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USE OF A KINETIC MODEL TO UNDERSTAND
THE EFFECT OF IRON(II) AND BICARBONATE
ON THE OZONATION OF 1,2-DICHLOROBENZENE

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USE OF A KINETIC MODEL TO UNDERSTAND THE EFFECT OF IRON(II) AND BICARBONATE ON THE OZONATION OF 1,2-DICHLOROBENZENE

By

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ABSTRACT

USE OF A KINETIC MODEL TO UNDERSTAND THE EFFECT OF IRON(II) AND BICARBONATE ON TEH OZONATION OF 1,2-DICHLOROBENZENE

By

Ming-Kuei Chiang

This study was conducted to investigate the effects of bicarbonate and ferrous iron on 1,2-dichlorobenzene oxidation using ozonation processes. A kinetic model was also developed to simulate experiments.

In the oxidation processes, the 1,2-dichlorobenzene removal efficiency was decreased and the ozone consumption was increased when the concentration of bicarbonate was increased from 0.002 M to 0.005 M. Thus, the effect of bicarbonate cannot be explained only the scavenging of the hydroxyl radicals which should decrease both 1,2-dichlorobenzene removal and ozone consumption. However, an additional explanation for the effect bicarbonate is the reaction of $^{\cdot}CO_3^{-}$ radical with ozone which consumes excess ozone.

The role of Fe^{2+} acting as an initiator or a scavenger in ozonation treatment systems depends on the ozonation condition. At neutral pH, the reaction of Fe^{2+} initiating ozone decomposition is a dominant in ozone treatment, but the reaction of Fe^{2+} scavenging hydroxyl radicals is the dominant reaction in O_3/UV and O_3/H_2O_2 treatments.

A model developed by using acuchem program shows a good agreement with the experimental results for O_3, O_3/UV, and O_3/H_2O_2 treatment systems at the pH range 5~8.

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CHAPTER 1

INTRODUCTION

GENERAL

Ozone is a very powerful oxidant (E^0 = 2.07 volts in alkaline solution), which is capable of reacting with numerous organic chemicals. It is more powerful than most of other oxidants currently used in water treatment (see Table 1.1). However, many organic matters (e.g., aliphatic amines) only react slowly with molecular ozone. For these matters, the processes involving the $\cdot OH$ radical generation may provide more

Table 1.1 Oxidation-Reduction Potentials of Water Treatment Agents

Reactions	Potential in Volts (E^0) at 25 ^{0}C
$F_2 + 2e^- = 2F^-$	2.87
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$	1.57
$HOCl + H^+ + 2e^- = Cl^- + H_2O$	1.49
$Cl_2 + 2e^- = 2Cl^-$	1.36
$HOBr + H^+ + 2e^- = Br^- + H_2O$	1.33
$Br_2 + 2e^- = 2Br^-$	1.07
$ClO_{2(aq)} + e^- = ClO_2^-$	0.95
$H_2O_2 + 2H_3O^+ + 2e^- = 4H_2O$ (base)	0.87

* Ozone Treatment of Industrial Wastewater, 1981. Noyes Data Corporation, New Jersey, p 17.

effective treatment.

The ·OH radical is an extremely strong and non-selective oxidant (E^0 = 3.06 volts). The processes resulting in the formation of ·OH radicals in sufficient quantity to affect water treatment are referred to as advanced oxidation processes (AOPs). These processes include ozone in combination with UV irradiation, ozone with added hydrogen peroxide, hydrogen peroxide in combination with Fe(II), hydrogen peroxide with UV irradiation, etc.. The processes of ozone in combination with UV irradiation (O_3/UV) and ozone with added hydrogen peroxide (O_3/H_2O_2) were the two AOPs studied in this work.

The application of ozone for the disinfection in water treatment began in Nice, France in 1907. By the 1960's, ozone was also used for odor control in wastewater treatment. Although the ozonation has been widely used in water and wastewater treatment facilities and more and more successful applications have been reported, these remain a lack of knowledgement of the mechanisms by which ozone decomposes. The lack of understanding the complex reactions of natural organic matter in aqueous ozone systems will become a major obstacle for further ozone applications.

In recent years, many possible reaction sequences in aqueous ozone solution were published (e.g., Bühler et al. 1984, Holcman et al. 1982, Gary et al. 1988, Sehested et al. 1982, 1984, 1991, Staehelin et al. 1982, 1984, 1985 ...). The mechanisms for ozone decomposition developed by Staehelin, Bühler and Hoigné (SBH) are widely accepted although some of reactions are in dispute (e.g., the existence of $^{\cdot}HO_4$). This mechanism is considered the most reliable system for ozone decomposition in pure water.

OBJECTIVES

In previous investigations, 1,3,5-trichlorobenzene and 1,2-dichlorobenzene have been studied in aqueous systems by using ozone, ozone/UV, and ozone/H_2O_2 treatments at various pH and portions of these studies have been published (Masten et al., 1993). Based upon the results of these series of investigations, the major objectives of this study were formulated to be (1) to investigate the effect of ferrous ion or/and bicarbonate ion on the efficiency of treatment of 1,2-DCB with advanced oxidative processes and (2) to develop a numerical model to describe the kinetics of oxidation and the efficiency of treatment processes.

BACKGROUND

The pathways of the ozonation for organic matters are: (i) direct attack by molecular ozone via cycle-addition or electrophilic reaction, and (ii) indirect attack by free radicals (primarily $^{\cdot}OH$) produced by the decomposition of ozone. In aromatic compounds, the ozonation of the compounds substituted with electron-donating groups (e.g., $-OH$ or $-NH_2$) is faster than it of the compounds substituted with electron-withdrawing groups (e.g., $-NO_2$, $-Cl$, $-COOH$). Hoigné and Bader

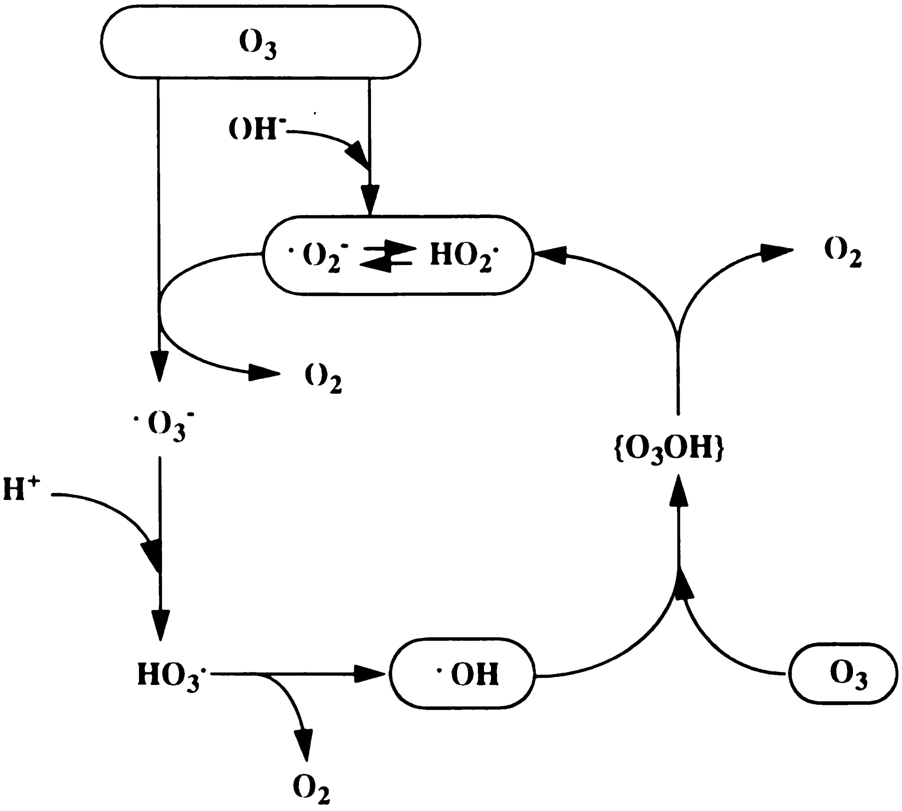

Figure 1.1 The decomposition of ozone in pure water
(Adapted from Staehelin and Hoigne, 1985)

(1983) determined the rate constants of the reaction of ozone with substituted benzenes, phenol > toluene > benzene > chlorobenzene > nitrobenzene. Generally, the more chlorinated compound is more difficult to be oxidized.

Ozone decomposition is a complex succession of reactions. It has been extensively studied (e.g., Sehested et al. 1982, 1984, 1991, Staehelin et al. 1982, 1984, 1985). Staehelin et al. have proposed a series of mechanisms that are widely accepted as a basic model for ozone decomposition in pure water (see Figure 1.1). The elementary steps of ozone decomposition are listed as follows :

Initiation :

$O_3 + OH^- \longrightarrow {}^{\cdot}O_2^- + {}^{\cdot}HO_2$ .... (1)

$({}^{\cdot}HO_2 \longleftrightarrow O_2^- + H^+)$

Propagation :

${}^{\cdot}O_2^- + O_3 \longrightarrow {}^{\cdot}O_3^- + O_2$ .... (2)

${}^{\cdot}O_3^- + H^+ \longleftrightarrow {}^{\cdot}HO_3$ .... (3)

${}^{\cdot}HO_3 \longrightarrow {}^{\cdot}OH + O_2$ .... (4)

${}^{\cdot}OH + O_3 \longleftrightarrow {}^{\cdot}HO_4$ .... (5)

${}^{\cdot}HO_4 \longrightarrow {}^{\cdot}HO_2 + O_2$ .... (6)

${}^{\cdot}HO_2 \longleftrightarrow {}^{\cdot}O_2^- + H^+$ .... (7)

The decomposition of ozone in pure water is initiated by reaction (1). Ozone (O_3) reacts with hydroxide ion (OH^-) to produce superoxide anion (${}^{\cdot}O_2^-$) and hydroperoxyl radical (${}^{\cdot}HO_2$). The chain propagation reactions: the transfer of an electron from ${}^{\cdot}O_2^-$ to O_3 forms the ozonide ion (${}^{\cdot}O_3^-$) with the release of

O_2 (reaction 2); the protonation of $\cdot O_3^-$ to form $\cdot HO_3$ followed by the decomposition of $\cdot HO_3$ to produce a hydroxyl radical ($\cdot OH$) with the release another O_2 molecule (reaction 3,4); the reaction of $\cdot OH$ and O_3 forms a charge-transfer complex ($\cdot HO_4$) which decays into $\cdot HO_2$ and O_2 (reaction 5,6); the decomposition of $\cdot HO_2$ forms $\cdot O_2^-$ and H^+ (reaction 7). The $\cdot O_2^-$ enters the first step of the cyclic reactions shown in Figure 1.1. In the propagation step, $\cdot O_2^-$ and $\cdot OH$ are both chain carriers which promote the cyclic reactions. Although some mechanisms of this model are still in dispute (ex. the existence of $\cdot HO_4$). It is the most reliable mechanism for ozone decomposition in pure water.

"Real" water systems contain many organic solutes or other impurities such as humic acid, carbonate species, iron, aromatic compounds, etc.. The mechanisms by which these solutes are involved in ozone decomposition are much more complex than that of which occurs in pure water. The solutes may act as initiators, promoters, or inhibitors in ozone decomposition or consume ozone only because of the direct reaction of the molecule with ozone (see Figure 1.2). Initiators react with ozone and form $\cdot O_3^-$ via an electron transfer reaction. Promoters are capable of regenerating $\cdot O_2^-$ by free radical reactions. Inhibitors scavenge free radicals such as $\cdot OH$ radicals resulting the decrease of $\cdot O_2^-$ formation.

Ferrous ion (Fe^{2+}) is a common metal ion that exists in ground water at concentration greater than 0.3 mg/L. In aqueous ozone systems, it has been proposed that ferrous ion

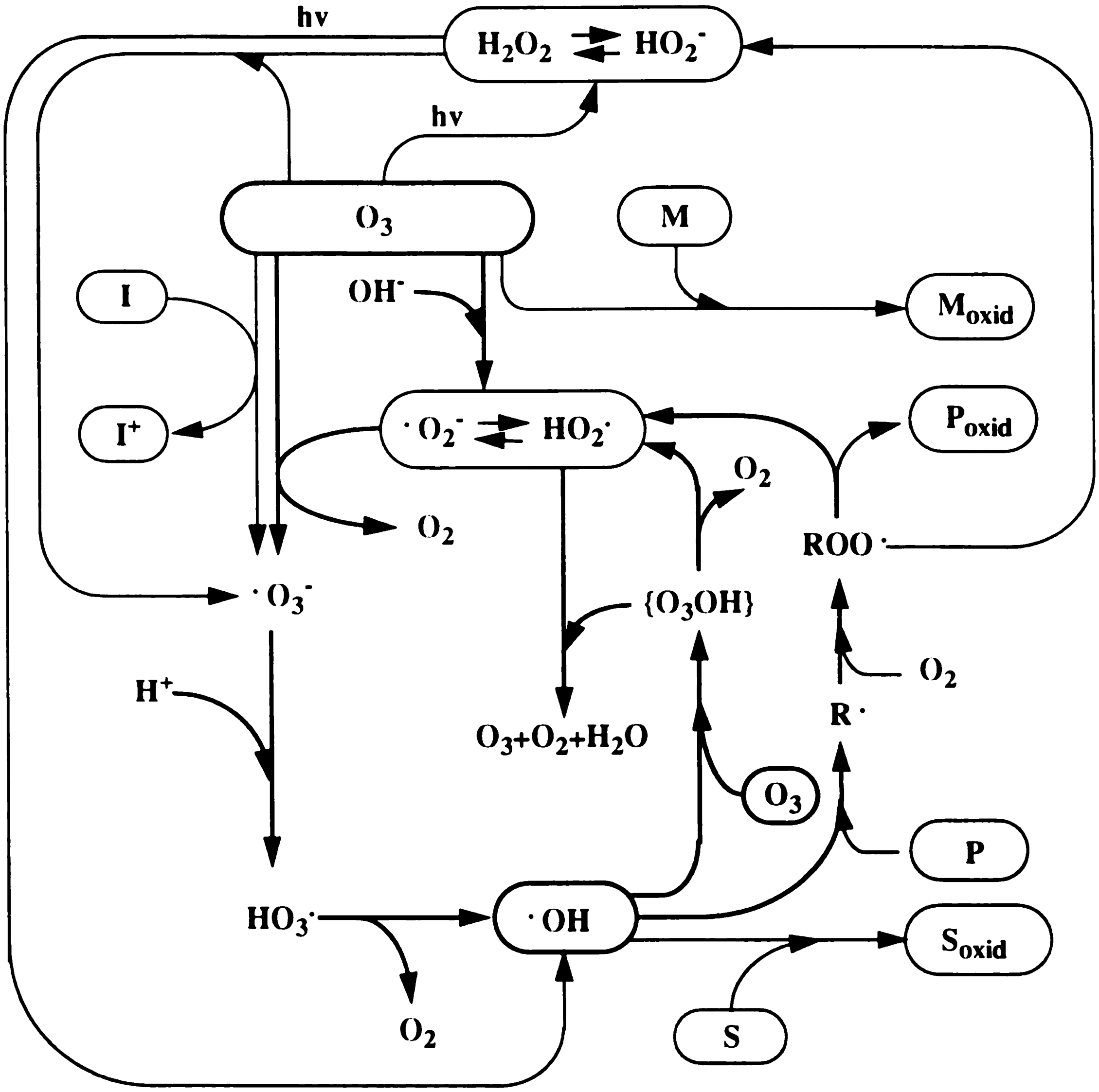

Figure 1.2 The decomposition of ozone containing reactant species.
M is a pollutant which reacts with ozone directly
I is an initiator which reacts with ozone to initiate the chain reaction
P is a promoter which reacts with ·OH to form a radical species
S is a scavenger which reacts with ·OH to terminate the chain reaction

reacts with ozone by an electron-transfer reaction and forms an ozonide ion (Hart et al., 1983), i.e. Fe^{2+} acts as an initiator. Protonation of $\cdot O_3^-$ results the formation of the hydroxyl radical. Thus, the net reaction is:

$$Fe^{2+} + O_3 + H^+ \longrightarrow Fe^{3+} + O_2 + OH \text{ .... } (8)$$

If there is excess Fe^{2+}, the $\cdot OH$ radical would oxidize a second Fe^{2+} (reaction 9).

$$Fe^{2+} + OH \longrightarrow Fe^{3+} + OH^- \text{ .... } (9)$$

Nowell and Hoigné (1987) suggested an alternative pathway by which an oxygen atom is transferred from O_3 to Fe^{2+} resulting in the formation of Fe^{4+} (reaction 10). The Fe^{4+} can oxidize with Fe^{2+} to Fe^{3+} (reaction 11).

$$Fe^{2+} + O_3 \longrightarrow (FeO)^{2+} + O_2 \text{ .... } (10)$$

$$(FeO)^{2+} + Fe^{2+} \longrightarrow 2Fe^{3+} \text{ .... } (11)$$

By this proposed pathway, no additional $\cdot OH$ radicals would be formed. On the other hand, according to this mechanism Fe^{2+} does not act as an initiator of ozone decomposition.

Carbonate species ($H_2CO_3{*}/HCO_3^-/CO_3^{2-}$), which are commonly found in natural water, are known to inhibit ozone decomposition, thus stabilizing ozone. HCO_3^-/CO_3^{2-} do not directly react with ozone (Hoigné al et., 1985) but react rapidly with $\cdot OH$ radicals to form $\cdot CO_3^-$ radical, a selective electrophilic reagent. The $\cdot CO_3^-$ radical also shows a wide range of reactivities with aromatic compounds however the rate constants for the reactions of these compounds and $\cdot CO_3^-$ radical are much less than that observed for the reaction of the same compounds with hydroxyl radicals.

Hydrogen peroxide and UV light are two initiators of ozone decomposition. Ozone/H_2O_2 is a cost effective technique of advanced oxidation processes. In water, H_2O_2 and HO_2^- are in an acid-base equilibrium of $pK_a = 11.65$ (reaction 12). The HO_2^- ion acts as an initiator of ozone decomposition resulting in the production of the superoxide ion (reaction 13). The superoxide ion may react with an additional ozone molecule to form the high reactive $^{\cdot}OH$ radical. At pH <12 when $[H_2O_2] > 10^{-7}M$, HO_2^- has a greater effect on the ozone decomposition rate than does the OH^- ion (Staehelin and Hoigné, 1982).

$$H_2O_2 \longleftrightarrow HO_2^- + H^+ \quad \ldots\ldots\ldots\ldots \quad (12)$$

$$HO_2^- + O_3 \longrightarrow OH + {}^{\cdot}O_2^- + O_2 \quad \ldots\ldots\ldots\ldots \quad (13)$$

As mentioned above, the higher concentration of hydrogen peroxide may produce more $^{\cdot}OH$ radicals. But at relatively high concentrations of hydrogen peroxide, H_2O_2 itself may scavenge the $^{\cdot}OH$ radical and inhibit the effect of the $^{\cdot}OH$ radical on the oxidation of the target chemical. It was found that with oxalic and 1,1,2-trichloroethane the rates of oxidation were fastest with a pH 7.5 and an initial hydrogen peroxide concentration of 60 to 70 μM (Paillard et al. 1988). The optimal H_2O_2 concentration for removing TCB in O3/H_2O_2 system was found to be 60 μM (Masten et al., 1993).

Ultraviolet light is another common initiator applied to decompose aqueous ozone in water treatment. In aqueous O_3/UV systems, UV light decomposes ozone and leads to the formation of hydrogen peroxide (reaction 14) at a rate closely matching the mass transfer rate of ozone into solution (Peyton and Glaze, 1988).

$$O_3 + H_2O + UV \longrightarrow H_2O_2 + O_2 \text{ .... } (14)$$

Hydrogen peroxide then reacts with ozone to produce the highly reactive $^{\cdot}OH$ radical as mentioned above (reaction 12, 13). At lower pH or higher UV intensities, hydrogen peroxide produces the hydroxyl radical directly by photolysis (reaction 15) before it has a chance to react with residual ozone.

$$H_2O_2 + hv \longrightarrow 2^{\cdot}OH \qquad \text{ .... } (15)$$

The reactions, both hydrogen peroxide undergoes direct photolysis and its conjugate base reacts with ozone, result in the formation of $^{\cdot}OH$ radicals that increase system's oxidation potential.

In short, The impurities existing in real water might affect the treatment efficiency of ozonation processes by acting as an initiator, promotor or scavenger. Therefore, in ozone application, the main chemical characteristics of an ozonation process should always be reviewed before planning and performing experiments to optimize an application.

CHAPTER 2

METHODS AND MATERIALS

SYSTEM CONFIGURATION

A continuous flow system was chosen to avoid the volatilization loss of target compounds and constant the mass transfer of ozone into solution. The system configuration was showed in Figure 2.1 and the experimental apparatus was summarized on Table 2.1. Basically, the continuous flow system can be partitioned into three parts, production of aqueous ozone, chemical pumping system, and continuously stirred flow-through reactor.

1) Production of Aqueous Ozone

A Polymetrics ozone generator (Model T-408, San Jose, CA) was used to generate ozone gas (approximately 3% v/v ozone in oxygen) by feeding dried high purity oxygen. The dielectric of the ozone generator was cooled by 10°C water supplied by a refrigerated circulator (Model 9500, Fisher Scientific) for the purpose of preventing the dielectric from overheating and stabilizing the rate at which the ozone gas was generated. Aqueous ozone solutions were prepared by continuously bubbling ozone gas into the ozone contactor, a three liter spherical flask, containing pH 2 water. In order to maintain a constant

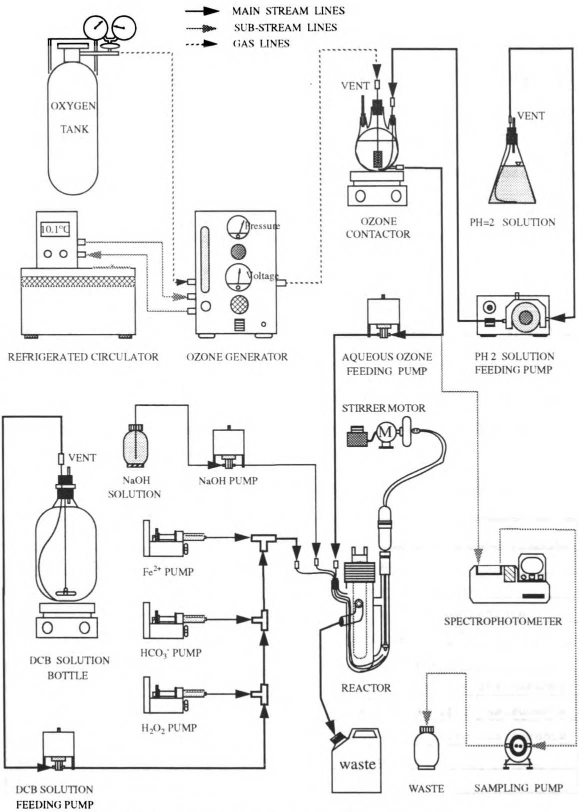

Figure 2.1 The Experimental Configuration of Ozonation system

water level in the contactor, a peristaltic pump (Model 7520-25, Cole-Parmer Instruments, Inc.) was used to continuously pump in pH 2 water and a piston pump (Model RHSY, Fluid Metering, Inc.) was used to continuously pump out aqueous ozone solution; both of the pumps were set at the same flowrate (~12.5 ml/min). In the ozone contactor, a stir bar was stirred by a magnetic stirrer to mix the aqueous ozone. A UV spectrophotometer (Model UV-1201, Shimadzu, Columbia, MD) was used to monitor aqueous ozone concentration continuously to ensure the system was stable.

2) Chemical Pumping System

DCB solution, Fe^{2+} solution, HCO_3^- solution, and H_2O_2 solution were respectively pumped by a piston pump (Model RHSY, Fluid Metering, Inc.), a syringe pump (Model A..E, Razel Scientific Instruments, Inc.), a syringe pump (Model A-99..ER,

Table 2.1 The List of Experimental Apparatus

NAME	MODEL	COMPANY
ozone generator	T-408	Polymetric
Refrigerated Circulator	9500	Fisher Scientific
pH 2 water Peristaltic Pump	7520-25	Cole-Parmer Instruments
Ozone Solution Piston Pump	RHSY	Fluid Metering
DCB Solution Piston Pump	RHSY	Fluid Metering
HCO_3^- Solution Syringe Pump	A-99..ER	Razel Scientific Instruments
Fe^{2+} Solution Syringe Pump	A..E	Razel Scientific Instruments
H_2O_2 Solution Syringe Pump	A..E	Razel Scientific Instruments
NaOH Solution Piston Pump	NSI-33R	Milton Roy
Photochemical Reactor	7868	Ace Glass
UV Spectrophotometer	UV-1201	Shimadzu

Razel Scientific Instruments, Inc.), and a syringe pump (Model A..E, Razel Scientific Instruments, Inc.). These chemicals were individually discharged to reactor. The flowrate for each pump was 12.5 mL/min, 1.0 mL/min, 0.6 mL/min, and 0.1 mL/min, respectively.

3) Continuously Stirred Flow-Through Reactor (CSFTR)

An impeller-stirred photochemical reactor (Model 7868, Ace Glass, Inc., Vineland, NJ) was used in all experiments. There are two chambers in the reactor and the total working volume is 250 mL. A stirred impeller installed in the smaller chamber provides a adequate mixing in the reactor by continuously circulating the solution between the two chambers. The impeller was driven by a stirrer motor, connected to the impeller by a flexible shaft. All of input lines were positioned below the impeller blades to mix influent streams rapidly. Trace studies have been done by Michael J. Galbraith (1993) and it proved that the reactor could be adequately described by a CFSTR model.

REAGENTS

1) pH 2 water : Deionized water was acidified with 36% hydrochloric acid to pH 2.
2) DCB solution : A six liter glass flask was filled with 6 L deionized water. 25 μL of 1,2-dichlorobenzene (99%, Aldrich Chemical Co., WI) was added in the flask then the flask was tightly sealed immediately. The solutions were stirred with magnetic stirrer for three days. The concentration of 1,2-

dichlorobenzene solutions resulting from this procedure was about 4ppm.

3) Fe^{2+} solution : 20 mL conc H_2SO_4 was slowly added to 50 mL deionized water and 0.351 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was dissolved into the acid solution. By diluting it with deionized water to 1 L, a 50 mg/L Fe^{2+} solution was prepared and stored in a dark bottle.

4) H_2O_2 solution : 85 μL of 30% H_2O_2 (Baker analyzed, Sigma, MO) was added into 50 mL deionized water to form 0.015 M H_2O_2 and it was standardized via direct UV absorption (ϵ_{240} = 40 M^{-1} cm_{-1}). It was prepared every time before used.

5) Indigo blue solution : 6 grams indigo blue was dissolved in 1 L deionized water and stored in a dark bottle as a stock solution. Proper amount of stock solution was diluted with deionized water to an absorbance of ~1.0000 at 600 nm every time before used.

ANALYTICAL METHODS

The inlet ozone concentration was determined by using direct UV-absorption method at 258 nm. Inlet aqueous solution was continuously pumped through a 2 mm quartz flow cell and was monitored by a UV spectrophotometer (Model UV-1201, Shimadzu Scientific Instruments, Inc., Columbia, MD). An extinction coefficient of 3000 $M^{-1}cm^{-1}$ was used to convert absorbance into mole concentration.

The ozone concentration in the reactor was determined by using the indigo method (Bader and Hoigné, 1982). While steady state condition was reached for each experiment, the effluent solution was directly sampled from the reactor outlet port with a 150 mL flask containing 100 mL indigo blue solution. The absorbances of the solution were measured at 600 nm before and after sampling.

1,2-Dichlorobenzene concentration was measured using head-space gas chromatograph (Autosystem, Perkin Elmer, Norwalk, CT) equipped with a flame ionization detector and a silica glass capillary column (PE624, Perkin Elmer, Norwalk, CT). The residual ozone was quenched by using sodium nitrite solution. Internal standard, 0.5 ppm 1,3,5-Trichlorobenzene, was used in DCB analysis.

The hydrogen peroxide concentration in the reactor was determined using the peroxidase N,N-diethy-p-phenylenediamine method with flow injection analysis technique (Galbraith, 1993). Samples were collected at reactor outlet port and were purged with nitrogen gas during sampling to remove residual ozone before analysis.

The ferrous ion concentration in reactor was determined by Phenanthroline method. Samples were also purged with nitrogen gas during sample collecting for 5 minutes to remove residual ozone. A standard curve was done for each set of experiments.

EXPERIMENTAL PROCEDURE

The experiments of this study were listed in Table 2.2. Each experiment was designed at the same pH including ozone,

ozone/UV, and ozone/H_2O_2 system with the same condition. Exp.1~Exp.6 were designed to investigate the effect of bicarbonate using O_3, O_3/UV, and O_3/H_2O_2 treatments at vary pH. Additional Fe^{2+} was added in Exp.7~Exp.10 for investigating the effect of Fe^{2+} when compare with Exp.4~Exp.6.

The experiments were started with pumping DCB solution and un-ozonated pH 2 water into the reactor. One hour later, the samples were taken for initial DCB concentration. NaOH piston pump was turned on to adjust pH in reactor when necessary. The ozone generator was turned on and ozone gas was bubbled into the contactor. The concentration of aqueous ozone in the contactor was monitored by UV spectrophotometer continuously and was controlled at 12 mg/L. HCO_3^- syringe pump and Fe^{2+} syringe pump were turned on, if necessary, after aqueous ozone concentration in the contactor was stable. All

TABLE 2.2 The List of Experiments in This Study

series	pH	[HCO_3^-] added	[Fe^{2+}] added	Process
Exp. 1	5.40	0.002 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 2	6.10	0.002 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 3	7.28	0.002 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 4	5.33	0.005 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 5	6.01	0.005 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 6	7.35	0.005 M	---	O_3, O_3/UV, O_3/H_2O_2
Exp. 7	2.24	0.005 M	2.0 mg/L	O_3, O_3/UV, O_3/H_2O_2
Exp. 8	4.13	0.005 M	2.0 mg/L	O_3, O_3/UV, O_3/H_2O_2
Exp. 9	5.79	0.005 M	2.0 mg/L	O_3, O_3/UV, O_3/H_2O_2
Exp.10	6.29	0.005 M	2.0 mg/L	O_3, O_3/UV, O_3/H_2O_2

necessary samples (e.g., remaining DCB, ozone, and Fe^{2+}) for the study of ozone system were taken from effluent stream after reactor had reached steady-state (one hour after all necessary pumps were turned on). After sampling, the UV light was turned on and all other equipments were kept at the same condition. When system reached steady state, effluent stream were sampled again for ozone/UV study. The UV light was turned off and H_2O_2 syringe pump was turned on. The system was again allowed to reach steady state before the effluent stream was sampled for ozone/H_2O_2 study. Whatever the system was changed, it is necessary to wait for one hour before steady state was reached. Table 2.3 summaries the experimental condition of all equipments.

Table 2.3 The Operation Condition for Equipments in Each System

Equipment	Initial Condition	Ozone system	Ozone/UV system	Ozone/H_2O_2 system
Ozone Generator	off	on	on	on
Ozone Pump	on	on	on	on
DCB Pump	on	on	on	on
HCO_3^- Pump	off	on	on	on
UV Light	off	off	on	off
H_2O_2 Pump	off	off	off	on
NaOH Pump	off	on(1)	on(1)	on(1)
Fe^{2+} Pump	off	on/off(2)	on/off(2)	on/off(2)

Note: (1) The NaOH pump was turned off in Exp.7.
(2) The Fe^{2+} Pump was turned off in Exp.1~Exp.6 and was turned on in Exp.7~Exp.10.

The effect of bicarbonate on DCB degradation was studied with [HCO_3^-] = 2 mM and 5 mM at pH 5, 6, and 7. The desired bicarbonate concentration in reactor was obtained by pumping proper concentration of sodium bicarbonate solution into the reactor with a fixed speed syringe pump.

CHAPTER 3

KINETIC MODEL

THE MODEL MECHANISMS

Based on basic mechanisms of ozone decomposition reported by Staehelin, Bühler, and Hoigné (has been discussed in chapter 1), an model to describe ozone decomposition along with contaminant degradation was developed using 72 reactions for O_3, O_3/UV,and O_3/H_2O_2 systems. The reactions used in this model are listed in Table 3.1.

It is generally accepted that O_3 decomposition is initiated by OH^- (R1) and HO_{2-} (R2). The ozone decomposition rate predicted by these two reactions is much slower than that observed in acid solution. Thus an additional initiation reaction, the thermal dissociation reaction of O_3 forming O and O_2 (R3) in acidic solution (Sehested et al., 1991), was incorporated into the kinetics model as well as the initiation reaction of O_3 with OH^- and HO_2^-. Contrary to the k_f value for R3 that was reported by Sehested et al. (1991), $10^{-7}s^{-1}$. Using this model, we estimated the k_f value to be $6.5*10^{-1}s^{-1}$. The quantum yield for the production O from H_2O_2 was also included in this model. In the presence of UV light, the reactions for the photolysis of aqueous ozone to produce H_2O_2 (R44) and

TABLE 3.1 A List of Reactions and Rate Constants Used in the Kinetic Model

No.	**REACTANTS**	**PRODUCTS**	**RATE CONSTANT**(a)		**Ref**
			k_f	k_r	
1	$O_3 + OH^-$	$\cdot HO_2 + \cdot O_2^-$	1.4E+02		33
2	$O_3 + HO_2^-$	$\cdot HO + \cdot O_2^- + O_2$	2.8E+06		33
3	O_3	$O + O_2$	6.5E-01(b)	1.0E+09	31
4	H_2O_2	$O + H_2O$	2.6E-04	2.2E+02(b)	28
5	$O + H_2O$	$\cdot HO + \cdot HO$	8.0E+01(b)		31
6	$\cdot O_2^- + H^+$	$\cdot HO_2$	2.0E+10	3.2E+05	38
7	$\cdot O_2^- + O_3$	$\cdot O_3^- + O_2$	1.6E+09		6
8	$\cdot O_3^- + H^+$	$\cdot HO_3$	5.2E+10	3.3E+02	6
9	$\cdot HO_3$	$\cdot OH + O_2$	1.1E+05		6
10	$\cdot OH + O_3$	$\cdot HO_4$	2.0E+09	1.0E+04	34
11	$\cdot HO_4$	$\cdot HO_2 + O_2$	2.8E+04		34
12	$\cdot O^- + O_2$	$\cdot O_3^-$	3.0E+09	3.3E+03	14
13	$\cdot O^- + \cdot O_3^-$	$2\cdot O_2^-$	7.0E+08		5
14	$\cdot O^- + \cdot OH$	HO_2^-	2.0E+10		30
15	$\cdot O^- + HO_2^-$	$\cdot O_2^- + OH^-$	4.0E+08		29
16	$\cdot O^- + H_2O_2$	$\cdot O_2^- + H_2O$	5.0E+08		5
17	$\cdot OH$	$\cdot O^- + H^+$	6.3E-02	5.0E+10	38
18	$\cdot OH + OH^-$	$\cdot O^- + H_2O$	1.2E+10	1.8E+06	5
19	$\cdot OH + \cdot O_3^-$	$\cdot HO_2 + \cdot O_2^-$	6.0E+09		30
20	$\cdot OH + HO_2^-$	$\cdot O_2^- + H_2O$	7.5E+09		5
21	$\cdot OH + H_2O_2$	$\cdot HO_2 + H_2O$	2.7E+07		24
22	$\cdot O^- + \cdot O_2^- + H_2O$	$2OH^- + O_2$	6.0E+08		5
23	$\cdot O_2^- + \cdot OH$	$OH^- + O_2$	1.0E+10		34
24	$\cdot O_2^- + 2\cdot HO_2$	$H_2O_2 + 2O_2$	9.7E+07		38
25	$\cdot O_2^- + \cdot HO_3$	$OH^- + 2O_2$	1.0E+10		34
26	$\cdot O_2^- + \cdot HO_4$	$OH^- + O_2 + O_3$	1.0E+10		34

TABLE 3.1 (Cont'd)

	REACTANTS	**PRODUCTS**	**RATE CONSTANT**(a)		**Ref**
			k_f	k_r	
27	$\cdot O_3^- + \cdot OH$	$OH^- + O_3$	2.5E+09		30
28	$\cdot OH + \cdot OH$	H_2O_2	5.0E+09		34
29	$\cdot OH + \cdot HO_2$	$H_2O + O_2$	6.6E+09		5
30	$\cdot OH + \cdot HO_3$	$H_2O_2 + O_2$	5.0E+09		34
31	$\cdot OH + \cdot HO_4$	$H_2O_2 + O_3$	5.0E+09		34
32	$\cdot HO_2 + \cdot HO_2$	$H_2O_2 + O_2$	8.7E+05		38
33	$\cdot HO_3 + \cdot HO_3$	$H_2O_2 + 2O_2$	5.0E+09		34
34	$\cdot HO_3 + \cdot HO_4$	$H_2O_2 + O_2 + O_3$	5.0E+09		34
35	$\cdot HO_4 + \cdot HO_4$	$H_2O_2 + 2O_3$	5.0E+09		34
36	$H_2O_2 + O_3$	$H_2O + 2O_2$	6.5E-03		38
37	$HO_2^- + H^+$	H_2O_2	5.0E+10	1.0E-01	38
38	H_2O	$H^+ + OH^-$	1.0E-03	1.0E+11	7
39	H_3PO_4	$H_2PO_4^- + H^+$	3.2E+08	5.0E+10	38
40	$H_2PO_4^-$	$HPO_4^{2-} + H^+$	3.2E+03	5.0E+10	38
41	HPO_4^{2-}	$PO_4^{3-} + H^+$	2.2E-01	5.0E+11	38
42	H_2CO_3	$HCO_3^- + H^+$	2.1E+04	4.7E+10	38
43	HCO_3^-	$CO_3^{2-} + H^+$	2.2E+00	4.7E+10	38
44	$O_3 + H_2O + hv$	$H_2O_2 + O_2$	1.5E-02(d)		24
45	$H_2O_2 + hv$	$\cdot OH + \cdot OH$	1.5E-03(d)		38
46	$Fe^{3+} + OH^- + hv$	$Fe^{2+} + \cdot OH$	5.0E+03		10
47	$H_3PO_4 + \cdot OH$	$\cdot H_2PO_4 + H_2O$	2.7E+06		5
48	$H_2PO_4^- + \cdot OH$	$\cdot H_2PO_4 + OH^-$	2.0E+04		5
49	$H_2PO_4^- + \cdot O_3^-$	$HPO_4^{2-} + \cdot HO_3$	9.1E+07	9.1E+06	6
50	$HPO_4^{2-} + \cdot OH$	$\cdot HPO_4^- + OH^-$	5.9E+05		17
51	$HPO_4^{2-} + \cdot O^-$	UNKNOWN	3.5E+06		5
52	$PO_4^{3-} + \cdot OH$	$\cdot PO_4^{2-} + OH^-$	7.0E+06		17
53	$H_2CO_3 + \cdot OH$	$\cdot HCO_3 + H_2O$	1.0E+05		5

TABLE 3.1 (Cont'd)

No.	REACTANTS	PRODUCTS	RATE CONSTANT(a)		Ref
			k_f	k_r	
54	HCO_3^- + $\cdot OH$	$\cdot CO_3^-$ + H_2O	1.5E+07		5
55	CO_3^{2-} + $\cdot OH$	$\cdot CO_3^-$ + OH^-	4.2E+08		5
56	CO_3^{2-} + $\cdot O^-$	$\cdot CO_3^-$ + O^{2-}	5.0E+05		14
57	$\cdot CO_3^-$ + O_3	UNKNOWN	1.0E+05		38
58	$\cdot CO_3^-$ + $\cdot O_2^-$	CO_3^{2-} + O_2	7.5E+08		14
59	$\cdot CO_3^-$ + $\cdot O_3^-$	CO_3^{2-} + O_3	6.0E+07		14
60	$\cdot CO_3^-$ + $\cdot OH$	UNKNOWN	5.0E+09		38
61	$\cdot CO_3^-$ + HO_2^-	HCO_3^- + $\cdot O_2^-$	5.6E+07		17
62	$\cdot CO_3^-$ + H_2O_2	HCO_3^- + $\cdot HO_2$	8.0E+05		17
63	Fe^{2+} + O_3	Fe^{3+} + $\cdot O_3^-$	1.7E+03(b)		12
64	Fe^{2+} + H_2O_2	Fe^{3+} + $\cdot OH$ + OH^-	76.5		37
65	Fe^{2+} + $\cdot OH$	Fe^{3+} + OH^-	4.3E+08		5
66	Fe^{2+} + $\cdot O^-$ + H_2O	Fe^{3+} + $2OH^-$	3.8E+09		5
67	DCB + O_3	PRODUCT	2.5E+00		(d)
68	DCB + $\cdot HO$	$\cdot$DCB + H_2O	4.0E+09		10
69(c)	DCB + $\cdot CO_3^-$	$\cdot$DCB + HCO_3^-	1.0E+05		(d)
70(c)	$\cdot$DCB + O_2	$\cdot$OODCB	1.0E+09		(d)
71(c)	$\cdot$OODCB + O_3	$\cdot$OODCB + $\cdot OH$	1.0E+01		(d)
72(c)	$\cdot$OODCB + $\cdot HO$	PRODUCT	4.0E+09		(d)

(a) The units for first and second order rate constants are s^{-1} and $M^{-1}s^{-1}$.
(b) Value estimulated from model simulation.
(c) This reactions are proposed in this work.
(d) Value estimated from structure-reactivity relationships.

decomposition of H_2O_2 to form hydroxyl radicals (R45) are considered.

Reactions R6~R11 describe the radical chain reaction of ozone decomposition as published by Staehelin, Bühler, and Hoigné (1984). Superoxide anion ($\cdot O_2^-$) and hydroxyl radical ($\cdot OH$) are two radical chain reaction carriers which promote ozone decomposition. The additional reactions reported by other authors (R12~R21) were also considered in the model including the reactions of oxygen anion radical ($\cdot O^-$) although $\cdot O^-$ is formed only at significant concentrations at high pH. A hypothetical radical-forming reaction, R5, (Sehested et al. 1991) that would be in direct competition with the reverse reaction of R3 was also included in the model. A rate constant of $8.0*10^1 s^{-1}$ was estimated for this reaction (R5) by fitting the data of Exp.1 to the model (as shown in Table 3.2).

Termination reactions are those reactions which consume free radicals and shorten the chain length of ozone decomposition. R22~R36 describe the radical termination reactions which were included in the model. R37~R43 describe the proton transfer reactions. These reactions were considered to be fast equilibrium processes. Since they were also involved in very fast propagation reactions, they may be in steady state but not equilibrium.

Carbonate and phosphate species are hydroxyl radical scavengers which inhibit the radical chain reactions. R47~R62 describe the relative reactions of carbonate and phosphate species with free radicals. However, the intermediate $\cdot CO_3^-$

Table 3.2 The Estimation of Rate Constants for Reactions R3 and R5

Rate Constant		Ozone Conc. (M)		DCB Conc. (M)	
k_{R3}	k_{R5}	$[O_3]_{obs}$	$[O_3]_{model}$	$[DCB]_{obs}$	$[DCB]_{model}$
1.0x10^{-7}	8.0x10^{-1}	4.99x10^{-5}	1.19x10^{-4}	5.05x10^{-6}	1.26x10^{-5}
1.0x10^{-7}	8.0x10^{0}	4.99x10^{-5}	1.19x10^{-4}	5.05x10^{-6}	1.26x10^{-5}
1.0x10^{-7}	8.0x10^{1}	4.99x10^{-5}	1.19x10^{-4}	5.05x10^{-6}	1.26x10^{-5}
1.0x10^{-7}	8.0x10^{2}	4.99x10^{-5}	1.19x10^{-4}	5.05x10^{-6}	1.26x10^{-5}
6.5x10^{0}	8.0x10^{-1}	4.99x10^{-5}	3.09x10^{-5}	5.05x10^{-6}	1.05x10^{-5}
6.5x10^{0}	8.0x10^{0}	4.99x10^{-5}	2.81x10^{-5}	5.05x10^{-6}	7.97x10^{-6}
6.5x10^{0}	8.0x10^{1}	4.99x10^{-5}	1.27x10^{-5}	5.05x10^{-6}	1.87x10^{-6}
6.5x10^{0}	8.0x10^{2}	4.99x10^{-5}	2.91x10^{-5}	5.05x10^{-6}	3.74x10^{-7}
6.5x10^{-1}	8.0x10^{-1}	4.99x10^{-5}	8.51x10^{-5}	5.05x10^{-6}	1.11x10^{-5}
6.5x10^{-1}	8.0x10^{0}	4.99x10^{-5}	7.95x10^{-5}	5.05x10^{-6}	1.01x10^{-5}
6.5x10^{-1}	8.0x10^{1}	4.99x10^{-5}	5.34x10^{-5}	5.05x10^{-6}	6.17x10^{-6}
6.5x10^{-1}	8.0x10^{2}	4.99x10^{-5}	1.50x10^{-5}	5.05x10^{-6}	1.60x10^{-6}
6.5x10^{-2}	8.0x10^{-1}	4.99x10^{-5}	1.14x10^{-5}	5.05x10^{-6}	1.24x10^{-5}
6.5x10^{-2}	8.0x10^{0}	4.99x10^{-5}	1.13x10^{-4}	5.05x10^{-6}	1.22x10^{-5}
6.5x10^{-2}	8.0x10^{1}	4.99x10^{-5}	1.00x10^{-4}	5.05x10^{-6}	1.06x10^{-5}
6.5x10^{-2}	8.0x10^{2}	4.99x10^{-5}	5.96x10^{-5}	5.05x10^{-6}	6.05x10^{-6}

acts as a promoter in its reaction with H_2O_2/HO_2^- (R61 and R62).

Fe^{2+} initiates ozone decomposition by an electron transfer reaction (R63, R64). In the meantime, Fe^{2+} also scavenges free radicals ($^{\cdot}OH$ and $^{\cdot}O^-$) and shortens the chain reaction (R65,R66). In the presence of UV light, Fe^{3+} is converted to Fe^{2+} by accepting an electron from OH$^-$ and forming the $^{\cdot}OH$ radical (R46).

Relatively little is known about the mechanism of the reaction of ozone with DCB. One of the possible reaction of $^{\cdot}OH$ radical with organic pollutants suggested by Hoigné (1988) is H-abstration (R68). The resulting radicals then add to the oxygen molecule rapidly forming peroxy radicals (R70). The peroxy radical scavenges another $^{\cdot}OH$ forming an unknow product (72). R71 is a possible reaction adepted from the model developed by Yao et al. (1992).

MODEL MODIFICATION FOR CONTINUOUS FLOW SYSTEM

A continuously stirred flow-through reactor was used in all experiments. Equation 16 shows the differential equation obtained from the mass balance of species X in continuous flow system. The species X could be O_3 or DCB or $^{\cdot}OH$ etc.. Any one of them should be expressed by its own differential equation.

$$\frac{d[X]}{dt}=\frac{1}{\theta}([X]_0-[X])+\sum_{i=1}^{n}(k_i*[reactants]_i) \qquad \textbf{(16)}$$

where [X] is the steady state concentration of species X in the reactor, $[X]_0$ is the initial concentration of species X in influent stream. θ is the hydraulic retention time of the reactor. There are n reactions involving species X. k_i is the rate constant of reaction i. The concentrations of reactants in the reaction are given by $[reactants]_i$. If the resction is second order overall (first order in each of the reactant) then there would be two reactants in the equation, e.g., $k_1*[reactant_1]_1*[reactant_2]_1$. If the reaction is first order then there would only be one reactant term in the equation and if the reaction is zero order then integer "1" replaces the $[\text{reactant}]_i$ term in the equation. The last term of equation 16 summarizes the reaction rates of all reactions involving species X. If the reaction produces species X, the value of $k_i*[\text{reactants}]_i$ is a positive. On the contrary, the reaction consumes species X, the value of $k_i*[\text{reactants}]_i$ is a negative. For each experiment, $[X]_0$ and θ are constants. Substituting $k'=[X]_0/\theta$ and $k''=1/\theta$ into equation 16, yields:

$$\frac{d[X]}{dt}=k'-k''[X]+\sum_{i=1}^{n}(k_i*[reactants]_i) \qquad \textbf{(17)}$$

In equation 17, the first term (k′) describes a zero order reaction forming species X (the reactant is replaced by integer "1" then the reaction rate is k′*1), and the second term (k") describes the kinetics of first order reaction involving species X (the reactant is X and reaction rate is k"*[X]). Then they can be summarized into the third term by adding two extra reactions (as shown in equation 18).

$$\frac{d[X]}{dt}=\sum_{i=1}^{n+2}(k_i*[reactants]_i) \qquad \textbf{(18)}$$

Where the $k_{n+1}=k'$, $[\text{reactants}]_{n+1}=$ "1" and $k_{n+2}=-k''$, $[\text{reactants}]_{n+2}=[X]$. Equation 18 is the simplest form of using differential equation to describe a homogeneous reaction system, e.g., the $\cdot HO_2$ generation rate in pure water system (see page 5) is:

$$d[{}^{\cdot}HO_2]/dt = k_1[O_3][OH^-] + k_6[{}^{\cdot}HO_4] + k_{f7}[{}^{\cdot}HO_2] - k_{r7}[{}^{\cdot}O_2^-][H^+]$$
$$= -\Sigma(k_i * [\text{reactants}]_i)$$

The reactions that occur in the CFCMR system used in this study can be modeled with using Acuchem program (Braun et al., 1988). The additional reactions for each species are added to replace the mass flux in/out the reactor.

unknown 1 $\longrightarrow$ X , $k' = [X]_0/\theta$, flux in equation

X $\longrightarrow$ unknown 2 , $k'' = 1/\theta$, flux out equation

where θ = 600 sec. for all experiments, thus, $k' = [X]_0/600$ M s^{-1} and $k'' = 1.67*10^{-3}$ s^{-1}. The model used in Acuchem program is attached in APPENDIX A.

CHAPTER 4

RESULTS AND DISCUSSIONS

The degradation rates of ozone and DCB in O_3, O_3/UV, and O_3/H_2O_2 treatment systems are summarized in Tables 4.1 to 4.3. Staehelin and Hoigné (1985) and Peyton and Glaze (1988) reported that bicarbonate and carbonate are hydroxyl radical scavengers which result in the loss of treatment efficiency of processes involving ·OH radical. The experimental results of this study agree with those of Staehelin and Hoigné (1985) and Peyton and Glaze. DCB removal efficiency decreases in O_3, O_3/UV, and O_3/H_2O_2 treatments (pH 5~7) when the bicarbonate concentration of the solution was increased from 0.002 M to 0.005 M (as shown in Table 4.4 and Figures 4.1 to 4.3). It was also reported that bicarbonate ions do not react with ozone (Hoigné et al., 1985) but react with hydroxyl radicals and inhibit ozone decomposition by acting as a hydroxyl radical scavenger and interrupting the chain reaction. In other words, ozone is more stable in solutions containing higher concentration of bicarbonate (Hoigné, 1988). The hypothesis mentioned above is contrary to the results of this study as shown in Figures 4.4 to 4.6. It was found that the degradation rate of ozone increases in O_3, O_3/UV, and O_3/H_2O_2 treatments

Table 4.1 Degradation Rate of DCB, O_3, and Fe^{2+} in Ozone Treatment

pH	$[HCO_3^-]$ (M)	$DCB^{(b)}$		$O_3^{(c)}$		$Fe^{2+(c)}$	
		Removal Efficiency (%)[a]	Degradation Rate (min^{-1})	Removal Efficiency (%)[a]	Degradation Rate (min^{-1})	Removal Efficiency (%)[a]	Degradation Rate (min^{-1})
5.40	0.002	64.49±4.34	0.184±0.029	59.51±1.92	0.149±0.009		
6.10	0.002	58.09±3.62	0.142±0.019	75.77±1.66	0.319±0.023		
7.28	0.002	50.67±3.40	0.104±0.013	60.38±1.20	0.154±0.006		
5.33	0.005	50.83±2.68	0.106±0.010	76.05±1.30	0.325±0.019		
6.01	0.005	51.39±2.34	0.109±0.009	75.95±1.88	0.327±0.027		
7.35	0.005	46.98±13.9	0.087±0.038	71.36±1.93	0.246±0.018		
2.24	0.005	14.12±9.34	0.017±0.012	61.60±0.72	0.164±0.004	88.51±3.27	0.789±0.225
4.13	0.005	72.34±4.91	0.284±0.058	90.29±0.45	1.010±0.048	76.09±0.57	0.346±0.009
5.79	0.005	67.74±1.41	0.223±0.011	90.38±0.30	0.997±0.031	73.32±2.20	0.292±0.026
6.29	0.005	68.87±7.51	0.237±0.071	86.73±0.56	0.700±0.030	77.46±1.21	0.368±0.201

Note : (a) Removal Efficiency = $(C_0-C)/C_0$,
where C_0 is the initial concentration of specie in reactor.
C is the final concentration of specie at steady state condition.
(b) Initial concentration of DCB is 1.84 ppm.
(c) Initial concentration of O_3 is 5.87 ppm.
(d) Initial concentration of Fe^{2+} is 1.9 ppm.

Table 4.2 Degradation Rate of DCB, O_3, and Fe^{2+} in Ozone/UV Treatment

pH	$[HCO_3^-]$	$DCB^{(b)}$		$O_3^{(c)}$		$Fe^{2+(d)}$	
	(M)	Removal Efficiency (%)[a]	Degradation Rate (min^{-1})	Removal Efficiency (%)[a]	Degradation Rate (min^{-1})	Removal Efficiency (%)[a]	Degradation Rate (min^{-1})
5.40	0.002	94.63±0.47	1.782±0.161	97.05±0.45	3.323±0.509		
6.10	0.002	88.61±0.94	0.795±0.071	98.99±0.21	10.057±2.195		
7.28	0.002	84.96±1.31	0.571±0.055	97.01±0.30	3.277±0.332		
5.33	0.005	89.90±0.69	0.910±0.063	98.76±0.38	8.152±2.502		
6.01	0.005	87.83±0.46	0.746±0.032	98.96±0.16	9.869±1.513		
7.35	0.005	81.96±2.71	0.448±0.078	98.36±0.34	5.913±1.256		
2.24	0.005	63.35±4.35	0.177±0.029	98.50±0.23	6.710±1.027	79.85±0.50	0.406±0.011
4.13	0.005	88.16±1.78	0.809±0.123	99.67±0.03	32.35±2.72	79.12±0.28	0.412±0.007
5.79	0.005	84.72±1.26	0.588±0.049	99.18±0.26	12.76±3.99	80.06±1.18	0.426±0.026
6.29	0.005	80.72±3.06	0.449±0.086	98.95±0.43	10.08±5.15	80.66±0.15	0.447±0.004

Note : (a) Removal Efficiency = $(C_0-C)/C_0$,
where C_0 is the initial concentration of specie in reactor.
C is the final concentration of specie at steady state condition.
(b) Initial concentration of DCB is 1.84 ppm.
(c) Initial concentration of O_3 is 5.87 ppm.
(d) Initial concentration of Fe^{2+} is 1.9 ppm.

Table 4.3 Degradation Rate of DCB, O_3, H_2O_2, and Fe^{2+} in Ozone/H_2O_2 Treatment

pH	$[HCO_3^-]$ (M)	DCB(b)		O_3(c)		H_2O_2(e)		Fe^{2+}(d)	
		Removal Efficiency (%)(a)	Degradation Rate (min^{-1})	Removal Efficiency (%)(a)	Degradation Rate (min^{-1})	Removal Efficiency (%)(a)	Degradation Rate (min^{-1})	Removal Efficiency (%)(a)	Degradation Rate (min^{-1})
5.40	0.002	88.21±1.39	0.759±0.094	77.28±1.13	0.345±0.018	18.81±0.42	0.024±0.001		
6.10	0.002	90.19±0.95	0.944±0.088	95.65±0.73	2.255±0.376	38.14±0.19	0.063±0.001		
7.28	0.002	89.08±1.17	0.828±0.095	93.57±0.25	1.477±0.059	54.17±0.74	0.120±0.003		
5.33	0.005	89.10±1.19	0.839±0.094	96.85±0.08	3.157±0.081	35.17±0.74	0.056±0.002		
6.01	0.005	89.21±0.48	0.858±0.042	98.91±0.38	9.434±3.310	59.05±0.91	0.150±0.004		
7.35	0.005	88.50±2.94	0.762±0.202	96.16±0.18	2.479±0.115	73.67±1.42	0.277±0.016		
2.24	0.005	34.05±6.66	0.053±0.015	88.46±0.32	0.789±0.393	67.59±2.64	0.251±0.019	80.61±.024	0.428±0.007
4.13	0.005	83.58±1.97	0.555±0.075	98.98±0.29	10.56±2.94	75.42±1.15	0.335±0.016	73.88±0.85	0.309±0.011
5.79	0.005	86.95±0.52	0.709±0.030	97.72±0.11	4.566±0.224	45.09±1.64	0.088±0.004	74.71±0.93	0.315±0.012
6.29	0.005	85.68±2.43	0.643±0.124	97.97±0.29	5.197±0.745	40.01±1.42	0.072±0.003	76.51±1.02	0.350±0.016

Note : (a) Removal Efficiency = $(C_0-C)/C_0$,
where C_0 is the initial concentration of specie in reactor.
C is the final concentration of specie at steady state condition.
(b) Initial concentration of DCB is 1.84 ppm.
(c) Initial concentration of O_3 is 5.87 ppm.
(d) Initial concentration of Fe^{2+} is 1.9 ppm.
(e) Initial concentration of H_2O_2 is 65 μM.

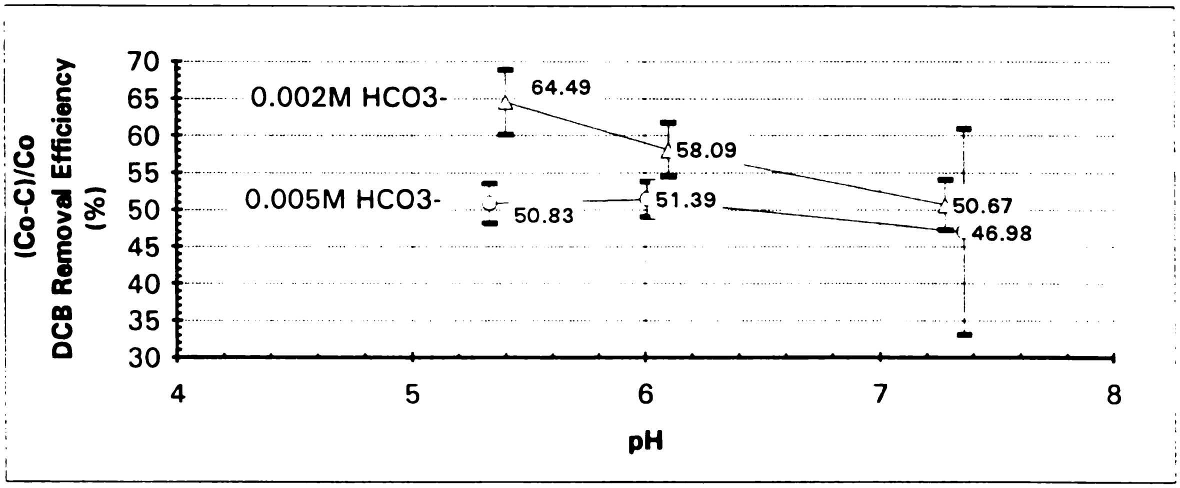

Figure 4.1 Effect of Bicarbonate Concentration on DCB Removal Efficiency in Ozone Treatment System

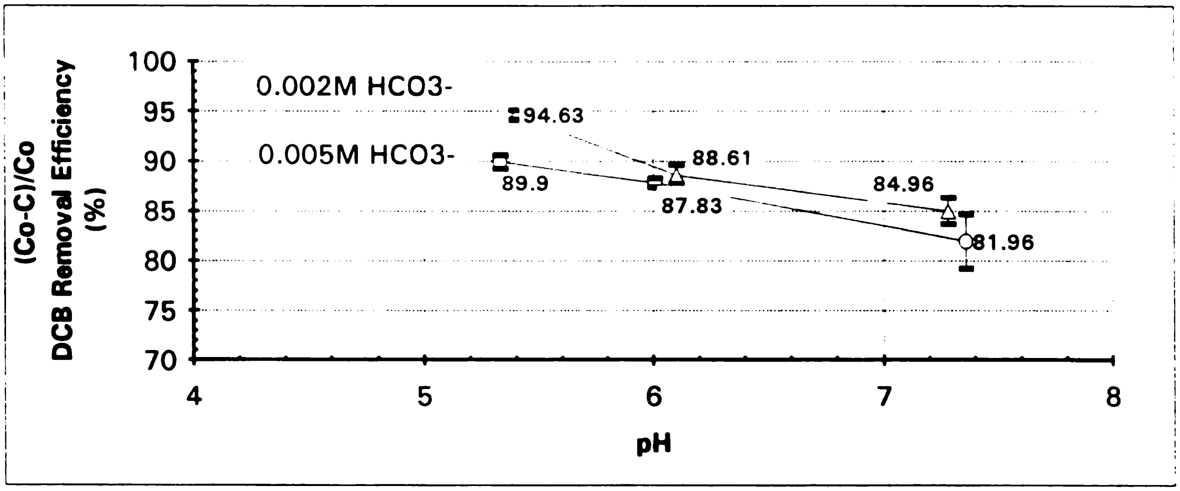

Figure 4.2 Effect of Bicarbonate Concentration on DCB Removal Efficiency in Ozone/UV Treatment System

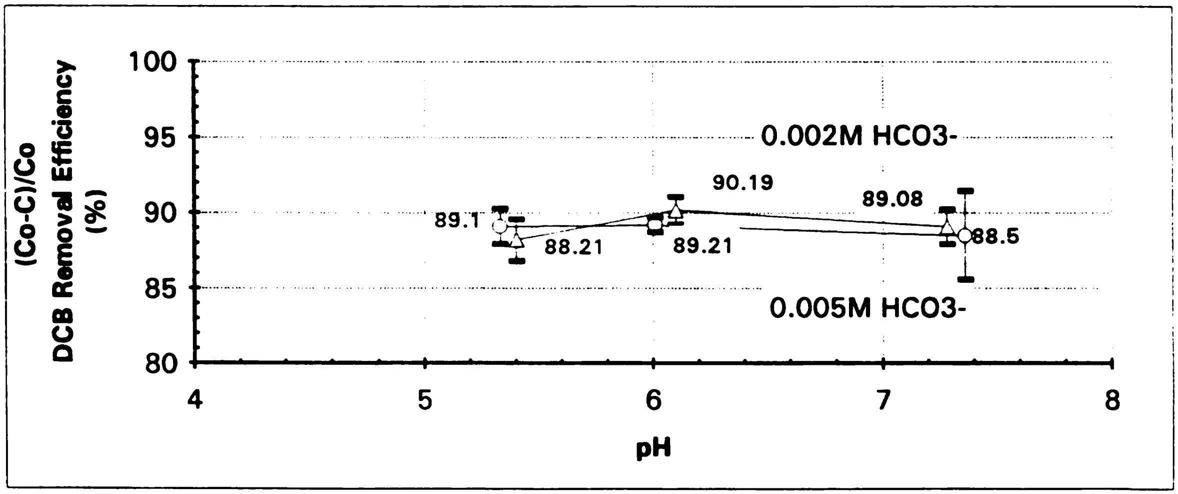

Figure 4.3 Effect of Bicarbonate Concentration on DCB Removal Efficiency in Ozone/H2O2 Treatment System

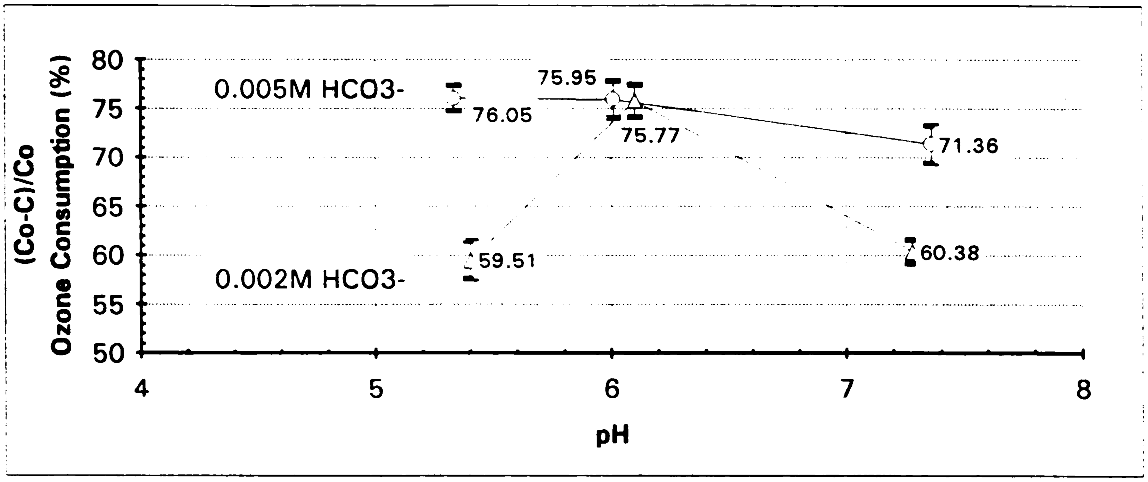

Figure 4.4 Effect of Bicarbonate Concentration on Ozone Consumption in Ozone Treatment System

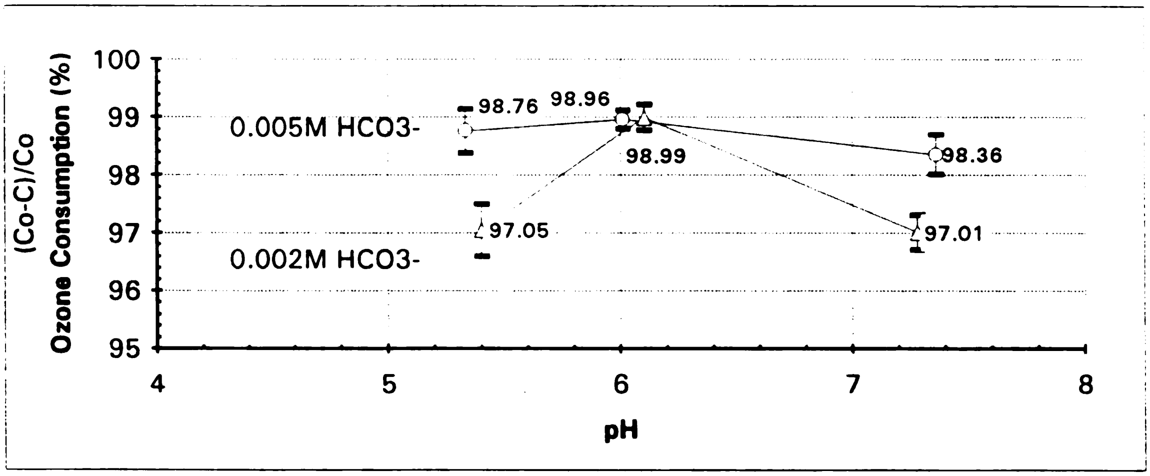

Figure 4.5 Effect of Bicarbonate Concentration on Ozone Consumption in Ozone/UV Treatment System

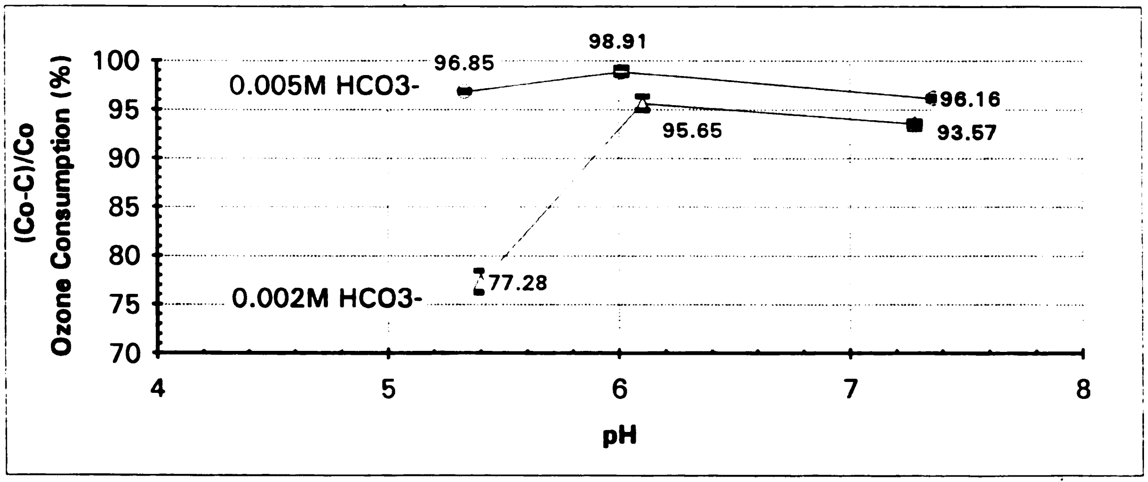

Figure 4.6 Effect of Bicarbonate Concentration on Ozone Consumption in Ozone/H2O2 Treatment System

(pH 5~7) when the bicarbonate concentration was increased from 0.002 M to 0.005 M (as shown in Table 4.5). Therefore, the effect of bicarbonate/carbonate ion cannot be explained simply by the scavenging of the hydroxyl radical by bicarbonate/ carbonate (Chelkowska, 1992). However, previous work has shown $\cdot CO_3^-$, which is formed when bicarbonate ions react with $\cdot OH$ radicals, could scavenge ozone (Nata et al., 1988). An increase in the bicarbonate ion concentration would result in a proportional increase in the consumption of hydroxyl radicals. This would reduce the possibility of the organic compound reacting with hydroxyl radicals and thus decrease

Table 4.4 The Effect of HCO_3^- on DCB Removal Efficiency

pH	O_3		O_3/UV		O_3/H_2O_2	
	0.002 M*	0.005 M*	0.002 M*	0.005 M*	0.002 M*	0.005 M*
5.4	64.5%	50.8%	94.6%	89.9%	88.2%	89.1%
6.1	58.1%	51.4%	88.6%	87.8%	90.2%	89.2%
7.3	50.7%	47.0%	85.0%	82.0%	89.1%	88.5%

* the bicarbonate concentration

Table 4.5 The Effect of HCO_3^- on O_3 Degradation Rate

pH	O_3		O_3/UV		O_3/H_2O_2	
	0.002 M*	0.005 M*	0.002 M*	0.005 M*	0.002 M*	0.005 M*
5.4	59.5%	76.0%	97.0%	98.8%	77.3%	96.8%
6.1	75.8%	75.9%	99.0%	99.0%	95.6%	98.9%
7.3	60.4%	71.4%	97.0%	98.4%	93.6%	96.2%

* the bicarbonate concentration

removal efficiency of the organic compound. Simultaneously, as more bicarbonate ions react with hydroxyl radicals producing more $\cdot CO_3^-$ this depletes additional ozone. This provides a reasonable explanation as to why bicarbonate ions would decrease the treatment efficiency of DCB and increase degradation rate of ozone.

In addition to these reactions, $\cdot CO_3^-$ could also react with excess H_2O_2/HO_2^- to form $\cdot HO_2/\cdot O_2^-$. These products would initiate the ozone decomposition chain reaction thus accelerating ozone degradation and increasing the concentration of hydroxyl radicals. Therefore, the reaction of H_2O_2/HO_2^- and $\cdot CO_3^-$ could lower the loss of hydroxyl radicals consumed by bicarbonate ions. This means the excess H_2O_2/HO_2^- would not only initiate ozone decomposition but would also reduce the effect that bicarbonate would have on the removal efficiency of DCB. In this study, higher H_2O_2/HO_2^- concentrations were present in the O_3/H_2O_2 treatment system than the other two treatments. As expected from this explanation, the results show that bicarbonate ion has less effect on DCB removal in ozone/H_2O_2 treatment than it in ozone and ozone/UV treatments (as shown in Table 4.4).

Fe^{2+} initiates ozone decomposition and results in the formation of the ozonide ion, which can then decompose to from the hydroxyl radical (Hoigné et al., 1985). As such, Fe^{2+} acts as an initiator. On the other hand, excess Fe^{2+} also consumes hydroxyl radicals and terminates the radical chain reaction. As such, Fe^{2+} can also act as a scavenger. For the ozone treatment process, the concentration of ozone in the reactor was ~30 μM before Fe^{2+} was added. Under these conditions, Fe^{2+} could react with ozone and accelerate ozone decomposition to form more hydroxyl radicals. Thus, both DCB removal efficiency and ozone consumption are increased. In our system, we observed an increases about 16.9% and 12.6% in the DCB removal and O_3 consumption, respectively, by the addition of Fe^{2+} at pH 6 (as shown in Table 4.6 and Figure 4.7 & 4.10). In ozone/UV and ozone/H_2O_2 treatments, the concentration of ozone remaining (less than 2 μM in ozone/UV and less than 4 μM in ozone/H_2O_2) before Fe^{2+} were added was very small. Fe^{2+} has to compete with other initiators for the small amount ozone present. Only a small portion of the Fe^{2+} added would compete with other initiators to react with ozone and the excess Fe^{2+} would scavenge the hydroxyl radical and thus inhibit the extent to which the the hydroxyl radical oxidizes DCB. Hence, the

Table 4.6 The Effect of Fe^{2+} on DCB and O_3 Degradation Rate at pH 6

	O_3		O_3/ UV		O_3/ H_2O_2	
	[DCB]	[O_3]	[DCB]	[O_3]	[DCB]	[O_3]
Exp.5[(1)]	51.4%	76.0%	87.8%	99.0%	89.2%	98.9%
Exp.9[(1)]	67.7%	90.4%	84.7%	99.2%	87.0%	97.7%
Exp.10[(1)]	68.9%	86.7%	80.7%	99.0%	85.7%	98.0%
Diff.[(2)]	16.9%	12.6%	-5.1%	0.1%	-2.9%	-1.1%

Note: (1) The experimental conditions are shown in Table 2.2

(2) Diff. = [(Exp.9 + Exp.10) / 2] - Exp.5

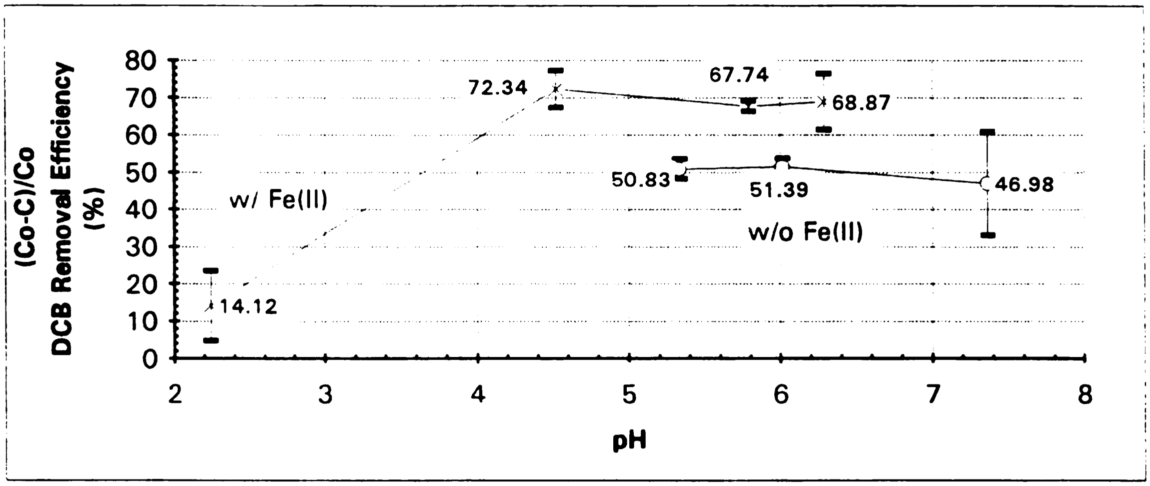

Figure 4.7 Effect of Fe(II) on DCB Removal Efficiency in Ozone Treatment System

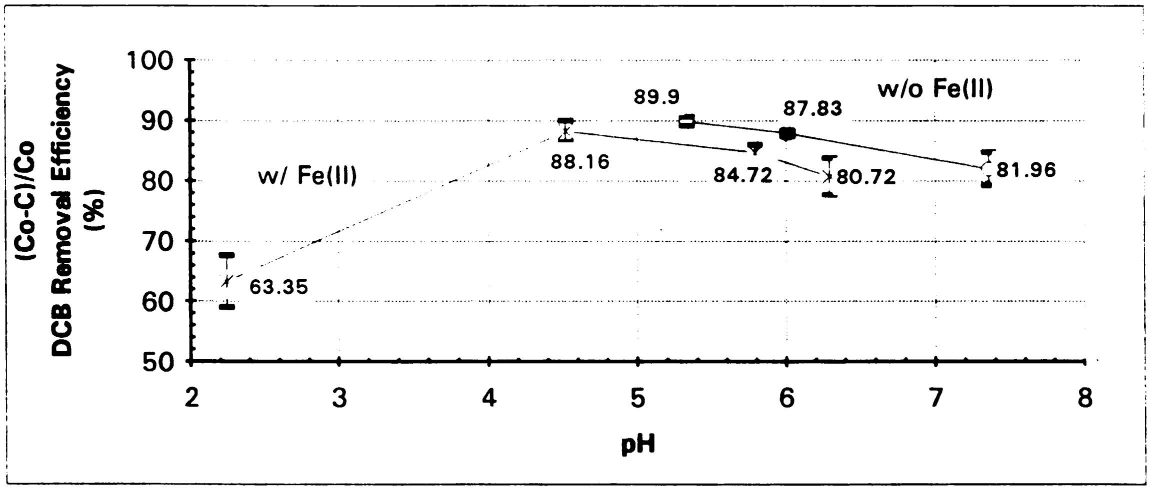

Figure 4.8 Effect of Fe(II) on DCB Removal Efficiency in Ozone/UV Treatment System

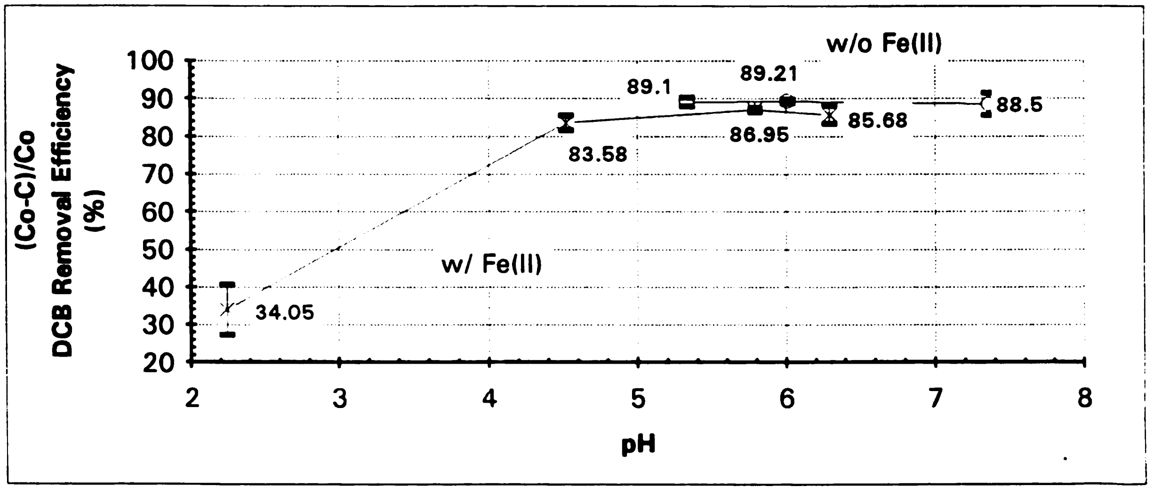

Figure 4.9 Effect of Fe(II) on DCB Removal Efficiency in Ozone/H2O2 Treatment System

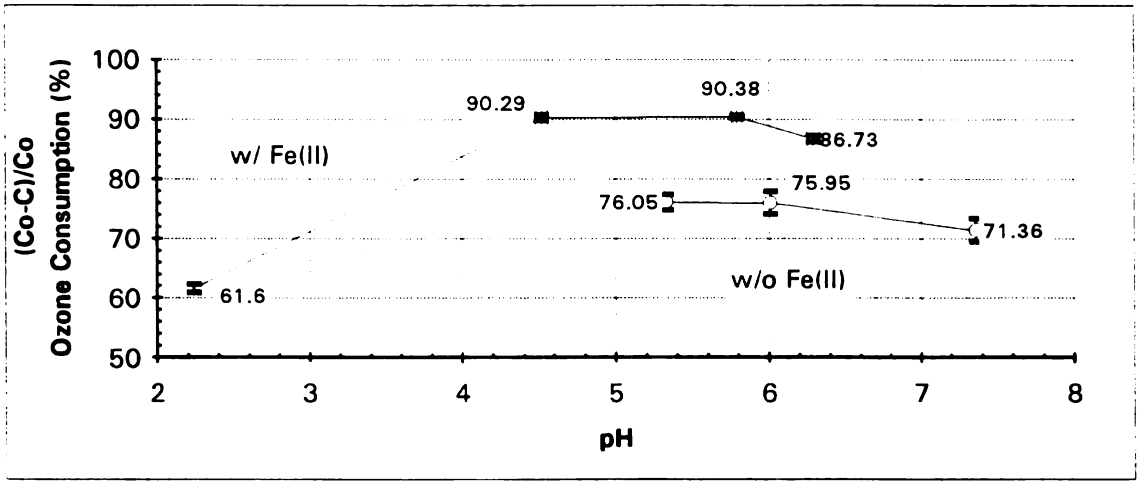

Figure 4.10 Effect of Fe(II) on Ozone Comsumption in Ozone Treatment System

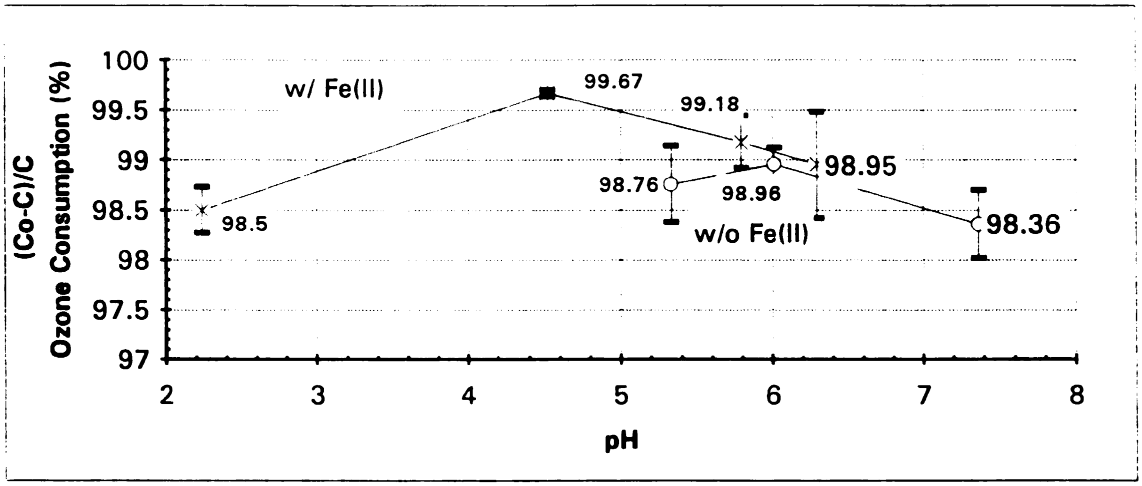

Figure 4.11 Effect of Fe(II) on Ozone Consumption in Ozone/UV Treatment System

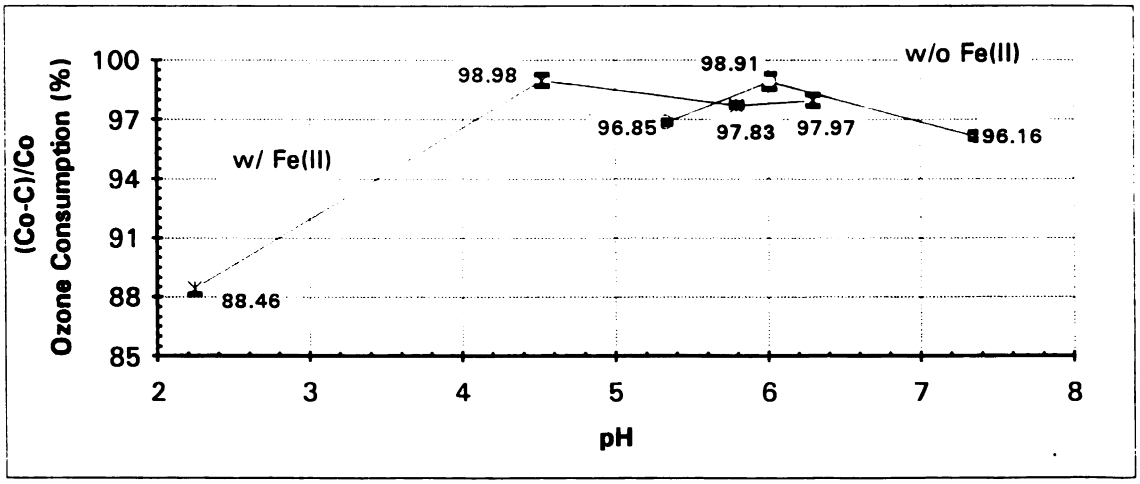

Figure 4.12 Effect of Fe(II) on Ozone Consumption in Ozone/H2O2 Treatment System

residual ozone concentration in O_3/UV and O_3/H_2O_2 treatment systems would not be expected to change significantly. At pH 6, the observations of less than 1% difference in the ozone consumption and the less than 6% and 3% decrease in DCB removal efficiency in O_3/UV and O_3/H_2O_2 treatment systems respectively (as shown in Table 4.6 and figure 4.8, 4.9, 4.11, 4.12) are consistent with the hypothesis mentioned above. As such, the role of Fe^{2+} as initiator or scavenger will depend on the competitive ability of Fe^{2+} with other initiators for ozone.

The rate constant of the Fe^{2+}/O_3 reaction was modified by using kinetic model simulation to get a better data fitting. When the value $5*10^5$ $M^{-1}s^{-1}$ (Hoigné,1985) was used in model, the model predicted that greater than 80% of ozone would have reacted with Fe^{2+} immediately and the extent of DCB removal was overpredicted. However, a smaller rate constant for Fe^{2+}/O_3 reaction ($1.7*10^3$ $M^{-1}s^{-1}$) was estimated using the model and used in this study (as shown in Table 4.7).

The results obtained from using the kinetic model to simulate the observations made in all experiments in this study are summarized in Appendix B. Comparing the model simulations for ozone consumption and DCB removal efficiency with those obtained experimentally, one observes that the best results for the model simulation are obtained for ozone/UV treatment followed by for ozone treatment and lastly for ozone/H_2O_2 treatment. The percentage difference between model simulations and experimental results for ozone consumption and

Table 4.7 The Estimation of the Rate Constant for Fe^{2+}/O_3 Reaction

System	Conc.	Rate Constant					
		Experi.	$1.7x10^{1}$	$1.7x10^{2}$	$1.7x10^{3}$	$1.7x10^{4}$	$5.0x10^{5}$
O_3 system	$[O_3]$	$1.56x10^{-5}$	$4.07x10^{-5}$	$2.69x10^{-5}$	$1.98x10^{-5}$	$1.83x10^{-5}$	$1.82x10^{-5}$
	[DCB]	$4.34x10^{-6}$	$5.44x10^{-6}$	$3.98x10^{-6}$	$3.11x10^{-6}$	$2.92x10^{-6}$	$2.91x10^{-6}$
	$[Fe^{2+}]$	$7.48x10^{-6}$	$2.00x10^{-5}$	$8.23x10^{-6}$	$1.54x10^{-6}$	$1.76x10^{-7}$	$6.08x10^{-9}$
O_3/UV system	$[O_3]$	$1.26x10^{-6}$	$6.46x10^{-6}$	$5.72x10^{-6}$	$4.06x10^{-6}$	$3.27x10^{-6}$	$3.12x10^{-6}$
	[DCB]	$2.69x10^{-6}$	$2.59x10^{-6}$	$2.45x10^{-6}$	$1.92x10^{-6}$	$1.46x10^{-6}$	$1.37x10^{-6}$
	$[Fe^{2+}]$	$6.42x10^{-6}$	$1.73x10^{-5}$	$1.43x10^{-5}$	$6.03x10^{-6}$	$1.01x10^{-6}$	$3.76x10^{-9}$
O_3/H_2O_2 system	$[O_3]$	$2.43x10^{-6}$	$1.98x10^{-5}$	$1.39x10^{-5}$	$5.97x10^{-6}$	$2.17x10^{-6}$	$1.86x10^{-6}$
	[DCB]	$2.00x10^{-6}$	$2.84x10^{-6}$	$2.38x10^{-6}$	$1.69x10^{-6}$	$1.24x10^{-6}$	$1.13x10^{-6}$
	$[Fe^{2+}]$	$7.80x10^{-6}$	$1.22x10^{-5}$	$8.33x10^{-6}$	$3.93x10^{-6}$	$1.44x10^{-6}$	$5.96x10^{-8}$
	$[H_2O_2]$	$3.80x10^{-5}$	$2.40x10^{-5}$	$2.64x10^{-5}$	$1.45x10^{-5}$	$4.70x10^{-6}$	$2.99x10^{-6}$

* The unit for rate constant and concentration are $M^{-1}s^{-1}$ and M, respectively.

DCB removal efficiency, respectively, at neutral pH are < 15% and < 16% for ozone treatment, < 4% and < 6% for ozone/UV treatment, and < 21% and < 14% for ozone/H_2O_2 treatment (see Table 4.8).

As stated previously, $\cdot CO_3^-$ might consume the excess ozone and react with other species. In the ozone/UV process, ozone is decomposed by UV light at a much faster rate than that observed for O_3 in the other two treatment processes. As such, $\cdot CO_3^-$ would be expected to deplete very little ozone in ozone/UV treatment system while the reaction of $\cdot CO_3^-$ and ozone might have only a very slight affect on the efficiency of DCB removal by the ozone/UV process. In contrast, the $\cdot CO_3^-/O_3$

Table 4.8 The % Difference Between Model Simulations and Experimental Results at Neutral pH

		Ozone Degradation Removal			DCB Removal Efficiency		
		Model	Experi.	Diff.*	Model	Experi.	Diff.*
O_3 System	Exp.2	61.1%	75.8%	-14.7%	60.5%	58.1%	2.4%
	Exp.3	68.8%	60.4%	8.4%	65.5%	50.7%	14.8%
	Exp.5	61.0%	76.0%	-15.0%	59.7%	51.4%	8.3%
	Exp.6	66.1%	71.4%	-5.3%	59.3%	47.0%	12.3%
	Exp.9	86.9%	90.3%	-3.4%	83.8%	67.8%	16.0%
	Exp.10	83.2%	86.7%	-3.5%	77.6%	68.9%	8.7%
O_3/UV System	Exp.2	95.2%	99.0%	-3.8%	89.8%	88.6%	1.2%
	Exp.3	95.3%	97.0%	-1.7%	85.0%	85.0%	0.0%
	Exp.5	95.2%	99.0%	-3.8%	86.5%	87.8%	-1.3%
	Exp.6	95.1%	98.4%	-3.3%	77.3%	82.0%	-4.7%
	Exp.9	96.7%	99.2%	-2.5%	89.8%	84.7%	5.1%
	Exp.10	96.6%	99.0%	-2.4%	86.2%	80.7%	5.5%
O_3/H_2O_2 System	Exp.2	77.3%	95.7%	-18.4%	77.3%	90.2%	-12.9%
	Exp.3	92.5%	93.6%	-1.1%	87.3%	89.1%	-1.8%
	Exp.5	78.1%	98.9%	-20.8%	76.3%	89.2%	-13.0%
	Exp.6	90.9%	96.2%	-5.3%	80.6%	88.5%	-7.9%
	Exp.9	94.9%	97.7%	-2.8%	91.2%	87.0%	4.2%
	Exp.10	95.0%	98.0%	-3.0%	87.8%	85.7%	2.1%

* Diff. is equal to Model(%) - Experi.(%).

reaction would be expected to affect the efficiency of the ozone, and ozone/H_2O_2 treatment systems more than observed in the ozone/UV process.

However, in the model, the rate constant used for the reaction of $\cdot CO_3^-$ and O_3 is small (10^5 dm^3 mol^{-1} s^{-1}) (Holcman et al., 1982).

As a result of the use of this rate constant, the model predicts that $\cdot CO_3^-$ would not influence the ozone consumption in either ozone/UV, ozone, ozone/H_2O_2 systems. However, only for the ozone/UV system is this prediction verified experimentally. As such, the model simulation and experimental results are comparable only for the ozone/UV system. However, the rate of the $\cdot CO_3^-/O_3$ reaction needs to be verified in a future study.

For the model simulation, the reactor was assumed to be a complete mixed system. However, the reactor would be more like a system between complete mixing and plug flow because all of the influent streams were installed in one location. The differences between complete mixed and plug flow systems would result some simulation error by using this model.

CHAPTER 5

CONCLUSIONS

CONCLUSIONS

The effect of bicarbonate on ozonation processes cannot be simply explained only by the scavenging of the $\cdot OH$ radical by bicarbonate. The competition of the intermediate $\cdot CO_3^-$ with other chemicals for ozone is an other important mechanism which should be considered when studying the influence of bicarbonate on ozonation processes. Thus, in O_3, O_3/UV, and O_3/H_2O_2 systems, the removal efficiency of DCB decreases and the consumption of ozone increases in the presence of bicarbonate. Furthermore, the reaction in which $\cdot CO_3^-$ reacts with H_2O_2/HO_2^- to form $\cdot HO_2/\cdot O_2^-$, thus initiating the ozone decomposition chain reaction to form $\cdot OH$ radicals would minimize the effect of bicarbonate on DCB removal efficiency. The O_3/H_2O_2 system has a higher H_2O_2 concentration than O_3 and O_3/UV systems do. Thus the bicarbonate has less effect on DCB removal efficiency in O_3/H_2O_2 system than it does in O_3 and O_3/UV systems.

The ferrous ion acts as of both an initiator and a $\cdot OH$ radical scavenger in ozonation processes. In the O_3 system,

Fe^{2+} acts as an initiator of ozone decomposition, resulting in the formation of additional $^{\cdot}OH$ radicals, thus increasing DCB removal. On the contrary, in O_3/UV and O_3/H_2O_2 systems, Fe^{2+} is unable to compete with UV and H_2O_2 as an initiator of ozone decomposition. Instead, Fe^{2+} acts as an $^{\cdot}OH$ radical scavenger, hence the DCB removal efficiency decreases. As such, the role of Fe^{2+} as an initiator or scavenger will depend on the competitive ability of Fe^{2+} with other initiators for ozone.

A rate constant of Fe^{2+}/O_3 reaction, 1.7×10^3 $M^{-1}s^{-1}$, was estimated by model fitting in this study. It is two order of magnitude lower than that reported by Hoigné et al. (1985). It may be caused by the difference of the water quality. Because the impurities existing in the water may react with Fe^{2+}, thus Fe^{2+} was consumed more than it should be on Fe^{2+}/O_3 reaction rate estimation. However, this rate constant needs to be confirmed in the future study.

Good agreement between data from experimental results and the kinetic model is observed for DCB and ozone degradation data in the pH range 5~8. This is especially true for the O3/UV system, where there are < 4% and < 6% differences between experiments and kinetics model for DCB and ozone degradation, respectively.

In water treatment, using ozonation processes is a good choice to remove lower concentrations of organic chemicals from water. For process engineers who want to apply ozone most effectively, the kinetic model can give a general idea of the target compound's treatment efficiency. However, due to lack of knowledge of the specifics of ozone chemistry, the kinetic model does not accurately predict the ozone decomposition rate or the extent of DCB removal for all conditions. As such, without such a model, it is always necessary to perform bench scale studies prior to design and implementation of the plan.

FUTURE RESEARCH

(1) In the study of O_3/H_2O_2 system, we found in the presence of Fe^{2+}, the remained H_2O_2 concentration increases when pH was increased. Lack of the knowledgement of the Fe^{2+}/H_2O_2 interaction, thus more mechanistic research is necessary to identify the effect of Fe^{2+} in O_3/H_2O_2 system.

(2) The rate constant of Fe^{2+}/O_3 reaction obtained by model fitting in this study is lower than the one reported by Hoigné et al. (1985). Thus it is necessary to identify the rate constant of Fe^{2+}/O_3 reaction in future research.

(3) The model was only applied in neutral pH in this study. At pH >10, the OH^- is predicted to be the dominate initiator. However, it is necessary to compare the experimental results and the kinetic model simulations at high pH when the OH^- ion becomes the dominate initiator.

(4) The reactions R67~R72 (see Table 3.1) are the proposed mechanisms of DCB oxidation. Thus the results of the model prediction might be changed if different mechanisms of DCB oxidation were proposed in the model. Thus identifying the mechanisms of DCB oxidation is necessary in future research.

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APPENDIX A

The Kinetic Model of Ozonation Processes for ACUCHEM Computer Program

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;This is a kinetic model of ozonation processes for ACUCHEM
;Ozone/Fe(II)/UV System at pH 6.3
 1111
;----- The Mechanisms -----
;----- Initiation Reactions -----
   , O3     + OH-   = .OH2   + .O2- , 1.4E2
   , O3     + HO2-  = .HO    + .O2- , 2.8E6
   , O3             =  O     +  O2  , 6.5E-1
   , O      + O2    =  O3           , 1.0E9
   , H2O2           =  O     + H2O  , 2.6E-4
   , O              =  H2O2         , 2.2E2
;----- Propagation Reactions -----
   , O              = .HO    + .HO  , 8.0E1
   , .O2-   + H     = .HO2          , 2.0E10
   , .HO2           = .O2-   + H    , 3.2E5
   , .O2-   + O3    = .O3-   + O2   , 1.6E9
   , .O3-   + H     = .HO3          , 5.2E10
   , .HO3           = .O3-   + H    , 3.3E2
   , .HO3           = .OH    + O2   , 1.1E5
   , .OH    + O3    = .HO4          , 2.0E9
   , .HO4           = .OH    + O3   , 1.0E4
   , .HO4           = .HO2   + O2   , 2.8E4
   , .O-    + O2    = .O3-          , 3.0E9
   , .O3-           = .O-    + O2   , 3.3E3
   , .O-    + .O3-  = .O2-   + .O2- , 7.0E8
   , .O-    + .OH   = HO2-          , 2.0E10
   , .O-    + HO2-  = .O2-   + OH-  , 4.0E8
   , .O-    + H2O2  = .O2-   + H2O  , 5.0E8
   , .OH            = .O-    + H    , 6.3E-2
   , .O-    + H     = .OH           , 5.0E10
   , .OH    + OH-   = .O-    + H2O  , 1.2E10
   , .O-            = .OH    + OH-  , 1.8E6
   , .OH    + .O3-  = .HO2   + .O2- , 6.0E9
   , .OH    + HO2-  = .O2-   + H2O  , 7.5E9
   , .OH    + H2O2  = .HO2   + H2O  , 2.7E7
;----- Termination Reactions -----
   , .O-    + .O2-  = OH-    + O2   , 6.0E8
   , .O2-   + .OH   = OH-    + O2   , 1.0E10
   , .O2-   + .HO2  = H2O2   + O4   , 9.7E7
   , .O2-   + .HO3  = OH-    + O4   , 1.0E10
   , .O2-   + .HO4  = OH-    + O5   , 1.0E10
   , .O3-   + .OH   = OH-    + O3   , 2.5E9
   , .OH    + .OH   = H2O2          , 5.0E9
   , .OH    + .HO2  = H2O    + O2   , 6.6E9
   , .OH    + .HO3  = H2O2   + O2   , 5.0E9
   , .OH    + .HO4  = H2O2   + O3   , 5.0E9
   , .HO2   + .HO2  = H2O2   + O2   , 8.7E5
   , .HO3   + .HO3  = H2O2   + O4   , 5.0E9
   , .HO3   + .HO4  = H2O2   + O5   , 5.0E9
   , .HO4   + .HO4  = H2O2   + O6   , 5.0E9
   , H2O2   + O3    = H2O    + O4   , 6.5E-3
   , O4             = O2     + O2   , 1.0E20
   , O5             = O3     + O2   , 1.0E20
```

```
   , O6             = O3     + O3   , 1.0E20
;----- Proton Transfer Equilibrium -----
   ,                = OH-    + H    , 1.0E-3
   , OH-    + H     =               , 1.0E11
   , H2O2           = HO2-   + H    , 1.0E-1
   , HO2-   + H     = H2O2          , 5.0E10
   , H3PO4          = H2PO4- + H    , 3.2E8
   , H2PO4- + H     = H3PO4         , 5.0E10
   , H2PO4-         = HPO4-2 + H    , 3.2E3
   , HPO4-2 + H     = H2PO4-        , 5.0E10
   , HPO4-2         = PO4-3  + H    , 2.2E-1
   , PO4-3  + H     = HPO4-2        , 5.0E11
   , H2CO3          = HCO3-  + H    , 2.1E4
   , HCO3-  + H     = H2CO3         , 4.7E10
   , HCO3-          = CO3-2  + H    , 2.2
   , CO3-2  + H     = HCO3-         , 4.7E10
;----- Effect of UV Light -----
   , O3             = H2O2   + O2   , 1.5E-2
   , H2O2           = .OH    + .OH  , 1.5E-3
   , Fe(III)+ OH-   = Fe(II) + .OH  , 5.0E3
;----- Effect of Phosphate Species -----
   , H3PO4  + .OH   = .H2PO4 + H2O  , 2.7E6
   , H2PO4- + .OH   = .H2PO4 + OH-  , 2.0E4
   , H2PO4- + .O3-  = HPO4-2 + .HO3 , 9.1E7
   , HPO4-2 + .HO3  = H2PO4- + .O3- , 9.1E6
   , HPO4-2 + .OH   = .HPO4- + OH-  , 5.9E5
   , HPO4-2 + .O-   = UNKNOWN1      , 3.5E6
   , PO4-3  + .OH   = .PO4-2 + OH-  , 7.0E6
;----- Effect of Carbonate Species -----
   , H2CO3  + .OH   = .HCO3  + H2O  , 1.0E5
   , HCO3-  + .OH   = .CO3-  + H2O  , 1.5E7
   , CO3-2  + .OH   = .CO3-  + OH-  , 4.2E8
   , CO3-2  + .O-   = .CO3-  + O-2  , 5.0E5
   , .CO3-  + O3    = UNKNOWN2      , 1.0E5
   , .CO3-  + .O2-  = CO3-2  + O2   , 7.5E8
   , .CO3-  + .O3-  = CO3-2  + O3   , 6.0E7
   , .CO3-  + .OH   = UNKNOWN3      , 5.0E9
   , .CO3-  + HO2-  = HCO3-  + .O2- , 5.6E7
   , .CO3-  + H2O2  = HCO3-  + .HO2 , 8.0E5
;----- Effect of Iron -----
   , Fe(II) + O3    = Fe(III)+ .O3- , 1.7E3
   , Fe(II) + H2O2  = Fe(III)+ .OH  , 76.5
   , Fe(II) + .OH   = Fe(III)+ OH-  , 4.3E8
   , Fe(II) + .O-   = Fe(III)+ OH-  , 3.8E9
;----- DCB Degradation -----
   , DCB    + O3    = DCB           , 2.5
   , DCB    + O3    = PRODUCT1      , 2.5
   , DCB    + .OH   = .DCB          , 4.0E9
   , DCB    + .CO3- = .DCB          , 1.0E5
   , .DCB   + O2    = .OODCB        , 1.0E9
   , .OODCB + O3    = .OODCB + .OH  , 1.0E1
   , .OODCB + .OH   = PRODUCT2      , 4.0E9
;----- Modification for Continuous Flow -----
```

```
;----- Hydraulic Detention Time is 600 Seconds -----
   , H         =          , 1.67E-3 ; Flux Out 1/600 s-1
   , OH-       =          , 1.67E-3 ; Flux Out 1/600 s-1
   , O3        =          , 1.67E-3 ; Flux Out 1/600 s-1
   , O2        =          , 1.67E-3 ; Flux Out 1/600 s-1
   , O         =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .O-       =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .O2-      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .O3-      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .OH       =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .HO2      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .HO3      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .HO4      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , H2O2      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , HO2-      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , H3PO4     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , H2PO4-    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , HPO4-2    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , PO4-3     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .HPO4-    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .PO4-2    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , H2CO3     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , HCO3-     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , CO3-2     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .HCO3     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .CO3-     =          , 1.67E-3 ; Flux Out 1/600 s-1
   , Fe(II)    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , Fe(III)   =          , 1.67E-3 ; Flux Out 1/600 s-1
   , DCB       =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .DCB      =          , 1.67E-3 ; Flux Out 1/600 s-1
   , .OODCB    =          , 1.67E-3 ; Flux Out 1/600 s-1
   , UNKNOWN1  =          , 1.67E-3 ; Flux Out 1/600 s-1
   , UNKNOWN2  =          , 1.67E-3 ; Flux Out 1/600 s-1
   , UNKNOWN3  =          , 1.67E-3 ; Flux Out 1/600 s-1
   , PRODUCT1  =          , 1.67E-3 ; Flux Out 1/600 s-1
   , PRODUCT2  =          , 1.67E-3 ; Flux Out 1/600 s-1
   ,          = H       , 9.58E-6 ; Flux In       [H]/600 M*s-1
   ,          = OH-     , 2.90E-15; Flux In     [OH-]/600 M*s-1
   ,          = O3      , 2.08E-7 ; Flux In      [O3]/600 M*s-1
   ,          = O2      , 3.33E-7 ; Flux In      [O2]/600 M*s-1
   ,          = DCB     , 1.95E-8 ; Flux In     [DCB]/600 M*s-1
   ,          = H2O2    , 0.00    ; Flux In    [H2O2]/600 M*s-1
   ,          = Fe(II)  , 5.70E-8 ; Flux In  [Fe(II)]/600 M*s-1
   ,          = H2CO3   , 8.00E-6 ; Flux In   [H2CO3]/600 M*s-1
   ,          = HCO3-   , 6.88E-10; Flux In   [HCO3-]/600 M*s-1
   ,          = CO3-2   , 7.43E-18; Flux In   [CO3-2]/600 M*s-1
   ,          = H3PO4   , 0.00    ; Flux In   [H3PO4]/600 M*s-1
   ,          = H2PO4-  , 0.00    ; Flux In  [H2PO4-]/600 M*s-1
   ,          = HPO4-2  , 0.00    ; Flux In  [HPO4-2]/600 M*s-1
   ,          = PO4-3   , 0.00    ; Flux In   [PO4-3]/600 M*s-1
END of Reaction Mechanism Statement:
;--- Initial Concentrations of Species (M) ---
  H      , 5.75E-3
```

```
  OH-     , 1.74E-12
  O3      , 1.25E-4
  O2      , 2.00E-4
  DCB     , 1.17E-5
  Fe(II)  , 3.42E-5
  H2O2    , 0.00
  H2CO3   , 4.80E-3
  HCO3-   , 4.13E-7
  CO3-2   , 4.46E-15
  H3PO4   , 0.00
  H2PO4-  , 0.00
  PO4-3   , 0.00
END of Species Concentration Sequence:
;--- Integration Tolerance ---
  1.0E-8
;--- Reaction Time (sec) ---
  6.0E2
```

APPENDIX B

The Results of Kinetic Model Simulation

Table B.1 The Input/Output Data of Kinetic Model for Ozone Treatment System

Exp. No.(1)		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
INPUT DATA	pH	5.40	6.10	7.28	5.33	6.01
	[H^+]	3.98E-6	7.94E-7	5.25E-8	4.68E-6	9.77E-7
	[OH^-]	2.51E-9	1.26E-8	1.91E-7	2.14E-9	1.02E-8
	[O_3]	1.23E-4	1.20E-4	1.23E-4	1.25E-4	1.22E-4
	[O_2](2)	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB]	1.42E-5	1.21E-5	1.21E-5	1.33E-5	9.69E-6
	[Fe^{2+}]	-----	-----	-----	-----	-----
	[H_2CO_3]	1.88E-3	1.32E-3	2.12E-4	4.53E-3	3.35E-3
	[HCO_3^-]	2.21E-4	7.78E-4	1.89E-3	4.65E-4	1.65E-3
	[CO_3^{2-}]	3.03E-9	5.34E-8	1.96E-6	5.84E-9	9.89E-8
MODEL OUTPUT	[O3]	5.34E-5	4.67E-5	3.84E-5	5.37E-5	4.76E-5
	[DCB]	6.17E-6	4.78E-6	4.18E-6	5.73E-6	3.90E-6
	[Fe^{2+}]	-----	-----	-----	-----	-----
	[H_2O_2]	1.19E-5	8.66E-6	2.17E-6	1.15E-5	7.70E-6
	[HO_2^-]	6.21E-12	2.28E-11	8.27E-11	5.26E-12	1.69E-11
	·OH	5.64E-13	6.52E-13	6.88E-13	5.67E-13	6.03E-13
	·HO_2	2.73E-13	1.88E-13	1.46E-13	3.02E-13	1.98E-13
	·HO_3	4.20E-13	4.52E-13	2.77E-13	4.35E-13	4.60E-13
	·HO_4	1.59E-12	1.60E-12	1.39E-12	1.60E-12	1.51E-12
EXP. RESULT	[O_3]Out	4.99E-5	2.90E-5	4.89E-5	3.00E-5	2.94E-5
	[DCB]Out	5.05E-6	5.09E-6	5.96E-6	6.54E-6	4.71E-6
	[Fe^{2+}]Out	-----	-----	-----	-----	-----

Table B.1 (Cont'd)

Exp. No.(1)		Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp.10
INPUT DATA	pH	7.35	2.24	4.13	5.79	6.29
	$[H^+]$	4.47E-8	5.75E-3	7.41E-5	1.62E-6	5.14E-7
	$[OH^-]$	2.24E-7	1.74E-12	1.35E-10	6.17E-9	1.95E-8
	$[O_3]$	1.31E-4	1.26E-4	1.15E-4	1.21E-4	1.18E-4
	$[O_2]$(2)	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB]	1.29E-5	1.17E-5	1.17E-5	1.35E-5	1.39E-5
	$[Fe^{2+}]$	-----	3.42E-5	3.42E-5	3.51E-5	3.32E-5
	H_2CO_3	4.25E-5	4.80E-3	4.77E-3	3.67E-3	2.48E-3
	HCO_3^-	4.57E-3	4.13E-7	3.08E-5	1.13E-3	2.32E-3
	CO_3^{2-}	6.01E-6	4.46E-15	2.44E-11	4.28E-8	2.65E-7
MODEL OUTPUT	$[O_3]$	4.44E-5	8.31E-6	8.25E-6	1.59E-5	1.98E-5
	[DCB]	5.25E-6	7.54E-7	8.54E-7	2.19E-6	3.11E-6
	$[Fe^{2+}]$	-----	3.08E-6	3.16E-6	1.98E-6	1.54E-6
	$[H_2O_2]$	1.90E-6	1.18E-6	1.13E-6	5.70E-7	7.31E-7
	$[HO_2^-]$	8.63E-11	4.13E-16	4.26E-14	8.07E-13	3.12E-12
	$\cdot OH$	4.65E-13	6.04E-12	5.28E-12	1.82E-12	1.11E-12
	$\cdot HO_2$	1.26E-13	1.99E-9	1.64E-11	3.21E-13	1.64E-13
	$\cdot HO_3$	2.34E-13	1.07E-12	9.91E-13	9.03E-13	7.70E-13
	$\cdot HO_4$	1.09E-12	2.64E-12	2.29E-12	1.52E-12	1.16E-12
EXP. RESULT	$[O_3]$Out	3.74E-5	4.86E-5	1.12E-5	1.17E-5	1.56E-5
	[DCB]Out	6.83E-6	1.00E-5	3.22E-6	4.35E-6	4.34E-6
	$[Fe^{2+}]$Out	-----	3.93E-6	8.18E-6	9.36E-6	7.48E-6

Note: (1) The experimental numbers are listed in Table 2.2
(2) The oxygen concentration is an estimated value in this work.

Table B.2 The Input/Output Data of Kinetic Model for Ozone/UV Treatment System

Exp. No.(1)		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
INPUT DATA	pH	5.40	6.1	7.28	5.33	6.01
	$[H^+]$	3.98E-6	7.94E-7	5.25E-8	4.68E-6	9.77E-7
	$[OH^-]$	2.51E-9	1.26E-8	1.91E-7	2.14E-9	1.02E-8
	$[O_3]$	1.26E-4	1.20E-4	1.23E-4	1.26E-4	1.24E-4
	$[O_2]$(2)	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB]	1.42E-5	1.21E-5	1.21E-5	1.33E-5	9.69E-6
	$[Fe^{2+}]$	-----	-----	-----	-----	-----
	H_2CO_3	1.88E-3	1.32E-3	2.12E-4	4.53E-3	3.35E-3
	HCO_3^-	2.21E-4	7.78E-4	1.89E-3	4.65E-4	1.65E-3
	CO_3^{2-}	3.03E-9	5.34E-8	1.96E-6	5.84E-9	9.89E-8
MODEL OUTPUT	$[O_3]$	6.14E-6	5.88E-6	5.78E-6	6.30E-6	6.05E-6
	[DCB]	1.10E-6	1.29E-6	1.82E-6	1.24E-6	1.33E-6
	$[Fe^{2+}]$	-----	-----	-----	-----	-----
	$[H_2O_2]$	1.31E-5	1.20E-5	7.99E-6	1.19E-5	9.76E-6
	$[HO_2^-]$	6.86E-12	3.17E-11	3.17E-10	5.46E-12	2.15E-11
	$\cdot OH$	4.90E-12	3.59E-12	2.13E-12	3.93E-12	2.51E-12
	$\cdot HO_2$	1.71E-12	5.83E-13	2.57E-13	1.98E-12	7.18E-13
	$\cdot HO_3$	5.62E-13	6.20E-13	4.08E-13	5.90E-13	6.97E-13
	$\cdot HO_4$	1.58E-12	1.11E-12	6.48E-13	1.30E-12	8.00E-13
EXP. RESULT	$[O_3]$Out	3.17E-6	1.21E-6	3.69E-6	1.56E-6	1.28E-6
	[DCB]Out	7.60E-7	1.38E-6	1.82E-6	1.34E-6	1.18E-6
	$[Fe^{2+}]$Out	-----	-----	-----	-----	-----

Table B.2 (Cont'd)

Exp. No.(1)		Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp.10
INPUT DATA	pH	7.35	2.24	4.13	5.79	6.29
	$[H^+]$	4.47E-8	5.75E-3	7.41E-5	1.62E-6	5.14E-7
	$[OH^-]$	2.24E-7	1.74E-12	1.35E-10	6.17E-9	1.95E-8
	$[O_3]$	1.31E-4	1.25E-4	1.15E-4	1.21E-4	1.19E-4
	$[O_2]$(2)	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB]	1.29E-5	1.17E-5	1.17E-5	1.35E-5	1.39E-5
	$[Fe^{2+}]$	-----	3.42E-5	3.42E-5	3.51E-5	3.32E-5
	H_2CO_3	4.25E-5	4.80E-3	4.77E-3	3.67E-3	2.48E-3
	HCO_3^-	4.57E-3	4.13E-7	3.08E-5	1.13E-3	2.32E-3
	CO_3^{2-}	6.01E-6	4.46E-15	2.44E-11	4.28E-8	2.65E-7
MODEL OUTPUT	$[O_3]$	6.41E-6	3.35E-6	3.27E-6	4.05E-6	4.06E-6
	[DCB]	2.93E-6	3.70E-7	4.27E-7	1.38E-6	1.92E-6
	$[Fe^{2+}]$	-----	4.12E-6	4.44E-6	5.79E-6	6.03E-6
	$[H_2O_2]$	7.21E-6	1.27E-5	1.14E-5	3.98E-6	2.58E-6
	$[HO_2^-]$	3.44E-10	4.45E-15	4.18E-13	5.62E-12	1.10E-11
	$\cdot OH$	1.11E-12	1.28E-11	1.10E-11	3.32E-12	1.98E-12
	$\cdot HO_2$	2.66E-13	4.46E-9	4.05E-11	1.13E-12	4.94E-13
	$\cdot HO_3$	3.98E-13	8.23E-13	7.86E-13	9.47E-13	8.89E-13
	$\cdot HO_4$	3.76E-13	2.25E-12	1.89E-12	7.07E-13	4.23E-13
EXP. RESULT	$[O_3]$Out	2.14E-6	1.88E-6	3.90E-7	9.90E-7	1.26E-6
	[DCB]Out	2.32E-6	4.27E-6	1.38E-6	2.06E-6	2.69E-6
	$[Fe^{2+}]$Out	-----	6.89E-6	7.14E-6	6.99E-6	6.42E-6

Note: (1) The experimental numbers are listed in Table 2.2.
(2) The oxygen concentration is an estimated value in this work.

Table B.3 The Input/Output Data of Kinetic Model for Ozone/H_2O_2 Treatment System

Exp. No.[1]		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
INPUT DATA	pH	5.40	6.1	7.28	5.33	6.01
	$[H^+]$	3.98E-6	7.94E-7	5.25E-8	4.68E-6	9.77E-7
	$[OH^-]$	2.51E-9	1.26E-8	1.91E-7	2.14E-9	1.02E-8
	$[O_3]$	1.25E-4	1.20E-4	1.22E-4	1.25E-4	1.24E-4
	$[O_2]$[2]	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB]	1.42E-5	1.21E-5	1.21E-5	1.33E-5	9.69E-6
	$[Fe^{2+}]$	-----	-----	-----	-----	-----
	$[H_2O_2]$	6.38E-5	6.23E-5	6.45E-5	6.92E-5	6.35E-5
	H_2CO_3	1.88E-3	1.32E-3	2.12E-4	4.53E-3	3.35E-3
	HCO_3^-	2.21E-4	7.78E-4	1.89E-3	4.65E-4	1.65E-3
	CO_3^{2-}	3.03E-9	5.34E-8	1.96E-6	5.84E-9	9.89E-8
MODEL OUTPUT	$[O_3]$	4.77E-5	2.73E-5	9.17E-6	4.71E-5	2.70E-5
	[DCB]	5.08E-6	2.74E-6	1.54E-6	4.69E-6	2.29E-6
	$[Fe^{2+}]$	-----	-----	-----	-----	-----
	$[H_2O_2]$	6.51E-5	5.07E-5	1.65E-5	6.88E-5	4.65E-5
	$[HO2^-]$	3.42E-11	1.34E-10	6.50E-10	3.16E-11	1.02E-10
	$\cdot OH$	7.79E-13	1.43E-12	2.64E-12	7.91E-13	1.32E-12
	$\cdot HO_2$	3.80E-13	3.27E-13	3.64E-13	4.31E-13	3.87E-13
	$\cdot HO_3$	5.68E-13	7.35E-13	6.47E-13	5.92E-13	8.06E-13
	$\cdot HO_4$	1.95E-12	2.05E-12	1.28E-12	1.96E-12	1.88E-12
EXP. RESULT	$[O_3]$Out	2.85E-5	5.22E-6	7.85E-6	3.95E-6	1.35E-6
	[DCB]Out	1.68E-6	1.19E-6	1.32E-6	1.45E-6	1.05E-6
	$[Fe^{2+}]$Out	-----	-----	-----	-----	-----
	$[H_2O_2]$Out	5.18E-5	3.85E-5	2.95E-5	4.48E-5	2.60E-5

Table B.3 (Cont'd)

Exp. No.[1]		Exp. 6	Exp. 7	Exp. 8	Exp. 9	Exp.10
INPUT DATA	pH	7.35	2.24	4.13	5.79	6.29
	$[H^+]$	4.47E-8	5.75E-3	7.41E-5	1.62E-6	5.14E-7
	$[OH^-]$	2.24E-7	1.74E-12	1.35E-10	6.17E-9	1.95E-8
	$[O_3]$	1.29E-4	1.23E-4	1.16E-4	1.19E-4	1.20E-4
	$[O_2]$	2.00E-4	2.00E-4	2.00E-4	2.00E-4	2.00E-4
	[DCB][2]	1.29E-5	1.17E-5	1.17E-5	1.35E-5	1.39E-5
	$[Fe^{2+}]$	-----	3.42E-5	3.42E-5	3.51E-5	3.32E-5
	$[H_2O_2]$	7.28E-5	6.25E-5	5.90E-5	6.66E-5	6.34E-5
	H_2CO_3	4.25E-5	4.80E-3	4.77E-3	3.67E-3	2.48E-3
	HCO_3^-	4.57E-3	4.13E-7	3.08E-5	1.13E-3	2.32E-3
	CO_3^{2-}	6.01E-6	4.46E-15	2.44E-11	4.28E-8	2.65E-7
MODEL OUTPUT	$[O_3]$	1.17E-5	7.71E-6	6.89E-6	6.07E-6	5.97E-6
	[DCB]	2.50E-6	6.65E-7	6.61E-7	1.19E-6	1.69E-6
	$[Fe^{2+}]$	-----	2.64E-6	2.87E-6	3.67E-6	3.93E-6
	$[H_2O_2]$	1.17E-5	4.96E-5	4.48E-5	2.68E-5	1.45E-5
	$[HO2^-]$	5.56E-10	1.74E-14	1.62E-12	3.80E-11	6.20E-11
	$\cdot OH$	1.45E-12	6.90E-12	6.94E-12	4.21E-12	2.78E-12
	$\cdot HO_2$	3.75E-13	2.54E-9	2.68E-11	1.37E-12	7.28E-13
	$\cdot HO_3$	6.29E-13	1.11E-12	1.08E-12	1.33E-12	1.33E-12
	$\cdot HO_4$	8.92E-13	2.80E-12	2.52E-12	1.35E-12	8.74E-13
EXP. RESULT	$[O_3]$Out	4.96E-6	1.42E-5	1.18E-6	2.72E-6	2.43E-6
	[DCB]Out	1.48E-6	7.69E-6	1.91E-6	1.76E-6	2.00E-6
	$[Fe^{2+}]$Out	-----	6.63E-6	8.93E-6	8.87E-6	7.80E-6
	$[H_2O_2]$Out	3.72E-5	2.03E-5	1.45E-5	3.66E-5	3.80E-5

Note: (1) The experimental numbers are listed in Table 2.2
(2) The oxygen concentration is an estimated value in this work.

APPENDIX C

Ozone, DCB, H_2O_2, and Fe^{2+} Sampling Summary for Each Experiment

EXP. 1 (1/2)

1) pH = 5.40

2) [HCO3-] = 0.0021 mole/L

3) Pump Flowrate :

Ozone =	12.301	mL/min.
DCB =	12.340	mL/min.
NaOH =	0.000	mL/min.
NaHCO3 =	0.628	mL/min.
H2O2 =	0.106	mL/min.

4) Hydraulic Retention Time = 9.89 min (w/o H2O2) 9.85 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw	Reactor	Wt. 1	Wt. 2	Initial	Final	Ozone Concentration (uM)				k'	Sk'
	Abs.	uM	(g)*	(g)**	Abs.	Abs.	Data	ub-Ave	Ave.	95%CI	min.-1	min.-1
1	0	**0.00**	---	---	---	---	#REF!	#REF!	**#REF!**	**#REF!**	**#REF!**	**#REF!**
						---	#REF!					
						---	#REF!					
				---	---	---	#REF!	#REF!				
						---	#REF!					
						---	#REF!					
			---	---	---	---	#REF!	#REF!				
						---	#REF!					
						---	#REF!					
2 O3	0.152	**123.32**	205.11	230.56	1.003	0.563	49.39	49.39	**49.93**	**2.37**	**0.149**	**0.009**
						0.563	49.39					
						0.563	49.39					
			202.84	226.69	1.003	0.588	49.44	49.36				
						0.589	49.21					
						0.588	49.44					
			205.15	229.59	1.003	0.572	50.89	51.03				
						0.571	51.10					
						0.571	51.10					
3 O3/ UV	0.155	**125.76**	206.00	230.54	1.003	0.789	3.54	3.54	**3.71**	**0.57**	**3.323**	**0.509**
						0.789	3.54					
						0.789	3.54					
			204.94	230.37	1.003	0.783	3.48	3.62				
						0.782	3.69					
						0.782	3.69					
			201.44	226.96	1.003	0.780	3.97	3.97				
						0.780	3.97					
						0.780	3.97					
4 O3/ H2O2	0.155	**125.23**	205.85	230.36	1.005	0.679	27.79	27.79	**28.45**	**1.42**	**0.346**	**0.018**
						0.679	27.79					
						0.679	27.79					
			201.97	225.80	1.005	0.682	28.90	28.83				
						0.682	28.90					
						0.683	28.68					
			203.03	227.85	1.005	0.671	28.73	28.73				
						0.671	28.73					
						0.671	28.73					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 1 (2/2)

DCB Standard Calibration Curve

Std. (uM)	DCB area	TCB area	Useful Sample	D/T
0.00	0	11267	1	**0.00**
1.70	8346	15034	1	**0.56**
3.40	21096	20245	1	**1.04**
5.10	23500	14374	1	**1.63**
6.80	32501	15377	1	**2.11**
10.20	42487	12747	1	**3.33**
13.61	87182	22575	1	**3.86**
20.41	60927	8527	1	**7.15**
27.21	123555	14138	1	**8.74**

Calibration Curve : Y = **0.05** + **3.11** X

r = 0.9999

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	51008	10897	5	4.6809	14.58	**14.23**	**0.98**	**0.000**	**#DIV/0!**
	41773	8941		4.6721	14.56				
	48325	10122		4.7743	14.87				
	73637	17833		4.1293	12.87				
	61111	13339		4.5814	14.28				
2	14701	8275	5	1.7766	5.56	**5.05**	**0.51**	**0.184**	**0.029**
O3	28731	19640		1.4629	4.59				
	25292	15909		1.5898	4.98				
	16950	9872		1.7170	5.38				
	27122	17903		1.5149	4.75				
3	4059	19100	5	0.2125	0.71	**0.76**	**0.04**	**1.782**	**0.161**
O3/	1870	7845		0.2384	0.79				
	2456	10345		0.2374	0.78				
	1233	5266		0.2341	0.77				
	2326	9989		0.2329	0.77				
4	5990	10641	5	0.5629	1.79	**1.68**	**0.16**	**0.759**	**0.094**
O3/	6395	11419		0.5600	1.79				
H2O2	8488	15793		0.5375	1.72				
	8545	17112		0.4994	1.60				
	8853	18954		0.4671	1.50				

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.088	0.087	0.090	0.088	0.09	0.089	0.0030
10	0.134	0.136	0.137	0.132	0.14	0.135	0.0024
25	0.217	0.228	0.227	0.221	0.22	0.223	0.0057
50	0.391	0.390	0.383	0.385	0.39	0.387	0.0042
75	0.538	0.541	0.540	0.544	0.54	0.540	0.0031
100	0.706	0.703	0.690	0.692	0.70	0.697	0.0087

Calibration Curve Y = **-12.62** + **162.06** X

r = 0.9996

where: "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM(raw)	uMinitial	Ave.	95% C.I	Abs.	uM	Ave.	95% C.I.	(min.-1)	min.-1
4	0.610	15250	63.70	**63.75**	**0.07**	0.396	51.56	**51.76**	**0.26**	**0.024**	**0.001**
	0.610	15250	63.70			0.397	51.72				
	0.611	15275	63.81			0.396	51.56				
	0.610	15250	63.70			0.398	51.88				
	0.611	15275	63.81			0.399	52.05				

EXP. 2 (1/2)

1) pH = 6.30

2) [HCO3-] = 0.0021 mole/L

3) Pump Flowrate :

Ozone =	12.301	mL/min.
DCB =	12.340	mL/min.
NaOH =	0.278	mL/min.
NaHCO3 =	0.628	mL/min.
H2O2 =	0.106	mL/min.

4) Hydraulic Retention Time 9.79 min (w/o H2O2) 9.75 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw	Reactor	Wt. 1	Wt. 2	Initial	Final	Ozone Concentration (mg/L)				k'	Sk'
	Abs.	uM	(g)*	(g)**	Abs.	Abs.	Data	ub-Ave	Ave.	95%C.I	min.-1	min.-1
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.149	**119.57**	205.33	231.58	1.008	0.658	28.43	28.56	**28.98**	**1.98**	**0.319**	**0.023**
						0.657	28.63					
						0.657	28.63					
			201.41	227.13	1.008	0.664	28.47	28.47				
						0.664	28.47					
						0.664	28.47					
			201.83	228.03	1.008	0.651	29.97	29.90				
						0.652	29.76					
						0.651	29.97					
3 O3/ UV	0.15	**120.38**	204.94	231.38	1.008	0.791	1.25	1.25	**1.21**	**0.26**	**10.057**	**2.195**
						0.791	1.25					
						0.791	1.25					
			202.86	230.56	1.008	0.784	1.03	1.09				
						0.783	1.22					
						0.784	1.03					
			204.65	230.50	1.008	0.795	1.22	1.29				
						0.794	1.43					
						0.795	1.22					
4 O3/ H2O2	0.15	**119.88**	205.58	231.57	1.008	0.774	5.33	5.26	**5.22**	**0.87**	**2.255**	**0.376**
						0.774	5.33					
						0.775	5.13					
			201.25	227.29	1.008	0.776	4.85	4.85				
						0.776	4.85					
						0.776	4.85					
			206.01	232.22	1.008	0.772	5.41	5.54				
						0.771	5.61					
						0.771	5.61					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 2 (2/2)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T
0.00	0	17893	1	**0.00**
1.70	5820	11005	1	**0.53**
3.40	8616	7396	1	**1.16**
5.10	15989	9654	1	**1.66**
6.80	20813	9783	1	**2.13**
10.20	35810	11577	1	**3.09**
13.61	51539	12900	1	**4.00**
20.41	61804	9111	1	**6.78**
27.21	72679	7842	1	**9.27**
34.01	118614	11133	1	**10.65**

Calibration Curve : Y = **0.11** + **3.15** X

r = 0.9987

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	Ave. uM	95% C.I.	k' (min-1)	Sk' 95% C.I.
1	33689	8339	4	4.04	12.85	**12.14**	**0.79**	**0.000**	**#DIV/0!**
	37205	9802		3.80	12.08				
	44590	11915		3.74	11.91				
	29938	7075		4.23	13.46				
	44866	12198		3.68	11.71				
2	17379	11121	4	1.56	5.04	**5.09**	**0.29**	**0.142**	**0.019**
O3	17510	11346		1.54	4.98				
	19555	12674		1.54	4.98				
	15316	9216		1.66	5.35				
	9064	4645		1.95	6.27				
3	3319	7983	4	0.42	1.42	**1.38**	**0.07**	**0.795**	**0.071**
O3/	3044	7685		0.40	1.36				
UV	4593	11886		0.39	1.33				
	3953	9584		0.41	1.41				
	2647	5819		0.45	1.55				
4	2055	5462	4	0.38	1.30	**1.19**	**0.07**	**0.943**	**0.088**
O3/	3165	9326		0.34	1.18				
H2O2	2688	7570		0.36	1.23				
	3089	8855		0.35	1.21				
	3397	10500		0.32	1.13				

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Average	95% C.I.
0	0.081	0.080	0.076	0.078	0.077	0.078	0.0026
10	0.121	0.124	0.127	0.123	0.122	0.123	0.0029
25	0.211	0.214	0.213	0.216	0.216	0.214	0.0026
50	0.366	0.366	0.361	0.369	0.366	0.366	0.0036
75	0.495	0.506	0.501	0.502	0.505	0.502	0.0054
100	0.664	0.662	0.667	0.666	0.664	0.665	0.0024

Calibration Curve Y = **-11.87** + **170.05** X

r = 0.9995

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM(raw)	uMinitial	Ave.	95% C.I	Abs.	uM	Ave.	95% C.I.	(min.-1)	min.-1
4	0.603	15075	62.29	**62.29**	**0.00**	0.296	38.46	**38.53**	**0.12**	**0.063**	**0.000**
	0.603	15075	62.29			0.297	38.63				
	0.603	15075	62.29			0.296	38.46				
	0.603	15075	62.29			0.296	38.46				
	0.603	15075	62.29			0.297	38.63				

EXP. 3 (1/2)

1) pH = 7.28

2) [HCO3-] = 0.0021 mole/L

3) Pump Flowrate :

Ozone	=	12.301	mL/min.
DCB	=	12.340	mL/min.
NaOH	=	0.000	mL/min.
NaHCO3	=	0.628	mL/min.
H2O2	=	0.106	mL/min.

4) Hydraulic Retention Time 9.89 min (w/o H2O2) 9.85 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

Exp.	INFLUENT		EFFLUENT								k'	Sk'
	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				min.-1	min.-1
							Data	ub-Ave	Ave.	95%C.I		
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.152	**123.32**	203.04	228.26	1.002	0.566	49.35	49.35	**48.86**	**1.48**	**0.154**	**0.006**
						0.566	49.35					
						0.566	49.35					
			205.25	230.89	1.002	0.565	48.20	48.20				
						0.565	48.20					
						0.565	48.20					
			202.02	227.40	1.002	0.565	49.04	49.04				
						0.565	49.04					
						0.565	49.04					
3 O3/ UV	0.152	**123.32**	202.62	228.48	1.002	0.778	3.72	3.86	**3.69**	**0.37**	**3.277**	**0.333**
						0.777	3.93					
						0.777	3.93					
			204.85	232.11	1.002	0.769	3.58	3.58				
						0.769	3.58					
						0.769	3.58					
			201.30	228.38	1.002	0.770	3.63	3.63				
						0.770	3.63					
						0.770	3.63					
4 O3/ H2O2	0.151	**122.00**	205.80	231.06	1.001	0.762	7.81	7.81	**7.85**	**0.31**	**1.477**	**0.059**
						0.762	7.81					
						0.762	7.81					
			205.85	231.60	1.001	0.757	8.05	7.99				
						0.758	7.85					
						0.757	8.05					
			204.85	230.71	1.001	0.757	7.88	7.74				
						0.758	7.67					
						0.758	7.67					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 3 (2/2)

DCB Standard Calibration Curve

Standar uM	DCB area	TCB area	Useful Sample	D/T
0.00	0	9472	1	**0.00**
1.70	8635	17378	1	**0.50**
3.40	13614	12474	1	**1.09**
5.10	24199	16064	1	**1.51**
6.80	36109	18639	1	**1.94**
10.20	43313	13553	1	**3.20**
13.61	72171	18610	1	**3.88**
20.41	89436	13914	1	**6.43**
27.21	131137	16019	1	**8.19**
34.01	149296	13933	1	**10.72**

Calibration Curve : Y = **0.25** + **3.20** X
r = 0.9990
where : X is the DCB/TCB ratio
Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Average uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	72324	20067	4	3.60	11.80	**12.09**	**0.69**	**0.000**	**#DIV/0!**
	73233	20530		3.57	11.68				
	55144	13544		4.07	13.30				
	65701	17527		3.75	12.26				
	59308	15355		3.86	12.63				
2	31805	20660	4	1.54	5.18	**5.96**	**0.23**	**0.104**	**0.013**
O3	22859	12463		1.83	6.13				
	26563	15369		1.73	5.79				
	23703	13379		1.77	5.93				
	20823	11569		1.80	6.02				
3	8980	19392	4	0.46	1.73	**1.82**	**0.12**	**0.571**	**0.055**
O3/	8223	17267		0.48	1.78				
UV	7187	14032		0.51	1.89				
	6035	10893		0.55	2.02				
	8227	16209		0.51	1.88				
4	5765	20193	4	0.29	1.16	**1.32**	**0.12**	**0.828**	**0.095**
O3/	3687	10782		0.34	1.35				
H2O2	5742	19233		0.30	1.21				
	3123	8854		0.35	1.38				
	4270	12417		0.34	1.35				

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Average	95% C.I.
0	0.075	0.072	0.072	0.075	0.073	0.073	0.0019
10	0.121	0.116	0.119	0.117	0.116	0.118	0.0027
25	0.213	0.205	0.210	0.205	0.212	0.209	0.0047
50	0.366	0.358	0.369	0.370	0.364	0.365	0.0059
75	0.512	0.514	0.502	0.502	0.504	0.507	0.0072
100	0.678	0.672	0.677	0.677	0.673	0.675	0.0034

Calibration Curve Y = **-10.33** + **165.32** X
r = 0.9994
where ; "X" is the UV absorption at 551 nm
"Y" is the concentration of H2O2 in uM
"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uMraw	uMinitial	Ave.	95% C.I	Abs.	uM	Ave.	95% C.I.	(min.-1)	min.-1
4	0.616	15400	64.33	**64.46**	**0.14**	0.242	29.67	**29.54**	**0.47**	**0.120**	**0.003**
	0.617	15425	64.44			0.238	29.01				
	0.617	15425	64.44			0.244	30.00				
	0.617	15425	64.44			0.240	29.34				
	0.619	15475	64.64			0.242	29.67				

EXP. 4 (1/2)

1) **pH = 5.40**

2) **[HCO3-] =** 0.0048 mole/L

3) **Pump Flowrate :**

Ozone =	12.301	mL/min.
DCB =	12.340	mL/min.
NaOH =	0.930	mL/min.
Fe(II) =	0.000	mL/min.
H2O2 =	0.106	mL/min.

4) **Hydraulic Retention Time** 9.78 min (w/o H2O2) 9.74 min (w/ H2O2)

5) **Volume of The Reactor =** 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				k' min.-1	Sk' min.-1
							Data	ub-Ave	Ave.	95%C.I		
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.156	**125.07**	205.44	234.71	0.995	0.607	29.54	29.48	**29.95**	**1.63**	**0.325**	**0.019**
						0.608	29.36					
						0.607	29.54					
			202.70	228.74	0.995	0.639	30.70	30.70				
						0.639	30.70					
						0.639	30.70					
			201.93	235.82	0.995	0.554	29.66	29.66				
						0.554	29.66					
						0.554	29.66					
3 O3/ UV	0.157	**125.88**	205.99	231.75	1.001	0.790	1.23	1.37	**1.56**	**0.48**	**8.152**	**2.502**
						0.789	1.44					
						0.789	1.44					
			201.29	227.22	1.001	0.787	1.62	1.75				
						0.786	1.82					
						0.786	1.82					
			201.71	227.38	1.001	0.789	1.56	1.56				
						0.789	1.56					
						0.789	1.56					
4 O3/ H2O2	0.157	**125.36**	204.98	232.82	0.999	0.760	4.09	3.90	**3.95**	**0.10**	**3.157**	**0.081**
						0.762	3.71					
						0.761	3.90					
			205.48	231.11	0.999	0.776	3.98	3.98				
						0.776	3.98					
						0.776	3.98					
			202.18	227.82	0.999	0.776	3.97	3.97				
						0.776	3.97					
						0.776	3.97					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 4 (2/2)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T
0.00	0	17893	1	**0.00**
1.70	10003	18741	1	**0.53**
3.40	22472	21128	1	**1.06**
5.10	40035	28396	1	**1.41**
6.80	52713	27065	1	**1.95**
10.20	58537	19443	1	**3.01**
13.61	100476	25627	1	**3.92**
20.41	159937	27187	1	**5.88**
27.21	209662	26864	1	**7.80**
34.01	263387	27164	1	**9.70**

Calibration Curve : Y = **-0.12** + **3.51** X

r = 0.9999

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	91354	23201	4	3.9375	13.68	**13.30**	**0.45**	**0.000**	**#DIV/0!**
	91234	23796		3.8340	13.32				
	85706	20571		4.1664	14.49				
	100834	26926		3.7449	13.01				
	103242	27196		3.7962	13.19				
2	50801	26011	5	1.9531	6.73	**6.54**	**0.28**	**0.106**	**0.010**
O3	53864	28185		1.9111	6.58				
	52372	28590		1.8318	6.30				
	43194	21906		1.9718	6.79				
	51340	27984		1.8346	6.31				
3	10870	25737	4	0.4223	1.36	**1.34**	**0.08**	**0.910**	**0.063**
O3/	10007	22929		0.4364	1.41				
UV	8724	19670		0.4435	1.43				
	9883	24329		0.4062	1.30				
	10850	26479		0.4098	1.31				
4	10084	22286	4	0.4525	1.46	**1.45**	**0.15**	**0.839**	**0.094**
O3/	11662	27299		0.4272	1.37				
H2O2	12188	28339		0.4301	1.38				
	5070	9157		0.5537	1.82				
	8908	18318		0.4863	1.58				

H2O2 Calibration Curve

Std. uM	Measruements						
	test 1	test 2	test 3	test 4	test 5	Average	95% C.I.
0	0.067	0.063	0.062	0.062	0.060	0.063	0.0032
10	0.109	0.108	0.107	0.104	0.104	0.106	0.0029
25	0.178	0.185	0.181	0.182	0.181	0.181	0.0031
50	0.312	0.308	0.312	0.312	0.308	0.310	0.0027
75	0.434	0.433	0.437	0.428	0.430	0.432	0.0044
100	0.570	0.564	0.567	0.568	0.567	0.567	0.0027

Calibration Curve Y = **-11.43** + **197.87** X

r = 0.9998

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM(raw)	uMinitial	Average	95% C.I	Abs.	uM	Average	95% C.I.	(min.-1)	min.-1
4	0.669	16725	69.04	**69.17**	**0.11**	0.281	44.17	**44.84**	**0.51**	**0.056**	**0.001**
	0.670	16750	69.15			0.285	44.96				
	0.671	16775	69.25			0.286	45.16				
	0.671	16775	69.25			0.284	44.76				
	0.670	16750	69.15			0.286	45.16				

EXP. 5 (1/2)

1) pH = 6.01

2) $[HCO_3^-]$ = 0.0048 mole/L

3) Pump Flowrate :

Ozone = 12.301 mL/min.
DCB = 12.340 mL/min.
NaOH = 1.205 mL/min.
Fe(II) = 0.000 mL/min.
H_2O_2 = 0.106 mL/min.

4) Hydraulic Retention Time 9.67 min (w/o H_2O_2) 9.63 min (w/ H_2O_2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

Exp.	INFLUENT		EFFLUENT								k'	Sk'
	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				min.-1	min.-1
							Data	ub-Ave	Ave.	5% C.I		
1	0	**0.00**	---	---	---	---	#####	#####	**#####**	**#####**	**#####**	**#####**
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O_3	0.154	**122.16**	201.58	227.56	1.000	0.655	28.39	28.46	**29.37**	**2.30**	**0.327**	**0.027**
						0.654	28.59					
						0.655	28.39					
			205.88	232.08	1.000	0.648	29.29	29.36				
						0.648	29.29					
						0.647	29.49					
			205.69	231.75	1.000	0.644	30.44	30.31				
						0.645	30.24					
						0.645	30.24					
3 O_3/ UV	0.156	**123.74**	201.62	228.77	1.000	0.780	1.27	1.27	**1.28**	**0.20**	**9.869**	**1.513**
						0.780	1.27					
						0.780	1.27					
			206.26	232.37	1.000	0.787	1.21	1.21				
						0.787	1.21					
						0.787	1.21					
			203.32	230.08	1.000	0.782	1.37	1.37				
						0.782	1.37					
						0.782	1.37					
4 O_3/ H_2O_2	0.157	**124.03**	204.79	228.36	1.000	0.803	1.41	1.41	**1.35**	**0.47**	**9.434**	**3.310**
						0.803	1.41					
						0.803	1.41					
			202.19	224.33	1.000	0.814	1.14	1.14				
						0.814	1.14					
						0.814	1.14					
			204.87	229.81	1.000	0.793	1.57	1.50				
						0.793	1.57					
						0.794	1.36					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 5 (2/2)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T
0.00	0	17893	1	**0.00**
1.70	---	---	1	**missing**
3.40	14836	14693	1	**1.01**
5.10	15700	8850	1	**1.77**
6.80	26215	12038	1	**2.18**
10.20	31022	8667	1	**3.58**
13.61	58176	14441	1	**4.03**
20.41	85994	12984	1	**6.62**
27.21	113841	13533	1	**8.41**
34.01	131858	11917	1	**11.06**

Calibration Curve : Y = **-0.01** + **3.13** X

r = 0.9984

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	Ave. uM	95% C.I.	k' (min-1)	Sk' 95% C.I.
1	-	-	4	######	#####	**9.69**	**0.33**	**0.000**	**#DIV/0!**
	44265	14541		3.0442	9.50				
	44448	13941		3.1883	9.95				
	45373	14826		3.0604	9.55				
	43567	13951		3.1229	9.75				
2	18946	12359	5	1.5330	4.78	**4.71**	**0.16**	**0.109**	**0.009**
O3	19138	12477		1.5339	4.78				
	18631	12708		1.4661	4.57				
	19661	13411		1.4660	4.57				
	17609	11325		1.5549	4.85				
3	5350	14067	5	0.3803	1.18	**1.18**	**0.02**	**0.746**	**0.032**
O3/	5208	13700		0.3801	1.18				
UV	5095	13522		0.3768	1.17				
	4684	11976		0.3911	1.21				
	5125	13567		0.3778	1.17				
4	4700	14181	4	0.3314	1.02	**1.05**	**0.03**	**0.858**	**0.042**
O3/	4760	13743		0.3464	1.07				
H2O2	4461	13072		0.3413	1.05				
	4692	15053		0.3117	0.96				
	4081	12176		0.3352	1.04				

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Average	95% C.I.
0	0.082	0.079	0.083	0.079	0.079	0.080	0.0024
10	0.130	0.135	0.128	0.137	0.129	0.132	0.0049
25	0.221	0.222	0.227	0.219	0.226	0.223	0.0042
50	0.379	0.375	0.370	0.376	0.375	0.375	0.0040
75	0.518	0.513	0.509	0.516	0.516	0.514	0.0044
100	0.668	0.674	0.678	0.667	0.679	0.673	0.0069

Calibration Curve Y = **-12.79** + **168.56** X

r = 0.9998

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM(raw)	uMinitial	Ave.	95% C.I	Abs.	uM	Ave.	95% C.I.	min.-1	min.-1
4	0.622	15550	63.51	**63.51**	**0.00**	0.227	25.47	**26.01**	**0.58**	**0.150**	**0.004**
	0.622	15550	63.51			0.229	25.81				
	0.622	15550	63.51			0.229	25.81				
	0.622	15550	63.51			0.232	26.31				
	0.622	15550	63.51			0.234	26.65				

EXP. 6 (1/2)

1) pH = 7.35

2) $[HCO_3^-]$ = 0.0050 mole/L

3) Pump Flowrate :

Ozone = 12.301 mL/min.
DCB = 12.340 mL/min.
NaOH = 0.000 mL/min.
Fe(II) = 0.000 mL/min.
H_2O_2 = 0.106 mL/min.

4) Hydraulic Retention Time 10.15 min (w/o H_2O_2) 10.10 min (w/ H_2O_2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

Exp.	INFLUENT		EFFLUENT								k'	Sk'
							Ozone Concentration (uM)					
	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Data	ub-Ave	Ave.	5% C.I	min.-1	min.-1
5	0	**0.00**	---	---	---	---	#####	#####	**#####**	**#####**	**#####**	**#####**
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O_3	0.157	**130.63**	202.28	227.22	0.993	0.614	38.52	38.52	**37.41**	**2.52**	**0.246**	**0.018**
						0.614	38.52					
						0.614	38.52					
			204.54	229.41	0.993	0.621	37.23	37.16				
						0.622	37.02					
						0.621	37.23					
			205.19	230.13	0.993	0.623	36.61	36.53				
						0.624	36.39					
						0.623	36.61					
3 O_3/UV	0.157	**130.63**	205.63	230.36	0.992	0.786	2.00	1.93	**2.14**	**0.45**	**5.913**	**1.256**
						0.787	1.79					
						0.786	2.00					
			201.28	225.97	0.993	0.786	2.23	2.23				
						0.786	2.23					
						0.786	2.23					
			204.93	229.63	0.992	0.785	2.26	2.26				
						0.785	2.26					
						0.785	2.26					
4 O_3/H_2O_2	0.156	**129.24**	204.77	229.63	0.992	0.771	5.02	5.02	**4.96**	**0.23**	**2.479**	**0.115**
						0.771	5.02					
						0.771	5.02					
			204.99	230.04	0.992	0.769	5.15	5.01				
						0.770	4.94					
						0.770	4.94					
			205.84	230.99	0.992	0.769	5.00	4.86				
						0.770	4.79					
						0.770	4.79					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 6 (2/2)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T
0.00	0	15334794	1	0.0000
3.40	14082330	16798820	1	0.8383
6.80	26115856	15395904	1	1.6963
13.61	52705164	15122005	1	3.4853
20.41	65246984	12855284	1	5.0755
27.21	108918464	16399562	1	6.6415

Calibration Curve :

Y = -0.12 + 4.07 X

r = 0.9997

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	Ave. uM	95% C.I.	k' (min-1)	Sk' 95% C.I.
5	42310060	13319260	3	3.1766	12.80	**12.88**	**1.62**	**0.000**	**#DIV/0!**
	35035196	10408399		3.3661	13.57				
	32171084	9067013		3.5481	14.31				
	50737080	16653456		3.0466	12.27				
	26554630	7467993		3.5558	14.34				
2 O3	25871216	7000310	3	3.6957	14.91	**6.83**	**1.58**	**0.087**	**0.038**
	7794684	3598859		2.1659	8.69				
	18995326	10096146		1.8814	7.53				
	25777322	16350205		1.5766	6.29				
	22220724	13320606		1.6681	6.66				
3 O3/ UV	9278464	16309450	5	0.5689	2.19	**2.32**	**0.19**	**0.449**	**0.079**
	8017264	12561038		0.6383	2.47				
	9193751	15429505		0.5959	2.30				
	8865530	15819229		0.5604	2.16				
	6791351	10600781		0.6406	2.48				
4 O3/ H2O2	5895520	16516268	4	0.3570	1.33	**1.48**	**0.33**	**0.765**	**0.203**
	4811330	10282525		0.4679	1.78				
	6521023	16987228		0.3839	1.44				
	6082735	16640806		0.3655	1.36				
	3091237	103559		29.8500	121.34				

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.068	0.067	0.071	0.066	0.063	0.067	0.0036
10	0.115	0.113	0.114	0.110	0.113	0.113	0.0023
25	0.193	0.198	0.194	0.196	0.202	0.197	0.0044
50	0.329	0.328	0.339	0.337	0.340	0.335	0.0071
75	0.477	0.484	0.483	0.481	0.484	0.482	0.0037
100	0.620	0.615	0.624	0.608	0.612	0.616	0.0079

Calibration Curve Y = **-10.94** + **180.02** X

r = 0.9998

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM(raw)	uMinitial	Ave.	95% C.I	Abs.	uM	Ave.	95% C.I.	(min.-1)	min.-1
4	0.677	16925	72.50	**72.77**	**0.28**	0.174	20.39	**19.16**	**1.02**	**0.277**	**0.016**
	0.682	17050	73.03			0.162	18.23				
	0.680	17000	72.82			0.166	18.95				
	0.678	16950	72.60			0.169	19.49				
	0.681	17025	72.92			0.165	18.77				

EXP. 7 (1/3)

1) pH = 2.24

2) [HCO3-] = 0.0048 mole/L

3) Pump Flowrate :
Ozone = 12.301 mL/min.
DCB = 12.340 mL/min.
NaOH = 0.000 mL/min.
Fe(II) = 0.984 mL/min.
H2O2 = 0.106 mL/min.

4) Hydraulic Retention Time 9.76 min (w/o H2O2) 9.72 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				k' min.-1	Sk' min.-1
							Data	ub-Ave	Ave.	95%C.I		
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.158	**126.41**	205.51	230.57	1.037	0.601	48.40	48.33	**48.55**	**0.91**	**0.164**	**0.004**
						0.602	48.18					
						0.601	48.40					
			205.64	230.55	1.037	0.601	48.90	48.97				
						0.601	48.90					
						0.600	49.11					
			202.47	234.66	1.037	0.491	48.45	48.34				
						0.492	48.29					
						0.492	48.29					
3 O3/ UV	0.156	**124.81**	201.69	227.52	1.030	0.810	1.76	1.76	**1.88**	**0.29**	**6.710**	**1.027**
						0.810	1.76					
						0.810	1.76					
			205.86	231.43	1.030	0.811	1.92	1.99				
						0.811	1.92					
						0.810	2.13					
			202.39	228.43	1.030	0.808	1.88	1.88				
						0.808	1.88					
						0.808	1.88					
4 O3/ H2O2	0.154	**122.70**	201.09	226.89	1.039	0.758	13.99	13.99	**14.16**	**0.39**	**0.789**	**0.022**
						0.758	13.99					
						0.758	13.99					
			201.77	227.84	1.039	0.754	14.30	14.30				
						0.754	14.30					
						0.754	14.30					
			201.75	228.71	1.039	0.747	14.07	14.20				
						0.746	14.27					
						0.746	14.27					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 7 (2/3)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T	Ave. (ppb)
0.00	0	10994926	1		0.0000
0.68	2709133	15521120	3	0.1745	0.1703
	2822517	16987612		0.1662	
	2745956	16142584		0.1701	
1.70	6871543	16668120	3	0.4123	0.4096
	6875499	16747235		0.4105	
	6690765	16485668		0.4059	
3.40	13057246	15762961	3	0.8283	0.8130
	13367006	16621329		0.8042	
	12637938	15671754		0.8064	
5.10	19683484	16073414	3	1.2246	1.2240
	18523668	15070709		1.2291	
	19661632	16137345		1.2184	
6.80	21615140	14528687	3	1.4878	1.4871
	22855978	15308210		1.4931	
	24313048	16422267		1.4805	
13.61	51689228	15674178	3	3.2977	3.2538
	51457456	15652338		3.2875	
	52288980	16463539		3.1760	

Calibration Curv Y = **0.03** + **4.22** X

r = 0.9989

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	46948456	18051014	5	2.6009	11.01	**11.66**	**1.00**	**0.000**	**#DIV/0!**
	44086540	17263168		2.5538	10.81				
	42161780	15532214		2.7145	11.49				
	33547360	11236201		2.9856	12.63				
	34653944	11895535		2.9132	12.33				
2	29283926	11315878	5	2.5879	10.96	**10.01**	**0.67**	**0.017**	**0.012**
O3	41260608	18137916		2.2748	9.63				
	37601592	16059582		2.3414	9.92				
	42656588	18578544		2.2960	9.72				
	41933352	18087354		2.3184	9.82				
3	12474441	12833113	3	0.9721	4.14	**4.27**	**0.35**	**0.177**	**0.029**
O3/	11479692	11060421		1.0379	4.41				
UV	12059614	12036641		1.0019	4.26				
	9628823	9117885		1.0560	4.49				
	10364590	9726083		1.0656	4.53				
4	25355524	13672650	3	1.8545	7.86	**7.69**	**0.41**	**0.053**	**0.015**
O3/	29374664	16242061		1.8086	7.67				
H2O2	19809200	9844410		2.0122	8.53				
	18282672	8838788		2.0685	8.76				
	32074568	18055012		1.7765	7.53				

EXP. 7 (3/3)

Effluent Fe(II)

Exp.	Sample	Measured with 10 cm cell				Fe(II) conc. (uM)			k'	Sk'
	No.	Absorbance			Ave.	Effluent	Ave.	95% C.I.	(min-1)	(min-1)
1	1	1.9736	1.9745	1.9704	1.9728	34.02	**34.21**	**0.40**	**0.000**	**#DIV/0!**
	2	1.9936	1.9895	1.9846	1.9892	34.31				
	3	1.9879	1.9879	1.9902	1.9887	34.30				
2	1	0.2215	0.2212	0.2216	0.2215	3.71	**3.93**	**1.11**	**0.789**	**0.225**
O3	2	0.2192	0.2175	0.2156	0.2174	3.64				
	3	0.2636	0.2645	0.2637	0.2640	4.45				
3	1	0.4024	0.4018	0.4017	0.4020	6.83	**6.89**	**0.15**	**0.406**	**0.011**
O3/UV	2	0.4108	0.4079	0.4081	0.4089	6.96				
	3	0.4045	0.4051	0.4066	0.4054	6.89				
4	1	0.3888	0.3900	0.3906	0.3898	6.62	**6.63**	**0.03**	**0.428**	**0.007**
O3/H2O2	2	0.3910	0.3900	0.3891	0.3900	6.63				
	3	0.3907	0.3911	0.3918	0.3912	6.65				

Calibration Curve : Y = -6.88 + 969.27 X

r = 0.9998

"X" is the value of Absorbance

"Y" is the Fe(II) concentration (ppb)

"r" is the correlation coefficient

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.072	0.074	0.065	0.068	0.067	0.069	0.0046
10	0.100	0.099	0.111	0.098	0.119	0.105	0.0115
25	0.177	0.164	0.165	0.165	0.173	0.169	0.0073
50	0.287	0.300	0.287	0.303	0.293	0.294	0.0091
75	0.417	0.429	0.427	0.421	0.427	0.424	0.0062
100	0.544	0.554	0.547	0.542	0.551	0.548	0.0061

Calibration Curve : Y = **-11.81** + **205.62** X

r = 0.9991

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM (raw)	M (initial	Ave.	95% C.I.	Abs.	uM	Ave.	95% C.I.	(min.-1	(min.-1)
4	0.606	15150	62.41	**62.51**	**0.13**	0.149	18.82	**20.26**	**1.65**	**0.215**	**0.019**
	0.608	15200	62.62			0.165	22.11				
	0.608	15200	62.62			0.152	19.44				
	0.607	15175	62.51			0.160	21.08				
	0.606	15150	62.41			0.154	19.85				

EXP. 8 (1/3)

1) pH = 4.52

2) $[HCO_3^-]$ = 0.0045 mole/L

3) Pump Flowrate :

Ozone = 12.301 mL/min.
DCB = 12.340 mL/min.
NaOH = 1.529 mL/min.
Fe(II) = 0.984 mL/min.
H_2O_2 = 0.106 mL/min.

4) Hydraulic Retention Time 9.21 min (w/o H_2O_2) 9.17 min (w/ H_2O_2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				k' min.-1	Sk' min.-1
							Data	ub-Ave	Ave.	95%C.I		
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O_3	0.152	**114.76**	205.56	232.94	1.038	0.757	11.24	11.11	**11.15**	**0.52**	**1.010**	**0.048**
						0.758	11.04					
						0.758	11.04					
			200.95	228.46	1.038	0.757	11.02	10.96				
						0.758	10.83					
						0.757	11.02					
			204.89	232.07	1.038	0.758	11.37	11.37				
						0.758	11.37					
						0.758	11.37					
3 O_3/ UV	0.153	**115.52**	205.11	230.80	1.038	0.824	0.38	0.38	**0.39**	**0.03**	**32.351**	**2.716**
						0.824	0.38					
						0.824	0.38					
			204.07	232.90	1.038	0.804	0.32	0.38				
						0.803	0.50					
						0.804	0.32					
			201.97	228.86	1.038	0.816	0.40	0.40				
						0.816	0.40					
						0.816	0.40					
4 O_3/ H_2O_2	0.154	**115.82**	200.93	228.36	1.039	0.810	1.04	1.04	**1.18**	**0.33**	**10.565**	**2.938**
						0.810	1.04					
						0.810	1.04					
			202.59	230.18	1.039	0.808	1.22	1.22				
						0.808	1.22					
						0.808	1.22					
			202.94	230.12	1.039	0.811	1.16	1.29				
						0.810	1.36					
						0.810	1.36					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 8 (2/3)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T	Ave.
0.00	0	10994926	1		0.0000
0.68	2709133	15521120	3	0.1745	0.1703
	2822517	16987612		0.1662	
	2745956	16142584		0.1701	
1.70	6871543	16668120	3	0.4123	0.4096
	6875499	16747235		0.4105	
	6690765	16485668		0.4059	
3.40	13057246	15762961	3	0.8283	0.8130
	13367006	16621329		0.8042	
	12637938	15671754		0.8064	
5.10	19683484	16073414	3	1.2246	1.2240
	18523668	15070709		1.2291	
	19661632	16137345		1.2184	
6.80	21615140	14528687	3	1.4878	1.4871
	22855978	15308210		1.4931	
	24313048	16422267		1.4805	
13.61	51689228	15674178	3	3.2977	3.2538
	51457456	15652338		3.2875	
	52288980	16463539		3.1760	

Calibrat Y = **0.03** + **4.22** X

r = 0.9989

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	46948456	18051014	5	2.6009	11.01	**11.66**	**1.00**	**0.000**	**#DIV/0!**
	44086540	17263168		2.5538	10.81				
	42161780	15532214		2.7145	11.49				
	33547360	11236201		2.9856	12.63				
	34653944	11895535		2.9132	12.33				
2	10695460	14018641	3	0.7629	3.25	**3.22**	**0.50**	**0.284**	**0.058**
O3	8598244	10757099		0.7993	3.41				
	12720079	18039950		0.7051	3.01				
	6632140	8077623		0.8211	3.50				
	6355219	7226741		0.8794	3.75				
3	3203340	9532392	3	0.3360	1.45	**1.38**	**0.17**	**0.808**	**0.128**
O3/	4496051	14806956		0.3036	1.32				
UV	2885068	8505703		0.3392	1.47				
	3107331	8633446		0.3599	1.55				
	4323156	13636830		0.3170	1.37				
4	6938908	16113692	4	0.4306	1.85	**1.91**	**0.16**	**0.555**	**0.075**
O3/	6798474	15514129		0.4382	1.88				
H2O2	4986220	10354560		0.4815	2.07				
	6581630	15290490		0.4304	1.85				
	3991012	7607872		0.5246	2.25				

EXP. 8 (3/3)

Effluent Fe(II)

Exp.	Sample Number	Measured with 10 cm cell				Fe(II) conc. (uM)			k'	Sk'
		Absorbance			Ave.	Effluent	Ave.	95% C.I.	(min-1)	(min-1)
1	1	1.9736	1.9745	1.9704	1.9728	34.02	**34.21**	**0.40**	**0.000**	**#DIV/0!**
	2	1.9936	1.9895	1.9846	1.9892	34.31				
	3	1.9879	1.9879	1.9902	1.9887	34.30				
2	1	0.4858	0.4836	0.4832	0.4842	8.26	**8.18**	**0.17**	**0.346**	**0.009**
O3	2	0.4771	0.4769	0.4768	0.4769	8.13				
	3	0.4779	0.4786	0.4768	0.4778	8.15				
3	1	0.4227	0.4210	0.4195	0.4211	7.17	**7.14**	**0.05**	**0.411**	**0.007**
O3/UV	2	0.4196	0.4198	0.4201	0.4199	7.14				
	3	0.4184	0.4187	0.4188	0.4186	7.12				
4	1	0.5221	0.5213	0.5208	0.5214	8.90	**8.89**	**0.11**	**0.310**	**0.006**
O3/H2O2	2	0.5181	0.5179	0.5183	0.5181	8.84				
	3	0.5230	0.5233	0.5234	0.5232	8.93				

Calibration Curve : Y = -6.88 + 969.27 X
r = 0.9998
"X" is the value of Absorbance
"Y" is the Fe(II) concentration (ppb)
"r" is the correlation coefficient

H2O2 Calibration Curve

Std. uM	Measruements						
	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.072	0.074	0.065	0.068	0.067	0.069	0.0046
10	0.100	0.099	0.111	0.098	0.119	0.105	0.0115
25	0.177	0.164	0.165	0.165	0.173	0.169	0.0073
50	0.287	0.300	0.287	0.303	0.293	0.294	0.0091
75	0.417	0.429	0.427	0.421	0.427	0.424	0.0062
100	0.544	0.554	0.547	0.542	0.551	0.548	0.0061

Calibration Curve : Y = **-11.81** + **205.62** X
r = 0.9991
where ; "X" is the UV absorption at 551 nm
"Y" is the concentration of H2O2 in uM
"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM (raw)	M (initial	Ave.	95% C.I.	Abs.	uM	Ave.	95% C.I.	(min.-1	(min.-1)
4	0.606	15150	58.91	**59.01**	**0.12**	0.129	14.71	**14.51**	**0.68**	**0.335**	**0.016**
	0.608	15200	59.10			0.125	13.89				
	0.608	15200	59.10			0.127	14.30				
	0.607	15175	59.01			0.127	14.30				
	0.606	15150	58.91			0.132	15.33				

EXP. 9 (1/3)

1) pH = 5.79

2) [HCO3-] = 0.0047 mole/L

3) Pump Flowrate :

Ozone =	12.301	mL/min.
DCB =	12.340	mL/min.
NaOH =	0.890	mL/min.
Fe(II) =	0.990	mL/min.
H2O2 =	0.106	mL/min.

4) Hydraulic Retention Time 9.43 min (w/o H2O2) 9.39 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

	INFLUENT		EFFLUENT									
Exp.	Raw	Reactor	Wt. 1	Wt. 2	Initial	Final	Ozone Concentration (uM)				k'	Sk'
	Abs.	uM	(g)*	(g)**	Abs.	Abs.	Data	ub-Ave	Ave.	95%C.I	min.-1	min.-1
1	0	0.00	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.157	121.37	204.47	231.17	0.999	0.729	11.84	11.84	11.67	0.36	0.997	0.031
						0.729	11.84					
						0.729	11.84					
			205.05	231.89	0.999	0.729	11.60	11.60				
						0.729	11.60					
						0.729	11.60					
			202.48	229.50	0.999	0.727	11.70	11.57				
						0.728	11.50					
						0.728	11.50					
3 O3/ UV	0.156	120.59	202.01	228.69	0.999	0.784	0.92	0.85	0.99	0.31	12.763	3.990
						0.784	0.92					
						0.785	0.72					
			205.14	232.18	0.999	0.781	1.05	1.05				
						0.781	1.05					
						0.781	1.05					
			205.58	232.29	0.999	0.783	1.08	1.08				
						0.783	1.08					
						0.783	1.08					
4 O3/ H2O2	0.155	119.34	201.35	228.65	0.997	0.769	2.76	2.76	2.72	0.13	4.566	0.224
						0.769	2.76					
						0.769	2.76					
			205.20	231.98	0.997	0.773	2.66	2.66				
						0.773	2.66					
						0.773	2.66					
			202.45	229.27	0.997	0.772	2.80	2.74				
						0.773	2.61					
						0.772	2.80					

Note : * weight of beaker only
** weight of beaker + indigo blue

EXP. 9 (2/3)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T	**Ave. (ppb)**
0.00	0	9551421	1		0.0000
3.40	10036036	11407443	2	0.8798	0.8650
	8895539	9228770		0.9639	
	14282330	16798820		0.8502	
6.80	13173816	6448658	2	2.0429	1.7416
	20498668	11226094		1.8260	
	25515856	15395904		1.6573	
13.61	20705164	5122005	3	4.0424	4.0592
	21243764	4984935		4.2616	
	27279174	7042437		3.8735	
20.41	50480372	9043517	3	5.5819	5.5102
	48600912	8567202		5.6729	
	62546984	11855284		5.2759	
27.21	102418464	16399562	2	6.2452	6.7071
	32029644	4050721		7.9071	
	77318960	10785319		7.1689	

Calibration Curv Y = **-0.12** + **4.07** X

r = 1.0000

where : X is the DCB/TCB ratio

Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	41524576	12620246	3	3.2903	13.267	**13.48**	**0.54**	**0.000**	**#DIV/0!**
	39617216	11660055		3.3977	13.704				
	43614064	630162		69.2109	281.6				
	19532540	5073315		3.8501	15.545				
	44010712	13177716		3.3398	13.469				
2 O3	10319936	9593831	3	1.0757	4.26	**4.35**	**0.19**	**0.223**	**0.017**
	7386303	6291530		1.1740	4.66				
	8777255	7897060		1.1115	4.40				
	8022378	6932605		1.1572	4.59				
	7939163	7182796		1.1053	4.38				
3 O3/ UV	5105688	8798553	3	0.5803	2.24	**2.06**	**0.17**	**0.589**	**0.057**
	6212633	11551221		0.5378	2.07				
	7108574	13740457		0.5173	1.99				
	3974543	6777215		0.5865	2.27				
	5974654	10849108		0.5507	2.12				
4 O3/ H2O2	5978974	12990972	3	0.4602	1.75	**1.76**	**0.07**	**0.710**	**0.044**
	5820559	12788305		0.4551	1.73				
	4056563	8031797		0.5051	1.94				
	4164827	8251756		0.5047	1.93				
	4827953	10288323		0.4693	1.79				

EXP. 9 (3/3)

Effluent Fe(II)

Exp.	Sample	Measured with 10 cm cell				Fe(II) conc. (uM)			k'	Sk'
	Number	Absorbance			Ave.	Effluent	Ave.	95% C.I.	(min-1)	(min-1)
1	1	2.0349	2.0216	2.0247	2.0270	34.96	**35.06**	**0.22**	**0.000**	**#DIV/0!**
	2	2.0359	2.0349	2.0324	2.0344	35.09				
	3	2.0351	2.0383	2.0376	2.0370	35.13				
2	1	0.5436	0.5432	0.5414	0.5427	9.27	**9.36**	**0.77**	**0.292**	**0.026**
O3	2	0.5328	0.5331	0.5322	0.5327	9.10				
	3	0.5664	0.5677	0.5680	0.5674	9.70				
3	1	0.4193	0.4203	0.4211	0.4202	7.15	**6.99**	**0.41**	**0.426**	**0.026**
O3/UV	2	0.4111	0.4123	0.4111	0.4115	7.00				
	3	0.3980	0.4010	0.4050	0.4013	6.82				
4	1	0.5133	0.5146	0.5145	0.5142	8.78	**8.87**	**0.32**	**0.315**	**0.012**
O3/H2O2	2	0.5155	0.5159	0.5161	0.5158	8.81				
	3	0.5279	0.5276	0.5285	0.5280	9.02				

Calibration Curve : Y = -6.88 + 969.27 X

r = 0.9998

"X" is the value of Absorbance

"Y" is the Fe(II) concentration (ppb)

"r" is the correlation coefficient

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.067	0.066	0.067	0.066	0.064	0.066	0.0015
10	0.122	0.116	0.121	0.119	0.120	0.120	0.0029
25	0.194	0.195	0.204	0.198	0.199	0.198	0.0049
50	0.324	0.321	0.325	0.324	0.323	0.323	0.0019
75	0.451	0.450	0.460	0.453	0.454	0.454	0.0049
100	0.593	0.595	0.596	0.595	0.594	0.595	0.0014

Calibration Curve : Y = -12.47 + **190.77** X

r = 0.9998

where ; "X" is the UV absorption at 551 nm

"Y" is the concentration of H2O2 in uM

"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM (raw)	M (initial	Ave.	95% C.I.	Abs.	uM	Ave.	95% C.I.	(min.-1	(min.-1)
4	0.669	16725	66.58	**66.64**	**0.07**	0.251	35.41	**36.59**	**1.09**	**0.087**	**0.004**
	0.670	16750	66.68			0.263	37.70				
	0.670	16750	66.68			0.257	36.55				
	0.669	16725	66.58			0.255	36.17				
	0.670	16750	66.68			0.260	37.13				

EXP. 10 (1/3)

1) pH = 6.29

2) [HCO3-] = 0.0046 mole/L

3) Pump Flowrate :
Ozone = 12.301 mL/min.
DCB = 12.340 mL/min.
NaOH = 1.153 mL/min.
Fe(II) = 0.984 mL/min.
H2O2 = 0.106 mL/min.

4) Hydraulic Retention Time 9.34 min (w/o H2O2) 9.30 min (w/ H2O2)

5) Volume of The Reactor = 250 mL

Ozone Concentration

Exp.	INFLUENT		EFFLUENT								k'	Sk'
	Raw Abs.	Reactor uM	Wt. 1 (g)*	Wt. 2 (g)**	Initial Abs.	Final Abs.	Ozone Concentration (uM)				min.-1	min.-1
							Data	ub-Ave	Ave.	95%C.I		
1	0	**0.00**	---	---	---	---	#####	#####	#####	#####	#####	#####
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
			---	---	---	---	#####	#####				
						---	#####					
						---	#####					
2 O3	0.154	**117.90**	206.19	232.75	1.004	0.716	15.47	15.47	**15.64**	**0.66**	**0.700**	**0.030**
						0.716	15.47					
						0.716	15.47					
			205.16	232.18	1.004	0.709	16.02	15.95				
						0.709	16.02					
						0.710	15.82					
			202.54	230.06	1.004	0.707	15.51	15.51				
						0.707	15.51					
						0.707	15.51					
3 O3/ UV	0.156	**119.44**	205.03	232.32	1.001	0.782	0.86	0.99	**1.26**	**0.64**	**10.082**	**5.146**
						0.781	1.05					
						0.781	1.05					
			201.30	228.08	1.001	0.782	1.50	1.50				
						0.782	1.50					
						0.782	1.50					
			204.26	231.21	1.001	0.782	1.28	1.28				
						0.782	1.28					
						0.782	1.28					
4 O3/ H2O2	0.157	**119.73**	205.53	232.50	1.002	0.777	2.40	2.40	**2.43**	**0.35**	**5.197**	**0.745**
						0.777	2.40					
						0.777	2.40					
			205.24	232.28	1.002	0.777	2.31	2.31				
						0.777	2.31					
						0.777	2.31					
			205.14	232.72	1.002	0.772	2.58	2.58				
						0.772	2.58					
						0.772	2.58					

Note : * weight of beaker only
** weight of beaker + indigo blue
*** Ozone concentration in experiments 1 & 6 are zero.

EXP. 10 (2/3)

DCB Standard Calibration Curve

Std. uM	DCB area	TCB area	Useful Sample	D/T	Ave.
0.00	0	10994926	1		0.0000
0.68	2709133	15521120	3	0.1745	0.1703
	2822517	16987612		0.1662	
	2745956	16142584		0.1701	
1.70	6871543	16668120	3	0.4123	0.4096
	6875499	16747235		0.4105	
	6690765	16485668		0.4059	
3.40	13057246	15762961	3	0.8283	0.8130
	13367006	16621329		0.8042	
	12637938	15671754		0.8064	
5.10	19683484	16073414	3	1.2246	1.2240
	18523668	15070709		1.2291	
	19661632	16137345		1.2184	
6.80	21615140	14528687	3	1.4878	1.4871
	22855978	15308210		1.4931	
	24313048	16422267		1.4805	
13.61	51689228	15674178	3	3.2977	3.2538
	51457456	15652338		3.2875	
	52288980	16463539		3.1760	

Calibration Curv Y = **0.03** + **4.22** X
r = 0.9989
where : X is the DCB/TCB ratio
Y is the DCB concentration (ppb)

Effluent DCB concentration

Exp. No.	DCB area	TCB area	Useful Sample	D/T	DCB uM	**Ave. uM**	**95% C.I.**	**k' (min-1)**	**Sk' 95% C.I.**
1	42656516	14153676	4	3.0138	12.75	**13.94**	**2.06**	**0.000**	**#DIV/0!**
	18558520	5249862		3.5350	14.95				
	19319944	5392414		3.5828	15.15				
	33437948	10963676		3.0499	12.91				
	37823840	756961		49.9680	210.91				
2 O3	7123910	14034804	4	0.5076	2.18	**4.34**	**0.83**	**0.237**	**0.071**
	8548897	7130518		1.1989	5.09				
	12037572	12035801		1.0001	4.26				
	13621071	14772329		0.9221	3.93				
	13190443	13739242		0.9601	4.09				
3 O3/ UV	4790381	7464607	4	0.6417	2.74	**2.69**	**0.16**	**0.449**	**0.086**
	12867412	15317227		0.8401	3.58				
	7449666	11821526		0.6302	2.69				
	6262754	10545058		0.5939	2.54				
	4713175	7264267		0.6488	2.77				
4 O3/ H2O2	3121084	6379119	5	0.4893	2.10	**2.00**	**0.17**	**0.643**	**0.124**
	4522149	10953430		0.4129	1.78				
	3844538	8085955		0.4755	2.04				
	3919295	8608885		0.4553	1.96				
	3241634	6595005		0.4915	2.11				

EXP. 10 (3/3)

Effluent Fe(II)

Exp.	Sample Number	Measured with 10 cm cell				Fe(II) conc. (ppb)			k'	Sk'
		Absorbance			Ave.	Effluent	Ave.	95% C.I.	(min-1)	(min-1)
1	1	1.9287	1.9218	1.9204	1.9236	33.17	**33.19**	**0.06**	**0.000**	**#DIV/0!**
	2	1.9253	1.9243	1.9290	1.9262	33.22				
	3	1.9233	1.9272	1.9209	1.9238	33.17				
2 O3	1	0.4352	0.4336	0.4322	0.4337	7.38	**7.48**	**0.40**	**0.368**	**0.021**
	2	0.4514	0.4498	0.4495	0.4502	7.67				
	3	0.4350	0.4342	0.4336	0.4342	7.39				
3 O3/UV	1	0.3789	0.3788	0.3788	0.3788	6.43	**6.42**	**0.05**	**0.447**	**0.004**
	2	0.3770	0.3765	0.3763	0.3766	6.40				
	3	0.3764	0.3797	0.3796	0.3786	6.43				
4 O3/H2O2	1	0.4509	0.4520	0.4527	0.4518	7.70	**7.80**	**0.34**	**0.350**	**0.016**
	2	0.4681	0.4663	0.4649	0.4665	7.95				
	3	0.4541	0.4546	0.4544	0.4544	7.74				

Calibration Curve : Y = -6.88 + 969.27 X
r = 0.9998
"X" is the value of Absorbance
"Y" is the Fe(II) concentration (ppb)
"r" is the correlation coefficient

H2O2 Calibration Curve

Std.	Measruements						
uM	test 1	test 2	test 3	test 4	test 5	Ave.	95% C.I.
0	0.064	0.069	0.063	0.066	0.063	0.065	0.0032
10	0.104	0.102	0.099	0.095	0.099	0.100	0.0043
25	0.177	0.178	0.177	0.173	0.177	0.176	0.0024
50	0.313	0.312	0.318	0.315	0.313	0.314	0.0030
75	0.451	0.447	0.448	0.459	0.448	0.451	0.0061
100	0.587	0.583	0.588	0.585	0.582	0.585	0.0032

Calibration Curve : Y = **-9.85** + **188.69** X
r = 0.9993
where ; "X" is the UV absorption at 551 nm
"Y" is the concentration of H2O2 in uM
"r" is the correlation coefficient

H2O2 Sample

Exp.	Influent					Effluent				k'	Sk'
	Abs.	uM (raw)	M (initial	Average	95% C.I.	Abs.	uM	Average	95% C.I.	(min.-1	(min.-1)
4	0.643	16075	63.38	**63.42**	**0.07**	0.260	39.21	**38.04**	**0.90**	**0.072**	**0.003**
	0.644	16100	63.48			0.255	38.27				
	0.643	16075	63.38			0.251	37.52				
	0.643	16075	63.38			0.251	37.52				
	0.644	16100	63.48			0.252	37.70				