This is to certify that the

thesis entitled

Oxidation of 1,3,5-Trichlorobenzene Using Advanced Oxidation Processes

presented by

Michael James Galbraith

has been accepted towards fulfillment
of the requirements for

M.S. degree in Environmental Engineering

Susan Jane Masten
Major professor

Date 31 March 1993

OXIDATION OF 1,3,5-TRICHLOROBENZENE USING ADVANCED OXIDATION PROCESSES

By

Michael James Galbraith

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Civil and Environmental Engineering

1992

ABSTRACT

OXIDATION OF 1,3,5-TRICHLOROBENZENE USING ADVANCED OXIDATION PROCESSES

By

Michael James Galbraith

A flow injection analysis (FIA) method for measuring dilute concentrations of hydrogen peroxide in the presence of ozone is presented. A peroxidase catalyzed oxidation of N,N-diethyl-*p*-phenylenediamine method was incorporated into a FIA system for use in advanced oxidation studies. Tracer studies determining mixing efficiencies of two commonly used photochemical reactors proposed for use in this research are also presented.

The potential for using advanced oxidation treatment processes to remove 1,3,5-trichlorobenzene (TCB) from aqueous solutions was investigated. Ozone, ozone/UV, ozone/peroxide, and ozone/UV/peroxide treatments were compared. The effect of pH, humic acid, and bicarbonate was investigated. At ozone and peroxide dosages of 6 mg/l and 60 μM, respectively, 99.6% of the TCB was oxidized in ten minutes, exceeding the removal efficiency obtained using the other processes. No advantage is gained by supplementing ozone with peroxide or UV light above a pH of 10.5. Significant trichlorobenzene removal was still achieved with humic acid and bicarbonate concentrations of 2 mg/l and 2 mM, respectively.

ACKNOWLEDGEMENTS

I wish to extend my appreciation to Dr. Susan J. Masten, Dr. Simon Davies, and Dr. Mackenzie Davis for serving on my committee and for their advice, encouragement, and professional guidance.

I also wish to thank Min Min Shu for the many hours of assistance with laboratory work and gas chromatography analysis.

Funding for this research was provided by the Office of Research and Development, U.S. Environmental Protection Agency under Grant R815750 to the Great Lakes and Mid-Atlantic Hazardous Substance Research Center, and also by the College of Engineering, Michigan State University.

TABLE OF CONTENTS

List of Tables vi

List of Figures viii

I. Introduction 1
1.1 General 1
1.2 Advanced Oxidation Chemistry 2

II. Determination of Hydrogen Peroxide in Aqueous Ozone Solutions Using Flow Injection Analysis 9
2.1 Introduction 9
2.2 Materials and Methods 11
2.3 Results 14
2.4 Discussion 15
2.5 Conclusions 16

III. Mixing Characteristic Comparison of Two Commercial Photochemical Reactors 17
3.1 Introduction 17
3.2 Materials and Methods 19
3.3 Results 23
3.4 Discussion 25
3.5 Conclusions 26

IV. Oxidation of 1,3,5-Trichlorobenzene Using Advanced Oxidative Processes . . 27
4.1 Introduction 27
4.2 Backround 28
4.3 Materials and Methods 31
4.4 Results 39
4.5 Discussion 48
4.6 Conclusion 53
V. Conclusions 55
5.1 Conclusions 55
5.2 Future Research 56

TABLE OF CONTENTS (cont.)

List of References 58

Appendix A. Indigo Blue Method for Sampling Aqueous Ozone 61

Appendix B. Trichlorobenzene Tracer Study Determining Time to Reach Steady State 65

Appendix C. Trichlorobenzene, Ozone, and Peroxide Sampling Summary for Each Experiment 68
Expt. 1 Hydrogen peroxide concentration optimization 68
Expt. 2 Aqueous ozone treatment at varying ph (low range) 70
Expt. 3 Aqueous ozone treatment at varying ph (high range) 72
Expt. 4 Ozone/Peroxide treatment at varying pH 74
Expt. 5 Ozone/UV treatment at varying pH 78
Expt. 6 Comparing treatment processes 80
Expt. 7 Comparing treatment processes with humic acid 83
Expt. 8 Comparing treatment processes with bicarbonate 85

Appendix D. Headspace Sampler, Gas Chromatograph Operating Parameters 87

LIST OF TABLES

Table 2.1 FIA System Parameter Optimization 14

Table 3.1 Batch Tracer Results for Reactor # 7863 25

Table 4.1 Ozone, Uv and Peroxide Reaction Rate Results 41

Table 4.2 Pseudo First Order Rate Constants for pH Variation Study 44

Table 4.3 Rate Constant Comparison with Humic Acid and Bicarbonate 47

Table 4.4 Hydroxyl Radical Concentration Results 48

Table C.1 Exp. 1 GC Data Summary 68

Table C.2 Exp. 1 Ozone and Peroxide Sampling Data 69

Table C.3 Exp. 2 GC Data Summary 70

Table C.4 Exp. 2 Ozone Sampling Data 71

Table C.5 Exp. 3 GC Data Summary 72

Table C.6 Exp. 3 Ozone Sampling Data 73

Table C.7 Exp. 4 GC data Summary 74

Table C.8 Exp. 4 Peroxide Sampling Data 76

Table C.9 Exp. 4 Ozone Sampling Data 77

Table C.10 Exp. 5 GC Data Summary 78

Table C.11 Exp. 5 Ozone Sampling Data 79

Table C.12 Exp. 6 GC Data Summary 80

Table C.13 Exp. 6 Ozone and Peroxide Sampling Data 82

Table C.14 Exp. 7 GC Data Summary 83

LIST OF TABLES (cont.)

Table C.15 Exp. 8 GC Data Summary 85

Table D.1 Headspace Sampler and GC Operating Parameters 87

LIST OF FIGURES

Figure 1.1 Reactions of Aqueous Ozone in "Pure Water" 3

Figure 1.2 Reactions of Aqueous Ozone in the Presence of Micropollutant M 4

Figure 2.1 FIA Configuration 11

Figure 2.2 Hydrogen Peroxide Standard Curve for the FIA System 15

Figure 3.1 Schematic of Photochemical Reactor # 7863 20

Figure 3.2 Schematic of Supermix Photochemical Reactor # 7868 21

Figure 3.3 Batch Tracer Analysis for Supermix Reactor # 7868 24

Figure 3.4 Continuous Flow Tracer Analysis on Supermix Reactor # 7868 24

Figure 4.1 Experimental Configuration 32

Figure 4.2 Hydrogen Peroxide Optimization 40

Figure 4.3 Ozone Treatment with Varying pH 42

Figure 4.4 Ozone/Peroxide Treatment with Varying pH 42

Figure 4.5 Ozone/UV Treatment with Varying pH 43

Figure 4.6 Effects of pH on Various Treatment Processes 43

Figure 4.7 Comparing Treatment Processes in the Presence of Humic Acid 45

Figure 4.8 Comparing Treatment Processes with Bicarbonate 45

Figure A.1 Indigo Blue/Ozone Calibration Curve 63

Figure B.1 Trichlorobenzene Tracer Study 67

CHAPTER I

INTRODUCTION

1.1 GENERAL

Growing concern over the quality of groundwater and surface water has led to the development of numerous techniques to treat contaminated waters. Remediation technique investigations are needed to develop effective treatment technologies. This research investigates the potential for using advanced oxidation processes to remove recalcitrant organics from contaminated aqueous wastes. Advanced oxidation processes are defined as processes that generate highly reactive hydroxyl radicals (Glaze et al., 1987). The efficiency of advanced oxidation processes using ozone, ozone/UV, ozone/hydrogen peroxide, and ozone/UV/hydrogen peroxide to treat aqueous wastes were evaluated in this study.

1,3,5-Trichlorobenzene was the chosen target compound. This compound has been shown to resist biological treatment (Kirk et al., 1989). It is commonly produced in the chemical industry as a pesticide manufacturing byproduct (Lamporski et al., 1980).

A rapid and simple flow injection analysis (FIA) technique to measure dilute concentrations of hydrogen peroxide in the presence of ozone was developed for this advanced oxidation study. This is discussed in Chapter 2.

A commercial photochemical reactor was modified to perform as a continuous flow through stirred reactor (CFSTR) . Tracer studies were performed to ensure the reactor could be modeled as a CFSTR. These studies are discussed in detail in

Chapter 3.

The advanced oxidation studies are discussed in Chapter 4. The optimal peroxide concentration for the ozone/peroxide process was determined. Individual ozone, UV, and peroxide oxidant rate constants with trichlorobenzene were determined. The effect of pH on each treatment process was then investigated. Finally, the efficiencies of each treatment process in the presence and absence of humic acid and bicarbonate were compared.

1.2 ADVANCED OXIDATION CHEMISTRY

Ozone can react with aromatic compounds directly or indirectly. The direct reaction is selective, favoring compounds with electron donating groups (i.e., OH and NH_2). Compounds with electron withdrawing groups (i.e., NO_2 and Cl), like 1,3,5-trichlorobenzene, are not easily oxidized by ozone. These compounds can, however, be oxidized with ozone indirectly using OH radicals.

OH radicals are the products of ozone decomposition. Figure 1.1 illustrates the reactions of aqueous ozone in pure water (Staehelin et al., 1985). Hydroxide ions initiate ozone decomposition by reacting with ozone, producing superoxide anions (O_2^-). Ozone then reacts with the superoxide anion to form ozonide radical ions and oxygen. The protonated ozonide ion rapidly decomposes to produce oxygen and hydroxyl radicals. The hydroxyl radicals decompose ozone further, producing more superoxide ions, which enter into the cyclic reaction.

Addition of solutes to the ozone reaction scheme complicates matters further. Figure 1.2 shows the effect of different solutes on ozone decomposition (Staehelin et

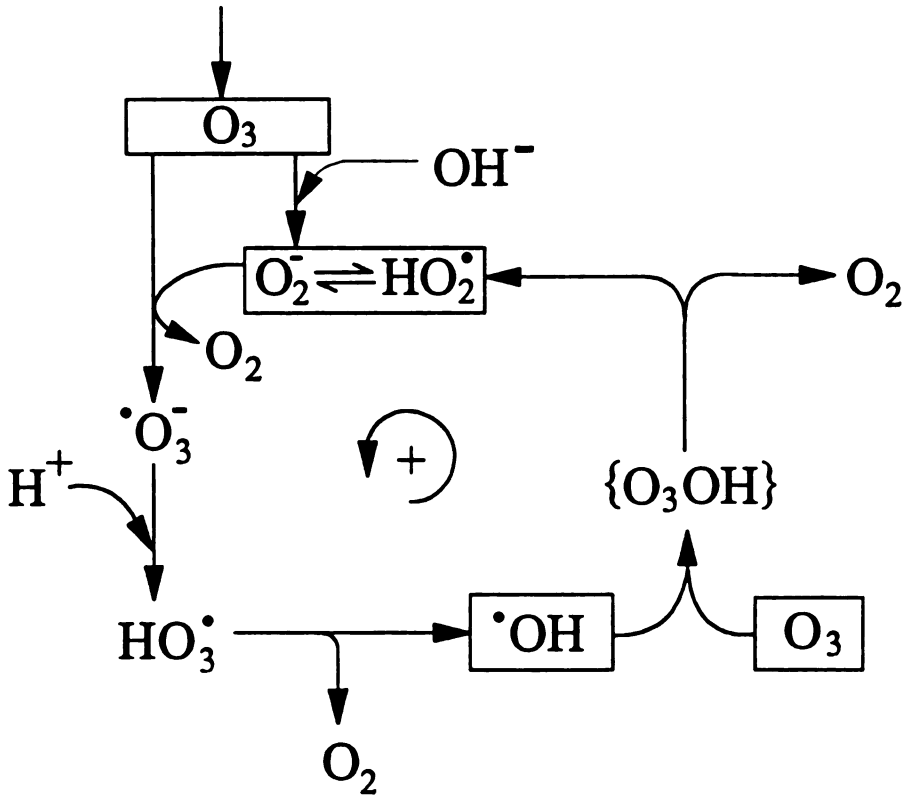
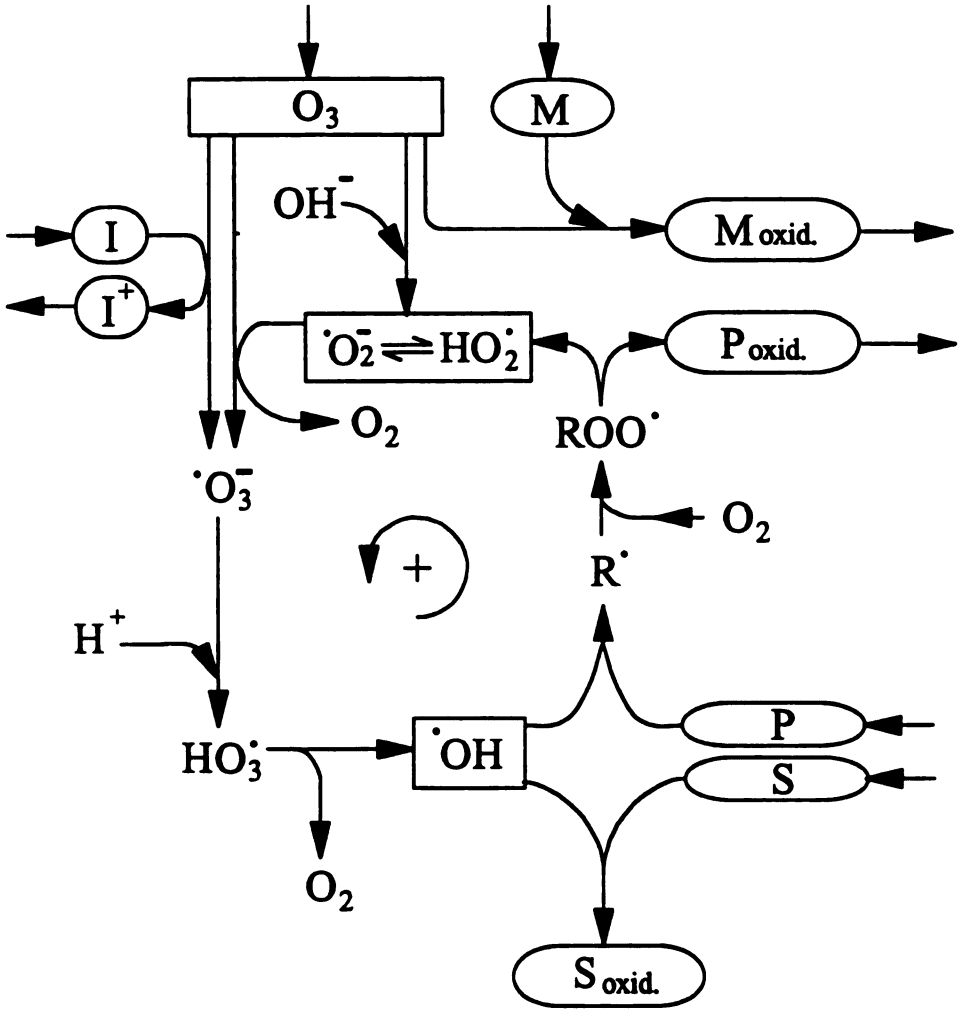


Figure 1.1 Reactions of Aqueous Ozone in "Pure Water"
(Adapted from Staehelin and Hoigné, 1985)



LEGEND

M -	Micropollutant (can also act as an initiator, scavenger, or promoter)
$M_{oxid.}$ -	Oxidized form of micropollutant
P -	Promoter
$P_{oxid.}$ -	Oxidized form of promoter
I -	Initiator
I^+ -	Protonated form of initiator formed by electron transfer reaction
S -	Scavenger
$S_{oxid.}$ -	Oxidized form of scavenger

Figure 1.2 Reactions of Aqueous Ozone in the Presence of Micropollutant M (Adapted from Staehelin and Hoigné, 1985)

al., 1985). Four types of reactive species can be identified. First are the micropollutants (M) that may be oxidized either by ozone directly or by secondary oxidants. Second are the initiators (I), such as hydroxide or hydroperoxide ions, that react with ozone to produce superoxide ions. Third are the promoters, e.g., formic and humic acids, that react with hydroxyl radicals to produce superoxide radicals. Last are the scavengers, such as carbonate and bicarbonate ions, that consume hydroxyl radicals without regenerating superoxide anions. The presence of these solutes effect the rate of ozone decomposition and secondary oxidant generation, and thus effect the rate at which the micropollutant will be degraded.

The initiators of ozone decomposition that were used in this study are hydroxide ions, ultraviolet light, and hydrogen peroxide. Ozone decomposition rates can be increased by increasing the hydroxide ion concentration. This is done by raising the pH. Hydroxyl radicals are produced from this ozone decomposition. Above a certain hydroxide ion concentration, however, the hydroxyl radicals produced are less available to react with the target chemical. This is due, in part, to the increased carbonate and bicarbonate concentrations found in open systems with elevated pH values. Carbonate and bicarbonate ions scavenge hydroxyl radicals, as shown (Staehelin et al., 1985):

$$\begin{matrix} HCO_3^- \\ \downarrow\uparrow \\ CO_3^{-2} \end{matrix} + OH\cdot \rightleftharpoons \begin{matrix} HCO_3^{\cdot} \\ \downarrow\uparrow \\ CO_3^{\cdot -} \end{matrix} + OH^- \qquad 1.1$$

This scavenging reduces the removal rate of the target chemical.

In water, hydrogen peroxide dissociates into hydroperoxide ions, as shown:

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \qquad 1.2$$

Hydroperoxide ions act as initiators of the ozone decomposition. They react readily with ozone, producing superoxide anions ($O_2^{\cdot}$). The superoxide ions in turn react with ozone to form hydroxyl radicals, as shown (Paillard et al. 1988):

$$O_3 + HO_2^- \rightarrow OH\cdot + O_2^- + O_2 \qquad 1.3$$

Hydroperoxide ions can act as hydroxyl radical traps at high concentrations because the ozone/peroxide reaction products react readily with hydroxyl radicals, as shown (Paillard et al., 1988):

$$OH\cdot + HO_2^- \rightarrow HO_2^{\cdot} + OH^- \qquad 1.4$$

$$OH\cdot + O_3 \rightarrow HO_2^{\cdot} + O_2 \qquad 1.5$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad 1.6$$

$$OH\cdot + HO_2^{\cdot} \rightarrow H_20 + O_2 \qquad 1.7$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad 1.8$$

$$OH^{\cdot} + O_2^{\cdot -} \rightarrow O_2 + OH^- \qquad 1.9$$

At elevated hydroperoxide ion concentrations, hydroxyl radicals are consumed by the competing reactions (equations 1.4 - 1.9), reducing the target chemical removal rate. At low hydroperoxide ion concentrations (i.e., below the experimentally determined optimal concentration), hydroxyl radical production decreases, also reducing the target chemical removal rate.

Ultraviolet light initiates ozone decomposition by producing hydrogen peroxide, as shown (Peyton et al., 1987):

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 \qquad 1.10$$

The peroxide formed can then react with ozone to produce hydroxyl radicals (equations 1.2 and 1.3). Peroxide can also undergo photolysis, producing hydroxyl radicals, as shown (Baxendale et. al., 1957):

$$H_2O_2 + h\nu \rightarrow 2(OH)^{\cdot} \qquad 1.11$$

Guittonneau et al. (1990), showed that ozone/UV systems had higher hydroxyl radical generation rates compared to H_2O_2/UV systems. Even though the quantum yield for the formation of hydroxyl radicals (via peroxide photolysis) is high, the molar absorptivity for peroxide is low compared to ozone (at wavelengths greater than 200 nm). This indicates the ozone reaction with hydrogen peroxide (formed by ozone photolysis) is the primary mechanism for the generation of hydroxyl radicals in

ozone/UV systems until the ozone is depleted. Once the ozone is depleted, the peroxide/UV reaction is the primary mechanism.

CHAPTER II

DETERMINATION OF HYDROGEN PEROXIDE IN AQUEOUS OZONE SOLUTIONS USING FLOW INJECTION ANALYSIS

2.1 INTRODUCTION

Hydrogen peroxide can be used in water and wastewater treatment to augment the production of OH radicals in advanced oxidation processes. Combining peroxide with ozone and/or ultraviolet light leads to the generation of hydroxyl radicals. The measurement of hydrogen peroxide at low concentrations is required to determine and maintain optimal peroxide concentrations in advanced oxidation processes. Hydrogen peroxide is also generated in water treatment systems using ozone, ultraviolet light, or a combination of both. Hydrogen peroxide measurement is required, in this instance, to determine reaction pathways, to better understand the advanced oxidation process, and to monitor process water for potentially high concentrations of hydrogen peroxide.

Several methods to measure hydrogen peroxide at low concentrations have been documented in recent years (Baga et al., 1988; Kieber et al., 1986; Wagner et al., 1984). These methods involve the use of manual titrations that are complicated and time consuming. An automated method, as opposed to manual titration, would facilitate the monitoring of hydrogen peroxide in continuously operating water treatment systems using advanced oxidation processes. It would also simplify sampling techniques in research conducted on advanced oxidation processes.

A colorimetric titration method can be automated using flow injection analysis (FIA). Flow injection analysis is based on the injection of a liquid sample into a

moving, non segmented continuous carrier stream of a suitable liquid. The injected sample forms a zone, which is then transported towards a spectrophotometer which continuously records the absorbance as it changes as a result of the passage of the sample material through the flow cell (Růžička et al., 1981). An automated flow injection analysis system has certain advantages, including higher sampling frequencies and greater reproducibility of the experimental procedure, which can lead to higher precision (Karlberg, 1989).

Bader et al. (1988), describes a photometric method for the determination of low concentrations of hydrogen peroxide by a peroxidase (POD) catalyzed oxidation of N,N-diethyl-*p*-phenylenediamine (DPD). This technique accurately measures hydrogen peroxide concentrations up to 100 μM. It has a lower detection limit of 6 nM, and is not effected by the dissolved material present in different natural waters. This method of measurement was incorporated into a flow injection analysis system for use in advanced oxidation studies.

Hydrogen peroxide samples are first bubbled with nitrogen gas to purge the ozone from solution. This purging technique has been used in other hydrogen peroxide methods (Peyton et al., 1987). The sample is then injected into a continuous flowing carrier stream of phosphate buffer solution, where it later mixes with DPD and POD reagents. The peroxide in the sample oxidizes the POD. The oxidized POD in turn oxidizes the DPD to the radical cation $DPD^{\cdot+}$ which forms a stable red color. This sample slug passes through a continuous flow cell positioned in a spectrophotometer where the $DPD^{\cdot+}$ is continuously measured at 551 nm. The sample slug produces an

absorbance peak whose height is directly proportional to the peroxide concentration. This paper describes the FIA system setup that produced the best peak height reproducibility and broadest measurement range.

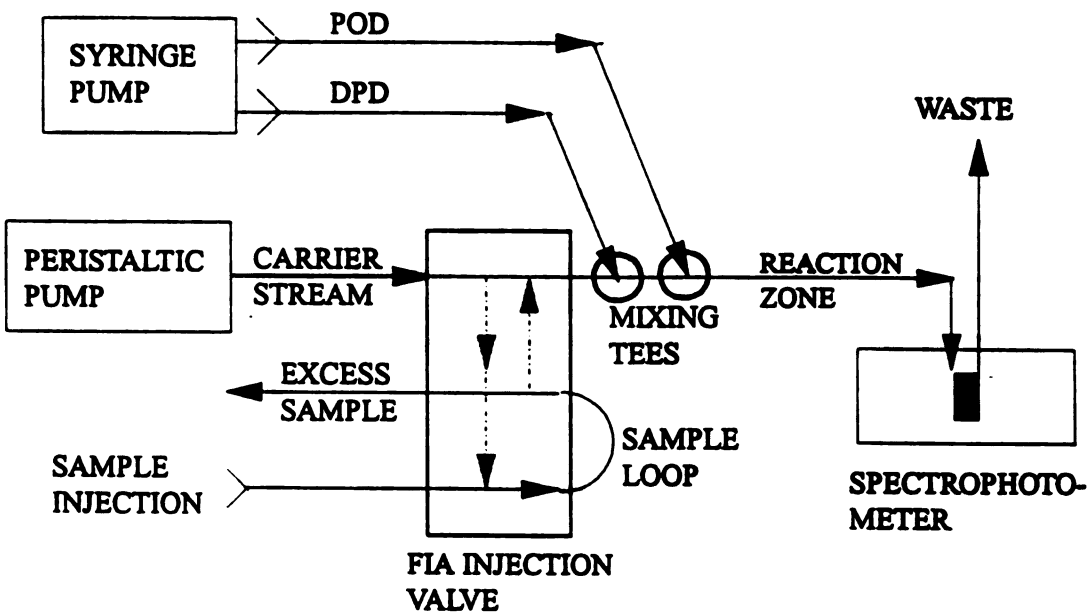


Figure 2.1 FIA Configuration

2.2 MATERIALS AND METHODS

FIA System Description

Figure 2.1 represents the experimental setup for measuring hydrogen peroxide with an FIA system. POD and DPD flows were driven with a syringe pump (Razel Scientific, Model A-E). A peristaltic pump (Cole Parmer-Master Flex, Model 7520-35) was used for the pH 6.0 phosphate buffer carrier stream. Using a plastic syringe, the sample was loaded into the sample loop of a Teflon® rotary valve (Reodyne, Type

50). This two-way valve has a load sample position and an inject sample position. When in the load position, the sample loop is not connected to the carrier stream. When the valve is switched to the inject sample position, the carrier stream is redirected to flush the sample loop into the carrier stream, where it later mixes with the POD and DPD flow streams. This flow path is represented with the dashed arrows in Figure 2.1. Teflon® tubing (0.031 inch inside diameter) was used for all flows. A one centimeter quartz continuous flow-through cell positioned in a UV/vis spectrophotometer (Model UV-1201, Shimadzu Scientific Instruments, Inc., Columbia, MD) was used to continuously record the absorbance.

Reagents

Buffer stock solution: 0.5 M NaH_2PO_4 was added to 0.5 M Na_2HPO_4 until a pH of 6.0 was obtained.

Hydrogen peroxide standard solution: 30% hydrogen peroxide (Baker Analyzed) was diluted to 0.01 M and standardized via direct UV absorption (ϵ = 40.0 $M^{-1}cm^{-1}$ at λ = 240 nm). Appropriate concentrations were obtained by diluting this solution.

DPD reagent: 0.5 grams N,N-Diethyl-*p*-phenylenediamine sulfate salt (DPD) (Sigma Chemical Co., St. Louis) was dissolved in 100 ml 0.1 N H_2SO_4.

POD reagent: 50 mg Type 1 peroxidase from horseradish (Sigma Chemical Co., St. Louis, 78 purpurogallin units/mg) was dissolved in 100 ml distilled water.

Procedure

FIA system optimization: FIA system parameters were varied to obtain broad operating ranges, lower detection limits, and reproducible absorbance peak heights.

Phosphate buffer, POD, and DPD flow rates and concentrations were optimized. Reaction zone length and sample loop size were also optimized. These parameters influence the reaction time in the tubing, the extent of reaction, and the extent of controllable sample dispersion.

Hydrogen peroxide standard curve: The FIA system was operated for 30 minutes before standard samples were injected to purge air from the lines and to allow the system to reach steady state. The spectrophotometer was then autozeroed at a wavelength of 551 nm. Blank samples were injected into the FIA system and the peak height was recorded. This value was subtracted off the peak heights for the standard solutions. Hydrogen peroxide samples ranging from 1 to 500 μM were injected in triplicate and absorbance peaks were recorded. The spectrophotometer was autozeroed between standards, if necessary. Calibration curves could not be done using hydrogen peroxide in the presence of ozone because ozone degrades hydrogen peroxide.

Sample preparation: Samples (not the standards) were immediately bubbled with nitrogen gas in a test tube to purge all ozone before injection into the FIA system. If the sample pH was lower than 6.0, a minimum of 5 minutes purging time was used. If the sample pH was above 6.0, a two minute purging time was used. Tests showed that no hydrogen peroxide was lost due to the bubbling of nitrogen gas. Before the first sample was taken, a blank was injected into the FIA system. The blank peak absorbance value was subtracted off the sample peak absorbance. Hydrogen peroxide concentrations were determined by correlating this value to the standard curve.

2.3 RESULTS

FIA System Optimization

Table 2.1 shows the results of the FIA system parameter optimization.

Table 2.1 FIA System Parameter Optimization

Buffer flow rate	6 ml/min.
Buffer concentration	0.5 M (NaH_2PO_4 / Na_2HPO_4)
POD flow rate	0.54 ml/min.
DPD flow rate	0.54 ml/min.
POD concentration	5 mg/l
DPD concentration	50 mg/l
Reaction zone length	15 feet
Sample loop size	0.1 ml

FIA Standard Curve

Figure 2.2 shows the standard curve for hydrogen peroxide using the FIA system. Error bars represent 95% confidence intervals on triplicate samples. Beyond 500 μM, absorbance readings deviate from linearity. From 0 to 500 μM, $[H_2O_2] = 29.7*A$, where A is the peak absorbance (blank corrected), and $[H_2O_2]$ is the concentration of hydrogen peroxide in μM. The correlation coefficient for this linear regression line fit was 0.999. The average standard deviation at the low end of the standard curve (between 1 and 10 μM) was 8.9×10^{-4} absorbance units, which corresponds to a lower detection limit of 26 nM (based on three times the standard deviation).

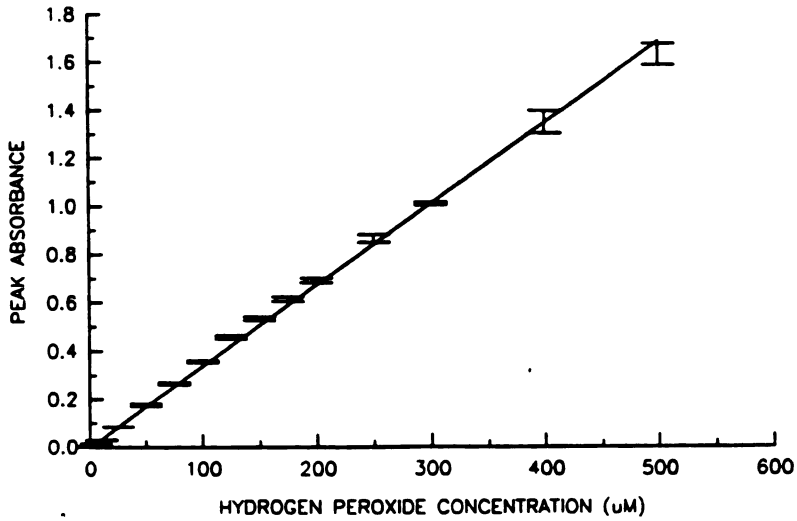


Figure 2.2 Hydrogen Peroxide Standard Curve for the FIA System

2.4 DISCUSSION

Hydrogen peroxide concentrations as high as 500 μM were accurately determined without dilution. Samples can be taken at a frequency of one sample every forty seconds. The range of this FIA method is five times greater than the manual method described by Bader et al. (1988). Total automation of this system could easily be accomplished by adding an in-line nitrogen bubbler between the sampling point and the sampling loop of the FIA system.

A concentrated phosphate buffer concentration of 0.5 M was needed to offset the pH dependence of this analysis. The formation of $DPD^{\cdot+}$ occurs optimally at a pH of 6.0. A phosphate buffer concentration of 0.05 M did not sufficiently buffer samples with a pH of less than 4.0 . These samples produced no FIA peaks. As the phosphate

concentration in the buffer was raised to 0.5 M to increase the buffer intensity, the absorbance peak for the blank increased. This can be attributed to a change in refractive index for the different buffer solutions. A peroxide sample adjusted to pH levels between 2 and 10 with phosphoric acid and sodium hydroxide yielded identical results when injected into the FIA system with the buffer concentration at 0.5 M.

2.5 CONCLUSIONS

Reproducible results were obtained for peroxide concentrations between 1 and 500 μM. The pH was controlled using a 0.5 M phosphate buffer. The DPD/POD method combined with flow injection analysis is a fast and accurate method for measuring dilute hydrogen peroxide concentrations in the presence of ozone.

CHAPTER III

MIXING CHARACTERISTIC COMPARISON OF TWO COMMERCIAL PHOTOCHEMICAL REACTORS

3.1 INTRODUCTION

Photoreactors are used to study photochemical reactions of interest. Batch reactors (Prat et al., 1988; Xu et al., 1988; Peyton et al., 1988) and continuous flow reactors (Peyton et al., 1987; Khan et al., 1985) have been used in waste treatment studies. Improper mixing could effect the results obtained in these studies. Despite the importance of good mixing in these reactors, little information is available on the mixing characteristics of commercial photochemical reactors. Simple mixing studies are an important first step in modeling photochemical reactor systems.

In batch experiments, complete mixing is desirable. Improper mixing in batch experiments could yield erroneous reaction rate results. The desired levels of mixing in continuous flow reactors depend on the type of system needed. Extensive mixing (i.e. with impeller blades), extensive recirculation, or a combination of both, help satisfy the requirements of continuous flow through stirred reactors (CFSTR). Poor mixing and/or recirculation in a continuous system help satisfy the requirements of plug flow reactors. Continuous flow systems can also be modeled as a CFSTR/plug flow combination (Nauman et al., 1983).

Mixing efficiencies in continuous flow systems can be determined by tracer analysis. A washout function (equation 3.1) can be generated by recording the reactor effluent concentration over time after implementing a negative step concentration

change, as discussed by Nauman et al., (1983). The washout function, W(t), is defined as;

$$W(t) = \frac{C(t)_{eff}}{C(0)_{eff}} \qquad 3.1$$

where C(t) is the reactor concentration after the step concentration change, and C(0) is the initial reactor concentration. For completely stirred vessels, the theoretical washout function is given by;

$$W(t) = \exp\left(-\frac{t}{\bar{t}_{hyd}}\right) \qquad 3.2$$

where t is the time after the step concentration change, and $\bar{t}_{hyd}$ is the reactor hydraulic retention time. Step changes in concentration can be easily achieved by switching reactor input lines to dye stock solutions. By integrating the washout function (equation 3.1), the actual reactor retention time can be determined (equation 3.3);

$$\bar{t}_{exp} = \int_0^{\infty} W(t)dt \qquad 3.3$$

where $\bar{t}_{exp}$ is the experimental reactor fluid retention time. The reactor dead volume is obtained by taking the difference between the hydraulic residence time and experimental residence time, i.e.;

$$dead\ volume = Q_r(\bar{t}_{hyd} - \bar{t}_{exp}) \qquad 3.4$$

where Q_r is the reactor flow rate.

This paper describes the tracer studies performed on two commercial photochemical reactors proposed for use with advanced oxidation research. A CFSTR system configuration was chosen to simplify sampling techniques and mathematical modeling, and to simulate a continuously flowing water treatment system.

3.2 MATERIALS AND METHODS

Photochemical Reactor System Description

Figure 3.1 represents the photochemical reactor chosen for our initial studies. This reactor (Ace Glass, Inc., Vineland, NJ, Model #7863) had a working volume of 500 ml. It was modified by adding a continuous flow outlet port, as shown. A quartz immersion well (Ace Glass, Inc., # 7874-38) was used in the reactor, providing a housing for the low pressure photochemical immersion lamp (ACE Glass, Inc., # 12128). Water was circulated through the jacket of the immersion well when the lamp was on. A magnetic stirrer (VWR Scientific, Model # 200) was used to stir the reactor. Herein, this reactor shall be referred to as Reactor A.

Figure 3.2 shows the second photochemical reactor used. This Supermix reactor (Ace Glass, Inc., Model #7868), equipped with a 85 ml recirculation loop, had a working volume of 250 ml. This reactor will be referred to as Reactor B. A quartz immersion well was also used in this reactor. A glass impeller shaft (Ace Glass, Inc., # 8068-08) was used to circulate the fluid in the reactor. The shaft was rotated in a water cooled glass bearing (Ace Glass, Inc., # 8040-10) using an electric motor (Ace Glass, Inc., # 13583) connected to a shaft through a flexible drive cable (Ace Glass, Inc., # 8081).

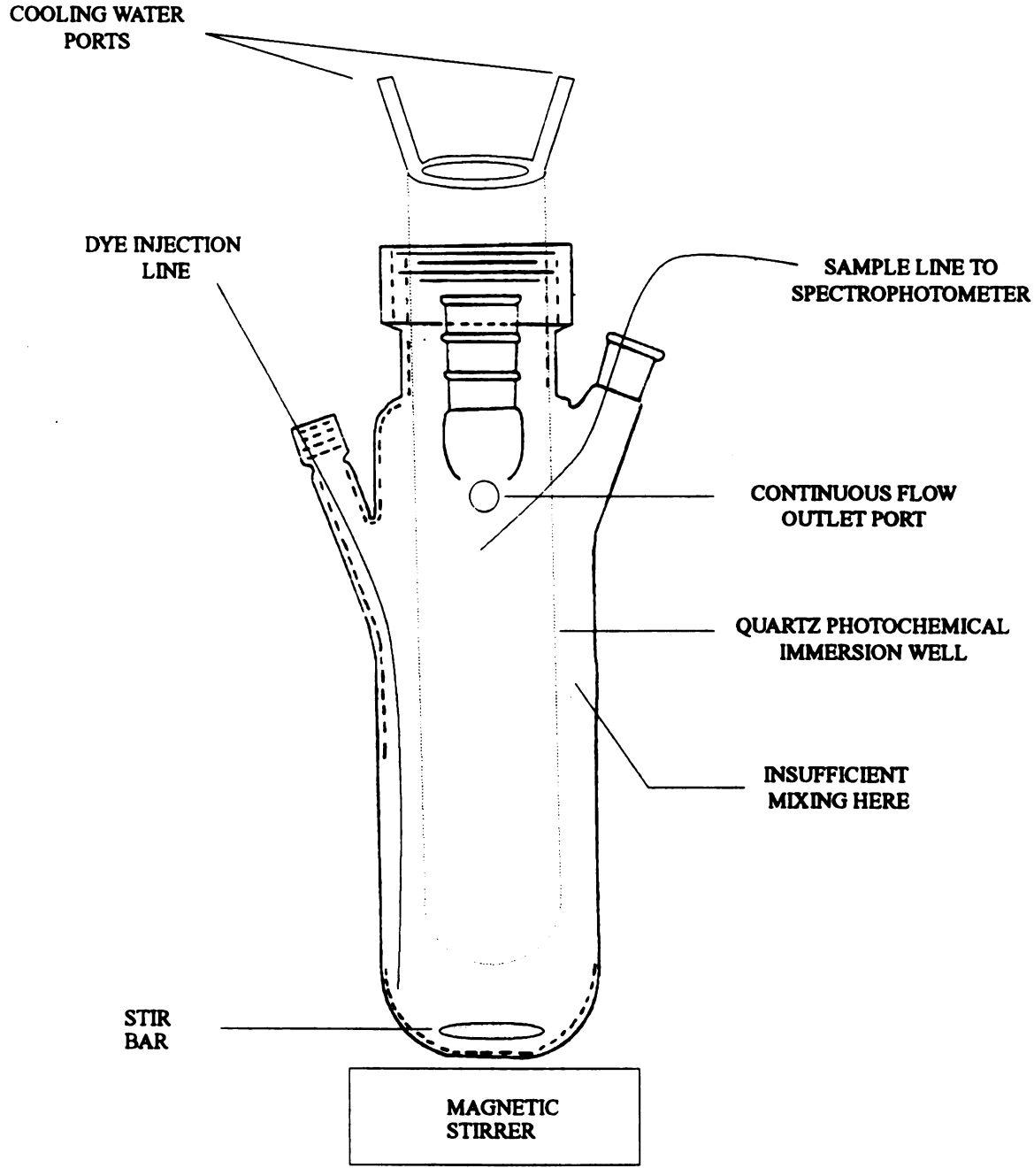


Figure 3.1 Schematic of Photochemical Reactor # 7863
(Reactor A)

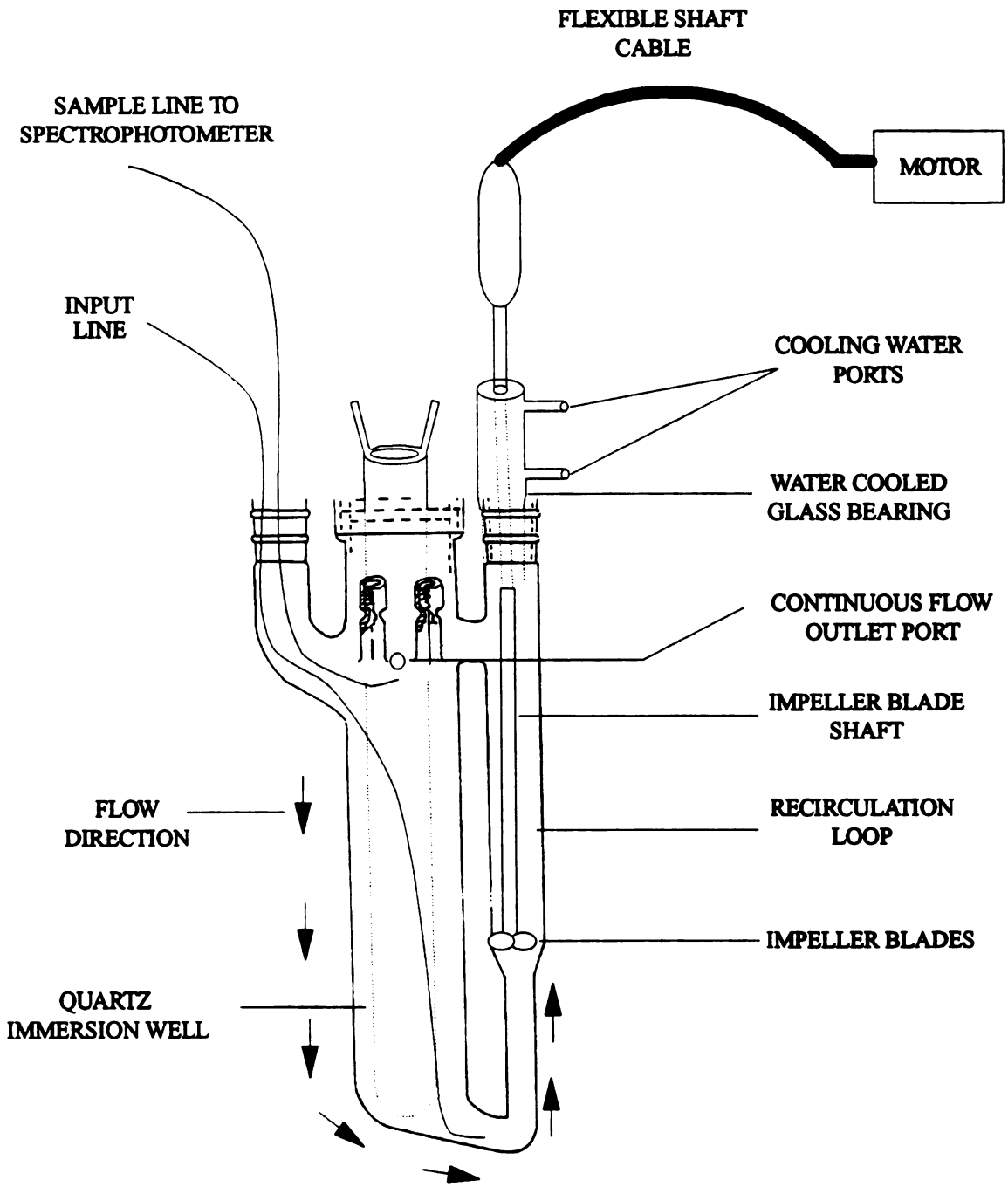


Figure 3.2 Schematic of Supermix Photochemical Reactor # 7868
(Reactor B)

Batch Tracer Analysis Procedure on Photochemical Reactor A

Reactor A was filled with deionized water to the level of the outlet port. A sample line (0.031 inch inside diameter Teflon® tubing) was positioned near the top of the reactor. A peristaltic pump (Cole Parmer, # 7520) continuously withdrew reactor fluid through this line into a one centimeter quartz continuous flow cell (Model # 178.710-QS, Hellma Cells, Inc., Forest Hills, N.Y.) that was positioned in a UV/vis spectrophotometer (Model UV-1201, Shimadzu Scientific Instruments, Inc. Columbia, MD). An injection line (0.031 inch inside diameter Teflon® tubing) was positioned in the bottom of the reactor. A magnetic stirrer rotated at the highest allowable speed to mix the reactor. A slug of concentrated methylene blue dye solution (Sigma Chemical Co., St. Louis) was injected into the bottom of the reactor. The absorbance of the effluent from the reactor was monitored with the spectrophotometer at 665 nm. The time for the liquid in the reactor to reach a steady state concentration was recorded. This experiment was repeated with three different types of magnetic stir bars.

Batch Tracer Analysis Procedure on Photochemical Reactor B

The same procedure used with Reactor A was used with Reactor B except the impeller blades provided mixing. Magnetic stir bars were not used. Different impeller blade shaft rotation speeds were used do determine how rotation speed affected reactor mixing. Shaft rotation speeds were determined with a tachometer.

Continuous Flow Tracer Analysis Procedure on Reactor B

Methylene blue dye solution with an absorbance of 0.40 (at 665 nm) was pumped into the reactor just below the impeller blades with a peristaltic pump (Cole Parmer,

Model # 7520-35) at a rate of 50 ml/minute. This provided for a hydraulic residence time of 5 minutes. Tubing positioned at the outlet port continuously sampled the reactor effluent. A peristaltic pump, continuous flow cell, and spectrophotometer was used for sampling, as before mentioned. The methylene blue input line was switched to clear deionized water after the reactor was filled and the sample line absorbance leveled to 0.40. Absorbance versus time was continuously monitored until the effluent absorbance was 0.00. The washout function was plotted and analyzed from these data points.

3.3 RESULTS

Table 3.1 shows the results of the batch tracer study done on Reactor A. The fastest time to achieve complete mixing was 8 minutes. Complete mixing was achieved when the reactor effluent absorbance leveled out to a constant value (within 1%).

Figure 3.3 shows the results of the batch tracer study on the Reactor B. The higher the shaft rotation speed, the better the mixing. At a rotation speed of 550 RPM, complete mixing was achieved in 90 seconds.

Figure 3.4 shows the results of the continuous flow tracer study with Reactor B. The washout data was plotted against the theoretical stirred tank response and theoretical plug flow response. A curve was fit to the experimental data points. By integrating this curve (equation 3.3), a reactor residence time was calculated to be 4.94 minutes. This indicates that the dead volume in the reactor is 3.1 ml (equation 3.4).

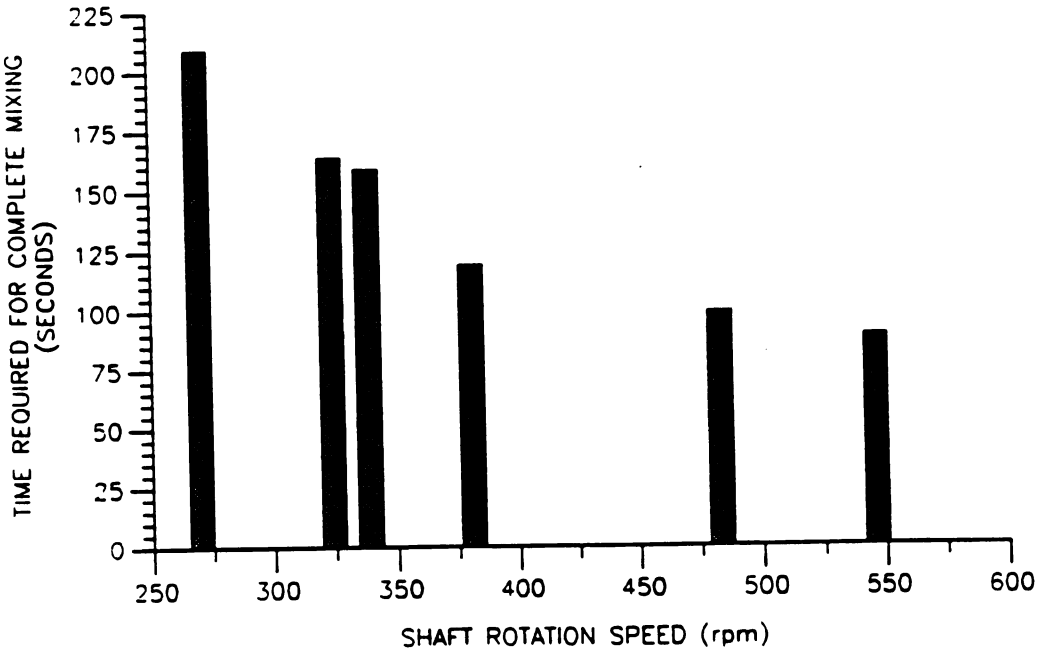


Figure 3.3 Batch Tracer Analysis for Supermix Reactor # 7868

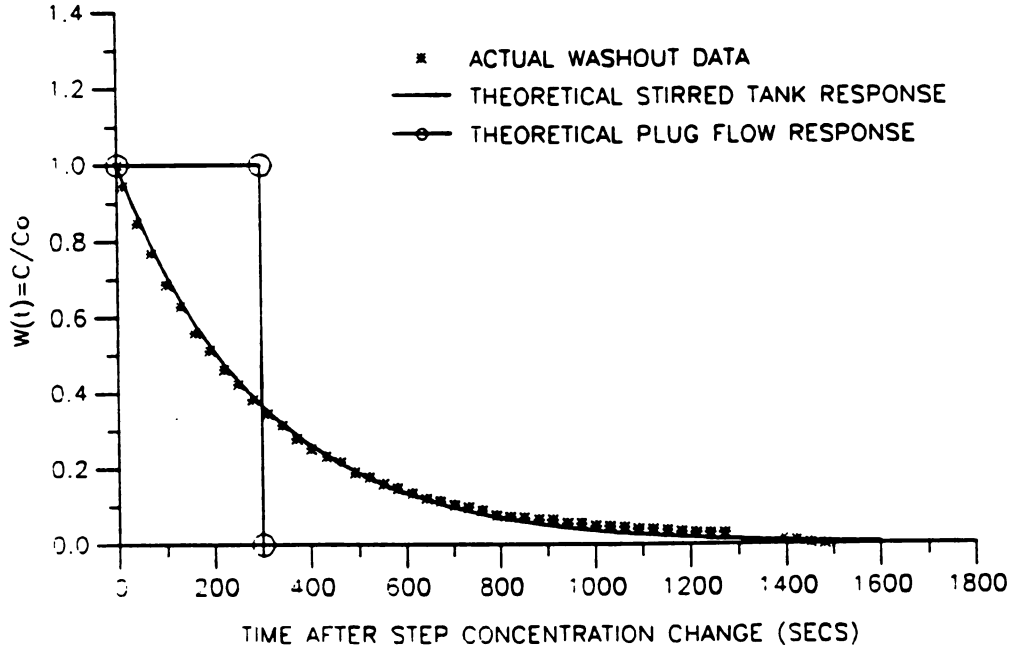


Figure 3.4 Continuous Flow Tracer Analysis on Supermix Reactor #7868

Table 3.1 Batch Tracer Results for Reactor A

Stir bar used	Time for complete mixing
Octagonal stir bar (2")	10 minutes
Star head stir bar (1-3/8")	8.5 minutes
Star head stir bar (1-3/4")	8.0 minutes

3.4 DISCUSSION

Batch tracer results for Reactor A revealed this reactor was poorly mixed. Visual observations showed the majority of the mixing occurred at the bottom of the reactor. Very little mixing occurred in the gap between the quartz immersion well and the inner wall of the reactor. The stir bars could not create sufficient turbulence to effectively mix the fluid in this gap, which was only 0.63 inches wide. Since this reactor was poorly mixed, no continuous flow tracer studies were performed. Continuous flow studies with this reactor would require modeling it as a CFSTR and plug flow reactor in series.

Batch tracer studies for the Reactor B proved this reactor was more efficiently mixed. Since only 90 seconds was required for complete mixing in the batch mode, a reactor retention time as low as five minutes (approximately three batch mixing retention times) would assure complete mixing in a continuous flow configuration. For this reason, a five minute retention time was chosen for the continuous flow tracer

study. Figure 3.4 shows that, as predicted, Reactor B behaved as a CFSTR at a retention time of five minutes. It follows that any reactor retention time greater than five minutes can be modeled as a CFSTR. The results indicate 3.1 ml of dead space exist, which is probably located in the three sampling port extensions at the top of the reactor.

3.5 CONCLUSIONS

Reactor A did not provide adequate mixing. Modeling this reactor requires an analysis of a CFSTR and plug flow reactor in series. Reactor B was sufficiently mixed to support CFSTR modeling criteria at reactor retention times greater than or equal to 5 minutes. Any future photochemical studies using reactors similar to Reactor A should test the mixing efficiency prior to any in depth study. Any past photochemical studies that used reactors similar to Reactor A should be checked to make sure the results were valid.

CHAPTER IV

OXIDATION OF 1,3,5 TRICHLOROBENZENE USING ADVANCED OXIDATIVE PROCESSES

4.1 INTRODUCTION

Many studies have been done on advanced oxidation treatment processes using ozone (Langlais et al., 1991), ozone/UV (Paillard et al., 1987), ozone/peroxide (Glaze et al., 1989), and ozone/peroxide/UV (EPA, 1990). These techniques center around the production of hydroxyl radicals, which are highly reactive, non selective oxidants. Aqueous ozone itself is a powerful, but selective, oxidant. Recalcitrant compounds that do not readily react with ozone often can be degraded by hydroxyl radicals. Advanced oxidation processes generate hydroxyl radicals by initiating formation of superoxide ions from ozone decomposition. These ions react with aqueous ozone to form hydroxyl radicals (Glaze et al., 1987).

The ability of advanced oxidation processes to degrade recalcitrant organics is effected, among others, by oxidant dose, UV light intensity, pH, retention time, the nature the organic micropollutant (Guittonneau et al., 1990), and the concentration of scavenging, promoting, or initiating solutes in the wastestream (Staehelin et al., 1985). Contaminated natural waters and industrial waste streams may vary in pH and contain significant quantities of these solutes. If advanced oxidation processes are used to remediate these contaminated waters, the effect these variables have on target compound removal efficiencies should be investigated.

1,3,5-Trichlorobenzene, a recalcitrant chlorinated organic, was the chosen target

compound for these studies. This compound has been shown to resist biological treatment (Kirk et al., 1989). It is commonly produced in the chemical industry as a pesticide manufacturing byproduct (Lamporski et al., 1980).

Experiments were conducted to determine:

1. The optimal hydrogen peroxide concentration for trichlorobenzene removal
2. UV, peroxide, and ozone rate constants for trichlorobenzene
3. Effects of pH on advanced oxidation treatment processes
4. A comparison of the efficiencies of advanced oxidation treatment processes in the presence and absence of humic acid and bicarbonate

4.2 BACKROUND

Hydrogen peroxide in water dissociates into hydroperoxide ions. These ions initiate ozone decomposition, producing superoxide ions and hydroxyl radicals. At certain concentrations, the hydroperoxide ions can act as hydroxyl radical scavengers (Paillard et al., 1988). The first stage of this study determined the optimal peroxide concentration for degrading trichlorobenzene in the presence of ozone.

The overall rate of reaction for these advanced oxidation processes can be formulated as:

$$\frac{-d[TCB]}{dt} = k_{O_3}[O_3][TCB] + k_{OH}[OH][TCB] + k_{photol}[\Phi\ I][TCB] + k_{H_2O_2}[H_2O_2][TCB] \qquad 4.1$$

where k is the reaction rate constant for the particular oxidant. [TCB], [O_3], [OH], and [H_2O_2] are the reactor trichlorobenzene, ozone, hydroxyl radical, and peroxide concentrations, respectively. I is the light intensity (irradiance) and Φ is the quantum

efficiency. Equation 4.1 assumes the individual reaction rates are first order with respect to the trichlorobenzene concentration (Glaze et al., 1980).

In the second stage of this study, the individual reaction rate constants for UV light, hydrogen peroxide, and ozone with trichlorobenzene were determined by simplifying and integrating equation 1:

$$k_{O_3} = - \frac{\ln\left(\frac{TCB_f}{TCB_i}\right)}{[O_3]\ \theta}, \quad k_{H_2O_2} = - \frac{\ln\left(\frac{TCB_f}{TCB_i}\right)}{[H_2O_2]\ \theta}, \quad k_{photo} = - \frac{\ln\left(\frac{TCB_f}{TCB_i}\right)}{[I\Phi]\ \theta} \qquad 4.2$$

where TCB_i and TCB_f are the steady state reactor trichlorobenzene concentrations before and after treatment, and θ is the reactor retention time. Ozone and peroxide concentrations represent steady state reactor concentrations after the treatment was initiated.

Hydroxide ions initiate ozone decomposition by reacting with ozone to form superoxide ions and hydroxyl radicals. In the third stage of this study, the effect of pH on the trichlorobenzene removal rates with ozone treatment, ozone/UV treatment, and ozone/peroxide treatment were determined. Pseudo first order oxidation rate constants were calculated and compared at different pH values by simplifying equation 4.1 to:

$$\frac{-d\ [TCB]}{dt} = k_{oxidant}[Oxidant][TCB] \qquad 4.3$$

If we assume that the oxidant concentration [oxidant] is constant over the course of the experiment (i.e., at steady state), the oxidant concentration and rate constant can be

combined, simplifying the equation further:

$$\frac{-d\,[TCB]}{dt} = k'\,[TCB] \qquad 4.4$$

Integrating equation 4.4 yields a pseudo first order rate constant, describing the reaction rate of the overall advanced oxidation process, as shown:

$$k' = -\frac{\ln\left(\frac{TCB_f}{TCB_i}\right)}{\theta} \qquad 4.5$$

In the fourth stage of this study, the reaction rates for each treatment process with and without the presence of humic acid and bicarbonate were determined. Dissolved humic substances can act as initiators, promoters, or inhibitors of ozone decomposition (Staehelin et al., 1985). Humic acid concentrations of 0.0, 2.0, and 10.0 mg/l were used. Bicarbonate and carbonate ions, common in natural water, act as ozone decomposition inhibitors, scavenging hydroxyl radicals. Bicarbonate concentrations of 0.0, 2.0, and 10.0 mM were used. Reaction rate constants (equation 4.5) were determined for ozone treatment, ozone/UV treatment, ozone/peroxide treatment and ozone/UV/peroxide treatment.

Hydroxyl radical concentrations for each treatment process not subjected to humic acid and bicarbonate were estimated by assuming a hydroxyl radical reaction rate with trichlorobenzene. The peroxide, photolysis and ozone rate constants from equation 4.2, along with the measured steady state concentrations of ozone, peroxide, and trichlorobenzene, were substituted into equation 4.1, solving for the term $k_{OH}[OH]$.

This calculation is shown in detail in the results section.

4.3 MATERIALS AND METHODS

General System Configuration

Figure 4.1 shows the experimental apparatus. A continuous flow system was used to eliminate sampling time constraints and to better simulate configurations likely to be used in actual treatment facilities. Gaseous ozone was produced using an ozone generator (Polymetrics Corp., San Hose, CA, Model T-408) and bubbled into an ozone contactor. The aqueous ozone solution was pumped into the reactor as opposed to bubbling ozone gas directly into the reactor. This provided a continuous input ozone flux. Ozone mass transfer corrections into reactor solutions due to varying concentration gradients across the ozone liquid-gas interface are avoided with this technique. Another advantage this method offers is its ability to treat volatile contaminants with low solubilities. Legube et al. (1983), reported that chlorobenzene removal in ozonation bubble columns was more a consequence of stripping action than oxidation reaction. Using this method, corrections due to volatilization of the contaminant would not be required.

Photochemical Reactor

A detailed schematic of the photochemical reactor is provided in Figure 3.2. This reactor has a working volume of 250 ml and is equipped with a recirculation chamber that houses an impeller blade that provides continuous mixing. A quartz immersion well houses a low pressure immersion lamp with a 254 nm principal wavelength output. Piston pumps (Model RHSY, Fluid Metering Inc., Oyster Bay, NY) were used

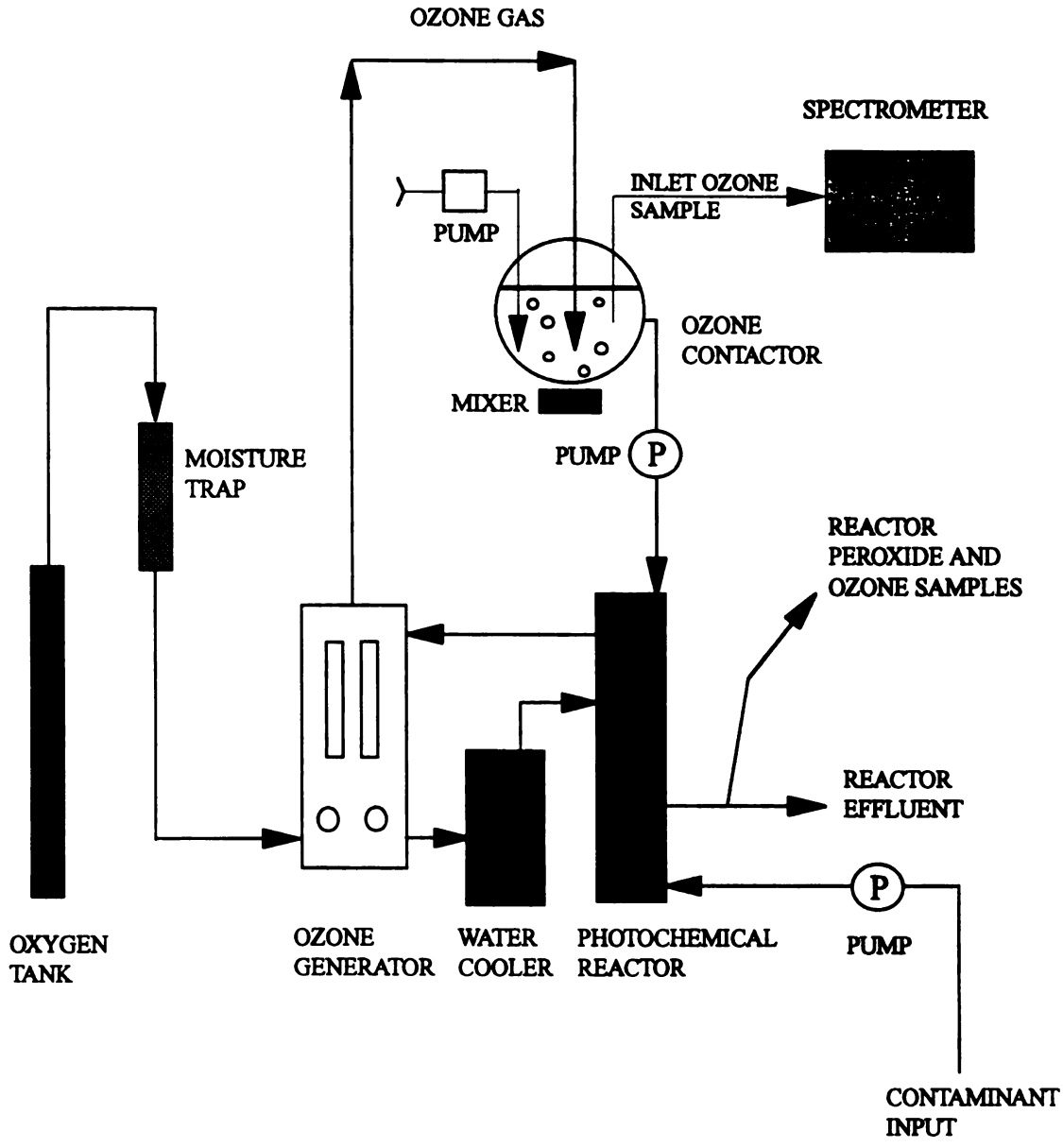


Figure 4.1 Experimental Configuration

to pump ozone and trichlorobenzene solutions into the reactor. Teflon® tubing was used for all input and sample lines. The input lines were positioned just below the impeller blades to ensure immediate mixing of the influent streams.

Ozone Gas Generation and Solution Preparation

Ozone gas (approximately 3%) was produced using an ozone generator (Polymetrics Corp., San Hose, CA, Model T-408) that was fed pure dried oxygen. The generator was cooled using water from a refrigerated circulating bath maintained at 10 °C. Aqueous ozone was made by continuously bubbling ozone gas into a three liter round bottom Pyrex flask containing deionized water that had been acidified to a pH of 2.0 using phosphoric acid. This solution was pumped into the reactor with piston pumps (Model RHSY, Fluid Metering Inc., Oyster Bay, NY) while a peristaltic pump (Cole Parmer-Master Flex, Model 7520-35) continuously replenished the buffer solution to the ozone contactor, maintaining a constant level. The contactor was stirred to ensure a consistent effluent ozone concentration.

Waste Stream Buffer Preparation

The waste stream was buffered with phosphate so that a pH of 7.0 ± 0.2 was maintained in the reactor after the ozone contactor buffer stream and waste stream were pumped in at equal flowrates. This was necessary because the ozone contactor solution was acidified to a pH of 2.0 with phosphoric acid.

1,3,5-Trichlorobenzene Stock Solution Preparation

Trichlorobenzene (Aldrich Chemical Co., Milwaukee, WI) stock solutions were prepared in 20 liter glass containers. Solid trichlorobenzene crystals were ground

using a mortar/pestle and added to the 20 liter vessel containing the waste stream buffer. Quantities in excess of the solubility of trichlorobenzene in water had to be added to obtain stock concentrations greater than 3 ppm. Stock solutions were mixed for two days and allowed to settle another day before being decanted into three separate 6 liter Pyrex flasks.

Humic Acid Preparation

Aldrich Humic Acid (sodium salt) was dissolved in deionized water (acidified to a pH of 3.0) and passed through glass fiber filters. Stock solutions were stored in the dark.

Analytical Methods

Analysis of inlet stream for ozone - The aqueous ozone in the inlet stream was continuously monitored with a flow cell positioned in a UV/vis spectrophotometer (Model UV-1201, Shimadzu Scientific Instruments, Inc., Columbia, MD). The ozone contactor solution was continuously drawn through the flow cell with a hand operated vacuum pump. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ was used to convert absorbance units into concentration.

Reactor ozone analysis - Reactor ozone concentrations could not be measured directly because of the possible presence of interfering compounds absorbing light at 258 nm. The indigo method (Bader et al., 1982) was used instead. Ozone samples were withdrawn from the reactor with a hand operated vacuum pump and delivered into 125 ml vacuum flasks containing known amounts of indigo blue solution. Ozone concentrations were determined by correlating the decrease in absorbance of an indigo

solution to the ozone concentration (see Appendix A).

Reactor peroxide analysis - Reactor peroxide concentrations were determined by flow injection analysis (FIA) using the peroxidase N,N-diethyl-*p*-phenylenediamine (DPD) method (Bader et al., 1988). The FIA technique is discussed in Chapter II. Samples were withdrawn from the reactor and immediately bubbled with nitrogen gas to purge the ozone before injection into the flow injection analysis system.

Trichlorobenzene sampling - Trichlorobenzene samples were collected at the reactor effluent port. The effluent was allowed to drain into glass vials that contained 0.125 ml of 0.09 M sodium nitrite solution. The sodium nitrite quenched the ozone to stop any further reaction. Aliquots of 10 ml were pipetted from these vials into separate vials suitable for gas chromatography analysis. Five trichlorobenzene samples were taken from the effluent for each steady state.

Headspace analysis of trichlorobenzene - 1,3,5-Trichlorobenzene was measured using a gas chromatograph (Perkin-Elmer Autosystem, Norwalk, CT) equipped with a flame ionization detector (FID) and a silica glass capillary column (Perkin-Elmer, Model 624). The carrier gas was helium. A five point calibration curve was performed for each experiment. Details of the gas chromatograph and headspace sampler operating parameters are provided in Appendix D.

UV Light Intensity - The quartz immersion well and photochemical lamp were cleaned with acetone before each experiment to maintain consistent UV light transmission into the reactor and to remove any adsorbed trichlorobenzene. The light intensity was measured with a potassium ferrioxalate actinometer (Murov, 1973) and

assumed to remain constant throughout the study.

Experimental Procedure

General - The reactor was operated with a hydraulic retention of 10 minutes by pumping ozone contactor buffer and trichlorobenzene solutions in at 12.6 ml/min for each experiment. The impeller blades that provided mixing were rotated at 500 RPM, as determined by a tachometer. A trichlorobenzene tracer study determined the reactor system required one hour (six retention times) to reach steady state after a step trichlorobenzene input change (see Appendix B).

Each experiment was started by pumping trichlorobenzene and ozone contactor solution (not ozonated) into the reactor. Effluent samples were taken one hour later to determine the initial steady state trichlorobenzene concentration. This initial trichlorobenzene steady state concentration was kept within the range of 1.17 ppm to 1.42 ppm for each experiment. The effluent concentration for the subsequent treatment processes were compared to this concentration to determine trichlorobenzene removal efficiencies.

The reactor was then subjected to a series of treatments using aqueous ozone, peroxide, UV light, pH adjusters, humic acid, or bicarbonate, depending on the process being studied. Oxygen gas was bubbled into the ozone contactor when aqueous ozone treatment was not being used. Aqueous ozone treatment was started by ozonating the ozone contactor buffer solution to obtain a concentration of 12 mg/l for each experiment, unless stated otherwise. This was easily accomplished by turning on the power to the ozone generator (since the oxygen was already flowing through the

generator and into the contactor). The ozone contactor required 15 minutes to reach a steady state ozone concentration after power was given to the generator. Effluent trichlorobenzene samples were therefore taken 75 minutes after the ozone generator was turned on.

Procedure to optimize hydrogen peroxide concentration- The contactor was ozonated after initial trichlorobenzene steady state was achieved, subjecting the waste stream to aqueous ozone. Effluent trichlorobenzene and aqueous ozone samples were taken one hour later, after which different peroxide solutions were successively pumped into the reactor using a syringe pump (Razel Scientific, Model A-E). In this way, reactor peroxide concentrations ranging from 6 μM to 6000 μM were achieved. Effluent trichlorobenzene, ozone and peroxide were measured one hour after each new peroxide input was initiated. The inlet ozone concentration for this experiment was 7.7 ± 0.2 mg/l. Reactor pH was maintained at 7.0 ± 0.2.

Determination of ozone, peroxide and UV rate constants- Individual rate constants were determined by treating trichlorobenzene with ozone, peroxide, or UV light. The reactor solution was subjected to these treatments after initial trichlorobenzene steady state concentration was reached. Reactor pH was maintained at 7.0 ± 0.2 for the peroxide and UV studies. The ozone reaction rate constant was calculated with the data obtained in the ozone treatment at varying pH study. The results from the reactor pH of 2.24 was used because hydroxyl radical formation due to ozone decomposition is minimal at low pH values.

pH variation studies - In each experiment, after the trichlorobenzene concentration

reached steady state, the solution in the reactor was subjected to either ozone, ozone/UV, or ozone/peroxide treatment. Sodium hydroxide or phosphoric acid were then pumped into the reactor with a variable speed syringe pump (Razel Scientific, Model A-99) at different rates to obtain the desired reactor pH. For each pH condition, concentrations of trichlorobenzene, ozone, and peroxide (for peroxide studies) were sampled from the effluent. The peroxide concentration determined by the peroxide optimization study was used in the ozone/peroxide treatment.

Humic acid, bicarbonate comparison studies - The effect of humic acid and bicarbonate on the efficiency of trichlorobenzene oxidation was assessed using four advanced oxidation treatment techniques (ozone, ozone/UV, ozone/peroxide, and ozone/peroxide/UV). This study consisted of three separate experiments. In the first experiment, the waste stream was successively treated with the four treatment methods without humic acid or bicarbonate. In the second experiment, the waste stream was also successively treated with the four treatment processes. However, the reactor solution first contained 2 mg/l humic acid for the four treatments. Once these studies were finished, the humic acid concentration in solution was increased to 10 mg/l. In the third experiment, the waste stream was successively treated with the four treatment processes . The reactor solution first contained 2 mM sodium bicarbonate. Once these studies were completed, the sodium bicarbonate concentration in solution was increased to 10 mM. Humic acid and sodium bicarbonate solutions were pumped into the reactor with a variable speed syringe pump (Razel Scientific, Model A-99) to obtain the desired reactor concentrations. Reactor pH was maintained at 7.0 ± 0.2 for

these studies.

4.4 RESULTS

Hydrogen Peroxide Concentration Optimization

The optimum removal of trichlorobenzene was obtained when a peroxide dosage of 60 μM was used, as shown in Figure 4.2. The concentration of the reactor ozone influent was 7.7 ± 0.2 mg/l. 97.8% of the trichlorobenzene was degraded in the reactor (t_d = 10 minutes). The residual ozone and peroxide concentrations were 0.5 ± 0.3 mg/l and 44.5 ± 0.5 μM, respectively. Detailed results of ozone, peroxide, and trichlorobenzene sampling for all experiments are provided in Appendix C.

Potassium Ferrioxalate Actinometer Results

Using a potassium ferrioxalate actinometer, the light intensity of the lamp emitted to the aqueous solution was determined to be 1.21 watts. Specifications of the low pressure immersion lamp list its output power to be 3.15 watts, indicating a 38% UV absorption efficiency into the reactor solution.

UV, Peroxide, and Ozone Rate Constant Determination

The ozone reaction rate constant was calculated with the data obtained in the ozone treatment at varying pH study (at a pH of 2.24). Results indicated that 49% of the trichlorobenzene was removed photolytically without the presence of ozone, 22% was removed with peroxide as the sole oxidant (with a reactor peroxide concentration of 60 μM), and 45% was removed with ozone as the sole oxidant (with a reactor ozone concentration of 4.9 mg/l). Table 4.1 lists the individual reaction rate constants calculated from equation 4.2. The errors associated with the rate constants were

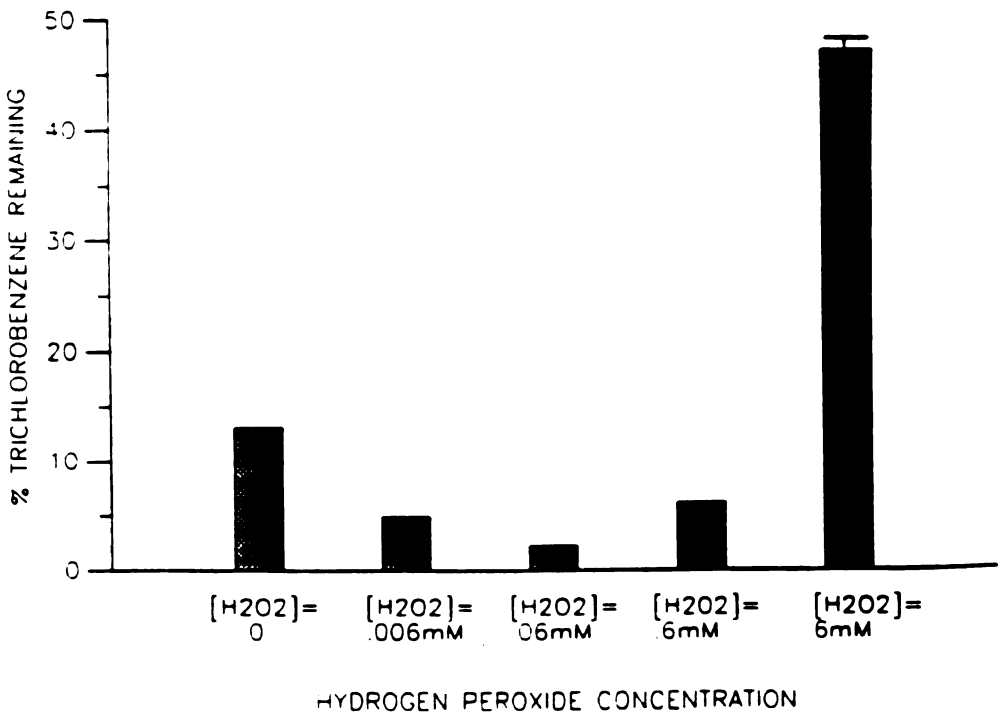


Figure 4.2 Hydrogen Peroxide Optimization

determined by incorporating the standard errors from the replicate samples into a propagation of error analysis.

Table 4.1 Ozone, UV and Peroxide Reaction Rate Constants

Process	pH	k	Units
Ozone	7.0 ± 0.2	9.6 ± 3.0	M^{-1} sec^{-1}
Photolysis	7.0 ± 0.2	8.9 ± 3.6 x 10^{-4}	$watt^{-1}sec^{-1}$
Peroxide	7.0 ± 0.2	6.6 ± 1.8	M^{-1} sec^{-1}

pH Effect on Treatment Process Results

The effect of pH on the ozone, ozone/peroxide, and ozone/UV treatment processes can be shown by plotting the percent trichlorobenzene remaining in the reactor effluent against reactor pH for each treatment process (see Figures 4.3 through 4.5). The data presented in these three figures is combined into Figure 4.6. Table 4.2 lists the pseudo-first order reaction rate constants for each treatment pH as calculated from equation 4.5. Standard errors represent 95% confidence intervals using the five replicate trichlorobenzene measurements.

Humic Acid and Bicarbonate Comparison Results

The results of studies in which the effect of humic acid and bicarbonate was compared are illustrated by plotting the percent trichlorobenzene remaining in the reactor effluent against the type of treatment process used (see Figures 4.7 and 4.8).

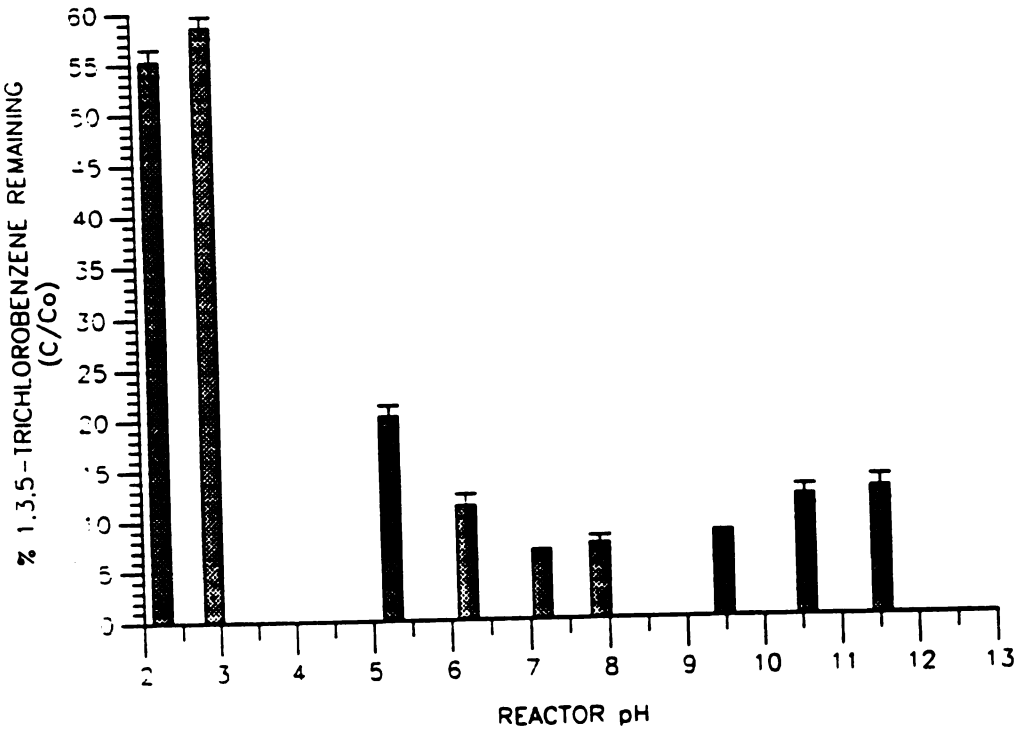


Figure 4.3 Ozone Treatment With Varying pH

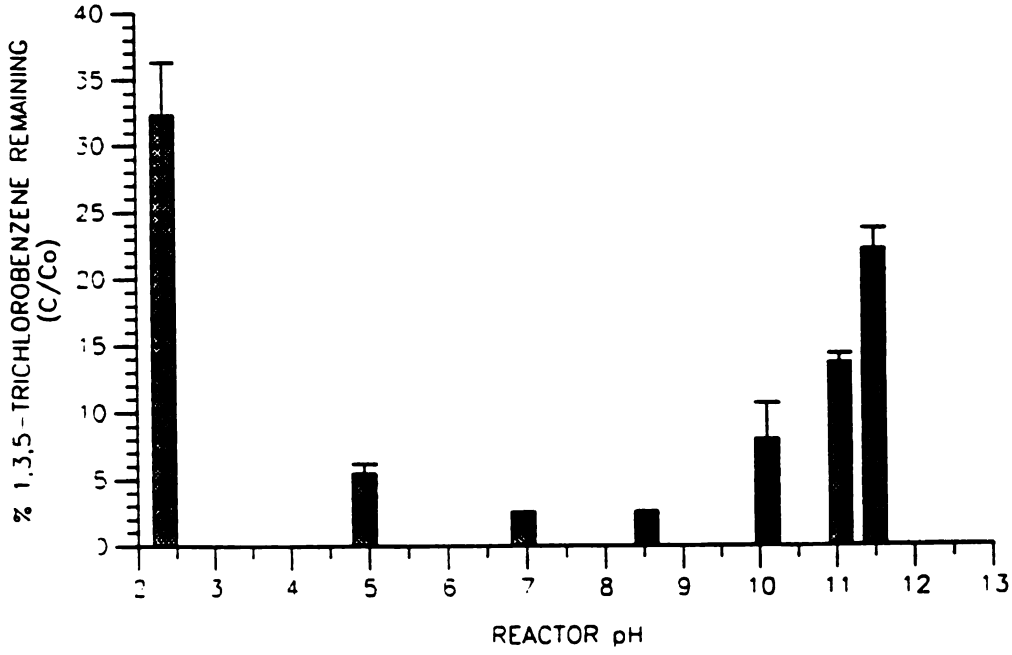


Figure 4.4 Ozone/Peroxide Treatment with Varying pH

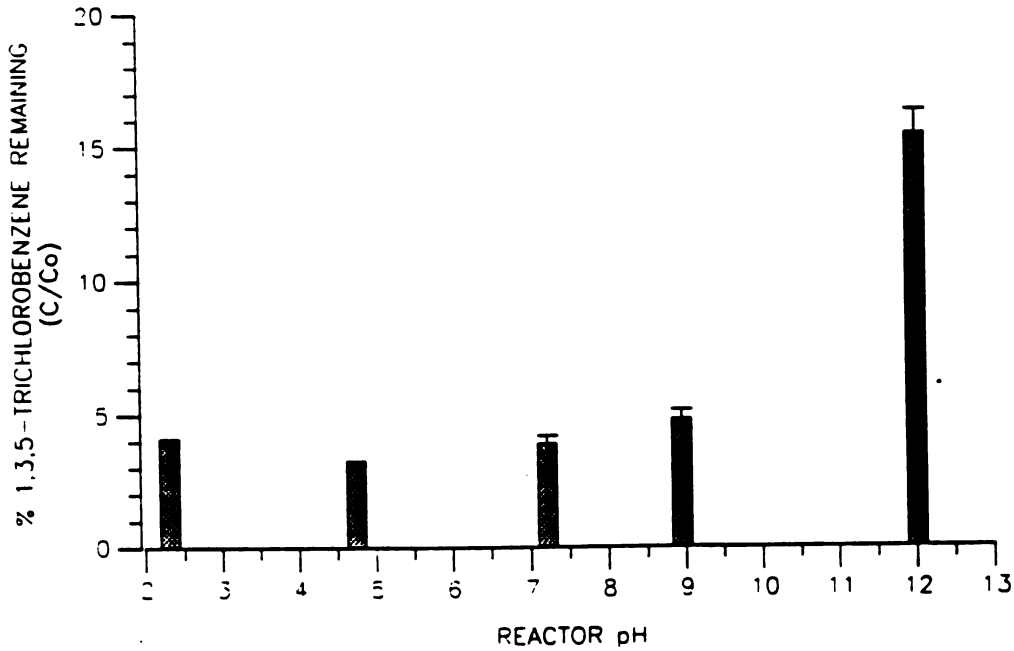


Figure 4.5 Ozone/UV Treatment With Varying pH

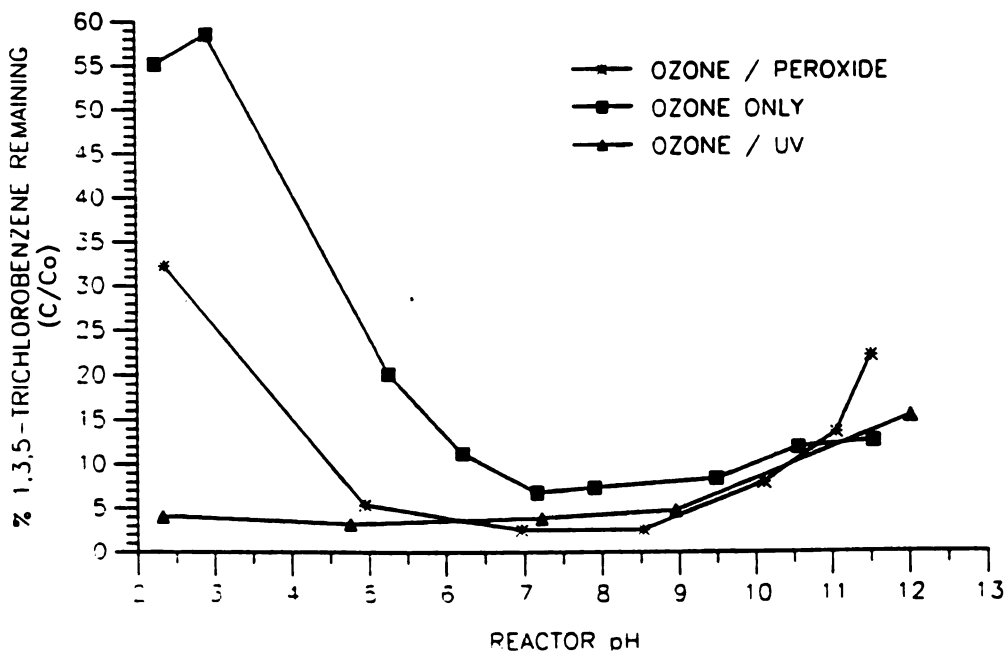


Figure 4.6 Effects of pH on Various Treatment Processes

Table 4.2 Pseudo First Order Rate Constants for pH Variation Study

Treatment Process	pH	k′ (min. $^{-1}$)
Ozone	2.24	0.059 ± .007
Ozone	2.92	0.053 ± .007
Ozone	5.25	0.160 ± .010
Ozone	6.21	0.218 ± .017
Ozone	7.17	0.242 ± .009
Ozone	7.90	0.261 ± .017
Ozone	9.48	0.248 ± .013
Ozone	10.55	0.213 ± .014
Ozone	11.53	0.207 ± .016
Ozone/Peroxide	2.35	0.113 ± .021
Ozone/Peroxide	4.94	0.291 ± .021
Ozone/Peroxide	6.96	0.367 ± .016
Ozone/Peroxide	8.53	0.366 ± .019
Ozone/Peroxide	10.10	0.253 ± .039
Ozone/Peroxide	11.05	0.199 ± .012
Ozone/Peroxide	11.50	0.151 ± .014
Ozone/UV	2.32	0.320 ± .013
Ozone/UV	4.75	0.343 ± .012
Ozone/UV	7.22	0.325 ± .016
Ozone/UV	8.95	0.303 ± .016
Ozone/UV	12.01	0.187 ± .013

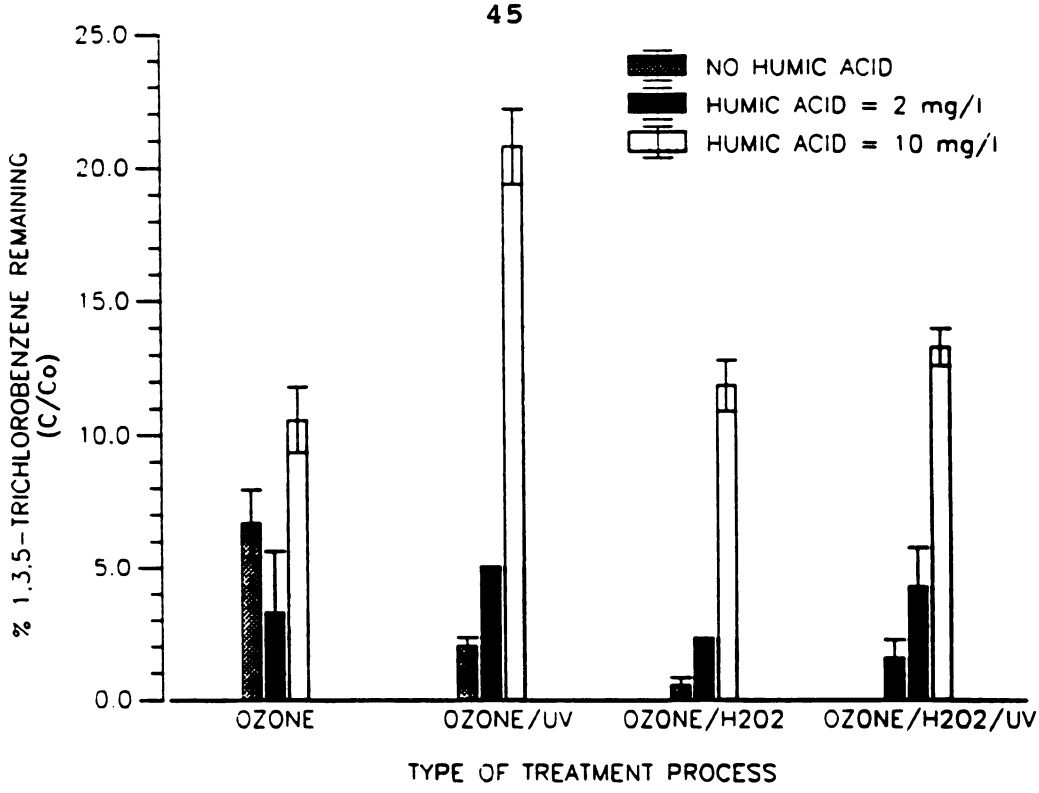


Figure 4 7 Comparing Treatment Processes in the Presence of Humic Acid

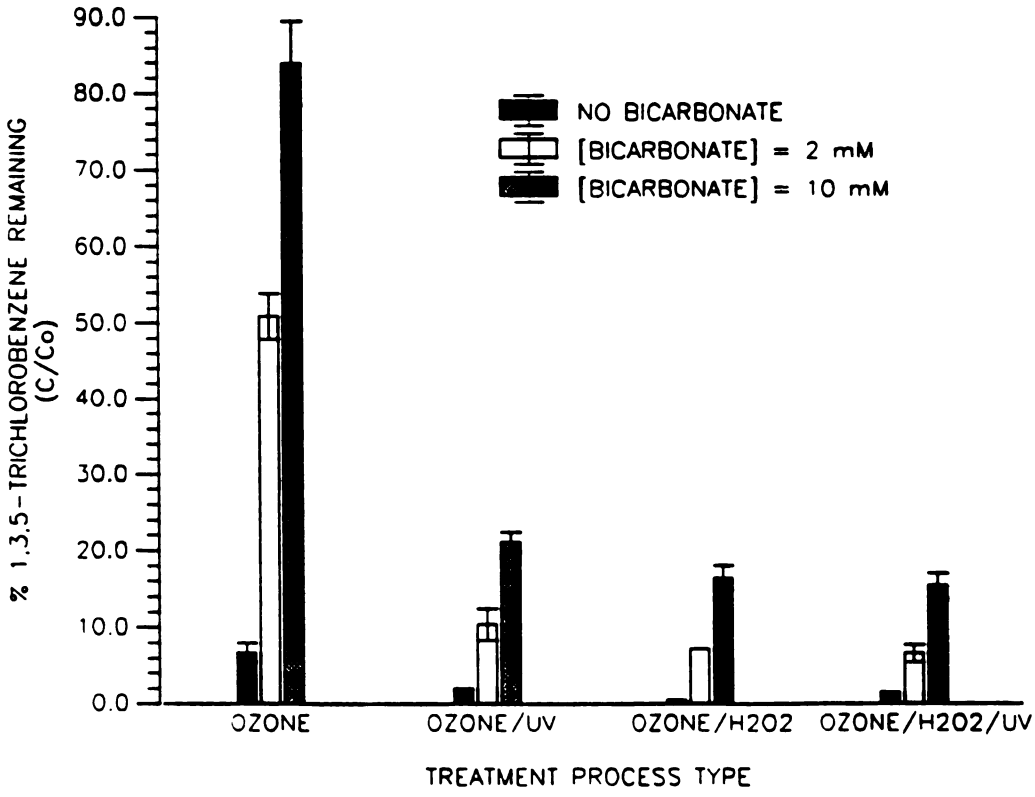


Figure 4 8 Comparing Treatment Processes with Bicarbonate

Table 4.3 lists the pseudo-first order rate constants determined from equation 4.5 for each process along with the treatment process concentration of humic acid or bicarbonate used. k'_{rel} is the relative pseudo-first order rate constant, i.e. the rate constant normalized to the rate constant with no humic acid or bicarbonate for that same process. The errors associated with the rate constants were determined by incorporating the standard errors from the replicate samples into a propagation of error analysis.

Equation 4.1 is integrated and solved for the term $k_{OH}[OH]$:

$$k_{OH}[OH] = \frac{-\theta\,(k_{O_3}[O_3] + k_{photo}[I\Phi] + K_{H_2O_2}[H_2O_2]) - \ln\frac{TCB_f}{TCB_i}}{\theta} \qquad 4.6$$

The results from the studies using no humic acid or bicarbonate were used to calculate $k_{OH}[OH]$ for the four treatment processes. Rate constants from Table 4.1 and results for measured ozone, peroxide, and trichlorobenzene concentrations were substituted into equation 4.6. The UV intensity was assumed to remain constant at 1.21 watts for processes using ultraviolet light. Calculated $k_{OH}[OH]$ values for each treatment process are shown in Table 4.4. Estimated hydroxyl radical concentrations were calculated assuming that the rate constant for the reaction of trichlorobenzene with OH radicals was 2.5×10^9 $M^{-1}sec^{-1}$. A structure-function relationship using vinyl chloride, dichloroehtylene (DCE), and trichloroethylene (TCE) was used to estimate this value. The reaction rate for chlorobenzene (Farhataziz et al., 1987) was multiplied by the ratio of the rate constants of vinyl chloride and TCE (Farhataziz et al., 1987) to obtain

Table 4.3 Rate Constant Comparison with Humic Acid and Bicarbonate

Treatment Process	Humic Acid Conc. (mg/l)	Bicarbonate Conc. (mM)	k' ($min.^{-1}$)	k'_{rel}	% Change in k'
Ozone	0	0	0.270 ± 0.028	1	0
Ozone	2	0	0.341 ± 0.111	1.26	-26.2
Ozone	10	0	0.225 ± 0.021	0.83	16.8
Ozone/UV	0	0	0.389 ± 0.024	1	0
Ozone/UV	2	0	0.299 ± 0.012	0.77	23.3
Ozone/UV	10	0	0.157 ± 0.015	0.40	59.6
Ozone/H_2O_2	0	0	0.555 ± 0.032	1	0
Ozone/H_2O_2	2	0	0.375 ± 0.018	0.68	32.4
Ozone/H_2O_2	10	0	0.213 ± 0.017	0.38	61.6
Ozone/UV/H_2O_2	0	0	0.415 ± 0.060	1	0
Ozone/UV/H_2O_2	2	0	0.316 ± 0.041	0.76	23.9
Ozone/UV/H_2O_2	10	0	0.202 ± 0.014	0.49	51.4
Ozone	0	0	0.270 ± 0.028	1	0
Ozone	0	2	0.067 ± 0.011	0.25	75.0
Ozone	0	10	0.017 ± 0.011	0.06	93.5
Ozone/UV	0	0	0.389 ± 0.024	1	0
Ozone/UV	0	2	0.226 ± 0.026	0.58	41.9
Ozone/UV	0	10	0.155 ± 0.011	0.40	60.1
Ozone/H_2O_2	0	0	0.555 ± 0.032	1	0
Ozone/H_2O_2	0	2	0.263 ± 0.011	0.47	52.6
Ozone/H_2O_2	0	10	0.180 ± 0.015	0.32	67.5
Ozone/UV/H_2O_2	0	0	0.415 ± 0.060	1	0
Ozone/UV/H_2O_2	0	2	0.272 ± 0.022	0.65	34.5
Ozone/UV/H_2O_2	0	10	0.187 ± 0.015	0.45	54.9

this estimate. The errors associated with the rate constants were determined by incorporating the standard errors from the replicate samples into a propagation of error analysis.

Table 4.4 Hydroxyl Radical Concentration Results

Treatment Process	pH	$k_{OH}[OH]$ (Sec^{-1})	[OH] (Moles/liter)
Ozone	7.0 ± 0.2	4.10 ± 0.6 x 10^{-3}	1.64 ± 0.2 x 10^{-12}
Ozone/UV	7.0 ± 0.2	5.35 ± 0.8 x 10^{-3}	2.14 ± 0.3 x 10^{-12}
Ozone/Peroxide	7.0 ± 0.2	9.04 ± 0.6 x 10^{-3}	3.60 ± 0.2 x 10^{-12}
Ozone/Peroxide/UV	7.0 ± 0.2	5.70 ± 1.6 x 10^{-3}	2.28 ± .6 x 10^{-12}

4.5 DISCUSSION

The hydrogen peroxide optimization results agree with work done by Paillard et al. (1988). They reported optimal trichloroethane oxidation occurred at initial peroxide concentrations of 60-70 μM. The optimal peroxide concentration in our study of 60 μM was determined for only one reactor ozone concentration. This occurred at reactor ozone and peroxide concentrations of 0.5 mg/l and 44.5 μM, respectively, and at an initial input ozone concentration of 3.9 mg/l (half of the concentration of the inlet stream). Paillard et al. also reported that in open systems, optimal conditions were obtained when 0.5 moles of peroxide were consumed per mole of ozone introduced.

Based on the above concentrations, our optimal peroxide concentration occurred when 0.2 moles of peroxide were consumed per mole of ozone introduced. Additional studies could be done to determine the optimal ratio of ozone and peroxide introduced to the reactor, as was done by Paillard et al. (1988).

The optimal pH for ozone treatment occurred at 7.90. The pseudo first order rate constant steadily decreased above and below this optimal pH value. A 77% decrease in the pseudo first order rate constant occurred when the pH was lowered from 7.9 to 2.2. A 21% decrease occurred when the pH was increased from 7.9 to 11.53. These results differ slightly from work done by Masten, (1992), who reported the removal efficiency for 1-chloropentane (CPA) with straight ozone treatment increased as the pH was raised from 2 to 10.5 . CPA is not reactive with ozone directly, much like trichlorobenzene. Masten's studies were done in a closed batch type system, unlike our continuous open system. This could explain why the results differed at high pH values. Hydroxyl radical scavenging by carbonate ions is the likely cause for the reduced trichlorobenzene removal efficiency in open systems at elevated pH values. When the pH exceeds 10.3, the carbonate ion is the dominant carbonate species. The carbonate ion scavenges hydroxyl radicals 20 times faster than the bicarbonate ion (Glaze et al., 1987). If carbon dioxide is prevented from entering the system at elevated pH values, a higher removal efficiency may be obtained. Reaction rates at lower pH values are reduced because ozone is stable at low pH values. Fewer hydroxyl radicals are formed at stable ozone conditions. This may not be the case for all chemicals, however. If a compound is reactive with ozone, the removal rate may

increase with decreasing pH values (Masten et al., 1992).

The optimal pH for the ozone/peroxide treatment occurred between a pH of 7.0 and 8.5. The pseudo first order rate constant also steadily decreased above and below this optimal pH value. A 69% decrease in the pseudo first order rate constant occurred when the pH was lowered from 7.0 to 2.3. A 59% decrease occurred when the pH was increased from 7.9 to 11.53. The decrease in removal efficiency as the pH was increased above 7.9 was probably due to carbonate scavenging. Ozone/peroxide treatment reaction rates are low at reduced pH's because fewer hydroperoxide ions are present, as shown:

$$H_2O_2 + H_2O \leftrightharpoons HO_2^- + H_3O^+ \qquad pK = 11.6 \qquad 4.7$$

Below a pH of 11.6, any decrease in pH will result in a decrease in hydroperoxide ion concentration. Hydroperoxide ions react with ozone faster than peroxide (Langlais et al., 1991). Decreased hydroperoxide concentrations result in decreased hydroxyl radical concentrations, causing lower reaction rates.

The optimal pH for the ozone/UV treatment occurred at a pH of 4.7. The reaction rate for this treatment process did not significantly decrease at lower pH values. The efficiency of ozone/UV treatment was only reduced at elevated pH values (above 9.0). A 7% decrease in the pseudo first order rate constant occurred when the pH was lowered from 4.7 to 2.3. A 45% decrease occurred when the pH was increased from 4.7 to 12.0. The decreased reaction rate at elevated pH values was probably caused by carbonate scavenging. Ozone/UV treatment is not effected at low pH values

because the UV light intensity is independent of reactor pH, unlike the hydroperoxide concentration. Even though ozone does not degrade at low pH values, the UV light is strong enough to degrade almost all the ozone, producing similar amounts of hydroxyl radicals.

From Figure 4.6, it is shown that above a pH of 10.5, no advantage is gained by supplementing ozone with peroxide or ultraviolet light. As the pH is increased above 10.5, the carbonate scavenging causes the advanced oxidation treatment techniques to become less efficient. Additional efforts to promote hydroxyl radical formation would be a waste of time and resources.

Reaction rates for the ozone/UV, ozone/peroxide, and ozone/UV/peroxide treatments with humic acid decreased with increasing humic acid concentrations. Humic acid did not seem to enhance radical chain reactions with these advanced oxidation processes, as has been observed for straight ozone treatment (Masten, 1991, Staehelin et al., 1985). Significant trichlorobenzene removal was obtained with 2 mg/l humic acid. Typical humic acid concentrations for groundwater range from 0.03-0.10 mg carbon per liter. Lake and river water range from 0.5 to 4.0 mg carbon per liter (Thurman, 1986). These concentrations can be converted to mg/l by assuming humic acid is 30-50% organic carbon.

The ozone treatment reaction rate increased when 2 mg/l humic acid was used. A two tailed t test determined the removal efficiencies for ozone treatment with 0.0 and 2 mg/l humic acid were statistically different based on the standard deviations of the five replicate samples taken for each process. The reaction rate increased 26% and

decreased 16.8% when humic acid concentrations of 2 mg/l and 10 mg/l were used, respectively. This agrees with the work by Masten and Staehelin, who reported that commercial humic acid may propagate radical chain reactions. Ozone treatment was the only process that showed this radical chain reaction propagation. This is probably because the steady state ozone concentrations for the other treatments were very low (in the range of 0.2 to 0.4 mg/l). The steady state ozone concentration for the straight ozone treatment was about 2.0 mg/l. The ozone was readily available to the humic acid in the ozone treatment process. This allowed sufficient time for the two compounds to react and propagate radical chain reactions. The other advance oxidation processes initiated ozone decomposition faster than humic acid, so no increase in reaction rate was observed when small amounts of humic acid were present.

As the reaction rates for all the processes studied decreased with increasing bicarbonate concentration, it is apparent that hydroxyl radicals play a significant role in the oxidation of trichlorobenzene using advanced oxidation processes. The ozone treatment reaction rate decreased 93.5% when the bicarbonate concentration was increased from 0 to 10 mM. Significant removal rates were still obtained for the ozone/UV, ozone/peroxide, and ozone/peroxide/UV treatment methods with a bicarbonate concentration of 2 mM. Bicarbonate concentrations in natural water vary. Paillard et al., (1987), reported specific ground water, river water, and pond water bicarbonate concentrations of 1.3 mM, 2.35 mM, and .2 mM respectively.

Table 4.4 shows the hydroxyl radical concentration calculated from equation 4.6 to

be very small. However, Glaze et al. (1989), reports that advanced oxidation treatment of organic substrates are practical with steady state hydroxyl radical concentrations in the range of 10^{-10} - 10^{-12} M. The ozone/peroxide treatment process had the highest estimated hydroxyl radical concentration, whereas the straight ozone treatment had the lowest.

The calculated reaction rate constants and hydroxyl radical concentrations indicate the ozone/hydrogen peroxide treatment was the most efficient advanced oxidation process for degrading 1,3,5-trichlorobenzene under the given experimental conditions. Glaze et al. (1987), reports that the ozone/peroxide process yields more hydroxyl radicals, is relatively cost effective, and is easier to adapt to current water treatment designs. Ozone/UV may be more effective in removing organics if they significantly undergo direct photolysis in the UV range.

4.6 CONCLUSIONS

Reaction rates for each treatment process are highest around a pH of 7.0. Ozone/UV treatment reaction rates are pH independent in the range of 2 to 7. At elevated pH the reaction rates decrease significantly. Compared to ozone/UV treatment, the reaction rates for trichlorobenzene oxidation decreased more dramatically in the ozone and ozone/peroxide treatment systems as the reactor pH deviated from the optimal pH of 7.0 . No advantage is gained by supplementing ozone with peroxide or ultraviolet light above a pH of 10.5.

Humic acid acts as both a hydroxyl radical promoter and scavenger. Ozone reaction rates can increase in the presence low humic acid concentrations. Otherwise,

reaction rates decrease with increasing humic acid and bicarbonate concentrations. Significant trichlorobenzene removals were still obtained with humic acid and bicarbonate concentrations of 2 mg/l and 2 mM, respectively.

Based on an indirect determination of hydroxyl radical concentration, the ozone/peroxide treatment was found to generate more hydroxyl radicals, making it the chosen treatment process to remove dissolved 1,3,5-trichlorobenzene from waste streams. The optimal input peroxide concentration for this process is 60 μM.

CHAPTER V

CONCLUSIONS

5.1 CONCLUSIONS

Ace Glass supermix photochemical reactor # 7868 (Reactor A) proved to be sufficiently mixed, supporting continuous flow through stirred reactor (CFSTR) criteria for reactor retention times greater than or equal to five minutes. Ace Glass photochemical reactor # 7863 (Reactor B) could only support CFSTR modeling criteria in series with a plug flow reactor. Mixing studies proved to be an essential first step in continuous flow reactor studies. The reactor first chosen looked as though it could easily satisfy CFSTR modeling criteria. Tracer studies proved otherwise and we were forced to modify the system so it could be accurately modeled.

The method developed for measuring dilute concentrations of hydrogen peroxide in the presence of ozone using the peroxidase catalyzed oxidation of N,N- diethyl-*p*-phenylene diamine proved to be fast, accurate, and reproducible. Hydrogen peroxide samples were accurately measured in the range from 1 to 500 μM, with a lower detection limit of 26 nM. This method worked well in the advanced oxidation studies. Total automation could easily be achieved by incorporating an in line nitrogen bubbler. This would allow for continuous peroxide monitoring and eliminate the need to manually sample the reactor effluent.

Advanced oxidation studies indicate ozone, ozone/UV, and ozone/peroxide treatment processes produce optimal oxidizing environments around a pH of 7.0.

Ozone/UV treatment reaction rates are not effected until elevated pH levels are reached, where reaction rates decrease significantly. Ozone and ozone/peroxide reaction rates decrease at pH levels above and below 7.0. No advantage is gained by supplementing ozone with peroxide or ultraviolet light above a pH of 10.5.

Humic acid acts as both a hydroxyl radical promoter and scavenger. Ozone reaction rates can increase in the presence low humic acid concentrations. Otherwise, reaction rates decrease with increasing humic and bicarbonate concentrations. Significant trichlorobenzene removal with humic acid and bicarbonate concentrations of 2 mg/l and 2 mM, respectively, is achievable.

The ozone/peroxide treatment process was more efficient for the oxidation of 1,3,5-trichlorobenzene when compared to the ozone, ozone/UV, and Ozone/UV/peroxide treatment processes. The optimal input peroxide concentration for this process was found to be 60 μM.

5.2 FUTURE RESEARCH

Based on the conclusions drawn from this research, the following areas should be researched:

1) Hydroxyl radical concentrations must be determined to accurately determine the reaction rate constant with trichlorobenzene. Hydroxyl radical probe analysis should be reviewed and implemented for this purpose.

2) Treatment process rate constants should be verified by repeating experiments at different retention times.

3) Other recalcitrant compounds should be studied to support the conclusions

of this research.

4) Reactor peroxide and ozone sampling techniques should be simplified and fully automated. More treatment processes could then be investigated in a given experiment.

5) Product identification studies should be included in future research.

LIST OF REFERENCES

LIST OF REFERENCES

Bader H., Sturzenegger V., and Hoigné J. (1988) Photometric Method for the Determination of Low Concentrations of Hydrogen Peroxide by the Peroxidase Catalyzed Oxidation of N,N-diethyl-*p*-phenylenediamine (DPD). *Wat. Res.* **22**, 1109-1115.

Bader H. and Hoigné J. (1982) Determination of Ozone in Water by the Indigo Method; A Submitted Standard Method. *Ozone Sci. Eng.* **4**, 169-176.

Baga A., Johnson G., Nazhat N., and Saadalla-Nazhat R. (1988) A Simple Spectrophotometric Determination of Hydrogen Peroxide at Low Concentrations in Aqueous Solutions. *Anal. Chem. Acta.* **204**, 349-353.

Baxendale J.H. and Wilson J.A. (1957) The Photolysis of Hydrogen Peroxide at High Light Intensities. *Trans. Farad. Soc.* **53**, 344-356.

EPA (1990) SITE Program Applications Analysis Report, *ULTROX International Ultraviolet Radiation/Oxidation Technology*, EPA-540/A5-89-012, U.S. Environmental Protection Agency, Washington, DC..

Farhataziz T. and Ross A.B. (1977) Selective Specific Rates of Reactions of Transients in Water and Aqueous Solutions. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **59**.

Glaze W.H. and Kang J.W. (1989) Advanced Oxidation Processes. Description of a Kinetic Model for the Oxidation of Hazardous Materials in Aqueous Media with Ozone and Hydrogen Peroxide in a Semibatch Reactor. *Ind. Eng. Chem. Res.* **28**, 1573-1580.

Glaze W.H., Kang J.W., and Chapin D.H. (1987) The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Sci. Eng.* **9**, 335-352.

Glaze W.H., Peyton G.R., Huang F.Y., Burleson J.L., and Jones P.C. (1980) *Oxidation of Water Supply Refractory Species by Ozone with Ultraviolet Radiation.* EPA-600/2-80-110. U.S. Environmental Protection Agency, Washington, DC.

Guittonneau S., De Latt J., Duguet J.P., Bonnel C., and Doré M. (1990) Oxidation of Parachloronitrobenzene in Dilute Aqueous Solution by O3 + UV and H2O2 + UV : A Comparative Study. *Ozone Sci. Eng.* **12**, 73-94.

Karlberg B. and Pacey G. (1989) *Flow Injection Analysis, a Practical Guide.* Elsevier, New York.

Khan S.R., Huang C.R., and Bozelli J.W. (1985) Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation. *Environ. Prog.* **4**, 229-238.

Kieber R. and Helz G. (1986) Two Method Verification of Hydrogen Peroxide Determinations in Natural Waters. *Anal. Chem.* **58**, 2312-2315. TP1. A5 (chem 1:6)

Kirk P.W.W., Rogers H.R., and Lester J.N. (1989) The Fate of Chlorobenzenes and Permethrins During Anaerobic Sewage Sludge Digestion. *Chemosphere.* **18**, 1771-1784.

Lamporski L.L., Langhorst M.L., Nesterick T.J., and Cutie S. (1980) *J. Assoc. Offic. Anal. Chem.* **63**, 27-32.

Langlais B., Reckhow D.A., and Brink D.R. (1991) *Ozone in Water Treatment: Application and Engineering.* Lewis Publishers, Chelsea, MI.

Legube B., Guyon S., Sugimitsu H., and Doré M. (1983) Ozonation of Some Aromatic Compounds in Aqueous Solution : Styrene, Benzaldehyde, Naphthalene, Diethylphthalate, Ethyl and Chlor Benzenes. *Ozone Sci. Eng.* **5**, 151-170.

Masten S.J. (1991) Ozonation of VOC's in the Presence of Humic Acids and Soils. *Ozone Sci. Eng.* **13**, 287-313.

Masten S.J. and Hoigné J. (1992) Comparison of Ozone and Hydroxyl Radical-Induced Oxidation of Chlorinated Hydrocarbons in Water. *Ozone Sci. Eng.* 14, 197-214.

Murov S.L. (1973) *Handbook of Photochemistry*, M. Dekker, New York.

Nauman E.B. and Buffham B.A. (1983) *Mixing in Continuous Flow Systems.* Wiley, New York.

Paillard H., Brunet R., and Doré M. (1988) Optimal Conditions for Applying an Ozone-Hydrogen Peroxide Oxidizing System. *Wat. Res.* **22**, 91-103.

Paillard H., Brunet R., and Doré M. (1987) Application of Oxidation by a Combined Ozone/Ultraviolet Radiation System to the Treatment of Natural Water. *Ozone Sci. Eng.* 9, 391-418.

Peyton G. and Glaze W. (1988) Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. *Environ. Sci. Technol.* **22**, 761-767.

Peyton G. and Glaze W. (1987) Mechanism of Photolytic Ozonation. *Photochemistry of Environmental Aquatic Systems.* **ACS Symposium Series 327**, 76-87.

Prat C., Vicente M., and Esplugas S. (1988) Treatment of Bleaching Waters in the Paper Industry by Hydrogen Peroxide and Ultraviolet Radiation. *Wat. Res.* **22**, 663-668.

Růžička J. and Hansen E.H. (1981) *Flow Injection Analysis.* Wiley, New York.

Staehelin J. and Hoigné J. (1985) Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions. *Environ. Sci. Technol.* **19**, 1206-1213.

Thurman E.M. (1986) *Organic Geochemistry of Natural Waters.* Martinus Nijhoff/Dr. W. Junk Publishers, Boston.

Wagner R. and Ruck W. (1984) Die Bestimmung von Wasserstoffperoxid und anderen Peroxyverbindungen. *Z. Wass. Abwass. Forsch.* **17**, 262-267.

Xu Y.M., Ménassa P., and Langford C. (1988) Photodecomposition of Several Chloroaromatics Using a Commercial Prototype Reactor. *Chemosphere.* **17**, 1971-1976.

APPENDICES

APPENDIX A

INDIGO BLUE METHOD FOR SAMPLING AQUEOUS OZONE

Appendix A. Indigo Blue Method For Sampling Aqueous Ozone

Introduction

Reactor ozone concentrations are measured to gain insight on what chemical reactions are taking place in solution and are needed to calculate the rate constants for advanced oxidation process. An indigo blue method for ozone determination similar to the one proposed by Bader (as before referenced) is used. Aqueous ozone quickly and stoichiometrically decolorizes indigo trisulfonate so that the change in absorbance of an indigo blue dye solution can be correlated to an aqueous ozone concentration with the aid of a calibration curve.

Calibration Curve Procedure

An aqueous ozone solution of 1.2 mg/l was generated by bubbling ozone gas into an ozone contactor filled with deionized water acidified to a pH of 2.0 with phosphoric acid. This solution concentration was determined by direct UV measurement at 260 nm with a molar absorptivity of 3000 $M^{-1}cm^{-1}$.

Indigo blue stock solution with an absorbance of 1.00 at 600 nm was prepared in deionized water acidified to a pH of 2.0 with phosphoric acid. 100 ml of this solution was pipetted into 150 ml vacuum flasks that contained mini stir bars. Samples were withdrawn from the ozone contactor into the flasks by creating a vacuum in the flask with a hand operated vacuum pump. Teflon tubing, pierced through rubber stoppers, carried the ozonated sample from the contactor to the flask. The flasks were positioned on a magnetic stirrer to provide adequate mixing while sampling. The

flasks were weighed before and after sampling to determine the sample volume. The absorbance of the indigo blue solution was taken after sampling. An ozone calibration curve was generated from this data by calculating the change in absorbance due to the dilution effect of the sample and subtracting this from the total change in absorbance in the indigo solution. The difference equals the change in absorbance due to ozone consumption. This value was plotted against the mg of ozone consumed to generate the indigo blue ozone calibration curve.

Reactor Ozone Sample Procedure

Reactor ozone samples were withdrawn from the reactor as described in the ozone/indigo blue calibration method. The sample line was positioned below the reactor effluent port. The flasks were weighed before and after sampling to determine the sample volume, and the change in absorbance of the indigo blue solution due to ozone consumption was compared to the calibration curve to obtain the weight of ozone in the reactor sample. This weight was divided by the volume of ozone sample to determine the reactor ozone concentration. The ozone calibration curve was not performed for each experiment due to time constraints. The slope of the ozone calibration curve was assumed to stay constant.

Results

Figure A.1 shows the ozone calibration curve using the indigo blue method. A linear relationship exists between the change in absorbance due to ozone consumption and amount of ozone added to the indigo solution. The results indicate a 0.0327 decrease in absorbance for every 10 μg of ozone added to the indigo blue solution.

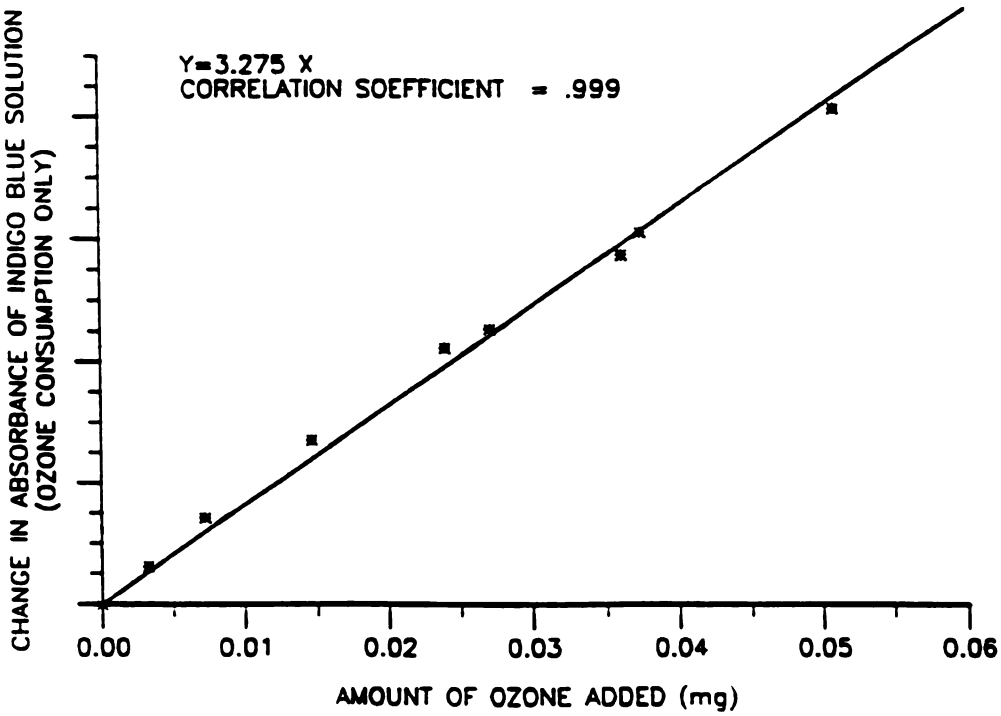


Figure A.1 Indigo Blue/Ozone Calibration Curve

Discussion

The indigo blue method is good for measuring reactor ozone concentrations, but it is time consuming and requires many manual operations. A more efficient way to measure reactor ozone concentrations would be to set up an automated flow injection analysis system that would continuously monitor the ozone by injecting reactor samples into a flowing stream of indigo solution while monitoring the absorbance on a spectrophotometer. This would eliminate weighing the flasks before and after sampling, and also eliminate pipetting 100 ml of indigo solution for each reactor sample taken.

APPENDIX B

TRICHLOROBENZENE TRACER STUDY DETERMINING TIME TO REACH STEADY STATE

Appendix B. Trichlorobenzene Tracer Study Determining Time to Reach Steady State

Introduction

Time for trichlorobenzene to reach steady state in the reactor was determined. This experiment supplements the methylene blue tracer analyses. A ten minute reactor retention time was used. Results from the dye tracer studies indicated 30 minutes would be required for the reactor to reach steady state. The extent to which TCB was degraded by ultraviolet light and peroxide alone, without ozone, was also determined.

Procedure

The photochemical reactor was initially filled with TCB free deionized water. The reactor effluent was sampled to determine if TCB was desorbing from the surfaces in the reactor. TCB solution and deionized water were then pumped in, each at a rate of 12.6 ml/min. Reactor effluent samples were taken in triplicate every 15 minutes for the first hour, and then every 30 minutes after that, for a total of 5 hours. After five hours, the UV light was turned on and triplicate samples were taken after one hour. The UV light was then turned off and peroxide was pumped into the reactor to obtain a concentration of 60 μM. Samples were again taken after 60 minutes to determine if TCB reacted with hydrogen peroxide alone. The reactor solution was kept at a pH of 7.0 ± 0.2.

Results

Figure B.1 indicates the reactor needs 60 minutes (or 6 retention times) to reach a steady state concentration. The UV light alone reduced the reactor TCB concentration from 1371 ppb to 694 ppb (49.4% removal). Hydrogen peroxide reduced the reactor TCB concentration from 1316 ppb to 1048 ppb (20.3% removal).

Discussion

The reactor took twice the amount of time originally predicted by the dye tracer study. Adsorption of TCB to the tubing or reactor walls or even losses to the air may account for this. Six reactor retention times should be allowed to reach steady state. Figure B.1 also shows the reactor concentration does not fluctuate very much when steady state is achieved. This indicates the pumps and mixing motor used in the these studies are capable of maintaining steady state and complete mixing conditions. TCB can be significantly degraded by UV light. Hydrogen peroxide alone was shown to remove a small portion of TCB. This removal is questioned, because the peroxide was pumped into the reactor right after the UV light was turned off. Significant amounts of ozone may have been generated in solution (while the UV light was on) which may have reacted with the peroxide to slow the return of TCB back to steady state.

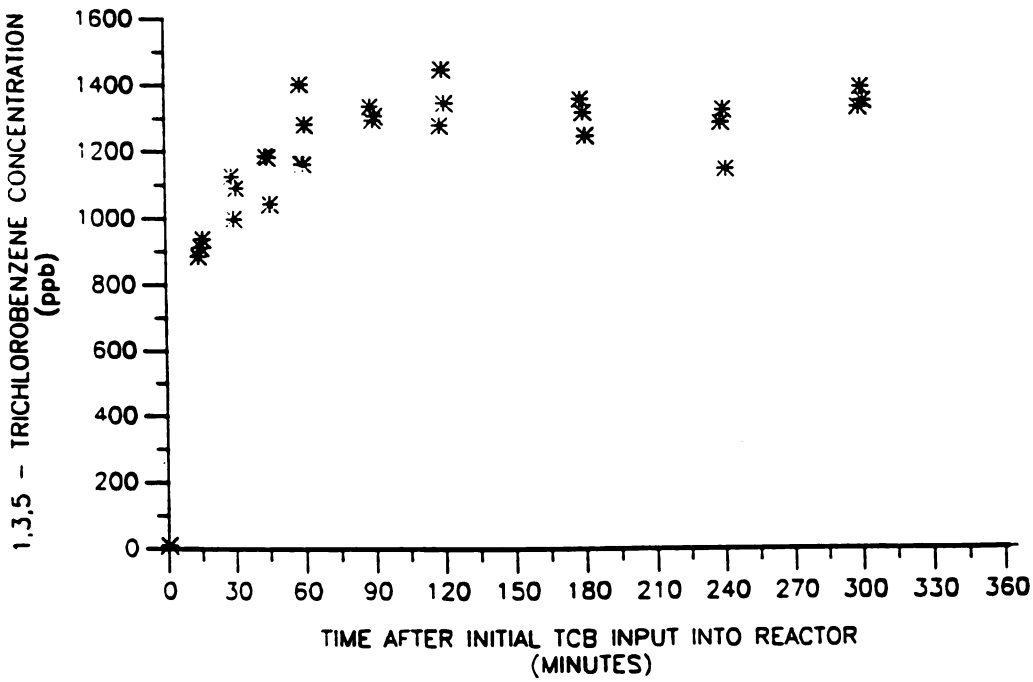


Figure B.1 Trichlorobenzene Tracer Study

APPENDIX C

TRICHLOROBENZENE, OZONE AND PEROXIDE SAMPLING SUMMARY FOR EACH EXPERIMENT

Exp. 1 Hydrogen Peroxide Concentration Optimization

Table C.1 Exp. 1 GC Data Summary

SAMPLE #	COMMENT		CCONC (ppb)	CAREA	IAREA	C.A/I.A	ICONC	CCONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		37.41	2961705	49922312	0.06	626.9	31.04	0.05	0.059
	std2		96.47	8921665	58326904	0.15	626.9	77.59	0.12	0.153
	std3		436.7	38248128	55231944	0.69	626.9	387.8	0.62	0.693
	std4		1381	122249952	55846024	2.19	626.9	1163	1.85	2.189
	std5		3006	269395712	56527916	4.77	626.9	3094	4.94	4.766
	CONT. S.S.									
1	AVG. CONC. =	971.32	935.4	92422176	46712716	1.98	469.9			
2	STD. DEV. =	26.814	993.9	99179664	47177468	2.1	469.9			
3	STD. ERROR =	33.289	978.4	95446008	46120144	2.07	469.9			
4			996.9	98296776	46615956	2.11	469.9			
5			952.1	92251872	45809892	2.01	469.9			
	OZONE ONLY									
6	AVG. CONC. =	126.9	127.8	12440268	46004872	0.27	469.9			
7	STD. DEV. =	3.4238	120.9	12113525	47371992	0.26	469.9			
8	STD. ERROR =	4.2506	129.5	12865593	46969488	0.27	469.9			
9	% REMAIN =	13.065	128.3	12710747	46828292	0.27	469.9			
10	% STD ERR =	0.3914	128	12197710	45065344	0.27	469.9			
	H202=6mM W/O3									
11	AVG. CONC. =	457.6	441.2	42471692	45510072	0.93	469.9			
12	STD. DEV. =	9.5872	463.8	42555864	43377206	0.98	469.9			
13	STD. ERROR =	11.902	463	42032472	42918116	0.98	469.9			
14	% REMAIN =	47.111	463.1	40053808	40888912	0.98	469.9			
15	% STD ERR =	1.096	456.9	36278880	37542720	0.97	469.9			
	H202=.6mM W/O3									
16	AVG. CONC. =	60.049	61.2	5660363	43727584	0.13	469.9			
17	STD. DEV. =	2.6975	55.27	5233329	44764976	0.12	469.9			
18	STD. ERROR =	3.3489	61.41	5647918	43477904	0.13	469.9			
19	% REMAIN =	6.1822	61.69	5765367	44183264	0.13	469.9			
20	% STD ERR =	0.3084	60.67	5421097	42241016	0.13	469.9			
	H202=.06mM W/O3									
21	AVG. CONC. =	21.793	20.26	1814124	42328408	0.04	469.9			
22	STD. DEV. =	2.6816	23.32	2136911	43329008	0.05	469.9			
23	STD. ERROR =	3.3291	20.61	1917696	43990656	0.04	469.9			
24	% REMAIN =	2.2437	25.71	1993744	36668112	0.05	469.9			
25	% STD ERR =	0.3066	19.07	1700024	42136792	0.04	469.9			
	H202=.006mM W/O3									
26	AVG. CONC. =	47.294	46.87	4191256	42277600	0.1	469.9			
27	STD. DEV. =	1.8799	45.43	4168146	43373260	0.1	469.9			
28	STD. ERROR =	2.3339	47.78	4212184	41677960	0.1	469.9			
29	% REMAIN =	4.8691	46.12	4274664	43821128	0.1	469.9			
30	% STD ERR =	0.2149	50.27	4267442	40131440	0.11	469.9			
	std2		54.2	6023783	52547812	0.11	469.9			
	jar	2244.8	2295	206543600	42549424	4.85	469.9			
	jar		2195	191794144	41315664	4.64	469.9			

Exp. 1 (cont.)

Table C.2 Exp.1 Ozone and Peroxide Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	STOCK SOLUTION ABSORB.	SAMPLE VOLUME (ml)	SAMPLE ABSORB.	CHANGE IN ABSORB. DUE DUE TO BOTH DILUTION AND CONSUMPTION	CHANGE IN ABSORB. DUE TO DILUTION EFFECT	CHANGE IN ABSORB. DUE TO OZONE CONSUMPTION	Rx. OZONE CONC. mg/l
1	201.88	225.15	1.06	23.3	0.85	0.2095	0.2	0.0095	0.12
2	201.17	217.97	1.06	16.8	0.89	0.1685	0.1524	0.01611	0.29
3	201.39	214.72	1.06	13.3	0.93	0.1335	0.1246	0.00888	0.20
4	200.93	218.02	1.06	17.1	0.89	0.17	0.1546	0.01536	0.27
5	204.93	224.66	1.06	19.7	0.87	0.185	0.1746	0.01041	0.16
6	200.97	218.19	1.06	17.2	0.88	0.175	0.1556	0.01936	0.34
7	201.26	215.98	1.06	14.7	0.89	0.1665	0.1359	0.03055	0.63
8	201.6	219.54	1.06	17.9	0.87	0.1855	0.1612	0.02434	0.41
9	202.23	221.34	1.06	19.1	0.86	0.1975	0.17	0.02751	0.44
10	201.77	218.97	1.06	17.2	0.8	0.2605	0.1555	0.10501	1.86
11	201.04	212.51	1.06	11.5	0.88	0.177	0.109	0.06798	1.81
12	203.88	222.66	1.06	18.8	0.8	0.2585	0.1675	0.09099	1.48

PEROXIDE SAMPLING DATA

H202 SAMP. #	AVERAGE FIA PEAK (MINUS BLANK)	PEROXIDE CONC. uM/l
1-1	0.209007	6751
1-2	0.209673	6772
2-1	0.197673	638
2-2	0.206673	668
3-1	0.128673	41.6
3-2	0.147113	47.5
4-1	0.016007	5.17
4-2	0.013673	4.42

SUMMARY

INPUT PEROXIDE CONC. (uM) H2O2	REACTOR PEROXIDE CONC. (uM) H2O2	REACTOR OZONE CONC. (mg/l)		STD ERROR (mg/l)	INLET OZONE CONC. (mg/l)
6000	6761.628	0.21	+/-	0.20843	7.68
600	653.0146	0.26	+/-	0.22789	7.68
60	44.53919	0.5	+/-	0.29755	7.68
6	4.793282	1.72	+/-	0.516	7.68

Exp. 2 Aqueous Ozone Treatment at Varying pH (Low Range)

Table C.3 Exp. 2 GC Data Summary

SAMPLE #	COMMENT		CCONC (ppb)	CAREA	IAREA	C.A/I.A	ICONC	CCONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		32.141	1975906	39485368	0.05	626.9	31	0.05	0.05
	std2		85.594	5866974	44025408	0.13	626.9	77.6	0.12	0.133
	std3		362.8	23022056	40757844	0.56	626.9	388	0.62	0.565
	std4		1083.7	71390440	42313000	1.69	626.9	1163	1.85	1.687
	std5		3100.4	234932816	48669388	4.83	626.9	3094	4.94	4.827
	CONT. S.S.									
1	AVG CONC. =	1427.7	1383.1	143878512	50087680	2.87	469.9			
2	STD DEV =	56.132	1486.2	143355744	46444244	3.09	469.9			
3	STD ERR =	69.685	1398.6	143718304	49478256	2.9	469.9			
4			1491.1	147467424	47617308	3.1	469.9			
5			1379.5	138833216	48456772	2.87	469.9			
	OZONE ONLY	pH=7.17								
6	AVG CONC. =	126.49	133.28	13571924	49030068	0.28	469.9			
7	STD DEV =	4.6559	127.64	12622064	47613416	0.27	469.9			
8	STD ERR =	5.7802	125.95	12785809	48877568	0.26	469.9			
9	% REMAINING	8.8599	120.38	12097206	48386956	0.25	469.9			
10	% STD ERR =	0.3621	125.21	12279910	47220532	0.26	469.9			
	OZONE ONLY	pH=6.21								
11	AVG CONC. =	160.94	163.79	16634004	48897928	0.34	469.9			
12	STD DEV =	14.849	174.45	17529516	48383016	0.36	469.9			
13	STD ERR =	18.435	135.57	13813850	49060500	0.28	469.9			
14	% REMAINING	11.273	167.37	16402914	47188112	0.35	469.9			
15	% STD ERR =	1.155	163.52	16255591	47866048	0.34	469.9			
	OZONE ONLY	Ph=5.25								
16	AVG CONC. =	288.26	276.31	26761748	46633156	0.57	469.9			
17	STD DEV =	14.225	275.81	27052184	47224792	0.57	469.9			
18	STD ERR =	17.66	287.13	30714152	51504544	0.6	469.9			
19	% REMAINING	20.191	310.63	32293076	50054676	0.65	469.9			
20	% STD ERR =	1.1064	291.42	29993116	49554764	0.61	469.9			
	OZONE ONLY	Ph=2.92								
21	AVG CONC. =	837.13	845.85	85001144	48385184	1.76	469.9			
22	STD DEV =	13.422	831.77	82042640	47492168	1.73	469.9			
23	STD ERR =	16.662	836.6	82158448	47284520	1.74	469.9			
24	% REMAINING	58.635	818.22	80522792	47383880	1.7	469.9			
25	% STD ERR =	1.0439	853.19	84005648	47407364	1.77	469.9			
	OZONE ONLY	Ph=2.24								
26	AVG CONC. =	789.1	793.13	78284424	47524352	1.65	469.9			
27	STD DEV =	16.013	812.26	76242672	45194464	1.69	469.9			
28	STD ERR =	19.88	791.07	75634920	46035092	1.64	469.9			
29	% REMAINING	55.271	769.84	73045480	45685368	1.6	469.9			
30	% STD ERR =	1.2455	779.19	73450624	45387168	1.62	469.9			

Exp. 2 (cont.)

Table C.4 Exp. 2 Ozone Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	STOCK SOLUTION ABSORB.	SAMPLE VOLUME (ml)	SAMPLE ABSORB.	CHANGE IN ABSORB. DUE DUE TO BOTH DILUTION AND CONSUMPTION	CHANGE IN ABSORB. DUE TO DILUTION EFFECT	CHANGE IN ABSORB. DUE TO OZONE CONSUMPTION
1	202.08	215.96	0.973	13.88	0.758	0.2155	0.1186	0.09691
2	201.89	216.34	0.973	14.45	0.753	0.22	0.1228	0.09715
3	203.09	218.46	0.973	15.37	0.74	0.2335	0.1296	0.10387
4	200.25	222.32	0.973	22.07	0.609	0.364	0.1759	0.18808
5	204.77	220.65	0.973	15.88	0.683	0.29	0.1333	0.15666
6	204.87	222.95	0.973	18.08	0.663	0.31	0.149	0.16102
7	200.81	213.05	0.973	12.24	0.64	0.333	0.1061	0.22689
8	205.96	224.32	0.973	18.36	0.603	0.3705	0.1509	0.21957
9	201.45	219.15	0.973	17.7	0.616	0.3573	0.1463	0.21098
10	199.84	222.7	0.973	22.86	0.385	0.588	0.181	0.40696
11	205.08	227.1	0.973	22.02	0.423	0.55	0.1756	0.37441
12	204.41	223.6	0.973	19.19	0.47	0.503	0.1567	0.34634
13	201.71	218.91	0.973	17.2	0.514	0.459	0.1428	0.3162
14	200.54	212.31	0.973	11.77	0.624	0.349	0.1025	0.24654
15	200.42	222.12	0.973	21.7	0.402	0.5715	0.1735	0.39801

SUMMARY

OZONE SAMPLE #	REACTOR OZONE CONC. (mg/l)	AVERAGE FOR TRIPLICATE (mg/l)		STD ERROR	pH	INLET OZONE CONC. (mg/l)	INLET OZONE ABSORBANCE (mg/l)
1	1.78109					11.92	0.149
2	1.71515	1.74009	+/-	0.089	7.17	11.92	0.149
3	1.72403					11.92	0.149
4	2.17402					11.92	0.149
5	2.51667	2.32086	+/-	0.437	6.21	11.92	0.149
6	2.2719					11.92	0.149
7	4.72882					11.92	0.149
8	3.05078	3.60678	+/-	2.408	5.25	11.92	0.149
9	3.04073					11.92	0.149
10	4.54138					11.92	0.149
11	4.33755	4.49435	+/-	0.345	2.92	11.92	0.149
12	4.60412					11.92	0.149
13	4.6898					11.92	0.149
14	5.34344	4.90405	+/-	0.943	2.24	11.92	0.149
15	4.67891					11.92	0.149

Exp. 3 Aqueous Ozone Treatment at Varying pH (High Range)

Table C.5 Exp. 3 GC Data Summary

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		33.495	2803429	50046320	0.06	626.9	31.04	0.05	0.06
	std2		76.975	6179142	47999204	0.13	626.9	77.59	0.12	0.13
	std3		387.33	33576728	51834216	0.65	626.9	387.8	0.62	0.65
	std4		1221.5	104313592	51062748	2.04	626.9	1163	1.85	2.04
	std5		3072.1	269110688	52379096	5.14	626.9	3094	4.94	5.14
	blank									
	CONT. S.S.									
1	average conc.=	1570.9	1662	166005696	44770176	3.71	469.9			
2	standard dev=	64.45	1527.2	144497520	42411552	3.41	469.9			
3	std. error =	80.013	1611.2	152393984	42394960	3.59	469.9			
4			1548.8	152831728	44230572	3.46	469.9			
5			1505.5	146513824	43622784	3.36	469.9			
	ozone only	pH=7.16								
6	average conc.=	106.91	110.29	10452030	42478824	0.25	469.9			
7	standard dev=	4.9684	105.43	9979315	42426620	0.24	469.9			
8	std. error =	6.1681	106.62	10363486	43569956	0.24	469.9			
9	% remaining =	6.8057	112.59	10553177	42013664	0.25	469.9			
10	% std error=	0.3512	99.644	9642318	43374620	0.22	469.9			
	ozone only	pH=7.9								
11	average conc.=	115.72	122.9	11473997	41846668	0.27	469.9			
12	standard dev=	10.77	128.36	12361594	43165236	0.29	469.9			
13	std. error =	13.371	106.35	10170830	42866916	0.24	469.9			
14	% remaining =	7.3661	103.07	9858496	42873256	0.23	469.9			
15	% std error=	0.7613	117.9	10898346	41435036	0.26	469.9			
	ozone only	pH=10.66								
16	average conc.=	187.39	164.16	15660004	42759412	0.37	469.9			
17	standard dev=	13.73	196.89	18585460	42310392	0.44	469.9			
18	std. error =	17.045	198.36	19993348	45180056	0.44	469.9			
19	% remaining =	11.929	188.74	17817678	42314136	0.42	469.9			
20	% std error=	0.9705	188.81	17379028	41257232	0.42	469.9			
	ozone only	pH=9.48								
21	average conc.=	132.21	121.85	11557052	42512932	0.27	469.9			
22	standard dev=	8.6582	132.59	12067652	40796608	0.3	469.9			
23	std. error =	10.749	125.44	13055726	46650692	0.28	469.9			
24	% remaining =	8.4162	142.35	13115812	41298796	0.32	469.9			
25	% std error=	0.612	138.83	13372054	43174544	0.31	469.9			
	ozone only	pH=11.53								
26	average conc.=	197.73	200.28	18444356	41279348	0.45	469.9			
27	standard dev=	17.006	188.18	17659184	42063180	0.42	469.9			
28	std. error =	21.112	215.87	19442464	40370128	0.48	469.9			
29	% remaining =	12.586	210.42	19167136	40829792	0.47	469.9			
30	% std error=	1.2021	173.88	16309344	42043590	0.39	469.9			

Exp. 3 (cont.)

Table C.6 Exp. 3 Ozone Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	STOCK SOLUTION ABSORB.	SAMPLE VOLUME (ml)	SAMPLE ABSORB.	CHANGE IN ABSORB. DUE DUE TO BOTH DILUTION AND CONSUMPTION	CHANGE IN ABSORB. DUE TO DILUTION EFFECT	CHANGE IN ABSORB. DUE TO OZONE CONSUMPTION
1	205.4	224.26	0.995	18.86	0.71	0.2825	0.157881	0.12462
2	203.28	221.94	0.995	18.66	0.71	0.281	0.15647	0.12453
3	201.15	222.6	0.995	21.45	0.7	0.291	0.175733	0.11527
4	199.75	214.71	0.995	14.96	0.8	0.191	0.129482	0.06152
5	199.9	222.32	0.995	22.42	0.73	0.2695	0.182224	0.08728
6	201.19	217.84	0.995	16.65	0.77	0.224	0.142021	0.08198
7	202.73	217.84	0.995	15.11	0.85	0.1415	0.130609	0.01089
8	202.8	218.03	0.995	15.23	0.85	0.1405	0.13151	0.00899
9	200.23	213.55	0.995	13.32	0.87	0.126	0.116956	0.00904
10	204.19	219.94	0.995	15.75	0.81	0.187	0.135389	0.05161
11	202.71	221.2	0.995	18.49	0.78	0.2175	0.155267	0.06223
12	203.95	218.57	0.995	14.62	0.82	0.178	0.126914	0.05109
13	204.3	217.74	0.995	13.44	0.88	0.116	0.117884	-0.0019
14	202.84	226.54	0.995	23.7	0.81	0.1885	0.190635	-0.0021
15	200.37	222.18	0.995	21.81	0.82	0.176	0.178154	-0.0022

SUMMARY

OZONE SAMPLE #	REACTOR OZONE CONC. (mg/l)	AVERAGE FOR TRIPLICATE (mg/l)		STD ERROR	pH	INLET OZONE CONC. (mg/l)	INLET OZONE ABSORBANCE (mg/l)
1	1.685612					12	0.15
2	1.702461	1.58631	+/-	0.463	7.16	12	0.15
3	1.370858					12	0.15
4	1.049029					12	0.15
5	0.993051	1.09937	+/-	0.343	7.9	12	0.15
6	1.256037					12	0.15
7	0.183866					12	0.15
8	0.150589	0.16922	+/-	0.042	10.6	12	0.15
9	0.173218					12	0.15
10	0.835945					12	0.15
11	0.858618	0.86198	+/-	0.069	9.48	12	0.15
12	0.891389					12	0.15
13	-0.03577					12	0.15
14	-0.02298	-0.02798	+/-	0.017	11.5	12	0.15
15	-0.0252					12	0.15

Exp. 4 Ozone/Peroxide Treatment at Varying pH

Table C.7 Exp. 4 GC Data Summary

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		31.827	2858768	52477424	0.054	626.9	31	0.05	0.05
	std2		80.39	7002482	50890064	0.138	626.9	77.6	0.12	0.14
	std3		381.25	34451760	52794188	0.653	626.9	388	0.62	0.65
	std4		1185	110240800	54349472	2.028	626.9	1163	1.85	2.03
	std5		2612.8	248349344	55531640	4.472	626.9	3094	4.94	4.47
	blank									
	blank *		23.717	1855054	45695532	0.041	626.9	3094	4.94	0.04
	blank *		27.119	2079382	44795960	0.046	626.9	3094	4.94	0.05
	CONT. S.S.									
1	average conc.=	1425.6	1492.9	155769776	45202396	3.409	469.9			
2	standard dev=	72.92	1384.4	141603632	45993804	3.161	469.9			
3	std. error =	90.527	1356.3	142690208	46077108	3.097	469.9			
4			1378.9	146444112	46513488	3.148	469.9			
5			1515.3	151491296	43784256	3.46	469.9			
	ozone/h2o2	**pH=6.96**								
6	average conc.=	36.452	41.237	4385030	46571176	0.094	469.9			
7	standard dev=	2.9306	36.578	3915893	46885568	0.084	469.9			
8	std. error =	3.6382	33.415	3566565	46745648	0.076	469.9			
9	% remaining=	2.557	35.036	3707843	46349448	0.08	469.9			
10	% std error=	0.2283	35.992	3783736	46041744	0.082	469.9			
	ozone/h2o2	**pH=11.5**								
11	average conc.=	316.2	285.56	29608656	45409760	0.652	469.9			
12	standard dev=	20.239	341.71	35700320	45756248	0.78	469.9			
13	std. error =	25.126	318.49	34067220	46846428	0.727	469.9			
14	% remaining=	22.18	313.14	31625920	44232408	0.715	469.9			
15	% std error=	1.5765	322.09	32167694	43740088	0.735	469.9			
	ozone/h2o2	**Ph=8.53**								
16	average conc.=	36.675	39.826	3625998	39874172	0.091	469.9			
17	standard dev=	3.8865	41.53	4389139	46286276	0.095	469.9			
18	std. error =	4.8249	34.851	3490700	43865984	0.08	469.9			
19	% remaining=	2.5727	35.085	3617496	45156520	0.08	469.9			
20	% std error=	0.3027	32.085	3354322	45786324	0.073	469.9			

Exp. 4 (cont.)

Table C.7 (cont.)

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC
21	average conc.=	194.7091	196.351	20399144	45500016	0.45	469.9
22	standard dev=	9.052153	180.429	17402340	42241128	0.41	469.9
23	std. error =	11.23793	194.877	19570358	43981612	0.44	469.9
24	% remaining=	13.65839	196.287	20560388	45874728	0.45	469.9
25	% std error=	0.705112	205.601	20835650	44382784	0.47	469.9
	ozone/h2o2	**pH =10.1**					
26	average conc.=	113.896	104.927	9996954	41726492	0.24	469.9
27	standard dev=	34.51431	85.5047	8436150	43210352	0.2	469.9
28	std. error =	42.8483	174.015	15345929	38622436	0.4	469.9
29	% remaining=	7.989542	100.867	9840492	42726864	0.23	469.9
30	% std error=	2.68847	104.166	10576532	44468408	0.24	469.9
	ozone/h2o2	**pH=4.94**					
31	average conc.=	77.67928	77.7992	8070696	45432776	0.18	469.9
32	standard dev=	9.15239	74.5431	7394539	43444720	0.17	469.9
33	std. error =	11.36237	81.3044	7619730	41044888	0.19	469.9
34	% remaining=	5.449021	89.863	8460548	41233576	0.21	469.9
35	% std error=	0.712919	64.8867	6360756	42932552	0.15	469.9
	ozone/h2o2	**pH=2.35**					
36	average conc.=	460.9127	414.6	40781144	43078836	0.95	469.9
37	standard dev=	31.04475	486.726	51227184	46094552	1.11	469.9
38	std. error =	49.39219	503.711	52323868	45493756	1.15	469.9
39	% remaining=	32.33196	438.614	45616660	45548508	1	469.9
	% std error=	4.000744					

*blank was injected with internal standard

Exp. 4 (cont.)

Table C.8 Exp. 4 Peroxide Sampling Data

SAMPLE #	AVERAGE PEAK ABS.	PEAK - BLANK	PEROXIDE CONC. (uM/l)	STANDARD CONC.	AVERAGE CONC. (uM/l)		std error on triplicate
blank	0.029	0	9.3548				
std1	0.0443	0.0153	14.301	5			
std2	0.12	0.091	38.71	25			
std3	0.301	0.272	97.097	75			
std4	0.473	0.444	152.58	125			
Rx. BLK	0.0267	0	0				
1-1	0.287	0.2603	72.923		72.27	+/-	1.7466
1-2	0.285	0.2583	72.362				
1-3	0.282	0.2553	71.522				
2-1	0.152	0.1253	35.107		34.45	+/-	2.8048
2-2	0.145	0.1183	33.147				
2-3	0.152	0.1253	35.107				
3-1	0.077	0.0503	14.099		13.07	+/-	2.231
3-2	0.072	0.0453	12.698				
3-3	0.071	0.0443	12.418				
4-1	0.109	0.0823	23.063		23.16	+/-	0.4007
4-2	0.109	0.0823	23.063				
4-3	0.11	0.0833	23.343				
5-1	0.071	0.0443	12.418		12.89	+/-	2.6275
5-2	0.07	0.0433	12.138				
5-3	0.077	0.0503	14.099				
6-1	0.069	0.0423	11.858		11.67	+/-	0.4007
6-2	0.068	0.0413	11.578				
6-3	0.068	0.0413	11.578				
7-1	0.236	0.2093	58.637		58.45	+/-	0.4007
7-2	0.235	0.2083	58.357				
7-3	0.235	0.2083	58.357				
8-1	0.253	0.2263	63.399		63.4	+/-	0.694
8-2	0.254	0.2273	63.679				
8-3	0.252	0.2253	63.119				

Exp. 4 (cont.)

Table C.9 Exp. 4 Ozone Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	INDIGO STOCK ABSORBL	SAMPLE VOLUME (ml)	SAMPLE ABSORBL	INDIGO ABSORBL CHANGE	ABSORBL CHANGE FROM DILUTION	ABSORBL CHANGE FROM OZONE REACTION	REACTOR OZONE CONC. (mg/l)
1	201.43	218.42	0.97	16.99	0.839	0.136	0.1415	-0.00595	-0.1069
2	203.46	219.48	0.97	16.02	0.845	0.129	0.1345	-0.00549	-0.1046
3	206.03	220.6	0.97	14.57	0.852	0.122	0.1239	-0.00186	-0.0391
4	200.82	215.7	0.97	14.88	0.846	0.128	0.1262	0.00184	0.0378
5	204.28	222.11	0.97	17.83	0.828	0.147	0.1474	-0.00089	-0.0152
6	204.57	221.84	0.97	17.27	0.829	0.146	0.1434	0.00206	0.0365
7	203.75	219.94	0.97	16.19	0.843	0.132	0.1357	-0.00422	-0.0795
8	205.07	223.06	0.97	17.99	0.826	0.148	0.1485	-0.00051	-0.0086
9	201.72	217.74	0.97	16.02	0.842	0.133	0.1345	-0.00199	-0.0379
10	200.3	220.97	0.97	20.67	0.809	0.165	0.1668	-0.00184	-0.0272
11	200.63	215.12	0.97	14.49	0.852	0.123	0.1233	-0.00077	-0.0162
12	201.58	214.48	0.97	12.9	0.865	0.11	0.1113	-0.00179	-0.0424
13	205.39	223.03	0.97	17.64	0.756	0.219	0.1461	0.07245	1.2541
14	201.61	216.09	0.97	14.48	0.786	0.188	0.1232	0.0648	1.3665
15	199.98	218.64	0.97	18.66	0.748	0.226	0.1532	0.07283	1.1918
16	201.37	211.71	0.97	10.34	0.742	0.232	0.0913	0.14073	4.1557
17	204.47	218.24	0.97	13.77	0.692	0.283	0.1179	0.16461	3.6502
18	206.86	220.75	0.97	13.89	0.677	0.298	0.1188	0.17871	3.9286

OZONE, PEROXIDE SAMPLING SUMMARY

REACTOR OZONE CONC. (mg/l)		STD ERROR	TREATMENT PROCESS	REACTOR pH	REACTOR PEROXIDE CONC. (uM/l)		STD ERROR	INITIAL REACTOR PEROXIDE CONC. (uM/l)	INLET OZONE CONC. (mg/l)
0	S.S. - NO OZONE			6.96	72.27	+/-	1.7466	72.2689	0
.	+/-	-	O3/H2O2	6.96	34.45	+/-	2.8048	72.2689	12
-0.1	+/-	0.0955	O3/H2O2	11.5	13.07	+/-	2.231	72.2689	12
0	+/-	0.0883	O3/H2O2	11.05	12.89	+/-	2.6275	72.2689	12
0	+/-	0.0325	O3/H2O2	10.1	11.67	+/-	0.4007	72.2689	12
0.02	+/-	0.0748	O3/H2O2	8.53	23.16	+/-	0.4007	72.2689	12
1.27	+/-	0.2194	O3/H2O2	4.94	58.45	+/-	0.4007	72.2689	12
3.91	+/-	0.6273	O3/H2O2	2.35	63.4	+/-	0.694	72.2689	12

Exp. 5 Ozone/UV Treatment at Varying pH

Table C.10 Exp. 5 GC Data Summary

SAMP. #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		42.88	3680543	55017168	0.07	627	31.04	0.05	0.07
	std2		83.89	6559281	50117284	0.13	627	77.59	0.12	0.13
	std3		416.5	34373628	52898776	0.65	627	387.8	0.62	0.65
	std4		1326	110545328	53431396	2.07	627	1163	1.85	2.07
	std5		3093	267536528	55437808	4.83	627	3094	4.94	4.83
	CONT. S.S.									
1			1187	104919264	42476596	2.47	470			
2	AVG CONC.=	1281	1303	116555576	42970780	2.71	470			
3	STD DEV.=	71.45	1341	126073256	45166336	2.79	470			
4	STD ERR.=	88.7	1347	123069312	43912520	2.8	470			
5			1225	109682648	43018324	2.55	470			
	uv/ozone pH=7.22									
6	AVG CONC.=	49.71	51.57	4721910	43999880	0.11	470			
7	STD DEV.=	3.598	43.45	4009085	44339272	0.09	470			
8	STD ERR.=	4.467	50.93	4802362	45305436	0.11	470			
9	% REMAIN.=	3.882	52.43	4609044	42242276	0.11	470			
10	% STD ERR.=	0.312	50.19	4691511	44917012	0.1	470			
	uv/ozone pH=2.32									
11	AVG CONC.=	52.44	53.59	5080594	45553908	0.11	470			
12	STD DEV.=	2.563	48.64	4553978	44990016	0.1	470			
13	STD ERR.=	3.182	54.11	5216417	46324140	0.11	470			
14	% REMAIN.=	4.095	54.83	5151349	45140388	0.11	470			
15	% STD ERR.=	0.222	51.03	4801756	45210028	0.11	470			
	uv/ozone Ph=4.75									
16	AVG CONC.=	41.67	39.35	3688140	45030732	0.08	470			
17	STD DEV.=	1.509	43.57	4120523	45443396	0.09	470			
18	STD ERR.=	1.873	41.78	4199960	48303756	0.09	470			
19	% REMAIN.=	3.254	42.02	4091923	46787360	0.09	470			
20	% STD ERR.=	0.131	41.64	3977700	45900012	0.09	470			
	uv/ozone Ph=8.95									
21	AVG CONC.=	61.62	64.27	6206876	46404764	0.13	470			
22	STD DEV.=	4.266	66.15	6300970	45768332	0.14	470			
23	STD ERR.=	5.296	55.21	5232202	45539536	0.11	470			
24	% REMAIN.=	4.811	62.61	5962949	45765100	0.13	470			
25	% STD ERR.=	0.37	59.85	5767900	46309772	0.12	470			
	uv/ozone Ph=12.01									
26	AVG CONC.=	197.8	201.1	19191324	45851728	0.42	470			
27	STD DEV.=	10.3	202.9	18907244	44779924	0.42	470			
28	STD ERR.=	12.78	208	19794552	45717096	0.43	470			
29	% REMAIN.=	15.45	196.1	18754024	45949360	0.41	470			
30	% STD ERR.=	0.893	181.1	16317085	43297504	0.38	470			

Exp. 5 (cont.)

Table C.11 Exp. 5 Ozone Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	STOCK SOLUTION ABSORB.	SAMPLE VOLUME (ml)	SAMPLE ABSORB.	CHANGE IN ABSORB. DUE DUE TO BOTH DILUTION AND CONSUMPTION	CHANGE IN ABSORB. DUE TO DILUTION EFFECT	CHANGE IN ABSORB. DUE TO OZONE CONSUMPTION
1	206.34	220.48	1.01	14.1	0.875	0.1305	0.125	0.006
2	206.14	227.4	1.01	21.3	0.808	0.197	0.176	0.0208
3	205.61	223.16	1.01	17.5	0.847	0.158	0.15	0.008
4	202.69	225.31	1.01	22.6	0.808	0.197	0.185	0.0116
5	201.34	217.8	1.01	16.5	0.851	0.1545	0.142	0.0125
6	200.48	220.13	1.01	19.7	0.828	0.177	0.165	0.0119
7	206.47	230	1.01	23.5	0.795	0.2105	0.191	0.0191
8	200.87	220.41	1.01	19.5	0.824	0.181	0.164	0.0167
9	201.06	216.7	1.01	15.6	0.854	0.151	0.136	0.0151
10	201.99	218.38	1.01	16.4	0.854	0.151	0.142	0.0095
11	202.16	224.71	1.01	22.6	0.808	0.1975	0.185	0.0126
12	204.29	222.9	1.01	18.6	0.837	0.1685	0.158	0.0108
13	201.22	217.01	1.01	15.8	0.861	0.144	0.137	0.007
14	203.78	223.81	1.01	20	0.834	0.171	0.168	0.0033
15	203.35	227.76	1.01	24.4	0.804	0.201	0.197	0.0038

SUMMARY

OZONE SAMPLE NUMBER	REACTOR OZONE CONC. (mg/l)	AVERAGE FOR TRIPLICATE (mg/l)		STD ERROR	pH	INLET OZONE CONC. (mg/l)	INLET OZONE ABSORBANCE (mg/l)
1	0.12951					12.24	0.153
2	0.2987	0.18888	+/-	0.24	7.22	12.24	0.153
3	0.13841					12.24	0.153
4	0.15666					12.24	0.153
5	0.23109	0.19115	+/-	0.09	2.32	12.24	0.153
6	0.18569					12.24	0.153
7	0.24744					12.24	0.153
8	0.26132	0.2677	+/-	0.06	4.75	12.24	0.153
9	0.29434					12.24	0.153
10	0.17654					12.24	0.153
11	0.17025	0.17475	+/-	0.01	8.95	12.24	0.153
12	0.17744					12.24	0.153
13	0.13441					12.24	0.153
14	0.05016	0.07742	+/-	0.12	12.01	12.24	0.153
15	0.0477					12.24	0.153

Exp. 6 Comparing Treatment Processes

Table C.12 Exp. 6 GC Data Summary

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		36.121	3420922	54065468	0.06	626.9	31.04	0.05	0.06
	std2		74.685	6564998	50180996	0.13	626.9	77.59	0.12	0.13
	std3		375.28	36136324	54969404	0.66	626.9	387.8	0.62	0.66
	std4		1166.8	113503296	55531168	2.04	626.9	1163	1.85	2.04
	std5		2838.7	269742400	54246144	4.97	626.9	3094	4.94	4.97
	CONT. S.S.									
1	average conc.=	1571.55	1434	162462432	47456980	3.42	469.9			
2	standard dev=	83.0977	1599.8	167773120	44026632	3.81	469.9			
3	std. error =	103.163	1557.8	173031872	46605196	3.71	469.9			
4			1624.5	174159760	45019572	3.87	469.9			
5			1641.6	177728736	45471376	3.91	469.9			
	ozone only	pH=7.29								
6	average conc.=	105.524	96.061	11728412	39501324	0.3	469.9			
7	standard dev=	18.2376	124.11	15975902	44076388	0.36	469.9			
8	std. error =	22.6413	89.36	13154551	46771044	0.28	469.9			
9	% remain =	6.71464	91.587	10824900	37788984	0.29	469.9			
10	% std error=	1.28864	126.5	13761370	37391028	0.37	469.9			
	O3 HIGH PH	PH=9.71								
11	average conc.=	117.869	127.38	16194422	43142128	0.38	469.9			
12	standard dev=	7.754	116.53	15912401	45460984	0.35	469.9			
13	std. error =	9.62631	124.24	16013914	43511404	0.37	469.9			
14	% remain =	7.50017	111.57	13753391	40639560	0.34	469.9			
15	% std error=	0.54789	109.63	14313340	42868880	0.33	469.9			
	blank		31.323	3099191	42341656	0.07	469.9			
	blank		35.194	3413571	41507584	0.08	469.9			
	OZONE/UV	PH=7.29								
16	average conc.=	32.1061	32.996	7204697	50437560	0.14	469.9			
17	standard dev=	4.35266	34.804	7202104	48971212	0.15	469.9			
18	std. error =	5.40367	36.516	6969824	46136312	0.15	469.9			
19	% remain =	2.04296	30.96	6083813	44058184	0.14	469.9			
20	% std error=	0.30755	25.254	6053545	48524524	0.12	469.9			
	blank		25.868	2681779	44365784	0.06	469.9			
	blank		30.398	2811325	39578076	0.07	469.9			

Exp. 6 (cont.)

Table C.12 (cont.)

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC
	OZONE/H2O2	pH=7.29					
21	average conc.=	6.093288	8.5063	4470761	47099612	0.0949	469.9
22	standard dev=	4.402661	6.2842	4262166	47500428	0.0897	469.9
23	std. error =	5.465749	10.205	4546636	45976296	0.0989	469.9
24	% remain =	0.387725	-1.2785	3436239	47687988	0.0721	469.9
25	% std error=	0.311086	6.7494	4082511	44953684	0.0908	469.9
	blank		32.423	3459986	45667124	0.0758	469.9
	blank		31.806	3315819	44613624	0.0743	469.9
	O3/H2O2/UV	pH=7.29					
26	average conc.=	24.77086	37.677	6161216	38228592	0.1612	469.9
27	standard dev=	9.682773	12.553	4749537	46355112	0.1025	469.9
28	std. error =	12.02082	28.107	6265203	45136408	0.1388	469.9
29	% remain =	1.576207	27.229	5806387	42458508	0.1368	469.9
30	% std error=	0.684171	18.287	5493002	47411208	0.1159	469.9
	blank		31.333	3138506	42865228	0.0732	469.9
	blank		31.254	3199328	43806480	0.073	469.9

Exp. 6 (cont.)

Table C.13 Exp. 6 Ozone and Peroxide Sampling Data

SAMPLE #	BEAKER WEIGHT BEFORE SAMPLE INJECTION	BEAKER WEIGHT AFTER SAMPLE INJECTION	INDIGO STOCK ABSORB.	SAMPLE VOLUME (ml)	SAMPLE ABSORB.	INDIGO ABSORB. CHANGE	ABSORB. CHANGE FROM DILUTION	ABSORB. CHANGE FROM OZONE REACTION	REACTOR OZONE CONC. (mg/l)
1	203.66	221.88	0.998	18.22	0.716	0.283	0.154	0.129	2.157
2	204.41	222.92	0.998	18.51	0.712	0.286	0.156	0.13	2.147
3	202.29	220.61	0.998	18.32	0.715	0.283	0.155	0.128	2.141
4	201.68	216.8	0.998	15.12	0.81	0.188	0.131	0.057	1.15
5	200.38	216.3	0.998	15.92	0.8	0.198	0.137	0.061	1.169
6	205.98	221.87	0.998	15.89	0.797	0.202	0.137	0.065	1.243
7	203.74	219.45	0.998	15.71	0.85	0.148	0.135	0.013	0.243
8	201.67	215.8	0.998	14.13	0.863	0.136	0.124	0.012	0.258
9	201.96	222.6	0.998	20.64	0.816	0.183	0.171	0.012	0.174
10	201.22	216.01	0.998	14.79	0.849	0.149	0.129	0.02	0.421
11	204.38	216.15	0.998	11.77	0.876	0.123	0.105	0.017	0.452
12	203.05	222.69	0.998	19.64	0.814	0.185	0.164	0.021	0.321
13	201.29	222.42	0.998	21.13	0.797	0.202	0.174	0.027	0.396
14	202.24	218.27	0.998	16.03	0.854	0.145	0.138	0.007	0.126
15	200.52	212.93	0.998	12.41	0.882	0.117	0.11	0.006	0.156

PEROXIDE SAMPLING DATA

SAMPLE #	AVERAGE PEAK ABS.	PEAK - BLANK	PEROXIDE CONC. (uM/l)	STANDARD CONC. (uM/l)	AVERAGE CONC. (uM/l)		std error on triplicate (uM/l)
blank	0.0313	0	10.1				
std1	0.043	0.0117	13.87	5			
std2	0.1236	0.0923	39.87	25			
std3	0.323	0.2917	104.2	75			
Rx BLK	0.0287	0	0				
1-1	0.033	0.0043	1.123				
1-2	0.034	0.0053	1.383		1.037	+/-	0.981
1-3	0.031	0.0023	0.605				
2-1	0.108	0.0793	20.57				
2-2	0.108	0.0793	20.57		20.66	+/-	0.371
2-3	0.109	0.0803	20.83				
3-1	0.152	0.1233	31.98				
3-2	0.155	0.1263	32.76		32.5		1.113
3-3	0.155	0.1263	32.76				

OZONE, PEROXIDE SAMPLING SUMMARY

REACTOR OZONE CONC. (mg/l)		STD ERROR (mg/l)	TREATMENT PROCESS	REACTOR pH	REACTOR PEROXIDE CONC. (uM/l)		STD ERROR (uM/l)	INITIAL PEROXIDE CONC. (uM/l)	INLET OZONE CONC. (mg/l)
2.1	+/-	0.0193	OZONE	7.29	---	+/-	---	60	
1.2	+/-	0.1217	OZONE	9.71	---	+/-	---	60	12
0.2	+/-	0.1112	O3/UV	7.29	1.037	+/-	0.981	60	12
0.4	+/-	0.1689	O3/H2O2	7.29	20.66	+/-	0.371	60	12
0.2	+/-	0.3669	O3/H2O2/UV	7.29	32.5	+/-	1.113	60	12

Exp. 7 Comparing Treatment Processes with Humic Acid

Table C.14 Exp. 7 GC Data Summary

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	BLANK									
	STD1		39.363	2819107	45622920	0.06	626.9	31.04	0.05	0.06
	std2		92.702	6526089	44846276	0.15	626.9	77.59	0.12	0.15
	std3		400.01	30478360	48538140	0.63	626.9	387.8	0.62	0.63
	std4		1157.3	94282104	51896936	1.82	626.9	1163	1.85	1.82
	std5		2769.5	232965952	53586776	4.35	626.9	3094	4.94	4.35
	blank									
	CONT. S.S.				HUMIC ACID = 2 mg/l					
1	average conc.=	1333.5	1381.6	144214640	49848084	2.89	469.9			
2	standard dev=	84.355	1433.2	151057184	50330852	3	469.9			
3	std. error =	104.72	1242.6	141609040	54423720	2.6	469.9			
4			1258.8	132482648	50258736	2.64	469.9			
5			1384.2	143092864	49365924	2.9	469.9			
	blank		11.769	1184800	48075492	0.02	469.9			
	blank		1.4559	150069	49222576	0	469.9			
	ozone only		pH=7.3		HUMIC ACID = 2 mg/l					
6	average conc.=	44.173	13.133	2118617	47318136	0.04	469.9			
7	standard dev=	28.008	73.486	6647356	38838072	0.17	469.9			
8	std. error =	34.77	61.164	7054005	48529872	0.15	469.9			
9	% remain.=	3.3126	15.21	2270413	46217684	0.05	469.9			
10	% std error=	2.3323	57.87	6728184	48594264	0.14	469.9			
	blank		7.2923	668956	43807360	0.02	469.9			
	blank		9.2053	886975	46013840	0.02	469.9			
	OZONE/UV		PH=7.3		HUMIC ACID = 2 mg/l					
11	average conc.=	67.368	68.037	7477529	47057224	0.16	469.9			
12	standard dev=	2.2779	64.55	6370517	42022052	0.15	469.9			
13	std. error =	2.8279	67.367	7260369	46098008	0.16	469.9			
14	% remain.=	5.0521	66.2	8008159	51647220	0.16	469.9			
15	% std error=	0.1897	70.685	7803032	47450268	0.16	469.9			
	blank		9.4344	850444	43047200	0.02	469.9			
	blank		6.2567	609971	46555956	0.01	469.9			
	OZONE/H2O2		PH=7.3		HUMIC ACID = 2 mg/l					
16	average conc.=	31.251	28.429	3582973	46331880	0.08	469.9			
17	standard dev=	2.5328	32.218	4143686	48596724	0.09	469.9			
18	std. error =	3.1444	33.933	4248655	47813524	0.09	469.9			
19	% remain.=	2.3436	28.69	3620123	46484224	0.08	469.9			
20	% std error=	0.2109	32.985	4262954	49070468	0.09	469.9			
	blank		6.6341	709304	51057920	0.01	469.9			
	blank		10.368	1060299	48838432	0.02	469.9			

Exp. 7 (cont.)

Table C.14 (cont.)

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC
	OZONE/UV/H2O2		**pH=7.3**		**HUMIC ACID = 2 mg/l**		
21	average conc.=	56.7862	50.497	6317741	50125824	0.126	469.93
22	standard dev=	18.0166	48.419	5713147	46950148	0.122	469.93
23	std. error =	22.367	88.761	10461345	50742816	0.206	469.93
24	% remain.=	4.25853	45.249	5969778	51889320	0.115	469.93
25	% std error=	1.50032	51.005	6193522	48728968	0.127	469.93
	blank		9.1781	980092	50995164	0.019	469.93
	blank		10.205	1030888	48241524	0.021	469.93
	OZONE ONLY		**pH=7.3**		**HUMIC ACID =10 mg/l**		
26	average conc.=	140.926	164.08	17498500	49773716	0.352	469.93
27	standard dev=	14.9242	146.58	13424540	42630264	0.315	469.93
28	std. error =	18.5278	132.46	15207836	53294792	0.285	469.93
29	% remain.=	10.5684	135.47	15140865	51912556	0.292	469.93
30	% std error=	1.2428	126.04	13212265	48591980	0.272	469.93
	blank		3.8059	484537	60797672	0.008	469.93
	OZONE/UV		**pH=7.3**		**HUMIC ACID =10 mg/l**		
21	average conc.=	277.233	283.93	32337684	52315840	0.618	469.93
22	standard dev=	16.8659	259.73	30489600	53732060	0.567	469.93
23	std. error =	20.9384	277.8	31926832	52746720	0.605	469.93
24	% remain.=	20.7904	263.19	29393454	51146320	0.575	469.93
25	% std error=	1.40449	301.51	33964532	51860480	0.655	469.93
	blank		12.601	1294990	49078484	0.026	469.93
	blank		9.8951	1033884	49895888	0.021	469.93
	OZONE/PEROXIDE		**pH=7.3**		**HUMIC ACID =10 mg/l**		
21	average conc.=	157.982	168.83	18782474	50810816	0.37	469.93
22	standard dev=	11.4927	158.79	17560190	50371680	0.349	469.93
23	std. error =	14.2678	146.63	17819278	55140868	0.323	469.93
24	% remain.=	11.8475	169.68	19245540	51814520	0.371	469.93
25	% std error=	0.95704	145.97	16484694	51228856	0.322	469.93
	blank		9.14	996714	52076068	0.019	469.93
	blank		6.2431	649048	49646612	0.013	469.93
	OZONE/UV/H2O2		**pH=7.3**		**HUMIC ACID =10 mg/l**		
21	average conc.=	177.229	190.92	20566518	49073728	0.419	469.93
22	standard dev=	8.39357	176.2	19280496	49656744	0.388	469.93
23	std. error =	10.4203	171.04	19571656	51851904	0.377	469.93
24	% remain.=	13.2909	178.11	19508136	49731156	0.392	469.93
25	% std error=	0.69897	169.87	19213408	51234228	0.375	469.93
	blank		11.731	1157082	47101260	0.025	469.93
	blank		6.6964	661858	47199688	0.014	469.93
	std 3		269.93	26260676	46459264	0.565	469.93

Exp. 8 Comparing Treatment Processes with Bicarbonate

Table C.15 Exp. 8 GC Data Summary

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC	C.CONC (STD) (PPB)	C.C/I.C.	C.A/I.A
	STD1		29.08	3454106	47383152	0.07	489.8	31.2	0.06	0.07
	std2		30.93	3744100	48275280	0.08	489.8	70.3	0.14	0.08
	std3		675.8	82966792	48968528	1.69	489.8	586	1.2	1.69
	std4		1153	140832768	48708168	2.89	489.8	1171	2.39	2.89
	std5		2054	247679104	48091680	5.15	489.8	1952	3.99	5.15
CONT. S.S. diluted 50%			**Sodium Bicarbonate = 2mM**							
1	average conc.=	1172.7	1304	70625616	47304016	1.49	469.9			
2	standard dev.=	697.72	832.1	53045168	54329832	0.98	469.9			
3	std. error =	866.19	1436	84183080	51423508	1.64	469.9			
4	corr.conc.=	1172.7	1522	82024656	47371368	1.73	469.9			
5			769.6	48997500	53967216	0.91	469.9			
CONT. S.S. not diluted			**Sodium Bicarbonate = 2mM**							
6	average conc.=	1361.7	1365	167588624	53732128	3.12	469.9			
7	standard dev.=	41.195	1396	166028192	52073440	3.19	469.9			
8	std. error =	51.142	1374	160524528	51137856	3.14	469.9			
9			1382	161859488	51266416	3.16	469.9			
10			1291	152491312	51561952	2.96	469.9			
	blank		59.71	6593537	50433284	0.13	469.9			
OZONE ONLY	**PH=6.85**		**Sodium Bicarbonate = 2mM**							
11	average conc.=	693.81	681.6	77066328	48256436	1.6	469.9			
12	standard dev.=	36.861	711.7	85579480	51458636	1.66	469.9			
13	std. error =	45.762	634.8	72622656	48589928	1.49	469.9			
14	% remaining =	50.951	715.3	80213872	48007264	1.67	469.9			
15	% std error=	3.0059	725.7	76837104	45365796	1.69	469.9			
	blank		47.85	4593655	43848736	0.1	469.9			
	STD1		47.87	3432444	45677012	0.08	626.9	31	0.05	0.08
	std2		80.6	4208664	33263044	0.13	626.9	77.6	0.12	0.13
	std3		427.4	32773476	48846764	0.67	626.9	388	0.62	0.67
	std4		1220	91141744	47608712	1.91	626.9	1163	1.85	1.91
	blank									
OZONE/UV	**PH=6.85**		**Sodium Bicarbonate = 2mM**							
16	average conc.=	141.81	180.1	17519176	38855416	0.45	469.9			
17	standard dev.=	25.572	145.8	17891422	47615424	0.38	469.9			
18	std. error =	31.747	108.9	14970963	50745808	0.3	469.9			
19	% remaining =	10.414	139.3	17020896	47085136	0.36	469.9			
20	% std error=	2.0853	135.1	17756600	50401228	0.35	469.9			
	blank		25.85	2800593	49478300	0.06	469.9			

Exp. 8 (cont.)

Table C.15 (cont.)

SAMPLE #	COMMENT		C.CONC (ppb)	C.AREA	I.AREA	C.A/I.A	I.CONC
	OZONE/H2O2	**pH=6.85**	**Sodium Bicarbonate = 2mM**				
21	average conc.=	98.014	99.493	13561902	49041572	0.276539	469.9
22	standard dev=	5.8703	88.889	12928769	51036812	0.253322	469.9
23	std. error =	7.2878	104.58	14218605	49424472	0.287683	469.9
24	% remaining =	7.1978	100.63	13702667	49106504	0.27904	469.9
25	% std error=	0.4787	96.47	13897192	51486196	0.269921	469.9
	blank		26.816	2588852	44093084	0.058713	469.9
	OZONE/UV/H2O2	**pH=6.85**	**Sodium Bicarbonate = 2mM**				
26	average conc.=	89.934	84.371	11969428	49915224	0.239795	469.9
27	standard dev=	13.771	93.087	12079587	46661128	0.258879	469.9
28	std. error =	17.096	74.232	10126761	46538964	0.217597	469.9
29	% remaining =	6.6044	111.38	10923202	36540364	0.298935	469.9
30	% std error=	1.1229	86.597	11748724	48018728	0.24467	469.9
	blank		25.155	2549045	46281324	0.055077	469.9
	OZONE ONLY	**pH=6.85**	**Sodium Bicarbonate = 10 mM**				
21	average conc.=	1143.5	1253.3	124047208	44314564	2.799242	469.9
22	standard dev=	70.064	1109.4	127153544	51187012	2.484098	469.9
23	std. error =	86.982	1125	119543504	47472476	2.518165	469.9
24	% remaining =	16.028	1067.8	125136896	52293080	2.392992	469.9
25	% std error=	5.7135	1161.8	132555880	51006308	2.598813	469.9
	OZONE/UV	**pH=6.85**	**Sodium Bicarbonate = 10 mM**				
21	average conc.=	288.37	314.48	35014336	47086780	0.743613	469.9
22	standard dev=	16.141	292.79	34724216	49881352	0.696136	469.9
23	std. error =	20.039	280.34	34724280	51915488	0.668862	469.9
24	% remaining =	78.823	273.72	33617652	51373436	0.654378	469.9
25	% std error=	1.3163	280.5	35261884	52691040	0.66922	469.9
	OZONE/H2O2	**pH=6.85**	**Sodium Bicarbonate = 10 mM**				
21	average conc.=	224.27	239.95	30200098	52029212	0.580445	469.9
22	standard dev=	19.334	209.89	26603388	51694344	0.514629	469.9
23	std. error =	24.002	245.37	30732644	51885828	0.592313	469.9
24	% remaining =	83.53	226.24	27762180	50438792	0.550413	469.9
25	% std error=	1.5766	199.91	24355208	49424748	0.492774	469.9
	OZONE/UV/H2O2	**pH=6.85**	**Sodium Bicarbonate = 10 mM**				
21	average conc.=	209.72	223.29	26514764	48744956	0.543949	469.9
22	standard dev=	19.934	238.15	29407086	51009540	0.576502	469.9
23	std. error =	24.747	198.02	25091760	51352224	0.488621	469.9
24	% remaining =	84.599	194.06	23996722	49997236	0.479961	469.9
25	% std error=	1.6255	195.06	24365780	50535080	0.482156	469.9
	TCB STOCK						
21	average conc.=	2019.8	1974.9	221560272	51265736	4.3218	469.9
22	standard dev=	127.54	1967.7	220506640	51207400	4.306148	469.9
23	std. error =	158.34	2192.3	227322240	47383376	4.79751	469.9

Note - peaks for the jug samples exceeded the limits for the FID det.

APPENDIX D

HEADSPACE SAMPLER AND GAS CHROMATOGRAPH

OPERATING PARAMETERS

Appendix D. Headspace Sampler and Gas Chromatograph Operating Parameters

1,3,5-Trichlorobenzene was measured using a gas chromatograph (Perkin-Elmer Autosystem, Norwalk, CT) equipped with a flame ionization detector (FID) and a silica glass capillary column (Perkin-Elmer, Model 624). The carrier gas was helium. Table D.1 summarizes the operating parameters of the headspace sampler and gas chromatographer used for the trichlorobenzene analysis.

Table D.1 Headspace Sampler and GC Operating Parameters

Flame Ionization Detector	
Temperature	250 °C
Injector	
Temperature	200 °C
Flow	8.0 ml/minute
GC Conditions	
Oven	
Equilibrium Time	1.0 minute
Temperature	90 °C
Hold Time	15 minutes
Carrier Gas	Helium (high purity)
Pressure	20 psi
Headspace Conditions	
Bath Temperature	90 °C
Transfer Line and Needle Temperature	100 °C
Carrier Gas Pressure	20 psi
Equilibrium Time	90 minutes