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**RESIN AND FATTY ACID TOXICITY REDUCTION BY
ADVANCED OXIDATIVE PROCESSES**

by

Craig William Young

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DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING

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THE UNIVERSITY OF ARIZONA

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ABSTRACT

Resin and fatty acids (RFAs) are the major toxic constituents of pulp and paper mill effluent. RFAs are toxic to aquatic life at low concentrations (< 2 ppm). The concentration and type of RFAs in the wastewater vary with wood source and mill process. The caustic extraction (E-stage) effluent contributes only 5 - 10% of the total plant wastewater discharges, yet more of the total wastewater toxicity and color is attributed to the E-stage than any other treatment stage. Toxicity reduction of E-stage effluent by Advanced Oxidative Processes (AOPs) could be economically more cost effective than the same treatment on the final plant effluent.

The focus of this research project was to determine which of four AOP processes produces the highest reduction of toxicity for a simulated E-stage wastewater. The processes studied were Ozone Only (O_3), O_3 with Hydrogen Peroxide (H_2O_2), O_3 with Ultraviolet (UV) 254 nm (UV_{254nm}) light, and O_3 with H_2O_2 and UV_{254nm} light. The treated water was characterized by UV absorbance scans, total organic carbon (TOC) analysis, and Gas Chromatography / Mass Spectroscopy (GC/MS). Toxicity of samples was determined by Microtox analysis. The highest reduction of toxicity was achieved by 30 minutes (min) O_3 only contact time for a total of 94.4 mg/L of O_3 transferred. Further ozonation resulted in marginal toxicity reduction.

A new procedure for analyzing RFAs by GC/MS using Solid Phase MicroExtraction was tested with results being given in Appendix F.

1.0 INTRODUCTION

1.1 Statement of Problem

In 1996, the U.S. produced 90.2 million tons of paper and paperboard products [Pulp and Paper, April 1997]. Pulp mill wastewater contains many chemicals that are toxic to marine life. Some toxic chemicals found in pulp and paper mill effluents include resin acids, fatty acids, and chlorinated phenols. It has been shown that approximately 80% of the toxic compounds found in the wastewater are resin acids [Leach, Thakore 1975, Walden, Howard 1973]. Walden and Howard (1973) attributed the remaining toxicity to unsaturated fatty acids.

Resin acids have been found toxic to young salmon at concentrations as low as 2 ppm [Rogers 1973, Maenpaa *et al.* 1968]. Others have reported toxic effects at concentrations as low as 0.4 ppm [Walden; Leach 1975]. The concentration and type of resin acids found in the wastewater varies with wood source, chemicals used, and mill staging. The three most common resin acids reported are isopimaric, abietic, and dehydroabietic acids [Walden; Howard 1973, Leach; Gietz; Thakore 1974, Leach; Howard; Walden 1974]. Values for abietic acid reported in the literature have been as high as 456 mg/L [Maenpaa *et al.* 1968]. Usually concentrations were reported between 13.4 and 121 mg/L [Leach; Howard; Walden

1974], 2.3 to 45.8 mg/L [Walden; Howard 1973], and 14.9 to 61.8 mg/L with an average of 31.9 mg/L [Howard; Walden 1974].

Resin and fatty acids are not regulated by name in the U.S. Code of Federal Regulation on pulp mill discharges (Chapter I, Subchapter N, Part 430). Instead the Biological Oxygen Demand (BOD₅), Total Suspended Solids (TSS), pentachlorophenol, trichlorophenol, and zinc are regulated by name [Code of Federal Regulation 1996].

Currently most pulp and paper mills' wastewater treatment facilities involve an aerobic biological system, the most common being activated sludge and aeration lagoons. These processes can remove more than 90% of the toxicity, but are subject to rapid increases in toxicity known as toxic breakthroughs. The chronic effects of pulp mill wastewater are not entirely known. Nestmann *et al.* (1979) determined that sub-lethal concentrations of pulp mill effluents had mutagenic effects on fish. Liver tumors have been reported in white sucker (Catostomus commersoni) fish near Bleached Kraft Mill Effluent (BKME) discharges in Lake Superior, [Smith; Rokosh 1989]. Skin neoplasms were reported on fish captured near kraft mill discharges in Japan [Yamashita *et al.* 1990].

1.2 E-stage Effluent

The E-stage extraction is one of the primary steps in the standard pulp making process. Sodium hydroxide is used to remove lignin and other extractable

material from the pulp. Lignin composes approximately 35% of the fibrous mass of a tree, but is not used in pulp production. The lignin dissolves in the high pH (> 10) solution and is removed in the wastewater. The lignin is highly colored and is responsible for most of the color of the final mill effluent [Biermann 1996]. The extractable materials include RFAs, terpenes, and phenolic compounds.

Generally, a pulp mill will have several E-stage extractions before and/or after the chlorination or bleaching stage(s). Loading of up to 5% NaOH may be used with 2-3% as a typical loading. Loading in the last few E-stages is usually less than 1% on pulp. The main advantage of the E-stage is to remove non-pulp material that would increase chemical usage in subsequent processes. Recently oxygen (O_2) gas has been added to the normal E-stage process. Typically the oxygen is added at 0.5% on pulp. This new process (called E_o) is becoming more widespread due to its low cost and reduced pollution output.

Due to the carboxyl group in their structures, RFAs are highly soluble as sodium salts in these caustic waters. The first stage caustic extraction effluent contributes a significant portion of the total wastewater toxicity and color. Yet, the E-stage effluents account for only 5 - 10% of the total plant discharges [Zaida *et al.* 1991]. Most of the toxic compounds are removed from the pulp in the E-stage washing. Treating the E-stage effluent could remove most of the final toxicity while treating only a fraction of the total plant wastewater. This makes E-stage treatment a potentially economically attractive option for wastewater detoxification.

2.0 OBJECTIVES

The primary objective of this research project was to determine the best treatment process for reducing resin and fatty acid toxicity in simulated and spiked E-stage pulp mill wastewater. This study tested four advanced oxidative processes; O₃ Only, O₃ with H₂O₂, O₃ with UV_{254nm} light, and O₃ with H₂O₂ and UV_{254nm} light. Along with this, a detailed explanation based upon water chemistry, specific oxidative processes, and chemical rate constants involved in the study was developed.

The second major objective was to determine if reduction of UV absorbance at 240 nm would be a good indicator of toxicity removal. Resin acids have a unique absorbance peak at 240 nm. UV absorbance reduction at 240 nm would be statistically analyzed, and if significant, an equation for UV_{240nm} reduction as an indicator of toxicity reduction would be derived.

A secondary objective was to investigate a new procedure, Solid Phase MicroExtraction (SPME), for analyzing RFAs by Gas Chromatograph / Mass Spectroscopy (GC/MS). If the new procedure was found useful, the best conditions for RFA analysis by SPME would be determined. Results of the SPME - GC/MS experiments are given in Appendix F.

3.0 LITERATURE REVIEW

3.1 Resin and Fatty Acids

Resin acids (RAs) are the predominant toxic compounds in many different types of pulp and paper mill wastewater. The most common RAs released during pulping include: abietic, dehydroabietic, neoabietic, pimaric, isopimaric, sandaracopimaric, levopimaric, and palustric acids. These eight RAs have been found in pulp mill effluent streams [Lockhart; Leach 1976, Walden; Leach 1975, Leach *et al.* 1973 - 1974 - 1975 - 1978]. Fatty acids (FAs) are not as toxic as RAs, but are found in sufficient quantities as to be toxic to aquatic organisms. Fatty acids have 96 hr lethal concentration (LC50) values of 2 - 8 mg/L verses 0.4 - 1.5 mg/L for RAs. Fatty acids are classified as either saturated or unsaturated acids. Examples of saturated FAs found in effluents include lauric, palmitic, stearic, and myristic, while unsaturated FAs include oleic, linoleic, palmitoleic, and pinolenic.

3.2 Chemical Characteristics of Resin and Fatty Acids

Resin acids are di-terpenoid carboxylic acids found in most softwoods. Resin acids usually have two double bonds in the three ringed structure except dehydroabietic acid, which has three double bonds in a benzene ring structure. Two methyl groups, an isopropyl group and a carboxyl group are attached to the

three rings. The methyl groups are found at the fourth and tenth carbon positions on the ring structure. The isopropyl group is attached to the thirteenth carbon and the carboxyl on the fourth. The isopropyl group may be replaced with a methyl/ethyl combination group for pimaric, isopimaric, and sandaracopimaric acid. Figure 3.2-1 shows the structures for the eight previously listed RAs.

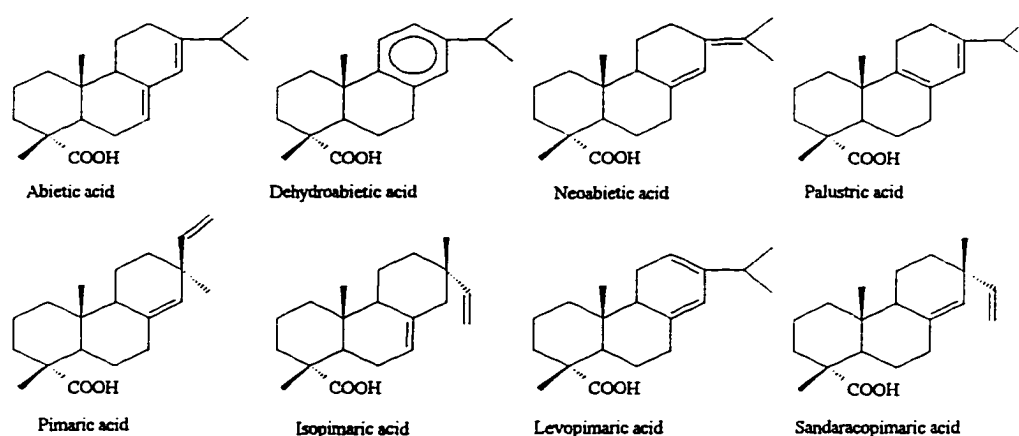


Figure 3.2-1. Structures of eight common resin acids found in pulp mill effluents.

The general chemical formula for a RA is $C_{20}H_{30}O_2$ with a molecular weight of 302 grams per mole. Dehydroabietic acid contains two less hydrogen atoms due to its extra double bond and thus has a formula of $C_{20}H_{28}O_2$ with a molecular weight of 300 grams per mole. The carboxyl group contained in the RAs is polar and makes the molecules slightly water soluble. The dissociation constant (pK_a) of most

carboxylic acids is approximately seven on the pH scale. The pK_a 's for abietic and dehydroabietic acids are 7.15 and 7.25 respectively. At pH 9, more than 95% of the RAs are present in the ionized form [Voss; Rapsomatiotis 1985]. McLeay *et al.* (1978) postulated that only under acidic conditions ($pH < 4.0$) should all of the RAs be in their neutral state. Equation 3.2 shows the dissociation of a typical carboxylic acid.



Fatty acids consist of long carbon chains with a carboxylic acid functional group at one end. Fatty acid may vary in length, side chains, and degree of unsaturation (number of double bonds). Two FAs were used in this study. They are oleic and linoleic acids. Both are eighteen carbon, straight chained carboxylic acids. Oleic acid is monounsaturated while linoleic acid is polyunsaturated with two double bonds. The chemical structures are shown in figure 3.2-2. Resin and fatty acids are highly soluble at pHs greater than 9, provided they are present as the ionized salt form.

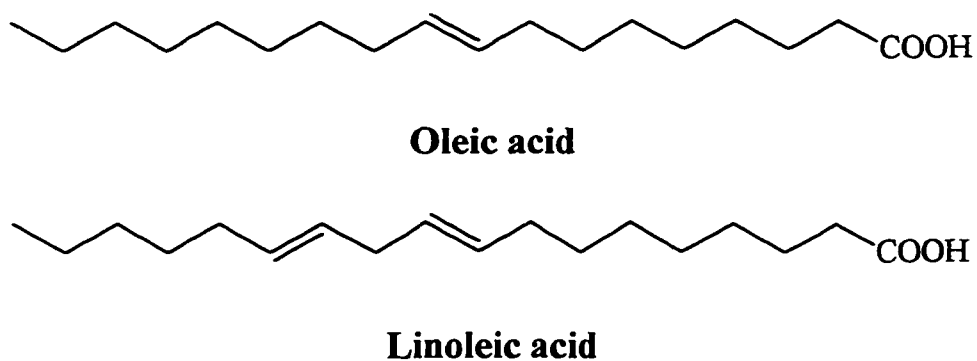


Figure 3.2-2. Structures of two common fatty acids.

3.3 Methods for Analysis of Resin and Fatty Acids

Gas Chromatography (GC) is the standard analytical method for determination of RFAs in pulp mill effluents. The sample preparation for GC analysis involves the extraction and derivatization of the RFAs. The current method in use is attributed to Voss and Rapsomatiatis (1985) of the Pulp and Paper Research Institute of Canada.

In this method, a 100 ml sample of aqueous solutions containing the RFAs is extracted with organic solvents. The extracted solution is dried over anhydrous magnesium sulfate and reacted with diazomethane to convert the RFAs to methyl derivatives. The solvent is evaporated under reduced pressure. The RFAs are dissolved in methanol, and internal standards of methyl heneicosanoate and

tricosanoic acid are then added. The solvent is evaporated and the RFAs are redissolved in 1.0 ml of ethyl acetate. This solution is then injected into the GC for analysis.

Li *et al.* (1996) determined that ethyl acetate was the best solvent for extracting RFAs from aqueous solutions. Resin and fatty acid extraction was greatest at pHs less than seven. It has been recognized that RFAs are more soluble in their ionized form and consequently are less extractable by organic solvents at higher pHs.

The method of RFA analysis by Voss and Rapsomatiatis has several disadvantages. It consumes large quantities of chemical to extract and derivatize the sample. Derivatization using diazomethane is a dangerous procedure as diazomethane is both highly toxic and explosive. The method is time consuming with extraction and derivitization taking from 15 to 30 min per sample depending on technician skill. The advantages of chemical extraction include less background noise and better peak resolution.

3.4 Resin and Fatty Acid Toxicity

Leach and Thakore (1973) reported that more than 80% of the total toxicity of a pulp mill effluent was caused by the sodium salts of isopimaric (55%), abietic (22%), and dehydroabietic (5%) acids. The pulp mill studied was using Douglas fir and western hemlock as its feed trees. Walden and Howard (1973) obtained

similar results for fir/hemlock feed trees. Maenpaa *et al.* (1968) found dehydroabietic acid to be the major resin acid present in a sulfite mill processing spruce trees. Maenpaa also determined that abietic and dehydroabietic acids were the major toxic constituents in kraft mill effluent. The toxicity of the samples depends on the type of chemical used to bleach the pulp. Chlorine bleaching produces chlorinated RAs increasing the wastewater toxicity. Chlorine dioxide, H₂O₂, O₂, or O₃ produce less toxic wastewater than chlorine bleaching. Clearly the RA concentrations and toxicity will vary depending upon the type of feed trees, and the pulping process used.

Resin acids are toxic to rainbow trout with 96-hr LC50s as low as 0.4 mg/L [Walden; Leach 1975]. Walden and Howard (1973) determined that pimaric type RAs tended to be more toxic than abietic type RAs. Both Rogers (1973) and Maenpaa *et al.* (1968) determined the lethal limit of dehydroabietic and abietic acids as 2.0 mg/L. Resin acid toxicity is pH dependent. Leach *et al.* (1972 - 1973 - 1974), and McLeay *et al.* (1978) studied the pH effect on resin acid toxicity. Their results indicate that toxicity increased greatly as the pH was lowered from 7.5 to 6.4. McLeay (1976) determined that the least toxic pH range to rainbow trout was 8.5 - 9.5 with the pH being lethal to the fish below 4 and above 10. Fatty acids are not as toxic as RAs and were considered minor toxicants by Leach and Thakore (1976). Figure 3.4 shows the 96hr LC50 concentrations for various RFAs found in pulp mill wastewater [Leach *et al.* 1978].

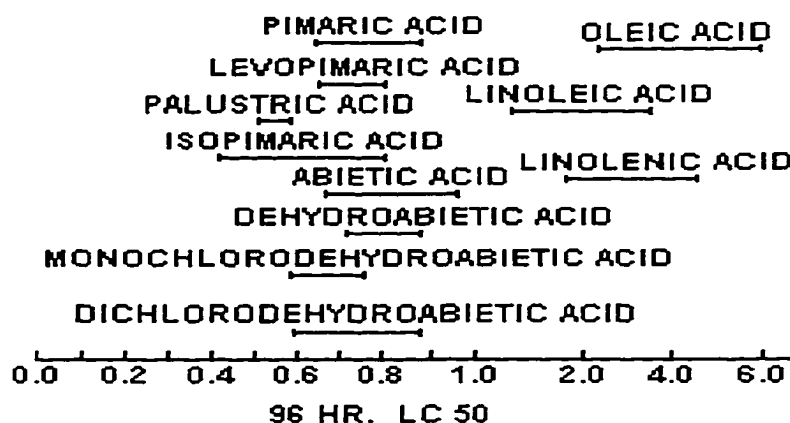


Figure 3.4. 96hr LC50 values for toxic constituents of pulp mill effluents [Leach *et al.* 1978].

Extracts from bleached kraft mills can have mutagenic activity. There was evidence that fish are at risk of developing tumors from exposure to bleached kraft mill effluent (BKME). Resin acids have been isolated from these mutagenic mixtures [Nestmann *et al.* 1979]. Liver tumors and "liver disease" have been reported for white sucker (*Catostomus commersoni*) near BKME discharges in Lake Superior Ontario [Smith; Rokosh 1989]. Skin neoplasms were reported for croaker (*Nibea mitsukuri*) and sea catfish (*Plotosus anguillaris*) captured near kraft mill discharge in Japan. Treatment of these fish with BKME resulted in similar lesions [Yamashita *et al.* 1990].

In a study by Metcalfe *et al.* (1994), extracts from BKME were tested for mutagenic and carcinogenic activity. A major fraction of the mutagenic activity was

caused by the water soluble extracts. The carcinogenicity tests involved the exposure of young rainbow trout to sub-carcinogenic concentration of BKME extracts. Preneoplastic lesions were observed on 5 out of 52 trout. The trout were injected with 500 ml equivalents per kg at 2 and 5 months. Trout were necropsied at eight months after initiation of the experiments.

3.5 Regulation of Pulp Mill Effluents

The regulation of resin and fatty acid discharge by pulp and paper mills falls under current mandates for total toxicity of effluent discharge. In Canada, regulations mandate that pulp and paper mill discharge be nontoxic to fish [Canada Gazette 1992]. Resin and fatty acid are regulated so that discharges must be lower than 2 mg/L. Regulation of U.S. wastewater discharge started at the turn of the century with the 1899 River and Harbor Act. In 1956, the Federal Water Control Act was passed to study the effects of pollution problems. It was amended in 1970 under the National Environmental Policy Act (NEPA) and the Environmental Quality Improvement Act. These amendments created the Environmental Protection Agency (EPA) as a regulatory agency to enact and enforce environmental standards [Casey 1980].

Pulp mill wastewater discharges are regulated under the Clean Water Act (CWA) and its amendments. The CWA established the National Pollutant Discharge Elimination System (NPDES) which issues permits of discharges to

surface waters. NPDES requires permit holders to meet effluent limitations based upon available technology [LaGrega *et al* 1994]. The CWA established 129 priority pollutants that are specifically regulated by name. The pulp and paper industry is required to test for three of the priority pollutants; pentachlorophenol, trichlorophenol, and zinc [Code of Federal Regulations 1996]. Furthermore the pH, five-day biological oxygen demand (BOD₅), and total suspended solids (TSS) are also regulated by the NPDES permit. Discharge quantities are regulated depending upon the mill process. The permits do not specify individual treatment processes but require that the Best Conventional Pollution Control technology (BCT) be used.

3.6 Treatment Techniques

3.6.1 Biological Treatment

The most widely used treatment of RFAs in wastewater is an aerobic biological treatment system. The two most common systems are activated sludge and aerated lagoon processes. Most treatment systems consist of a primary clarifier to remove suspended solids before biological treatment. Lo *et al.* (1990) determined that the primary clarifier did not remove any RFAs from the effluent. Lo, also determined that anaerobic treatment was insufficient to detoxify chemithermomechanical (CTMP) pulping waste. Lo found that chemicals including RFAs in the CTMP waste were toxic to anaerobic bacteria.

Aerobic treatment is quite effective in reducing toxicity. Elefsiniotis *et al.* (1995) removed more than 90% of RFAs using a 10 L biological sequencing batch reactor system with a hydraulic retention time of 48 hrs. The wastewater tested had an average of 17 mg/L of unspecified RAs, 11 mg/L of unspecified FAs, TOC = 1050 mg/L, COD = 3480 mg/L, and a pH of 7.26. The experimental data did not indicate whether the RFAs were degraded or were simply adsorbed by the biomass. Tardif and Hall (1996) repeated Elefsiniotis' experiments obtaining similar results. Liu *et al.* (1996) extensively studied aerobic biological treatment of RFAs. Untreated chemithermomechanical pulp (CTMP) effluent with a RFA concentration of approximately 45 mg/L was used in all of the experiments. Adsorption onto the sludge, biooxidation, and static air oxidation experiments were performed. The results obtained showed that 92% of the RFAs could be removed in an activated sludge treatment system with only an 8 hour hydraulic retention time. Their results suggested that biooxidation and adsorption were the two main pathways for RFA removal in aerobic biological treatment. Approximately 70% of the RFAs were removed by static adsorption onto inactive (dead) sludge within 30 min of contact. Further contact time with the sludge produced no additional removal. Air oxidation played a small role in RFA reduction with only 10% of RFA removal after 12 hr of static air oxidation. The biooxidation experiments indicated that biooxidation dominates as the main removal mechanism for long retention periods. Adsorption

dominated for the first hour before biooxidation removal increased. Final adsorption removal was only 25% after 12 hr of contact with active sludge.

Wood-inhabiting fungi have been studied as a method to detoxify wood chips before processing. Wang *et al.* (1995) studied four fungal strains, *Ophiostoma piceae*, *Ophiostoma ainoae*, *Ophiostoma piliferum*, and *Lecythophora sp.* to determine their effectiveness at removing RAs from wood chips. All four strains gave similar results of about 67% reduction of RAs. There was a large discrepancy among the removals of various RAs. Palustric acid, which is one of the more toxic RAs, had the highest removal of 96%. Dehydroabietic acid, the most common RA, had the lowest removals of 35 to 52%. The four fungal strains were chosen for their ability to remove wood extractives and not the wood structure. The fungal experiments indicate that biological pretreatment could be an efficient way to remove RAs from wood chips to reduce resulting effluent toxicity.

3.6.2 Membrane Treatment

Membrane treatment has been studied as a process for wastewater cleanup and reuse. Elefsiniotis *et al.* (1995) studied the potential use of ultrafiltration to remove RFAs from simulated wastewater. Two polyethersulfone negatively charged membranes were tested with nominal molecular weight cut-offs (MWCO) of 100,000 and 10,000 Daltons (D). Experiments were performed at a pH of 7.26 at temperatures ranging from 20 to 50 °C, and 90% permeate recovery. Total RFA

removals averaged 69% and 55%, respectively. The FAs were almost completely removed (> 90%) while resin acid removal ranged from 25 to 45%. Individual resin acid removals varied greatly. Isopimaric and abietic acids had more than 50% removals while dehydroabietic acid removal was only about 10%.

Tardif and Hall (1996) produced almost identical results as Elefsiniotis. The average fatty acid removal was 94% while the average resin acid removal was 36%. Total RFA removals were 67% and 57% for the 100,000 and 10,000 D membranes. Neither set of experimenters accounted for the large discrepancies in fatty acid removal verses resin acid removal or the individual resin acid removal rates.

In a study by Dorica (1986), membrane filtration using a 6000 D molecular weight cut off (MWCO) membrane resulted in 68 to 90% RFA removal. Zaidi *et al.* (1991) studied thirteen different membranes for separation of pure solutions of toxic constituents of pulp mill effluents. A mixture of 4,5-dichlorocatechol, 4,5-dichloroguaiacol, dehydroabietic acid, chlorodehydroabietic acid, dichlorodimethylsulfone, and sulfonated lignin each at 200 mg/L in distilled water was used as a test water. The experiments were conducted at room temperature. The solution pH and experimental recoveries were not included in the article. Polysulfone and polyethersulfone membranes, with MWCOs ranging from 1000 to 30,000 D, were the main membranes used in this study. Dehydroabietic acid rejections ranged from 40 to 90%, while chlorodehydroabietic acid rejections ranged

from 76 to 97%. It was concluded that the rejection of RAs by ultrafiltration membranes with large MWCOs was due to solute-membrane interaction.

3.6.3 Ozone Treatment

Dorica and Wong (1979) studied the use of O₃ in the detoxification of liner board effluent by RFA destruction. Roy-Arcand and Archibald (1996) studied the use of low dosages of O₃ in the treatment of thermomechanical (TMP) and CTMP pulp mill effluents. A 75% decrease in RFAs and total toxicity was obtained by the application of only 50 mg/L of O₃. Cross and Myers (1968) reported that partial oxidation of abietic and dehydroabietic acids virtually eliminated their toxicity to trout. Roy-Arcand and Archibald reported that RFAs were sensitive to applied O₃ doses of 10-50 mg per liter of effluent. This is only 1-5% of the total O₃ needed to mineralize the total RFA present in the effluent studied. Approximately 60% of the total toxicity, as tested by Microtox toxicity, was removed using a dose of just 10 mg/L. Toxicity reduction decreased rapidly after the first 10 mg/L and was only 80% with a dose of 100 mg/L. They postulated that the tendency of nearly non-polar solutes such as RFAs to adhere to bubble surfaces may be the cause of the high RFA removals.

3.6.4 Ozone with H₂O₂ Treatment

Ozone in combination with H₂O₂ has been studied for chemical oxygen demand (COD) and toxicity reduction by Hostachy *et al.* (1996) who determined that the addition of peroxide inhibited the removal of COD. COD removal was lowest when O₃ and H₂O₂ were used together. The higher pH tested produced the lower results for both the O₃ only and O₃ / H₂O₂ with the O₃ / H₂O₂ at pH 10 having the lowest COD removal. Hostachy postulated that peroxide may act as a radical scavenger inhibiting oxidation at high pHs.

The Electric Power Research Institute (EPRI) report on pulp and paper mill effluent treatment using advanced oxidative processes (1993) studied O₃ / H₂O₂ treatment of E-stage effluent extensively. Twenty one experiments were performed specifically on caustic wastewater. The pH of the experiments varied from 7.4 to 11.5. Ozone transferred ranged from 300 to 584 mg/L while H₂O₂ values ranged from 176 to 1025 mg/L. The toxicity reduction varied greatly with the highest reduction of 95.5%. Some experiments were not tested for toxicity reduction and some were more toxic after treatment than before.

3.6.5 Ozone with UV_{254nm} Light Treatment

The EPRI report was the only study found that contained information on O₃ / UV treatment of E-stage wastewater. Six experiments were performed with O₃ transfer ranging from 314 to 475 mg/L and one or two UV lamps used. The report

did not indicate what wavelength of UV light was produced by the lamps. The pH of the samples ranged from 10.7 to 11.5. The toxicity reduction (by Microtox) ranged from 58.2 to 94.5%. No experiments using O_3 / H_2O_2 / UV light were found in the literature.

3.7 Ozone Oxidative Strength

Ozone is one of the most powerful oxidants known to man. Only fluorine (F_2), the hydroxide radical ($OH\cdot$) and elemental oxygen radicals ($O\cdot$) have higher oxidative potentials than O_3 . Table 3.7 shows the oxidative potentials of most common oxidants used in oxidative treatment of water and wastewater.

Oxidative Species	Oxidative Potential ¹
Fluorine (F_2)	2.25
Hydroxide Radical ($OH\cdot$)	2.05
Elemental Oxygen Radical ($O\cdot$)	1.78
Ozone (O_3)	1.52
Hydrogen Peroxide (H_2O_2)	1.30
Per Hydroxide Radical ($HO_2\cdot$)	1.25
Hypochlorous Acid ($HOCl$)	1.10
Chlorine (Cl_2)	1.00

¹ Based on Chlorine as reference point (= 1.00)

Table 3.7. Relative oxidative potentials for common oxidants (Rice 1981).

3.8 Ozone Reactions

Ozone directly reacts with organic molecules by three distinct pathways. The first reaction pathway is the cyclo addition also known as the Criegee mechanism [Langlais 1991]. Ozone can react across unsaturated bonds forming a cyclic intermediate. In aqueous solutions, this cyclic structure quickly decomposes forming a carbonyl (aldehyde or ketone) and a zwitterion. The zwitterion will decompose into another carbonyl compound and H_2O_2 . Figure 3.8-1 shows the cyclic addition with cyclic intermediate production.

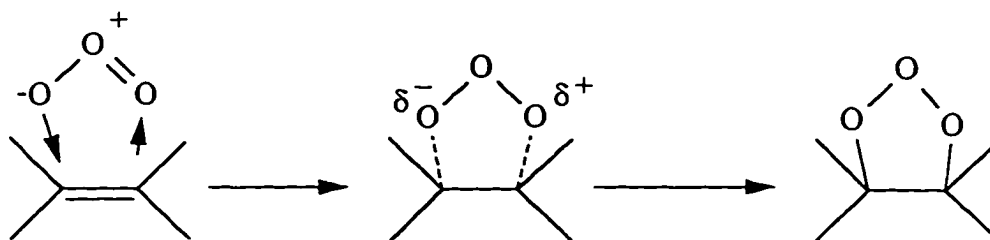


Figure 3.8-1. Cyclo addition (Criegee) mechanism (Langlais 1991).

A second O_3 attachment intermediate possibility has been published by William H. Brown [Brown 1995]. Ozone combines with the double bond to form a different ring structure. This new ring structure is known as an Ozonide. The Ozonide structure is shown in figure 3.8-2.

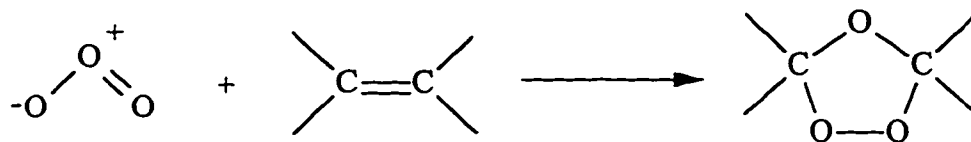


Figure 3.8-2. Ozonide formation (Brown 1995).

Both of the Criegee and Ozonide products further react to cleave the double bond forming the carbonyl compounds (aldehydes and ketones) and H_2O_2 . Figure 3.8-3 shows this cleavage starting with the Criegee intermediate product.

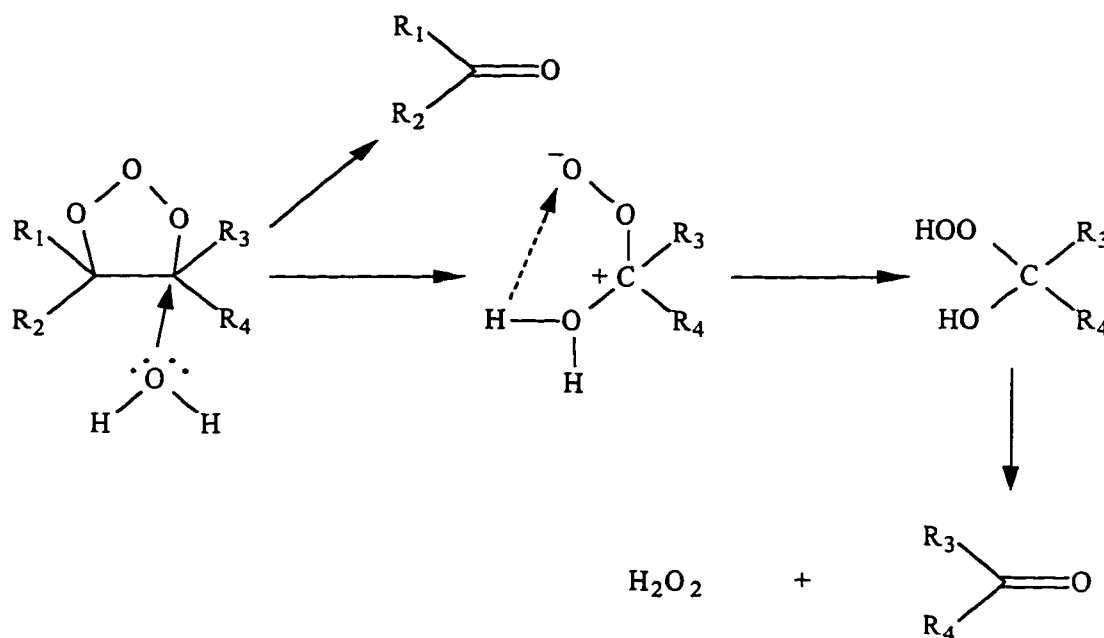


Figure 3.8-3. Cleavage products from Criegee mechanism (Langlais 1991).

The second possible reaction mechanism is the electrophilic addition pathway. Electrophilic addition occurs mainly on aromatic compounds with electron donating groups substituted onto the aromatic ring. The electron donor groups (OH, NH₂, etc.) increase the electronic density allowing the O₃ addition at the ortho and para positions. The O₃ quickly reacts with water to add a hydroxide group to the aromatic ring and produce oxygen gas. The hydroxylated product is much more susceptible to further oxidation. Further ozonation will open the ring structure of the product producing carbonyl and carboxyl compounds. Figure 3.8-4 schematically represents the initial reaction (D = electron donating group).

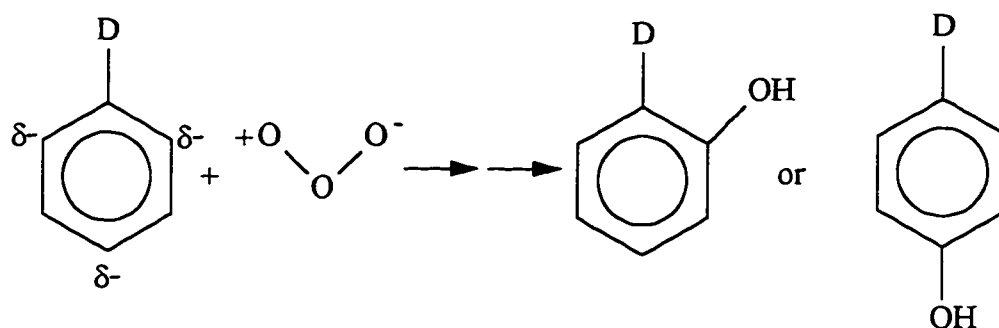


Figure 3.8-4. Electrophilic ozone reaction.

The last reaction pathway is nucleophilic addition. Nucleophilic addition occurs in a limited number of cases on electronic deficient molecules. Compounds with electron withdrawing groups such as -COOH, and -NO₂ are most likely to undergo nucleophilic O₃ reactions. Ozone addition occurs at the meta position and

generally is weakly O_3 reactive. Figure 3.8-5 shows a nucleophilic O_3 reaction (W = electron withdrawing group).

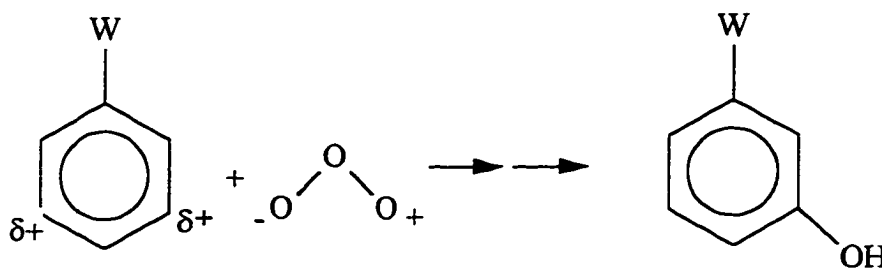


Figure 3.8-5. Nucleophilic ozone reaction.

3.9 Advanced Oxidative Processes

Advanced Oxidative Processes (AOPs) is the general term for a set of oxidation reactions involving the production of hydroxide radicals ($OH\cdot$) and their subsequent reactions. The $OH\cdot$ is a much more powerful and reactive oxidant than O_3 having a relative oxidative potential of 2.05 verses 1.52 for O_3 [Rice 1981]. The hydroxide radical can be formed from reactions involving O_3 and H_2O_2 or UV_{254nm} light.

In the presence of organic compounds represented by HMH , $OH\cdot$ will react to form an organic radical $HM\cdot$ (Equation 3.9-1-1 in Table 3.9-1). The organic radical can quickly react with oxygen forming an oxygenated organic radical ($HMO_2\cdot$) (Equation 3.9-1-2). This oxygenated radical can dissociate to form a

hydrogen ion (H^+), a superoxide ion (O_2^-), and a neutral oxidized organic molecule (M) (Equation 3.9-1-3). The superoxide ion may react with O_3 to produce more hydroxyl radicals (Equations 3.10-4 to 3.10-6 in Table 3.10).

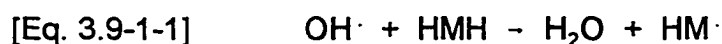


Table 3.9-1. Hydroxide radical reactions with organic compounds and O_2 (Peyton 1987).

A second possible reaction pathway is given in table 3.9-2. The hydroxyl radical reacts with the organic compound as before to produce an organic radical $HM\cdot$ (Equation 3.9-2-1 in Table 3.9-2). The organic radical can quickly react with hydrogen peroxide forming an alcohol ($HMOH$) and another $OH\cdot$ (Equation 3.9-2-2).

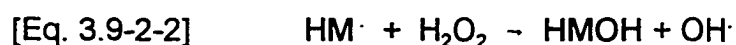
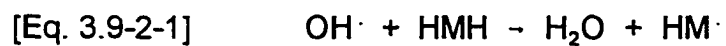


Table 3.9-2. Hydroxide radical reactions with organic compounds and H_2O_2 .

3.10 Ozone with H₂O₂

Hydrogen peroxide is a weak acid that dissociates into a hydroperoxide ion (HO₂⁻) and a hydrogen ion (H⁺) (Equation 3.10-1 in Table 3.10). Ozone will react with the hydroperoxide ion to form a hydroxide radical (OH·), superoxide ion (O₂⁻) and O₂ (Equation 3.10-2). The superoxide ion can further react to initiate OH· production as postulated by Staehelin *et al.* (1984) in table 3.10. Equation 3.10-7 gives the summarized reaction between H₂O₂ and O₃.

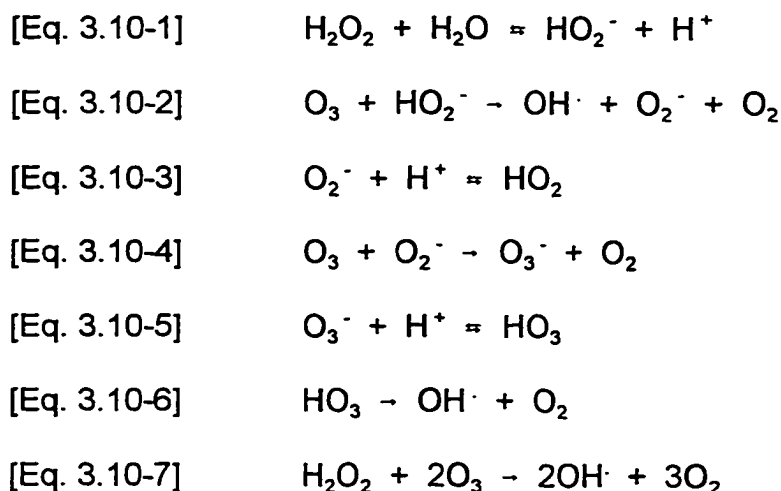


Table 3.10. Hydrogen peroxide catalyzed decomposition of O₃ [Staehelin *et al.* 1984].

3.11 Ozone with UV_{254nm} Light

UV_{254nm} light, like H₂O₂, decomposes O₃ and produces OH·. The maximum wavelength that O₃ will absorb is at 253.7 nm. UV_{254nm} radiation will photolyze O₃ to form a dioxygen molecule and an elemental oxygen radical (Equation 3.11-1 Table 3.11). The elemental oxygen radical may react with water to produce hydroxide radicals (Equation 3.11-2). The hydroxide radicals may combine to form H₂O₂ as seen in equation 3.11-3. The direct production of H₂O₂ is written as equation 3.11-4. Hydrogen peroxide may react with the O₃ as above (Table 3.10).

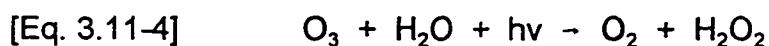


Table 3.11. Ozone decomposition with UV_{254nm} light (Peyton and Glaze 1983).

3.12 Ozone with H₂O₂ and UV_{254nm}

Ozone with H₂O₂ and UV_{254nm} should react in a similar manner to the O₃ with UV_{254nm} and the O₃ with H₂O₂ reactions in sections 3.9 and 3.10. Ozone with UV_{254nm} and H₂O₂ should produce OH· more quickly than the O₃ with UV_{254nm}.

4.0 EXPERIMENTAL METHODS

4.1 Oxidation Reactor

The oxidation reactor used in this study is shown as figure 4.1. It consisted of a cylindrical glass container, used as a reservoir, in which mixing and O₃ contacting were accomplished. A centrifugal pump was employed to recirculate the 5 L water sample. The cylindrical glass reactor was 22 inches in diameter and 19 inches long. This reactor can hold more than 5 L of wastewater with sufficient head space for gas disengagement. Ozone in oxygen was added to the reactor through a porous stainless steel diffuser. The one-speed pump used for the experiments was manufactured by Teel (IP767A) and had a magnetic drive and polypropylene wetted parts. Its flow rate was measured as 2.99 ± 0.25 L/min.

4.2 Ozone Generator

An Ozone Research and Equipment Corporation (OREC) ozonator (OREC # 03V5-0) was used in this study. It produced O₃ by corona discharge (Figure 4.2) using medical grade oxygen carrier gas at a flow rate of 2 SL/min (SL-standard liters) into the generator. The rated output of the ozonator was 0 - 0.25 pounds - O₃/day. The generator pressure dial was set at 4.5 to 5.0 pounds per square inch (psi).

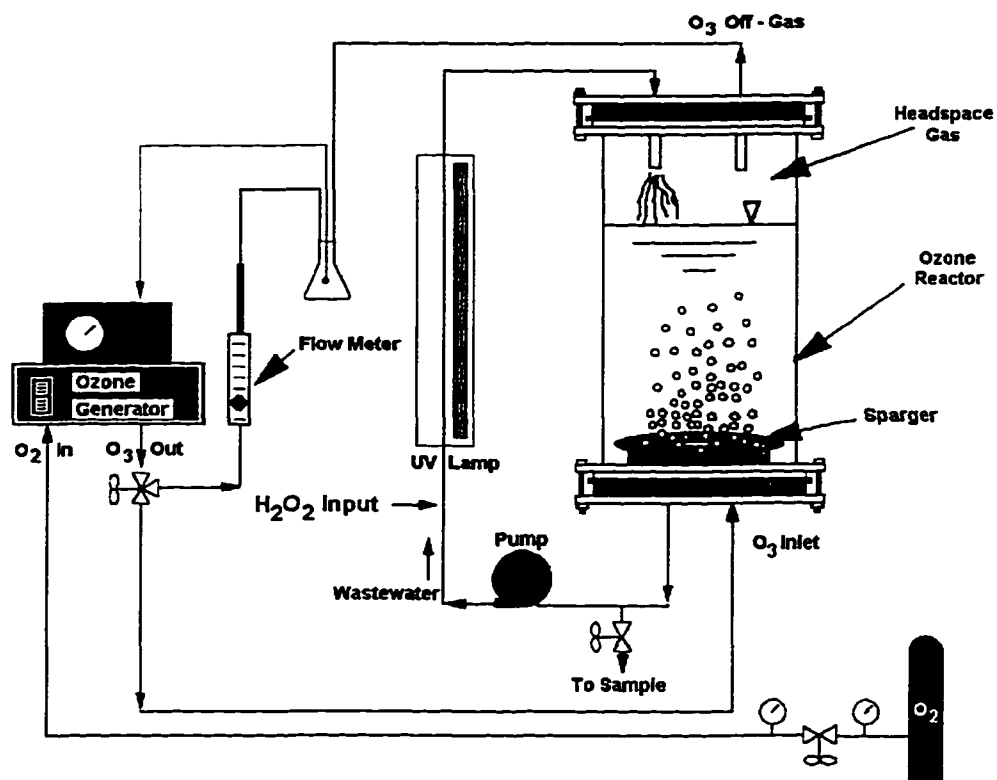


Figure 4.1. Oxidation reactor.

Ozone and oxygen gas flow rate through the glass diffuser was regulated to a constant flow rate of 2.0 SL/min for all experiments. Unused gas from the ozonator was vented to the fumehood. The ozonator output and exit gases from the reactor were measured by an OREC Gas Phase Monitor (Model # O3DM-110).

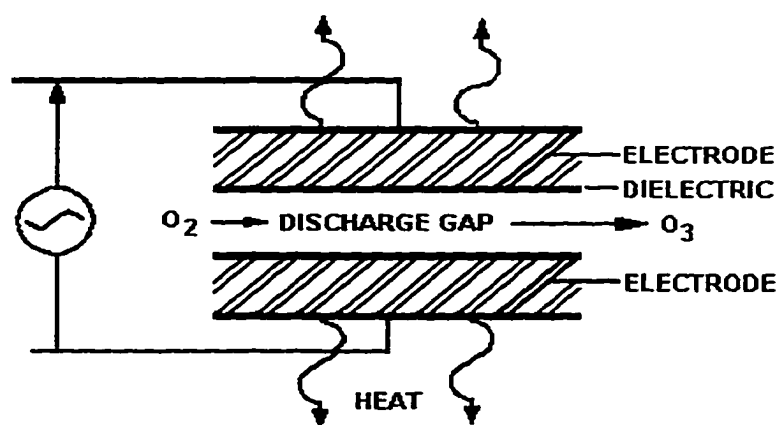


Figure 4.2. Corona discharge ozone generator.

4.3 UV_{254nm} Light Source

A NIS G15T8 15 watt 253.7 nm germicidal UV light bulb was used as the UV_{254nm} radiation source. Wastewater was circulated in a quartz tube next to the UV_{254nm} light source. The quartz tube was situated 3 mm away from the bulb in a parallel position. The light was turned on 10 min before the experiments to warm up the bulb and was on continuously during all of the UV_{254nm} experiments. The UV_{254nm} light and quartz tube were housed in an unpainted tin container as a

reflective surface and to minimize UV_{254nm} exposure to the operator. During the non-UV_{254nm} experiments, the wastewater was not exposed to the UV_{254nm} lamp.

4.4 Analytical Methods

All of the samples were analyzed for total organic carbon (TOC), Ultraviolet (UV) absorbance, pH, Gas Chromatography / Mass Spectrum (GC/MS), Microtox Toxicity, and chemical oxygen demand (COD). The E-stage samples were analyzed by TOC, UV absorbance at 240 nm, Integrated Scan Area (ISA), pH, Microtox, COD, and for color.

4.4.1 Total Organic Carbon

The samples were measured for TOC by a Shimadzu 5000 TOC Analyzer. The measurement system is based on the combustion / non-dispersive infrared gas analysis method. The samples were diluted to one twenty-fifth of the original concentration to meet the standard range of analysis. All the samples were acidified to pH 2.0 and N₂-stripped prior to the measurement of the non-volatile dissolved organic carbon (NVDOC). Duplicate measurements were made for each sample and the TOCs reported as the averages.

4.4.2 UV-vis Absorbance Spectroscopy

A wavelength scan was run on the samples using a Shimadzu UV-Vis Spectrophotometer UV-160A (P/N 204-04550), a microcomputer controlled double-beam recording spectrophotometer with a variable wavelength and 2.0 nm band width. Absorbance measurements were recorded using 1.0 cm cuvettes in increments of 10 nm from 200 nm to 400 nm. The areas under the curves are determined using the trapezoidal method of integration and is known as the Integrated Scan Area (ISA). Fixed readings were taken at 240 nm.

4.4.3 pH

The pH measurements were made use a Beckman Φ -11 pH/millivolt meter equipped with a combination pH electrode. The pH meter was calibrated prior to use with standards of 7 and 10.

4.4.4 Gas Chromatography - Mass Spectroscopy

Resin and fatty acid concentrations were performed on a Varian 3400 Gas Chromatograph with a Finnigan MAT 700 Ion Trap detector. Helium was used as a carrier gas. Sample addition was done in split-less mode with an injection port temperature of 200 °C and a column temperature of 150 °C. The column used was a 30m x 0.25 mm ID x 0.20 μ m film DB-5. The DB-5 is a poly 5% - phenyl / 95%

methyl silicone fused silica column. The DB-5 is a general use column capable of a variety of analysis.

4.4.5 Solid Phase Micro Extraction (SPME)

Solid Phase Micro Extraction (SPME) is a new technique for the extraction of volatile and nonvolatile compounds from both liquid and gaseous samples. SPME was developed in 1993 by Dr. Janusz Pawliszyn and associates at the University of Waterloo in Ontario, Canada. The SPME technology is licensed exclusively to Supelco Inc.

The SPME unit consists of a 1-cm piece of fused silica fiber phase coated with a polyacrylate or polydimethylsiloxane phase. The fiber is retractable in a needle for use with sample vials. The fiber is placed in or above the sample and allowed to absorb the analytes for a few seconds to 15 min. The fiber is removed and injected directly into the GC injection port where the analytes thermally desorb onto the column.

SPME can sample either the head space or liquid portions for numerous chemicals. Aromatics, FAs and trihalomethanes are just a few of the compounds extracted using SPME. Various phase coatings and fiber sizes are available depending on the compound(s) being extracted. A 100 μm polydimethylsiloxane fiber was used approximately 25 times for RFA extraction. A diagram of the manual SPME fiber holder is shown in figure 4.4.5.

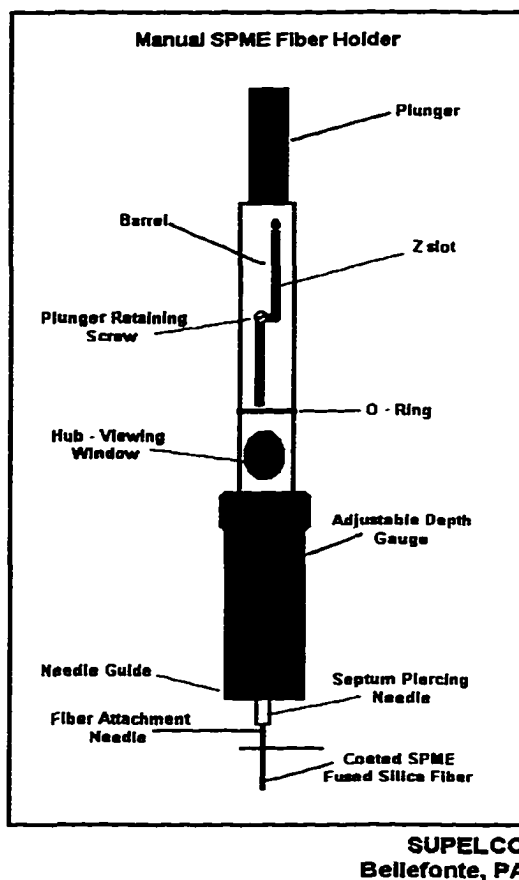


Figure 4.4.5. Manual SPME fiber holder. (Supelco 1995)

4.4.6 Microtox

Microtox is a system developed by the Microbics Corporation (now AZUR Environmental) that detects and measures toxicity. A suspension of luminescent microorganisms (*Photobacterium phosphoreum*) is used as the standard reagent in the Microtox system. These microorganisms emit light as a product of respiration. When toxic chemicals inhibit the microbes' respiration, the light output

drops in proportion to the toxicity of the sample. The microbes respond within minutes of exposure allowing for rapid toxicity evaluation. Light output is compared with the control sample. The difference in light is attributed to the sample's effect on the microbes.

A dose-response curve is automatically determined from the light output. The effective concentration (EC) of a particular percent of light loss is found on the dose-response curve. Toxicity Units can be determined by dividing 100 by the effective concentration. The percent reduction in toxicity was calculated by subtracting the final toxicity ($T.U._{(final)}$) from the initial toxicity ($T.U._{(initial)}$) divided by the initial toxicity and multiplied by 100 (Equation 4.4.6).

$$[\text{Eq. 4.4.6}] \quad \text{Percent Toxicity Reduction} = \frac{(T.U._{(initial)} - T.U._{(final)})}{T.U._{(initial)}} \times 100$$

4.4.7 Chemical Oxygen Demand (COD)

The COD of the samples was determined using Hach COD test vials. A 2-ml sample is pipetted into the Hach vials containing sulfuric acid, mercuric sulfate, chromic acid and silver sulfate. The vials are heated at 200 degrees Celsius ($^{\circ}\text{C}$) for two hours and allowed to cool. UV-vis absorbance readings were taken at 620 nm. The COD, in mg/L, was calculated using a standard calibration curve.

4.4.8 Color

The color of a sample was determined using the standard color measurement procedure for pulp mill wastewater. The pH of a colored sample is adjusted to 7.6 ± 0.1 . UV-vis readings at 465 nm were taken for the adjusted samples. The color of the sample, in platinum cobalt color units (PCCU), was calculated by multiplying the absorbance reading by 100 and dividing by 0.029.

4.5 Ozone Dosage

The O_3 transferred to the sample was calculated from the applied O_3 and off-gas measurements. The O_3 off-gas was subtracted from the total applied O_3 to give the total O_3 transferred. The trapezoidal integration method was used in determining the total O_3 transferred. The trapezoidal integration method calculated the applied O_3 by multiplying the average O_3 concentration by the contact time and the O_3 flow rate (Equation 4.5).

$$[\text{Eq. 4.5}] \quad [(O_{3(\text{beginning})} + O_{3(\text{ending})}) / 2] \times (t_2 - t_1) \times (2) = \text{applied ozone dose}$$

$$\text{Units:} \quad [\text{mg / SL}] \times [\text{min}] \times [\text{SL / min}] = [\text{mg}]$$

The O_3 off-gas was determined by the same calculations as the applied ozone dose using the measured off-gas O_3 concentrations for the $O_{3(\text{beginning})}$ and $O_{3(\text{ending})}$ values.

4.6 Standard Water Solution

The simulated E-stage water (Standard Water) used contained the following chemicals and concentrations (Table 4.6) in MilliQ water. The standard water was a close approximation of E-stage inorganic constituents as provided by the literature [Sierka 1995]. The pH for the experiments was adjusted with NaOH to 11.5. Five liter batches of standard water were used in the experiments.

Sodium Chloride (NaCl)	250 mg/L
Sodium Carbonate (Na ₂ CO ₃)	3,500 mg/L
Sodium Sulfite (Na ₂ SO ₃)	160 mg/L
Sodium Sulfate (Na ₂ SO ₄)	75 mg/L
Potassium Sulfate (K ₂ SO ₄)	50 mg/L
Abietic acid (70%)	60 mg/L
Dehydroabietic acid	20 mg/L
Oleic acid	10 mg/L
Linoleic acid	10 mg/L

<u>Ion</u>	<u>Concentration (mg/L)</u>
Na ⁺	1900
K ⁺	23
SO ₄ ⁻²	78
SO ₃ ⁻²	102
Cl ⁻	152
Alkalinity	3800

Table 4.6. Simulated E-stage wastewater composition.

4.7 Actual E-stage Effluent Characteristics

Actual E-stage effluent was obtained from a pulp mill in the midwestern portion of the United States. The effluent was characterized for TOC, UV absorbance at 240 nm, ISA, pH, color, COD, and Microtox toxicity. The E-stage effluent was filtered through a 0.45 μm filter to remove suspended particles. The E-stage water was spiked with 60 mg/L of abietic acid, 20 mg/L of dehydroabietic acid, 10 mg/L of oleic acid, and 10 mg/L of linoleic acid to determine the effect of O_3 on RFA in actual E-stage wastewater. The spiked and unspiked E-stage Effluent had the following characteristics (Table 4.7).

	pH	TOC (mg/L)	COD (mg/L)	UV _{240nm}	ISA	Color	Toxicity (EC50)
Unspiked	12.25	603	1501	0.621	1909	655	63.4
Spiked	12.40	679	1707	0.740	2100	834	6.5

Table 4.7. E-stage effluent characteristics.

The theoretical TOC and COD for the 100 mg/L of RFAs are 79 mg/L and 281.6 mg/L respectively. The difference in TOC from the unspiked to spiked samples is almost exactly that of the RFAs, while the change in COD is lower than expected. The COD difference may be due to errors in sample mixing or in the COD analysis. The ISA for the RFAs was 155 which is approximately the difference between the spiked and unspiked ISA.

4.8 2³ Experimental Setup

The 2³ experimental setup is used for experiments when three factors are being studied at two levels each. A total of eight experiments (matrix experiments) are performed with optional replication of zero to all of the experiments. The experiments performed in this 2³ setup are shown in table 4.8-1. The repeat experiments are shown in table 4.8-2.

Experimental Number	UV _{254nm} Illumination	Total H ₂ O ₂ (30%) added	Total O ₃ Input	Actual O ₃ Transferred
1	None	None	64.0 mg/L	57.4 mg/L
a	None	None	128.0 mg/L	94.4 mg/L
b	None	0.9 ml	64.3 mg/L	63.3 mg/L
ab	None	1.8 ml	128.5 mg/L	126.7 mg/L
c	On	None	67.0 mg/L	64.6 mg/L
ac	On	None	134.0 mg/L	109.5 mg/L
bc	On	0.9 ml	62.0 mg/L	61.1 mg/L
abc	On	1.8 ml	124.0 mg/L	116.4 mg/L

Where

- 1 = Base Experiment (Low O₃ Dose)
- a = High O₃ Dose
- b = Nominal 2 to 1 O₃ to H₂O₂ Dose
- c = UV_{254nm} Illumination (One bulb at full strength)

Table 4.8-1. 2³ statistical matrix experiments.

The peroxide dose was equivalent to a nominal 2 to 1 molar ratio of O₃ input to H₂O₂. Repeat runs were performed on the low O₃ (1), the high O₃ (a), the H₂O₂ - low O₃ (b), and the H₂O₂ - high O₃ (ab) experiments (Table 4.8-2).

Experimental Number	UV _{254nm} Illumination	Total H ₂ O ₂ (30%) added	Total O ₃ Input	Actual O ₃ Transferred
1	None	None	63.5 mg/L	62.1 mg/L
a	None	None	126.9 mg/L	101.7 mg/L
b	None	0.9 ml	59.9 mg/L	58.1 mg/L
ab	None	1.8 ml	119.8 mg/L	116.4 mg/L

Table 4.8-2. 2³ repeat experiments.

4.9 General Experimental Procedure

Simulated E-stage wastewater was produced as described in section 4.6. The standard water (SW) was heated to 40 °C and the pH was adjusted to approximately 11.5. The SW was pumped into the reactor as in section 4.1. The SW was ozonated for 30 min in the matrix experiments and for 60 min in the repeat experiments. Ozone was applied at a rate of 10 mg/SL. Ozone off-gas measurements were taken every minute. The reactor contents were sampled every five minutes. Samples were analyzed for pH, TOC, and UV absorbance at 240 nm. Additional analysis (GC/MS, UV spectrum, and COD) were performed at fifteen-

minute intervals. Color analysis was performed on the E-stage wastewater only. The simulated wastewater was not colored.

4.9.1 GC/MS Procedure

The samples were tested as is by the GC/MS instrument. The SPME syringe was lowered into the sample and allowed to adsorb for fifteen seconds. The syringe was extracted from the sample and injected into the sampling port on the GC. The sample adsorbed to the syringe was desorbed from the syringe for five to ten seconds in the port. The temperature of the sampling port was 200 °C and the column temperature was 150 °C. The instrument started recording after 30 seconds. Total run time was 30 min.

5.0 RESULTS

Eight experiments were performed to determine the best combination of O₃, H₂O₂, and UV_{254nm} light for toxicity reduction of RFAs in simulated E-stage effluents. Two preliminary experiments were conducted to determine the approximate contact time for O₃ addition. Results for the preliminary experiments are given in section 5.1.1. The main experiments performed in this study are known as the matrix experiments. Samples were taken at 15 and 30 min for the matrix experiments and were analyzed as in section 4.4. Two repeat experiments were performed on the matrix experiments. These were analyzed for O₃ contact times of 15, 30, 45, and 60 min.

Actual E-stage wastewater was tested using the best oxidative method from the matrix experiments. The actual E-stage wastewater was spiked with 100 mg/L of RFAs (spiked experiments) at the same concentrations in the matrix experiments. Experiments were performed on E-stage wastewater without additional RFAs (unspiked experiments). The results of the spiked, unspiked, and the duplicate E-stage experiments are given in section 5.1.3.

Four experiments were performed to determine the O₃ transfer and decomposition in the SW solution. No RFAs were present in these experiments.

5.1 Experimental Results

5.1.1 Preliminary Experiments

Two preliminary experiments were performed on the simulated wastewater. These experiments were conducted to determine the approximate O_3 contact time required to reach the maximum UV_{240nm} absorbance reduction. The reduction of UV absorbance reached an approximate maximum (97% of the 60 min reduction) at approximately 30 min of contact time. Both experiments were run for 60 min with 100 mg/L of 70% abietic acid and 30% unidentified RAs as the substrate. A calibration formula (Table G - 1) for concentration versus UV_{240nm} absorbance was derived by performing a linear regression on varying RA concentrations and UV_{240nm} measurements. This formula was used for determining UV_{240nm} reduction. Resin acids have a distinct peak at 240 nm as seen in figure 5.1.1-1. Figure 5.1.1-2 shows the UV absorbance reduction with cumulative O_3 transferred for the two test experiments. Appendix G contains the data for the two test experiments.

UV Scan for 60 mg/L of Resin Acids

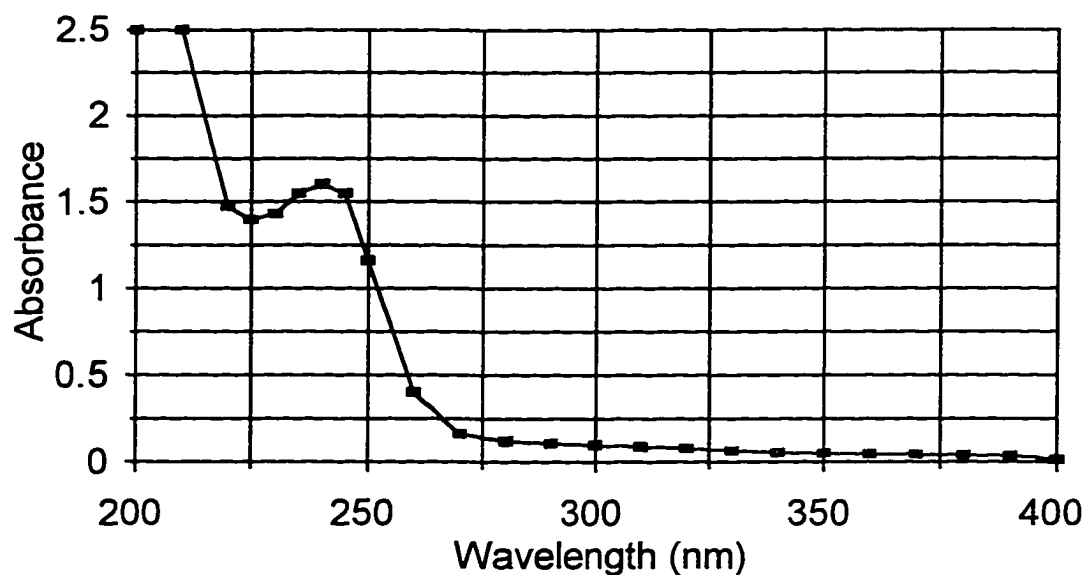


Figure 5.1.1-1. UV absorbance scan for 60 mg/L mixture of 70% abietic, 30% unidentified resin acids.

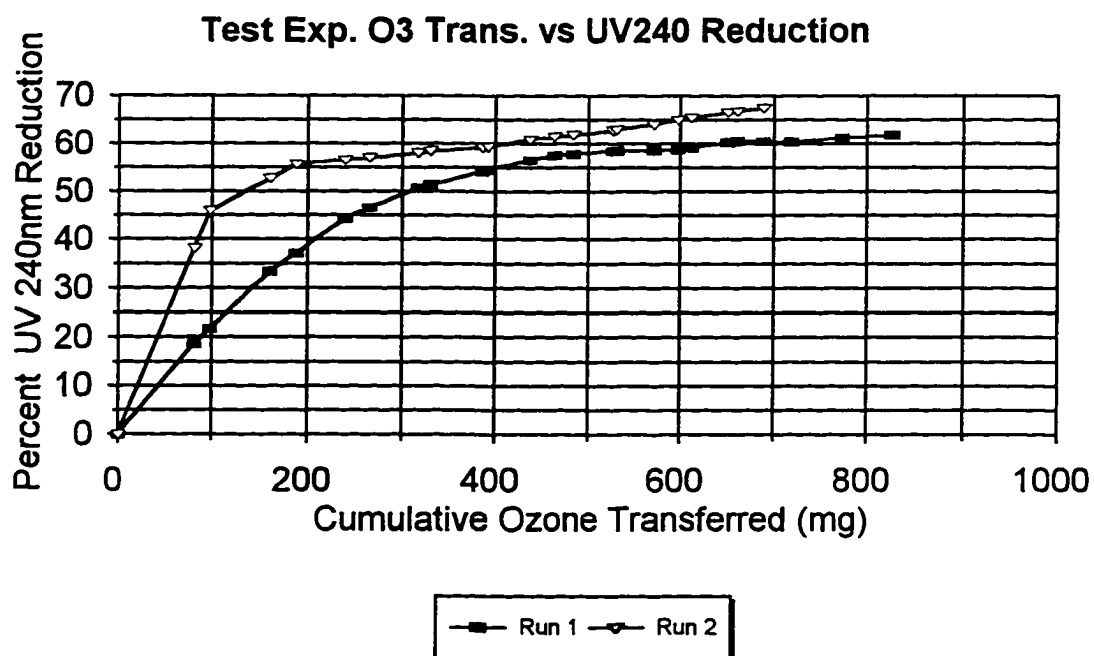


Figure 5.1.1-2. Results of test experiments.

5.1.2 Matrix and Repeat Results

The data for the matrix experiments is given in Appendix A. Appendix B contains the calculations for O₃ transferred. A summary of the matrix experimental results is summarized in the following tables.

Table 5.1.2-1 O₃ Only Matrix Experiment Run

Table 5.1.2-2 O₃ / H₂O₂ Matrix Experiment Run

Table 5.1.2-3 O₃ / UV_{254nm} Light Matrix Experiment Run

Table 5.1.2-4 O₃ / H₂O₂ / UV_{254nm} Light Matrix Experiment Run

Table 5.1.2-5 O₃ Only Repeat Run

Table 5.1.2-6 O₃ / H₂O₂ Repeat Run

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.38	2.272	205	50.80	9.7	0.00	-
5	20.58	11.41	1.479		58.07			
10	40.24	11.38	0.973		59.92			
15	57.44	11.38	0.818	192	64.56	22.7	57.3	0.199
20	71.05	11.37	0.813		67.59			
25	82.98	11.34	0.804		70.33			
30	94.40	11.31	0.793	203	70.22	89.4	89.2	0.189

Table 5.1.2-1. Analytics for O₃ only matrix experiment run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.49	2.434	186	116.10	24.4	0.00	-
5	21.23	11.43	1.595		100.27			
10	42.28	11.29	1.003		111.07			
15	63.34	11.44	0.676	189	107.26	36.5	33.1	0.105
20	84.44	11.35	0.727		108.77			
25	105.58	11.34	0.694		111.68			
30	126.71	11.34	0.659	189	115.94	64.6	62.2	0.098

Table 5.1.2-2. Analytics for O₃ / H₂O₂ matrix experiment run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.83	1.477	205	46.71	44.1	0.00	-
5	22.18	11.85	1.001		43.07			
10	43.93	11.87	0.586		46.38			
15	64.64	11.84	0.380	202	46.21	43.1	-1.7	-0.005
20	82.30	11.85	0.429		46.94			
25	96.53	11.82	0.427		51.41			
30	109.48	11.78	0.429	201	54.15	61.8	28.5	0.052

Table 5.1.2-3. Analytics for O₃ / UV_{254nm} light matrix experiment run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.35	1.445	205	55.50	36.8	0.00	-
5	20.50	11.31	1.301		48.11			
10	40.83	11.20	0.788		52.53			
15	61.13	10.89	0.590	203	55.83	39.1	5.9	0.019
20	80.83	11.21	0.577		66.63			
25	98.75	11.10	0.655		66.69			
30	116.44	11.24	0.629	203	73.57	49.4	25.6	0.044

Table 5.1.2-4. Analytics for O₃ / H₂O₂ / UV_{254nm} light matrix experiment run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.47	1.878	204	46.52	6.2	0.00	-
5	20.95	11.45	1.600		53.59			
10	41.65	11.45	1.256		57.98			
15	62.07	11.42	0.882	197	66.28	17.1	63.6	0.205
20	79.24	11.39	1.098		57.98			
25	91.65	11.37	1.022		77.36			
30	101.73	11.34	0.998	199	76.99	104.8	94.1	0.185
35	111.07	11.31	1.018		78.92			
40	119.91	11.29	1.022		83.36			
45	128.38	11.28	1.038	198	78.92	125.8	95.0	0.148
50	136.62	11.26	1.016		80.65			
55	144.67	11.22	0.946		81.69			
60	152.67	11.20	0.952	201	84.46	190.1	96.7	0.127

Table 5.1.2-5. Analytics for O₃ only repeat run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	TOC (mg/L)	Microtox EC50	Microtox % Red.	% Tox Red / O ₃ Trans.
0	0.00	11.84	2.314	189	83.85	8.9	0.00	-
5	19.56	11.76	1.856		74.40			
10	38.79	11.75	1.310		78.25			
15	58.14	11.74	1.087	191	79.90	21.1	57.8	0.199
20	77.51	11.67	1.216		83.90			
25	96.93	11.69	1.130		85.30			
30	116.40	11.71	1.049	187	88.75	25.6	65.2	0.112
35	135.85	11.63	1.220		90.75			
40	155.25	11.62	1.140		88.45			
45	174.51	11.65	1.115	187	91.85	29.9	70.2	0.080
50	193.81	11.58	1.274		92.70			
55	213.21	11.55	1.231		95.20			
60	232.53	11.57	1.183	187	93.15	36.6	75.7	0.065

Table 5.1.2-6. Analytics for O₃ / H₂O₂ repeat run.

5.1.3 E-stage Experiment Results

The results of the E-stage, spiked E-stage, and repeat experiments are given in the following tables. The experimental data and graphs are included in Appendix E. Microtox results are included in Section 5.2.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	Color PCCU	TOC (mg/L)	Microtox EC50	Microtox % Red.	Tox Red / O ₃ Trans.
0	0.00	12.40	0.740	1707	834	679	6.5	0.0	-
5	20.16	12.40	0.669			657			
10	40.09	12.40	0.631			640			
15	60.04	12.37	0.599	1570	431	645	38.3	83.2	0.264
20	79.91	12.35	0.578			630			
25	99.72	12.30	0.569			627			
30	119.55	12.24	0.549	1510	290	641	41.9	84.6	0.135

Table 5.1.3-1. Spiked E-stage analytical results for O₃ only run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	Color PCCU	TOC (mg/L)	Microtox EC50	Microtox % Red.	Tox Red / O ₃ Trans.
0	0.00	12.37	0.695	1686	938	651	7.2	0.0	-
5	20.25	12.34	0.634			666			
10	40.36	12.31	0.594			629			
15	60.46	12.27	0.582	1548	445	618	34.4	79.1	0.249
20	80.34	12.26	0.554			601			
25	100.05	12.23	0.552			617			
30	119.72	12.18	0.529	1592	300	607	49.8	85.6	0.136

Table 5.1.3-2. Spiked E-stage analytical results for repeat run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	Color PCCU	TOC (mg/L)	Microtox EC50	Microtox % Red.	Tox Red / O ₃ Trans.
0	0.00	12.25	0.621	1501	655	603	63.4	0.0	-
5	20.82	12.24	0.593			622			
10	41.41	12.22	0.577			653			
15	61.93	12.20	0.543	1426	555	623	69.8	9.2	0.029
20	82.29	12.17	0.552			633			
25	102.41	12.14	0.533			614			
30	122.29	12.10	0.518	1382	414	650	83.9	24.4	0.039

Table 5.1.3-3. Unspiked E-stage analytical results for O₃ only run.

Time (Min)	O ₃ Trans (mg/L)	pH	UV _{240nm} Abs.	COD (mg/L)	Color PCCU	TOC (mg/L)	Microtox EC50	Microtox % Red.	Tox Red / O ₃ Trans.
0	0.00	12.18	0.579	1448	583	581	25.8	0.0	-
5	20.78	12.20	0.576			601			
10	41.37	12.18	0.550			623			
15	61.83	12.16	0.543	1439	483	597	39.1	34.2	0.108
20	82.12	12.14	0.531			594			
25	102.22	12.12	0.507			608			
30	122.08	12.06	0.496	1495	341	602	47.2	45.4	0.073

Table 5.1.3-4. Unspiked E-stage analytical results repeat run.

5.1.4 Standard Water Without Resin and Fatty Acids

Four experiments without RFAs were performed to determine the transfer and decomposition of O₃ to the simulated water. Figure 5.1.4-1 is a plot of the O₃ transferred for the four oxidative processes studied. Figure 5.1.4-2 compares the O₃ off-gas measurements for O₃ and O₃ / UV_{254nm} with and without RFAs. Figure 5.1.4-3 compares the O₃ off-gas measurements for O₃ / H₂O₂ and O₃ / H₂O₂ / UV_{254nm} with and without RFAs.

The transfer rates for the O₃ only and O₃ / UV_{254nm} experiments (figure 5.1.4-2) were approximately equal with O₃ only transferring more O₃ for the first few minutes of run time. Likewise the O₃ / H₂O₂ and O₃ / H₂O₂ / UV_{254nm} experiments (figure 5.1.4-3) transferred identically for the first 17 min. Hydrogen peroxide was added at the start of both experiments, and again at 15 min for the O₃ / H₂O₂

experiment. The addition of H_2O_2 at 15 min for the $\text{O}_3 / \text{H}_2\text{O}_2$ experiment changed the O_3 off-gas curve from being identical to that of the $\text{O}_3 / \text{H}_2\text{O}_2 / \text{UV}_{254\text{nm}}$ experiment. The off-gas data for the $\text{O}_3 / \text{H}_2\text{O}_2 / \text{UV}_{254\text{nm}}$ experiment suggests that without additional H_2O_2 , the O_3 off-gas would rise toward the same levels as the O_3 and $\text{O}_3 / \text{UV}_{254\text{nm}}$ experiments.

The difference between the O_3 transferred for the SW, with and without RFAs, does not necessarily equal the O_3 reacted with the RFAs as either O_3 or $\text{OH}\cdot$. The O_3 transferred to the SW without RFAs is equal to the O_3 reacted with inorganic material, the O_3 decomposed in the water, and the dissolved O_3 present in the water. There is an additional demand competing for O_3 and $\text{OH}\cdot$ when RFAs are present.

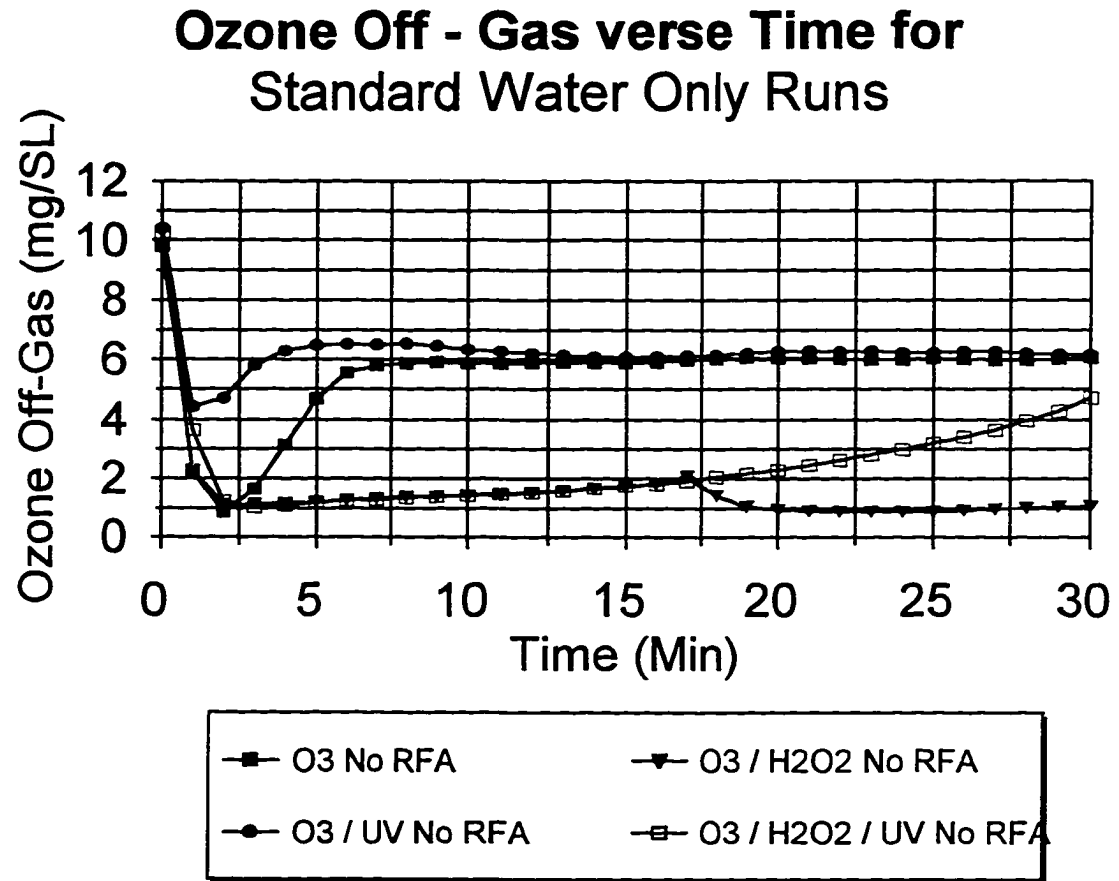


Figure 5.1.4-1. Ozone off-gas verses time for the four oxidative processes.

Note: 0.9 ml of 30% H₂O₂ was added at the beginning of the two H₂O₂ experiments.

An additional 0.9 ml was added after 15 min for the O₃ / H₂O₂ experiment.

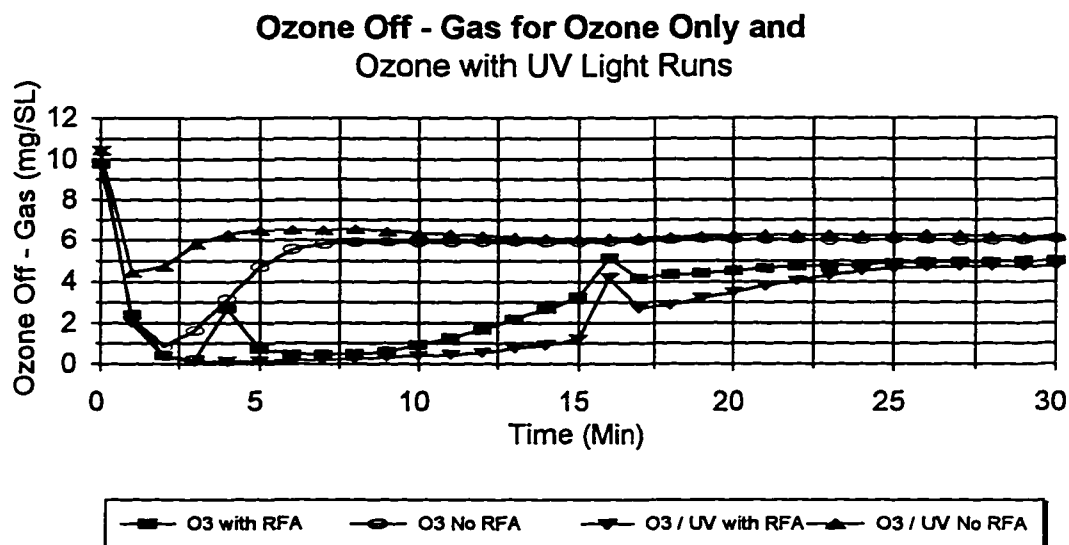


Figure 5.1.4-2. Ozone off-gas for O_3 and O_3 / UV_{254nm} experiments.

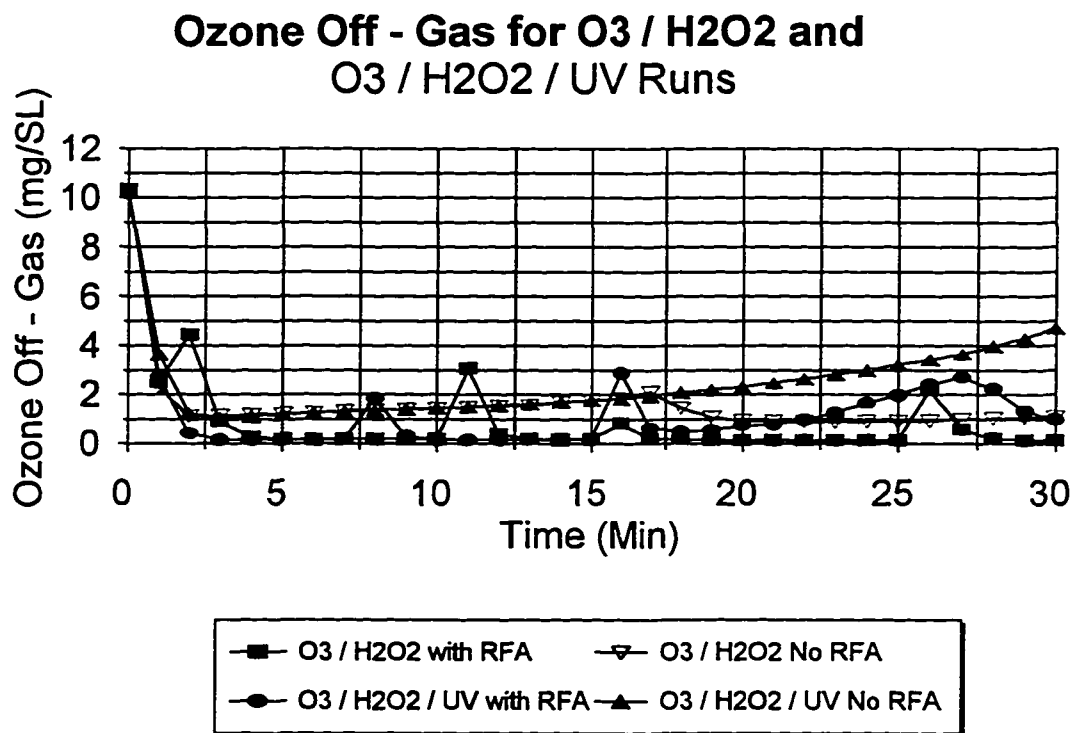


Figure 5.1.4-3. Ozone off-gas for O_3 / H_2O_2 and $O_3 / H_2O_2 / UV$ experiments.

Note: Spikes in experiments with RFAs are due to stoppage of gas flow in the experiment for foam settling. H_2O_2 was added at time = 0 and 15 min for the $\text{O}_3 / \text{H}_2\text{O}_2$ experiments. H_2O_2 was added at time = 0 and 27 min for the $\text{O}_3 / \text{H}_2\text{O}_2 / \text{UV}$ with RFAs experiment, and at time = 0 for the $\text{O}_3 / \text{H}_2\text{O}_2 / \text{UV}$ No RFA experiment.

5.1.5 $\text{UV}_{254\text{nm}}$ Light Only Experiment Results

A 5 L sample of SW with RFAs was recirculated through the oxidative reactor while being exposed to the $\text{UV}_{254\text{nm}}$ light source. The temperature, pH, recirculation rate, and time of exposure were identical to the matrix experiments. No O_3 or H_2O_2 was used in this experiment. Samples were taken at 0, 5, 10, 15 and 30 min and analyzed for UV absorbance and Microtox toxicity. The Microtox data are tabulated in table 5.1.5 while the UV absorbance is plotted in figure 5.1.5. Microtox analysis typically has a range of error of 16% [Microtox Manual 1992]. The 10 min value falls within the error range, suggesting that the 10 min value may be the same as the feed value. The other values were outside the error range indicating that those values are distinct from the feed value.

	Feed	5 Min	10 Min	15 Min	30 Min
EC 50	9.1	6.7	8.0	10.6	10.9
Tox. Units	11.0	14.9	12.5	9.4	9.1
Percent Reduction	0.0	-35.6	-13.8	14.3	16.8

Table 5.1.5. Microtox data for UV_{254nm} only experiment.

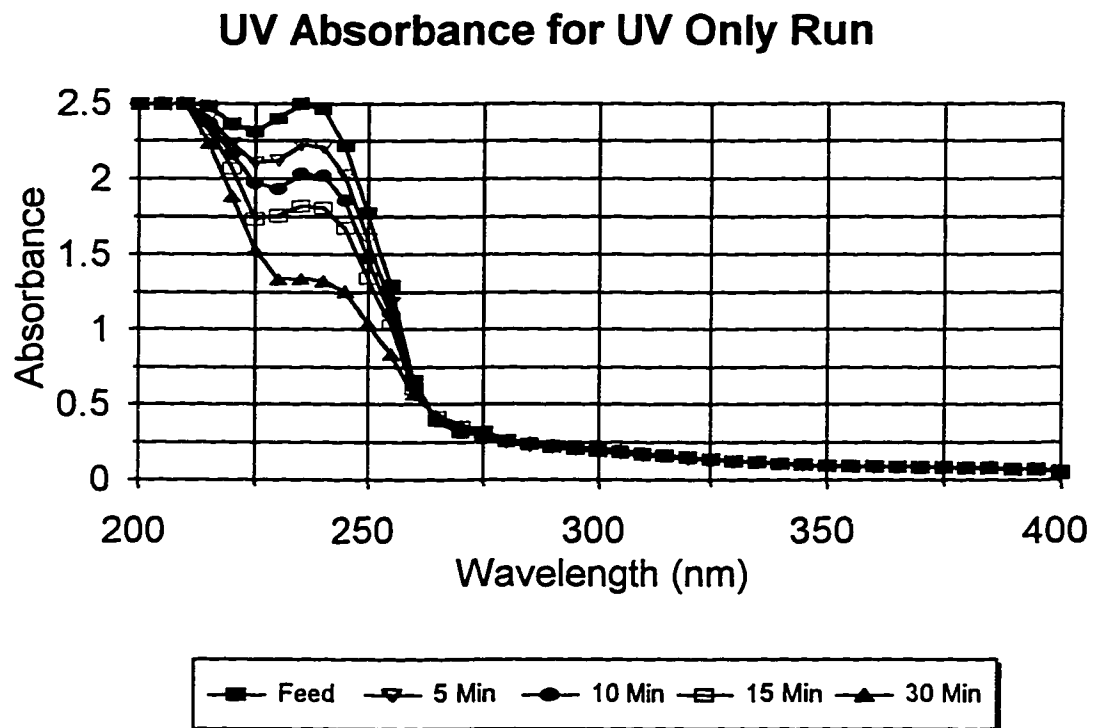


Figure 5.1.5. UV absorbance scan for UV_{254nm} only experiment.

5.2 Microtox Toxicity

The results of all of the Microtox toxicity measures are given in table 5.2-1 including the Microtox EC50, Toxicity Units, and Percent Toxicity Reduction values. The EC50 values are the calculated values given by the Microtox software. The Toxicity Units are calculated by taking the EC50 value divided into 100. The Percent Toxicity Reduction is calculated as the percentage decrease in Toxicity Units compared with the initial feed values. Table 5.2-2 shows the Microtox results for the actual E-stage O₃ only runs.

EC50

Time	O ₃ Only Run 2	O ₃ Only Run 1	O ₃ / H ₂ O ₂ Run 2	O ₃ / H ₂ O ₂ Run 1	O ₃ / UV _{254nm} Run	O ₃ / H ₂ O ₂ / UV _{254nm} Run
0	6.2	9.7	8.9	24.4	44.1	36.8
15	17.1	22.7	21.1	36.5	43.4	39.1
30	104.8	89.4	25.6	64.6	61.8	49.4
45	125.8		29.9			
60	190.1		36.6			

Toxicity Units

Time	O ₃ Only Run 2	O ₃ Only Run 1	O ₃ / H ₂ O ₂ Run 2	O ₃ / H ₂ O ₂ Run 1	O ₃ / UV _{254nm} Run	O ₃ / H ₂ O ₂ / UV _{254nm} Run
0	16.0	10.3	11.2	4.1	2.3	2.7
15	5.8	4.4	4.7	2.7	2.3	2.6
30	1.0	1.1	3.9	1.6	1.6	2.0
45	0.8		3.3			
60	0.5		2.7			

Percent Toxicity Reduction

Time	O ₃ Only Run 2	O ₃ Only Run 1	O ₃ / H ₂ O ₂ Run 2	O ₃ / H ₂ O ₂ Run 1	O ₃ / UV _{254nm} Run	O ₃ / H ₂ O ₂ / UV _{254nm} Run
0	0.0	0.0	0.0	0.0	0.0	0.0
15	63.6	57.3	57.8	33.1	-1.7	5.9
30	94.1	89.2	65.2	62.2	28.5	25.6
45	95.0		70.2			
60	96.7		75.7			

Table 5.2-1. Microtox data for simulated and simulated repeat runs.

Time	EC50			
	Spiked 1	Spiked 2	Unspiked 1	Unspiked 2
0	6.5	7.2	63.4	25.7
15	38.3	34.4	69.8	39.1
30	41.9	49.8	83.9	47.2

Time	Toxicity		Units	
	Spiked 1	Spiked 2	Unspiked 1	Unspiked 2
0	15.5	13.9	1.6	3.9
15	2.6	2.9	1.4	2.6
30	2.4	2.0	1.2	2.1

Time	Percent		Reduction	
	Spiked 1	Spiked 2	Unspiked 1	Unspiked 2
0	0.0	0.0	0.0	0.0
15	83.2	79.1	9.2	34.2
30	84.6	85.6	24.4	45.4

Table 5.2-2. Microtox results for O₃ only E-stage, spiked E-stage, and repeat runs.

5.3 Regression Analysis Results

The results of the regression analysis calculations indicate that the three treatment variables (O_3 , H_2O_2 , UV_{254nm}) did not have a significant impact on the UV absorbance at 240 nm of the wastewater. Regression analysis calculations were done with the percent toxicity reduction as the dependant variable and the UV_{240nm} percent toxicity reduction as the independent variable. Regression analysis was performed on the individual experiments and the combined data. Table 5.3-1 contains the results of the regression analysis for the matrix experiments along with the R^2 for the analysis. Table 5.3-2 contains the regression analysis results for the E-stage, UV only and combined experimental results. Appendix C contains the data used and complete results of the regression analysis.

Experiment	X - Coefficient	Constant	R^2
O_3 Only	1.1403	-0.2609	0.8851
O_3 Only Repeat	1.6930	4.2210	0.8018
O_3 / H_2O_2	0.6593	-0.1379	0.7888
O_3 / H_2O_2 Repeat	1.2600	1.2426	0.9179
O_3 / UV	0.1706	0.7029	0.1779
$O_3 / H_2O_2 / UV$	0.2596	0.4752	0.4205

Table 5.3-1. Regression analysis of UV_{240nm} reduction and toxicity reduction for matrix experiments.

Experiment	X - Coefficient	Constant	R ²
Spiked E-Stage	3.5157	3.2985	0.9444
Spiked E-Stage Repeat	3.7818	4.2143	0.9394
Unspiked E-Stage	1.2923	-1.3714	0.8257
Unspiked E-Stage Repeat	3.0869	5.4463	0.8754
UV Only	0.7239	-18.7755	0.3741
Combined Result	0.0649	51.7769	0.0022

Table 5.3-2. Regression analysis of UV_{240nm} reduction and toxicity reduction for E-stage, UV only, and combined experiments.

6.0 DISCUSSION OF RESULTS

The four AOP processes studied produced a variety of toxicity responses. The highest toxicity reduction (90%) of the matrix experiments was achieved after transfer of 94.4 mg/L of O₃ only. Approximately 60% of the toxicity was removed after 57.4 mg/L of O₃ only had been transferred. The processes in descending order of toxicity removal were (values of O₃ transferred in parentheses) O₃ - (94.4 mg/L), O₃ / H₂O₂ - (126.7 mg/L), O₃ - (57.4 mg/L), O₃ / H₂O₂ - (63.6 mg/L), O₃ / UV_{254nm} - (109.5 mg/L), O₃ / H₂O₂ / UV_{254nm} - (116.4 mg/L), O₃ / H₂O₂ / UV_{254nm} - (61.1 mg/L), and O₃ / UV_{254nm} - (64.6 mg/L). The repeat runs with O₃ and O₃ / H₂O₂ produced higher (< 5% for 30 min results) toxicity removals than the matrix experiments. Toxicity reductions were not directly related to O₃ transferred, but were dependent on the oxidative processes employed particularly if UV_{254nm} illumination was present. The repeat runs were conducted to 60 min instead of the 30 min contact time of the matrix experiments. This was done to determine the amount of additional toxicity reduction with additional ozonation. Toxicity reduction was minimal (2% increase in toxicity reduction) with an additional 30 min of contact time (50.94 mg/L O₃ transferred).

The spiked E-stage experiments produced better results for 15 min of O₃ contact time (60.0 mg/L O₃ transferred) than the O₃ only matrix experiments. The E-stage toxicity was reduced by approximately 81% verses approximately 60% for

the matrix experiments. The toxicity reduction only increased to 85% with an additional 15 min of contact time (119.6 mg/L of O₃ transferred). The matrix experiments produced higher toxicity reductions for less O₃ transferred due to the lower O₃ demand of the wastewater employed in the matrix experiments.

The unspiked E-stage experiments produced lower toxicity reduction than the spiked or matrix experiments. The unspiked run only reduced the toxicity by 9% with 61.8 mg/L of O₃ and by 24% with 122.2 mg/L of O₃ transferred. The unspiked repeat run produced 34% and 45% toxicity reductions for the same quantities of O₃ transferred. The large difference in toxicity reductions for the two unspiked runs may be due to wastewater character. The first unspiked run used water from the bottom of a bucket while the second used water from the top of a different bucket. The unspiked water contained more COD (+ 53 mg/L), TOC (+ 22 mg/L), and color (+ 72 PCCU) than the unspiked repeat water. The unspiked water was less toxic than the repeat run was (63.4 vs. 25.7 EC50 values).

The toxicity reduction was normalized by dividing it by the O₃ transferred. These values indicate that O₃ only was the most effective at reducing the toxicity with O₃ / H₂O₂ the next most effective and O₃ / UV and O₃ / H₂O₂ / UV being the least effective treatment processes. It is interesting to note that both the O₃ / UV and O₃ / H₂O₂ / UV increased in treatment effectiveness with time while the most effective (O₃ and O₃ / H₂O₂) processes decrease in effectiveness with time. This was accounted for by the initial increase in toxicity due to UV_{254nm} illumination. The

effectiveness of the spiked E-stage runs was higher than the most effective of the matrix experiments (0.264 for spike E-stage verses 0.199 for SW O₃ only).

The UV absorbance at 240 nm did not correlate with toxicity reduction. However, the UV absorbance scans indicated a peak at 250 nm increased with increasing toxicity reduction (See figures D-1 through D-6 in Appendix D). Maier and Conroy (1981) determined that the addition of oxygen to organic molecules would shift the UV absorbance of the compound to a longer wavelength. The increase in UV_{250nm} absorbance correlates well with toxicity reduction and could possibly be used to estimate toxicity reduction if toxicity reduction was only caused by oxygen addition to the RFAs. Toxicity reduction can be accomplished by the reduction of larger molecular weight molecules into smaller nontoxic molecules and thus UV_{250nm} absorbance may not be an accurate estimator of the amount of toxicity reduction. The UV_{250nm} peak is largest and most pronounced on the O₃ only runs which also produced the largest toxicity reductions.

The SPME - GC/MS method developed did not produce the desired results. The spectrum peaks were small and hard to distinguish from the background noise. The SPME syringe was not able to adsorb the RFAs at the standard water pH of 11.5. The pH was decreased to less than 4 to convert the RFAs to the free acid forms. These free acid forms adsorbed to the syringe but most of the RFAs precipitated out of solution at the low pH. Appendix F contains the information on the SPME/ GC-MS results.

6.1 Oxidative Pathways

The O_3 / H_2O_2 , O_3 / UV_{254nm} , and $O_3 / H_2O_2 / UV_{254nm}$ AOPs all produce hydroxyl radicals (OH^\cdot) by the decomposition of O_3 . Ozone, in the presence of OH^- , decomposes to produce hydroxyl radicals. Direct O_3 reactions with organic material predominate since O_3 decomposition at the high pHs is slow compared with the reaction rates of O_3 with organic molecules. Staehelin and Hoigne (1982) derived a reaction rate constant of $k = 70 \text{ M}^{-1}\text{s}^{-1}$ for the decomposition of O_3 by hydroxide ions (OH^-). The decomposition of O_3 by hydroperoxide anion (HO_2^-) is $2.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. The HO_2^- ion is formed by the dissociation of H_2O_2 in water. At pH of 11.5, the rate of O_3 decomposition by OH^- is $d[O_3] / dt = 0.22 [O_3]$. The O_3 decomposition by HO_2^- at pH of 11.5 with the H_2O_2 added in the matrix experiments was $d[O_3] / dt = 6941 [O_3]$. The decomposition by HO_2^- is 31,550 times faster than by OH^- .

Two pathways for hydroxyl radical attack are postulated. A representation of the hydroxyl radical attack with O_2 addition is given in figure 6.1-1, while the hydroxyl radical attack with H_2O_2 addition is shown in figure 6.1-2. The direct O_3 attack pathway is shown in figure 6.1-3.

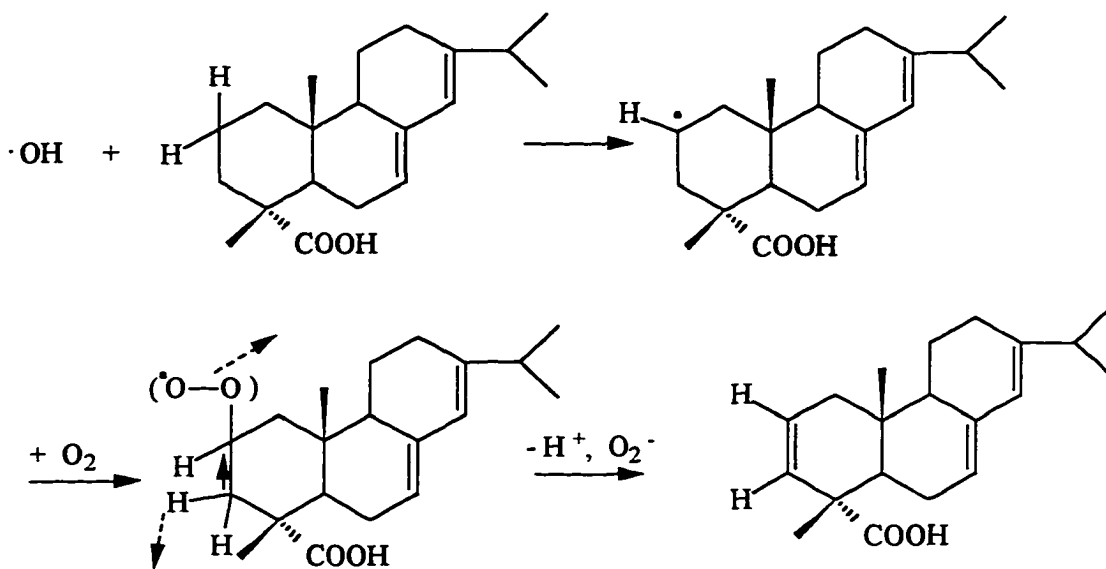


Figure 6.1-1. Hydroxyl radical attack of abietic acid with O_2 addition.

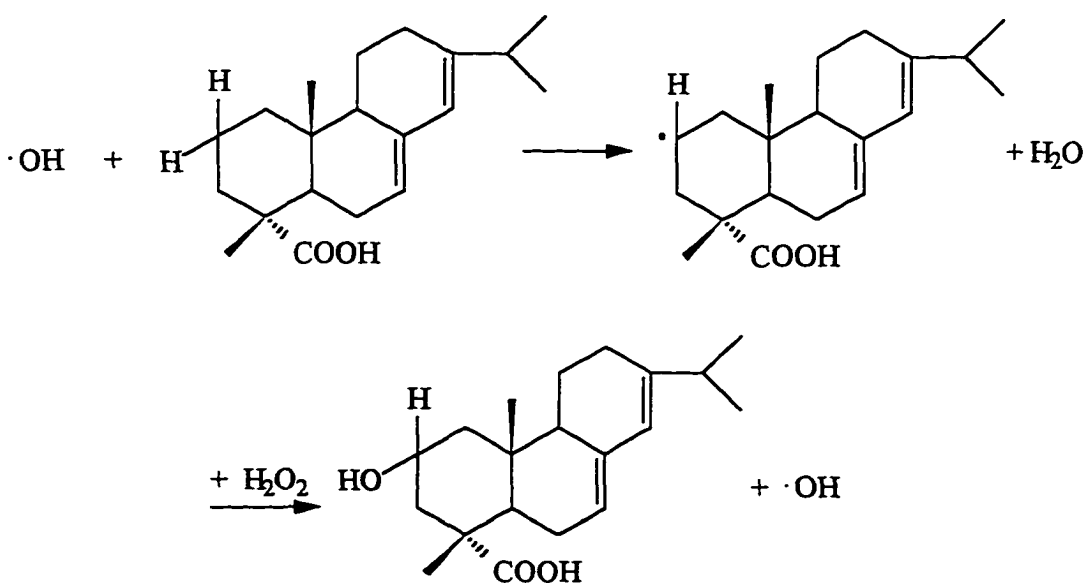


Figure 6.1-2. Hydroxyl radical attack of abietic acid with H_2O_2 addition.

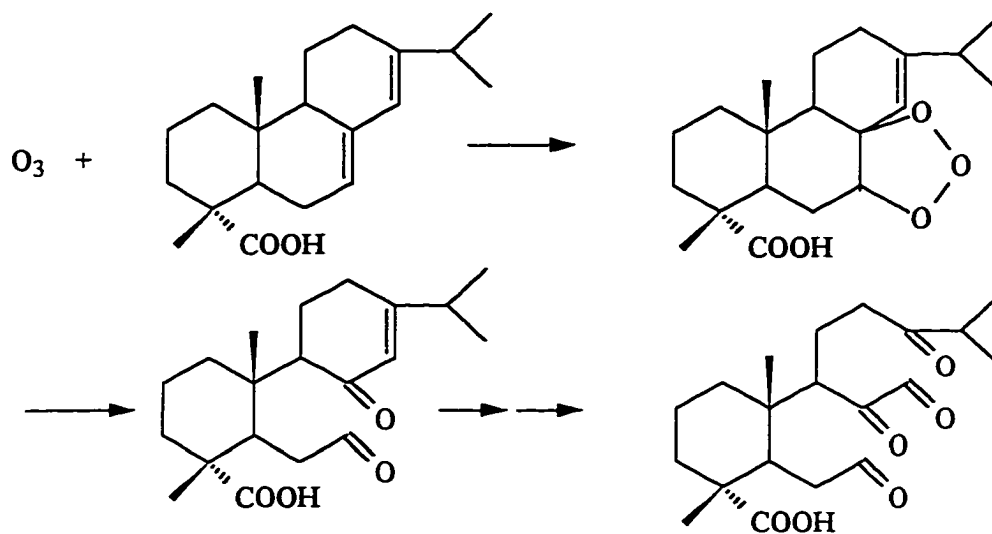


Figure 6.1-3. Direct O_3 attack of abietic acid.

The direct O_3 attack of the RAs produced the most rapid structural changes and oxygen addition of the oxidative pathways studied. The breaking of the ring structure and the addition of the oxygen to the structure produced the toxicity reduction seen in the O_3 only runs. Ozone reacts rapidly with double and triple bonds and slowly with atoms carrying negatively charged compounds such as nitrogen (N), phosphorus (P), oxygen (O), sulfur (S), and nucleophilic carbons [Langlais *et al* 1991]. The rapid toxicity reduction seen in the first 15 to 30 min of the O_3 only runs, followed by the slower toxicity reduction would be accounted by the O_3 order of reactivity. Another factor in the differences in treatment efficiencies is believed to be the effect of radical scavengers. The simulated and actual E-stage

wastewater both contain large concentration of carbonates (CO_3^{-2}) and bicarbonates (HCO_3^{-1}). Both ions are known to terminate radical reactions by reacting with hydroxyl radicals [Hoigne and Bader 1981]. The rate constants for the reactions of CO_3^{-2} and HCO_3^{-1} with $\text{OH}\cdot$ are $K = 4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $K = 1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ respectively.

Using the rate constants for the reactions of CO_3^{-2} and HCO_3^{-1} with $\text{OH}\cdot$, and the concentration of RFAs of 100 mg/L ($3.333 \times 10^{-4} \text{ M}$) the efficiency (as a percent) of the $\text{OH}\cdot$ reaction with the RFAs was derived using equations 6.1-1 and 6.1-2. The rate constant for the reaction of $\text{OH}\cdot$ with RFAs is unknown. Rate constants for the reaction of $\text{OH}\cdot$ with organic species are commonly between 10^8 and $10^{10} \text{ M}^{-1}\text{s}^{-1}$ [Glaze *et al* 1987]. The equation was modified for RFAs from Glaze's work. Hoigne and Bader (1981) measured rate constants for varying organic species ranging from < 0.01 to $10^9 \text{ M}^{-1}\text{s}^{-1}$.

$$[\text{Eq. 6.1-1}] \quad E = \frac{R}{(R + 1)} * 100$$

$$[\text{Eq. 6.1-2}] \quad R = \frac{K_{\text{RFA}} * [\text{RFA}]}{K_{\text{HCO}_3} * [\text{HCO}_3^{-1}] + K_{\text{CO}_3} * [\text{CO}_3^{-2}]}$$

Where:

$$[\text{RFA}] = 3.333 \times 10^{-4} \text{ M}$$

$$K_{\text{HCO}_3} = 1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

$$K_{\text{CO}_3} = 4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$

$$[\text{HCO}_3^{-1}] = 0.0038 \text{ M}$$

$$[\text{CO}_3^{-2}] = 0.0342 \text{ M}$$

K_{RFA}	R	E (%)
1×10^7	2.3114×10^{-4}	0.023
5×10^7	1.1557×10^{-3}	0.115
1×10^8	2.3114×10^{-3}	0.231
5×10^8	1.1557×10^{-2}	1.142
1×10^9	2.3114×10^{-2}	2.259
5×10^9	1.1557×10^{-1}	10.359
1×10^{10}	2.3114×10^{-1}	18.773

Table 6.1. Efficiency of OH[·] reaction with RFAs.

Using Hoigne and Bader work, the K_{RFA} was likely less than 1×10^9 which gave an efficiency for the reaction of less than 2.3%. Due to the low efficiency of OH[·] with the RFAs and the rapid ring breakage and oxygen addition of direct ozonation only, O₃ only should have been the best process for reducing the RFA toxicity of simulated E-stage effluents.

Roy-Arcand and Archibald (1995) studied the effects of direct O₃ reactions on RA, FA, COD, toxicity, and juvabione removal. Their study focused on CTMP primary clarifier effluent with a pH of 4.9 to 6.6, and a total RFA concentration of approximately 10 mg/L. The toxicity of their samples was reduced by 60% with only 10 mg/L of O₃ transferred and 75% with 50 mg/L. Further O₃ up to 100 mg/L only eliminated an additional 5% of the total toxicity. Individual RFA and juvabione removals gave similar results with a high initial removal followed by a slower removal with additional O₃.

Although the wastewaters studied and the RFA concentrations were dissimilar, comparisons of this project with the research of Roy-Arcand do have some relevance. At an O_3 dose of 60.0 mg/L the toxicity of the spiked E-stage wastewater used in this study was reduced by 83%. The same 60.0 mg/L O_3 dose produced 80% toxicity reduction in Roy-Arcand's research. While at an O_3 dose of 119.6 mg/L, 84.6% of the toxicity was reduced, versus 86% at 100 mg/L for Roy-Arcand. Roy-Arcand's research and this study produced almost identical toxicity reductions for the same amount of O_3 transferred, though different effluents and RFA concentrations were used.

The EPRI report results do not correlate well with the results of the O_3 / H_2O_2 and O_3 / UV results obtained in the author's research. The characteristics of the E-stage wastewater used in the EPRI study and this study varied greatly. The water used in the EPRI study came from the Bowater mill in Catawba, South Carolina. The Bowater mill is a kraft type softwood pulping mill having a bleaching sequence of $C_D-E_O-H-E-D$ (D=Chlorine Dioxide- ClO_2 in acid, $C_D=Cl_2/ClO_2$ in acid, H=Hypochlorite in base). The Bowater E-stage had the following range of characteristics: pH 10.5 to 11.5, TOC 560 to 1250, color 9000 to 14000, and Microtox EC50 1.9 to 38.1. The pH of the EPRI experiments ranged from 7.34 to 11.13. The characteristics for the E-stage used in this study were: pH 12.4, TOC 650 to 680, color 834 to 938, and Microtox EC50 6.4 to 7.2. The bleaching sequence used in the mill that provided the E-stage for this study was C_D-E_O-D-D .

The EPRI results varied greatly in toxicity reduction for the O₃ / H₂O₂ experiments with the toxicity reduction ranging from -214.9 to 92.7%. The toxicity reductions for the O₃ / UV experiments were substantial in the EPRI report ranging from 58.2 to 94.5%. The toxicity reduction obtained for the simulated water (-1.65 to 28.53%) in this study did not parallel these results. The O₃ only results had good correlation between the EPRI report and this study. The EPRI toxicity reduction for the O₃ only ranged from 50.2 to 91.2%. This study's E-stage toxicity reduction ranged from 79.1 to 85.6%. It should be noted that the EPRI experiments were performed on actual E-stage wastewater with varying pHs, O₃, H₂O₂, and UV levels and no additional RFAs. The different pHs at which the experiments were performed would produce different oxidative pathways.

6.1.1 SW without RFAs and UV_{254nm} Only Experiments

The reactor O₃ off-gas results indicated that the O₃ only and O₃ / UV_{254nm} experiments transferred the O₃ in a similar pattern. Likewise the O₃ / H₂O₂ and O₃ / H₂O₂ / UV_{254nm} experiments were similar in O₃ transferred. The toxicity reductions within each of these pairs varied greatly due to the effect of UV_{254nm} illumination. The experiments involving illumination with UV_{254nm} light produced both increases and decreases in toxicity. The UV_{254nm} only experiment was performed to characterize the effect of UV_{254nm} light on the RFAs to explain the large differences in toxicity reductions between the experiments with and without UV_{254nm} illumination.

The toxicity of the SW increased for the first 10 min of illumination and decreased after 15 min. The UV_{254nm} illumination of the RFAs produced photolyzed products with an increase in toxicity. The low toxicity reductions obtained from the O₃ / UV_{254nm} and O₃ / H₂O₂ / UV_{254nm} experiments would be due to competition between the UV_{254nm} increasing the toxicity and the O₃ and O₃ / H₂O₂ reducing the toxicity.

While the toxicity was increasing, the UV absorbance scans showed a decrease in absorbance at 240 nm with time. This decrease in UV_{240nm} absorbance confirms the conclusion that UV_{240nm} absorbance is not a good indicator of toxicity.

6.2 pH Change with Time

As seen in table 6.2-1, the pH of the solution decreased with time in all of the experiments performed. The change in pH can best be seen in the two repeat experiments of O₃ and H₂O₂. Both of the duplicate experiments lowered the pH by 0.27 pH units over a one hour period. In the repeat O₃ only run, the pH changed from an initial 11.47 to 11.20 after one hour of ozonation. The repeat O₃ / H₂O₂ run pH was reduced from 11.84 to 11.57. These decreases in pH are attributed to the dissociation of alcohols produced as in figure 6.1-1 and of carboxylic acids if they are produced. The EPRI report noted that organic acids produced by oxidation tend to lower the wastewater pH.

The results from the actual E-stage wastewater experiments show the same decrease in pH with ozonation. The average decrease in pH was 0.15 pH units over the 30 min reaction times. Results of pH decreases for the E-stage experiments are shown in table 6.2-2.

The standard and actual E-stage waters are both highly buffered solutions. The alkalinity of the waters were 3800 mg/L and 2800 mg/L as CaCO₃ respectively. The high buffering capacity of the water decreases the change in pH. Therefore, the actual quantity of hydrogen ions (H⁺) produced from the ozonation of the wastewater is greater than the change in pH indicates. The pH changes are minor and did not affect the treatment processes in any noticeable manner.

Time (Min)	UV _{254nm}	O ₃ /H ₂ O ₂	O ₃ Only	O ₃ / H ₂ O ₂ /		UV _{254nm}
	Only	Repeat	Repeat	O ₃ /H ₂ O ₂	O ₃ Only	
0	11.83	11.84	11.47	11.49	11.38	11.35
5	11.85	11.76	11.45	11.43	11.41	11.31
10	11.87	11.75	11.45	11.29	11.38	11.20
15	11.84	11.74	11.42	11.44	11.38	10.89
20	11.85	11.67	11.39	11.35	11.37	11.21
25	11.82	11.69	11.37	11.34	11.34	11.10
30	11.78	11.71	11.34	11.34	11.31	11.24
35		11.63	11.31			
40		11.62	11.29			
45		11.65	11.28			
50		11.58	11.26			
55		11.55	11.22			
60		11.57	11.20			

Table 6.2-1. pH change with time for matrix experiments.

Time (min)	E-stage pH Data			
	Spiked	Spiked Repeat	Unspiked	Unspiked Repeat
0	12.40	12.37	12.25	12.18
5	12.40	12.34	12.24	12.20
10	12.40	12.31	12.22	12.18
15	12.37	12.27	12.20	12.16
20	12.35	12.26	12.17	12.14
25	12.30	12.23	12.14	12.12
30	12.24	12.18	12.10	12.06

Table 6.2-2. pH data for E-stage experiments.

6.3 COD, TOC and Color Results

The data for the chemical oxygen demand (COD) and total organic carbon (TOC) results are tabulated in Appendix D. The COD did not change significantly even after one hour of oxidation. The theoretical COD for the feed was 301.0 mg/L while the experimentally determined COD values were lower than the theoretical by approximately 100 mg/L. High concentrations of chlorine (> 1000 mg/L) are known to inhibit COD results, but chlorine concentrations were only at 152 mg/L.

The COD for the E-stage experiments decreased between 3 and 12%. Most of the COD reduction was obtained in the first 15 min of ozonation. The spiked E-stage had a higher initial COD and COD removal than the unspiked samples. The addition of the RFAs accounted for the higher initial COD (1707 mg/L for spiked

verses 1501 mg/L for unspiked). The higher COD removals in the spiked samples indicate a greater affinity of O_3 to the RFAs than to the other organic compounds in the E-stage wastewater. This would indicate that the other organics found in the E-stage contain fewer unsaturated bonds than the RFAs.

The TOC values tended to increase with time of oxidation. The initial TOC values were with one exception lower than the 79.1 mg/L theoretical TOC feed. The FAs are only slightly soluble in water with a solubility of less than 2.9 mg/L. Both oleic and linoleic acids were added at 10 mg/L. The FAs formed an organic layer on the top of the water during the initial mixing. Removing the FAs (TOC = 15.4 mg/L) from the theoretical TOC calculations would account for the discrepancy between the theoretical and measured TOC readings. The TOC measurements increased with time of oxidation indicating that the FAs were being solubilized. The FAs could be solubilized by oxidation to more soluble compounds and by reactions with the solution to form soluble ionized salts.

The EPRI report likewise produced TOC results that increased with oxidative treatment. All of the E-stage O_3 / UV experiments tested for TOC analysis showed an increase of 61 mg/L to 160 mg/L in TOC after treatment. Similarly half the O_3 / H_2O_2 TOC results increased from 9 mg/L to 502 mg/L after oxidation [EPRI 1993]. This phenomenon was not accounted for in their report.

The color analysis was only completed for the actual E-stage wastewater experiments. The color of the E-stage and its percentage reduction is given in table

E - 6. The color reduction correlates well with the color reduction obtained in the EPRI report. The EPRI color reduction for the O₃ only experiments ranged from 57.5 to 73.1%, while in this research color reduction for the spiked E-stage experiments ranged from 48.3 to 68.0%. The unspiked E-stage experiments had color reductions of only 15.3 to 41.4%. The addition of the RFAs increased the color of the spiked E-stage by approximately 300 PCCU. Although the RFAs did not color the SW solutions, the double bonds of the RFAs increased the color of the E-stage effluent. The RFAs were oxidized by the O₃ reducing the color of the spiked E-stage proportionately.

7.0 CONCLUSIONS

Toxicity reduction of the RFAs in simulated wastewater was best achieved by O₃ only which produced a rapid molecular structure change (e.g., double bond cleavage and ring rupture) and oxygen addition to the RFAs. Radical oxidation did not produce the rapid structure changes that direct O₃ reaction did since most of the radicals were scavenged by bicarbonate and carbonate ions. Less than 2.3% of the OH· are believed to have reacted with the RFAs.

The experiments involving UV_{254nm} produced minor toxicity reductions or produced small increases in toxicity. The UV_{254nm} only experiment indicated that the UV_{254nm} light was producing photolyzed molecular products with higher toxicities than the starting RFAs.

The use of UV-vis absorbance at 240 nm is not a good indicator of resin acid destruction for even simulated water solutions only containing RFAs. A regression analysis determined that the UV_{240nm} reduction was not a significant descriptor of toxicity reduction with a R² of 0.0022. Therefore, no general equation for UV_{240nm} was derived. The ISA for the E-stage experiments is not a good correlation with toxicity reduction either. The ISA was only slightly reduced for varying toxicity reduction levels. UV absorbance at 250 nm may have some use as a quantitative indicator for the production of partial oxidative products which correlate with toxicity reduction.

Chemical Oxygen Demand tests for the simulated wastewater showed no significant change with oxidation. Total organic carbon analysis may indicate that the fatty acids were solubilized with oxidation.

7.1 Recommendations and Possible Future Work

1. A study comparing AOP processes for the low pH C-Stage, the final combined effluents, and mixtures of treated and untreated waste streams would prove useful in determining the best stage(s) to treat to reduce total effluent toxicity.
2. The biodegradability of the wastewater after treatment as by biological oxygen demand should be studied as biological treatment would follow any AOP treatment.
3. The Solid Phase Micro Extraction - GC/MS method still holds great promise in reducing time, materials and cost of Gas Chromatograph work. The pH effect on solubility and SPME absorption, along with other SPME tips ought to be researched.
4. Future studies involving RFAs would find it easier to use the sodium salts of the compounds as solubility seemed to affect the analytical results. This is especially true of the FAs. The FAs may want to be eliminated from future

experiments due to their low solubility, lower toxicity and the high degree of foaming associated with solutions containing them.

5. The toxicity increases in the RFA solution when exposed to UV_{254nm} should be studied further. The more toxic products of UV_{254nm} irradiation should be determined and characterized.

Appendix A - Experimental Data

O₃ Only Run April 28, 1997 Raw Data

Initial pH = 11.52, Initial O₃ input = 9.80 mg/SL

Foam produced, but manageable with silicon defoamer.

Run stopped after 3 min to settle foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	9.80	Sampled	16	5.14	
1	2.39		17	4.16	
2	0.42		18	4.33	
3	0.23	Foam Stop	19	4.39	
4	2.70		20	4.51	Sampled
5	0.76	Sampled	21	4.64	
6	0.49		22	4.75	
7	0.49		23	4.78	
8	0.51		24	4.83	
9	0.62		25	4.90	Sampled
10	0.92	Sampled	26	4.94	
11	1.27		27	4.96	
12	1.68		28	4.95	
13	2.17		29	5.01	
14	2.68		30	5.02	End of Run / Sampled
15	3.22	Stopped / Sampled	End	11.54	

Table A - 1. Data for O₃ only matrix experiment run.

O₃ / H₂O₂ Run April 28, 1997 Raw Data
 Initial pH = 11.45, Initial O₃ input = 10.33 mg/SL
 0.9 ml of 30% H₂O₂ added at 0 and 15 min.
 Large amounts of foam even with silicon defoamer.
 Run stopped at 1, 10, and 25 min to settle foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	10.33	Sampled	16	0.85	
1	2.51	Foam Stop	17	0.23	
2	4.46		18	0.19	
3	0.92		19	0.14	
4	0.26		20	0.14	Sampled
5	0.19	Sampled	21	0.14	
6	0.17		22	0.14	
7	0.18		23	0.14	
8	0.18		24	0.14	
9	0.18		25	0.14	Foam Stop / Sampled
10	0.18	Foam Stop / Sampled	26	2.20	
11	3.07		27	0.58	
12	0.40		28	0.22	
13	0.19		29	0.15	
14	0.17		30	0.15	End of Run / Sampled
15	0.18	Sampled / Added H ₂ O ₂	End	11.09	

Table A - 2. Data for O₃ / H₂O₂ matrix experiment run.

O₃ / UV_{254nm} Light Run May 2, 1997 Raw Data

Initial pH = 11.48, Initial O₃ input = 10.44 mg/SL

Little foam produced. Run not stopped for foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	10.44	Sampled	16	4.20	
1	2.03		17	2.72	
2	0.39		18	2.88	
3	0.15		19	3.19	
4	0.13		20	3.48	Sampled
5	0.16	Sampled	21	3.79	
6	0.18		22	4.04	
7	0.22		23	4.30	
8	0.27		24	4.52	
9	0.35		25	4.63	Sampled
10	0.43	Stopped / Sampled	26	4.70	
11	0.47		27	4.73	
12	0.55		28	4.74	
13	0.78		29	4.72	
14	0.94		30	4.76	End of Run / Sampled
15	1.20	Sampled	End	11.90	

Table A - 3. Data for O₃ / UV_{254nm} light matrix experiment run.

O₃ / H₂O₂ / UV_{254nm} Light Run May 2, 1997 Raw Data

Initial pH = 11.35, Initial O₃ input = 10.18 mg/SL

0.9 ml of 30% H₂O₂ added at 0 and 27 min.

Large amounts of foam even with silicon defoamer.

Run stopped after 7 min to settle foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	10.18	Sampled / H ₂ O ₂ added	16	2.88	
1	2.74		17	0.65	
2	0.43		18	0.49	
3	0.17		19	0.55	
4	0.17		20	0.77	Sampled
5	0.17	Sampled	21	0.80	
6	0.18		22	0.97	
7	0.18	Foam Stop	23	1.25	
8	1.83		24	1.66	
9	0.32		25	1.98	Sampled
10	0.17	Sampled	26	2.43	
11	0.18		27	2.70	H ₂ O ₂ added
12	0.19		28	2.23	
13	0.18		29	1.32	
14	0.19		30	1.00	End of Run / Sampled
15	0.20	Stopped / Sampled	End	10.49	

Table A - 4. Data for O₃ / H₂O₂ / UV_{254nm} light matrix experiment run.

O₃ Only Repeat Run May 28, 1997 Raw Data

Initial pH = 11.48, Initial O₃ input = 9.80 mg/SL

Large amounts of foam even with silicon defoamer.

Run stopped at 1.5, 2.5, 5, 7.5, and 10 min to settle foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	9.80	Sampled	31	5.88	
1	2.45	Foam Stop	32	5.94	
2	7.21	Foam Stop	33	5.98	
3	6.37		34	5.98	
4	1.04		35	5.98	Sampled
5	0.20	Foam Stop / Sampled	36	6.06	
6	7.70		37	6.09	
7	0.80	Foam Stop	38	6.15	
8	8.39		39	6.24	
9	1.33		40	6.33	Sampled
10	0.25	Foam Stop / Sampled	41	6.39	
11	3.24		42	6.37	
12	0.55		43	6.37	
13	0.30		44	6.32	
14	0.35		45	6.35	Sampled
15	0.48	Sampled	46	6.41	
16	0.83		47	6.39	
17	1.43		48	6.40	
18	2.04		49	6.47	
19	2.79		50	6.56	Sampled
20	3.50	Sampled	51	6.56	
21	4.03		52	6.57	
22	4.43		53	6.62	
23	4.73		54	6.56	
24	4.97		55	6.54	Sampled
25	5.24	Sampled	56	6.59	
26	5.41		57	6.60	
27	5.62		58	6.59	
28	5.71		59	6.63	
29	5.79		60	6.61	End of Run / Sampled
30	5.83	Sampled	End	11.35	

Table A - 5. Data for O₃ only repeat run.

O₃ / H₂O₂ Repeat Run May 28, 1997 Raw Data
 Initial pH = 11.84, Initial O₃ input = 9.89 mg/SL
 Large amounts of foam even with silicon defoamer.
 Run stopped at 5 and 10 min to settle foam.

Time	O ₃ Out	Notes	Time	O ₃ Out	Notes
0	9.89	Sampled / Added H ₂ O ₂	31	0.27	
1	1.55		32	0.25	
2	0.58		33	0.23	
3	0.43		34	0.24	
4	0.41		35	0.25	Sampled
5	0.40	Foam Stop / Sampled	36	0.25	
6	5.01		37	0.30	
7	0.77		38	0.31	
8	0.36		39	0.30	
9	0.33		40	0.31	Sampled
10	0.33	Foam Stop / Sampled	41	0.32	
11	1.66		42	0.33	
12	0.40		43	0.34	
13	0.31		44	0.37	
14	0.29		45	0.39	Sampled
15	0.28	Sampled	46	0.40	
16	0.28		47	0.37	
17	0.28	H ₂ O ₂ added	48	0.29	
18	3.21		49	0.27	
19	0.50		50	0.27	Sampled
20	0.31	Sampled	51	0.26	
21	0.25		52	0.27	
22	0.24		53	0.28	
23	0.24		54	0.27	
24	0.24		55	0.29	Sampled
25	0.23	Sampled	56	0.30	
26	0.23		57	0.31	
27	0.24		58	0.32	
28	0.24		59	0.32	
29	0.25		60	0.35	End of Run / Sampled
30	0.26	Sampled	End	10.07	

Table A - 6. Data for O₃ / H₂O₂ repeat run.

Appendix B - Ozone Calculations

<u>OZONE IN</u>		<u>APPLIED</u>			
<u>TIME (min)</u>	<u>OZONE (mg/SL)</u>	<u>OZONE (mg/L)</u>			
0.00	9.80	0.00			
15.00		64.02			
30.00	11.54	128.04			
<u>OZONE OUT</u>		<u>OZONE</u>	<u>OZONE</u>	<u>TOTAL</u>	<u>OZONE</u>
<u>TIME</u>	<u>READING</u>	<u>OUT</u>	<u>OZONE OUT</u>	<u>TRANSFERRED</u>	
min	mg/SL	mg	mg	mg/L	
0.00	0.00				
5.00	0.76	3.80	3.80	20.58	
10.00	0.92	8.40	12.20	40.24	
15.00	3.22	20.70	32.90	57.44	
20.00	4.51	38.65	71.55	71.05	
25.00	4.90	47.05	118.60	82.98	
30.00	5.02	49.60	168.20	94.40	

Table B - 1. Ozone calculations for O₃ only matrix experiment run.

Notes: Ozone out is calculated by multiplying the average ozone reading by the five minute time period of that average reading. Total ozone out is the sum of the ozone out reading up to that time. Ozone input is equal to the average of the ozone input readings (at time = 0 and 30 min) multiplied by 2 SL/min and the time of ozonation. Ozone transferred is equal to the total ozone out subtracted from the ozone input. Ozone applied and transferred values are given in mg/L by dividing the O₃ values (mg) by the volume of the water samples (5 L).

Time (Min)	O ₃ / H ₂ O ₂ run O ₃ Trans. (mg/L)	O ₃ / UV _{254nm} run O ₃ Trans. (mg/L)	O ₃ / H ₂ O ₂ / UV _{254nm} run O ₃ Trans. (mg/L)	O ₃ only repeat run O ₃ Trans. (mg/L)	O ₃ / H ₂ O ₂ repeat run. O ₃ Trans. (mg/L)
5	21.23	22.18	20.50	20.95	19.56
10	42.28	43.93	40.83	41.65	38.79
15	63.34	64.64	61.13	62.07	58.14
20	84.44	82.30	80.83	79.24	77.51
25	105.58	96.53	98.75	91.65	96.93
30	126.71	109.48	116.44	101.73	116.40
35				111.07	135.85
40				119.91	155.25
45				128.38	174.51
50				136.62	193.81
55				144.67	213.21
60				152.67	232.53

Table B - 2. Ozone transferred for remaining matrix experiments.

Appendix C - Regression Analysis of UV_{240nm} Reductions

	Toxicity Reduction	UV _{240nm} Reduction		Toxicity Reduction	UV _{240nm} Reduction
H ₂ O ₂ 0	0.00	0.00	O ₃ / UV 0	0.00	0.00
H ₂ O ₂ 15	33.12	72.23	O ₃ / UV 15	-1.65	74.27
H ₂ O ₂ 30	62.17	72.93	O ₃ / UV 30	28.53	70.95
H ₂ O ₂ 2 0	0.00	0.00	Spiked 1 0	0.00	0.00
H ₂ O ₂ 2 15	57.76	53.03	Spiked 1 15	83.15	19.10
H ₂ O ₂ 2 30	65.15	54.67	Spiked 1 30	84.60	25.80
H ₂ O ₂ 2 45	70.22	51.82			
H ₂ O ₂ 2 60	75.67	48.88	Spiked 2 0	0.00	0.00
			Spiked 2 15	79.11	16.30
O ₃ 0	0.00	0.00	Spiked 2 30	85.56	23.90
O ₃ 15	57.28	64.00			
O ₃ 30	89.15	65.10	Unspiked 1 0	0.00	0.00
			Unspiked 1 15	9.22	12.60
O ₃ 2 0	0.00	0.00	Unspiked 1 30	24.40	16.60
O ₃ 2 15	63.64	53.04			
O ₃ 2 30	94.05	46.86	Unspiked 2 0	0.00	0.00
O ₃ 2 45	95.04	44.73	Unspiked 2 15	34.20	6.20
O ₃ 2 60	96.72	49.31	Unspiked 2 30	45.42	14.30
O ₃ / H ₂ O ₂ / UV 0	0.00	0.00	UV Only 0	0.00	0.00
O ₃ / H ₂ O ₂ / UV 15	5.90	59.17	UV Only 5	-35.60	10.40
O ₃ / H ₂ O ₂ / UV 30	25.55	56.47	UV Only 10	-13.80	18.00
			UV Only 15	14.30	28.00
			UV Only 30	16.80	48.00

Table C-1. Toxicity reduction and UV_{240nm} reduction for all experiments.

O₃ Only Regression Output:

Constant	-0.2609
Std Err of Y Est	21.6509
R Squared	0.8851
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	1.1403
Std Err of Coef.	0.4108

O₃ Only Repeat Run Regression Output:

Constant	4.2210
Std Err of Y Est	21.2902
R Squared	0.8018
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	1.6930
Std Err of Coef.	0.4860

O₃ / H₂O₂ Regression Output:

Constant	-0.1379
Std Err of Y Est	20.2158
R Squared	0.7888
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	0.6593
Std Err of Coef.	0.3411

O₃ / H₂O₂ Repeat Run Regression Output:

Constant	1.2426
Std Err of Y Est	10.1786
R Squared	0.9179
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	1.2600
Std Err of Coef.	0.2175

O₃ / H₂O₂ / UV_{254nm} Regression Output:

Constant	0.4752
Std Err of Y Est	14.4021
R Squared	0.4205
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	0.2596
Std Err of Coef.	0.3048

O₃ / UV_{254nm} Regression Output:

Constant	0.7029
Std Err of Y Est	21.7580
R Squared	0.1779
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	0.1706
Std Err of Coef.	0.3667

Spiked E-stage Regression Output:

Constant	3.2985
Std Err of Y Est	16.1443
R Squared	0.9444
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	3.5157
Std Err of Coef.	0.8527

Repeat Spiked E-stage Regression Output:

Constant	4.2143
Std Err of Y Est	16.5860
R Squared	0.9394
No. of Observations	3
Degrees of Freedom	1
X Coefficient(s)	3.7818
Std Err of Coef.	0.9604

<u>Unspiked E-Stage Regression Output:</u>		<u>Unspiked Repeat Regression Output:</u>	
Constant	-1.3714	Constant	5.4463
Std Err of Y Est	7.2753	Std Err of Y Est	11.8106
R Squared	0.8257	R Squared	0.8754
No. of Observations	3	No. of Observations	3
Degrees of Freedom	1	Degrees of Freedom	1
X Coefficient(s)	1.2923	X Coefficient(s)	3.0869
Std Err of Coef.	0.5938	Std Err of Coef.	1.1646

<u>UV_{254nm} Only Regression Output:</u>	
Constant	-18.7755
Std Err of Y Est	19.7919
R Squared	0.3741
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	0.7239
Std Err of Coef.	0.5406

<u>Combined Results Regression Output:</u>	
Constant	51.7764
Std Err of Y Est	32.5097
R Squared	0.0022
No. of Observations	25
Degrees of Freedom	23
X Coefficient(s)	0.0649
Std Err of Coef.	0.2853

Table C-2. Regression output for individual experiments and combined results.

Appendix D - Analytical Results

COD Results	A 420	unadjusted mg/L	adjusted mg/L
MQ	0.513	4	0
O ₃ - 0	0.068	205	201
O ₃ - 15	0.097	192	188
O ₃ - 30	0.072	203	199
H ₂ O ₂ - 0	0.111	186	181
H ₂ O ₂ - 15	0.104	189	184
H ₂ O ₂ - 30	0.104	189	184
UV _{254nm} - 0	0.068	205	201
UV _{254nm} - 15	0.075	202	198
UV _{254nm} - 30	0.077	201	197
H ₂ O ₂ /UV _{254nm} - 0	0.068	205	201
H ₂ O ₂ /UV _{254nm} - 15	0.073	203	198
H ₂ O ₂ /UV _{254nm} - 30	0.073	203	198
O ₃ - 2 - 0	0.071	204	199
O ₃ - 2 - 15	0.085	197	193
O ₃ - 2 - 30	0.081	199	195
O ₃ - 2 - 45	0.084	198	193
O ₃ - 2 - 60	0.077	201	197
H ₂ O ₂ - 2 - 0	0.104	189	184
H ₂ O ₂ - 2 - 15	0.098	191	187
H ₂ O ₂ - 2 - 30	0.107	187	183
H ₂ O ₂ - 2 - 45	0.107	187	183
H ₂ O ₂ - 2 - 60	0.107	187	183

COD(mg/L) = - 450.945 * A420 + 235.6868 - MQ value.

Table D - 1. Chemical Oxygen Demand (COD) results.

	TOC Reading		
	0.507	Ave MQ	
MQ 2	0.529	0.5	
MQ 3	0.484		
MQ 4	0.48		
		ppm -MQ	Factor
5 ppm Standard	4.457	3.96	1.26
10 ppm Standard	10.62	10.12	0.99
20 ppm Standard	21.23	20.73	0.96

30 ppm Standard	32.7	32.20	0.93	
	TOC Reading	TOC - MQ	Factor Adjusted	Actual
O ₃ - 0	10.86	10.36	10.24	51.19
O ₃ - 5	12.16	11.66	11.52	57.61
O ₃ - 10	12.49	11.99	11.85	59.24
O ₃ - 15	13.32	12.82	12.67	63.34
O ₃ - 20	13.86	13.36	13.20	66.01
O ₃ - 25	14.35	13.85	13.69	68.43
O ₃ - 30	14.33	13.83	13.67	68.33
H ₂ O ₂ - 0	22.53	22.03	21.77	108.84
H ₂ O ₂ - 5	19.70	19.20	18.97	94.86
H ₂ O ₂ - 10	21.63	21.13	20.88	104.40
H ₂ O ₂ - 15	20.95	20.45	20.21	101.04
H ₂ O ₂ - 20	21.22	20.72	20.47	102.37
H ₂ O ₂ - 25	21.74	21.24	20.99	104.94
H ₂ O ₂ - 30	22.50	22.00	21.74	108.70
UV _{254nm} - 0	10.13	9.63	9.52	47.58
UV _{254nm} - 5	9.48	8.98	8.87	44.36
UV _{254nm} - 10	10.07	9.57	9.46	47.28
UV _{254nm} - 15	10.04	9.54	9.43	47.13
UV _{254nm} - 20	10.17	9.67	9.56	47.78
UV _{254nm} - 25	10.97	10.47	10.35	51.73
UV _{254nm} - 30	11.46	10.96	10.83	54.15
H ₂ O ₂ /UV _{254nm} - 0	11.70	11.20	11.07	55.34
H ₂ O ₂ /UV _{254nm} - 5	10.38	9.88	9.76	48.81
H ₂ O ₂ /UV _{254nm} - 10	11.17	10.67	10.54	52.72
H ₂ O ₂ /UV _{254nm} - 15	11.76	11.26	11.13	55.63
H ₂ O ₂ /UV _{254nm} - 20	13.69	13.19	13.03	65.17
H ₂ O ₂ /UV _{254nm} - 25	13.70	13.20	13.04	65.22
H ₂ O ₂ /UV _{254nm} - 30	14.93	14.43	14.26	71.29
O ₃ Run 2 - 0	9.31	8.91	9.30	46.52
O ₃ Run 2 - 5	10.66	10.26	10.72	53.59
O ₃ Run 2 - 10	11.50	11.10	11.60	57.98
O ₃ Run 2 - 15	13.09	12.69	13.26	66.28
O ₃ Run 2 - 20	11.50	11.10	11.60	57.98
O ₃ Run 2 - 25	15.21	14.81	15.47	77.36
O ₃ Run 2 - 30	15.14	14.74	15.40	76.99
O ₃ Run 2 - 35	15.51	15.11	15.78	78.92
O ₃ Run 2 - 40	16.36	15.96	16.67	83.36
O ₃ Run 2 - 45	15.51	15.11	15.78	78.92

O ₃ Run 2 - 50	15.84	15.44	16.13	80.65
O ₃ Run 2 - 55	16.04	15.64	16.34	81.69
O ₃ Run 2 - 60	16.57	16.17	16.89	84.46
H ₂ O ₂ Run 2 - 0	16.45	16.05	16.77	83.85
H ₂ O ₂ Run 2 - 5	14.64	14.24	14.88	74.40
H ₂ O ₂ Run 2 - 10	15.38	14.98	15.65	78.25
H ₂ O ₂ Run 2 - 15	15.70	15.30	15.98	79.90
H ₂ O ₂ Run 2 - 20	16.46	16.06	16.78	83.90
H ₂ O ₂ Run 2 - 25	16.73	16.33	17.06	85.30
H ₂ O ₂ Run 2 - 30	17.39	16.99	17.75	88.75
H ₂ O ₂ Run 2 - 35	17.77	17.38	18.15	90.75
H ₂ O ₂ Run 2 - 40	17.33	16.93	17.69	88.45
H ₂ O ₂ Run 2 - 45	17.99	17.59	18.37	91.85
H ₂ O ₂ Run 2 - 50	18.15	17.75	18.54	92.70
H ₂ O ₂ Run 2 - 55	18.63	18.23	19.04	95.20
H ₂ O ₂ Run 2 - 60	18.23	17.83	18.63	93.15

Table D - 2. Total Organic Carbon (TOC) results.

Ozone Run UV Absorbance

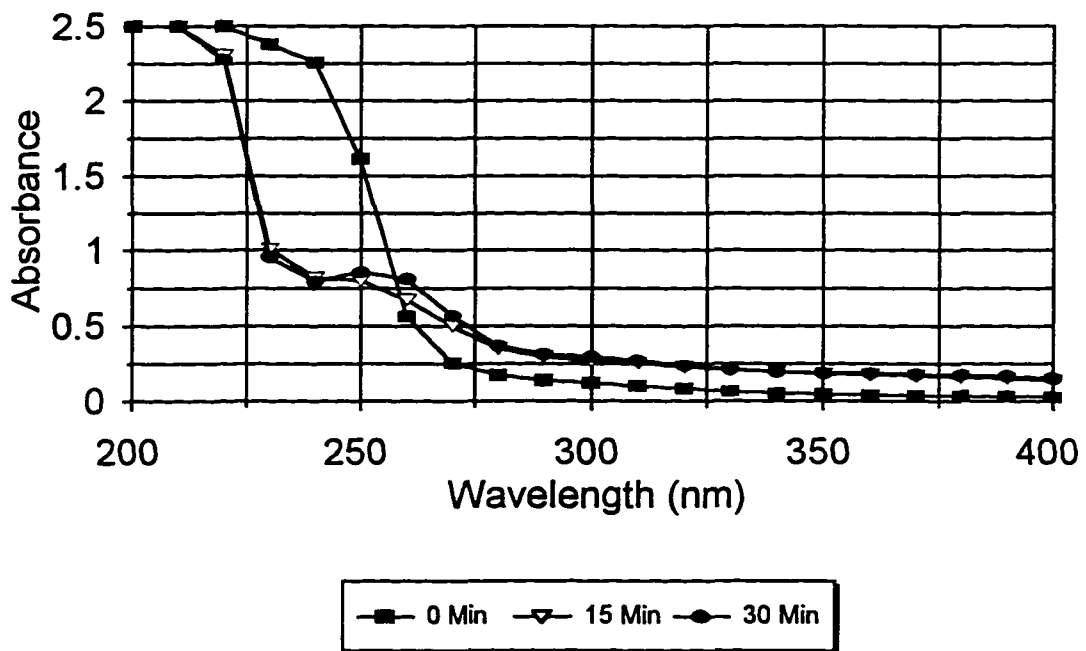


Figure D - 1. UV results for O₃ only run.

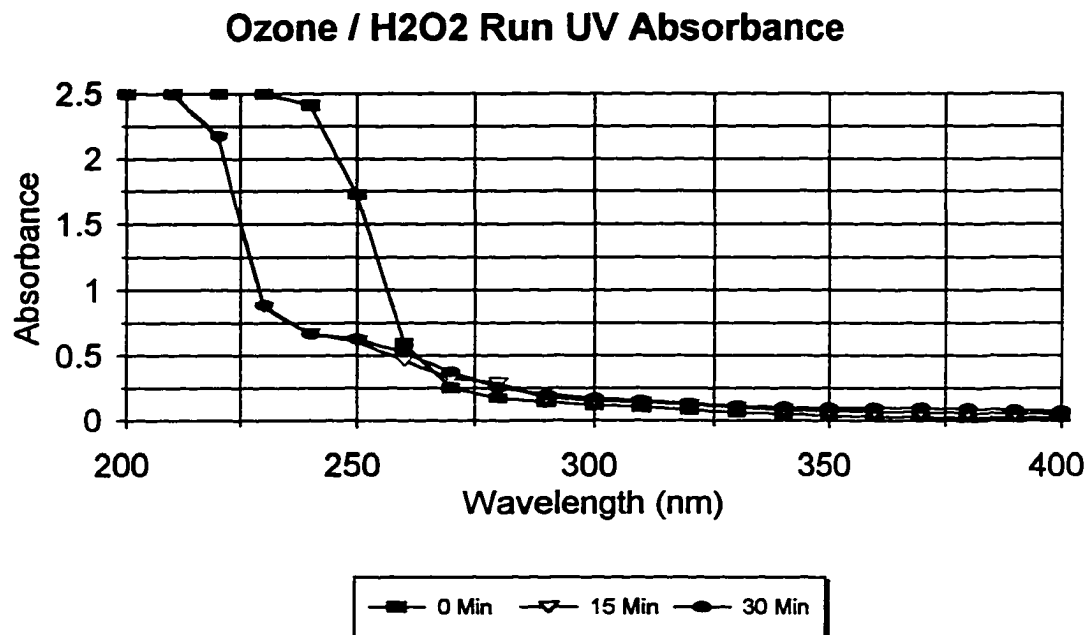


Figure D - 2. UV results for O₃ / H₂O₂ run.

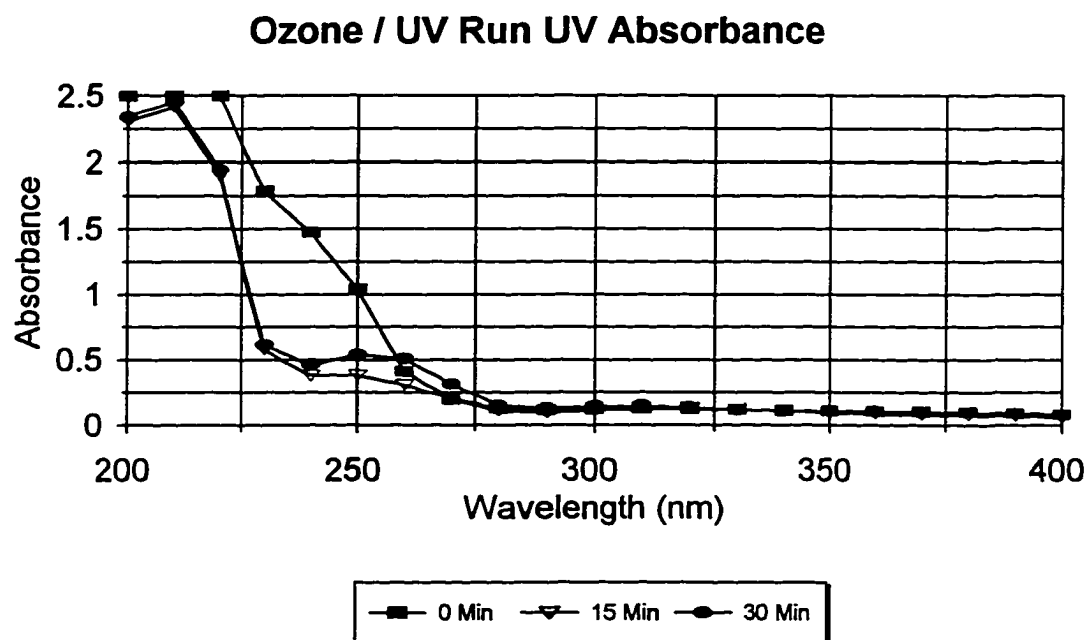


Figure D - 3. UV results for O₃ / UV_{254nm} light run.

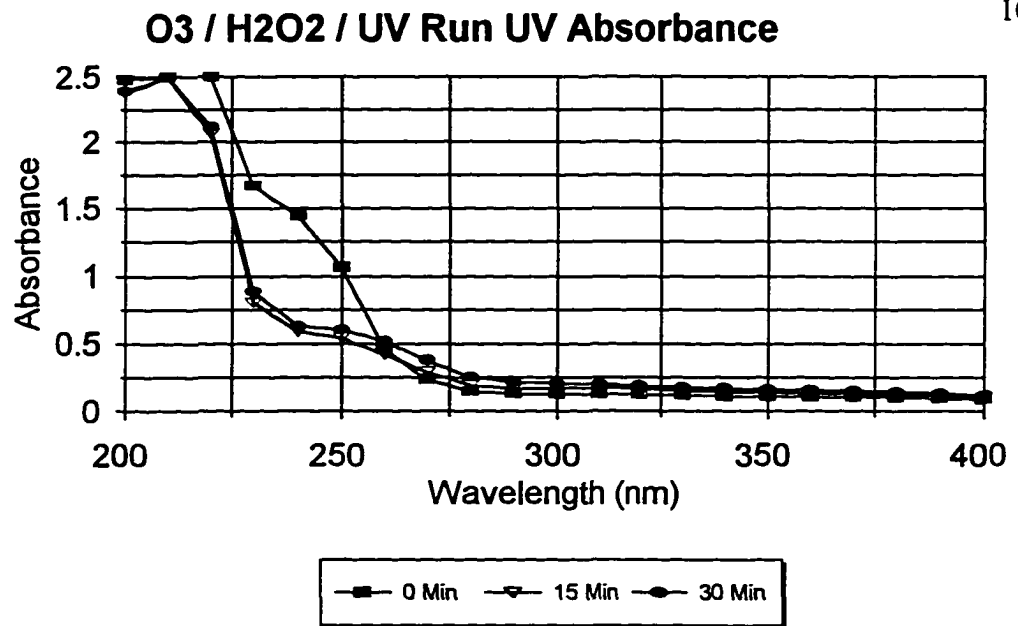


Figure D - 4. UV results for O₃ / H₂O₂ / UV_{254nm} light run.

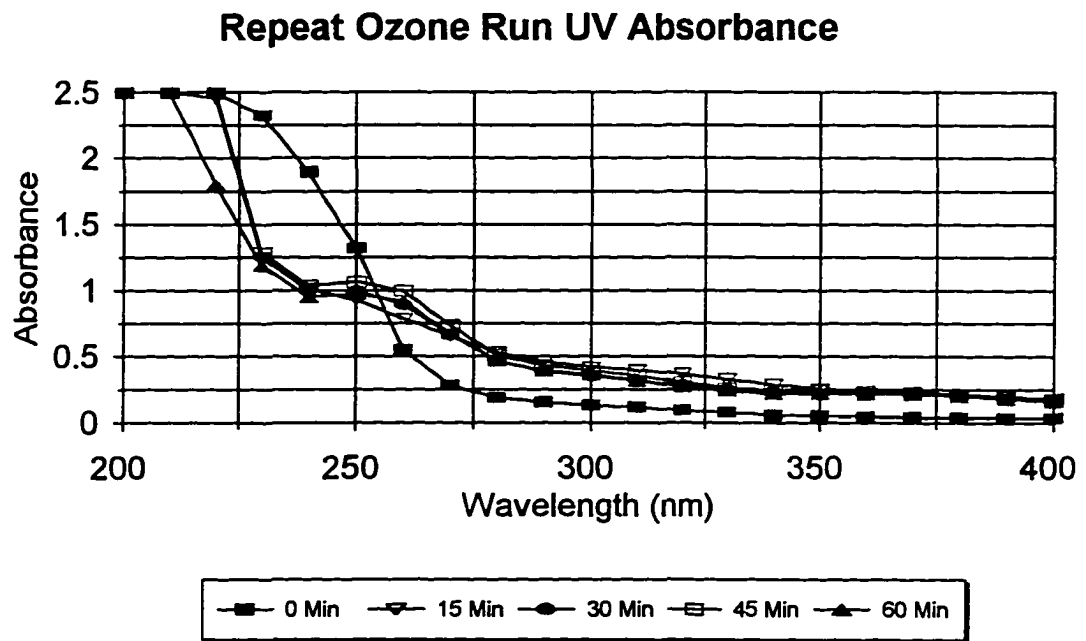


Figure D - 5. UV results for O₃ only repeat run.

Repeat O3 / H2O2 Run UV Absorbance

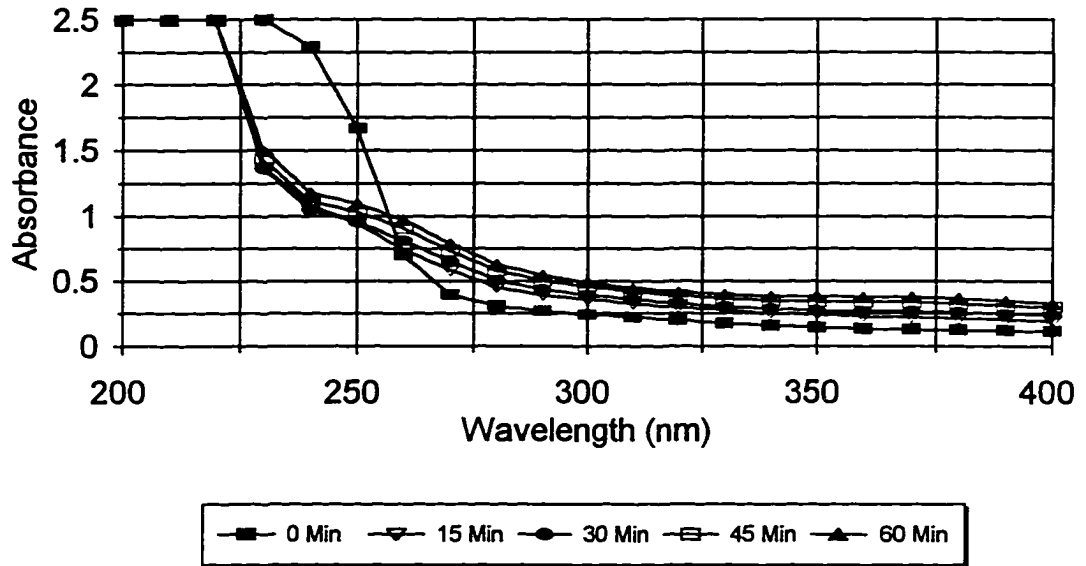


Figure D - 6. UV results for O₃ / H₂O₂ repeat run.

**UV Scans for Spiked
E-stage and Simulated Wastewater**

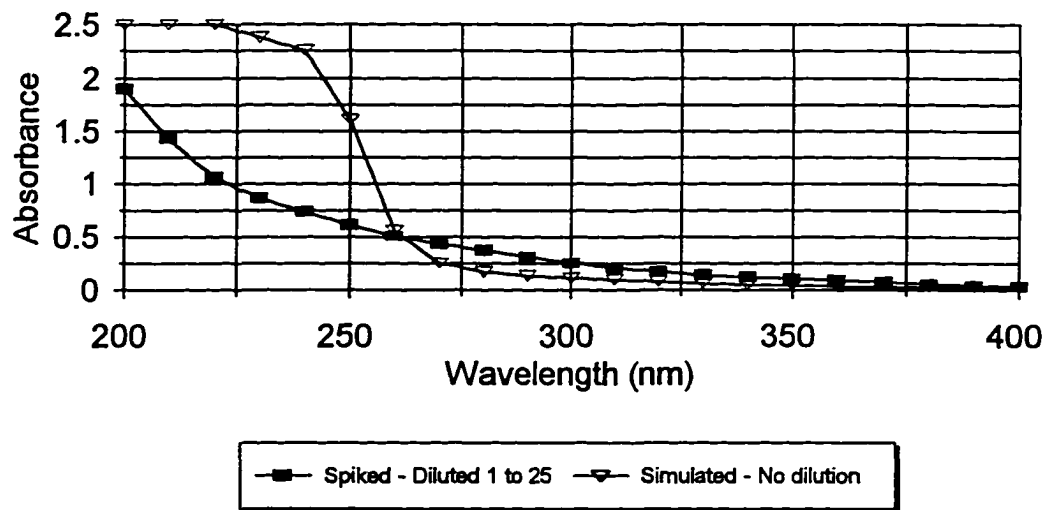


Figure D - 7. UV scan comparison for spiked E-stage and simulated wastewater feeds.

Appendix E - E-stage Results

Spiked E-stage Run Raw Data

60 mg/L Abietic, 20 mg/L Dehydroabietic, 10 mg/L Oleic, 10 mg/L Linoleic

Initial pH = 12.40, O₃ input = 9.61 mg/SL.

Run stopped due to foam at 12 and 15 min.

Time	O ₃	Notes	Time	O ₃	Notes
0	9.61	Sampled	16	2.04	
1	2.14		17	0.67	
2	0.38		18	0.30	
3	0.24		19	0.30	
4	0.23		20	0.31	Sampled
5	0.24	Sampled	21	0.30	
6	0.24		22	0.29	
7	0.24		23	0.29	
8	0.24		24	0.27	
9	0.24		25	0.28	Sampled
10	0.23	Sampled	26	0.29	
11	0.23		27	0.29	
12	0.23	Foam Stop	28	0.30	
13	1.20		29	0.30	
14	0.37		30	0.29	End of Run / Sampled
15	0.22	Stopped / Sampled	End	10.79	

Table E - 1. Data for spiked E-stage run.

Spiked E-stage Repeat Run Raw Data

60 mg/L Abietic, 20 mg/L Dehydroabietic, 10 mg/L Oleic, 10 mg/L Linoleic

Initial pH = 12.37, O₃ input = 10.53 mg/SL.

Run stopped due to foam at 11 and 15 min.

Time	O ₃	Notes	Time	O ₃	Notes
0	10.53	Sampled	16	1.03	
1	1.14		17	0.18	
2	0.21		18	0.15	
3	0.14		19	0.13	
4	0.14		20	0.36	Sampled
5	0.13	Sampled	21	0.29	
6	0.13		22	0.28	
7	0.13		23	0.28	
8	0.13		24	0.30	
9	0.14		25	0.31	Sampled
10	0.14	Sampled	26	0.34	
11	0.14	Foam Stop	27	0.35	
12	2.24		28	0.37	
13	0.35		29	0.38	
14	0.17		30	0.40	End of Run / Sampled
15	0.14	Stopped / Sampled	End	9.85	

Table E - 2. Data for spiked E-stage repeat run.

Unspiked E-stage Run Raw Data
Initial pH = 12.25, O₃ input = 10.24 mg/SL

Time	O ₃	Notes	Time	O ₃	Notes
0	10.24	Sampled	16	0.28	
1	2.73		17	0.31	
2	0.45		18	0.34	
3	0.20		19	0.37	
4	0.18		20	0.39	Sampled
5	0.20	Sampled	21	0.42	
6	0.20		22	0.43	
7	0.21		23	0.46	
8	0.21		24	0.49	
9	0.23		25	0.51	Sampled
10	0.23	Sampled	26	0.54	
11	0.24		27	0.55	
12	0.26		28	0.57	
13	0.26		29	0.59	
14	0.27		30	0.63	End of Run / Sampled
15	0.27	Sampled	End	10.78	

Table E - 3. Data for unspiked E-stage run.

Unspiked E-stage Repeat Run Raw Data

Initial pH = 12.18, O₃ input = 9.79 mg/SL

Time	O ₃	Notes	Time	O ₃	Notes
0	9.79	Sampled	16	0.28	
1	2.30		17	0.31	
2	0.25		18	0.32	
3	0.20		19	0.35	
4	0.13		20	0.37	Sampled
5	0.14	Sampled	21	0.39	
6	0.15		22	0.42	
7	0.15		23	0.44	
8	0.17		24	0.45	
9	0.18		25	0.46	Sampled
10	0.19	Sampled	26	0.49	
11	0.21		27	0.52	
12	0.22		28	0.54	
13	0.23		29	0.57	
14	0.26		30	0.60	End of Run / Sampled
15	0.27	Sampled	End	11.13	

Table E - 4. Data for unspiked E-stage repeat run.

Time (min)	Spiked E-stage O ₃ Trans. (mg/L)	Spiked E-stage Repeat O ₃ Trans. (mg/L)	Unspiked E-stage O ₃ Trans. (mg/L)	Unspiked E-stage Repeat O ₃ Trans. (mg/L)
5	20.16	20.25	20.82	20.78
10	40.09	40.36	41.41	41.37
15	60.04	60.46	61.93	61.83
20	79.91	80.34	82.29	82.12
25	99.72	100.05	102.41	102.22
30	119.55	119.72	122.29	122.08

Table E - 5. Ozone transferred for E-stage runs.

Spiked E-Stage UV Scans

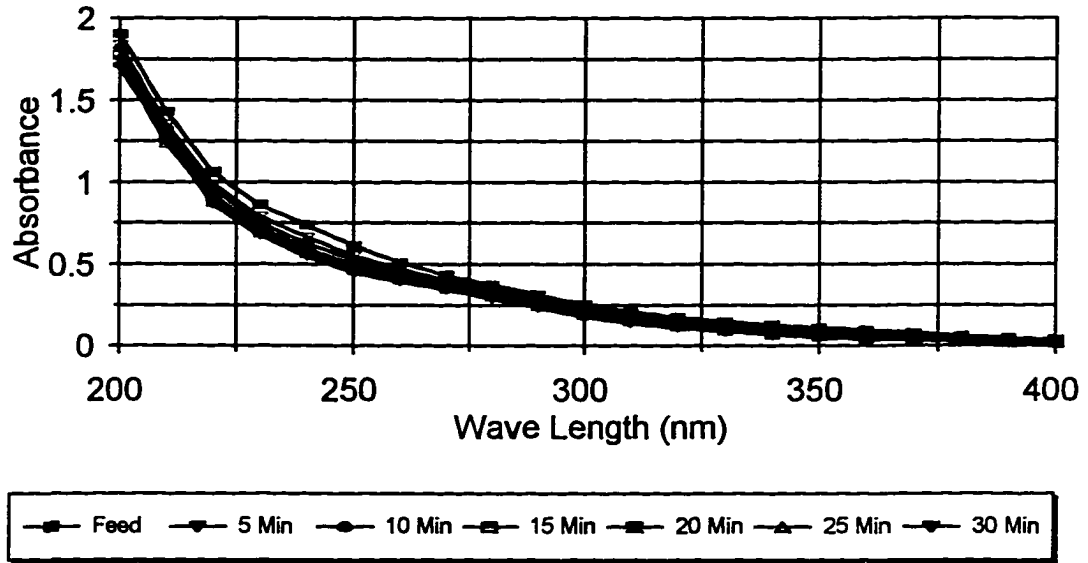


Figure E - 1. UV scan for spiked E-stage run.

Spiked E-Stage Repeat Run UV Scans

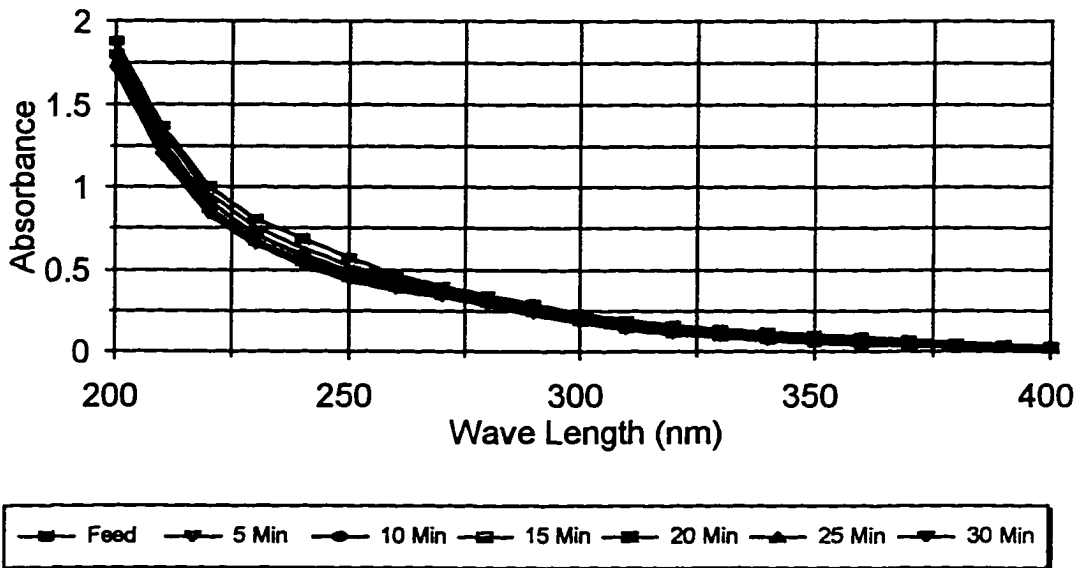


Figure E - 2. UV scan for spiked E-stage repeat run.

Unspiked E-Stage Run UV Scans

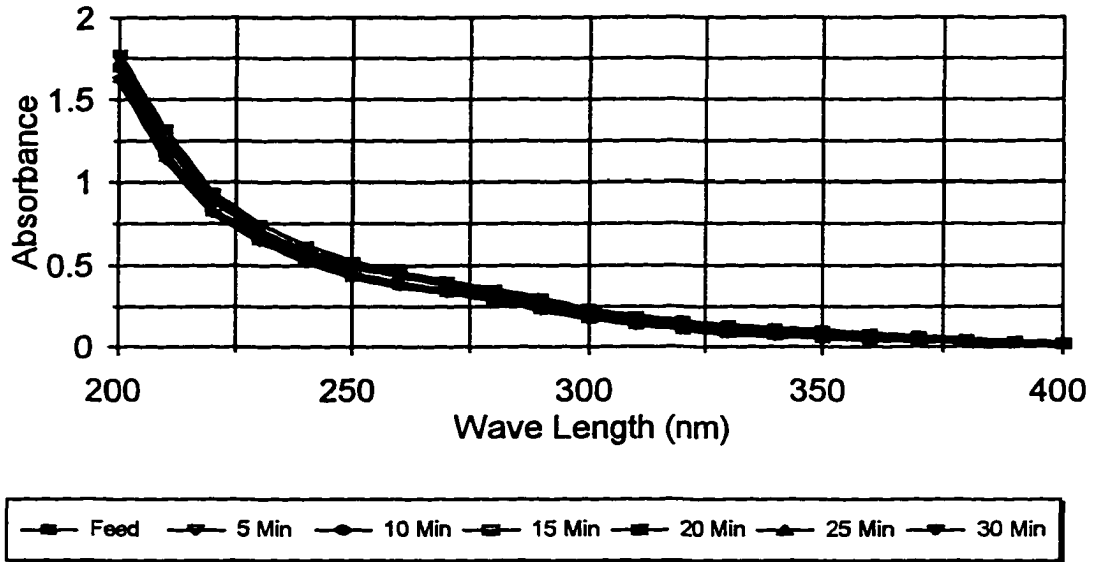


Figure E - 3. UV scan for unspiked E-stage run.

Unspiked E-Stage Repeat Run UV Scans

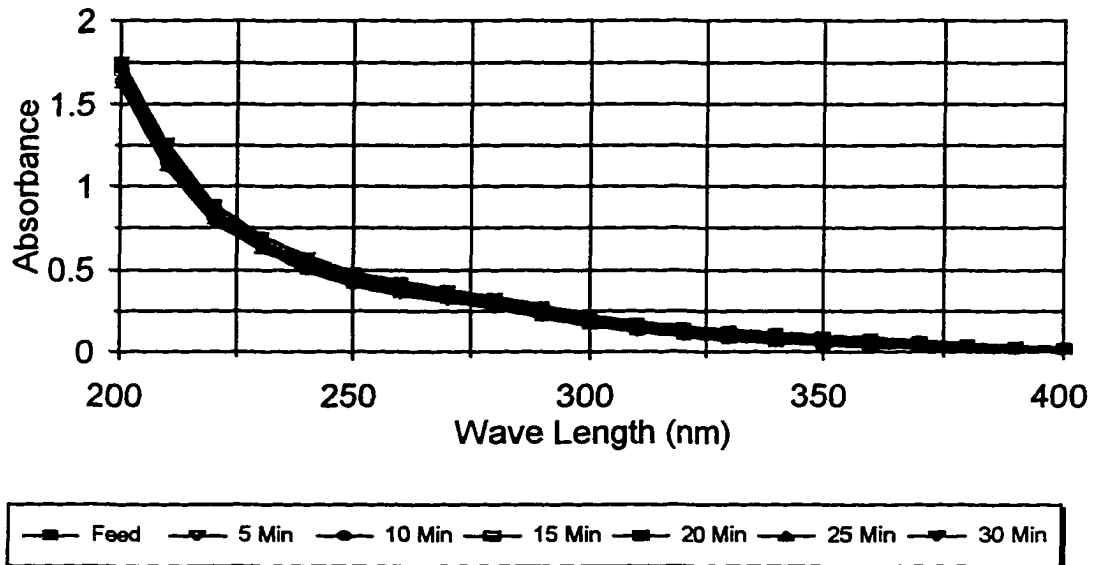


Figure E - 4. UV scan for unspiked E-stage repeat run.

	465 abs.	COD	% Red	620 abs.	Color	% Red.		
S1 Feed	0.558	1707	0.0	0.242	834	0.0		
S1 15 min	0.514	1570	8.0	0.125	431	48.3		
S1 30 min	0.495	1510	11.5	0.084	290	65.3		
S2 Feed	0.551	1686	0.0	0.272	938	0.0		
S2 15 min	0.504	1539	8.7	0.129	445	52.6		
S2 30 min	0.490	1495	11.3	0.087	300	68.0		
U1 Feed	0.492	1501	0.0	0.190	655	0.0		
U1 15 min	0.468	1426	5.0	0.161	555	15.3		
U1 30 min	0.454	1382	7.9	0.120	414	36.8		
U2 Feed	0.475	1448	0.0	0.169	583	0.0		
U2 15 min	0.461	1404	3.0	0.140	483	17.2		
U2 30 min	0.451	1373	5.2	0.099	341	41.4		
						Value	- MQ	X 25
TOC	Value				S1 15 min	35.70	25.82	645
MQ	2.204				S1 20 min	34.87	25.18	630
MQ	1.913				S1 25 min	34.73	25.07	627
MQ	1.795	- MQ			S1 30 min	35.47	25.64	641
5	10.36	8.39			U2 Feed	32.35	23.25	581
10	17.21	15.24			U2 5 min	33.36	24.02	601
20	30.20	28.23			U2 10 min	34.55	24.94	623
30	43.02	41.05	X 25		U2 15 min	33.16	23.87	597
U1 Feed	33.51	24.14	603		U2 20 min	33.00	23.75	594
U1 5 min	34.48	24.88	622		U2 25 min	33.74	24.31	608
U1 10 min	36.11	26.13	653		U2 30 min	33.41	24.06	602
U1 15 min	34.54	24.93	623		S2 Feed	35.98	26.03	651
U1 20 min	35.06	25.33	633		S2 5 min	36.79	26.65	666
U1 25 min	34.04	24.54	614		S2 10 min	34.82	25.14	629
U1 30 min	35.93	25.99	650		S2 15 min	34.26	24.71	618
S1 Feed	37.46	27.17	679		S2 20 min	33.37	24.03	601
S1 5 min	36.28	26.26	657		S2 25 min	34.21	24.67	617
S1 10 min	35.40	25.59	640		S2 30 min	33.72	24.30	607

Table E - 6. COD, Color, and TOC data for E-stage runs.

Appendix F - SPME / GC - MS Results

Plots of the GC/MS results are given as figures F- 1 through F- 6. The Solid Phase MicroExtraction (SPME) method did not produce high quality data. The chromatograph peaks were very small and difficult to distinguish from the background noise. One peak was quite distinct in the plot for the O₃ only run at 15 min. The peak at approximately 28 min was attributed to the production of a partial oxidative product. It is not known what specific product caused the peak.

It is believed that the small peaks were due to the solubility of the RFAs and their inability to adsorb to the SPME syringe. The syringe tip used in the experiments was a 100 um polydimethylsiloxane coated tip designed for mid to non-polar semivolatiles. At pH's of greater than 11, the RFAs were present in their highly soluble sodium salt forms. These salts did not adsorb onto the syringe tip and no peaks were observed at these high pHs. When the pH was lowered to below 4, the RFAs were present as free carboxylic acids. The free acids adsorbed onto the syringe tip, but most of it precipitated out of solution due to their low solubility. The results of the GC/MS work are questionable due to the solubility problem.

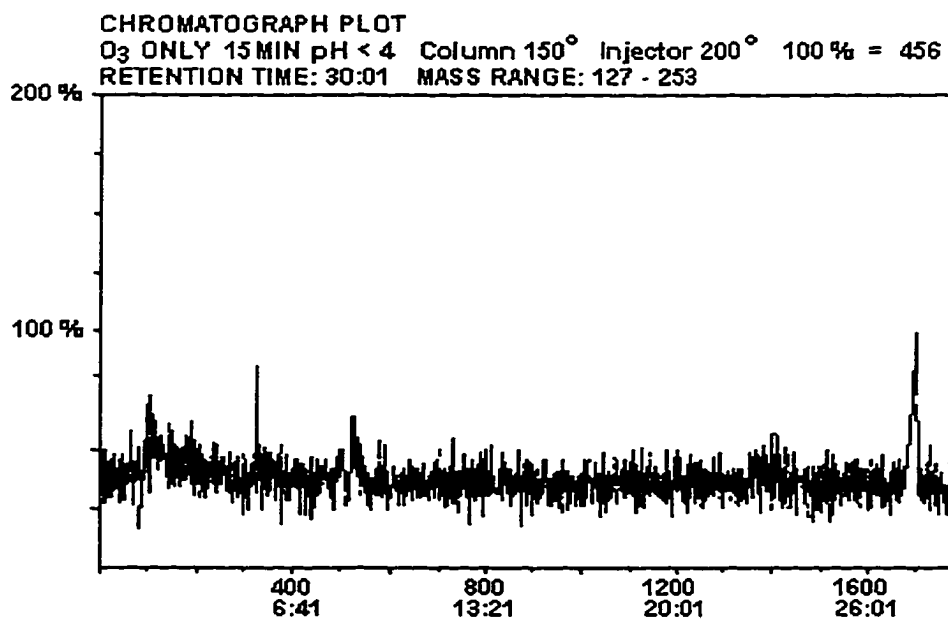
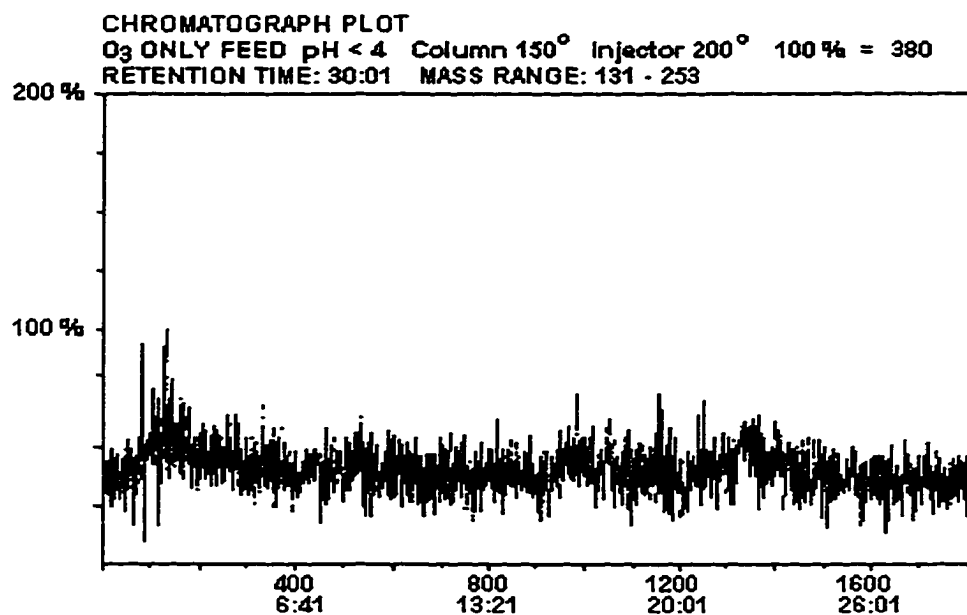


Figure F - 1. GC/MS plot for O₃ only feed and 15 min results.

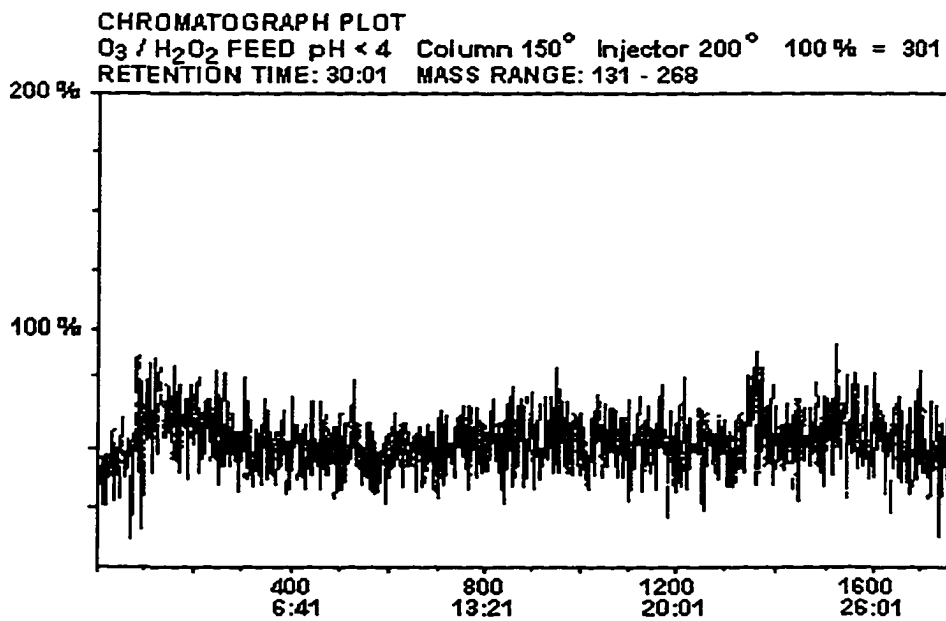
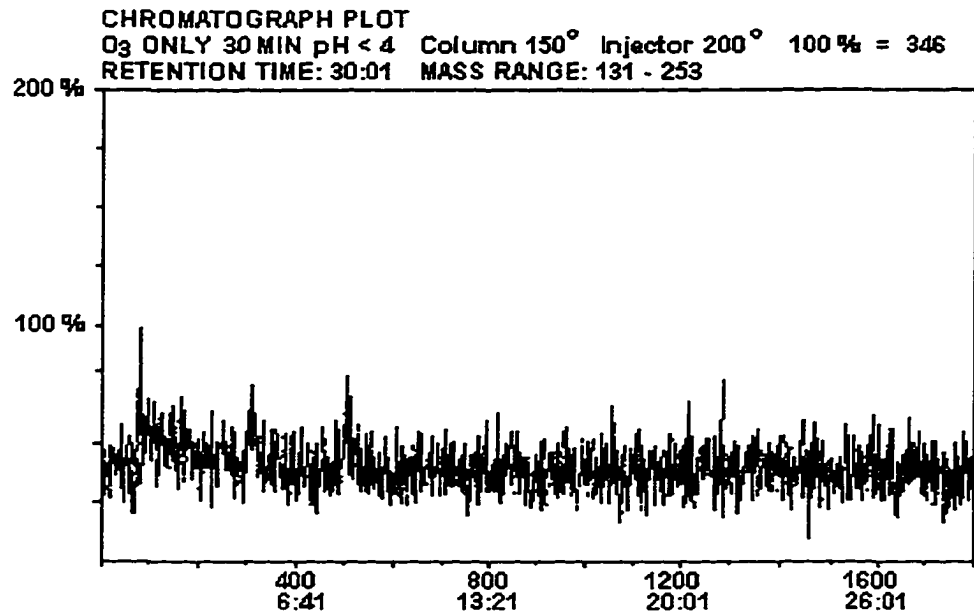


Figure F - 2. GC/MS plot for O₃ only 30 min and O₃ / H₂O₂ feed results.

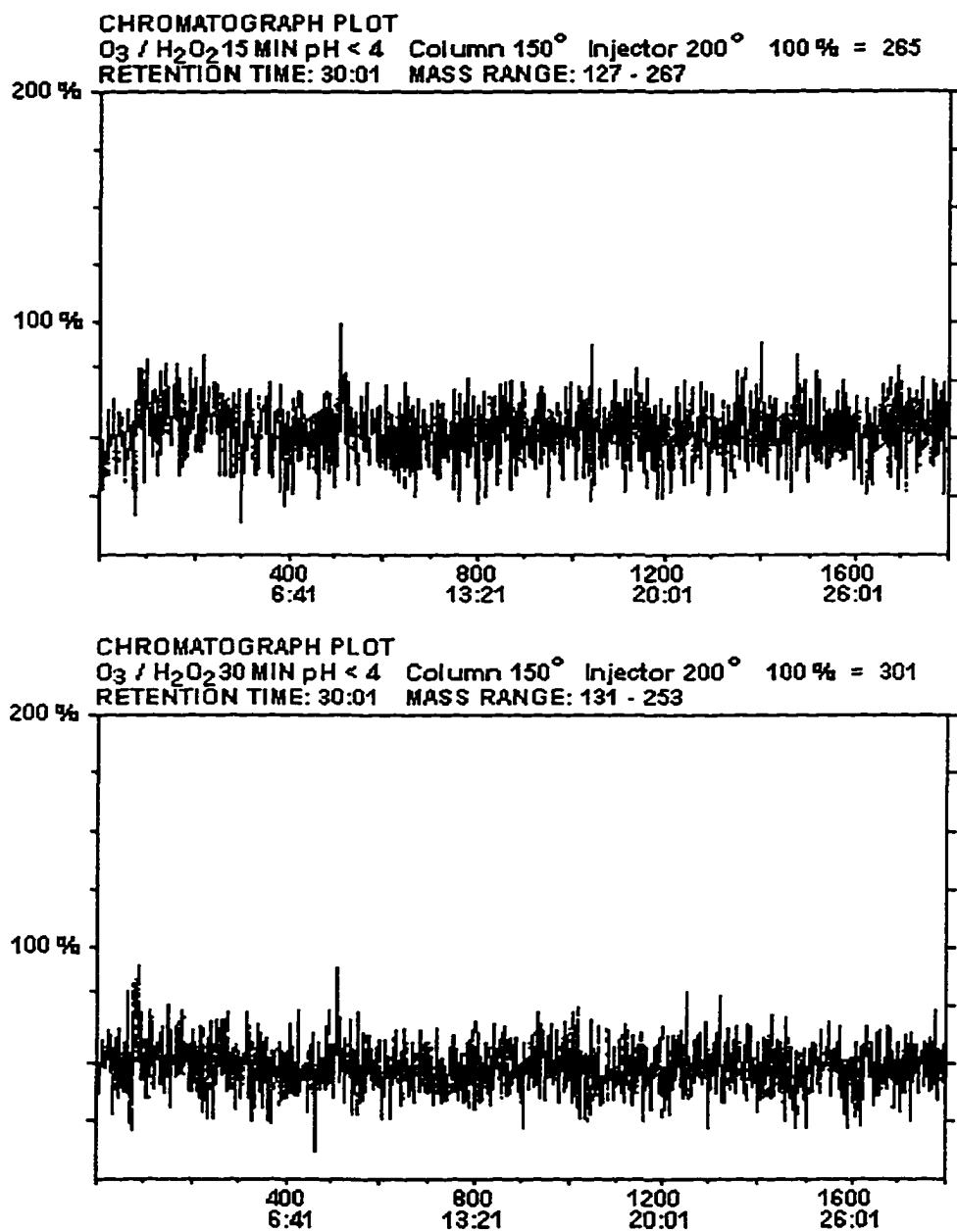


Figure F - 3. GC/MS plot for O₃ / H₂O₂ 15 min and 30 min results.

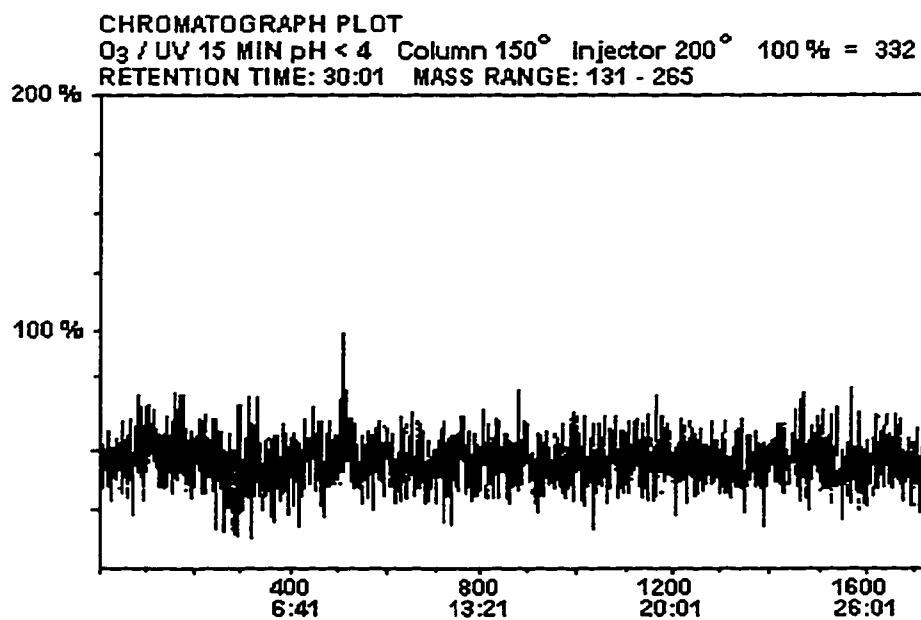
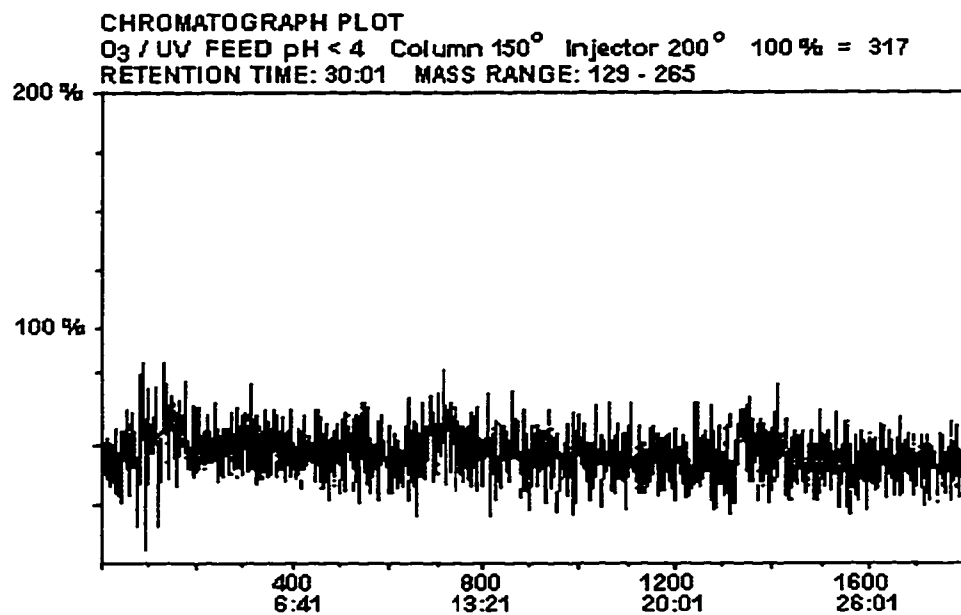


Figure F - 4. GC/MS plot for O₃ / UV_{254nm} feed and 15 min results.

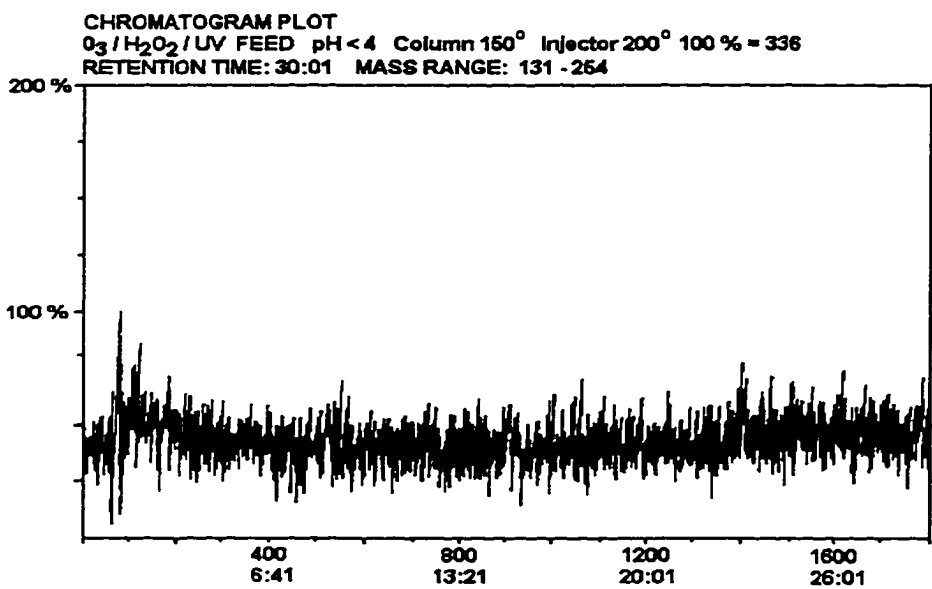
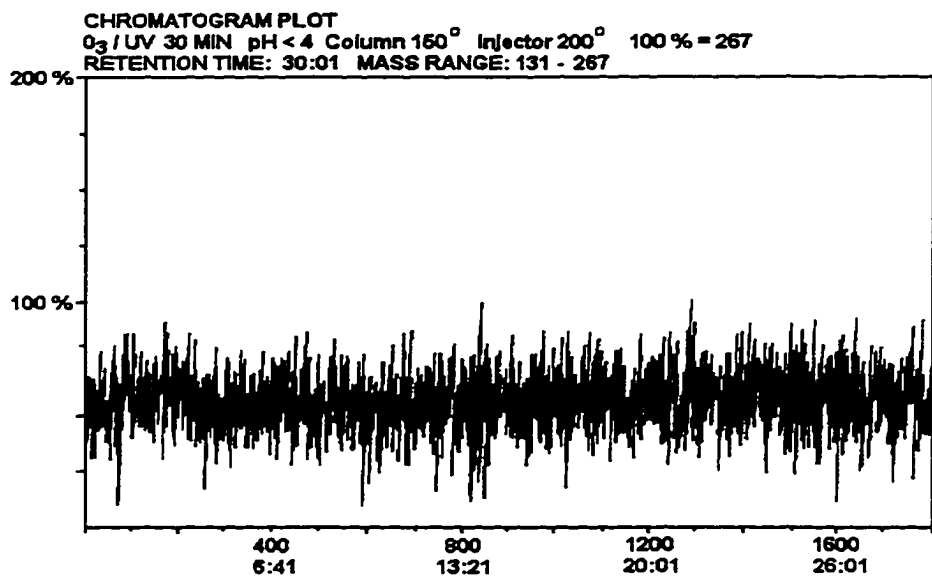


Figure F - 5. GC/MS plot for O₃ / UV_{254nm} 30 min and O₃ / H₂O₂ / UV_{254nm} feed results.

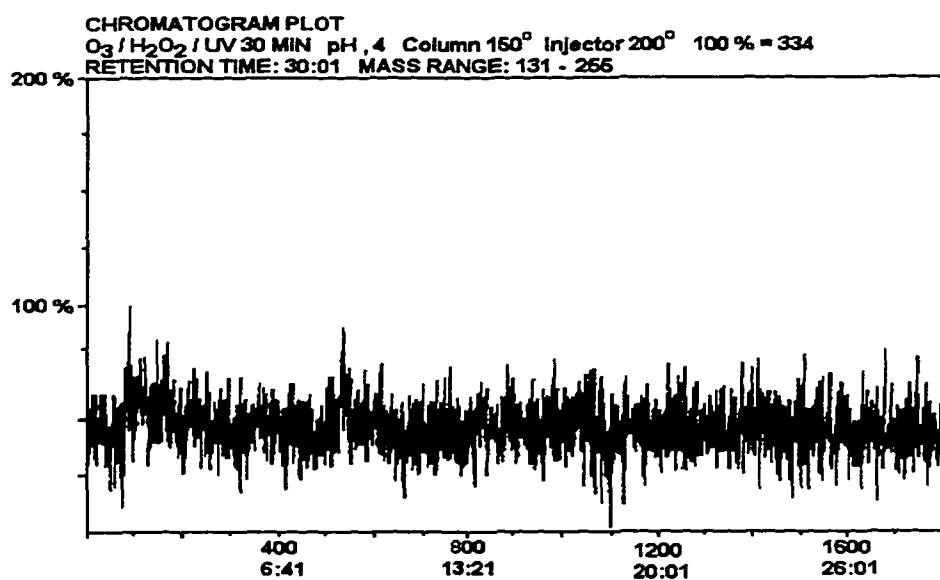
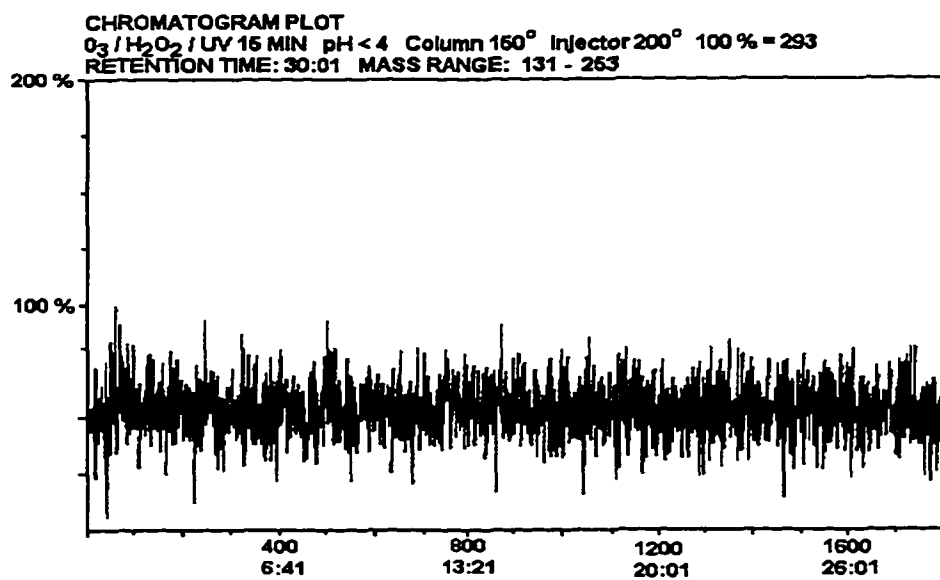


Figure F - 6. GC/MS plot for O₃ / H₂O₂ / UV_{254nm} 15 min and 30 min results.

Appendix G - Test Experiments Results

UV-vis Photometric Spectrum - General Resin Acid Absorbance at 240 nm

Concentration mg/L	Absorbance	
80	2.468	
50	1.362	
25	0.640	
10	0.248	
5	0.094	
1	0.016	
		Regression Output:
Constant		0
Std Err of Y Est		2.9962
R Squared		0.9906
No. of Observations		6
Degrees of Freedom		5
X Coefficient(s)		33.7642
Std Err of Coef.		1.0322
Formula		
Concentration = 33.7642 * Absorbance		

Table G - 1. UV_{240nm} absorbance standard regression.

Time	Absorbance	UV _{240nm} Destruction	pH
0	2.235	0.00	10.81
5	1.818	18.66	10.75
10	1.487	33.47	10.68
15	1.242	44.43	10.83
20	1.101	50.74	10.83
25	1.013	54.68	10.65
30	0.946	57.67	10.82
35	0.925	58.61	10.59
40	0.919	58.88	10.78
45	0.880	60.63	10.78
50	0.884	60.45	10.77
55	0.866	61.25	10.67
60	0.851	61.92	10.69

Table G - 2. UV_{240nm} and pH results for test experiment #1.

Time	Absorbance	UV _{240nm} Destruction	pH
0	1.570	0.00	11.49
5	0.849	45.92	11.51
10	0.696	55.67	11.46
15	0.674	57.07	11.48
20	0.652	58.47	11.48
25	0.640	59.24	11.47
30	0.613	60.96	11.00
35	0.598	61.91	11.44
40	0.583	62.87	11.43
45	0.564	64.08	11.41
50	0.542	65.48	11.37
55	0.525	66.56	11.36
60	0.51	67.52	11.36

Table G - 3. UV_{240nm} and pH results for test experiment #2.

Test Experiment #1

Time (Min)	O ₃ Read	O ₃ Trans.
0.0	10.10	
5.0	0.30	81.50
10.0	0.35	161.25
15.0	0.60	239.50
20.0	0.58	316.60
25.0	1.07	391.35
30.0	1.30	462.50
35.0	1.57	531.15
40.0	1.83	597.15
45.0	2.10	660.50
50.0	2.80	719.00
55.0	2.96	773.20
60.0	3.06	826.10

Test Experiment #2

Time (Min)	O ₃ Read	O ₃ Trans.
0.0	10.05	
5.0	0.46	98.10
10.0	1.69	187.75
15.0	2.88	265.30
20.0	4.25	330.05
25.0	4.73	385.55
30.0	5.16	436.50
35.0	5.56	483.30
40.0	5.64	527.90
45.0	5.82	570.80
50.0	6.10	611.60
55.0	6.27	650.15
60.0	6.58	688.60

Table G - 4. Ozone readings from preliminary test experiments.

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