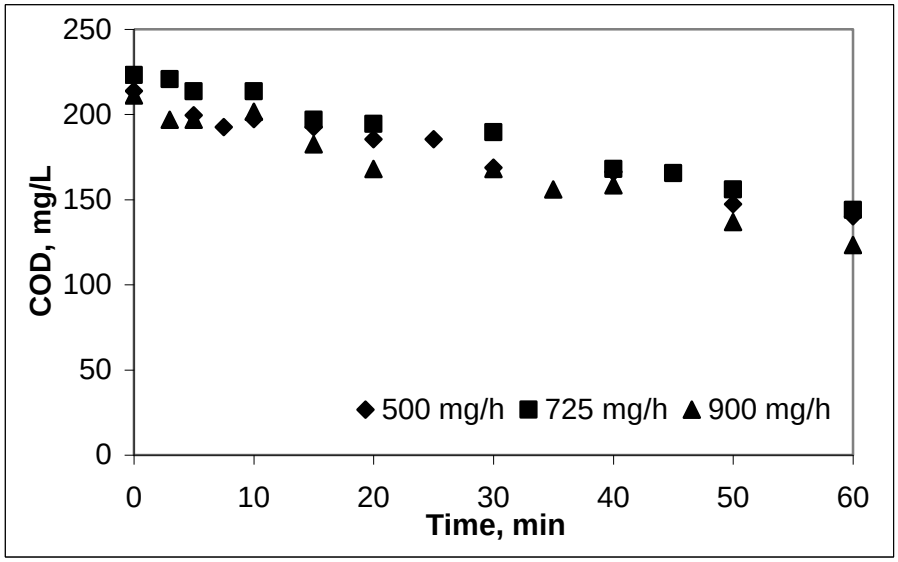

Figure 4.14. : COD Removal for BII as a Function of Treatment Time at Varying Ozone Feed Rates; Experimental Conditions: COD_o = 217 ± 7 mg/L; pH = 7.0; t = 60 min.

4.2.1.2 UV Absorbance Abatement

UV_{280} and UV_{254} were also monitored at different ozone feed rates and pH = 7.0 for the selected textile biocides. Figures 4.15 and 4.16 present UV_{280} and UV_{254} abatement rates as a function of ozonation time at varying ozone feed rates for BI.

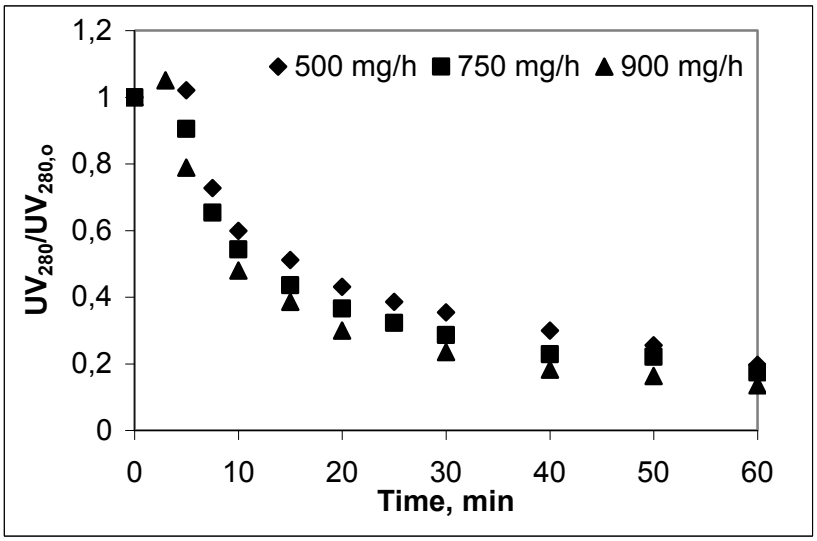

Figure 4.15. : Normalized UV_{280} Removal for BI as a Function of Rreatment Time at Varying Ozone Feed Rates; Experimental Conditions: $UV_{280,o}$ = 0.37 ± 0.02 cm^{-1}; pH = 7.0; t = 60 min.

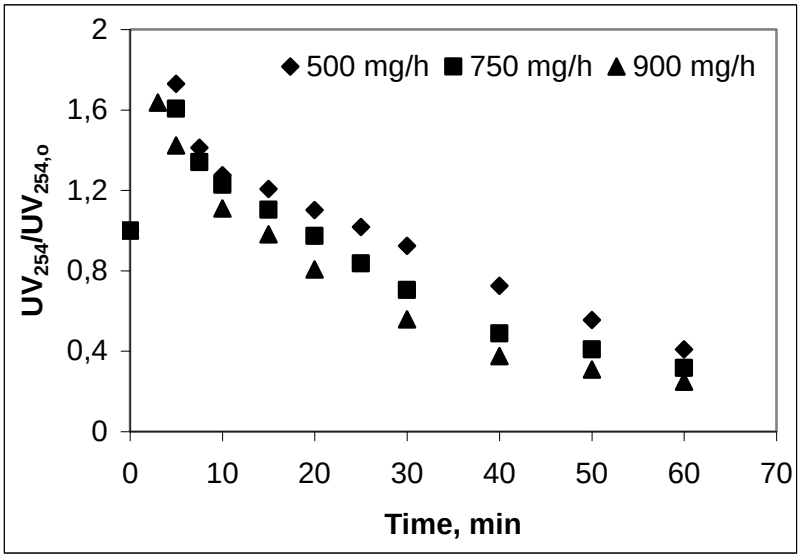

Figure 4.16. : Normalized UV_{254} Removal for BI as a Function of Treatment Time at Varying Ozone Feed Rates; Experimental Conditions: $UV_{254,o}$ = 0.30 ± 0.01 cm^{-1}; pH = 7.0; t = 60 min.

UV_{280} and UV_{254} removals slightly increased with increasing ozone feed rates and these are not significant improvements.

In Figures 4.17 and 4.18, normalized UV_{280} and UV_{254} abatements obtained for the ozonation of BII at pH = 7.0 and varying ozone feed are depicted.

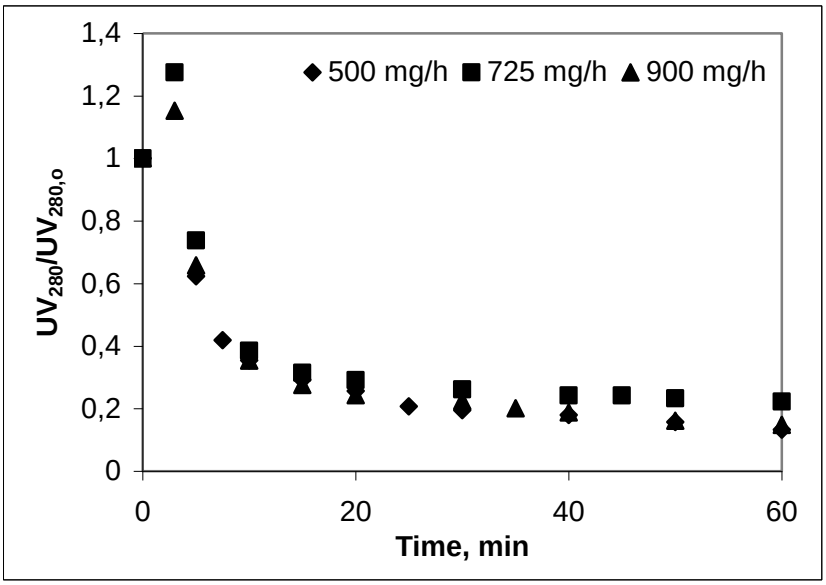

Figure 4.17. : Normalized UV_{280} Removal for BII as a Function of Treatment Time at Varying Ozone Feed Rates; Experimental Conditions: $UV_{280,o}$ = 0.26 ± 0.02 cm^{-1}; pH = 7.0; t = 60 min.

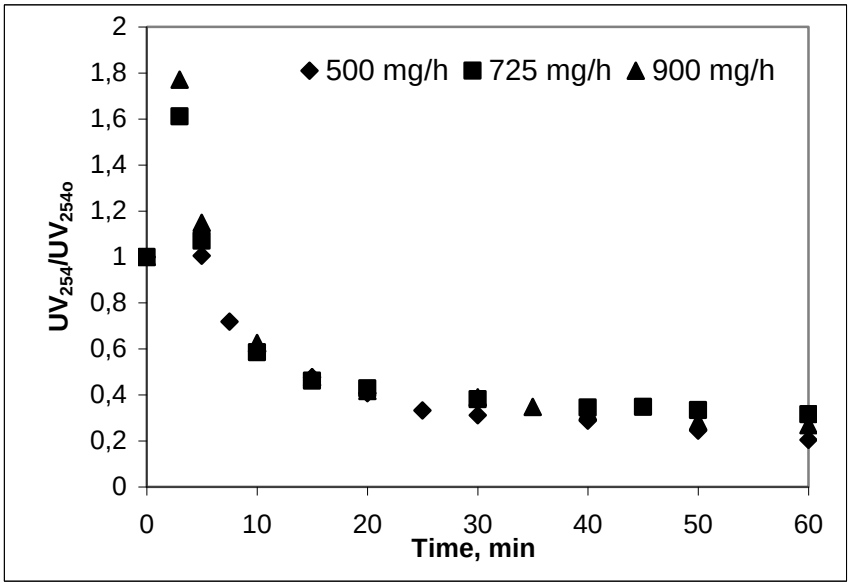

Figure 4.18. : Normalized UV_{254} Removal for BII as a Function of Treatment Time at Varying Ozone Feed Rates; Experimental Conditions: $UV_{254,o}$ = 0.18 ± 0.01 cm^{-1}; pH = 7.0; t = 60 min.

As it is clear in Figures 4.17 and 4.18, UV_{280} and UV_{254} removals did not differ for the ozonation of BII at pH = 7.0 and varying ozone feed rates. From Figures 4.17 and 4.18 it is evident that UV_{254} and UV_{280} increased rapidly to a maximum and then declined. Kuo and Huang (1995) explained this increase in absorbance by the formation of one or more intermediates of incomplete oxidation during the early stages of ozonation.

In Tables 4.9 and 4.10, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} are summerized for BI under the experimental conditions indicated.

Table 4.9. : Effect of Ozone Feed Rate on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for BI; Experimental Conditions: COD_o = 191 ± 9 mg/L; pH = 7.0; t = 60 min.

O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} (mg COD/mg O_{3A})	Y_{O3} (mg O_{3A}/COD_o)	D_{O3} (mg O_{3o}/COD_o)
500	42	0.27	1.33	3.16
763	49	0.19	2.56	5.23
893	47	0.19	2.63	5.59

It can be seen from Table 4.9 that the optimum ozone feed rate is 500 mg/h where the maximum COD removal yield is observed although the first order rate constants of both COD removal UV_{280} removal increased as the ozone feed rate increased.

Table 4.10. : Effect of Ozone Feed Rate on Percent COD Removal, k_{COD}, and k_{UV280} Values for BI; Experimental Conditions: COD_o = 191 ± 9 mg/L; pH = 7.0; t = 60 min.

O_3 Dose (mg/h)	COD_o (mg/L)	COD Removal (%)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
500	197	36	0.008	0.039
763	182	47	0.011	0.046
893	200	49	0.016	0.063

In order to optimize ozone feed rates for BI and BII, it is important to evaluate the COD removal yields for all ozone feed rates that are given in Tables 4.9 to 4.11.

In Table 4.11 and 4.12, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, k_{UV280} with varying ozone feed rates for 60 min experiments are summerized for BII in the experimental conditions indicated.

Table 4.11. : Effect of Ozone Feed Rate on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for BII; Experimental Conditions: COD_o = 217 ± 7 mg/L; pH = 7.0; t = 60 min.

O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} (mg COD/mg O_{3A})	Y_{O3} (mg O_{3A}/COD_o)	D_{O3} (mg O_{3o}/COD_o)
533	37	0.30	1.15	3.11
744	53	0.16	2.21	4.17
898	52	0.15	2.79	5.31

Table 4.12. : Effect of Ozone Feed Rate on Percent COD Removal, k_{COD}, and k_{UV280} Values for BII; Experimental Conditions: COD_o = 217 ± 7 mg/L; pH = 7.0; t = 60 min.

O_3 Dose (mg/h)	COD_o (mg/L)	COD Removal (%)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
533	214	34	0.007	0.085
744	223	35	0.008	0.082
898	211	42	0.010	0.090

As the ozone feed rate increased, first order rate constants for COD removal and UV_{280} removal and COD removals showed no significant increase for BII. 533 mg/h was found to be the optimum ozone feed rate since the maximum ozone yield coefficient was observed at this ozone feed rate. The differences in COD and UV_{280} removals between BI and BII can be explained by the stuctural differences of the tested biocides.

4.2.2 Effect of pH

In order to explore the effect of reaction pH on the ozonation of BI and BII, 60 and 120 min experiments were performed at pH = 7.0 and pH = 12.0. The reaction pH of the biocide solutions was kept constant at desired values using appropriate pH buffers given in Table 3.3 in the Materials and Methods Section.

4.2.2.1 COD Abatement

The effect of increasing the pH from 7.0 to 12.0 on COD removal from biocidal finishing effluent (aqueous BI and BII samples) was questioned by running ozonation experiments at a fixed ozone dose (=900 mg/h) and varying pH (Figures 4.19 and 4.20).

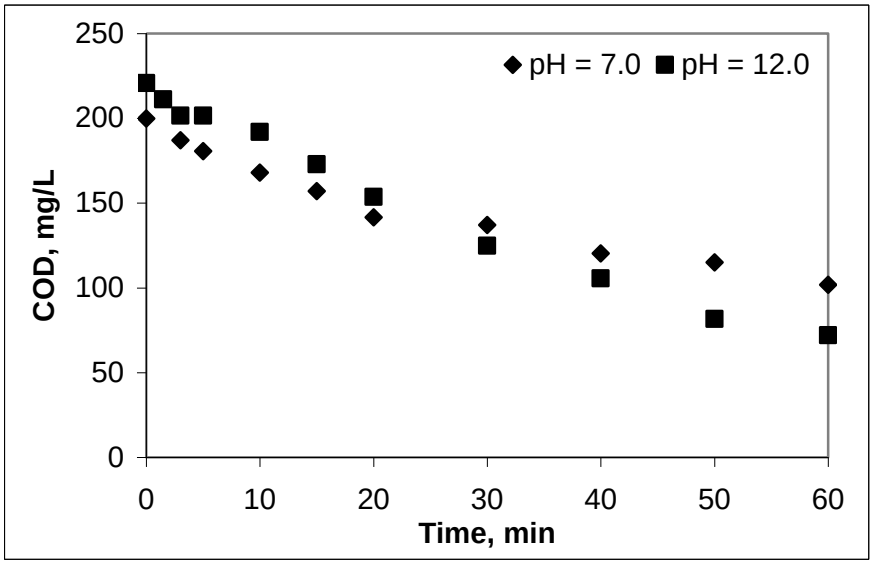

Figure 4.19. : COD Removal for BI as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 890 ± 12 mg/h; COD_o = 210 ± 10 mg/L; t = 60 min.

As it can be observed in Figure 4.19, COD abatement rates only slightly increased at elevated pH. The increase in COD removal became more apparent towards the end of the oxidation due to more effective destruction of ozonation products.

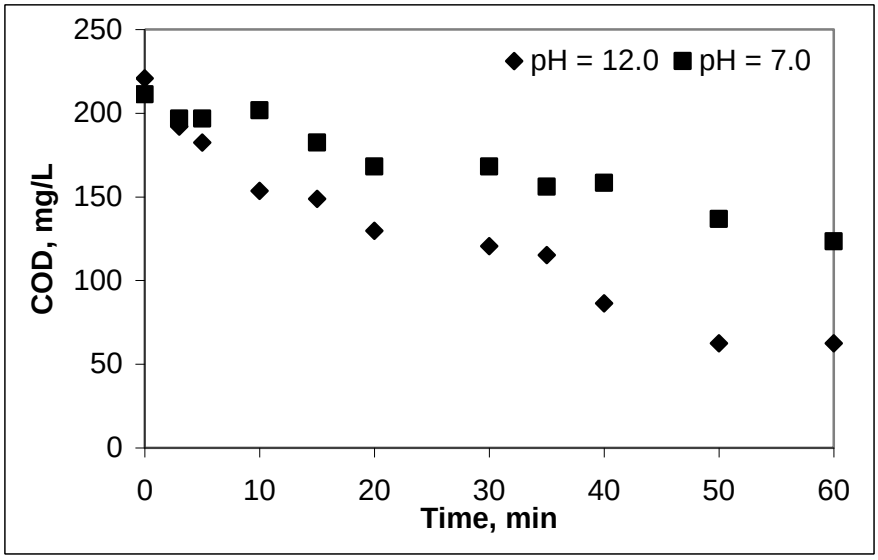

Figure 4.20. : COD Removal for BII as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 ± 2 mg/h; COD_o = 216 ± 5 mg/L; t = 60 min.

According to Figure 4.19 and 4.20, COD removal at elevated pH showed more improvement for BII than for BI. It can be concluded that $OH^{\bullet}$ radical reactions of oxidation intermediates are more evident for BII.

4.2.2.2 UV absorbance abatement

For both studied textile biocides, UV_{280} and UV_{254} were also followed during the ozonation experiments conducted at pH = 7.0 and 12.0 at a fixed ozone feed rate of 900 mg/h to observe the effect of pH on ozonation efficiency. The experimental results for BI were depicted in Figures 4.21 (UV_{280}) and 4.22 (UV_{254}).

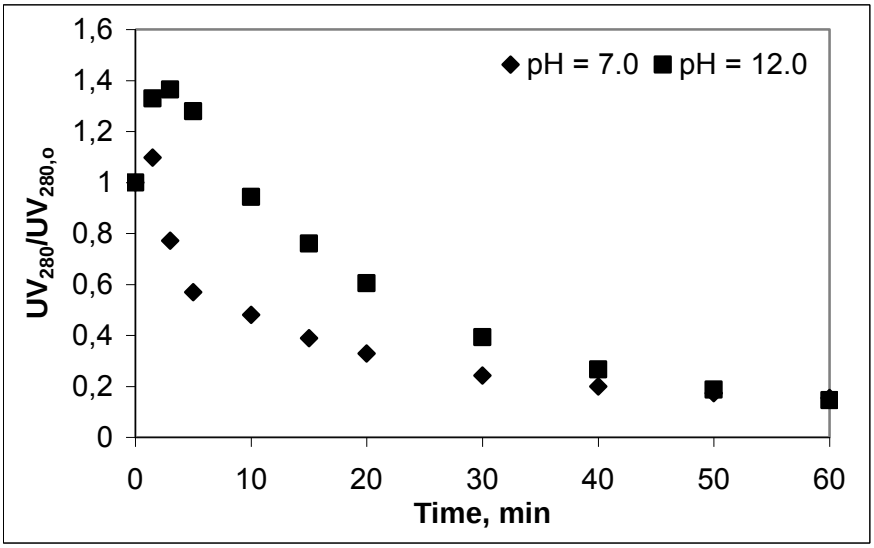

Figure 4.21. : Normalized UV_{280} Removal for BI as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 890 ± 12 mg/h; $UV_{280,o}$ = 0.34 ± 0.03 cm^{-1}; t = 60 min.

According to Figure 4.21, the UV_{280} abatement rates are almost the same for BI at pH = 7.0 and pH =12.0

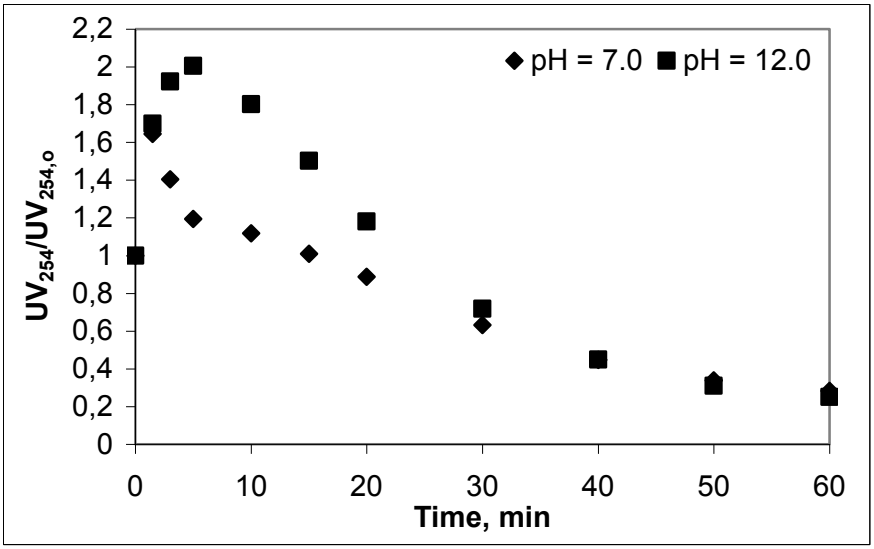

Figure 4.22. : Normalized UV_{254} Removal for BI as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 892 ± 12 mg/h; $UV_{254,o}$ = 0.33 ± 0.03 cm^{-1}; t = 60 min.

Although the final UV_{254} values were the same for both reaction pH for BI, the UV_{254} removal rates were higher at pH = 12.0 compared to removal rates at pH = 7.0. A rapid increase in absorbance value during the early stages of ozonation, was observed. The increment in absorbance value being more significant at pH = 12.0, h is a consequence of the differences in type and number of oxidation intermediates

due to the different reaction mechanisms of ozone dominant at pH = 7.0 and 12.0 (Kuo and Huang, 1995).

Normalized UV_{280} and UV_{254} removals are depicted in Figures 4.23 and 4.24, respectively, at a feed rate of 900 mg/h and varying reaction pH for BII.

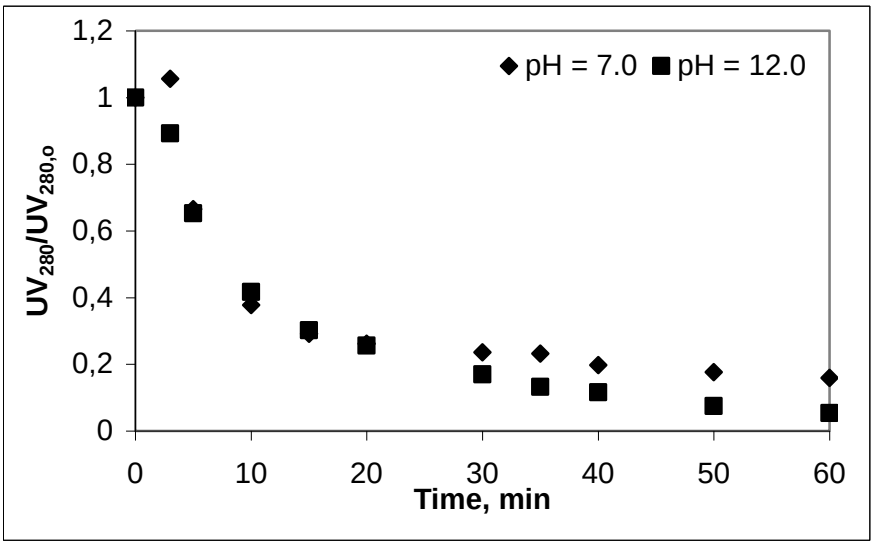

Figure 4.23. : Normalized UV_{280} Removal for BII as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 ± 2 mg/h; $UV_{280,o}$ = 0.24 cm^{-1}; t= 60 min.

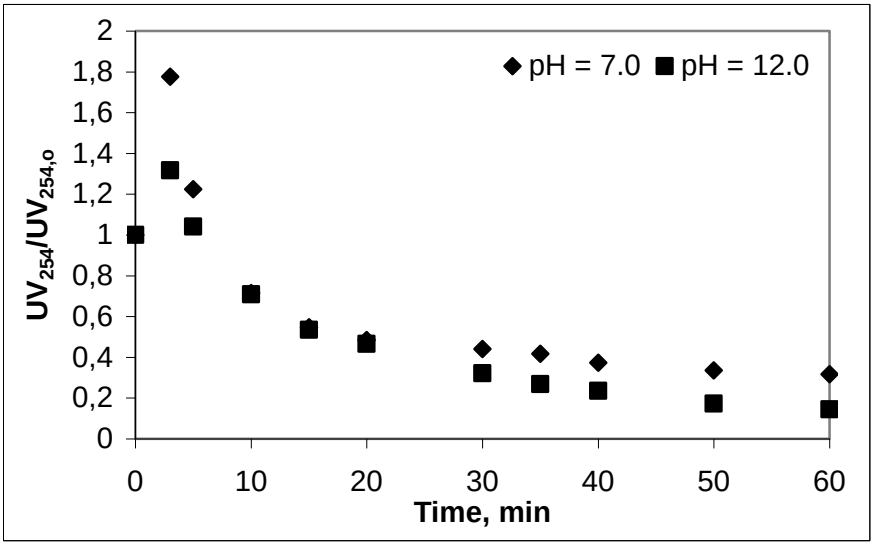

Figure 4.24. : Normalized UV_{254} Removal for BII as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 ± 2 mg/h; $UV_{254,o}$ = ; 0.20 ± 0.04 cm^{-1}; t = 60 min.

Although the first order COD removal rate increased by a factor of 2.5 at elevated pH, UV_{254} and UV_{280} removals were the same at both pH values for BII showing that ozone decomposition to free radicals did not improve the destruction of the parent compound, BII, while more efficient oxidation of the ozonation products resulted in higher COD removal.

In Tables 4.13 and 4.14, O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} with varying reaction pH for 60 min and 120 min experiments are summerized for BI under the experimental conditions indicated.

Table 4.13. : Effect of pH on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for BI; Experimental Conditions: Ozone Feed Rate = 890 ± 12 mg/h; COD_o = 210 ± 10 mg/L (t = 60 min); Ozone Feed Rate = 902 mg/h; COD_o = 195 ± 5 mg/L (t = 120 min).

Ozonation Time (min)	pH	O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} ($mgCOD/mgO_{3A}$)	Y_{O3} (mgO_{3A}/COD_o)	D_{O3} (mgO_{3o}/COD_o)
60	7.0	902	53	0.17	2.97	5.65
	12.0	878	83	0.16	4.12	4.97
120	7.0	902	38	0.14	4.65	12.40
	12.0	902	39	0.18	4.62	11.90

Table 4.14. : Effect of pH on Percent COD removal, k_{COD}, and k_{UV280} values for BI; Experimental Conditions: Ozone Feed Rate = 890 ± 12 mg/h; COD_o = 210 ± 10 mg/L (t = 60 min); Ozone Feed Rate = 902 mg/h; COD_o = 195 ± 5 mg/L (t = 120 min).

Ozonation Time (min)	pH	COD_o (mg/L)	COD Removal (min)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
60	7.0	200	49	0.012	0.056
	12.0	221	67	0.019	0.045
120	7.0	200	61	0.011	0.056
	12.0	190	85	0.019	0.039

Tables 4.15 and 4.16 list the O_{3A}, Y_{O3}, Y_{COD}, D_{O3}, k_{COD}, and k_{UV280} values obtained for BII under the experimental conditions indicated and 60 – 120 min ozonation experiments.

Table 4.15. : Effect of pH on O_{3A}, Y_{COD}, Y_{O3}, D_{O3} Values for BII; Experimental Conditions: Ozone Feed Rate = 900 ± 2 mg/h; COD_o = 216 ± 5 mg/L (t = 60 min); Ozone Feed Rate = 890 ± 8 mg/h; COD_o = 215 ± 15 mg/L (t = 120 min).

Ozonation Time (min)	pH	O_3 Dose (mg/h)	O_{3A} (%)	Y_{COD} ($mgCOD/mgO_{3A}$)	Y_{O3} (mgO_{3A}/COD_o)	D_{O3} (mgO_{3o}/COD_o)
60	7.0	898	52	0.15	2.79	5.31
	12.0	902	70	0.20	3.56	5.11
120	7.0	883	54	0.09	6.46	9.58
	12.0	898	87	0.12	7.71	11.27

Table 4.16. : Effect of pH on Percent COD removal, k_{COD}, and k_{UV280} Values for BII; Experimental Conditions: Ozone Feed Rate = 900 ± 2 mg/h; COD_o = 216 ± 5 mg/L (t = 60 min); Ozone Feed Rate = 890 ± 8 mg/h; COD_o = 215 ± 15 mg/L (t = 120 min).

Ozonation Time (min)	pH	COD_o (mg/L)	COD Removal (min)	k_{COD} (min^{-1})	k_{UV280} (min^{-1})
60	7.0	211	42	0.010	0.070
	12.0	221	72	0.025	0.073
120	7.0	230	54	0.011	0.049
	12.0	199	87	0.016	0.057

As is evident in Tables 4.14 and 4.16 that the improvement of k_{UV280} with increasing pH was more pronounced for BI as compared with BII, most probably due to their structural differences.

4.2.3 AOX Results

Adsorbable organic halogens is a measure of total halogenated organic matter in a water sample. This parameter shows total molar amount of organically bound halogen, giving no information about the nature of organic compounds to which the halogens are bound or about the individual halogens present (APHA, 1989).

Due to the molecular structure of BI (active ingredient: 2,4,4'-trichloro-2'-hydroxydiphenyl ether) and its chlorine content, the AOX parameter was followed during ozonation of BI at pH = 7.0 and 12.0. The experimental results are presented in Figure 4.25.

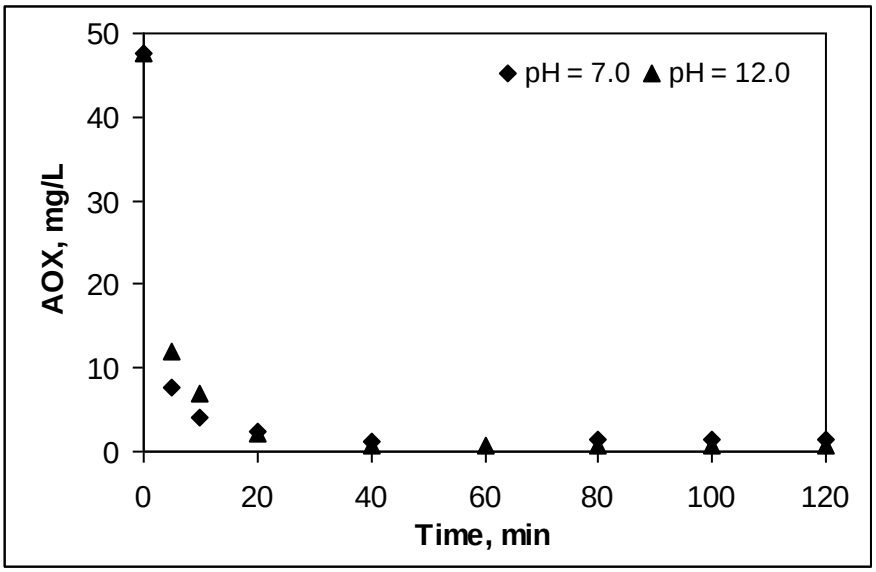

Figure 4.25. : AOX Removal for BI as a Function of Treatment Time at pH = 7.0 and pH = 12.0; Experimental Conditions: Ozone Feed Rate = 900 mg/h; AOX_o = 47.5 mg/L; COD_o =195 ± 5 mg/L; TOC_o = mg/L; t = 120 min.

Ozone reacts selectively with AOX-causing halogenated functional groups as a result of its electrophilic nature (Gamal El-Din and Smith, 2002). At pH = 7.0, when both direct molecular ozone reactions and indirect free radical reactions are of almost equal importance, the rate of AOX removal was almost the same as compared to the AOX removal rate obtained at pH = 12.0. The selective reaction of ozone with AOX-causing moieties, resulted in sufficient AOX removal rate at pH = 7.0. From Figure 4.25 it is evident that the AOX removal was practically complete after 20 min ozonation corresponding to 300 mg ozone.

AOX abatement also followed first-order kinetics. The first order AOX removal rate constants were found to be 0.250 min^{-1} (R^2 = 0.92) at pH = 7.0 and 0.149 min^{-1} (R^2 = 0.95) at pH = 12.0. When the AOX removal and UV_{280} removal rates were compared, it could be concluded that AOX removal proceeded four times faster than UV_{280} removal. Higher AOX removal rates can be explained by the mechanism proposed by Chen and Ni (1998) to describe the sequence of 2,4-dichlorophenol ozonation which proceeded in the following order: hydroxylation (increase in UV optical density), dechlorination (AOX removal) and ring-cleavage (dearomatization).

4.3 Effect of ozone on mineralization rates

120 min experiments were conducted to follow TOC removal (mineralization) of the studied tannins at pH = 3.5 and 7.0 and for the selected biocides at pH = 7.0 and 12.0 at an ozone feed rate of 900 mg/h. As was expected, TOC removals were lower than COD removals, since TOC represents the degree of ultimate oxidation to inorganic end products.

4.3.1 Tannins

TOC removals for NT and ST were examined at pH = 3.5 and pH = 7.0 at an ozone feed rate of 900 mg/h. In order to evaluate the selectivity of oxidation changes in UV_{280}/COD and UV_{280}/TOC ratios were shown separately. The effectiveness of ozonation on the degree of partial oxidation of the textile tannins was examined as well. TOC removals for NT and ST with respect to ozonation time at pH = 3.5 and 7.0 are given in Figures 4.26 and 4.27, respectively.

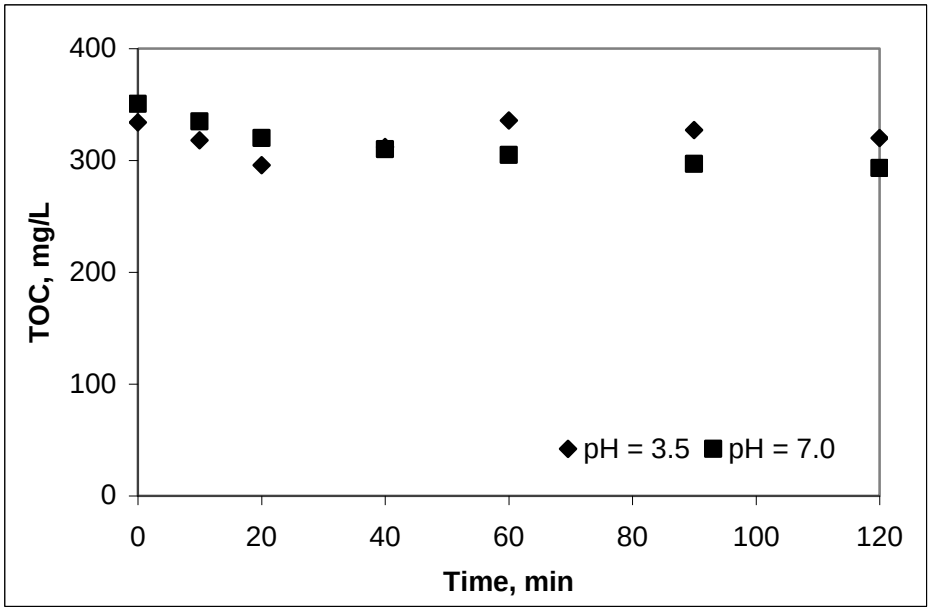

Figure 4.26. : TOC Removal for NT as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 mg/h; TOC_o = 342 ± 8 mg/L; t = 120 min.

As a result of ozonation, no significant TOC removal was observed at both reaction pH showing inefficient oxidation for NT.

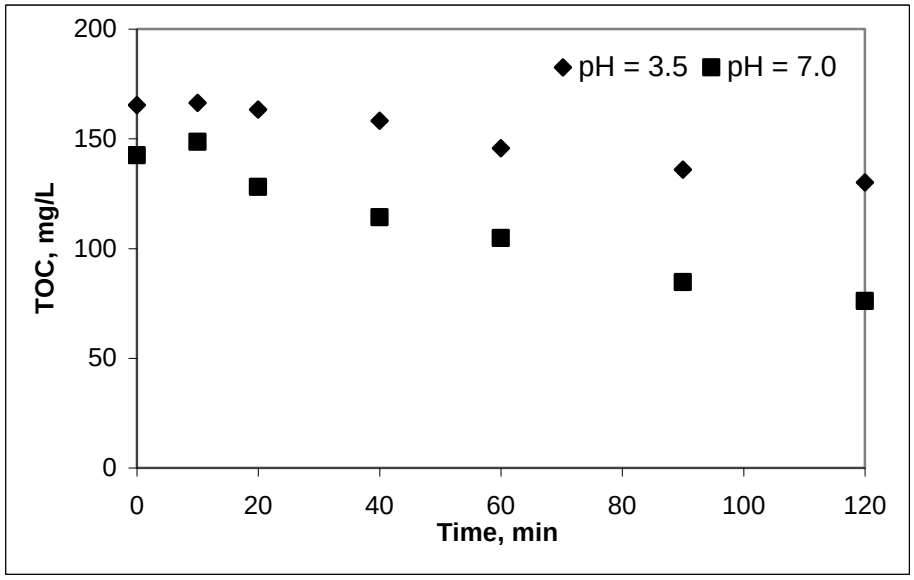

Figure 4.27. : TOC Removal for ST as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 mg/h; TOC_o = 154 ± 12 mg/L; t = 120 min.

While ozone is a strong and relatively selective oxidant to remove unsaturated and aromatic compounds, $OH^{\bullet}$ is much stronger and hence less selective. Direct ozone reactions would lead to removal of polyphenols and other aromatics and unsaturated compounds. On the other hand, the oxidation by $OH^{\bullet}$ should bring

about wastewater mineralization and therefore significant reductions in COD and TOC (Beltran et al., 2001). This explains the increment of TOC removal from 21% to 47% for ST when the pH increased from 3.5 to 7.0. In Table 4.17, TOC removals together with the final TOC values for NT and ST at obtained different pH values were presented.

Table 4.17. : TOC Removal for NT and ST at Varying pH; Experimental Conditions: Ozone feed rate = 900 mg/h; TOC_o (NT) = 342 ± 8 mg/L; TOC_o (ST) = 154 ± 12 mg/L; t = 120 min.

Textile Tannin	pH	TOC_{Final}, mg/L	TOC removal, %
NT	3.5	320	4
	7	293	16
ST	3.5	130	21
	7	76	47

The ozone selectivity towards the tannin structure can be explained by evaluating TOC, COD and UV_{280} removals together. The selectivity of ozone towards aromaticity can be expressed in the form of relative UV_{280}/TOC and UV_{280}/COD ratios against applied ozone dose which are given in Figures 4.28 and 4.29 for NT, respectively.

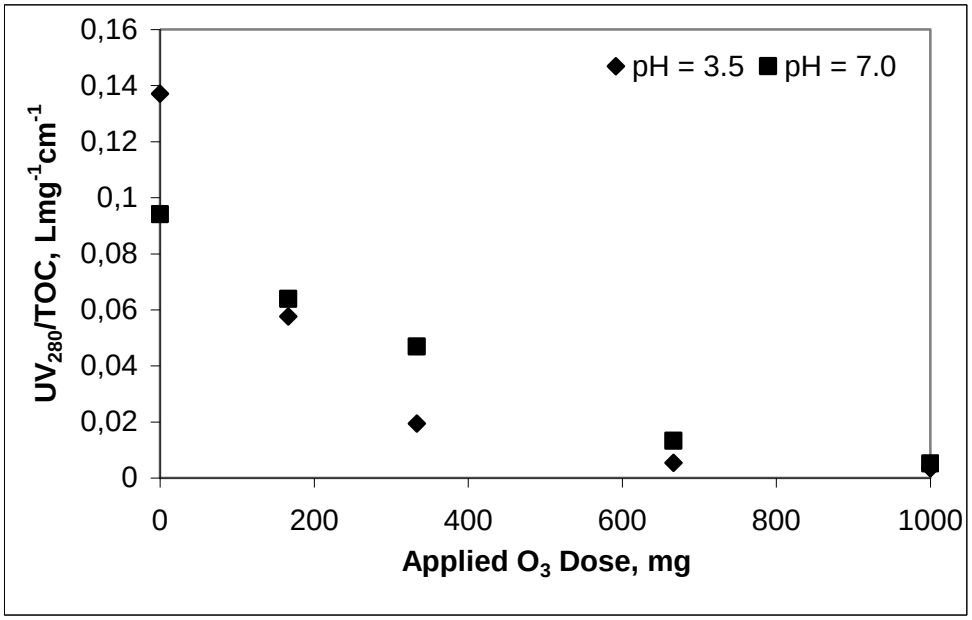

Figure 4.28. : Changes in UV_{280}/TOC Ratio at pH 3.5 and pH 7.0 for NT; Experimental Conditions: Ozone Feed Rate = 1000 mg/h; TOC_o = 342 ± 8 mg/L; $UV_{280,o}$ = 0.780 ± 0.12 cm^{-1} (after 50 fold dilution); t = 60 min.

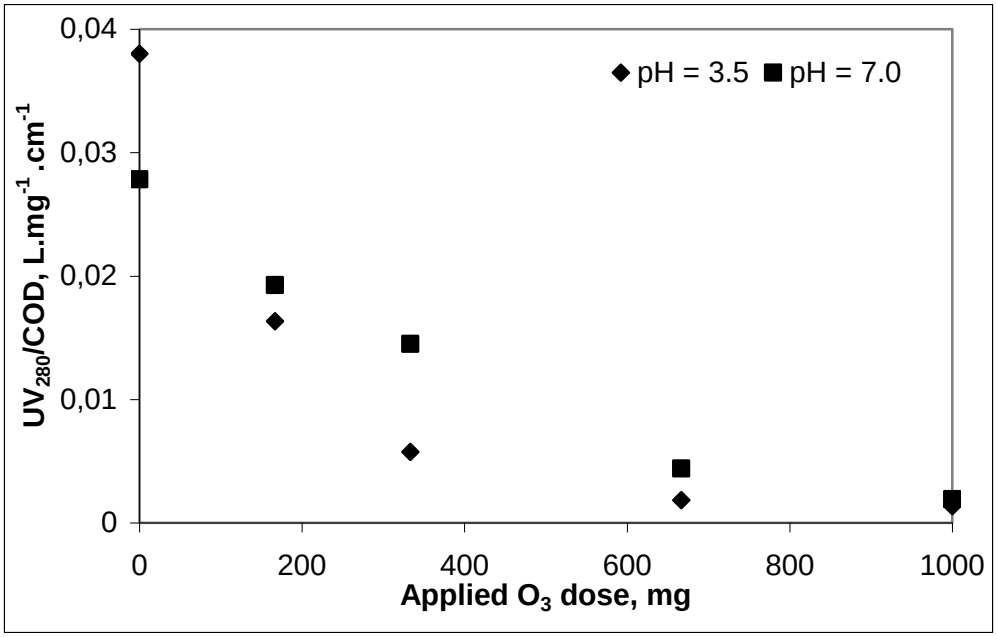

Figure 4.29. : Changes in UV_{280}/COD Ratio at pH 3.5 and pH 7.0 for NT; Experimental Conditions: Ozone Feed Rate = 1000 mg/h; $UV_{280,o}$ = 0.780 ± 0.12 cm^{-1} (after 50 fold dilution); t = 60 min.

From the figures it is evident that there is a significant difference in UV_{280}/COD and UV_{280}/TOC ratios at pH = 3.5 compared with the ratios obtained at pH = 7.0 for NT. In particular, up to 40 min ozonation at acidic pH, the ozone selectivity curve appeared to be much steeper than at pH = 7.0, at which pH dearomatization and COD abatement went parallel to each other. This observation reveals the inherent affinity of ozone specially towards the high-molecular-weight, polyaromatic NT structure.

The pH-dependent selectivity of ozone towards aromaticity, expressed as the changes in UV_{280}/COD and UV_{280}/TOC ratios, are displayed as a function of the applied ozone dose for ST Figures 4.30 and 4.31 for ST, respectively.

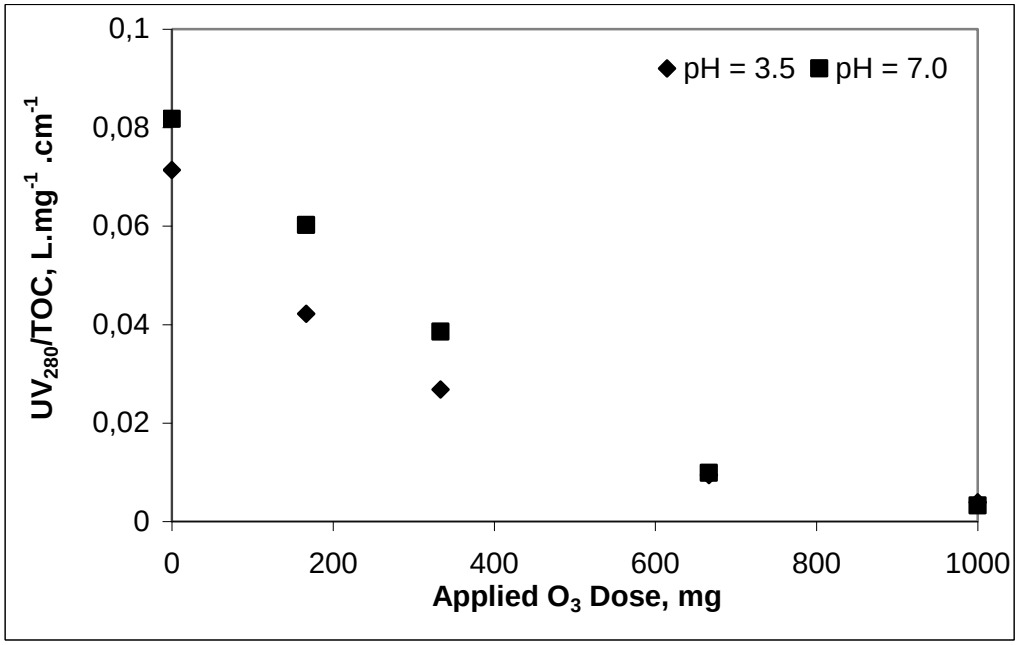

Figure 4.30. : Changes in UV_{280}/TOC Ratio at pH 3.5 and pH 7.0 for ST; Experimental Conditions: Ozone Feed Rate = 1000 mg/h; $UV_{280,o}$ = 0.575 cm^{-1} (after 20 fold dilution); t = 60 min.

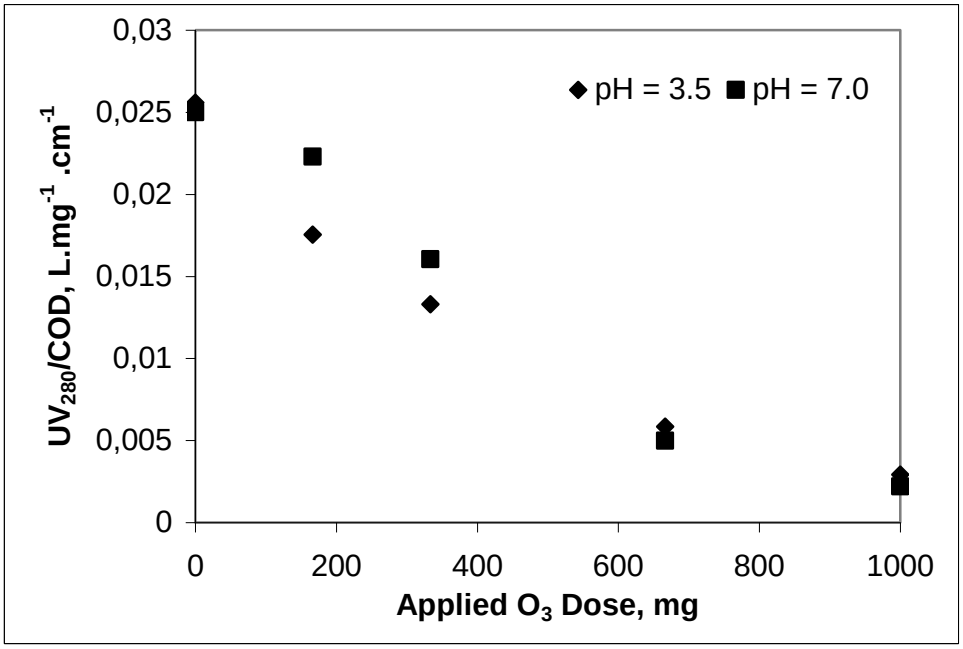

Figure 4.31. : Changes in UV_{280}/COD Ratio at pH 3.5 and pH 7.0 for ST; Experimental Conditions: Ozone Feed Rate = 1000 mg/h; $UV_{280,o}$ = 0.575 cm^{-1} (after 20 fold dilution); t = 60 min.

After 40 min ozonation, the oxidation of intermediate ozone products levelled off for ST as well as NT at both studied pH values, mainly because of the fragmentation of aromatic structures being practically complete for both studied tannins.

In order to examine the effectiveness of ozonation on partial oxidation under different reaction conditions, the following calculations were made in accordance with the approach suggested by Fiehn et al. (1998);

COD removal in total:

$$COD_{oxi} = 1 - \frac{COD_t}{COD_0} \tag{4.3}$$

COD removal due to mineralization:

$$COD_{min} = 1 - \frac{TOC_t}{TOC_0} \tag{4.4}$$

COD removal due to partial oxidation:

$$COD_{partoxi} = COD_{oxi} - COD_{min} = \frac{TOC_t}{TOC_0} - \frac{COD_t}{COD_0} \tag{4.5}$$

In Figures 4.32 and 4.33, COD removal (%) versus applied specific O_3 dose ($gO_3/gCOD_o$) plots are given for NT and ST.

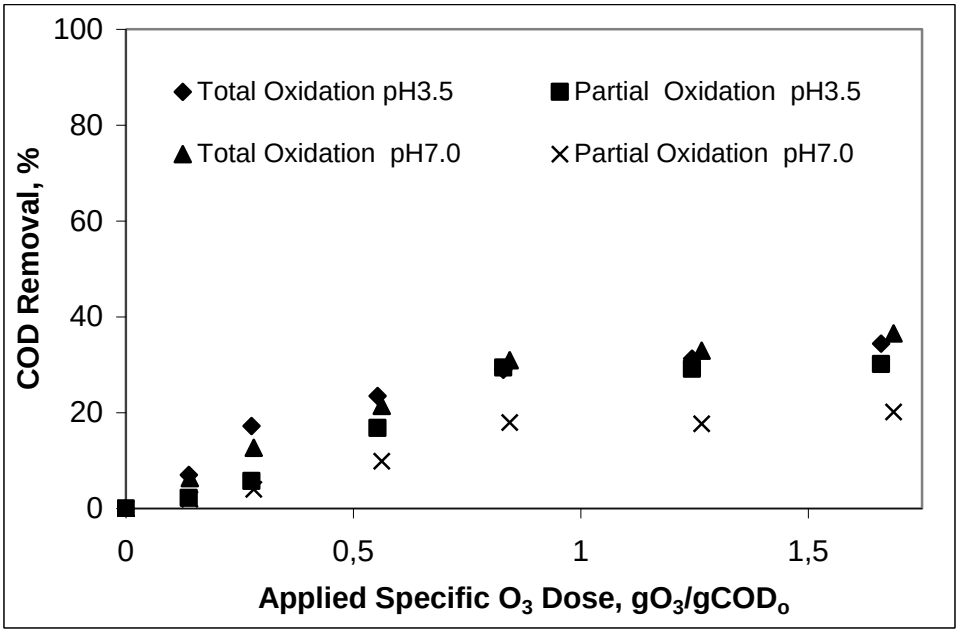

Figure 4.32. : Changes in Percent Total COD Removal and COD Abatement due to Partial Oxidation at pH = 3.5 and pH = 7.0 as a Function of the Applied Specific Ozone Dose (g Ozone Introduced per g of Initial COD) for NT; Experimental Conditions: Ozone Feed Rate = 1000 mg/h; COD_o = 1195 ± 10 mg/L; TOC_o = 342 ± 8 mg/L; t = 120 min.

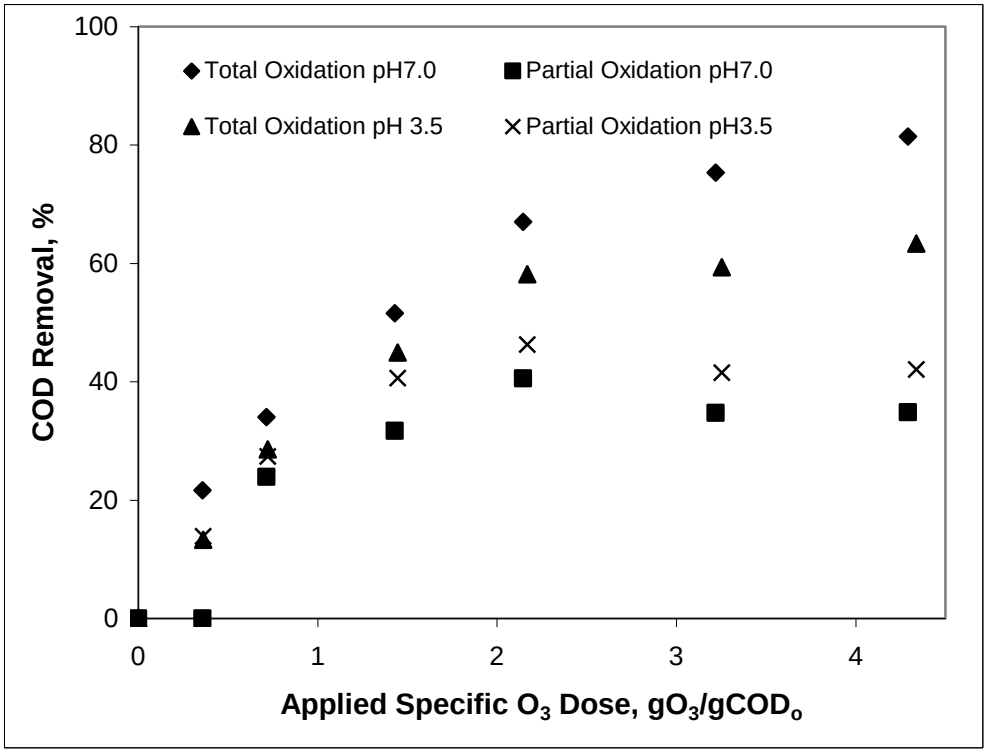

Figure 4.33. : Changes in Percent Total COD Removal and COD Abatement due to Partial Oxidation at pH = 3.5 and pH = 7.0 as a Function of the Applied Specific Ozone Dose (g Ozone Introduced per g of Initial COD) for ST; Experimental Conditions: Ozone feed rate = 1000 mg/h; COD_o = 463 ± 3 mg/L; TOC_o = 154 ± 12 mg/L; t = 120 min.

The difference between the total and partial COD removals in the established figures indicates the degree of mineralization. At pH = 3.5 and pH = 7.0, the degree of mineralization for NT and ST is evaluated in Figures 4.24 and 4.25. At pH = 3.5, total COD removal and COD removal due to partial oxidation were practically identical for NT implying that no mineralization occured for tannic acid, whereas at pH = 7.0, negligible mineralization was achieved. On the other hand, at pH = 7.0, there was significant difference between the total oxiation and partial oxidation mainly due to mineralization for ST.

4.3.2 Biocides

For BI and BII, mineralization and ozone selectivity towards the biocide structure were evaluated in terms of TOC removal and changes in the UV_{280}/COD and UV_{280}/TOC ratios at pH = 7.0 and 12.0. In addition, total and partial oxidation rates were compared in order to evaluate the extent of mineralization of BI and BII.

In Figures 4.34 and 4.35, the TOC abatements for BI and BII were depicted as a function of ozonation time at different pH values, respectively.

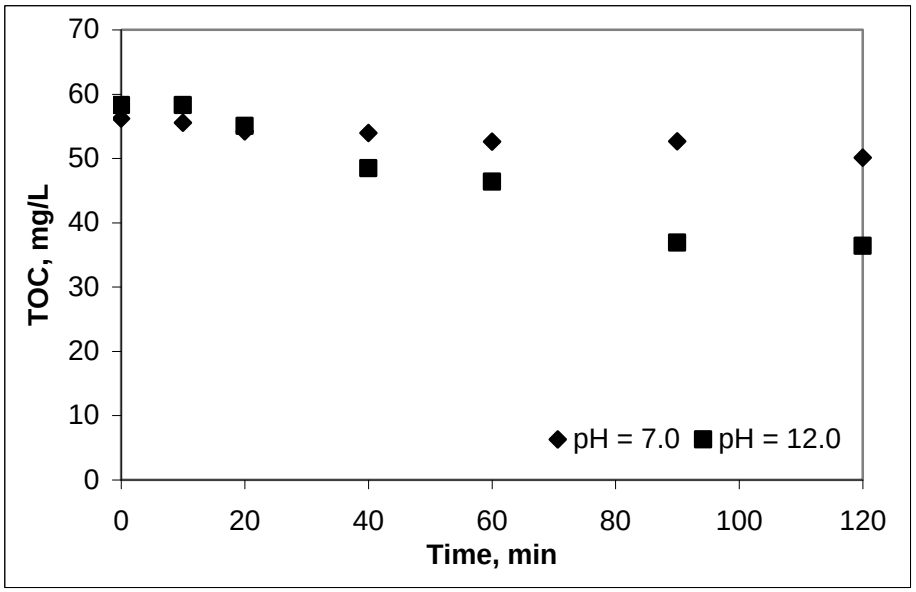

Figure 4.34. : TOC Removal for BI as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 mg/h; TOC_o = 57 ± 1 mg/L; t = 120 min.

As expected, TOC removal of BI increased when the pH was increased from 7.0 to 12.0 as a result of enhanced ozone decomposition to hydroxyl free radicals (Staehelin and Hoigné, 1982).

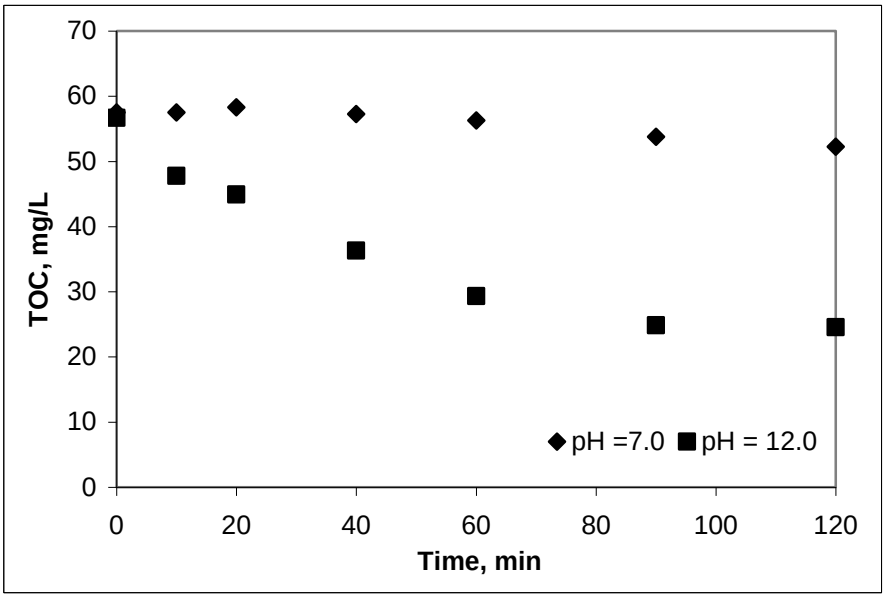

Figure 4.35. : TOC Removal for BII as a Function of Treatment Time at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 mg/h; TOC_o = 57 mg/L; t = 120 min.

The enhancement of TOC abatement rate at pH = 12.0 was even more obvious in the case of BII, where differences in the TOC removal rates were apparent from the very begining of ozonation.

TOC removals and final TOC values (obtained after 120 min ozonation) for BI and BII are given in Table 4.18 at pH = 7.0 and 12.0. Again, the improvement in TOC removal at pH = 12.0 was more evident for BII compared to BI. Overall TOC removals increased from 11% and 9% to 38% and 56% for BI and BII, respectively.

Table 4.18. : TOC removal for BI and BII at Varying pH; Experimental Conditions: Ozone Feed Rate = 900 mg/h; TOC_o (BI) = 57 $\pm$ 1 mg/L; TOC_o (BII) = 57 mg/L; t = 120 min.

Pollutant	**pH**	**TOC_{final}, mg/L**	**TOC removal, %**
Biocide I	7	50	11
	12	36	38
Biocide II	7	52	9
	12	25	56

The reason of the more significant improvement observed in the TOC abatement of BII as compared to with BI may be attributed to the structural differences of the biocidal formulations; BI is a triple-chlorinated diphenyl ether and hence difficult to oxidize even with whereas BII, a diphenyl alkane derivative is very prone to $OH^{\bullet}$oxidative attack.

The pH-dependent relative selectivity of ozone towards aromaticity, expressed as the changes in UV_{280}/TOC and UV_{280}/COD, are displayed for both textile biocides as a function of the applied ozone dose in Figures 4.36 (UV_{280}/TOC for BI) to 4.39 (UV_{280}/COD for BII).

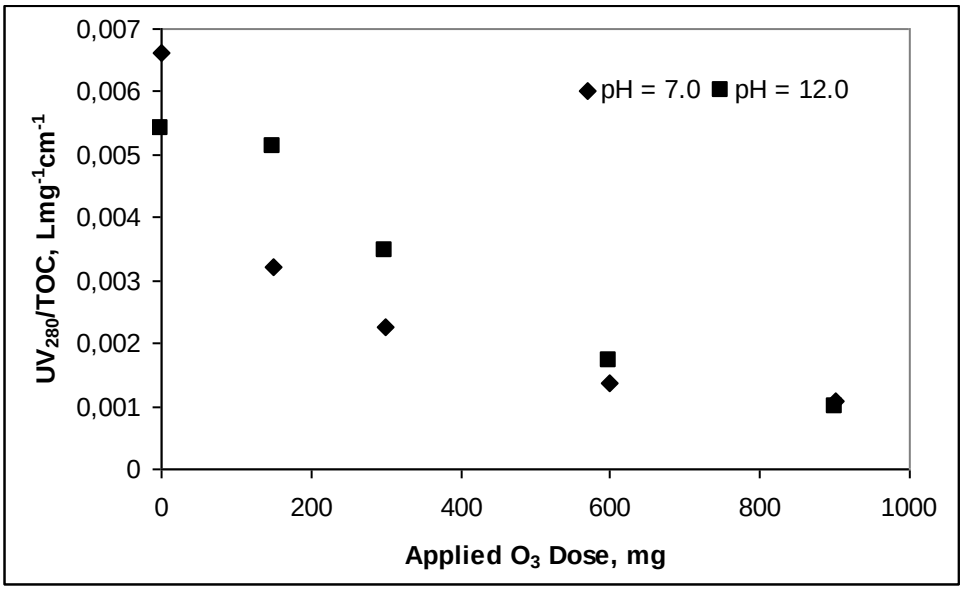

Figure 4.36. : Changes in the UV_{280}/TOC Ratio at pH 7.0 and pH 12.0 for BI; Experimental Conditions: Ozone Feed Rate = 900 mg/h; $UV_{280,o}$ = 0.35 cm^{-1}; t = 60 min.

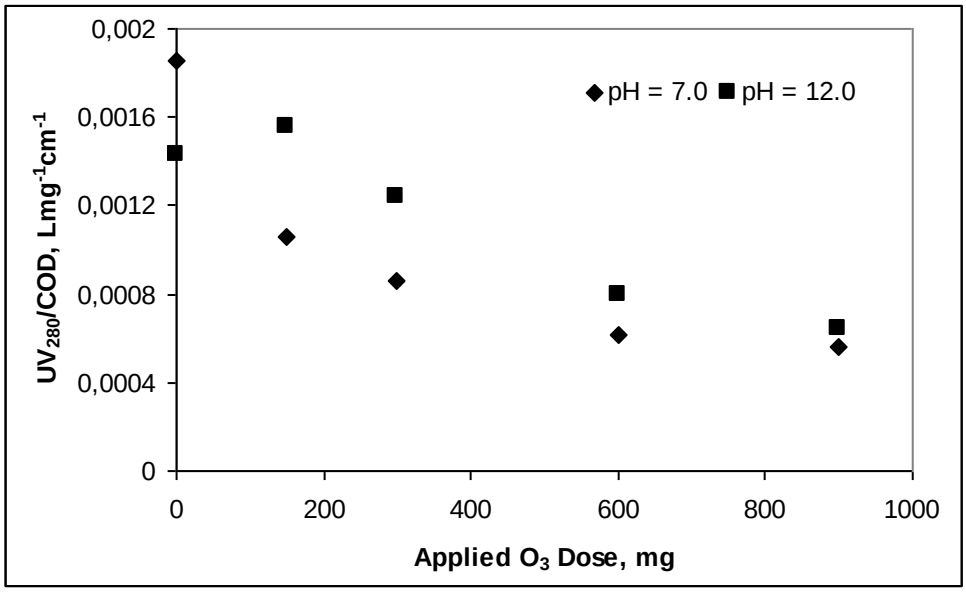

Figure 4.37. : Changes in UV_{280}/COD Ratio at pH 7.0 and pH 12.0 for BI; Experimental Conditions: Ozone Feed Rate = 900 mg/h; $UV_{280,o}$ = 0.35 cm^{-1}; t = 60 min.

According to Figures 4.36 and 4.37 showing the relative reduction in aromatic content of BI, the ozone selectivity curves appeared to be much steeper at pH = 7.0 compared to the curves at pH = 12.0 showing more effective removal of the aromatic structure of BI at pH = 7.0 than at pH = 12.0. This can be supported by the relatively higher UV_{280} removal rate for BI at pH = 7.0.

In the case of BII, there was no significant difference in UV_{280}/COD and UV_{280}/TOC ratios at pH = 7.0 compared with the ratios obtained at pH = 12.0 indicating that there is no difference for the removal of BII structure at both pH which can also be explained by the same UV_{280} removal rates obtained for pH = 7.0 and 12.0.

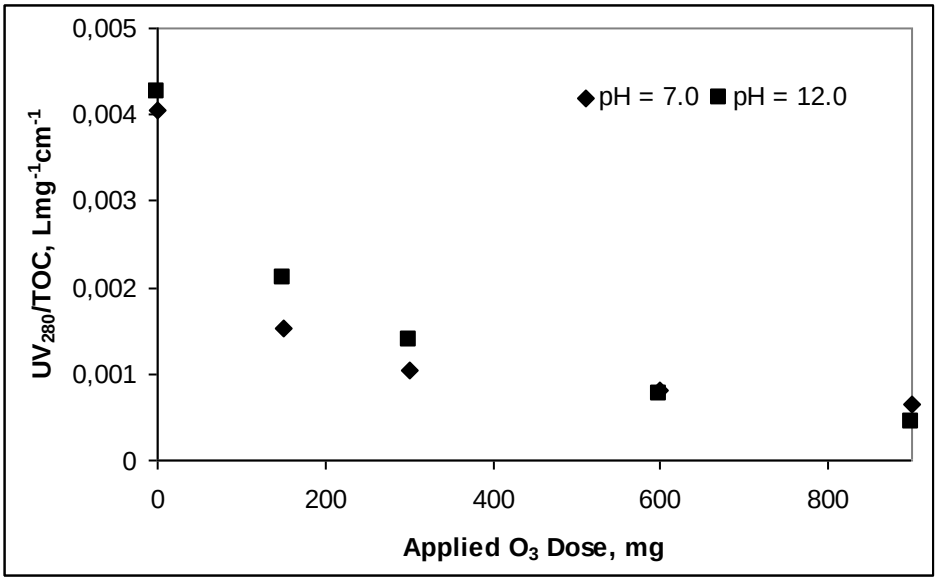

Figure 4.38. : Changes UV_{280}/TOC Ratio at pH 7.0 and pH 12.0 for BII; Experimental Conditions: Ozone Feed Rate = 900 mg/h; $UV_{280,o}$ = 0.24 cm^{-1}; t = 60 min.

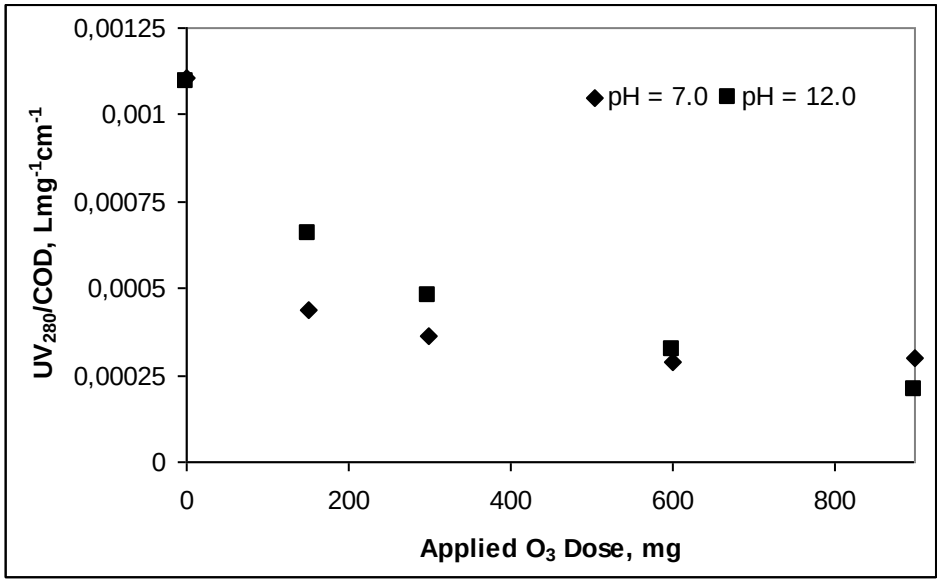

Figure 4.39. : Changes in UV_{280}/COD Ratio at pH 7.0 and pH 12.0 for BII; Experimental Conditions: Ozone Feed Rate = 900 mg/h; $UV_{280,o}$ = 0.24 cm^{-1}; t = 60 min.

According to the approach suggested by Fiehn et al. (1998) the effectiveness of ozonation on partial oxidation under different reaction conditions is examined for BI

and BII. In Figures 4.40 and 4.41, percent COD removal versus applied specific O_3 plots are given for BI and BII, respectively.

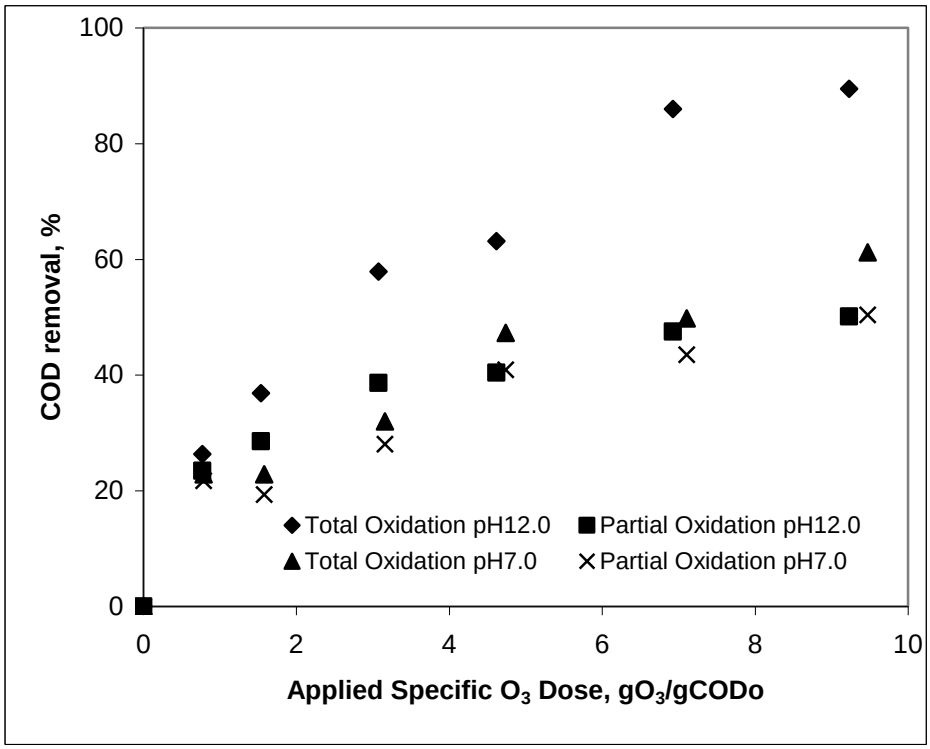

Figure 4.40. : Changes in Percent Total COD removal and COD Abatement due to Partial Oxidation at pH = 7.0 and pH = 12.0 as a Function of the Applied Specific Ozone Dose (g ozone introduced per g of initial COD) for BI; Experimental Conditions: Ozone Feed Rate = 900 mg/h; COD_o = 195 ± 5mg/L; TOC_o = 57 ± 1 mg/L; t = 120 min.

From Figures 4.40 (for BI) and 4.41 (for BII) at pH = 7.0, total COD removal and COD removal due to partial oxidation were practically identical for both biocides, revealing that the degree of mineralization is negligible. On the other hand, at pH = 12.0, the degree of partial oxidation was low as compared with pH = 7.0 for BII, however the total COD removal and COD abatement due to mineralization were rather high. In the case of BI, the degree of partial oxidation was identical at both studied pH and the increase in total COD removal was mainly due to mineralization.

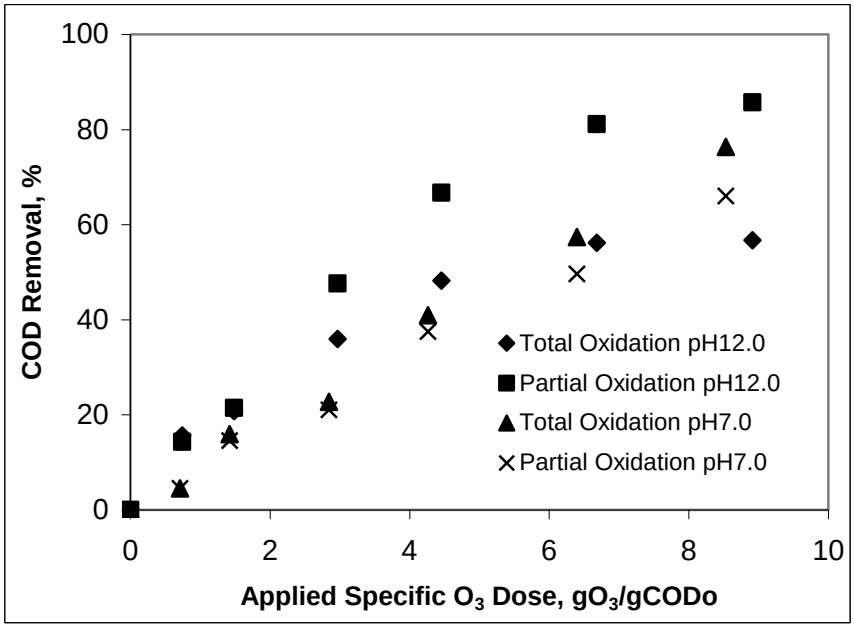

Figure 4.41. : Changes in Percent Total COD Removal and COD Abatement due to Partial Oxidation at pH = 7.0 and pH = 12.0 as a Function of the Applied Specific Ozone Dose (g ozone Introduced per g of Initial COD) for BII: Experimental Conditions: Ozone Feed Rate = 900 mg/h; COD_o = 215 ± 15 mg/L; TOC_o = 57 mg/L; t = 120 min.

4.4 Effect of Ozone on Biodegradability

Most aromatic compounds are difficult to be decomposed by microorganisms, while ozonation products may be more susceptible to microbial decomposition (Gilbert, 1987, Hsu et al., 2004). It has been previously suggested that increasing the ozone contact time first produces more biodegradable intermediates, and that upon extension of the ozonation period biodegradability levels off (Balcıoğlu Akmehmet, and Arslan, 2001), decreases (Takahashi et al., 1994, Jochimsen and Jekel, 1997, Imai et al., 1998) or in some cases even further increases (Gilbert, 1987; Benitez et al., 2001) depending on the specific pollutant type (Akmehmet Balcıoğlu, and Ötker, 2003). Since ozonation can considered as a pre-treatment method for textile tannins, it is crucial to evaluate the biodegradability of NT and ST before and after ozonation. In order to assess the effect of ozonation on the biodegradability of NT and ST, the BOD_5/COD ratio was determined before and after ozonation for 40 min at a feed rate of 1000 mg/h and pH = 3.5. It was thought that the biodegradability of NT and ST can be improved as a result of the conversion of the high-molecular-weight organic compounds to low-molecular-weight organic compounds with oxidation by ozonation.

In Table 4.19, the BOD_5 and COD values together with the established biodegradability ratios (BOD_5/COD) are summerized for NT and ST before and after ozonation.

Table 4.19. : BOD_5, and BOD_5/COD Ratio of NT and ST Before and After Treatment with Ozone: Experimental Conditions: Ozone Feed Rate = 1000 mg/h; pH = 3.5; t = 40 min.

	NT		ST	
Ozonation (pH = 3.5, 1000 mg/h)	**Before**	**After**	**Before**	**After**
BOD_5, mg/L	86	15	6	135
COD, mg/L	1200	920	460	255
BOD_5/COD	0.072	0.016	0.013	0.529

As it can be seen in Table 4.19, BOD_5/COD ratio for NT, decreased from 0.072 to 0.016. On the other hand, the BOD_5/COD ratio for ST increased from 0.013 to 0.529 which shows a significant increase in biodegradability of ST even at low pH.

As a result of ozonation for 40 minutes at a feed rate of 1000 mg/h and pH = 3.5, a reasonable improvement in the biodegradability of ST was achieved, whereas for NT no biodegradability improvement could be obtained.

The toxicity of a variety of refractory compounds towards heterotrophic biomass has already been evaluated using activated sludge in previously published work (Gutiérrez, at al., 2002). In the present study, in addtion to biodegradability tests, activated sludge inhibition experiments were conducted within the scope of an ongoing COST Action (EU Cost Action 628) in order to examine the effect of ozonation on the acute toxicity of the selected pollutants. Activated sludge inhibition experiments which are used for acute toxicity evaluation were performed in accordance with an organic loading (COD/MLVSS)–balanced, ISO (1986) test procedure. For that purpose, activated sludge inhibition tests were conducted with previously acclimated (fed with a synthetic medium resembling readily biodegradable, “domestic” wastewater, called SWW herein) with heterotrophic biomass for two months at a constant temperature of 20 ± 2^{o}C. Different dilutions of tannin and biocide sample solutions with appropriate amounts of SWW resulting in a series of varying COD fractions were prepared, thereby keeping the total COD in the pollutant + SWW effluent mixture constant. The raw and ozonated textile auxiliaries + SWW mixtures were continuously aerated for up to 60 min in test beakers containing proper amounts of sewage sludge acclimated to SWW. The decrease in

dissolved oxygen concentration (in mg/L) in the synthetic wastewater control (SWW) and different dilutions of raw and ozonated tannin and biocide effluent samples were monitored for up to 5 min using a WTW Oxi Digi 2000 model oxygen meter. Microbial oxygen uptake rates (OUR, in mg L^{-1} h^{-1}) in the test blank (SWW only) and in the diluted tannin and biocide effluent samples were calculated based on the linear part ($R^2 > 0.95$) of the dissolved oxygen concentration curves as a function of aeration (i.e. biological treatment) time. The percent inhibition of OUR, i.e. I_{OUR}, % for every tested sample dilution was calculated using the following equation;

$$I_{OUR}\ (\%) = \quad [(R_B - R_T) \times 100] / R_B \qquad (4.6)$$

where R_B and R_T are the OUR's calculated for the blank and test samples, respectively. The COD content of raw and ozonated solutions resulting in 50 % decrease of OUR's (i.e. the EC_{50} values; in mg/L COD) after t = 30 min aeration was calculated by interpolation of the linear "lnCOD" versus "percent I_{OUR}" plots obtained for the raw and ozonated samples.

Experimental results of the activated sludge inhibition test conducted for NT and ST are summerized in Table 4.20.

Table 4.20. : EC_{50} values for raw and ozonated NT and ST. Experimental conditions: Ozonation for 40 min; Ozone dose = 1000 mg/h; Ozonation pH = 3.5; Bioaeration experiments conducted for 30 min; F/M ratio = 0.17 mg COD mg $MLVSS^{-1}$ d^{-1}; $COD_{40min,NT}$ = 970 mg/L ; $COD_{40min,ST}$ = 280 mg/L.

	NT		**ST**	
Type of sample	Raw	Ozonated	Raw	Ozonated
EC_{50}, mg/L COD	381	431	259	No Inhibition

As is obvious in Table 4.20, the EC_{50} value (i.e. mg/L COD coming from the tested toxicant and causing 50% activated sludge inhibition after 30 min aeration in batch bioreactors fed with SWW+test samples) of NT slightly increased from 381 mg/L to 431 mg/L COD after ozonation at pH = 3.5 at a rate of 1000 mg/h, whereas ST, that had an original EC_{50} value of 259 mg/L COD and hence exerted more toxicity than NT, exhibited no inhibition towards activated sludge microorganisms upon exposure to ozonation at identical reaction conditions (pH & ozone dose). These results were obtained in parallel to the BOD_5 results.

Experimental results obtained for BI and BII (in mg/L COD) before and after ozonation are given Table 4.21.

Table 4.21. : EC_{50} values for raw and ozonated BI and BII. Experimental conditions: Ozonation for 40 min; Ozone dose = 600 mg/h; Ozonation pH = 3.5; Bioaeration experiments conducted for 30 min; F/M ratio = 0.10 mg COD mg $MLVSS^{-1}$ d^{-1}; $COD_{40min,BI}$ = 135 mg/L ; $COD_{40min,BII}$ = 166 mg/L.

	BI		**BII**	
Type of sample	Raw	Ozonated	Raw	Ozonated
EC_{50}, mg/L COD	188	No Inhibition	151	No Inhibition

Both investigated textile biocides exerted a significant acute toxicity towards activated sludge microorganisms, i.e. the initial EC_{50} (in terms of COD equivalents) values were found as 188 mg/L for BI and 151 mg/L COD for BII. Oxidation processes are effective in elimination of toxic compounds (Marco et al., 1997). Results of the activated sludge inhibition tests demonstrated that ozonation at a specific ozone dose of 1 mg O_3 /mg COD_o (applied ozone dose = 900 mg/h at pH = 3.5 for 40 min) for ST and 2 mg O_3 /mg COD_o (applied ozone dose = 600 mg/h at pH = 7.0 for 60 min) for both biocides accounted for practically complete detoxification of the aqueous ST, BI and BII revealing that partial oxidation was sufficient for detoxification of tested pollutants.

4.5 Kinetic studies

In order to follow the concentration of BI, UV_{280} was monitored since it is the characteristic peak value in the absorption spectrum of BI. The kinetics of heterogeneous reactions is governed by absorption theories of gases in liquids accompanied by chemical reactions. Kinetic studies were accomplished only for BI of which the exact molecular strucure of the active substance is exactly known (2,4,4'-trichloro-2'-hydroxydiphenyl ether). In order to determine the kinetic regime of the reaction between mlecular ozone and BI, the volumetric mass transfer coefficient (k_La) and the first order UV absorbance abatement rate constant at 280 nm (k_{UV280}) which is the characteristic wavelength of BI were compared.

The volumetric mass transfer coeffcient, k_La value was found by measuring the liquid phase ozone concentation with time at pH = 2.0 in distilled water and at and ozone feed rate of 900 mg/h. By using this data ($O_{3,l}$ vs time) $\ln((C_{O3,b}^* - C_{O3,b})/C_{O3,b}^*)$ was established and plotted against ozonation time. The slope of this

curve gave the volumetric mass transfer coefficient k_La (in min^{-1}) that had to be determined and compared with UV_{280} abatement kinetics. The $ln((C_{O3,b}^* - C_{O3,b})/C_{O3,b}^*)$ versus ozonation time curve is presented in Figure 4.42.

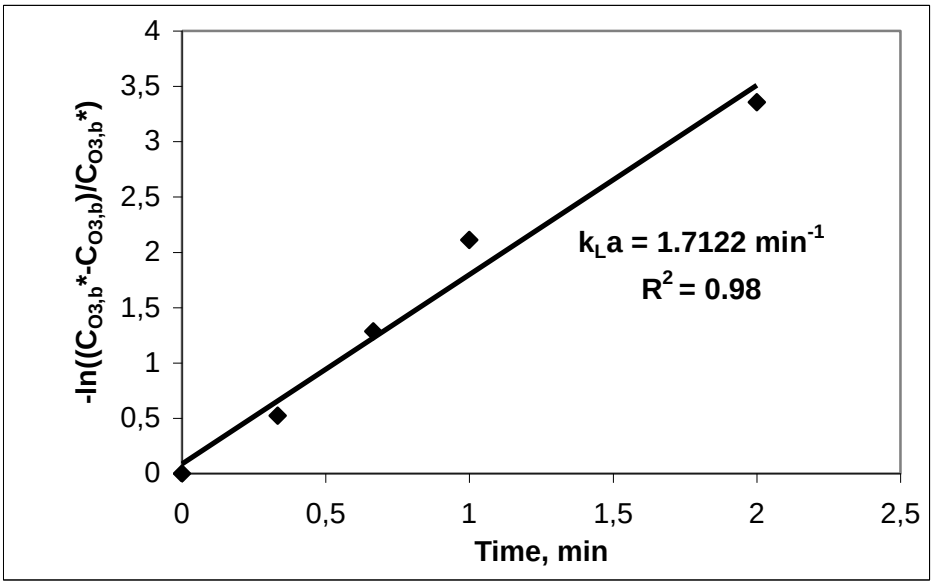

Figure 4.42. : Determination of the Volumetric Mass Transfer Coefficient, k_La; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 2.0; t = 120 min.

Since the characteristic UV absorbance of BI is very close to the absorbance value that is generally accepted as a “collective” parameter representing “aromaticity” (Nakamura et al., 2004),this value was followed to describe the fate of xenobiotic removal. Figure 4.43 presents the linearized form of UV280 abatement kinetics for BI during ozonation at a dose of 900 mg/h and pH = 7.0.

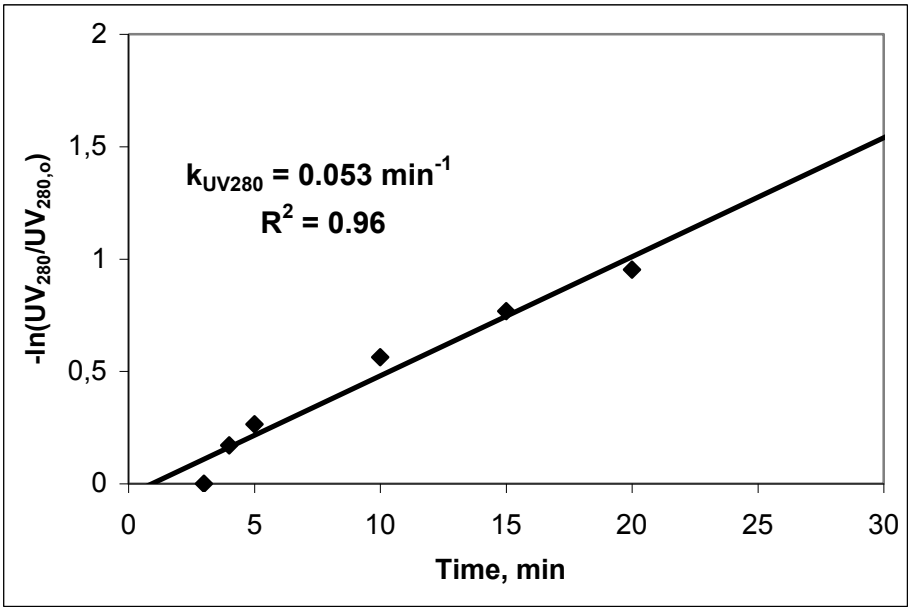

Figure 4.43. : Determination of First Order UV_{280} Abatement Rate Constant, k_{UV280} for BI; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with 50 mL, 0.1M $NaHCO_3$); t = 120 min.

Upon closer inspection of Figures 4.42 and 4.43 it is obvious that $k_La > k_{UV280}$, indicating that the reaction between molecular ozone (bicarbonate buffer was used in proper amounts to scavenge all OH• and to enable the evaluation of direct O_3-BI reaction) and BI (presented as UV_{280}) is not mass transfer-, but kinetically limited.

For slow kinetic regimes, the gas liquid reaction is a two series process where mass transfer through the film layer first occurs and then the chemical reaction develops in the bulk liquid as explained in Section 2.3.4. Hence, the presence of liquid phase ozone is the sign of slow reactions in water (Appendix A, Figure A.5 and A.6). For a slow kinetic regime, since there is no mass transfer limitation, $k_La > k_1$. In this case, once the indirect reactions are eliminated, the rate constant of the direct reaction between ozone and the pollutant (BI) can be obtained from the mass balance of BI in the reactor:

$$r_{BI} = -\frac{dC_{BI,b}}{dt} = k_{O_3,BI} C_{O3,b} C_{BI,b} \qquad (4.6)$$

where

r_{BI} : Ozonation rate of BI, Ms^{-1}

$C_{BI,b}$: Concentration of BI in the bulk liquid, M

$k_{O3,BI}$: bimolecular rate constant of direct reaction ozone-BI, $M^{-1}s^{-1}$

$C_{O3,b}$: Concentration of ozone in the bulk liquid, M

$r_{BI,b}$ can be expressed as

$$r_{BI} = k_1 C_{BI,b} \quad (4.7)$$

where k_1 is the first order pollutant abatement rate constant of BI. As was described previously parent compound degradation can also be monitored by examining absorbance at wavelength where the maximum absorption band in the visible region of the spectrum for coloured samples and at the appropriate ultraviolet characteristic wavelength for aromatic and other organic compounds (Alvares et al., 2000). In order to convert absorbance values to molar concentrations, a calibration line for the concentration of BI (mol/L) versus the corresponding UV_{280} value was plotted and shown in Figure 4.44.

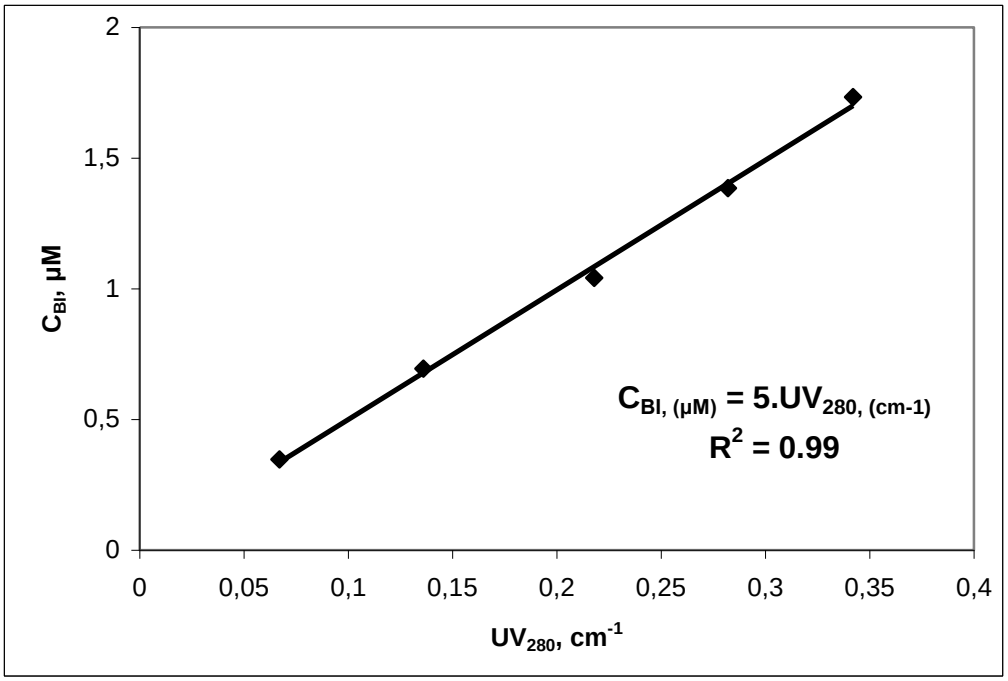

Figure 4.44. : Calibration curve, concentration of BI, C_{BI}, (µM) versus corresponding UV_{280} (cm^{-1}).

For the evaluation of the kinetic regime of the direct reaction of ozone with BI, the effect of ozone decomposition reaction must eliminated by the addition of $OH^{\bullet}$ scavengers. Bicarbonate, which is an effective $OH^{\bullet}$ scavenger was used to inhibit the decomposition of ozone and to eliminate indirect reactions (Glaze and Kang, 1989). Ozonation experiments were conducted at pH = 7.0 in the presence of sodium bicarbonate with 900 mg/h ozone feed rate.

In Figure 4.45, BI abatement converted to molar concentrations is given with respect to ozonation time (pH = 7.0; 900 mg/h O_3; HCO_3^-buffer).

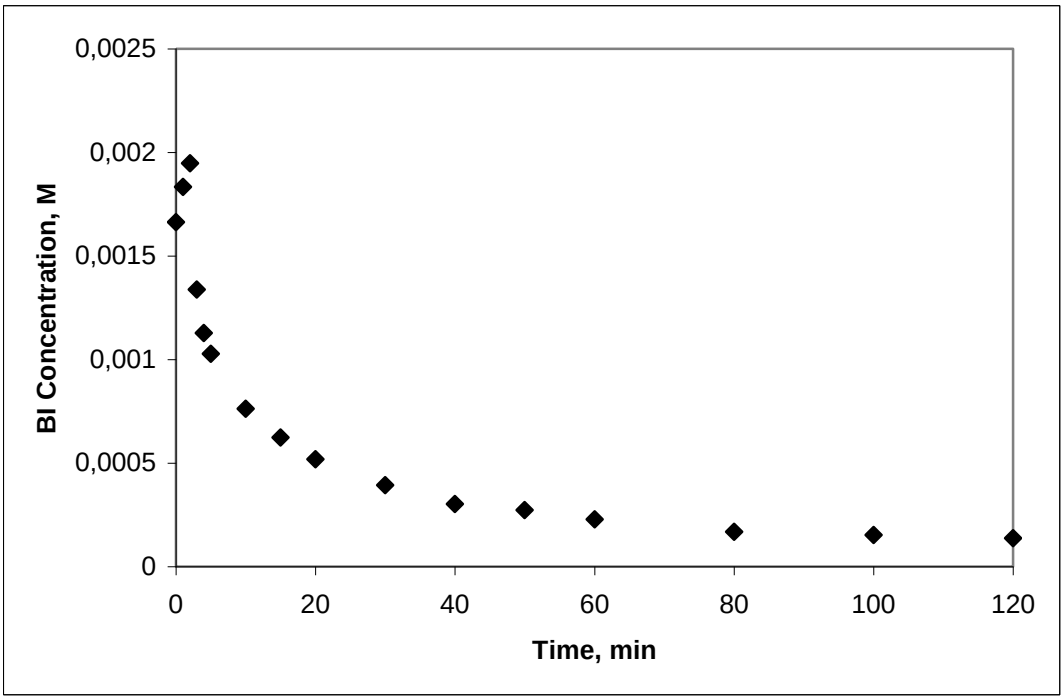

Figure 4.45. : Changes in BI Concentration with respect to Ozonation Time; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0 (adjusted with 50 mL, 0.1M $NaHCO_3$); t = 120 min.

Once the UV_{280} values for BI are converted to BI concentration (mol/L) according to the calibration line, the first order rate constant for BI degradation (i.e. k_1 in min^{-1}) could be calculated by forming a logarithmic molar concentration versus ozonation time curve (Figure 4.46).

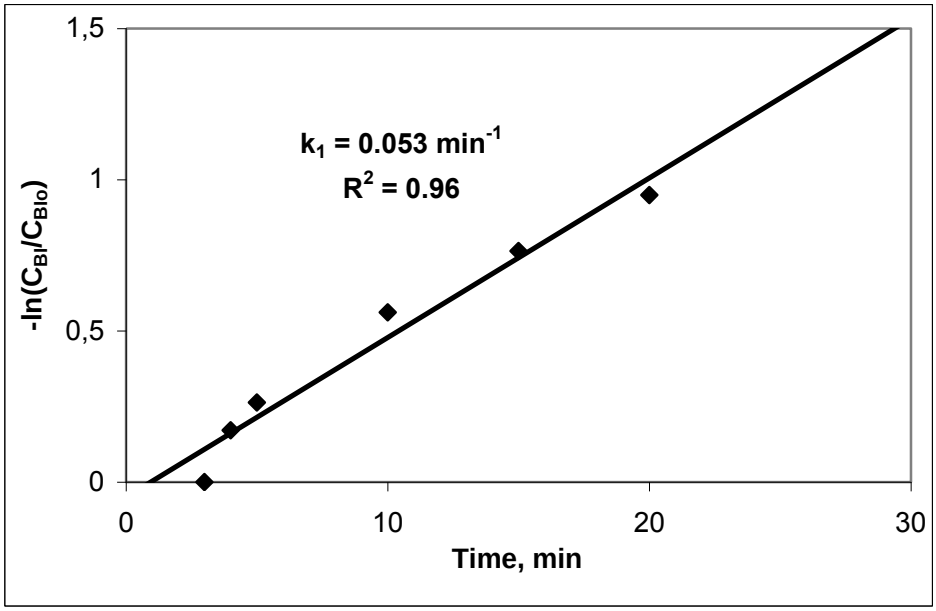

Figure 4.46. : Logarithmic and molar abatement rates for ozonation of BI; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with 50 mL, 0.1M $NaHCO_3$); t = 120 min.

From Figure 4.46, the first order BI abatement rate constant was found to be 0.053 min^{-1}.

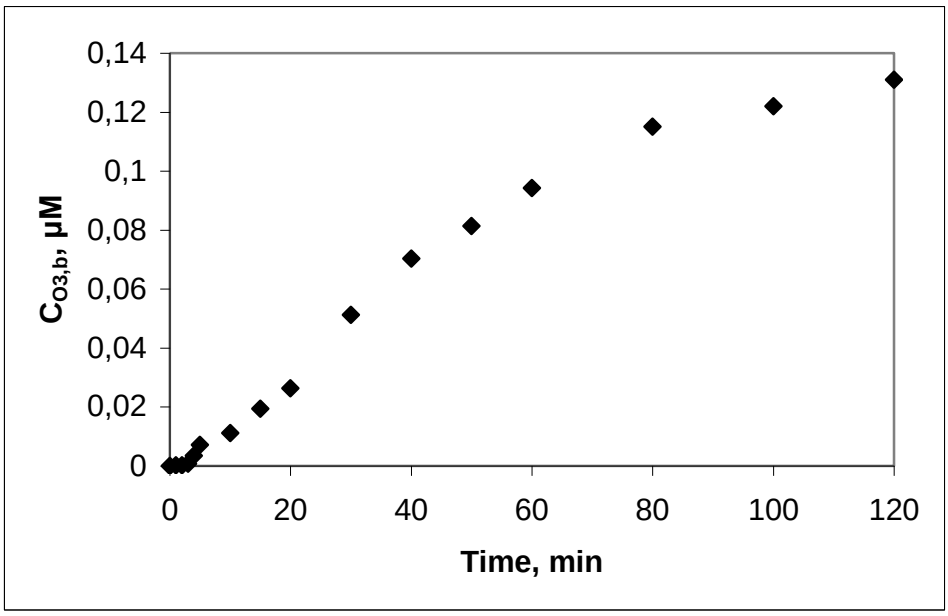

Figure 4.47. : Changes in Molar O_3 in the Bulk Liquid with respect to Ozonation Time; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with 50 mL, 0.1M $NaHCO_3$); t = 120 min

After the determination of the variables k_1, $C_{BI,b}$, and $C_{O3,b}$, the slope of the plot $-r_{BI}$ against the product of concentrations of BI and ozone ($C_{BI,b}$, and $C_{O3,b}$) which led to

a straight line according to equation 4.6, gave the bimolecular rate constant for the ozonation od BI.

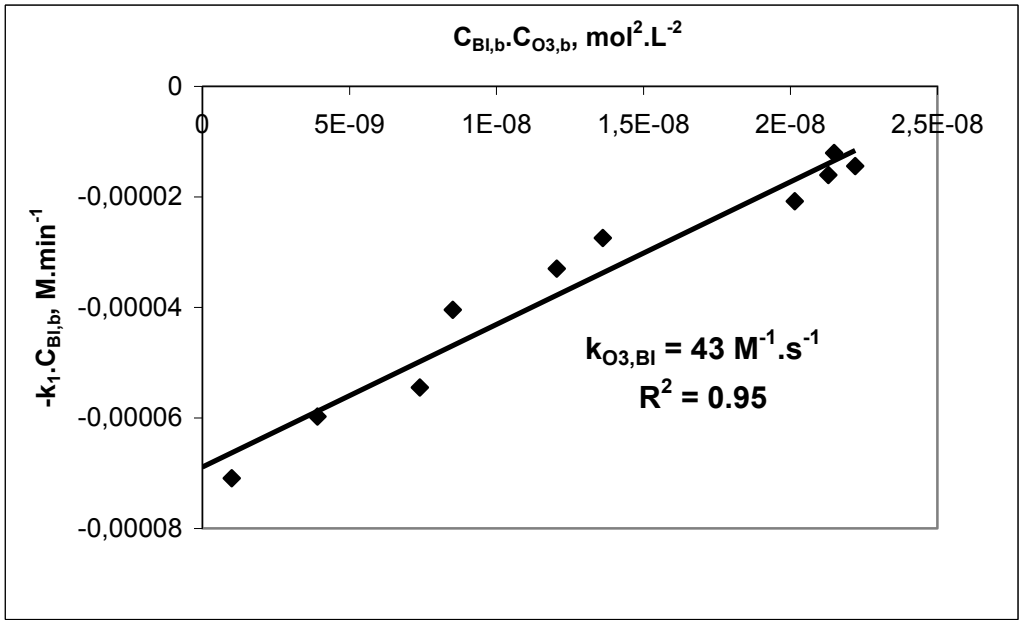

Figure 4.48. : Determination of Bimolecular Reaction Rate Constant of BI Experimental Conditions: pH = 7.0 (adjusted with 50 mL, 0.1M $NaHCO_3$); Ozone Feed Rate = 900 mg/h; t = 120 min.

The bimolecular rate constant for the direct reaction of ozone with BI was found as $k_2 = 43\ M^{-1}s^{-1}$ ($R^2 = 0.95$) from the slope of the curve in the above figure. This value lies in the range of direct reactions of ozone with aromatic compounds and hence is acceptable.

5 SUMMARY AND CONCLUSIONS

The textile dyeing & finishing industry is particularly known for its high water and chemical consumption among all industrial sectors. In addition, most of the dyestuffs and auxiliaries originating from this industry resist biodegradation and hence require special treatment. If not treated properly, they will remain in the dyehouse untreated and impart serious aesthetic and environmental concern in the receiving, discharged water bodies. In order to alleviate this problem, in the present experimental work the effect of ozonation on the treatability of two commercial textile tannins (abbreviated as NT and ST) and two frequently employed biocidal finishing agents (abbreviated as BI and BII) was investigated. The effects of ozonation on the partial oxidation, acute toxicity and biodegradability of the selected refractry chemicals were assessed in terms of the collective environmental parameters COD, TOC, UV_{254} (presenting unsaturated moities) UV_{280} (presenting aromatic structure) and BOD_5 as well as AOX (Adsorbable Organic Halogens) for BI. The following results and conclusions could be drawn from the study:

- Increasing the ozone feed rate (from 450 to 1100 min the case of NT. However, in the case of ST, an increase in COD removal was observed when the ozone feed rate was increased. In addition, as a result of the accelerated accelerated ozone decomposition to free radicals, COD removal increased at elevated pH only for ST.

- In the case of NT, 698 mg ozone was used for 26% COD and 4% TOC removals at pH = 3.5, whereas 764 mg ozone was used by the reaction system to achieve 28% COD and 16% TOC removals after ozonation for 60 min at pH = 7.0 at an ozone dose of 900 mg/h. For ST, when the reaction pH was increased from 3.5 (452 mg ozone used) to 7.0 (706 mg ozone used), the overall COD removal increased from 52% to 64% and the TOC removal from 21% to 47% at the same applied ozone dose.

- The BOD_5/COD ratio known as a common indicator of bidegradability increased appreciably for ST, but slightly decreased for NT after 40 min

ozonation at a dose of 900 mg/h and at pH = 3.5. The results of the activated sludge inhibition experiments were in complete agreement with the BOD_5 measurements; ST showed no inhibiton towards activated sludge after ozonation for 40 min at a dose of 900 mg/h and pH = 3.5. The inhibitory effect of NT did not change after ozonation under the same reaction conditions.

- The results obtained for COD, TOC, as well as BOD_5 and activated sludge inhibition tests all implied that ozonation was not effective for the treatment of NT. However, ozonation proved to be fairly effective in degrading ST both in terms of COD as well as TOC, either via direct molecular ozone attack or indirect oxidation with •OH radicals.

- Since only partial oxidation (45 % COD removal for ST after 40 min ozonation at pH 3.5) resulted in complete detoxification and acceptable biodegradability improvement for otherwise refractory ST, ozonation appeared to be an economically feasible and promising option for the effective pre-treatment of ST.

- After the application of 900 mg ozone at pH = 7 (absorbed ozone = 478 mg), the COD removal was obtained as 49%; whereas at pH = 12 (absorbed ozone = 730 mg) COD incresed to 67 % for the biocide BI. In the case of biocide BII, by applying the same ozone dose, the COD removal efficiency increased from 42% at pH = 7 (absorbed ozone = 467 mg) to 72% at pH = 12 (absorbed ozone = 631 mg). In the same manner, the TOC removal rates obtained for BI and BII increased from around 10 % at pH = 7 to 38 % for BI and to 56 % for BII at pH = 12 after 120 min ozonation (1800 mg ozone). Conclusively, elevated ozone doses and pH (indirect, free radical type oxidation pathway) were required for the effective mineralization of the tested biocides.

- When AOX, UV_{280} and COD removal rates were compared for ozonation of BI, it was evident that AOX abatement rates were higher which can be explained by the individual reaction modes of ozonation, namely hydroxylation, dechlorination (AOX removal), followed ring-cleavage (UV_{280} removal), double bond fission (UV_{254} removal), oxygenation (COD abatement) mineralization to oxidation end products (TOC reduction).

- Both investigated textile biocides exerted a significant acute toxicity towards activated sludge microorganisms, i.e. the initial EC_{50} (in terms of COD equivalents) values were found as 188 mg/L for BI and 151 mg/L COD for BII. Results of the activated sludge inhibition tests demonstrated that ozonation at a specific ozone dose of 2 mg O_3 /mg COD_o (applied ozone dose = 600 mg/h at pH = 7.0 for 60 min) accounted for practically complete detoxification of the aqueous biocides revealing that partial oxidation was sufficient for detoxification of both biocides.

- Ozonation proved to be a promising and economically feasible alternative for the effective treatment of both biocides originating from the textile finishing industry.

- As a result of the kinetic study condcuted with BI, the bimolecular reaction rate constant for the direct, bimolecular reaction of BI with ozone was found to be 43 $M^{-1}s^{-1}$ which is in the range of reaction rate constants of ozone with certain aromatic compounds.

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7 APPENDIX

APPENDIX A. Change in $C_{O3,b}$ with Respect to Ozonation Time for the Selected Textile Auxiliaries in the Experimental Conditions Indicated.

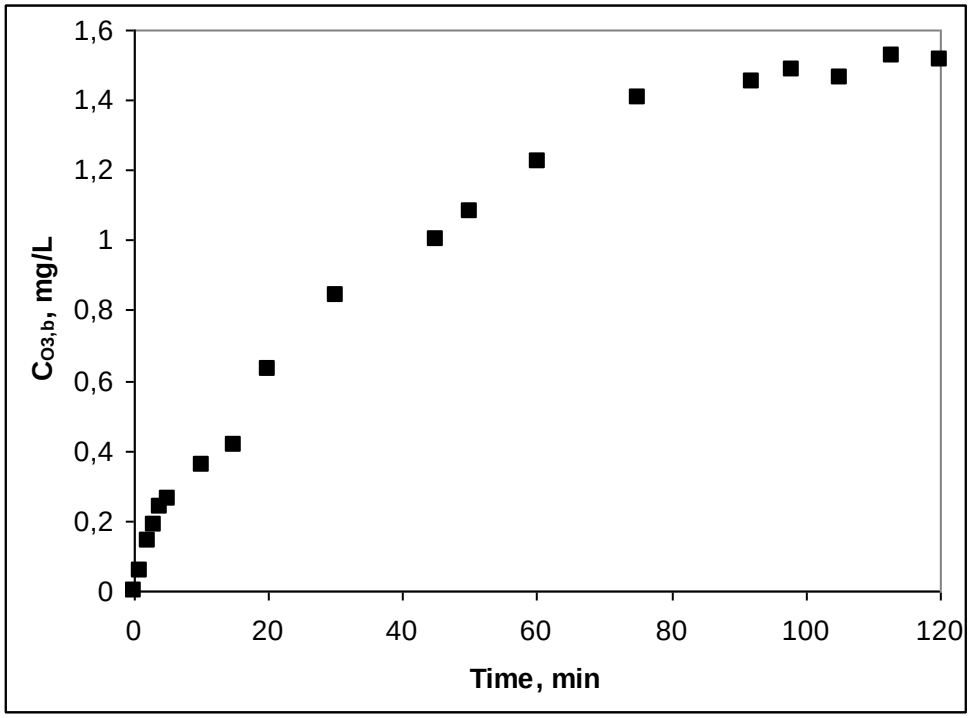

Figure A.1. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for NT on Mass Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 3.5; (adjusted with H_3PO_4 Buffer); COD_o = 1200 mg/L; TOC_o = 340 mg/L; $UV_{280,o}$ = 0.928 cm^{-1}; $UV_{254,o}$ = 0.552 cm^{-1} (after 50 fold dilution); t = 120 min.

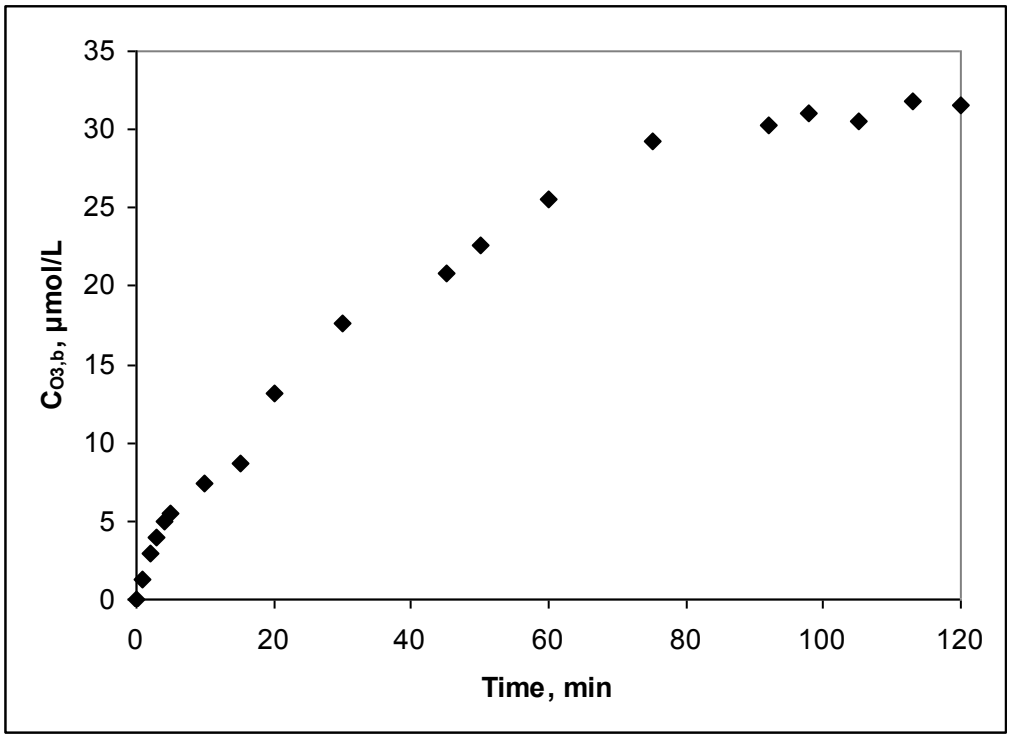

Figure A.2. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for NT on Molar Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 3.5; (adjusted with H_3PO_4 Buffer); COD_o = 1200 mg/L; TOC_o = 340 mg/L; $UV_{280,o}$ = 0.928 cm^{-1}; $UV_{254,o}$ = 0.552 cm^{-1} (after 50 fold dilution); t = 120 min.

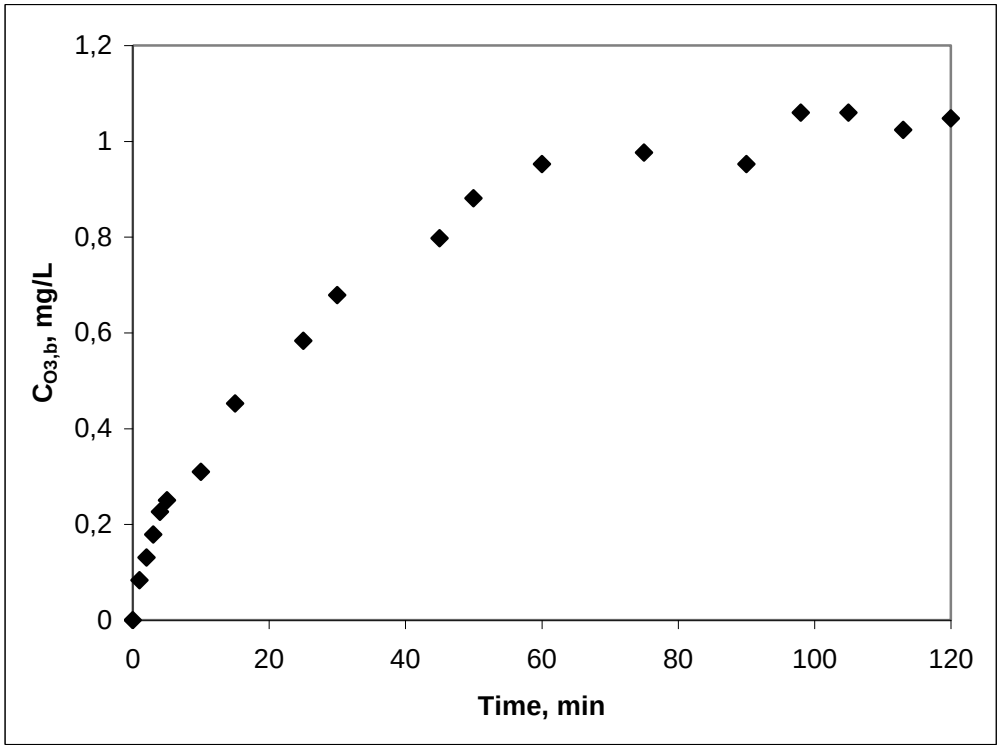

Figure A.3. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for ST on Mass Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with H_3PO_4 Buffer); COD_o = 460 mg/L; TOC_o = 155 mg/L; $UV_{280,o}$ = 0.575 cm^{-1}; $UV_{254,o}$ = 0.799 cm^{-1} (after 20 fold dilution); t = 120 min.

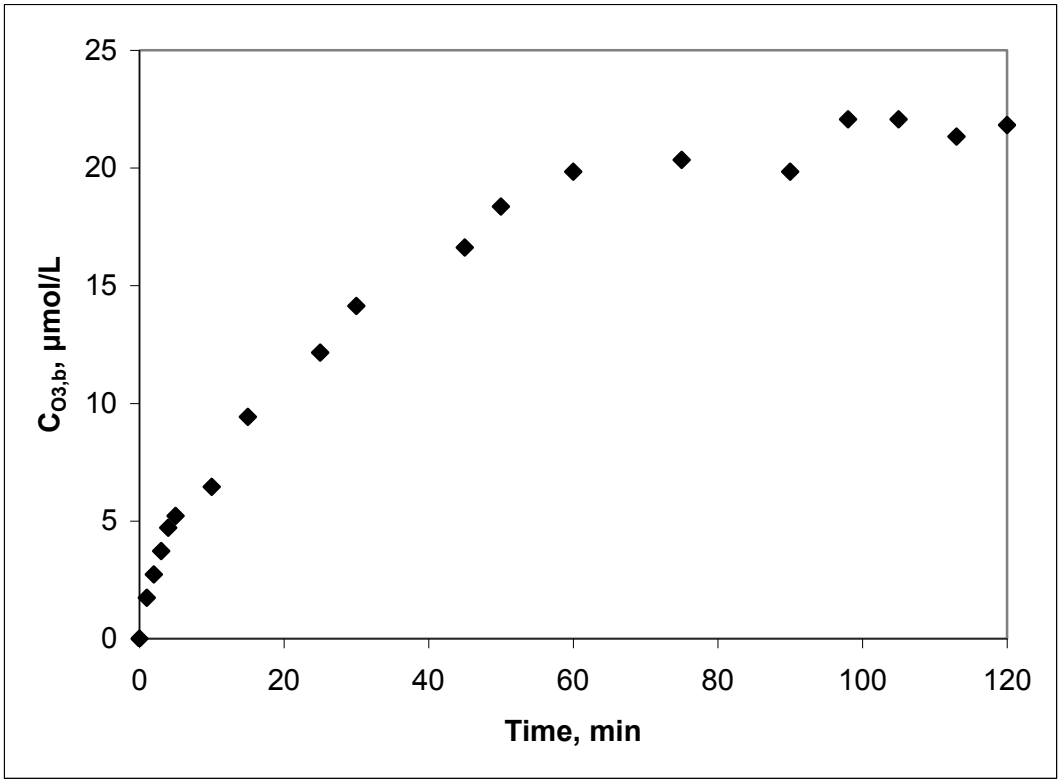

Figure A.4. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for ST on Molar Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with H_3PO_4 Buffer); COD_o = 460 mg/L; TOC_o = 155 mg/L; $UV_{280,o}$ = 0.575 cm^{-1}; $UV_{254,o}$ = 0.799 cm^{-1} (after 20 fold dilution); t = 120 min.

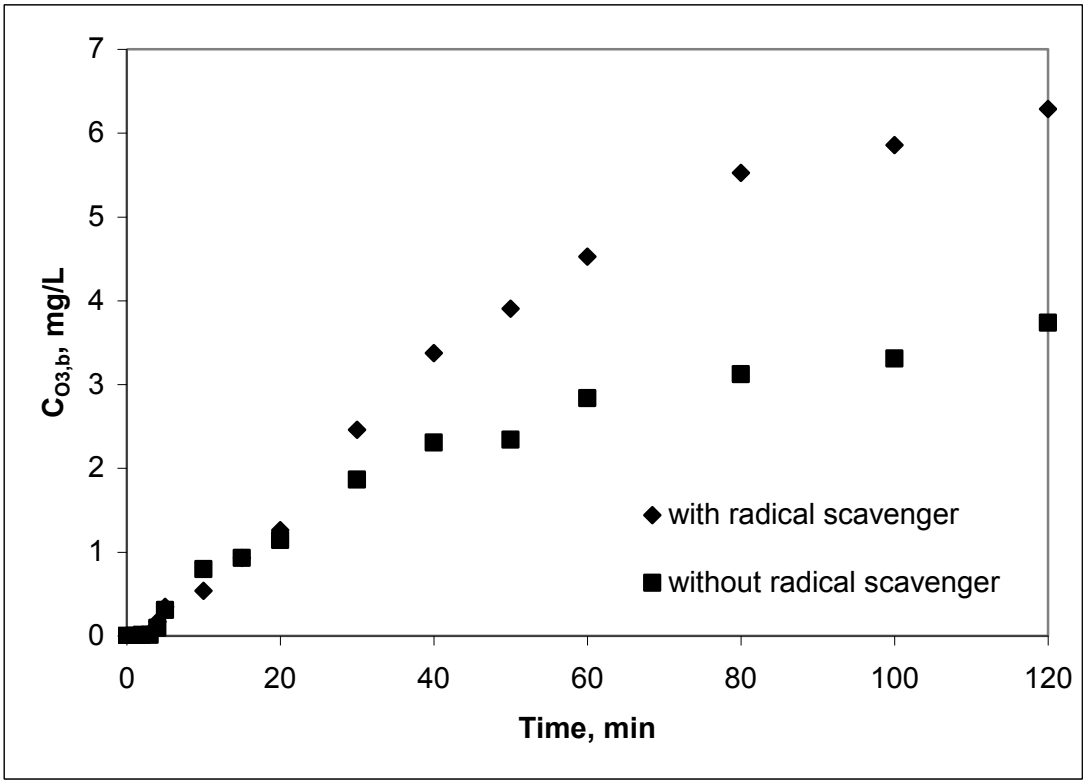

Figure A.5. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for BI on Mass Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with KH_2PO_4/NaOH Buffer (Ozonation without Scavenger) and 6.25 mM $NaHCO_3$ (Ozonation with Scavenger)); COD_o = 195 mg/L; TOC_o = 57 mg/L; $UV_{280,o}$ = 0.37 cm^{-1}; $UV_{254,o}$ = 0.30 cm^{-1}; t = 120 min.

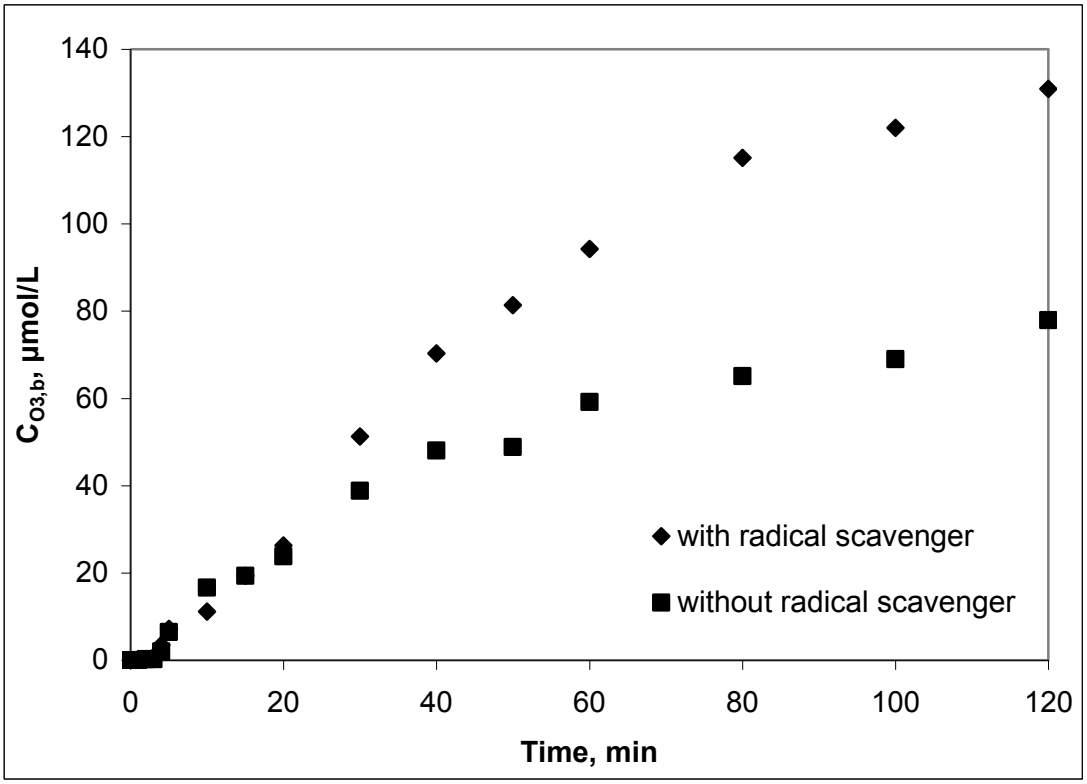

Figure A.6. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for BI on Molar Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with KH_2PO_4/NaOH Buffer (Ozonation without Scavenger) and 6.25 mM $NaHCO_3$ (Ozonation with Scavenger)); COD_o = 195 mg/L; TOC_o = 57 mg/L; $UV_{280,o}$ = 0.37 cm^{-1}; $UV_{254,o}$ = 0.30 cm^{-1}; t = 120 min.

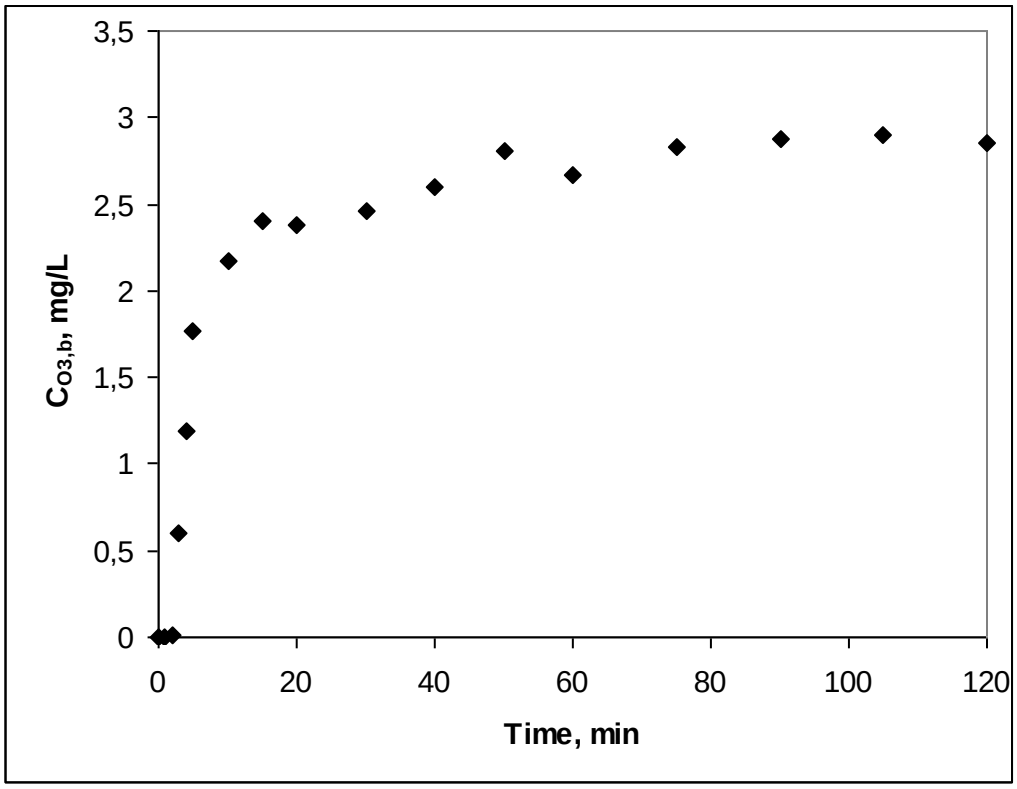

Figure A.7. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for BII on Mass Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with KH_2PO_4/NaOH Buffer); COD_o = 215 mg/L; TOC_o = 57 mg/L; $UV_{280,o}$ = 0.26 cm^{-1}; $UV_{254,o}$ = 0.18 cm^{-1}; t = 120 min.

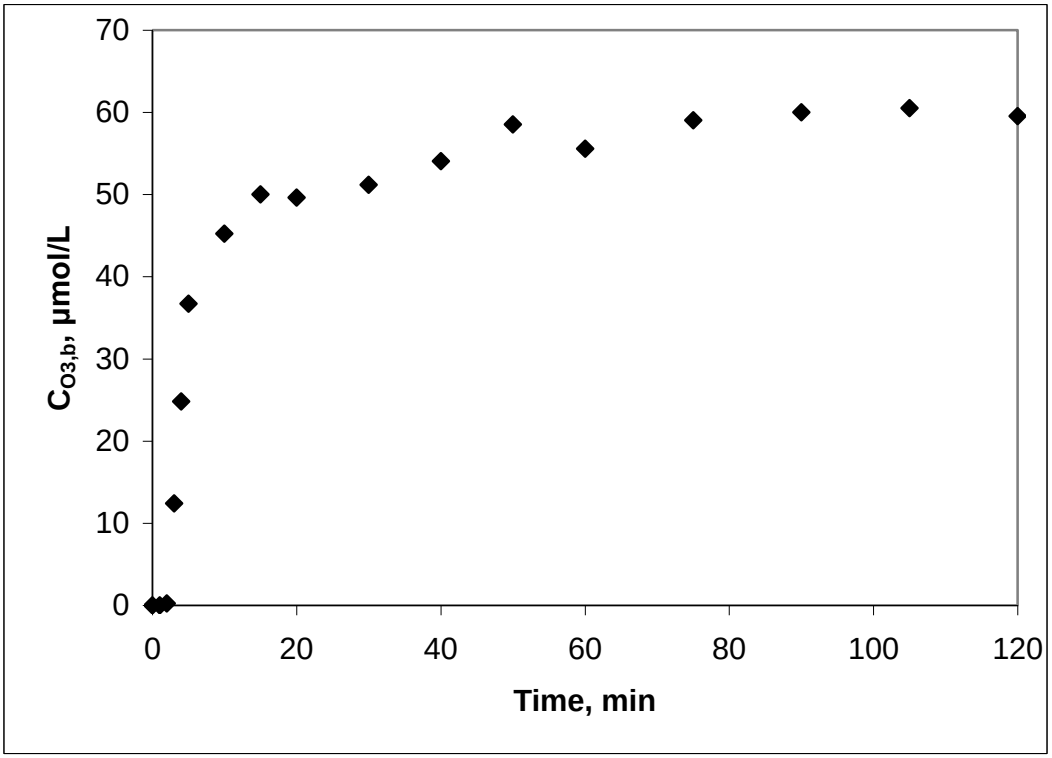

Figure A.8. : Changes in $C_{O3,b}$ with Respect to Ozonation Time for BII on Molar Basis; Experimental Conditions: Ozone Feed Rate = 900 mg/h; pH = 7.0; (adjusted with KH_2PO_4/NaOH Buffer); COD_o = 215 mg/L; TOC_o = 57 mg/L; $UV_{280,o}$ = 0.26 cm^{-1}; $UV_{254,o}$ = 0.18 cm^{-1};t = 120 min.

CURRICULUM VITEA

Şebnem Koyunluoğlu was born in İstanbul in 1979. She graduated from Beyoğlu Anatolian High School in 1997. She received her undergraduate degree from İstanbul Technical University (İTÜ), Environmental Engineering Department in 2001. She has been working as a research assistant in Yeditepe University, Chemical Engineering Department since 2003.