This is to certify that the

thesis entitled

AN EVALUATION OF ADVANCED OXIDATION PROCESSES
FOR THE TREATMENT OF
CHLORINATED BENZENE IN AQUEOUS SYSTEMS

presented by

Minmin Shu

has been accepted towards fulfillment
of the requirements for

M.S. degree in Environmental Engineering

Susan J. Masten
Major professor

Date April 6, 1995

O-7639

AN EVALUATION OF ADVANCED OXIDATION PROCESSES
FOR THE TREATMENT OF
CHLORINATED BENZENE IN AQUEOUS SYSTEMS

By

Minmin Shu

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

1995

ABSTRACT

An Evaluation of Advanced Oxidation Processes for the Treatment of Chlorinated Benzene in Aqueous Systems

By

Minmin Shu

The purpose of this study is to improve the understanding of the potential of using advanced oxidation processes (AOPs) for the oxidation of chlorinated benzenes in aqueous systems.

The efficiency of oxidation of 1,2-dichlorobenzene using ozone, ozone/UV, ozone/peroxide, and ozone/UV/peroxide treatment was evaluated. The effect of pH, humic acid and bicarbonate was investigated. Pentanoic acid was used as an OH radical probe to estimate the steady state hydroxyl radical concentration and thus, compare the processes studied in terms of their efficiency to generate hydroxyl radicals.

The results indicate that the highest removal rate of 1,2 -dichlorobenzene can be obtained using the ozone/peroxide process in the optimum pH region (pH 6.8-8.5). There is no significant effect on treatment efficiency by humic acid and bicarbonate at concentrations of 2 mg/l and 2 mM, respectively. The results of experiments investigating the oxidation of pentanoic acid, the OH radical probe, supported the hypothesis that the highest treatment efficiency of AOPs is obtained with the system that generates the greatest concentration of OH radicals.

Dedicated to my family members and my friends for their support, encouragement and understanding

ACKNOWLEDGMENTS

I would like to thank my advisors Dr. Susan Masten and Dr. Simon Davies for their encouragement, support and professional guidance throughout my graduate study. Also I thank Dr. Craig Criddle for serving on my committee and for his concern with this research.

I wish to extend my appreciation to all people who provided me with guidance and assistance. In particular, I like to thank M. K. Chiang for the many hours of assistance in the laboratory.

Funding for this research was provided by the Office of Research and Development, US. Environmental Protection Agency under Grant R-816922-01-0 and by the Great Lakes and Mid-Atlantic Hazardous Substance Research Center under grant R-81575-01-0. This work was also financially supported by Dow Chemical Company through the Environmental Enhancement Grant. The content of this publication does not necessarily represent the views of those agencies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATORS

AOPs	Advanced oxidation processes
DCB	1, 2-dichlorobenzence
TCB	1, 3, 5-trichlorobenzene
PA	Pentanoic Acid
$[\mathrm{DCB}]_o$	Initial steady DCB concentration
$[\mathrm{DCB}]$	DCB concentration in the reactor
$[\cdot\mathrm{OH}]$	Hydroxyl radical concentration
k_i	The reaction rate constant for the particular oxidant i
k'	The conditional rate constant for the degradation of DCB
I	The light intensity
ϕ	The quantum efficiency
τ	The hydraulic retention time

I. INTRODUCTION

I-1 General

The chlorobenzenes which are widely used in chemical industries, have been associated with groundwater and surface water contamination. They are potentially toxic and can impart a foul taste and odor to drinking water (Anselme, et al., 1987). The concern for maintaining the quality of water supplies has led to the development of numerous remediation techniques. Advanced oxidation process is one of the several environmentally sound remediation techniques that will destroy the pollutant instead of merely transferring it from one phase to another.

Advanced oxidation processes (AOPs) are defined as those techniques that involve the generation of highly reactive radical intermediates particularly the hydroxyl radical (·OH) at ambient temperature (Glaze and Kang, 1990). Ozone is combined with hydrogen peroxide and /or ultraviolet radiation in AOPs. The efficiency of advanced oxidation processes depends on the oxidant dose, pH, retention time, UV light intensity, the nature of the organic compound, and the concentration of scavenging, promoting, or initiating solutes involved (Masten and Davies, 1993).

Previous research with chlorinated compounds by Masten and Davies (1992), and Galbraith (1993) has shown that the high removal rate of chlorinated compounds occurs at those conditions where ozone degrades to form secondary oxidants, because peroxide and ozone are themselves relatively unreactive with the target compounds and are selective oxidants for only a few classes of organic compounds that contain electron donating groups.

In the previous studies certain compounds were used as kinetic probe to measure the relative reactivity of AOPs. The work conducted by Yao points out that the hydroxyl radical (HO·) is the dominant oxidant in all AOPs (Yao, et al., 1992).

I-2. Objectives of this Study

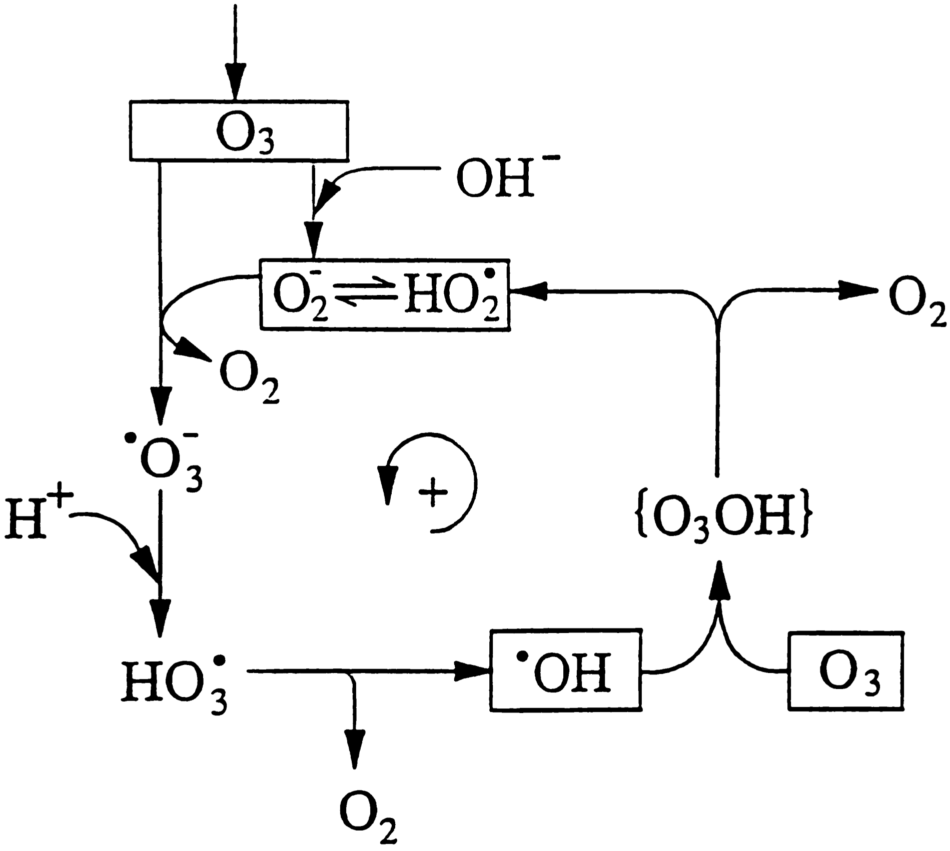
The purpose of this research is to assess the potential of AOPs for the oxidation of dichlorobenzene and to improve our understanding of the mechanism by which AOPs decompose target organic chemicals in aqueous systems. 1, 2- Dichlorobenzene was chosen as the target compound because (1) it is reactive with both ozone and OH radicals, (2) it is semi- volatile, (3) it is on the EPA list of priority pollutants and (4) it is resistant to biological treatment (Kirk et al., 1989). Pentanoic acid anion was chosen as OH radical probe because it is analytically detectable at low concentrations, it produces no chloride ions upon oxidation, it does not absorb light at wavelengths above 240 nm, it reacts with OH radical, and it does not react appreciably with ozone or such secondary radicals as $HO_2\cdot$ and $RO_2\cdot$(Yao et al., 1992).

Experiments were conducted to:

- Select and evaluate compounds to be OH radical probe;
- Determine the effect of pH on the efficiency of the advanced oxidation treatment processes studied;
- Compare the efficiencies of advanced oxidation treatment processes in the presence and absence of humic acid or bicarbonate.

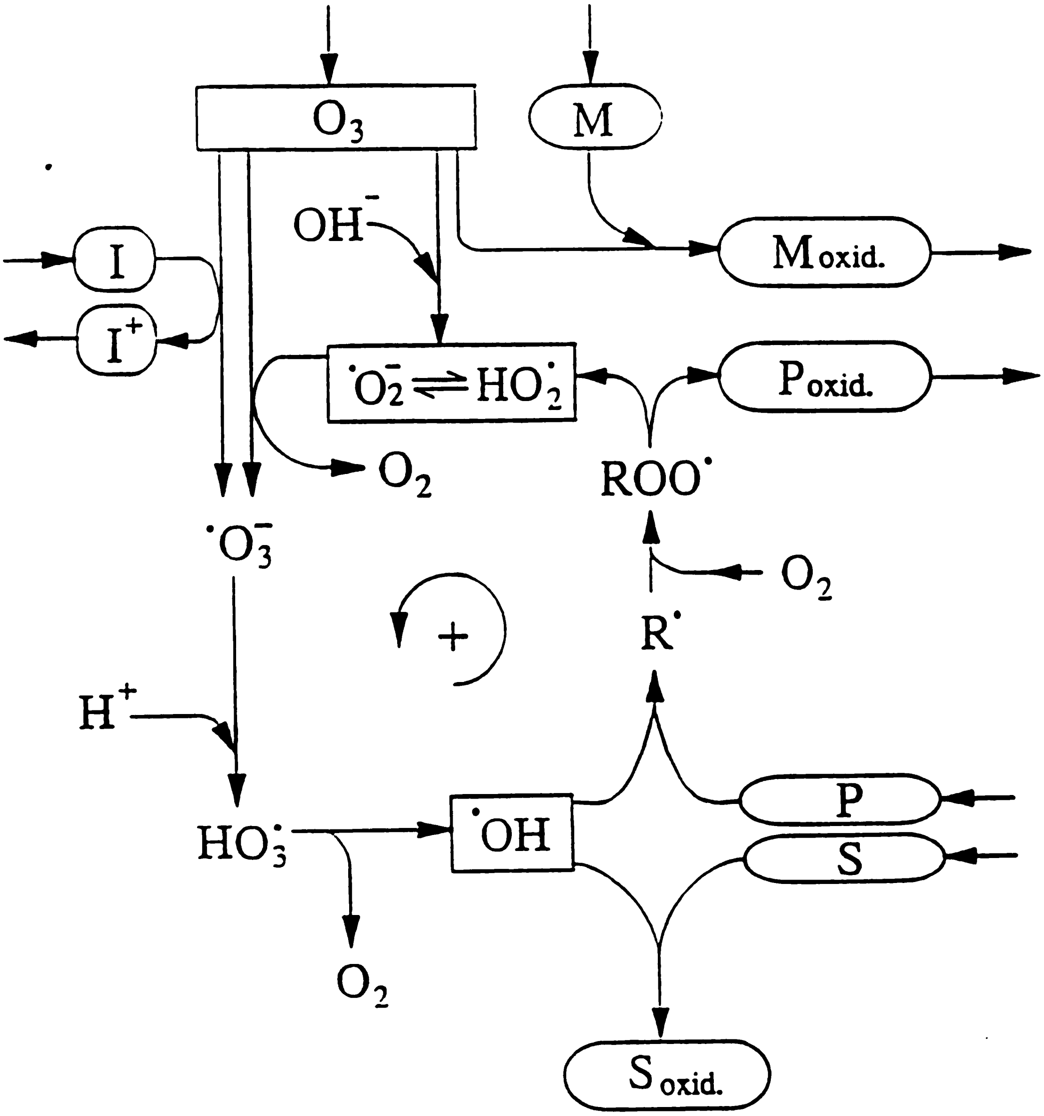
I-3. The Formation of OH Radicals in AOPs

In water ozone decomposes rapidly to form more reactive secondary oxidants, such as $\cdot OH$, $\cdot O^-_2$, and $HO_2^\cdot$. The mechanism by which ozone decomposes in water has been extensively studied. Figure 1-1 illustrates the reactions of ozone in



The oxidants that can oxidize organic chemicals are indicated in the boxes. (Adpapted from Staehelin and Hoigné, 1985)

Figure 1-1
The Decomposition of Ozone in Pure Water



M : a micropollutant which reacts directly with ozone;
I : an initiator which reacts with ozone to initiate the chain reaction mechanism;
S : a scavenger which reacts with OH radicals to terminate the chain reaction;
P : a promoter which reacts with OH radicals to form a radical species which result in chain propagation.

Oxidant species are indicated in boxes. (Adapted from Staehelin and Hoigné, 1985)

Figure 1-2
The Decomposition of Ozone in Waters Containing Reactant Species

pure water (Staehelin and Hoigné, 1985). Hydroxide ions initiate ozone decomposition to form superoxide anions which react via a cyclic mechanism to form a hydroxyl radical. Figure 1-2 shows the complex mechanisms by which ozone decomposes in waters containing species such as humic acid, carbonate/ bicarbonate, iron, carboxylic acid and primary alcohols (Staehelin and Hoigné, 1985). These species can act either as initiators, promoters or inhibitors of free radical reactions. Initiation reactions involve superoxide ion ($O_2^-\cdot$) formation from ozone while promoters are capable of regenerating this ion. Inhibitors decrease the amount of superoxide formed resulting in a decrease in the rate of hydroxyl radical formation. Scavengers directly consume hydroxyl radicals.

Previous studies indicate that there are three ways to initiate ozone decomposition to produce OH radicals in the AOP system (Hoigné and Bader, 1987).

1) By increasing the hydroxide ion concentration (i.e., increasing the pH value), more hydroxide ions will be available to react with O_3, thus increasing the rate of ·OH radical formation. Although there has been much dispute as to the order of the reaction of ozone with OH^- ions, it is widely accepted that the rate of ozone decomposition is proportional to the concentration of OH^- ion.

$$\frac{d[O_3]}{dt} = -k[O_3]^a[OH^-]^b \qquad (1\text{-}1)$$

where a, b >0

In an open system, where bicarbonate and/or carbonate is present, as the pH above 6 there are fewer ·OH radicals to attack the target compound due to bicarbonate and/or carbonate scavenging.

$$\begin{array}{c} HCO_3^- \\ \uparrow\downarrow \\ CO_3^- \end{array} + \cdot OH = \begin{array}{c} HCO_3^{\cdot} \\ \uparrow\downarrow \\ CO_3^{-\cdot} \end{array} + HO^- \qquad (1\text{-}2)$$

2) Hydrogen peroxide dissociates to form hydroperoxide ions, which initiate ozone decomposition to produce superoxide anions, which ultimately produce OH radicals through a chain reaction. Unfortunately, the ozone/peroxide reaction products consume OH radicals via a competition reaction if the hydrogen peroxide concentration is too high.

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \qquad (1\text{-}3)$$

$$O_3 + HO_2^- \rightarrow \cdot OH + O_2^- + O_2 \qquad (1\text{-}4)$$

$$HO_2^- + \cdot OH \rightarrow HO_2^{\cdot} \qquad (1\text{-}5)$$

$$O_3 + \cdot OH \rightarrow HO_2^{\cdot} \qquad (1\text{-}6)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (1\text{-}7)$$

$$HO_2^{\cdot} + \cdot OH \rightarrow H_2O + O_2 \qquad (1\text{-}8)$$

$$2(\cdot OH) \rightarrow H_2O_2 \qquad (1\text{-}9)$$

$$\cdot OH + O_2^{\cdot} \rightarrow OH^- + O_2 \qquad (1\text{-}10)$$

3) Ultraviolet light initiates ozone decomposition to produce hydrogen peroxide

$$O_3 + hv + H_2O \rightarrow H_2O_2 \qquad (1\text{-}11)$$

The hydrogen peroxide formed then either react with ozone to produce OH radicals (Eq.1-3, 1-4) or undergo photolysis to generate the hydroxyl radical

$$H_2O_2 + hv \rightarrow 2\,(\cdot OH) \qquad (1\text{-}12)$$

Hoigné (1987) indicated that ozone decomposition initiated by either OH^- or H_2O_2/ HO_2^- results in similar yield of OH radical production. UV light (255 nm) converts aqueous ozone primarily into OH radicals only at higher pH values (above 7 or 8, depending on the system), where the rate of reaction between H_2O_2/ HO_2^- and O_3 proceeds faster than the rate in low pH range, or at lower light intensities, where ozone photolyzes more slowly, allowing the H_2O_2/ HO_2^- initiated decomposition of ozone to occur.

II. MATERIALS AND METHODS

II-1 Materials

General

Figure 2-1 shows the system configuration used in this study. The system contains three major parts: 1) the aqueous ozone generation and contacting system; 2) the central reactor; 3) the monitoring system. Experimental conditions were controlled by up to nine pumps.

Photochemical Reactor

A Supermix photochemical reactor (Model 7868, Ace Glass Inc., NJ) was used in this study (Figure 2-1). This reactor has two chambers with a total working volume of 250 mL . In the smaller chamber an impeller is rotated using a stirrer motor operated (Model 13583, Ace Glass, Inc., NJ) at 425 rpm to provide efficient mixing by recirculating the liquid in the reactor between the two chambers. A quartz immersion well is located in the main chamber of the reactor to house a low pressure mercury lamp.

UV light

A low pressure immersion lamp having a principal wavelength output 254 nm was housed in a quartz immersion well in the reactor. Using a potassium ferrioxalate actinometer developed by Murov (1973), Galbraith (1993) determined the light intensity of the lamp emitted to the aqueous solution to be 1.21 watts. It is 1.94 watts below its list output power value. This indicates UV absorption efficiency in the reactor aqueous phase is 38 %.

Ozone Generation and Ozone Solution Preparation

A Polymetrics ozone generator (Model T-408, San Jose, CA) was fed with pure dried oxygen to produce gaseous ozone (approximately 3% v/v ozone in oxygen). The dielectric in the ozone generator was cooled by using of a circulating refrigerated water bath system maintained at 10 °C. Aqueous ozone solutions were prepared by continuously bubbling gaseous ozone into a three liter round -bottom flask which was continuously replenished with deionized water that had been acidified to pH 2 with phosphoric acid. The solution was continuously mixed using a magnetic stirrer.

1, 2 -Dichlorobenzene (DCB) Solution Preparation

25 µl 99% spectrophotometric grade 1, 2-dichlorobenzene (99% spectrophotometric grade, Aldrich, Chem. Co., WI) was mixed with 6 L deionized water for three days in a sealed glass flask. This solution was stored in the dark and at room temperature for a maximum of 10 days.

Pentanoic Acid (PA) Solution Preparation

A solution of sodium pentanate (0.1 M) was prepared by dissolving 0.1 M pentanoic acid (99%, Sagam, MO.) and 0.1M NaOH in 1 L of deionized water. The stock solution was stored in the dark, and at room temperature. It was diluted to the appropriate concentration level before it was fed into the reactor.

Humic Acid (HA) Solution Preparation

Humic acid (Sodium salt, Aldrich, Chem. Co., WI) was dissolved in deionized water which had been acidified to pH 2 with phosphoric acid. The suspension was passed through glass fiber filters. Stock solutions were stored in the dark and at 4 °C for up to 3 weeks.

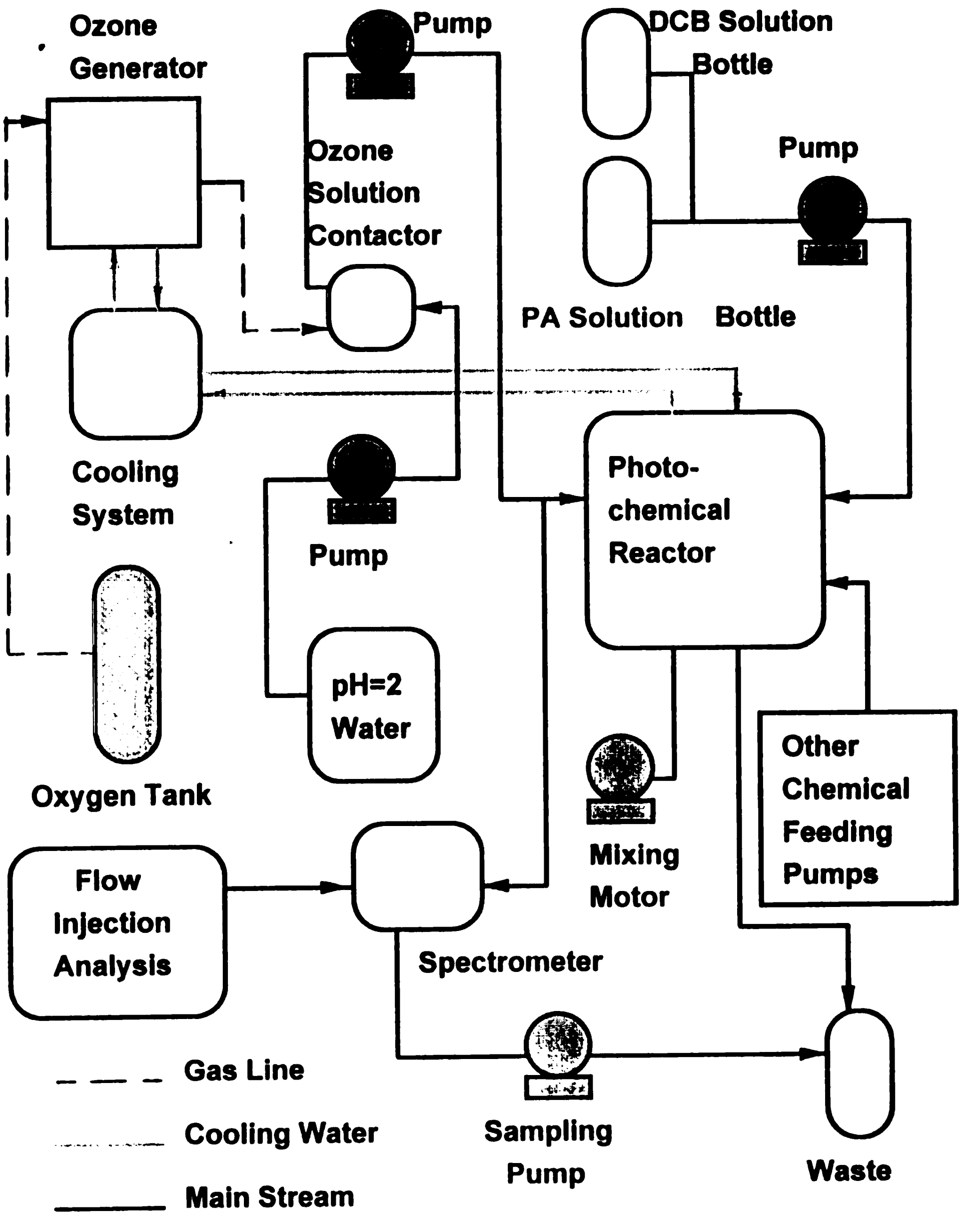
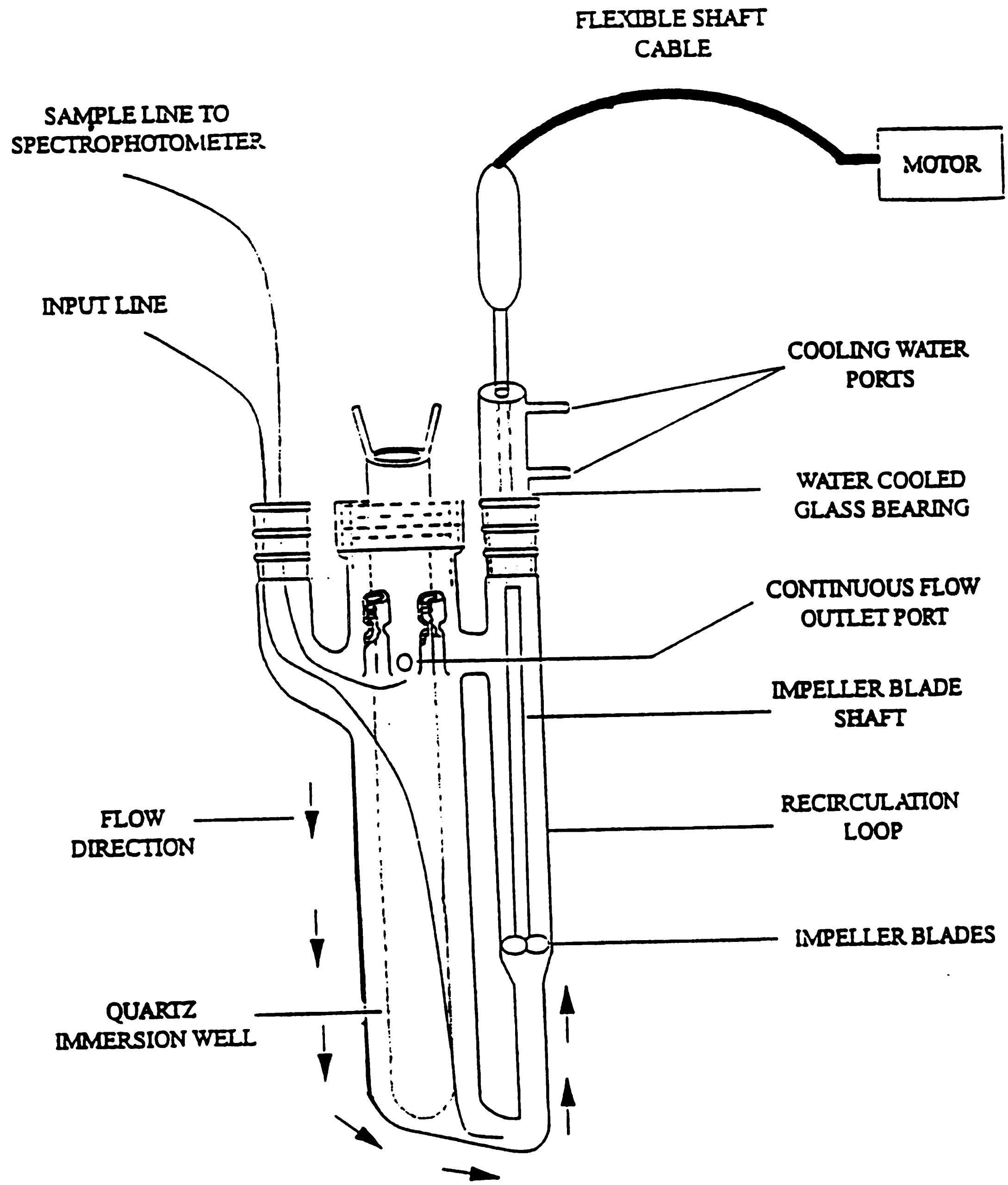


Figure 2-1 System Configuration



(Adapted from Masten and Davies, 1992)

Figure 2-2 The Photochemical Reactor Used in this Research

H_2O_2 Solution Preparation

Hydrogen peroxide (30% solution, Sigma, MO.) was diluted to 0.01 M and standardized by direct UV absorption ($\epsilon = 40.0$ $M^{-1}cm^{-1}$ at $\lambda = 240$ nm). This standard solution was diluted to an appropriate concentration level based on the experimental requirement.

Bicarbonate Solution Preparation

Sodium bicarbonate (Analytical reagent, J.T. Baker Inc., NJ) was dissolved in deionized water at the appropriate concentration level.

1,3, 5-Trichlorobenzene Stock Solution

1, 3, 5-Trichlorobenzene (99%, Aldrich, Chem. Co., WI) was used as internal standard for headspace GC analysis, A stock standard solution (1000mg/L) was prepared by dissolving trichlorobenzene in methanol.

II-2 Analytical Methods

Ozone Analysis

The aqueous ozone concentration in the inlet stream to the reactor was determined using a UV/vis spectrophotometer (Shimadzu Scientific Instruments, Inc., Model UV-1201, Columbia, MD) The solution was pumped through a flow cell to continuously monitor the absorbance at wavelength of 258 nm. An extinction coefficient of 3000 M^{-1} cm^{-1} (Galbraith, et al.,1992) was used to convert absorbance units to concentration. A small portion of the inlet stream to the reactor was continuously drawn through the flow cell by a pump.

The concentration of ozone in the reactor was determined by the indigo blue method (Bader et al., 1982) to avoid the possibility of interfering compounds absorbing light at 258 nm. The samples were collected from the reactor outlet into volumetric flasks containing known amounts of indigo blue solution. Calibration curves for the determination of ozone concentration were made daily.

Headspace Analysis of 1, 2-Dichlorobenzene

1, 2 -Dichlorobenzene and 1, 3, 5 -trichlorobenzene were determined by head-space gas chromatography (Perkin Elmer, GC Model, Autosystem, Sampler Model : HS-40, Norwalk, CT) equipped with a flame ionization detector (FID) and a 30 meter, 0.53 mm ID silica glass capillary column (Perkin Elmer, Model 624, Norwalk, CT). An internal standard was used in all samples and in calibration and check standards. GC and sampler operating parameters are provided in Table 2-1.

Analysis of Pentanoic Acid: Esterification of Acid using BF_3 in Methanol

Pentanoic acid concentrations were determined in water by a method that involves the esterification of the acid using BF_3 in methanol. The ester is then quantified using head-space gas chromatography with an autosampler (Perkin Elmer, GC Model : Autosystem, Sampler Model : HS-40, Norwalk, CT) equipped with a flame ionization detector (FID) and a 50 meter, 0.53 mm ID silica glass capillary column (Perkin Elmer, Model 624, Norwalk, CT). This method gives good linearity from 90 ppb to 5.5 ppm. The GC and sampler operating parameters are provided in Table 2-2. The details of this method are presented in Appendix 1.

Effluent H_2O_2 Analysis : Flow Injection Analysis

Flow injection analysis is based on the colorimetric titration of a liquid sample, that has been injected into a non-segmented, continuously moving carrier stream of a suitable liquid. The injected sample mixes with the carrier liquid to form a zone of colored liquid, which is then transported through a flow cell that is positioned in the spectrophotometer . The absorbance of the stream is continuously monitored.

The effluent hydrogen peroxide concentration was determined by flow injection analysis (FIA) (Galbraith, 1993) with a UV/vis spectrophotometer at a wavelength of

Table 2-1
Headspace GC and Sampler Operation Conditions for DCB and TCB Analysis

Flame Ionization Detector (FID)	
Temperature	250 °C
Injection	
Temperature	250 °C
Pressure	20 psi
Column	DB-624, 30m × 0.53mm ID
GC Condition	
Oven	
Equilibration. Time	1.0 min
Temp.erature	110 °C
Program Time	12 min
Carrier Gass	Helium (high purity)
Pressure	20 psi
Sampler Condition	
Equilibration Time	45 min
Equili. Temperature	90 °C
Transfer line and NeedleTemp.	100 °C
Carrier Gas	Helium (high purity)
Pressure Time	2.0 min
Injection Time	0.5 min

Table 2-2
Headspace GC Operation Conditions for Pentanoic Acid Analysis

Flame Ionization Detector (FID)	
Temperature	250 °C
Injection	
Temperature	250 °C
Pressure	20 psi
Column	DB-624, 50m × 0.53mm ID
GC Condition	
Oven	
Equilibration Time	1.0 min
Initial Temperature	70 °C
Holding Time	18 min
Program Rate	40 °C/ min
Final Temperature	230 °C
Hold Time	17 min
Carrier Gass	Helium (high purity)
Pressure	20 psi
Sampler Condition	
Equilibration Time	20 min
Equilibration Temperature	70 °C
Transfer Line and Needle Temp.	100 °C
Carrier Gas	Helium (high purity)
Pressure Time	2.0 min
Injection Time	0.5 min

551 nm (Shimadzu Scientific Instrument, Inc., Columbia, MD) using a modification of the peroxidase N,N-diethyl-*p*-phenylenediamine (DPD) method (Bader et al., 1988). This method is based upon the hydrogen peroxide in the sample oxidizing the peroxidase in the carrier stream. The oxidized peroxidase then oxidizes the DPD to the radical cation DPD^{+} which has a relatively stable red color that can been monitored by a UV/vis spectrophotometer. The FIA system configuration is shown in Appendix 2.

II-3 Experimental Approach

Experimental Condition Control

The hydraulic retention times in the reactor were controlled by the influent flow rates of ozone solution and target compound solution which were pumped by two piston pumps (Fluid Metering Inc., Model RHSY,Oyster Bay, NY) at an equal flow rates of 12.5 ml/min.

The pH value in the reactor were controlled by a syringe pump (RAZEL Scientific Instruments, Model A-99.ER Conn.) which pumped a NaOH solution (0.5 or 1.0 N) into reactor at the speed required to achieve the desired pH values.

The aqueous ozone solution was maintained at a constant level in the contactor by a peristaltic pump (Cole Parmer, Model 7520-35, Niles, IL) which was used to continuously replenish the phosphoric acid solution in the contactor while the aqueous ozone solution was pumped out at a same flow rate.

Influent humic acid, bicarbonate and hydrogen peroxide solutions were pumped into the reactor by syringe pumps (RAZEL Scientific Instruments, Model A.Z Conn.) at the appropriate speeds.

Sampling

The DCB, PA samples were collected at the reactor effluent exit. The aliquots were added to 150 μL sodium nitrite solution (0.9 M) contained in 20 mL head space GC vials. Effluent hydrogen peroxide samples were collected into a test tube at the reactor effluent exit, then immediately bubbled with nitrogen gas to purge all ozone before the sample was injected into the FIA system.

Experimental Procedure

Nitrobenzene, 1-chlorobutane, propionic acid (salt), butyric acid (salt) and pentanoic acid (salt) were examined as OH radical probes. The choice of an appropriate probe were made upon evaluating (1) the solubility, volatility and reactivity of these compounds with ozone; (2) the results of GC analysis to determine if these compounds interfered with the analysis of DCB; (3) the results of experiments to determine a suitable analytical method for the probe compounds. PA was chosen as the probe (see Section III-1).

Experiments were conducted to investigate the effects of pH, humic acid and bicarbonate on the efficiency of AOPs to oxidize DCB and PA. A 10 min retention time was used. Before turning on the ozone generator, the solutions containing the target compound and an acidified solution (from ozone contactor) were pumped into reactor. Based upon the results of tracer mixing study, after six retention times the system reached steady state (Appendix 3). As such, after one hour, the initial samples were obtained. The effluent concentrations determined during various treatments were compared to this initial concentration to determine the treatment efficiency of each process. All of the DCB and PA degradation results were compared with 1,3, 5-trichlorobenzene (TCB) degradation results obtained by Galbraith (1993).

PA and DCB were not oxidized in the same solution. However, as we wished to compare the results obtained with DCB with that of PA, it was necessary to control the experimental system so that the same experimental conditions could be used for DCB and PA. As such, either PA or DCB could be pumped into the experimental system by simply turning a swtching valve.

The Ozone/UV process was used as a cleaning process for the system after each experiment, detergent/water washing, followed by organic solvent cleaning were used when necessary.

III. RESULTS

III-1 •OH Radical Probe Selection

Based on the examination of the physical and chemical characteristics of the probe chemicals, the results of our analytical method development, pentatonic acid (salt) was found to be the most appropriate OH radical probe among the five examined compounds (pentanoic acid (salt), propionic acid (salt), butyric acid (salt), nitrobenzene and 1-chlorobutane) examined.

Pentanoic acid (salt) has a high water solubility and dissolves in water instantly, it is nonvolatile and does not have UV/vis spectum above 240 nm (Fig 3-1). It produces no chloride ions upon oxidation, it reacts with OH radical and does not react appreciably with ozone (See Fig 3-2) or the secondary radicals such as $HO_2^{\cdot}$or $RO_2^{\cdot}$ (Yao, et al. 1992), and it is analytically detectable at low concentrations.

Propionic acid (salt) and butyric acid (salt) have similarly physical and chemical characteristics as those of pentanoic acid (salt). Methanol was used in esterification of the acid in the headspace GC/FID analysis and coeluding peaks were the major problem in propionic acid (salt) analysis. Coelution also resulted in a slight reduction in the reproducibility of butyric acid (salt) measurement.

Nitrobenzene was analyzed using same GC program as DCB, and reproducibility was excellent. This GC program was modified by decreasing the start temperature to 49 °C for 1-chlorobutane analysis, but both of these compounds were ruled out as :

(1) Nitrobenzene has a no negligible reactivity with ozone and functions as a promoter of radical chain reactions by increasing the rate of formation of OH radical (Akata et al., 1992).

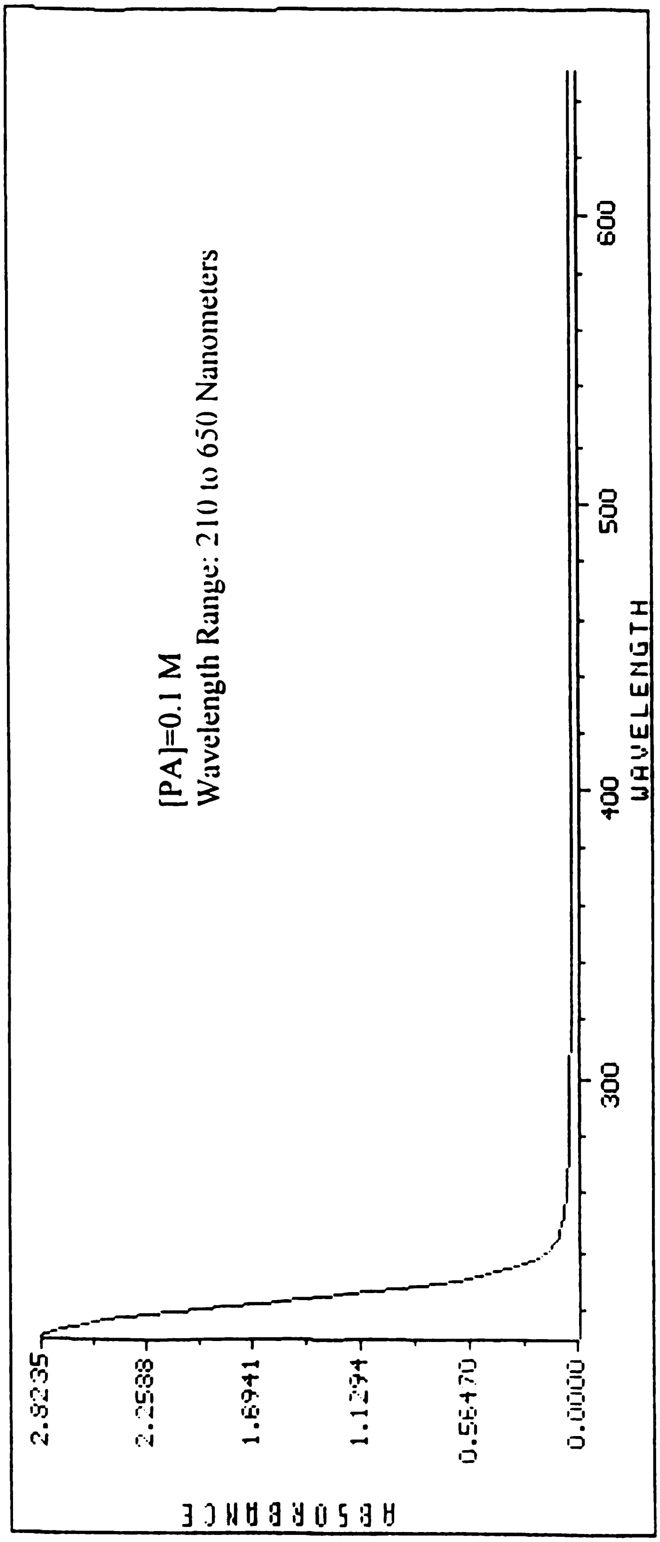


Figure 3-1 UV/Vis Spectrum for Pentanoic Acid (pH = 2.5)

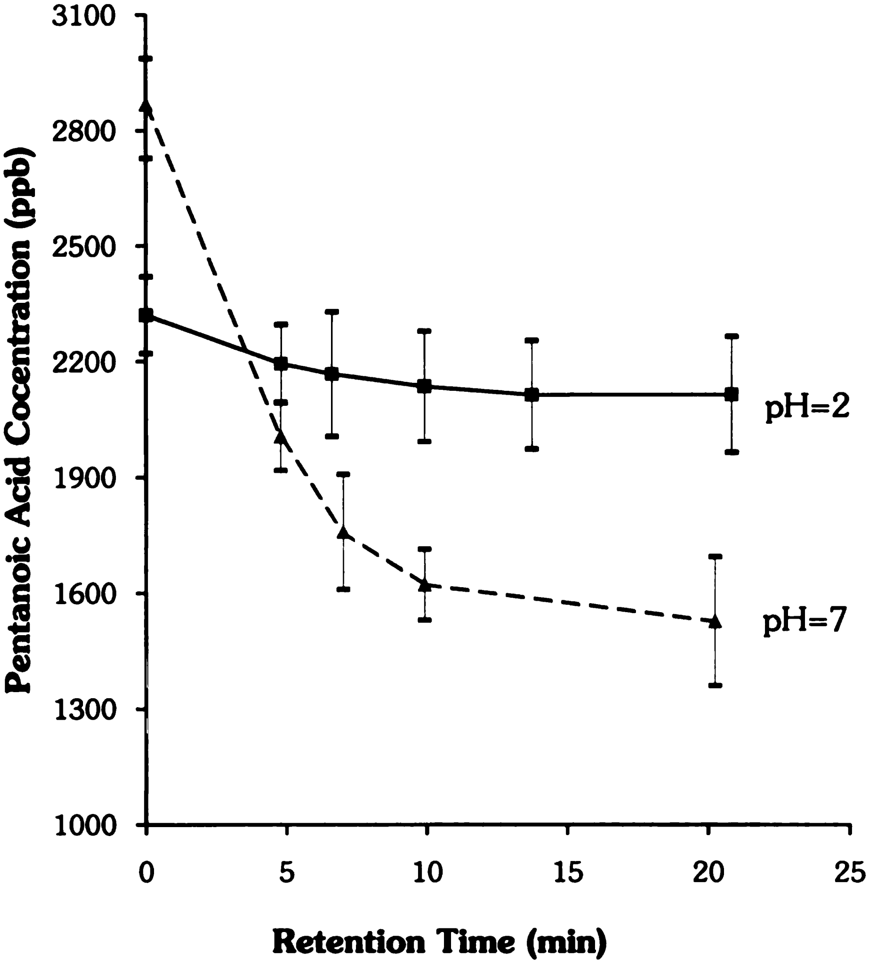


Figure 3-2
Variation of the Effluent Pentanoic Acid Concentration with Retention Time

(2) 1- Chlorobutane may produce chloride ions upon oxidation.

(3) Three days are required to prepare solutions of nitrobenzene and 1- chlorobutane.

III-2. The Effect of pH on Dichlorobenzene Degradation

Figure 3-3 shows the effect of pH on the efficiency of oxidation of DCB in ozone, ozone /UV and ozone /H_2O_2 treatment processes. The percentage of DCB remaining in the reactor effluent is plotted against reactor pH for each treatment process. For all of three processes, the decomposition of DCB occurred fastest at a pH between 7.0 to 8.5 . The efficiencies of ozone and ozone/H_2O_2 treatment for the oxidation of DCB increased with pH in the pH region below 7, whereas, the efficiencies decreased slightly with increasing pH in the pH region above 9. Ozone/UV treatment was relatively insensitive to changes in pH. Figure 3-4 illustrates the comparison of each treatment process efficiency at optimum pH region (pH about 7.0 to 8.5). The results indicate that ozone/H_2O_2 is most efficiency treatment process. This can also be observed from the overall reaction rate constants (see Table 3-2). Similar results were observed with both DCB and TCB.

III-3 The Effect of Humic Acid and Bicarbonate on Ozone/UV Treatment

Figure 3-5 and Figure 3-6 illustrate the effect of humic acid and bicarbonate on DCB degradation in the ozone/UV system. For all experimental conditions, greater than 84% degradation of DCB was obtained. The addition of humic acid (2 and 10 mg/l) and bicarbonate (2 and 10 mM) resulted in decreases in the extent of degradation of DCB and TCB. However, the decrease in the efficiency of DCB oxidation is small compared to that observed for TCB degradation with a bicarbonate concentration

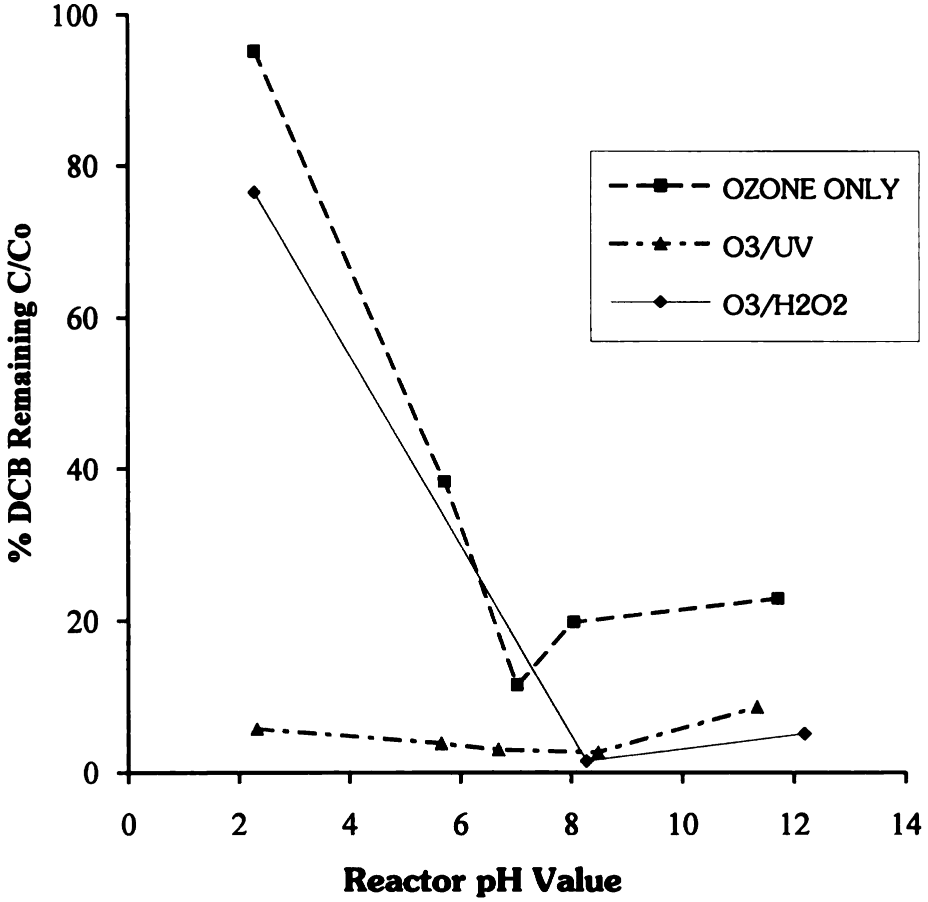


Figure 3-3
Effect of pH on Various Treatment Processes

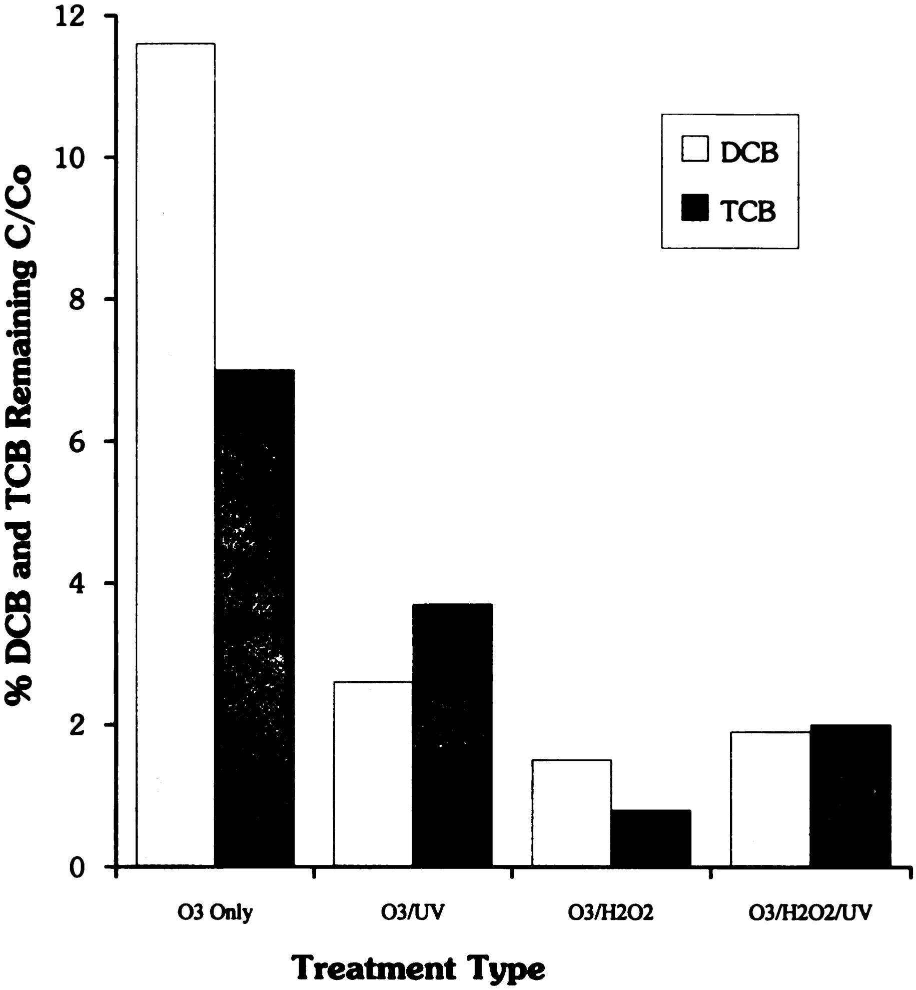


Figure 3-4
Comparison of Treatment Efficiency at
Optimum pH Region (pH=7.0-8.5)

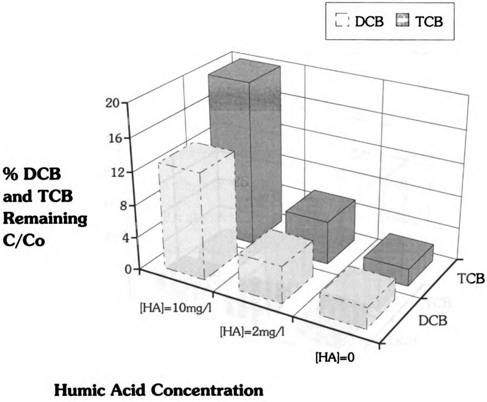


Figure 3-5
Efficiciency of O_3/UV for the Oxidation of DCB and TCB in the Presence of Humic Acid at Optimum pH Region (pH=7.0-8.5)

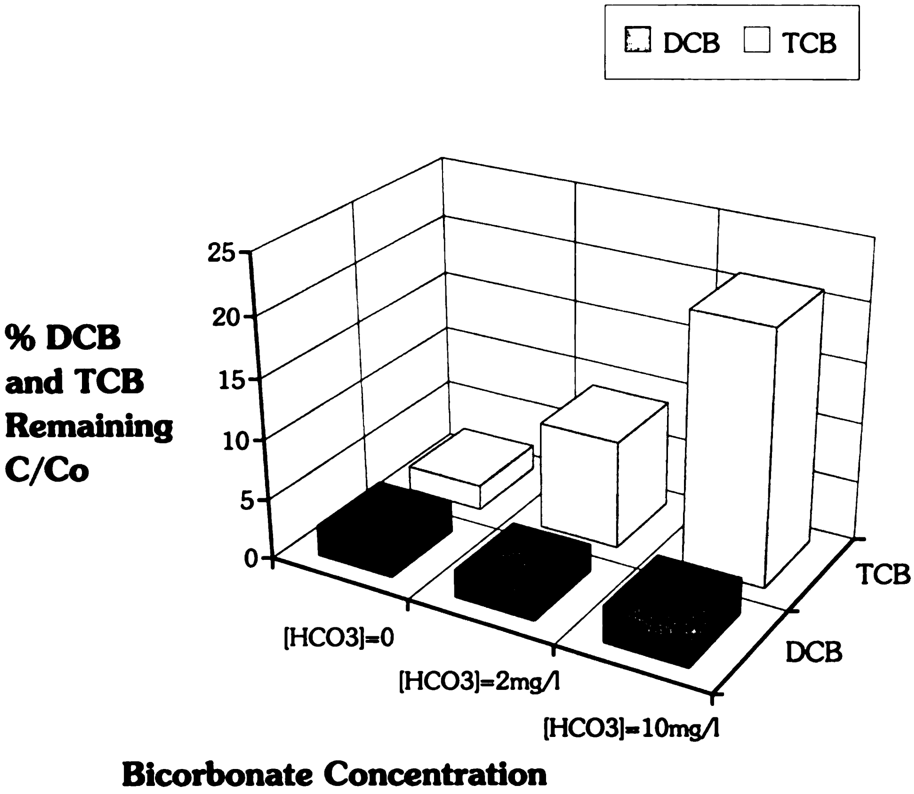


Figure 3-6
Efficiency of Ozone/UV for the Oxidation of DCB and TCB in the Presence of Bicarbonate

of 10 mM. At the lower scavenger concentrations (2 mg/l humic acid and 2 mM bicarbonate), which are similar to that observed in natural waters, the extent of degradation of DCB exceeded 94%. Similar results were observed for TCB degradation, where at these concentrations the extent of TCB degradation exceeded 92%.

III-4 OH Radical Probe — The Degradation of Pentanoic Acid

As stated previously, pentanoic acid was used as the OH radical probe. The extent of DCB degradation was compared to the extent of PA degraded (Fig. 3-7 to Fig. 3-10). Experimental results showed that the extent of DCB degradation was always greater than the extent of PA reaction over the pH region studied for all treatment processes. In the low pH region ($pH < 2.5$), DCB may degrade by the direct reaction of DCB with ozone. However, at pH value above 6.8, the OH radical reaction is expected to be important ($k_{OH} = 4.0 \times 10^9 M^{-1}s^{-1}$ for DCB, $k_{OH} = 2.9 \times 10^9 M^{-1}s^{-1}$ for PA), (Haag and Yao, 1992). As the rate constant k_{OH} for DCB is only 0.33 times higher than that for PA, the relative concentrations become one considerable factor for the removal rate of DCB or PA if they both present in the system at the same time. Figure 3-10 shows that the percentage of DCB remaining ($100\% \times C/Co$) increased from 36.04% to 69.19%, when the concentration ratio of PA over DCB was increaseed from 0.125 to 1.0. The presence of humic acid or bicarbonate had similar effects on degradation of PA and DCB.

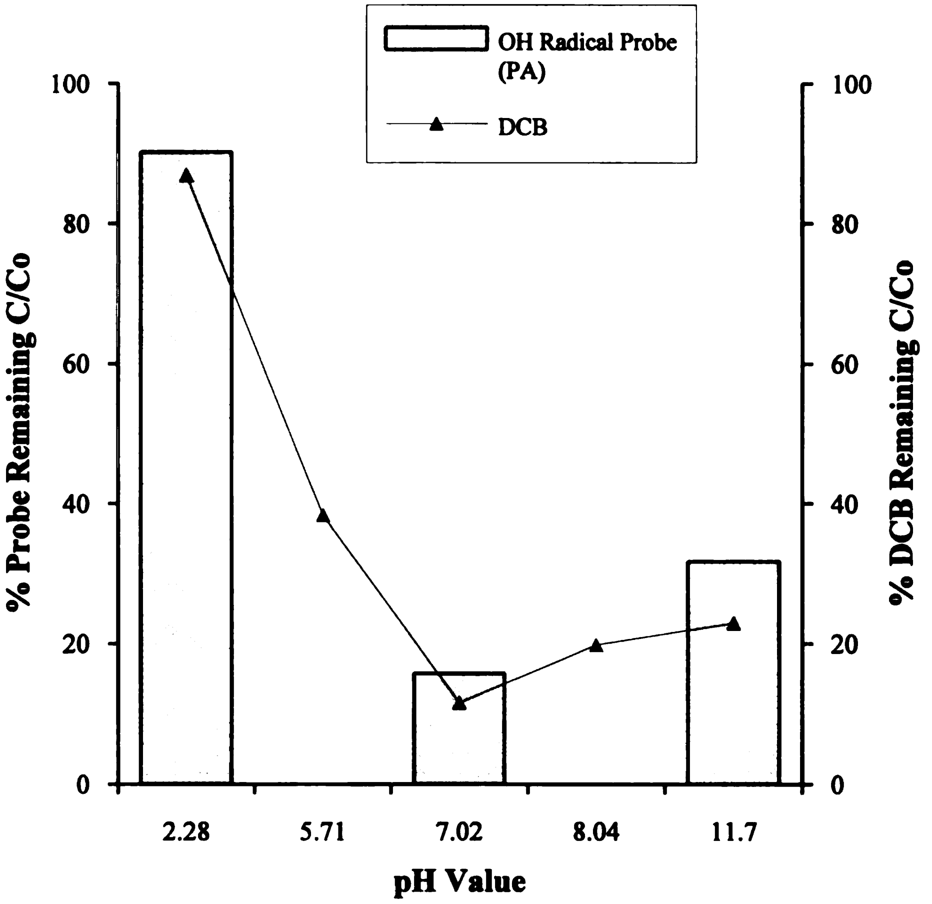


Figure 3-7
Comparison of DCB and OH Radical Probe Degradation Using Ozone Treatment

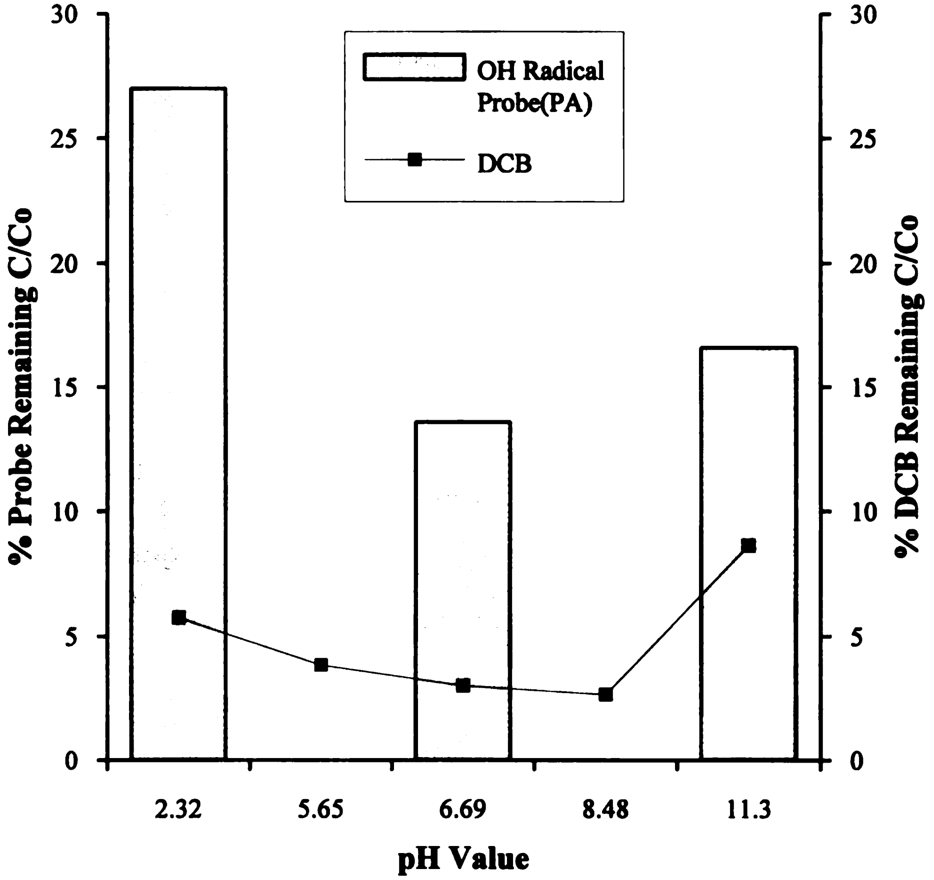


Figure 3-8
Comparison of DCB and PA Degradation Using Ozone/UV Treatment

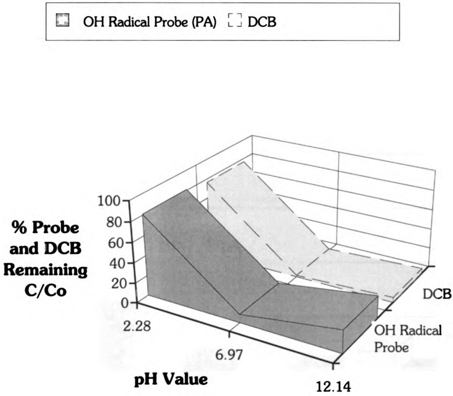


Figure 3-9
Effect of Ph on the Oxidation of DCB and OH Radical Probe Using Ozone/Hydrogen Peroxide Treatment

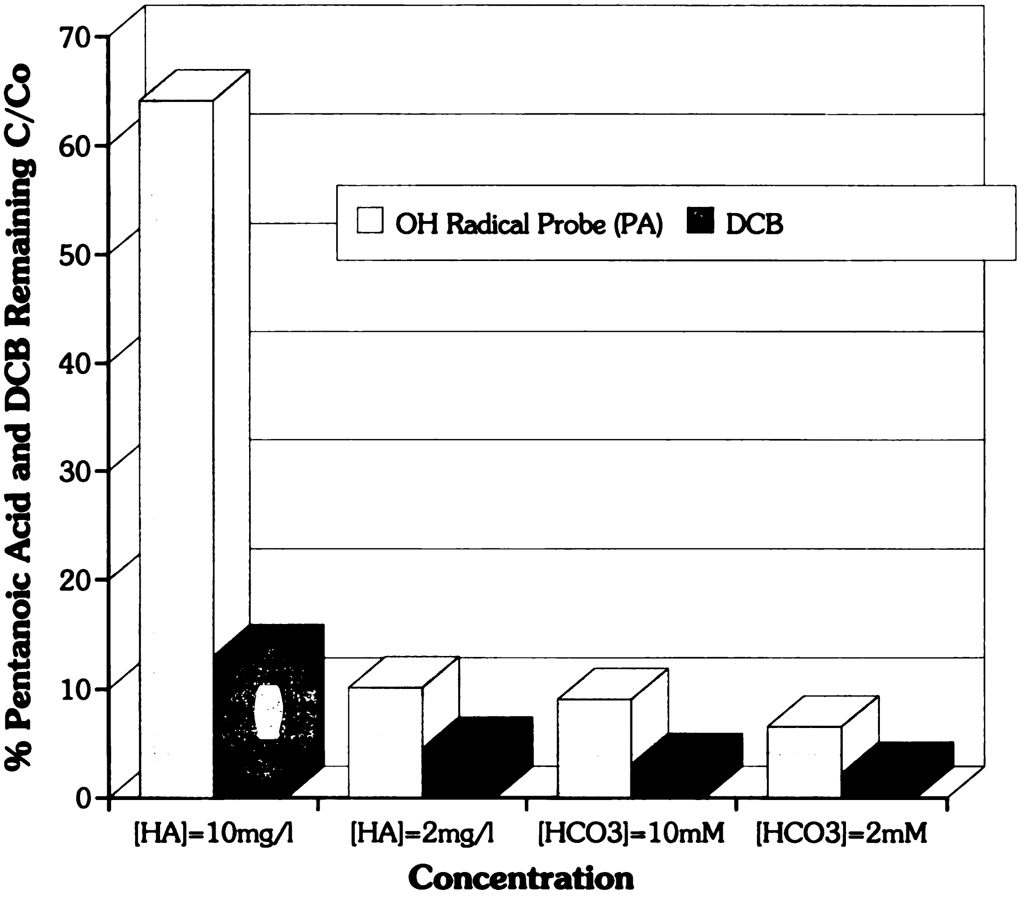


Figure 3-10
Effect of Humic Acid and Bicarbonate on the Oxidation of DCB and Pentanoic Acid Using Ozone/UV Treatment

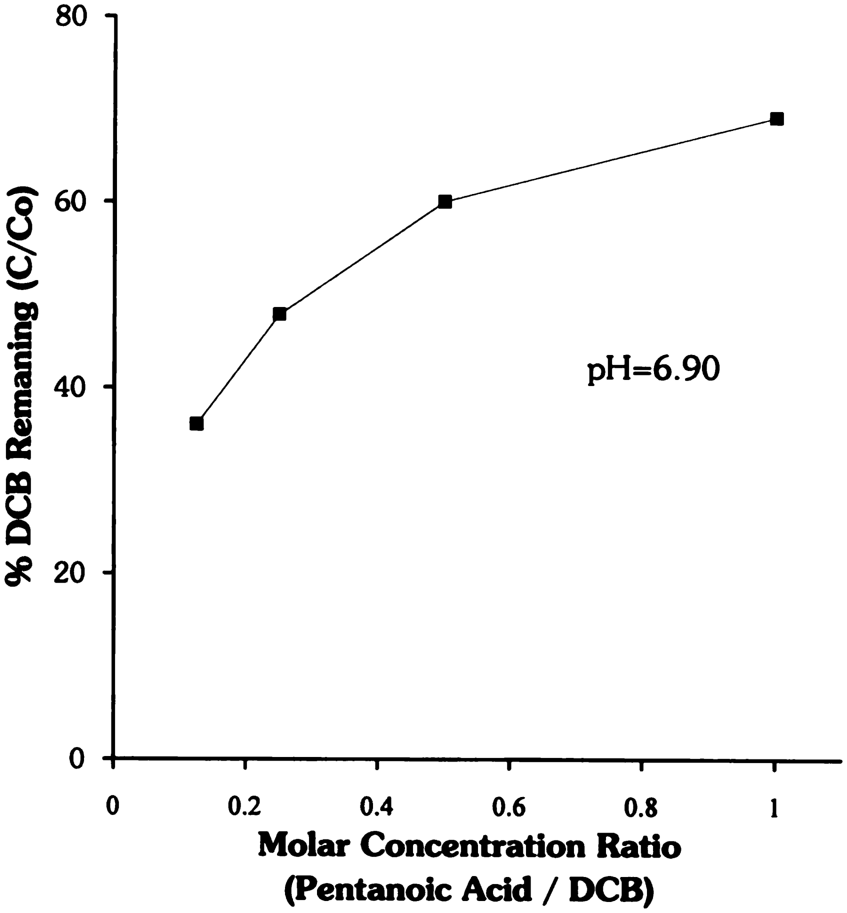


Figure 3-11
Ozone Treatment of DCB and
Pentanoic Acid at pH=6.90

III-5. Overall Reaction Rate Constant

The reactor used in this study was a continuously flowing stirred-tank reactor (CFSTR). Based on the studies of other aromatic compounds (Langlais et al., 1991) the rate of degradation of DCB is assumed to be first order in the concentration of DCB. In a CFSTR at steady-state, the rate of degradation of DCB is given by the equation :

$$\frac{d[DCB]}{dt} = \frac{1}{\tau}([DCB]_0 - [DCB]) - k[DCB] = 0 \qquad (3\text{-}1)$$

Where $k[DCB] = k_{O_3}[O_3][DCB] + k_{OH}[OH][DCB] + k_{photo}[I\Phi][DCB]$ (3-2)

k_i is the reaction rate constant for the particular oxidant; $[O_3]$, [OH] and [DCB], are the reactor ozone , OH radical and DCB concentrations, respectively; $[DCB]_o$ is the initial steady state concentration of DCB in the reactor; I is the light intensity and Φ is the quantum efficiency; τ is the hydraulic retention time and k' is a conditional rate constant for the degradation of DCB. From equation (3-1) k' can be expressed as :

$$k = \frac{1}{\tau}\left(\frac{[DCB]_0 - [DCB]}{[DCB]}\right) \qquad (3\text{-}3)$$

The conditional rate constant is useful in engineering design to evaluate the conditions that control the rate of oxidation of the target chemical and to size the reactor. The conditional rate constants calculated from the experiment results are classified and are provided in Tables 3-1 and 3-2.

Table 3-1 Effect of pH on TCB, DCB and Pentanoic Acid Degradation

Treatment Process	pH	k' (min^{-1}) TCB	pH	k' (min^{-1}) DCB	pH	k' (min^{-1}) PA
Ozone	2.24	0.08 ± 0.009	2.28	0.015 ± 0.009	2.21	0.011 ± 0.017
Ozone	2.92	0.07 ± 0.009				
Ozone	5.25	0.04 ± 0.035	5.71	0.161 ± 0.018		
Ozone	6.21	0.79 ± 0.100				
Ozone	7.17	1.03 ± 0.07	7.02	0.765 ± 0.056	7.02	0.533 ± 0.113
Ozone	7.90	1.25 ± 0.16	8.04	0.405 ± 0.032		
Ozone	9.48	1.09 ± 0.11				
Ozone	10.55	0.74 ± 0.07				
Ozone	11.53	0.69 ± 0.085	11.71	0.336 ± 0.052	11.5	0.215 ± 0.035
Ozone/H_2O_2	2.35	0.20 ± 0.03	2.26	0.037 ± 0.008	2.28	0.024 ± 0.035
Ozone/H_2O_2	4.94	1.70 ± 0.28				
Ozone/H_2O_2	6.96	3.8 ± 0.45			6.97	1.104 ± 0.334
Ozone/H_2O_2	8.53	3.8 ± 0.55	8.27	6.580 ± 0.807		
Ozone/H_2O_2	10.10	1.2 ± 0.44				
Ozone/H_2O_2	11.05	0.63 ± 0.06				
Ozone/H_2O_2	11.50	0.35 ± 0.44	12.19	1.879 ± 1.828	12.1	0.343 ± 0.156
Ozone/UV	2.32	2.3 ± 0.22	2.28	1.638 ± 0.181	2.31	0.271 ± 0.106
Ozone/UV	4.75	3.0 ± 0.25	5.65	2.505 ± 0.094		
Ozone/UV	7.22	2.5 ± 0.29	6.69	3.218 ± 0.429	6.77	0.635 ± 0.240
Ozone/UV	8.95	2.0 ± 0.22	8.48	3.693 ± 0.244		
Ozone/UV	12.01	0.55 ± 0.22	11.34	1.059 ± 0.055	11.00	0.503 ± 0.133
Ozone/UV/H_2O_2			8.34	5.125 ± 0.618	8.19	0.658 ± 0.213

Table 3-2
Effect of Humic Acid and Bicarbonate on TCB, DCB and Pentanoic Acid Degradation

Treatment Process	Humic Acid (mg/l)	Bicarbonate (mM)	k' (min^{-1}) TCB	k' (min^{-1}) DCB	k' (min^{-1}) PA
Ozone/UV	0	0	4.8 ± 0.87	3.22 ± 0.429	0.64 ± 0.24
Ozone/UV	1.6	0	1.9 ± 0.18		
Ozone/UV	2	0		2.13 ± 0.17	0.89 ± 0.30
Ozone/UV	10	0	0.49 ± 0.07	0.67 ± 0.10	0.06 ± 0.04
Ozone/UV	0	0	4.8 ± 0.87	3.22 ± 0.43	0.64 ± 0.24
Ozone/UV	0	2	0.86 ± 0.20	4.32 ± 0.64	1.44 ± 0.59
Ozone/UV	0	10	0.37 ± 0.03	3.23 ± 0.35	1.02 ± 0.14

Equation 3-2 represent three pathway of DCB degradation: direct ozone oxidation; sensitized photolysis and direct photolysis. Results show that about 13% and 28% of $[DCB]_o$ were degraded by direct ozone oxidation and direct photolysis, respectively.

PA degradation can be expressed by similar forms of equations 3-1, 3-2 and 3-3. Yao indicates that k_{O_3} for PA is about 3.6 $\times 10^{-8}$ and direct photolysis is unimportant (Yao et al.,1992).

$$HO\cdot + HCO_3^- = {}^{\cdot}CO_3^- + H_2O \qquad (3\text{-}3)$$

$$HO\cdot + CO_3^{2-} = {}^{\cdot}CO_3^- + HO^- \qquad (3\text{-}4)$$

$$O_3 + {}^{\cdot}CO_3^- = dd \qquad (3\text{-}5)$$

The results indicated that the highest conditional rate constant occurred with ozone/H_2O_2 treatment at pH=8.27 (Table 3-1). Under this condition turning on UV light did not have any beneficial for the removal of the target compound. An interesting phenomenon is that the conditional rate constants did not decrease for both DCB and PA, when 2 or 10 mM bicarbonate presented in the system. This is contrary to what was observed by Galbraith (1993) with TCB. A possible explanation for the results with DCB and PA is that $\cdot CO_3^-$, produced from the reaction of HCO_3/CO_3^{2-} with $\cdot OH$ may be capable of oxidizing DCB and PA. Another explanation could be that $\cdot CO_3^-$ promotes the degradation of ozone and the product of this reaction (dd) is a secondary oxidant capable of oxidizing DCB and PA. Further work needs to be conducted to determine if these results are an experimental artifact or if they are "real", then research needs to be conducted to determine the reactive oxidant species.

IV. DISCUSSION

IV-1. Optimum Condition

The overall reaction rate constant is highest for the most efficienct treatment conditions. For ozone treatment, the optimum condition for DCB degradation occurs at approximately pH 7. The overall reaction rate constant decreased quickly when the pH was either increased or decreased. At pH < 7, less hydroxide ion is available to promote ozone decomposition; at pH > 7, bicarbonate/carbonate ions scavenge the OH radical. The highest overall reaction rate constant of PA was also observed at pH 7, suggesting that the reaction with OH radical predominates under this condition (See Figure 3-2, Table 3-2).

Similar results were observed for the ozone/UV and ozone/H_2O_2 processes. The optimum pH for contaminant oxidation occurred between 7.0 to 8.5 . Specially, for ozone/UV process, it should be emphasized that in a very broad pH region, the overall reaction rate constant of DCB did not change significantly as the rate of OH radical formation is independent of pH, but dependent on light intensity which was constant over the experiment. This hypothesis is supported by the estimated OH radical concentration which are calculated from PA degradation results. (see Table 4-1)

The estimated steady state OH radical concentration in the reactor can be calculated by following equation: (Masten et al., 1993).

$$\frac{d[PA]}{dt} = \frac{1}{\tau}([PA]_0 - [PA]) - k_{OH}[\bullet OH][PA] = 0 \qquad (4\text{-}1)$$

$$[\bullet OH] = \frac{1}{\tau}\left(\frac{[PA]_0 - [PA]}{[PA]k_{OH}}\right) \qquad (4\text{-}2)$$

where k_{OH} is the rate constant for the reaction of OH radical with PA , and equals to 0.29 ×10^{10} ($M^{-1}s^{-1}$ or s^{-1}) (Buxton, C. V. et al 1988). The OH radical concentrations are essentially constant over the pH region 2.3 to 11.4 under steady state conditions,

Table 4-1
Estimated Steady State OH Radical Concentration

	pH	DCB Remaining (C/Co) %	DCB Overall Reaction Constant k'(min^{-1})	Estimated [·OH] (M)
O3	2.28	86.91	0.015 ± 0.009	$(0.62 \pm 1.01) \times 10^{-13}$
	7.02	11.56	0.765 ± 0.056	$(3.06 \pm 0.65) \times 10^{-12}$
	11.5	22.94	0.336 ± 0.052	$(1.24 \pm 0.20) \times 10^{-12}$
O3/UV	2.28	5.75	1.638 ± 0.181	$(1.56 \pm 0.61) \times 10^{-12}$
	8.48	2.64	3.693 ± 0.244	$(3.65 \pm 1.38) \times 10^{-12}$
	11.39	8.63	1.059 ± 0.244	$(2.89 \pm 0.76) \times 10^{-12}$
$O3/UV/H_2O_2$	8.34	1.91	5.125 ± 0.618	$(3.79 \pm 0.95) \times 10^{-12}$
$O3/H_2O_2$	2.26	76.52	0.037 ± 0.008	$(1.36 \pm 1.60) \times 10^{-13}$
	8.27	1.50	6.580 ± 0.807	$(6.35 \pm 1.49) \times 10^{-12}$
	12.19	5.05	1.879 ± 1.828	$(1.97 \pm 0.70) \times 10^{-12}$

The ozone /H_2O_2 treatment (pH of 8.27) was most efficient process in terms of both OH radical generation and DCB degradation. Table 4-1 shows a good agreement for the percentages of DCB remaining, the DCB overall rate constant and the steady state OH radical concentration.

IV-2. OH Radical Scavenger and Reaction Competition

In AOPs, humic acid and bicarbonate/carbonate act as OH radical scavengers since they consume OH radicals and form products that do not enter the cyclic reaction involved in the decomposition of ozone (see Fig 1-2). (Peyton & Gee, 1989; Yao, 1992). From the following reactions and rate constants, one can see ·OH scavenging reactions involving such scavengers as humic acid and carbonate and the rate constants for the oxidation of PA and DCB occur at rates that are on the same order of magnitude. Thus, one would expect that CO_3^{2-}, HA, PA and DCB would compete for the available OH radicals.

Reaction	Rate Constant k ($M^{-1}s^{-1}$)	
$HO\cdot + CO_3^{-2} = HO^- + CO\cdot_3^-$	0.39×10^9	(4-3)
$HO\cdot + HCO_3^- = CO\cdot_3^- + H_2O$	0.85×10^7	(4-4)
$HO\cdot + HA = A\cdot + H_2O$	0.30×10^{10}	(4-5)
$HO\cdot + PA = P\cdot + H_2O$	0.29×10^{10}	(4-6)
HO· + 1, 2 - dichlorobenzene	0.40×10^{10}	(4-7)
$HCO_3^- = H^+ + CO_3^{2-}$	0.22×10	(4-8)
$O_3 + CO\cdot_3^- = dd$	0.10×10^6	(4-9)

As such, the scavenging effect of humic acid is likely to depend on the relative concentrations of humic acid , PA and any other reactants in the system. Figure 3-9 shows that when the concentration of humic acid was increased from 2 to 10 mg/l, the degradation rate of PA decreased significantly when using ozone/UV treatment (pH ≅ 7.3). It is very interesting that the addition of bicarbonate /carbonate did not result in a decrease in the degradation rates of DCB and PA, in fact the rates of degradations of both DCB and PA increased somewhat. Three possible explanations for this result are: (1) as the rate constant of OH radical with DCB is approximately two orders of magnitude higher than the rate constant of OH radical with bicarbonate, 10 mM bicarbonate did not show a scavenging effect on both DCB (2.590 mg/L) and PA (4.560 mg/L). Although carbonate has a higher ·OH rate constant than bicarbonate (Eq. 4-3), at pH 7.3, carbonate would not play an important role (Eq 4-8), as its concentration would be approximately three orders of magnitude lower than the concentration of bicarbonate. (2) $CO{\cdot}_3^{-\cdot}$, the product of reactions show in Eq 4-10 and Eq 4-11 initiates ozone decomposition, and the unknown product (dd) of the reaction shown in Eq 4-12 (Yao et al., 1992) may be an OH radical promoter. The function of bicarbonate, as a scavenger or promotor, may depend on the experimental condition in the system. (3) $\cdot CO_3^{2-}$ or the product formed from the reaction of ozone with $CO{\cdot}_3^{-}$ may be an oxidant capable of reacting with PA and DCB.

Because the k_{OH} of DCB is only 0.33 times higher than that of PA ($k_{OH}=4.0 \times 10^9 M^{-1}s^{-1}$ for DCB, $k_{OH}=2.9 \times 10^9 M^{-1}s^{-1}$ for PA, Haag and Yao, 1992), their relative concentrations may contribute to the phenomena discussed above (if they both present in the system at the same time). Figure 3-11shows that concentration of DCB remaining (C/Co) increased from 36.04% to 69.19%, when the concentration ratio of PA to DCB increased from 0.125 to 1.0. This result suggests that concentrations of OH radical probe must be as low as possible to avoid interference with target compound degradation.

V. CONCLUSIONS

Of the five compounds evaluated, pentanoic acid (PA) was found to be most appropriate OH radical probe due to its low volatility, low reactivity with ozone, high solubility and low detection limit.

Variations in the pH had the greatest effect on ozone treatment. The efficiency of ozone/UV treatment was essentially independent of pH.

While in the AOPs system the addition of humic acid reduced the efficiency of oxidation of DCB, removal efficiencies of > 80% were observed. Contrary to expectation, 2 or10 mM bicarbonate did not affect the efficiency of DCB oxidation.

Results indicate that the competition reactions between OH radicals with PA and OH radicals with humic acid are strong. The scavenging effect of humic acid depends on the relative concentrations of PA and humic acid. The degradation rates of PA increased slightly when 2 or 10 mM bicarbonate was added.

The results of DCB, TCB and PA are qualitatively similar, suggesting a similar mechanism for the degradation of all three compounds.

As a result of this research, the optimum condition and optimum process for the treatment of 1, 2-dichlorobenzene using AOPs were found. The conditional rate constant of each process was obtained. And useful information for engineering design was provided.

VI. FURTHER WORKS

Although our results show that the OH radical is the principal oxidant in AOPs, to fully understand the mechanism involved in these complex systems, it is necessary to develop detailed kinetic models that accurately describe the rates of production and/or losses of oxidants and the other reactions involved.

An economic evaluation should be done for the application of AOPs for the treatment of hazardous wastes.

Practice is the way to make the public recognize and accept a novel technology, so that, it is imperative to move AOPs out of the laboratory and to apply this technique into the field for the remediation of a site contaminated with hazardous chemical(s).

LIST OF REFERENCES

Anselme, C.; Duget,J. P.; Mazounie, P. and Mallevialle, J. (1987). Development of an Integrated Analytical Approach for Evaluating toxic Compound Removal from Groundwater Treated by Ozone/Hydrogen Peroxide. Proc. of AWWA Water Quality Technology Conference, pp. 655-664 .

Akata, A and Gurol M. D. (1992). Oxidation of Nitrobenzene by Ozone and Ozone/UV Processes. Proc. of Second International Symposium Chemical Oxidation Technology for The Nineties, Nashlille, Tennessee. pp153-165.

Akane, A.; Fukushima, S.; Matsubara, K.; Takahashi, S.and Shiono, H. (1990). Analysis of Blood Bcetate by Head-space Gas Chromatography: Comparative of Reagents for The Methyl Esterification. Journal of Chromatography, **529**, 155-160.

Atkinson, R. (1987). Estimation of OH Radical Reaction Rate Constants and Atmospheric Lifetime for Polychlorobiphenyls, Dibenzo-p-dioxins, and Dibenzofurans. Environ. Sci. Technol., **21**, 305-307,

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

Buxton, G. V.; Greenstock, C.; Helman, W.P. and Ross, BA.B. (1988). Critical Review of Rate Constants for Reactions of Hydrrated Electrons,Hydrogen Atoms and Hydroxyl Radicals (·OH/·O-) in Aqueous Solution. J. Phys. Chem. Ref. Data. **17**(2) , 2560-2564.

Galbraith J. M. (1993). Oxidation of 1, 2, 3- Trichlorobezene Using Advanced Oxidation Processes. Master Thesis, Michigan State University, East Lansing, MI 48823.

Galbraith J. M.; Shu, M.; Davies, S.and Masten, S. (1992). Use of Ozone, Ozone/Peroxide, and Ozone/UV for the Generation of OH Radicals to Oxidize Chlorinated Organics. Proceeding of the Twenty- Fourth Mid- Atlantic Industrial West Conference, West Virginia University, pp 411-420.

Glaze, H. W. and Kang, J. (1984). 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.

Gurol D. M. and Nekoulnaini, S. (1984). Kinetic Behavior of Ozone in Aqueous Solution of Substituted Phenols. Ind. Eng. Chem. Fundam., **23**(1), 54-60.

Haag, R. W. and Yao, C. C. D. (1992). Rate Constant for Reaction of Fydroxyl Radicals with Several Drinking Water Contaminants. Environ. Sci. Technol., **26**, 1005-1013.

Hoigné, J. (1982). Mechanisms, Rates and Selectivities of Oxidations of Organic Compounds Initiated by Ozonation of Water. Handbook of Ozone Technology and Applications, ANN Arbor Science. **1**(12), 341-377.

Hoihné, J. and Bader, H. (1983). Rate Constant for Reaction of Ozone with Organic and Inorganic Compounds in Water —I. Non-Dissociation Organic Compounds. Water Res., **17**. 173-183.

Hoigné, J. and Bader, H. (1987). Combination of Ozone/UV and Ozone/hydrogen Peroxide; Formation of Secondary Oxidants. Proc. of the 8th Ozone World Congress, pp K83-K97.

Hoigné, J and Bader, H. (1989). Ozone/UV Process for Water-treatment; Formation of Hydrogen Peroxyde (H_2O_2)-Residual. 2nd International Conference on UV/Ozone in the Treatment of Water and Other Liquids. Berlin, German.

Killops, S. (1986) Volatile Ozonization Products Aqueous Humic Material. Water Res., **20** (2), 153-165.

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.

Masten, S. and Davies, S. (1992). The Using of Ozone/UV for the Oxidation of Chlornated Benzenes and Biphenyls. Progress Report to the Great Lakes and Mid-Atlantic Hazardous Research Center, Michigan State University, MI.

Masten, J. S.; Galbraith, J. M. and Davies ,H. R. S. (1993). Oxidation of Trichlorobezene Using Advanced Oxidation Processes. Proc. of the 11th Annual IOA World Congress. Aug./Sept., San Francisco, CA. pp S-20-35 -S-20-50

Masten, S and Davies, S (1994) Use of Ozone and Other Strong Oxidants for Hazardous Water Management, Chapter 18 of Environmental Oxidants. J. O. Nriagu and M. S. Simmons, Eds., J. Wiley and Sons, New York, NY. pp 517-547.

Method 612 — Chlorinated Hydrocarbons (1984). Federal Register/Rules and Regulations. **49** (209), 128-135.

Peyton, G.; and Glaze, H. (1987). Mechanism of Photolytic Ozonation, Chapter 6 of Photochemistry of Environmental Aquatic Systems, ACS Symposium Series, **327**, 76-87.

Peyton, R. G.; and Glaze, H. W.(1988). Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. 3. Photolysis of Aqueous Ozone. Environ. Sci. Technol., **22**, 1761-767.

Peyton, G.; Gee, C.; Bandy J. and Maloney, S. (1989). Catalytic Competition Effects of Humic Substances on Photolytic Ozonation of Organic Compounds. American Chemical Society, Advance in Chemistry Series, **219**, 639-661.

Roth, A. J.; Moench L. W. and Debalak, A. K. (1983). Kinetic Modeling of the Ozonation of Phenol in Water. Journal of WPCF., **54** (2), 135-139.

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

Yao, J. J. (1991). Ozoneation of Soils Contaminated with Polycyclic Aromatic Hydrcarbons (PAHs). Master Thesis, Michigan State University.

Yao, C. C. D.;Haag, R. W. and Mill, T. (1992). KineticFeatures of Advanced Oxidation Processes for Treating Aqueous Chemical Mixtures. Proc. of Second International Symposium Chemical Oxidation Technology for The Nineties. Nashlille, Tennessee. pp 124-152.

APPENDIXES

1. Pentanoic Acid Estertification Followed By Head-space GC/FID Method
2. Flow Injection Analysis System Configuration
3. Reactor Tracer Mixing Experimental Result
4. Data Summary Of DCB And PA Degradation
5. Data Summary Of TCB Degradation

Appendix 1

Pentanoic Acid Estertification Followed By Head-space GC/FID Method

Reference

Atsushi Akane, Shoju Fukushima, Kazuo Matsubara, Setsunori Takahashi and Hiroshi Shiono, (1990) "Analysis of blood acetate by head-space gas chromatography: comparative of reagents for the methyl esterification", Journal of Chromatography, **529**, 155-160.

Basic Reaction

$$C_4H_9\text{-}COOH + HO\text{-}CH_3 \overset{BF_3}{\Rightarrow} C_4H_9\text{-}CO_2\text{-}CH_3 + H_2O$$

$C_4H_9\text{-}CO_2\text{-}CH_3$, the product of the esterification reaction of PA and CH_3OH can be measured by using a head-space gas chromatography with flame ionization detection. A calibration curve ($C_4H_9\text{-}COOH$ concentrations against $C_4H_9\text{-}CO_2\text{-}CH_3$ response areas) was prepared daily.

Reagents and Procedure

In a 20 ml head-space GC vial

(1) Add 3.5 ml water sample which contain $C_4H_9\text{-}COO^-$ anions;
(2) Add 0.1 ml 2 N HCl solution, to maintain the sample pH <4;
(3) Add 0.4 ml boron trifluoride 10% in methanol solution (GC Analysis, Fluka Chemical Corp., Ronkonkoma, NY);
(4) Seal the vials and store them at 37 °C for 60 hours:
(5) GC analyze by GC.

Discussion

This method can directly measure $C_4H_9\text{-}COO^-$ anion in water solution at a low concentration level (Figure A-1-1, A-1-2). However, this method is time consumpting and sensitive to pH, storage temperature and storge time. Where pH > 4, other reactions may occur and result in the formation of other compounds which showed up, in our studies, as a double peak in GC analysis (Figure A-1-3). When storge temperature was higher than 37°C, a good base line could not be acheved (storge 60 hours). When temperature lower than 37°C, the esterification reaction was not completed in 60 hours.

Result

1) The product rate of C_4H_9-CO_2-CH_3 is 0.44 ± 0.03

2) The results of headspace GC analysis

Pentanoic Acid Concentration (mg/L)
(Mean ± 95% confident limit)

Ozone Treatment	O_3/UV Treatment	O_3/H_2O_2 Treatment	$O_3/UV/H_2O_2$
3.549 ± 0.109	4.404 ±0.702	3.252± 0.691	3.252± 0.691
3.202 ± 0.420	1.188 ± 0.233	2.630± 0.239	0.429± 0.022
0.561 ± 0.089	0.135 ± 0.135	0.270± 0.009	
1.125 ± 0.121	0.730 ± 0.051	0.735± 0.157	

3) Pentanoic Acid Calibration Curve

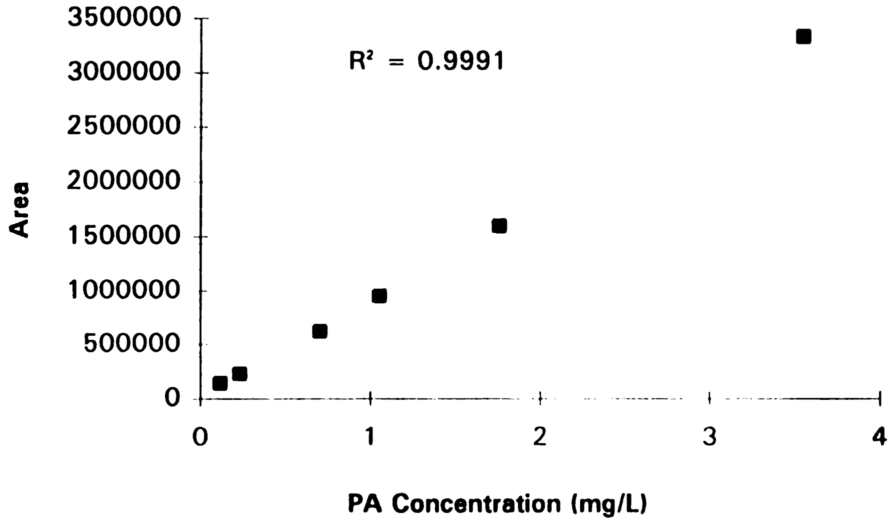


Figure A-1-1
Pentanoic Acid Calibration Curve

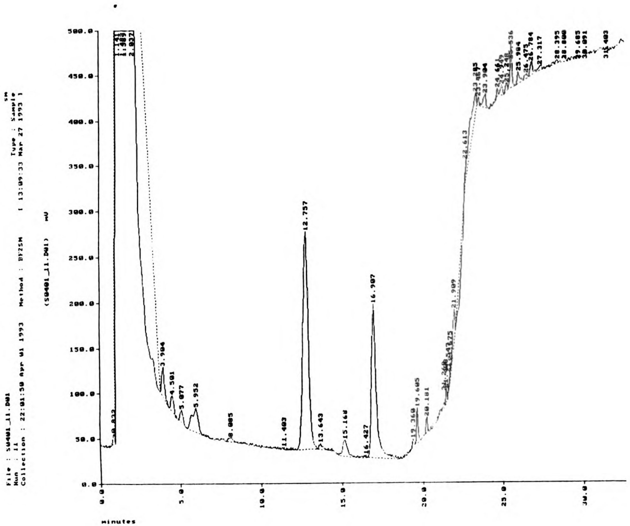


Figure A-1-2 GC Analysis Result

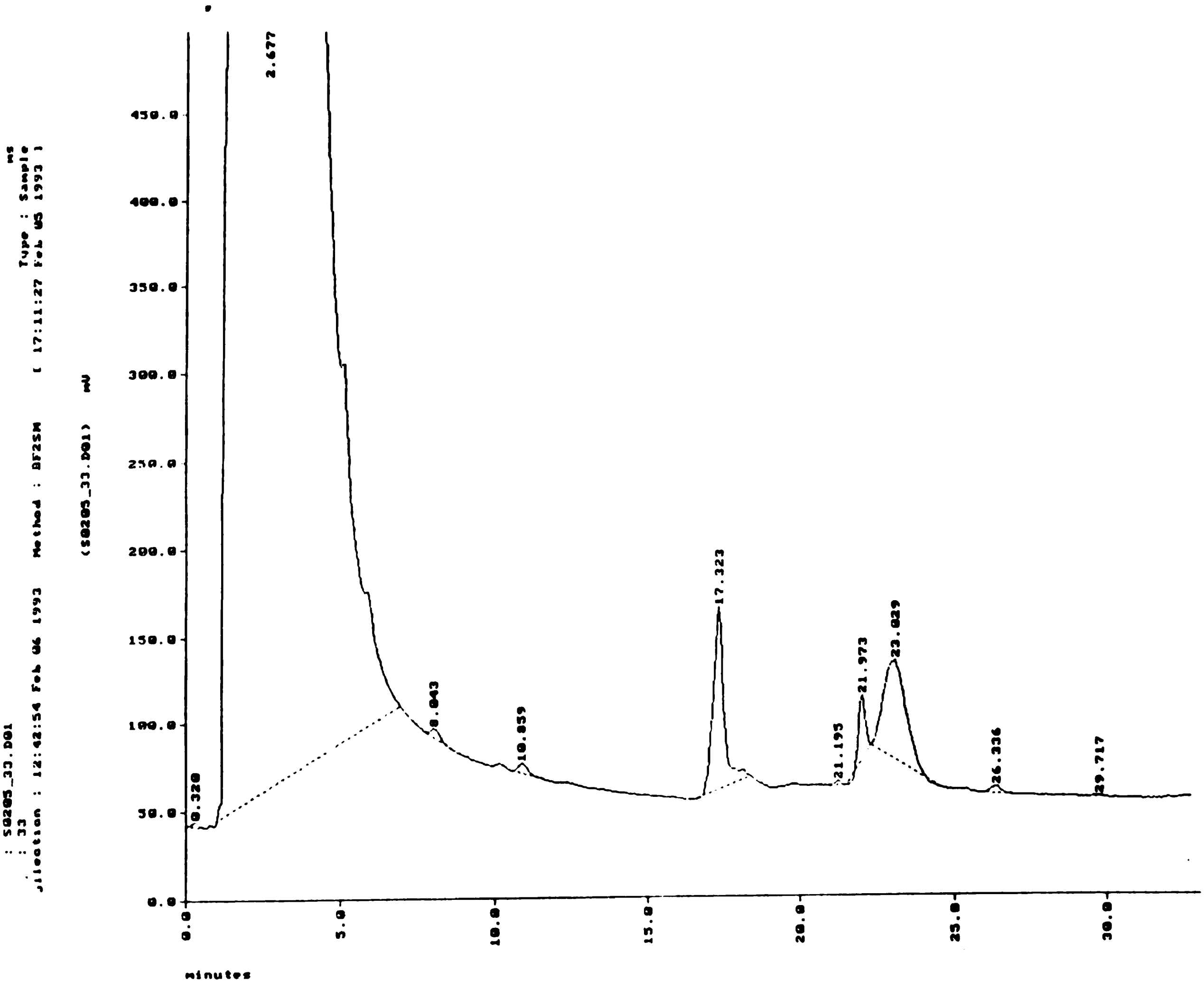
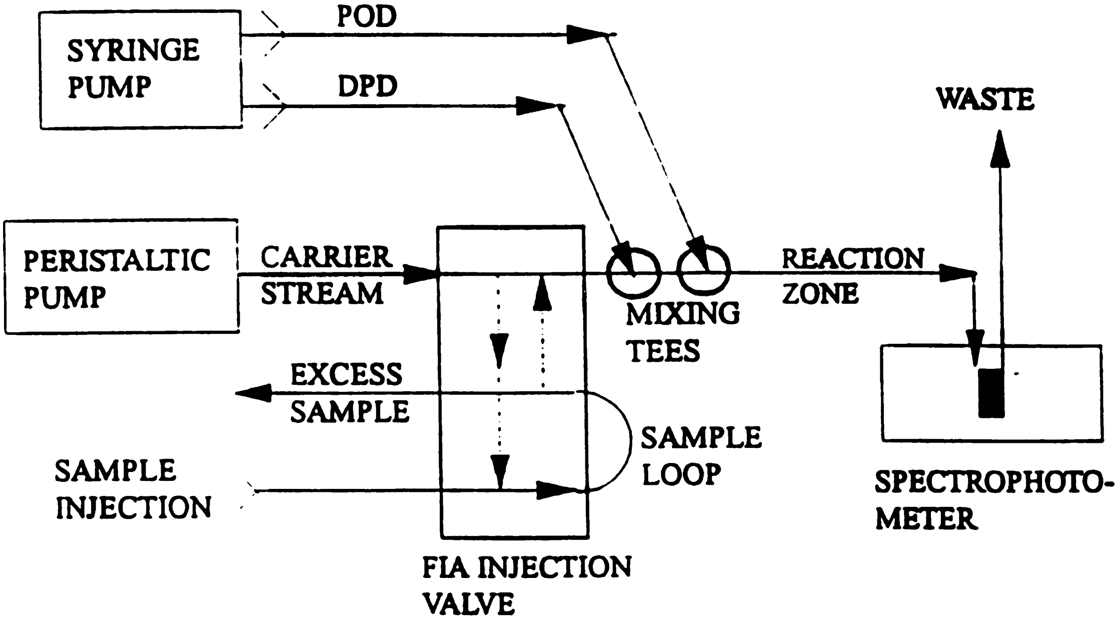


Figure A-1-3 GC Analysis Result

Appendix 2

Flowing Injection Analysis System Configuration



(Adapted from Galbraith, 1993)

Figure A-2-1 FIA System Configuration

Appendix 3

Reactor Tracer Mixing Experimental

(Motor Speed 425 rpm)

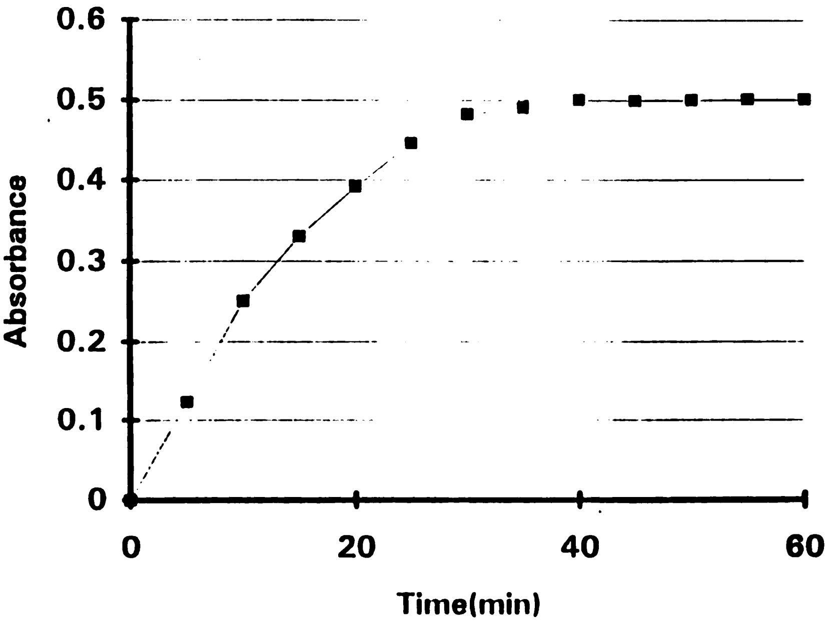


Figure A-3-1 Reactor Tracer Mixing Experimental Result

Appendix 4

Data Summary Of DCB And PA Degradation

Experimental A. Ozone Treatment at Varying pH

Table A-1. Target Compound: DCB

Hydraulic Retention Time (min)	10	10	10	10	10
UV Light	no	no	no	no	no
Reactor pH	2.28	5.71	7.02	8.04	11.71
Inlet Ozone Concentration (mg/l)	12.16	12.16	12.08	12.08	12.08
Flow Rate Of Inlet Ozone Solution (ml/hr)	750	750	750	750	750
Reactor Ozone Concentration (mg/l)	3.394	1.478	1.163	0.320	0.036
Humic Acid Concentration (mg/l)	0	0	0	0	0
Bicarbonate Concentration (mM)	0	0	0	0	0
Hydrogen Peroxide Concentration (mM)	0	0	0	0	0
Target Compound Initial Concentration (mg/l)	2.720 ± 0.147	2.720 ± 0.147	2.720 ± 0.147	2.720± 0.147	2.720± 0.147
Reactor Effluent Target Compound Concentration (mg/l)	2.364 ± 0.147	1.043 ± 0.062	0.315 ± 0.012	0.539 ± 0.021	0.624 ± 0.083
% Remaining of Target Compound	86.91	38.34	11.56	19.80	22.94

Table A-2. Target Compound: Pentanoic Acid

Hydraulic Retention Time (min)	10	10	10
UV Light	no	no	no
Reactor pH	2..21	7.02	11.53
Inlet Ozone Concentration (mg/l)	12.00	12.08	12.08
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750
Reactor Ozone Concentration (mg/l)	3.197	2.066	0.658
Humic Acid Concentration (mg/l)	0	0	0
Bicarbonate Concentration (mM)	0	0	0
Hydrogen Peroxide Concentration (mM)	0	0	0
Target Compound Initial Concentration (mg/l)	3.549 ± 0.109	3.549± 0.109	3.549 ± 0.109
Reactor Effluent Target Compound Concentration (mg/l)	3.202 ± 0.420	0.561 ± 0.089	1.125 ± 0.121
% Remaining of Target Compound	92.22	15.81	31.70

Experimental B. Ozone/UV Treatment at Varying pH

Table B-1. Target Compound: DCB

Hydraulic Retention Time (min)	10	10	10	10	10
UV Light	on	on	on	on	on
Reactor pH	2.32	5.65	6.69	8.48	11.34
Inlet Ozone Concentration (mg/l)	12.64	12.32	12.80	12.00	12.48
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750	750
Reactor Ozone Concentration (mg/l)	0.188	0.167	0.226	0.029	0.017
Humic Acid Concentration (mg/l)	0	0	0	0	0
Bicarbonate Concentration (mM)	0	0	0	0	0
Hydrogen Peroxide Concentration (mM)	0	0	0	0	0
Target Compound Initial Concentration (mg/l)	2.284 ± 0.078	2.284 ± 0.078	2.284 ± 0.078	2.284± 0.078	2.284± 0.078
Reactor Effluent Target Compound Concentration (mg/l)	0.162 ± 0.017	0.108± 0.003	0.085± 0.011	0.074± 0.004	0.244 ± 0.010
% Remaining of Target Compound	5.75	3.84	3.01	2.64	8.63

Table B-2. Target Compound : Pentanoic Acid

Hydraulic Retention Time (min)	10	10	10
UV Light	on	on	on
Reactor pH	2.31	6.77	11.00
Inlet Ozone Concentration (mg/l)	12.48	12.48	12.72
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750
Reactor Ozone Concentration (mg/l)	0.310	0.028	0.143
Humic Acid Concentration (mg/l)	0	0	0
Bicarbonate Concentration (mM)	0	0	0
Hydrogen Peroxide Concentration (mM)	0	0	0
Target Compound Initial Concentration (mg/l)	4.404 ± 0.702	4.404± 0.702	4.404 ± 0.702
Reactor Effluent Target Compound Concentration (mg/l)	1.188± 0.233	0.135± 0.135	0.730± 0.051
% Remaining of Target Compound	26.97	13.60	16.58

Experimental C. Ozone/H_2O_2 Treatment at Varying pH

Table C-1. Target Compound : DCB

Hydraulic Retention Time (min)	10	10	10	10
UV Light	No	No	on	No
Reactor pH	2.26	8.27	8.34	12.19
Inlet Ozone Concentration (mg/l)	12.24	12.24	12.24	12.24
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750
Reactor Ozone Concentration (mg/l)	2.682	0.068	0.243	0.112
Humic Acid Concentration (mg/l)	0	0	0	0
Bicarbonate Concentration (mM)	0	0	0	0
Input Hydrogen Peroxide Rate (μ mol./hr)	90	90	90	90
Reactor Effluent Hydrogen Peroxide Concentration (μM)	41.480 ± 1.867	19.604 ± 1.867	22.729 ± 1.867	10.039 ± 0.880
Target Compound Initial Concentration (mg/l)	2.879 ± 0.160	2.879± 0.160	2.879 ± 0.160	2.879 ± 0.160
Reactor Effluent Target Compound Concentration (mg/l)	2.203± 0.072	0.043± 0.004	0.055± 0.006	0.141±0.141
% Remaining of Target Compound	76.52	1.50	1.91	5.05

Table C-2 Target Compound : Pentanoic Acid

Hydraulic Retention Time (min)	10	10	10	10
UV Light	No	No	on	No
Reactor pH	2.28	6.79	8.19	12.19
Inlet Ozone Concentration (mg/l)	12.24	12.24	12.24	12.24
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750
Reactor Ozone Concentration (mg/l)	2.740	0.227	0.327	0.183
Humic Acid Concentration (mg/l)	0	0	0	0
Bicarbonate Concentration (mM)	0	0	0	0
Input Hydrogen Peroxide Rate (μ mol./hr)	90	90	90	90
Reactor Effluent Hydrogen Peroxide Concentration (μM)	44.037 ± 1.412	21.403 ± 1.078	22.350 ± 0.815	13.732 ± 1.051
Target Compound Initial Concentration (mg/l)	3.252 ± 0.0.691	3.252 ± 0.691	3.252 ± 0.691	3.252 ± 0.691
Reactor Effluent Target Compound Concentration (mg/l)	2.630 ± 0.239	0.270 ± 0.009	0.429 ± 0.022	0.735 ±0.157
% Remaining of Target Compound	80.87	8.30	13.18	22.59

Experimental D. Ozone/UV Treatment in The Presence of Humic Acid and Bicarbonate

Table D-1. Target Compound : DCB

Hydraulic Retention Time (min)	10	10	10	10
UV Light	on	on	on	on
Reactor pH	7.33	7.32	7.43	7.46
Inlet Ozone Concentration (mg/l)	12.18	12.00	12.08	12.00
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750
Reactor Ozone Concentration (mg/l)	0.005	0.013	0.141	0.248
Humic Acid Concentration (mg/l)	10	2	0	0
Bicarbonate Concentration (mM)	0	0	10	2
Input Hydrogen Peroxide Rate (μ mol./hr)	0	0	0	0
Reactor Effluent Hydrogen Peroxide Concentration (μM)	0	0	0	0
Target Compound Initial Concentration (mg/l)	2.592 ± 0.113	2.592± 0.113	2.592± 0.113	2.592 ± 0.113
Reactor Effluent Target Compound Concentration (mg/l)	0.338 ± 0.045	0.117± 0.007	0.079± 0.008	0.059 ±0.008
% Remaining of Target Compound	13.04	4.49	3.00	2.26

Table D-2. Target Compound : Pentanoic Acid

Hydraulic Retention Time (min)	10	10	10	10
UV Light	No	No	No	No
Reactor pH	7.34	7.37	7.50	7.49
Inlet Ozone Concentration (mg/l)	12.08	12.16	12.08	12.00
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750
Reactor Ozone Concentration (mg/l)	0.0633	0.439	0.195	0.078
Humic Acid Concentration (mg/l)	10	2	0	0
Bicarbonate Concentration (mM)	0	0	10	2
Input Hydrogen Peroxide Rate (µ mol./hr)	0	0	0	0
Reactor Effluent Hydrogen Peroxide Concentration (µM)	0	0	0	0
Target Compound Initial Concentration (mg/l)	4.560 ± 0.344	4.560 ± 0.344	4.560 ± 0.344	4.560 ± 0.344
Reactor Effluent Target Compound Concentration (mg/l)	2.924 ± 0.795	0.461± 0.114	0.409 0.029	0.296 ±0.092
% Remaining of Target Compound	64.12	10.11	8.97	6.49

Experimental E. Ozone Treatment of DCB and Pentanoic Acid of Humic at pH=6.90

Table E. Target Compound : DCB

Hydraulic Retention Time (min)	10	10	10	10
UV Light	No	No	No	No
Reactor pH	6.89	6.91	6.90	6.82
Inlet Ozone Concentration (mg/l)	12.24	12.40	12.24	12.32
Flow Rate of Inlet Ozone Solution (ml/hr)	750	750	750	750
Reactor Ozone Concentration (mg/l)	2.205	2.185	2.844	1.803
Humic Acid Concentration (mg/l)	0	0	0	0
Bicarbonate Concentration (mM)	0	0	0	0
Input Hydrogen Peroxide Rate (μ mol./hr)	0	0	0	0
Reactor Effluent Hydrogen Peroxide Concentration (μM)	0	0	0	0
DCB Initial Concentration (mg/l)	2.195 ± 0.072	2.431 ± 0.203	2.398 ± 0.082	2.418 ± 0.161
$\frac{[\text{Pentanoic Acid}]}{[\text{DCB}]}$	0.125	0.250	0.500	1.000
Reactor Effluent DCB Concentration (mg/l)	0.778 ± 0.044	1.164 ± 0.072	1.429 ± 0.048	1.673 ±0.059
% Remaining of Target Compound	36.04	47.88	59.59	69.19

Appendix 5

Data Summary Of TCB Degradation

Effect of pH on TCB Degradation using Ozone, Ozone/H_2O_2 and Ozone/UV Treatment.

Treatment Process	pH	k′, min^{-1}
Ozone	2.24	0.08 ± .009[1]
Ozone	2.92	0.07 ± .009
Ozone	5.25	0.40 ± .035
Ozone	6.21	0.79 ± .10
Ozone	7.17	1.03 ± .07
Ozone	7.90	1.25 ± .16
Ozone	9.48	1.09 ± .11
Ozone	10.55	0.74 ± .07
Ozone	11.53	0.69 ± .085
Ozone/H_2O_2	2.35	0.20 ± .03
Ozone/H_2O_2	4.94	1.7 ± .28
Ozone/H_2O_2	6.96	3.8 ± .45
Ozone/H_2O_2	8.53	3.8 ± .55
Ozone/H_2O_2	10.10	1.2 ± .44
Ozone/H_2O_2	11.05	0.63 ± .06
Ozone/H_2O_2	11.50	0.35 ± .04
Ozone/UV	2.32	2.3 ± .22
Ozone/UV	4.75	3.0 ± .25
Ozone/UV	7.22	2.5 ± .29
Ozone/UV	8.95	2.0 ± .22
Ozone/UV	12.01	0.55 ± .06

[1] mean ± 95% confidence limits

(Adapted from Masten et al., 1993)

Effect of Humic Acid and Bicarbonate on TCB Degradation using Ozone, Ozone/H_2O_2 and Ozone/UV Treatment.

Treatment Process	Humic acid mg/L	HCO_3^- mM	k′ min^{-1}	k'_{rel}
Ozone	0	0	1.4 ± .31[1]	1.00
Ozone	1.6	0	2.9 ± 2.3	2.11
Ozone	10	0	0.85 ± .13	0.61
Ozone/UV	0	0	4.8 ± .87	1.00
Ozone/UV	1.6	0	1.9 ± .18	0.39
Ozone/UV	10	0	0.49 ± .07	0.10
Ozone/H_2O_2	0	0	3.8 ± .45	1.00
Ozone/H_2O_2	1.6	0	4.2 ± .53	1.10
Ozone/H_2O_2	10	0	0.74 ± .10	0.18
Ozone/H_2O_2/UV	0	0	6.2 ± 3.0	1.00
Ozone/H_2O_2/UV	1.6	0	2.2 ± .89	0.36
Ozone/H_2O_2/UV	10	0	0.65 ± .07	0.10
Ozone	0	0	1.4 ± .31	1.00
Ozone	0	2	0.10 ± .012	0.07
Ozone	0	10	0.02 ± .009	0.01
Ozone/UV	0	0	4.8 ± .87	1.00
Ozone/UV	0	2	0.86 ± .20	0.18
Ozone/UV	0	10	0.37 ± .03	0.08
Ozone/H_2O_2	0	0	3.8 ± .45	1.00
Ozone/H_2O_2	0	2	1.3 ± .11	0.34
Ozone/H_2O_2	0	10	0.51 ± .06	0.13
Ozone/H_2O_2/UV	0	0	6.2 ± 3.0	1.00
Ozone/H_2O_2/UV	0	2	1.4 ± .28	0.23
Ozone/H_2O_2/UV	0	10	0.55 ± .07	0.09

---

[1] mean ± 95% confidence limits