10-31-1992

Catalytic ozone/ultraviolet light oxidation of organics in water : integrated charcoal/ozonation/UV radiation

Dawei Wang
New Jersey Institute of Technology

Recommended Citation

Wang, Dawei, "Catalytic ozone/ultraviolet light oxidation of organics in water : integrated charcoal/ozonation/UV radiation" (1992). *Theses*. 2384.
https://digitalcommons.njit.edu/theses/2384

ABSTRACT
Catalytic Ozone/Ultraviolet light Oxidation Of Organics In Water: Integrated Charcoal/Ozonation/UV Radiation

By
Dawei Wang

A novel heterogeneous catalytic-oxidation technology where activated carbon is used as a catalyst-adsorbent, ozone serves as the oxidant and UV light as activation agent, is developed in a lab scale study. We demonstrate this process for destruction of recalcitrant organics in water i.e: combined oxidation by ozone, UV light plus activated carbon. The investigation includes evalution of various operating conditions: ozone levels, activated carbon levels; time for complete destruction of the individual target pollutants, plus evalution of activity of the continuously recativated carbon surface in-situ. All experiments were performed at room temperature in a semi-batch reactor. Seven representative chemicals was used as target pollutants: Phenol, N,N-dimethyl Formamide, O-cresol, Aniline, Pyridine, Trichloroethlene, Dioxane.

The experiments indicate that activated carbon may function as effective catalyst besides being an adsorbent. This new process can achieve more complete and rapid oxidation to recalcitrant compounds when compared to either photocatalytic-ozonation or adsorption operations as seperate treatment processes. It is observed that in adsorption only experiment, 8% of phenol removal was obtained after 10.5 min, while photolytic-ozonation process decomposed 50% of the phenol in this time. However, in the new process, 66% of phenol removal was obtained. we also found that carbon adsorption capacities were significantly increased and activity regenerated by continuously activating the carbon with UV light and in-situ reaction.

Rate constants, characteristic constants of carbon uptake test for this C/O3/UV process compared to O3/UV process are:

Table 1: Rate constants

Compound	Rate Ratio*
Aniline	1.17
Pyridine	1.80
N,N-dimethyl Formamide	1.98
O-cresol	1.63
Trichloroethylene	1.50
Dioxane	1.38
Phenol	1.50

* Ratio of rate for this process to photolytic ozonation (no carbon present)

Table 2: Characteristic constants of carbon Uptake Test

For equation: $q(mg/mg)=K_f*Ce^{(1/n)}$
(1): C/O3/UV process:

$Kf=10^{(-7.03)}$; $n=0.519$.
(2): Carbon only process:

$Kf=10^{(-20.03)}$; $n=0.169$.
(Phenol as Adsorbate)

We also describe and characterize on increased rate of ozone mass transfer from the gas to the liquid phase with the UV/carbon present.

CATALYTIC OZONE/ULTRAVIOLET LIGHT OXIDATION OF ORGANICS IN WATER: INTEGRATED CHARCOAL/OZONATION/UV RADIATION

by
Dawei Wang

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science
Department of Civil and Environmental Engineering
October 1992

APPROVAL PAGE

Catalytic Ozone/Ultraviolet Light Oxidation Of Organics In Water: Integrated Charcoal/Ozonation/UV Radiation

By
Dawei Wang

MAY 11 \ 1992

Dr. Joseph W. Bozzelli, Thesis Advisor
Professor of Chemical Engineering, Chemistry, and
Environmental Science Department, NJIT

May 11/1992

Dr. John W. Liskowitz, Committee Member
Professor of Civil and Environmental Engineering
Department, NJIT

May 11, 1992

Dr. Su Ling Cheng, Committee Member
Professor of Civil and Environmental Engineering
Department, NJIT

BIOGRAPHICAL SKETCH

Author: Dawei Wang

Degree: Master of Engineering in Environmental Engineering

Date: October, 1992

Date of Birth:

Place of Birth:

Undergraduate and Graduate Education:

- Master of Engineering in Environmental Engineering, New Jersey Institute of Technology, Newark, NJ, 1992
- Master of Engineering in Environmental Engineering, TongJi University, Shanghai, P.R. China, 1990
- Bachelor of Engineering in Water Supply and Discharge Engineering, Construction Engineering Branch of TongJi University, Shanghai, P.R. China, 1984

Major: Environmental Engineering

Publications:

Wang, Dawei. "A Study On The High Strengthen Gourmet-Powder Process Wastewater Using An Anoxic-Aerobic Two-Phase Submerged Biological Filters." Master Thesis, TongJi University, Shanghai, P.R. China, 1990.

ACKNOWLEDGMENT

I wish to express my sincere thanks to Dr. Joseph W. Bozzelli for his valuable guidance and encouragement throughout the course of the thesis. I am specially indebted to him for his insightful and constructive criticisms at every stage of this thesis. This thesis would never have been completed if it were not for his assistance.

Also, I sincerely thank Dr. Gutli. and Mr. Yu Gi for the timely help and suggestions involving in my thesis.

In addition, I would like to express my appreciation to my wife for her support and large amount of time spent on the thesis preparation. Last but not the least I would like to thank all those who have helped me in one way or the other during the entire course of this thesis.

TABLE OF CONTENTS

PAGE

LIST OF FIGURES

LIST OF TABLE

CHAPTER 1
INTRODUCTION

Toxic and hazardous organic compounds are often present in industrial discharges and water supplies. Due to the continuous industrialization, more and more rivers, lakes and seas are being contaminated by industrial discharges. The potential health effects and other adverse environmental implications of toxic and carcinogenic organic pollutants has made the removal of these materials from the contaminated potable water supplies a major focus of environmental concern and regulations. The need for cleaning and decontaminating industrial discharging streams to lower levels has become extremely important especially in the industrial nations. This is because these waters are used for drinking or run off into other waters that affect our environment.

In general, many toxic and hazardous organic compounds belong to the class of recalitrant compounds. The basic processes that can be implemented for treatment of hazardous compounds involve: 1). Detoxification. 2). Volume reduction. 3). Isolation of the material from environment. With respect to water purification, commonly accepted approachs by federal, state and local water pollution abatement and control agencies include: 1). Physical Treatment; 2). Chemical Treatment; 3) Biological Treatment; 4) Thermal Treatment; 5). Fixation/encapsulation.

Physical Treatment: such as activated carbon absorption only alters the hazardous constitutents to a more convenient form for further processing or disposal. It does not convert the pollutants to harmless products. Biological treatment suffers from limitations such as large required land area, limited operating temperature, poor or no mobility of the treatment unit, long biological reaction times, and the presence of organic constitutents that are not biodegrable in water matrices which are not easily treated. Further processing and disposal of the treatment sludge requires careful planning, otherwise potential releases of adsorbed constitutents will occur due to bioadsorption. Thermal treatment, examples are incineration and wet air oxidation, is suitable for streams with higher concentrations of organic compounds. Here the organics are used as an energy source for the proceses. Fixation/Encapsulation must be taken a tempory solution because there is the uncertainy about it's long-term effectiveness and there are concerns about eventual biodegradation products or leaching of hazardous constitutents into groundwater. Comparatively, chemical oxidative processes have long been recognized as an effective and practical means to treat toxic and hazardous organics in wastewater, especially for recalcitrant pollutants. This method can usually completely destroy (mineralize) the organic pollutant,i.e. convert it to CO_2 and H_2O. Mineralization, does not require long reaction times, and has high efficiencies. For each of the above process classes there is a range of conditions for which the process is most suitable (28-29). The rules to the engineer for selecting these treatment methods are only relative at present and research is needed to further quantitate and define the optimun operation stages.

CHAPTER 2
LITERATURE SURVEY

Ozonation technology has received a significant amount of attention for destruction and/conversion of organic and inorganic compounds in aqueous phase during the past decade (8-11). Due to its high oxidation potential (-2.07v) which is secondary only to fluorine among the commercially available molecular oxidizing agents as shown in table 2, ozonation is now being used as an attractive reagent in the destruction of organic contaminants in both hazardous waste and potable water treatment systems (3).

Aqueous phase ozone reaction chemistry is complex. Dissolved ozone may react along two major pathways: ether directly with dissolved solutes or by spontaneous decomposition resulting in secondary oxidants (34). Oxidation products found in water after application of ozone include decomposition products of ozone itself and oxidation products from the organic materials present. The former products consists of oxygen (O_2), the ozonide radical anion (O_3^-), superoxide ion ($O2^-$), perhydroxyl radical (HO_2^-) and hydroxyl free radical (OH). In addition, hydrogen peroxide is produced in small quantities by decomposition of ozone in water (via combination of OH radical), or as by-product of ozone oxidation of dissolved organic materials (3,4).

Although ozone's high oxidation potential makes ozonation thermodynamically favorable, the reaction proceeds only if the kinetics are also favorable. Researchers have indicated that the direct reactions of ozone are highly selective and the ozonation of organic solutes often are kinetically limited while the overall reaction is exothermic or thermodynamically spontaneous; This implies that the initiation reaction is endothermic or rate limiting (5). In order to accelerate oxidation reactions, catalysts are sometimes added to ozonation systems. Catalysts added to ozonation processes enhance ozone's decomposition into more highly reactive radical oxidants which react more rapidly with organic solutes along alternative pathways (30).

Recently, ozonation technology has been improved by addition of various promoters such as peroxide or ultraviolet light, resulting in process collectively called Advanced Oxidation Process (AOP) (31).

Activated carbon has been reported to catalyze oxidation reactions at its surface (32-33). Surface catalysis provides an alternative pathway for oxidation reactions to proceed and has been found to increase the rate of reaction (31). Weber and Corapaoglu (1981) reported that molecular oxygen was capable of efficiently oxidizing cyanides which had been adsorbed onto activated carbon.

Among the general treatment methods commonly used, both ozonation and carbon adsorption have been utilized for the treatment of hazardous compounds seperately, but associated costs, inefficient treatment (incomplete oxidation), and post treatment requirements (spent carbons need to be regenerated) have limited use of these technologies (31-33).

A new heterogeneous catalytic-oxidation technology Integrated Adsorption Oxidation (IAO) has been developed and studied in this laboratory recently (30). This is also a new AOP process which combines activated carbon (catalysts) with ozone in a single reactor to enhance the oxidation reaction rate. The bench-scale feasibility studies indicate that half of the compounds tested were destroyed twice as fast by IAO as by direct ozonation. Process economics indicate an 18% savings in capital costs for this improved reaction system (31). For the ozonation of Acetamide and Dimethl Formamide, adding activated carbon significantly accelerated their oxidations: Acetamide by a factor of 1.68 and of Dimethl Formamide by a factor of 1.59 (30). Our experiments show that IAO is an effective treatment.

CHAPTER 3
OBJECTIVE

The objective is to describe an investigation of a new IAO process which combines O3/UV and activated carbon for the treatment of recalcitrant organic in water.

The scope of this study is to investigate on a lab scale the application of this novel heterogeneous catalytic-oxidation technology for destruction of several recalcitrant organic pollutants in water. Specifically we collect kinetic data on activated carbon catalyzed O3/UV oxidation of organic contaminants in aqueous solution, evaluate destruction removal efficiencies, verify the the existance of a catalytic effect for destruction of several target compounds, and evaluate increased adsorption capacities effected by this combined oxidation process. A preliminary mathematic model for the process will also be illustrated. This study is the preparation to further engineering application and scale up for commercial units. A Pilot-scale reactor will also be described.

CHAPTER 4
EXPERIMEMTAL SECTION

4.1 Materials

Target Compounds: The following seven compounds are used as target pollutants throughout this work:

Component	Formula	Concentration	Source	Purity
Phenol	C6H5OH	1000mg/l	FisherSci.	Co. 92%
N,N-dimethyl Formamide	HCON(CH3)2	2000mg/l	Aldrich Co.	99%
Pyridine	C5H5N	1000mg/l	Aldrich Co.	99%
Aniline	C6H5NH2	1000mg/l	Aldrich Co.	99%
Trichloro-ethlene	CHCLCCL2	2000mg/l	Aldrich Co.	98%
O-cresol	CH3C6H4OH	2000mg/l	Fluka	Co. 99%
Dioxane	C4H8O2	2000mg/l	Fluka	Co. 98%

FisherSci. Co: 52 Faden Road, Springfield, NJ 07081.

Aldrich Co: 1001 West Saint Paul Avenue, Milwaukee, MI53233.

Fluka: 980 South Scand Street, Ronkonkoma, NY 11779.

The concentration of target compounds for this study depends on the specific solubility and reactivity of each compound.

Indigo reagent for determination of ozone concentration in water: The stock solutions of indigo reagent were prepared by dissolving 0.6 g/l (1mM) potassium indigo trisulfonate (purchased from Fluka Co.) in 20 mM phosphoric acid (17).

Activated carbon: Powdered activated carbon (PAC, mesh No. 50 to 200 (84%), large than 50 mesh (2%), less than 200 mesh (14%) by weight) was used as both a catalyst and adsorbant in the experiments dealing with the seven compounds. Granular activated carbon (GAC, mesh No. 10 to 30 (80%), No. 30 to 50 (20%) by weight) was only used in the investigation for activated carbon equilibrium studies and catalyzing oxidation reaction on the carbon surface. The detailed quantities of PAC utilized are listed in table 4, and 7.

Ozone: Comes from the ozone generator (Model T-23, Welsbach Systems Corporation, Philadelphia, PA. Now serviced by Polymetrics, Inc.,200 Rittenhouse Circle #2 west Bristol, PA 19007).

Water: Distilled water was used as a solvent for each target compound.

4.2 Experimental System and Instrumentation:

4.2.1 Charcoal/Ozone/UV Reaction System:

A schematic diagram of the reaction system is shown in Figure 1. The reactor used in this study is a cylinder glass jar, fitted with three ports at the top and one port at the bottom near the vertical axis. It has a liquid holdup volume of 1000 mililiters and is semi-batch type (H:D=15:4). Ozone gas is introduced into the reactor from the bottom through a stainless steel sparger of medium porousness (Alltech Hastalog C Mobile Phase Filters, with 1/8" tubing, pore size of 2 microns. 2051 Wankegan Road, Deerfield, Illinos). Excess ozone gas exits from a top port of the reactor to an exhaust hood via a vent line. No mechanical agitators are used in the reactor. Complete mixing is achieved by bubbling the gas up through the reactor plus use of a recycle pump. A sampling port is located at the recycle in flow line at the bottom. Activated carbon (powdered activated carbon) is put into reactor from the top port. Stainless steel fittings and PTFE (Teflon) tubling are used for all connections.

The UV lamp is installed in a central cylinder section of the reactor along the vertical axis. It is an immersion type high pressure mercury vapor lamp. It emits principally at 2537A, and is rated at 20W. In this system, the UV lamp is encased in two concentric wells made of quartz, these immersion wells provide a cooling jacket around the lamp. We do not measure the UV light intensity but the manufacturer's specification on the lamp are included.

Ozone is produced using an ozone generator. It is a water cooled, corona discharge type. The ozone-oxygen mixture gas could be varied between 0 to 8% ozone output, fitted with a flowrate of gas effluent from 0.015 to 0.16 SCFM. Operation of the ozone generator is straightforward and required no maintainene during the period of use as long as water cooling is turned on. Feed gas is pure oxygen pressure for this study. Output ozone concentratiuons into reactor dissolved in water were determined by Indigo method (17).

4.2.2 Instrumentation

4.2.2.1 Gas Chromatograph:

Analysis of liquid samples organics in water were collected directly from reactor into a vial, quenched, the O3 was then analyzed is by a Perkin-Elmer 910 Gas Chromatograph equipped with a Flame Ionization Detector (FID). Hydrogen is used as its flame source (30ml/min), With excess air at 300 ml/min flow as oxidant. Carried gas nitrogen (30ml/min), flows through the analytical separation column and then to the detector to carry the vaporized sample from injection port. A soap-film (bubble meter) is usually used to calibrate gas flowrates for the GC.

A packed column, 2 meters in length, 1/8" O.D.stainless column is used isothermally to achieve the necessary reactant and product separation. Columns are packed in this lab and chosen according to the adsorption characteristic of the target compounds. Details are summarized in Table 3.

4.2.2.2 Syringe:

A Hamilton* Syringe(Model 701, capacity 0-10ul, Fisher Scientific Co.) is used to collect samples and put them into GC for testing the concentration of all target compounds. A plastic syringe (3cc Syringe. Bection Dickinson Co., Rutherford, NJ) with a membrane mounted filter is used to seperate carbon from the solution containing carbon (see below).

4.2.2.3 Syringe Holder:

In our experiment, we adopted a Fisherbrand 304 stainless syringe holder (13mm) (Fisher Scientific Co.) to filter or clarify small carbon particles from the sample before analysis (capacity: 0-200ul). After our separating, we just to change the membrane filters (Micro Sep Membrane: Dia:13mm) (Fisher Scientific Co.).

4.2.2.4 Spectrophotometer:

Generally, the absorption measurement for analysis of aqueous ozone using the indigo method is performed at 600nm on a spectrophometer. In this study, a spectronic 20 spectrophotometer (spectral range of 340-950, 115v/60Hz, Fisher Scientific Co.) is used. Cuvette holders allowing thermostating were selected. The cuvette path-lengths is 1 cm and has to be left in positions in the instrument during filling and flushing, when residual ozone is determined by the indigo method.

4.2.2.5 Magnetic stirring appratus:

This apparatus is used for carbon adsorption test. we adopted five Economic Magnetic Stirriers (speed ranged: 200-1650 rpm, surface area 7.5m2, 120v/60Hz, 0.14A, 16w, Fisher Co.).

4.2.2.6 PH meter:

PH values of target solution are monitored by A 6071 microcomputer based bench top PH meter from Jenco Electronics, Ltd. Probe model is: A triaxle 3-in-1 pH/Ref/Tem electrode.

4.3. Experimental Procedures:

All reactor liquid feed was prepared by dissolving the desired amount of each target compound in distilled water. The volume of target solution is 800 ml. The details of each concentration of target compound are listed in Table 3. Reaction solutions were buffered at pH=7 with diluted sodium hydroxide & phosphate buffer solutions.

4.3.1 Experimental procedure for O3/UV plus carbon process:

Prior to an experimental run, 800 ml of target solution was placed in the reactor. To achieve complete mixing of the solution, we would first run the recycle pump, and then switch on the ozone generator to the desired ozone flowrate. At this same time, the UV lamp was turned on and the desired amount of activated carbon was added into the reactor. After a warm up period of 30 seconds, water samples (4-5 ml) for analysis of concentration were withdrawn from the sample port. Because the decomposition rate for target solution using this process was relatively fast, all procedures required a uniform precision, especially for the sampling time. 4-5 ml volume samples were collected from the sampling port at appropriate time intervals. Details can be seen to Table 4. A total of 6-8 samples were taken during an average period of reaction time. The system was operated at room temperature and atmospheric pressure.

Immediately after drawing a sample from the reactor, a syringe holder is used to remove the carbon particles in the sample so as to quench the catalytic-adsorption reaction (carbon surface reacting with sample). Then, the sample was placed into sampling vial, which contained 2-3 drops of 10% sodium thiosulfate solution for the sake of quenching the liquid phase ozone oxidation reactions. This also eliminated any possibility of continued reaction and decomposed the remaining peroxides. The total time for sample withdraw to sodium thiosulfate quench was 30 seconds.

All samples collected from these experiments were subjected to GC analysis within 8-10 minutes (the sample were analyzed immediately). Concentrations of target compound solution were measured by Gas Chromatograph.

4.3.2 Experimental procedure for determination of aqueous ozone:

For the determination of ozone in water by the indigo method, we refer to the paper by Bader, H., and Hoigne, J. (17).

Several 100 ml volumetric flasks were used for sample, blank and background ozone analysis. To each 100 ml flask, 1 ml of indigo reagent and 10 ml of 0.5M phosphate buffer reagent for pH 2 (17) were added to all except the blank flask without indigo reagent. A 1 ml reactor liquid/carbon sample (filtered for removing the carbon) was immediately put into the flask and diluted to 100 ml (after collection from the reactor). The 1 cm I.D. cuvette was then filled with this solution and inserted into the spectrometer (600nm) for analysis. Due to the unstability of the spectrophotometer, at least two readings for the same cuvette were taken to insure reproducibility. According to the standard indigo method (17), the absorbance of the residual indigo present in the sample solutions was measured at 600 nm in the cuvette. The absorbance change (ΔA) at 600 nm for indigo method -20,000 $M^{-1}cm^{-1}$ given in the reference (17) is utilized. We can use formula $A=k*l*C$ and $k=-20{,}000\ M^{-1}cm^{-1}$ to caculate the aqueous ozone concentration {Where: k: molar absorptivity $m^{-1}cm^{-1}$. l: length of cuvette (cm). C: ozone concentration (ppm)}.

In this study, three different operation conditions were run for the ozone mass transfer from gas to liquid phase. That is: carbon only; carbon plus UV; no carbon plus no UV. We wanted to determine the ozone concentration in water comparision of each of the different conditions.

4.3.3 Experimental procedure for activated carbon test:

In our experiment, two types of adsorption equilibrium experiments, (carbon-O3/UV-phenol) and (carbon-phenol), were performed to verify whether there were differences between carbon adsorption capacities for carbon only and the combined C/O3/UV processes using phenol as a adsorbate. The initial concentration of phenol is 2000 mg/l. Adsorption isotherms for carbon-phenol were determined by adding carefully determined amounts of absorbent (0.2, 0.4, 0.6, 1.0, 1.2 gm, see Tables 9, 10 ,11) carbon to five 250 ml bottles containing 100 ml of phenol (concentration: 2000mg/l) solution. The bottles were sealed and mechanically tumbled for 7 days to ensure equilibrium conditions.

A adsorption isotherms forcarbon from the catalytic-oxidation process (carbon/O3/UV/phenol) were performed at: Carbon, ozone, phenol (2000mg/l) and UV inlet conditions identical to those used in the kinetic experiments (see Table 4, and 5). The experiment was run for 10 minutes with UV & ozone both on. The phenol level was determined by GC. The carbon was then removed and dryed at 298K for 24 hours. The carbon, 12 gms, was then divided into mass quantities of 0.2, 0.4, 0.6, 0.8, and 1.0gms. The carbon was then input into five 250 ml bottles for isotherm equilibrium tests (7 days reaction). Phenol 2000mg/l was used as the adsorbate. Simultaneously phenol was treated with O3/UV process (No carbon) to determine the phenol concentration after 10 minutes. The difference in phenol concentration between the two experiments is assigned to carbon adsorption for this 10 minutes duration. The assumed phenol uptake on the O3/UV activated carbon is now used (added) to the 7 days carbon uptake test. From these two experiments: O3/UV/C/Phenol and O3/UV/No C/Phenol and the corresponding adsorption isotherm data on treated carbon vs non treated carbon, we obtain adsorption data on the two types of carbon. The data consists of Freundlich Isotherm parameters K_f anf n. If we assume that all of the difference in phenol concentrations O3/UV/C vs O3/UV only is due to reaction of phenol on the surface of the carbon, then the adsorption study results indicate that the treated carbon adsorbs less phenol than non treated carbon.

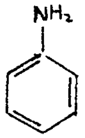
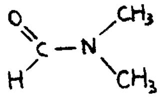
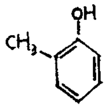
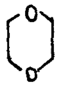
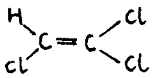
CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 Results

5.1.1 Rate Studies

5.1.1.1 Investigation Of C/O3/UV Process

The seven pollutants which were investigated in this study include:

Type	Name	Formula	Structure
1) Aromatic Amine Compounds---			
	Aniline	C6H5NH2	
2) Amide Compounds---			
	N,N-dimethyl Formamide	HCON(CH3)2	
3) Phenolic Compounds---			
	O-cresol	CH3C6H4OH	
	Phenol	C6H5OH	
4) Aromatic Compounds---			
	Pyridine	C5H5N	
5) Cyclicoxy compounds---			
	Dioxane	C4H8O2	
6) Chlorocarbon compounds---			
	Trichloro-ethlene	CHCLCCL2	

Reactions were conducted on all of compounds at 298 K in H_2O solution, PH=7, and are at atmospheric pressure. Experiments of combined Ozone/UV plus activated carbon and Ozone/UV were both carried out for each compound. The initial concentrations are listed for each compound depended on the individual compound's degradability and solubility and are listed in table 4.

Experimental results on decomposition of pollutants are illustrated in Figure 5 through 10, which show normalized concentration (C/C_0) as a function of the average residence time for both O3/UV and C/O3/UV processes. It is seen that target compound concentration consistently decreased with increasing reaction time for all the reactions. Within a fixed reaction time, the combination of O3/UV plus activated carbon was much more effective than O3/UV alone in destroying all target compounds. Figure 17 through 22 show best fit, first order decay plots for the reaction of Aniline, Pyridine, Phenol, Dioxane, Trichloroethlene, O-cresol, N,N-dimethyl Formamide in both O3/UV and charcoal catalyzed O3/UV systems. Overall rate constants for first order decay of Aniline and N,N-dimethyl Formamide fit the experimental data very well. Trichloroethlene and Phenol, also obey pseudo-first order decay. Degradation of Pyridine, O-cresol and Dioxane are, however, not well fit by the pseudo-first order rate law.

5.1.1.2 Investigation Of Destruction Rate

5.1.1.2.1 Mathematic Model For The Destruction Rate Kinetics

The overall (global) reaction were analyzed by fitting the following rate model to the data:

$$-\frac{d[M]}{dt} = k'^{*} [M]^{a} * [O3]^{b} * [I]^{d} * [C]^{e} \qquad (1)$$

Where [M], [O3], and [C] are the concentration of target compound, ozone and carbon respectively. [I] is the flux of radiation actually transferred into the reactor. a, b, d, and e are the order of the reaction determined from the experiments respectively. k' is the overall or global reaction rate constant. * means Times (defined).

The concentration and respective reaction order of Ozone, UV radiation and carbon Solids during the reaction are assumed to be constant. Equation (1) can then be arranged into the format:

$$-\frac{d[M]}{dt} = k * [M]^a \qquad (2)$$

Where $k = k' * [O3]^b * [I]^d * [C]^e$

This also assumes that the rate of disappearance of target compound is a first-order process ($a=1$); so, the rate may be written as:

$$-\frac{d[M]}{dt} = k * [M] \qquad (3)$$

Where M is concentration of target pollutant

When dosages of Ozone, UV radiation ([I]), and/or carbon are changed, the pseudo-first order rate constant k in equation (3) would be changed as:

$$\frac{k_2}{k_1} = \frac{k'_2 * [O3]^{b}{}_2 * [I]^{d}{}_2 * [C]^{e}{}_2}{k'_1 * [O3]^{b}{}_1 * [I]^{d}{}_1 * [C]^{e}{}_1} \qquad (4)$$

Where k_2, k'_2 is the value after changing $[I]_1$, $[C]_1$ and $[O3]_1$ to $[I]_2$, $[O3]_2$, and $[C]_2$.

Equation (4) shows that k is proportional to concentration of Ozone [3], UV radiation [I], and Carbon [C]. The rate constant k increases linearly with corresponding increase in the dosage of ozone and carbon if k' and [I] are assumed constant.

In order to analyze the pollutant decomposition rate, we use equation (3), and obtain:

$$\ln([M]/[M]o) = -k * t \qquad (5)$$

Where [M]o: Initial conc. of target compound;

[M]: Concentration of target compound at time t;

k: Reaction rate constant for pseudo-first order;

t: Contact time of reaction.

The fractional conversion x of target compound as reactant is defined as the fraction of reactant converted into product or

$$X = 1 - ([M]/[M]_o) \qquad (6)$$

So, equation (5) becomes:

$$\ln (1-X) = -k * t \qquad (7)$$

Defining the half-life of the reaction, $t_{1/2}$ as the time for the concentration of reactants to drop to one-half the original value:(6)

$$[M] = 1/2 * [M]_o \qquad (8)$$

Then, from equation (5) and (8), the half-life time is given by:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (9)$$

Plots of integrated rate equation (5), $-\ln([M]/[M]_o)$ versus time, are shown in Figure 15 through 22 for a range of initial concentration and conversions. The specific rate constants are obtained from the slopes on the curves. Table 7 through 9 list the rate constants and calculated half-lives for both O3/UV and O3/UV plus carbon process runs on each compound.

5.1.1.2.2 Experimental Results

Analysis for Destruction Rate of Pollutants:

Of the seven chemicals studied, decomposition was most rapid for Trichloroethlene with $X=0.83$ at contact time 10.5 min, and slowest for N,N-Dimethyl Formamide $X=0.253$ and Dioxane with $X=0.184$ for contact times of 20.5 min. As shown in Table 6, degradation of Trichloroethlene, N,N-dimethyl

Formamide, and Dioxane to X=0.5 requires 4.10, 25.77, and 63.77 minutes respectively. Here it is also seen that N,N-Dimethyl Formamide and Dioxane are not reactive with O3/UV alone to a significant extent. The reason is probably that there is an oxidation selectivity of the system (12) and stability assigned to each chemical structure i.e. each compound. Degradation of Aniline, Pyridine, O-cresol, and Phenol to X=0.5 requires only 7.70, 19.9, 8.24, and 7.19 minutes respectively for C/O3/UV process.

5.1.1.2.3 Effect Of Activated Carbon

In the reaction systems that have carbon added, the observed reaction rates have been increased significantly. Figure 5 through 10 indicate that an appreciable increase in conversion of all target compounds is observed when the reaction system is changed to O3/UV plus carbon from O3/UV alone.

Two forms of activated carbon: GAC (25-50 mesh) and PAC were utilized in our experiments. GAC has surface area of 1200-1500 m^2/G and PAC has 1500-2000 m^2/G (1). Therefore, PAC possesses slightly more surface area than GAC for the surface reactions. For our rate studies, only PAC was used due to its better adsorption. We used GAC instead of PAC in the carbon adsorption tests however because it is easier to separated GAC from the solution. The PAC's specific gravity is less than water and it is in a fine powdwer like form, so filtering and drying with quantitative weighing is difficult. 0.4 grams of PAC were added to 800 ml reagent volume for all target compounds. Kinetics results can be seen from Tables 4, 5, and 7.

The effect of different PAC loading was investigated while the dosage of ozone was held constant for phenol studies. Level were changed from 0.25 g/l to 0.5 g/l. One can see from Figure 2, and 15 that the rate of destruction for phenol is increased 30 percent (from 0.0736 to 0.0964 1/min) with the contact time 10.5 min.

Clearly the lower amount of PAC in the experiment, the slower observed decay of phenol. It should be noted that there is a maximun loading for PAC in our process because if there is too much PAC added into liquid it will cause the liquid to become opaque so that the UV light can not be transmitted. Figures 2, and 15, alongwith Table 7 show that the rate is decreased from 0.0964 to 0.0728 when the PAC dosage added into system is changed from 0.5 g/l up to 0.6 g/l. So, in our system the maximum dosage of PAC is around 0.5 g/l. All seven compounds are investigated at this of PAC loading.

5.1.1.2.4 Effect of Oxidant Dosages

Figure 3, and Table 7 give a good example on the effect of ozone dosage loading in phenol reaction and show that dosage of ozone is an important factor in this process. The concentration of ozone dissolved in water can be obtained from relevant conversion of O3 flowrate value in ozone generator manual. Table 8 gives a summary of phenol experiments. The rate constants in Table 8 show that when the flowrate of O3/O2 gas is increased from 0.025 to 0.06 SCFM (0.88 l/min to 2.12 l/min) the destruction rate constant k is increased from 0.087 to 0.134 l/min. This demonstrates that increasing the dosage of ozone is important in ozone oxidation process.

5.1.1.3 Mathematic Model For O3/UV Plus Carbon Process

The reactor results were analyzed by making a material balance for each target compound. The performance equation obtained is:

Accumulation = - Oxidation - Absorption + desorption (10)

Or:

Oxidation: $r_o = k^*[O3]^{a*}[I]^{b*}[C]^d$

Adsorption: $r_a = k_a^*\{C_m\text{-}(C_1\text{-}C)\}$

Desorption: $r_d = k_d*(C_1-C)$

Where:

V: Reactor volume;

k: Oxidation reaction rate constant;

k_a: rate constant of adsorption;

k_d: rate constant of desorption;

a, b, and d are the exponents and are equal to 1 when the assumption of first-order oxidation reaction for each condition is made.

I: Light Intensity.

C: Concentration of target compound at contact time t for C/O3/UV process;

C_1: Concentration of target compound by oxidation (O3/UV) reaction only (Nocarbon) through reaction time t;

C_o: Initial concentration in reactor;

C_m: Amount of solute adsorbed per unit adsorbent maximums;

According to equation (10), we have:

$$V*\frac{dC}{dt} = - V*k*[O3]*[I]*C - V*k_a*\{C_m-(C_1-C)\} + V*k_d*(C_1-C) \qquad (11)$$

Assume: 1). $k*[O3]*[I]=k_3$

2). Due to $\frac{dC}{dt} = k*[O3]*[I]*C$, So, $C_1=C_o*e^{-k_3 t}$

Put k_3 and C_1 into equation (11), we obtain:

$$\frac{dC}{dt} = -k_3*C-k_a*\{C_m-(C_o*e^{-k_3*t}-C)\} + k_d*(C_o*e^{-k_3*t}-C) \qquad (12)$$

Assume again:

$k_4 = -(k_3 + k_a + k_d)$

$k_5 = -k_a*C_m$

$k_6 = C_o * (k_a + k_d)$

Equation (12) can be rearranged to

$$\frac{dC}{dt} = k_4 * C + k_5 + k_6 * e^{-k_3 t} \qquad (13)$$

To solve equation (13), we obtain:

$$C = \frac{e^{(k_3 + ka + k_d) * t} * \{k_a C_m - (k_a + k_d) * C_o\} - k_a * C_m}{k_3 + k_a + k_d} + \frac{(k_3 + k_a + k_d) * e^{(k_3 + k_a + k_d) * t}}{k_3 + k_a + k_d}$$

The above equation then applies to the system given the above major assumptions. If k_a, and k_d are known, we can plot data for O3/UV plus carbon process destruction of the target organics. This analysis will be improved and further developed in future studies.

5.1.2 Equilibrium And Continuously Regeneration Of Catalyst Studies

5.1.2.1 Investigation Of Activated Carbon Adsorption

Two types of adsorption equilibrium experiments were carried out to deterimine whether the adsorption capacility compared to carbon only process. Phenol is used to as an absorbate. The detailed experimental procedure can be found in the preceeding experimental section.

The equilibrium data were found to be best fit by the Freundlich Isotherm Equation:

$q_e = k_f * C_e^{(1/n)}$

or, in linear form,

$\mathrm{Log}(q_e) = \mathrm{Log}(K_f) + 1/n * \mathrm{Log}(C_e)$

Where:

q_e = amount of phenol adsorbed per unit of weight of carbon;

C_e = concentration remaining in solution phase;

K_f and $1/n$ are characteristic conatants related to adsorption capacity and activation intensity, respectively.

The experimental equilibrium data were normalized by plotting $\mathrm{Log}(q_e)$ versus C_e. Two constants K_f and n can be obtaind from the plots. The details are shown in Figure 14 (For both carbon only and the O3/UV plus carbon process). The summary of characteristic constants K_f and n can be seen in Table 10, 11, and 12. From our experimental equilibrrium data, (carbon-phenol) and (carbon-O3/UV-phenol), we found that characteristic constants K_f and n of the activated carbon to be increased from $n=0.169$ and $K_f=10^{(-20.03)}$ up to $n=0.519$ and $K_f=10^{(-7.03)}$. The experimental results verified that the adsorption capacity of activated carbon can be enhanced by photolytic-ozone/oxidation reaction. The process provides us a alternative method i.e. use of this heterogneous catalytic-oxidation process, to extend the adsorption saturation time for activated carbon.

5.1.2.2 Mathematic Model For Equilibrium Studies

For catalytic-oxidation on the surface of activated carbon (C/O3/UV):

5.1.2.2.1 Basing On The Freundlich Isotherm Theropy:

I). Case I: (carbon only)

C_o ---------○--------- C_{eo} (14)

Case II: (O3/UV plus carbon)

C_o ---------○--------- C_{e1} (15)

C_o: Phenol input concentration in the system;

C_{eo}: Phenol output concentration in the system (case I);

C_{e1}: Phenol output concentration in the system (case II);

t_o: adsorption time;

II). According to the Freundlish Isotherm Equation $Q_e=K_f*C_e^{(1/n)}$, we obtain two equations from conditions with and without carbon:

Case I: $q_1=K_{f1}*C_{e1}^{(1/n1)}=(C_o-C_{e1})*(1/m)$ (16)

Case II: $q_o=K_{fo}*C_{eo}^{(1/no)}=(C_o-C_{eo})*(1/m)$ (17)

Assumption: the weight of adsorbent here is equal to m=1;

III). Due to the oxidation, we have:

$$-\frac{dC}{dt} = r = k_3*[O3]*[I]*[C] \tag{18}$$

Where:

C: The concentration of target compound in reactor at time t;

Exponents now assumed equal to 1;

k_3: Rate constant of oxidation reaction;

[O3], [I] are the conc. of ozone and UV radiation respectively;

Take $k_4=k_3*[O3]*[I]$,

Therefore, we have:

$$-\frac{dC}{dt} = k_4*C \tag{19}$$

After reaction for to time, t_o, and integrating the rate equation (18), we obtain:

$$C_{e1}=C_o*e^{(-k_4*T_o)} \tag{20}$$

IV). According to the mass balance and assumption q(mg/mg) is the adsorption capacity "value" which is increased by the catalytic-oxidation process O3/UV, the following equation can be obtained:

$$q = q_1 - q_o = K_{f1} * C_{e1}^{(1/n1)} - K_{fo} * C_{eo}^{(1/no)} = C_{eo} - C_{e1} \qquad (21)$$

= adsorption capacities increased by O3/UV process

Put equation (20) into (21), we got:

$$K_{f1} = \frac{C_{eo} + K_{fo} * C_{eo}^{(1/no)} - C_{fo} * e^{(-k_4 * T_o)}}{(C_o * e^{(-k_4 * T_o)})(1/n1)} \qquad (22)$$

From these parameters K_{fo}, n_o, t_o, C_{eo}, k_4, and n1, we can obtain from the experiment and through plotting the data on paper and get K_{f1} using equation (22) calculation.

The equilibrium time for GAC adsorption test requires 7 days. If we want to get K_o, n_o, t_o, C_{eo}, k_4, and n1 it is idealy effective only after operating the system 7 days. But, in our Lab-scale it is impossible to maintain the C/O3/UV system operating this long period of time in order to get these above parameters. Therefore, here we can not use experimental data(reacting 7 days) (k_o, n_o etc.) to match and calculate the above mathematic model (equation 22). We adopt the method mentioned before (please see the experimental section), that is 10 min for (carbon-O3/UV-phnol) process, then 7 days for (carbon-phenol) process). This allows us to reach some initial conclusions to overall (only uncertainy from quantities).

5.1.2.2.2 Basing On The Langumir Adsorption Isotherm Theory

5.1.2.2.2.1 O3/UV Plus Activated Carbon Process:

I). According to the Langumir Adsorption Isotherm Theory, we have:

(a). Rate of desorption: $r_d = K_d * @$ (23)

(b). Rate of adsorption: $r_s = K_s * (1 - @)$ (24)

Where:

K_d: rate of constant of desorption;

K_s: rate of constant of absorption;

@: the fraction of the sites already filled by adsorbed molecules;

II). According to the oxidation, under O3/UV process, the following equation can be obtained:

$$r_@ = \frac{d@}{dt} = k*[O3]*[I]*@ \qquad (25)$$

Where:

$r_@$: rate of oxidation on th surface of activated carbon;

k: rate constant of oxidation reaction;

[O3], [I] is the concentration of ozone and UV radiation respectively;

III). According to mass balance, the following equation can be obtained when equilibrium is reached:

(a). Net of desorption = Adsorption;

(b). Desorption - Oxidation = Net desorption;

From equation 23, 24, 25, we have:

$K_d*@-k*[O3]*[I]*@=K_s*(1-@)$

$$@ = \frac{K_s}{K_d+K_s-k*[O3]*[I]} \qquad (26)$$

5.1.2.2.2.2 Activated Carbon Only Process

When the equilibrium is reached, the following equation is valid:

$r_d=r_s$,

$$\text{So, } @_1 = \frac{K_s}{K_d+K_s} \qquad (27)$$

Where:

$@_1$: The fraction of the sites already filled by adsorbed molecules under this carbon only process;

r_d, r_s, K_s, and K_d are the same as before;

5.1.2.2.2.3 Comparision Of Two Processes

Adsorption capacity "value" increased by catalytic-oxidation using O3/UV process @ is:

$$@ = @ - @_1 = \frac{K_s * k * [O3] * [I]}{(K_d + K_s - k * [O3] * [I] * (K_d + K_s)} > 0$$

Through the this analysis, we observe that the adsorption capacity under the O3/UV plus carbon process is larger than in the normal carbon adsorption case (see discussion).

5.1.3 Investigation Of Ozone Dissolved In Liquid Phase:

5.1.3.1 Ozone Mass Transfer

---Condition: UV lamp off, No carbon added----

As ozone is bubbled into the buffered distilled water with the UV lamp off, the concentration of aqueous ozone rises rapidly until an equilibrium level is reached. The mass balance of ozone over the liquid gives(19):

$$V * \frac{dC_{o3l}}{dt} = K_{lo3} * a * V * (C_{o3i} - C_{o3l}) \qquad (28)$$

Where:

K_{lo3}: mass transfer coefficient for gas absorption;

a: bubble surface area;

V: reaction volume;

C_{o3i}: O3 conc. at H_2O-O3 bubble interface;

C_{o3I}: O3 conc. of O3 in solution;

C_{o3i} is assumd constant integrating the equation (28) at the boundary conditions: $t=0$, $C_{o3I}=0$; $t=t$, $C_{o3I}=C_{o3I}$;

$$1-(C_{o3I}/C_{o3i})=Exp(-K_{Io3}*a*t) \qquad (29)$$

This equation can be solved for K_{Io3} by linear regression of experimental data of C_{o3I} versus time. Ozone concentration versus time in the aqueous solution is shown in Figures 11, 12, and 13 in our experiments.

5.1.3.2 Effect Of UV Lamp On Ozone Mass Transfer:

----Condition: No carbon addition-----

The effect of ultraviolet radiation on ozone in aqueous solution is shown in Figure 13. When the UV lamps are turned on, the dissolved ozone attenuates rapidly. Subsequent runs give lower values of both the equilibrium ozone concentration and the mass-transfer coefficient, as shown in Figure 13. Once the UV lamps are turned on, some of ozone dissolved in solution is destroyed and changed to other radical species by the UV radiation. This data is verified by previous research of Peyton (25-28).

Peyton suggested: ozone removed from the feed gas system can be photolyzed in solution by ultraviolet light at 254nm to produce hydrogen peroxide intermediate product, not hydroxyl radical as has been frequently speculated in the past. Hydrogen peroxide is a very weak acid, and its conjugate base HO_2^- reacts with ozone to yield hydroxyl radical (OH^*)(28). The hydroxyl radical OH*'s oxidation potential (2.80 volts) is larger than ozone's oxidation potential (2.07 volts) (See table 1). This is the reason why ozone photolysis is more effective than ozone without photolysis process only for the cleanup of recalitrant pollutants in water.

5.1.3.3 Effect Of PAC On Ozone Mass Transfer

-----Condition: No UV lamp -----

When the PAC is added and then ozone bubbled into purified water, the dissolved ozone was observed to increase rapidly with the increased dosage of PAC. This effect of PAC addition on ozone in aqueous solution is shown in Figure 12.

The PAC may act by absorbing and scavenging the ozone molecules effectively increasing the concentration difference between ozone gas and ozone liquid. The actual transfered amount from ozone gas is, therefore, increased as shown in equation 28. The other possible explanation for this is that PAC stabilizes the presence of ozone dissolved in solution. The ultimate result is to make the ozone concentration higher in solution with PAC added ozone in solution plus active ozone on carbon surface. This gives us some insight into why the catalytic-ozonation by activated carbon process (IAO) destroys the organics faster and more effectively than the ozone alone system, i.e. more ozone may be present. It also suggests that activated carbon can function as a catalyst-absorbent. The increased rate of transfer suggests that a higher input of ozone to the reactor (higher capacity ozone generatior) may be beneficial to the conversion process.

5.1.3.4 Effect Of PAC On O3/UV Process:

-----Condition: UV lamp is on plus carbon added-----

The experimental data show that ozone dissolved in solution increases with increased amounts of PAC added. Now we report that the concentration of ozone in (carbon-O3/UV) case is less than concentration in (carbon-O3) case (See Figure 13). This results is because that the ozone is being photolyzed by UV and is being reacted into other active radical and stable species.

In summary: Ozone in solution is changed into other radical species by UV radiation. Ozone in solution can be adsorbed onto carbon surfaces and ozone gas transfer will increase with the increasing PAC dosage.

5.2 Discussions

Charcoal catalyzed O3/UV is a new and effective heterogeneous catalytic-oxidation technology being developed and tested in our research labs. It is an extension and a sister process to the Integrated Adsorption/Oxidation (IAO) process, which was created by J.W. Bozzelli, D. Vaccari and co-workers (31). Data are presented in two sections on initial resulits from this process.

This present work also has further investigated and evaluated the heterogeneous catalytic-oxidation technology from both analysis of conversion through various operation conditions including measurement of increased a adsorption capacity of carbon for phenol.

The experiment results indicate that there are several plausable reasons that explain the catalytic-oxidation reactions:

1). The use of activated carbon in the reaction system produces an active surface for both adsorption and catalysis of the target molecule oxidation processes. Both stable molecules and active intermediates (OH^* and other Radical species of target compound which are produced from the Ozonation and UV radiation) can be adsorbed on the carbon surface. There (on the carbon surface) reagents can then come into contact with the adsorbed radicals/molecules and react or further react inclusive of supplying or providing oxygen or active oxygen species to the carbon.

2). From the above experimental results and analysis of destruction rate, the apparent heterogeneous catalytic destruction rate k is larger than the homogeneous catalytic-oxidation reaction rate under the same operation conditions. The removal rate of target compound for O3/UV plus carbon is also larger than for the homogeneous process alone.

3) There can be increased adsorption of the organic molecules on the surface of the carbon due to insitu activation of the surface from combined effects of the system. O3 active radicals resulting from photolytic decomposition of the ozone and photolytic processes at the surface itself. From the kinetic expression analysis for Freundlich Isotherm Theory and Langmuir adsorption Isotherm (see equations 13 to 26), we can find that in the adsorption and oxidation (C/O3/UV) process adsorption value in the quilibrium @ is large than @1 in the carbon only process. From the aspect of regenerating activated carbon, this is equivalent to extending the adsorption capacity of the activated carbon. This process also produces much less spent carbon as waste by product.

4). There also the possibility that there is an increase in oxidizing radicals in solution resulting from the increased ozone mass transfer. A caution should be made with respect to the maximum extension of the carbon adsorption "capacity" and/or the observed Frendlich Isotherm constants. If essently complete oxidation of organic occurs after adsorption and the carbon surface is still active, the capacity of the carbon for further adsorption of organic is then theroretically infinite. The reasons for this not being practically realizable, even at equilibrium are two fold. First, it is likely that oxidation of organics at the carbon surface is not absolutely complete, thereby leaving a residual amount adsorbed at the surface which may diminish the capacity of the carbon for further adsorption. Second, other background constitutents can adsorb or otherwise deposit (e.g. precipitate) on the carbon. It should be noted that even if this occurs to only a minor extent with respect to solute removal, it may be significant with respect to utilization of adsorption sites on the carbon. In summary photolytic/O3/Treatment is a valuable method for regeneration activated carbon at the same time as catalyzing the oxidation reactions.

An additional caution should be made that the dosage of activated carbon needs to be limited because if too much is put into solution the UV light can not be transmitted into the solution sufficiently.

CHAPTER 6
CONCLUSIONS

A new photolytic heterogeneous catalytic-oxidation process which combines ozone, ultraviolet light and activated carbon is shown to be an effective method in destroying a wide variety of recalcitrant organic pollutants (Hazardous and/or toxic) present in water at low levels (500-2000ppm). The destruction rates of reaction were up to 1.98 times faster with O3/UV plus activated carbon than with the O3/UV homogeneous process alone. For the seven target compounds, the observed reaction rates were fastest for N,N-dimethyl Formamide with an increased rate of 1.98 and slowest for Aniline with the increased rate of 1.17.

Activated carbon is shown to possess either a catalytic effect or on enhanced adsorption in photolytic-ozonation oxidation. Comparisions of activated carbon adsorption process (carbon only), photolytic-ozonation process (O3/UV), and activated carbon catalysis (C/O3/UV) for the treatment of phenol showed that the removal rate was increased with the activated carbon /O3/UV by 45%. Our initial analysis suggests that the effect is a catalytic one.

We have also demonstrated that the adsorption capacity of activated carbon may be enhanced by photolytic-ozonation oxidation reaction. Comparision of two kinds of equilibrium tests: (carbon-phenol) and (carbon-O3/UV-phenol) show that the characteristic constants for Freundlich adsorption equation log (K_f) and n were both increased from -20.03, and 0.169 to -7.03, and 0.519 , respectively. This implies that it is possible to continuously regenerate activated carbon while catalyzing the oxidation reaction using the photolytic catalytic-oxidation (C/O3/UV) process. This process also produces less spent carbon as waste by product.

Possibilities for further study are to estabilish a pilot-scale reactor to investigate the scale up parameters and research on the kinetic and adsorption processes for more realistic estimates of its potential benefits from our Integrated Photolytic-Adsorption process, as well as better understanding.

Catalytic Ozone/Ultraviolet Light Oxidation Of Organics In Water: Integrated/Charcoal/UV Radiation

Appendix

TABLE 1

Oxidation Potential Of Commercially Avaiable Oxidizing Agents

	Species	Oxidation Potential (volts)	Relative Oxidation Power
1.	Fluorine, F2	3.06	2.25
2.	Hydroxyl Radical, OH **	2.80	2.05
3.	Atomic Oxygen, O **	2.42	1.78
4.	Ozone, O3	2.07	1.52
5.	Hydrogen Peroxide, H2O2 **	1.77	1.30
6.	Perhydroxyl Radical, HO2	1.70	1.25
7.	Hypochlorous Acid, HOCL	1.49	1.10
8.	Chlorine, CL2	1.36	1.00

* Based on CL2 as a reference
** Not a stable molecule must be generated in-situ

TABLE 2

Packed Columns and Operating Conditions Chromatographic Columns

Column Description Stationary on Packing Phase	Target Compound	Column Temp.(oC)	Reaction Time(min.)
4% Carbowax 20M+0.8% KOH on Graphpac-GB, 60/80	Pyridine	180	2.4
1% Alltech At-1400 on Chromosorb W-HP, 100/200	O-cresol	110	1.6
	Phenol	120	1.7
Chromosorb 101	Trichloro-ethlene	170	3.1
	N,N-dimethyl Formamide	200	3.5
	Dioxane	200	2.0
5% SP2100 on Supelcoport, 80/100	Aniline	100	1.2

TABLE 3

Initial Concentrations And Reaction Time For Target Compounds

Target Compound	Molecular Weight	Concentration PPM	Mol/l	Reaction Time (min.)
Phenol C6H5OH	94.05	1000	0.01063	10.5
Pyridine C5H5N	79.10	1000	0.01264	10.5
Trichloro-ethlene CHCLCCL2	131.37	2000	0.01522	10.5
Aniline C6H5NH2	93.12	1000	0.01074	10.5
O-cresol CH3C6H4OH	108.14	2000	0.01849	20.5
N,N-dimethyl Formamide HCON(CH3)2	73.06	2000	0.02736	10.5
Dioxane C4H8O2	88.00	2000	0.0227	20.5

TABLE 4

List Of Conditions For Reactor Operation

Compound	Reaction Time (Min.)	Sampling Interval (Min.)	Flowrate of O3/O2 (L/Min)	Dosage of PAC (Grams)
Aniline	10.5	2	1.41	0.4
Pyridine	10.5	2	1.41	0.4
N,N-dimethyl Formamide	10.5	2	1.41	0.4
O-cresol	20.5	4	1.41	0.4
Trichloro-ethlene	10.5	2	1.41	0.4
Dioxane	20.5	4	1.41	0.4
Phenol	10.5	2	0.88	0.4
			1.41	0.4
			2.12	0.4
Phenol	10.5	2	1.41	0.20
			1.41	0.32
			1.41	0.40
			1.41	0.40

Volume of Reactor = 1000 ml; Reaction Volume = 800 ml

TABLE 5

Concentrations Of Target Compound, Ozone And Charcoal For The O3/UV Plus Carbon Studies

Compound	Initial Conc. (PPM)	Final Conc. (PPM)	[O3] (Mg/l)	[PAC] (g/l)
Aniline	1000		67.7	0.5
Pyridine	1000		67.7	0.5
N,N-dimethyl Formamide	2000		67.7	0.5
O-cresol	2000		67.7	0.5
Trichloroethlene	2000		67.7	0.5
Dioxane	2000		67.7	0.5
Phenol	1000		67.7	0.5

Volume of Reaction = 800 ml; Flowrate of O3 = 1.41l/min

TABLE 6

Rate Constants And Half-Lives For Target Compounds Comparsion Of C/O3/UV & O3/UV Processes

Compound	Initial Conc. (PPM)	O3/UV Process		C/O3/UV process		ko
		k value (1/min)	t1/2 (min)	k value (1/min)	t1/2 (min)	
Aniline	1000	0.0767	9.04	0.090	7.70	1.17
Pyridine	1000	0.0193	35.9	0.0348	19.9	1.80
N,N-diemthyl Formamide	2000	0.0136	50.9	0.0269	25.8	1.98
O-cresol	2000	0.0515	13.5	0.0841	8.24	1.63
Trichloro ethlene	2000	0.1130	6.13	0.1690	4.10	1.50
Dioxane	2000	0.00785	88.3	0.0187	63.8	1.38
Phenol	1000	0.0643	10.8	0.0964	7.19	1.50

Volume of Reaction = 800 ml; [O3]: 67.7 mg/l;

t1/2 = Ln2/k; ko: ratio for C/O3/UV to O3/UV process (Improvement factor).

TABLE 7

Rate Constants And Half-Lives For Phenol Comparision Of Varied PAC Dosage And Varied Ozone Dosage

Description	[PAC]=0.5g/l		Description	[O3]=50.9 mg/l	
[O3] (mg/l)	k value (1/min)	t1/2 (min)	[PAC] (g/l)	k value (1/min)	t1/2 (min)
42.3	0.0873	7.94	0.25	0.0736	9.42
67.7	0.126	5.50	0.40	0.0787	8.81
101.8	0.134	5.17	0.50	0.0964	7.19
			0.60	0.0728	9.52

Vol.of Reaction:800 ml; Init.of Conc. of Phenol:1000 PPM

TABLE 8

Rate Constant, Half-Lives And Conversion For Phenol Comparision Of C/O3/UV, O3/UV and Carbon Only

Description	k value (1/min)	t1/2 (min)	Initial Conc. (PPM)	Final Conc. (PPM)	Conv.(%) X=1-C/Co
Carbon only process	0.00837	82.81	1000	916	8%
O3/UV process (NO Carbon)	0.0643	10.78	1000	496	50%
C/O3/UV process	0.0964	7.190	1000	343	66%

Reaction Conditions:

Volume of Reaction: 800 ml; Reaction Time: 10.5 min;

[O3]: 50.9 mg/l; [PAC]: 0.5g/l

TABLE 9

Activated Carbon Uptake Test
CASE I: Carbon Only (7 Days)

Carbon (g)	Ini. Conc. Co(mg/l)	Fin. Conc. Ce(mg/l)	X=Co-Ce (mg/l)	q=X/M (mg/mg)	Log(Ce)	Log(q)
0.2	2000	1815.2	184.8	0.185	-0.733	3.259
0.4	2000	1737.9	262.1	0.131	-0.883	3.240
0.6	2000	1660.0	340.0	0.113	-0.947	3.220
1.0	2000	1616.0	384.0	0.077	-1.114	3.208
1.2	2000	1550.46	449.5	0.075	-1.125	3.190

Reaction Conditions:

Uptake time: 7 days; Reaction volume: 250 ml;

TABLE 10

Activated Carbon Uptake Test
CASE II: Carbon Under O3/UV Process (10 Min) Plus Carbon Only (7 Days)

(1): Carbon under O3/UV process (10 min)

Description	Reaction Time (Min)	Phenol Concentration Ini.(PPM)	Fin.(PPM)
O3/UV process	10	2000	1769.3
C/O3/UV process	10	2000	1516.3

Carbon Uptake Phenol:

{O3/UV} - {C/O3/UV} = 1769.3 -1516.3 = 253 mg/l.

Each Carbon Uptake Phenol:(equivalent)

(253 mg/l * 41)/12 g = 84.33 mg phenol/g carbon
= Q

Reaction Volume: 4 l;

(2): Carbon only (7 days uptake test)

Carbon (g)	Ini. Conc. Co(mg/l)	Fin. Conc. Ce(mg/l)	X=Co-Ce (mg/l)	q=X/m+Q (mg/mg)	Log(q)	Log(Ce)
0.2	2000	1888	112	112*0.2/0.2+Q =0.196	-7.08	3.276
0.6	2000	1714	286	286*0.2/0.6+Q =0.180	-0.745	3.234
1.0	2000	1682	318	318*0.2/1.0+Q =0.148	-0.830	3.226

Reaction Volume: 250 ml;

TABLE 11

Characteristic Constants Kf, n Relating To Activated Carbon Adsorption Capacity And Intensity Comparision Of C/O3/UV And Carbon Only Process

Description	Kf	n
Carbon only process	10(-20.03)	0.169
O3/UV plus carbon process	10(-7.03)	0.519

Schematic Diagram of Experimental Apparatus

Integrated Charcoal/Ozonation/UV radiation

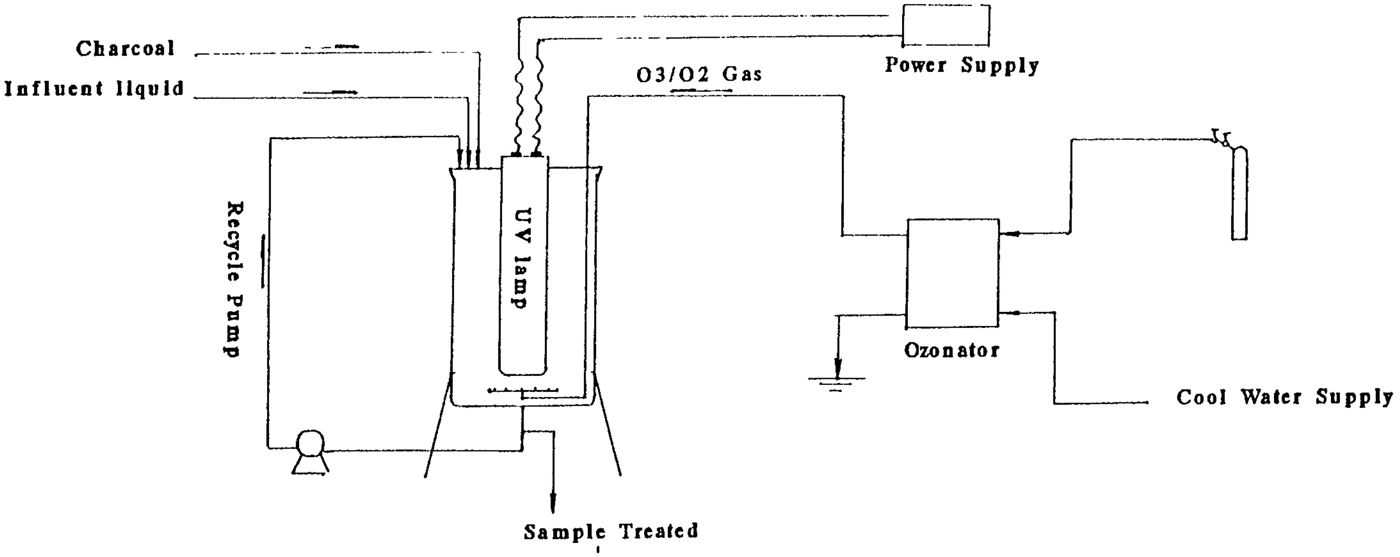
- Semi-batch Reactor
- Ozone Generator
- GC Analysis
- Spectrophotometer

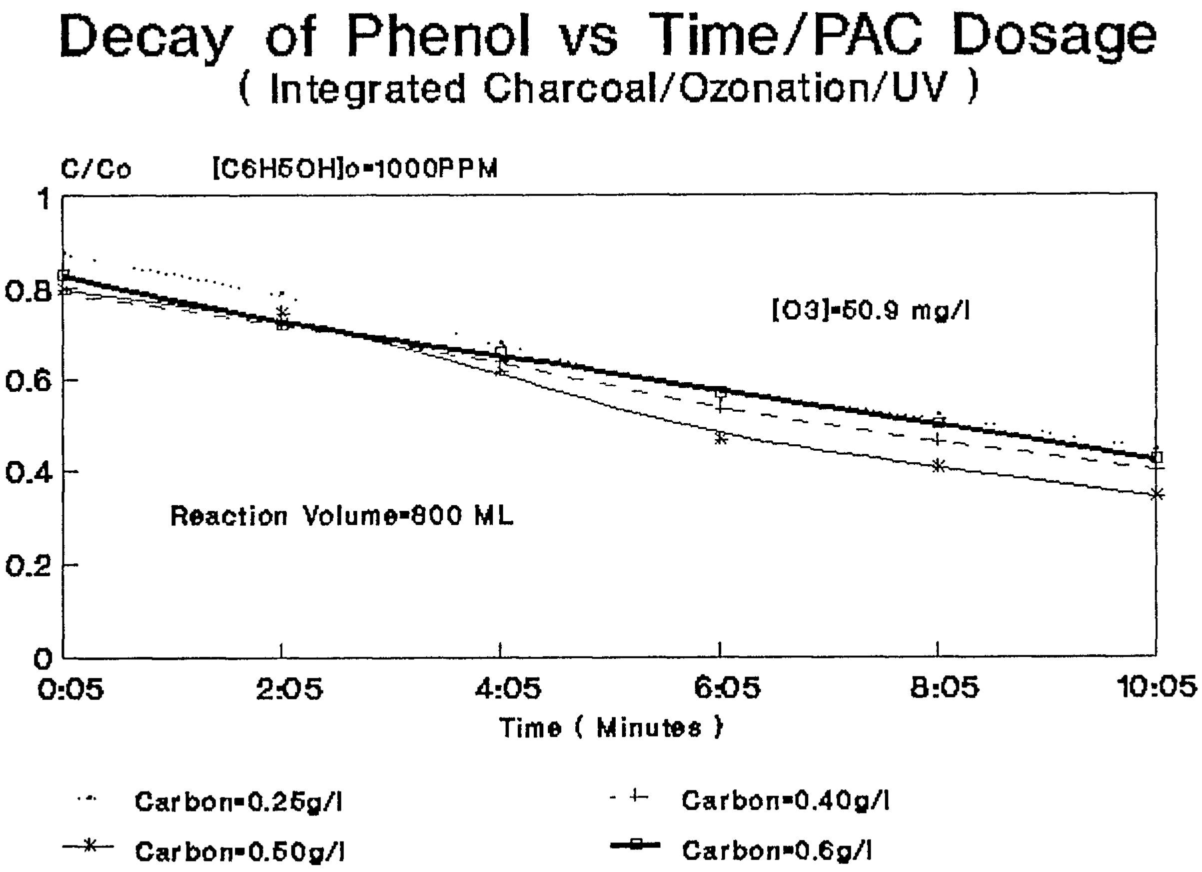
VARIABLE

-Reaction Time (10.5 min)

-Reaction Volume (800 ml)

-Reaction Temperature (Room)

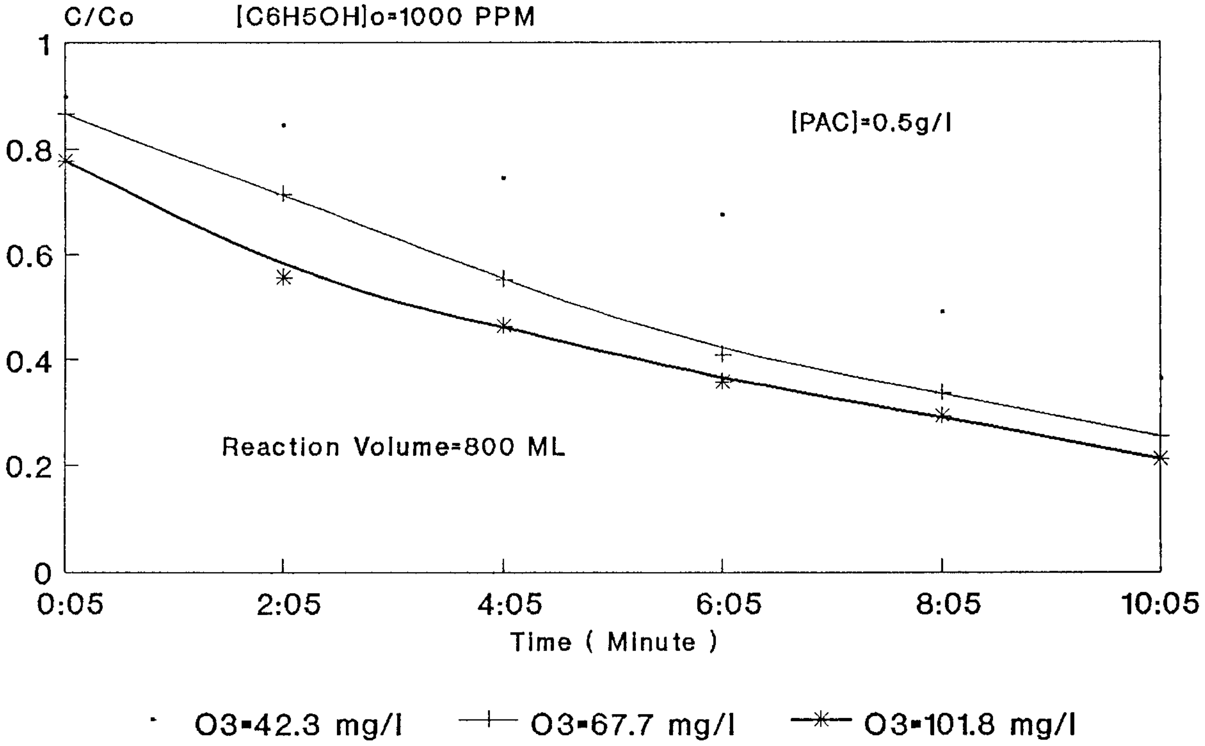




Comparision of Varied PAC Dosage

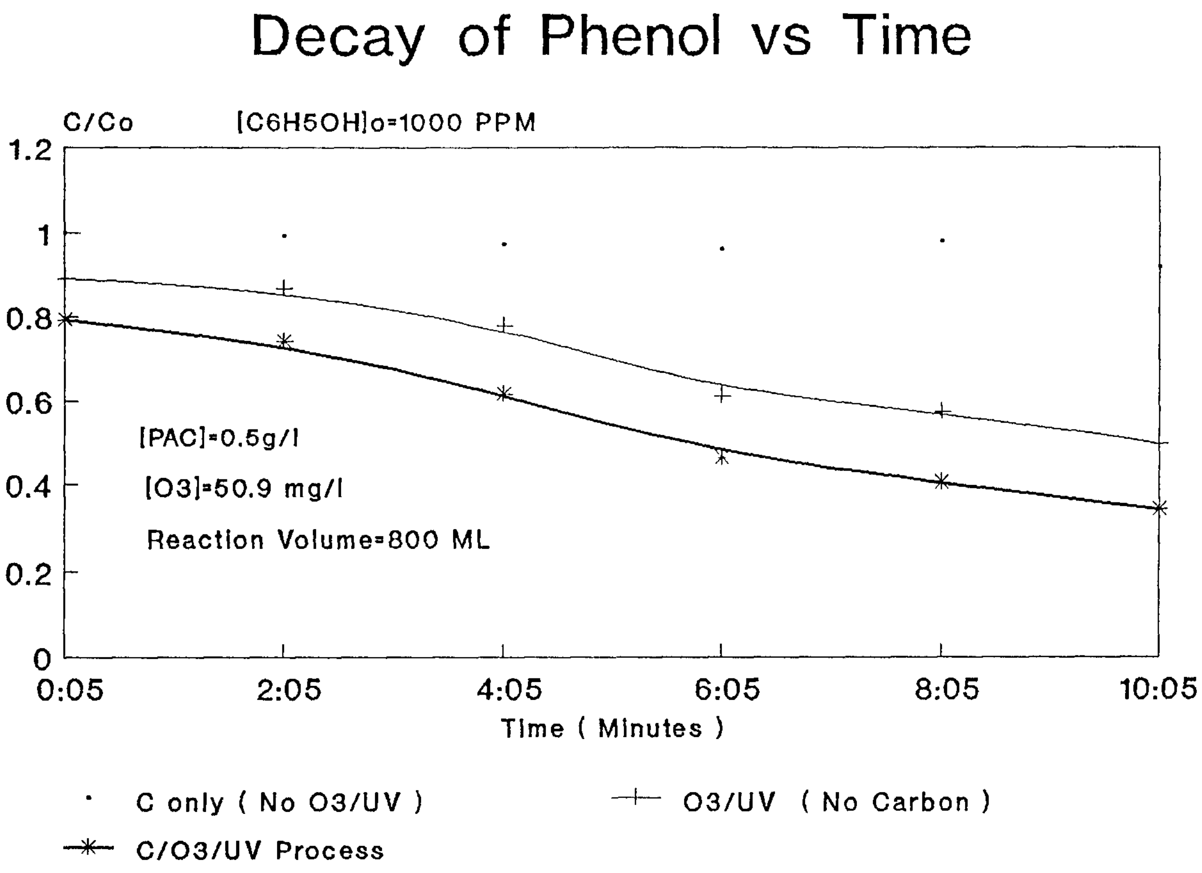
Figure 2

Decay of Phenol vs Time/Ozonation Dosage
(Integrated Charcoal/Ozonation/UV)



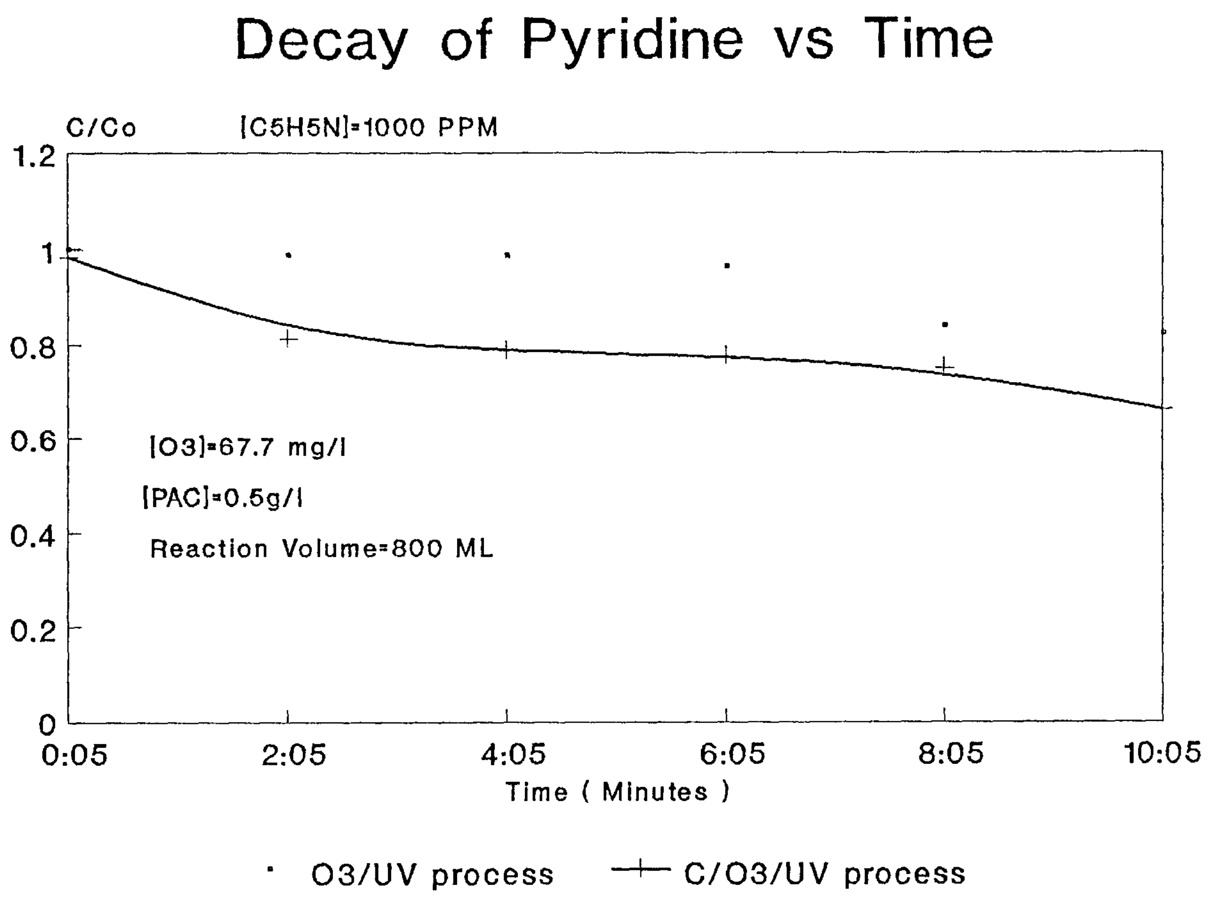
Comparision of Varied O3 Dosage

Figure 3



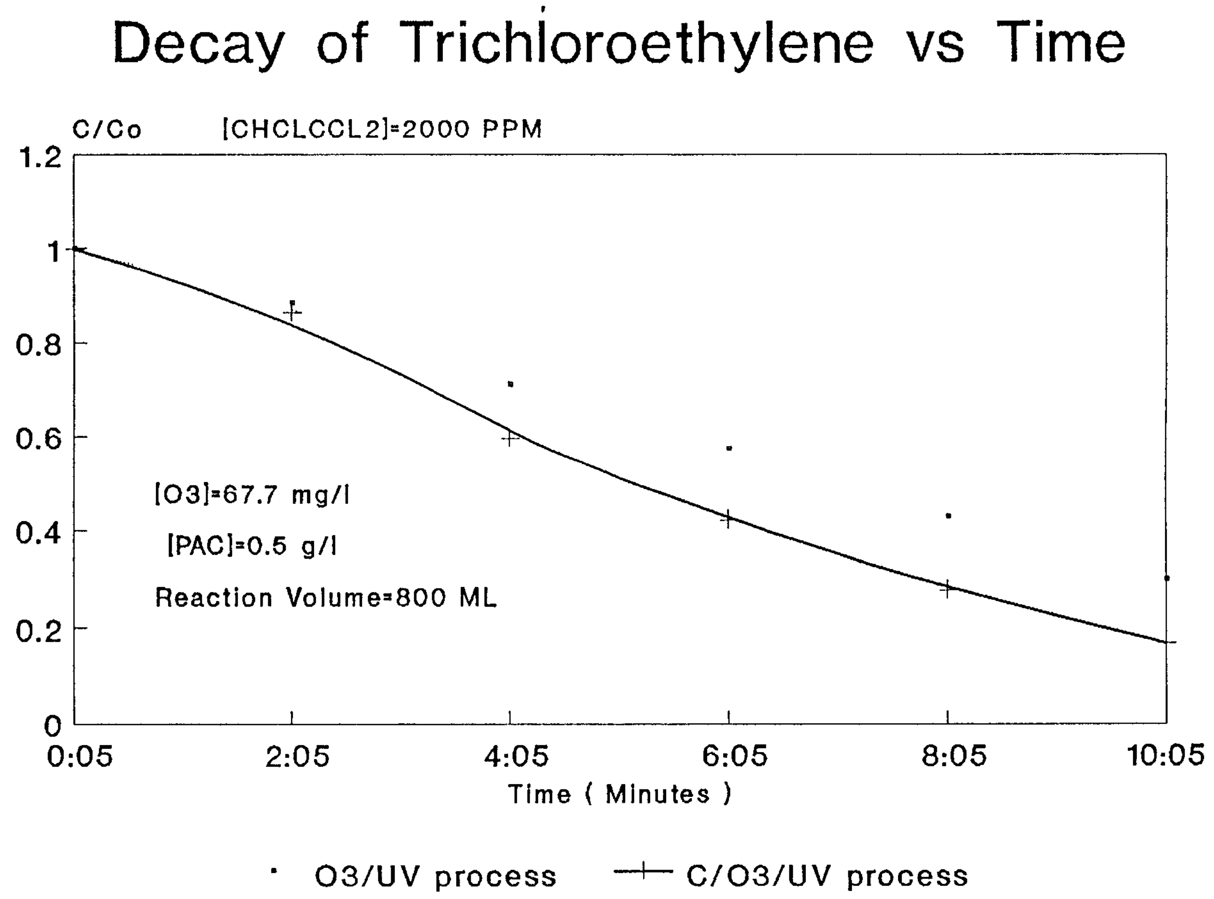
Comparision of C/O3/UV & O3/UV & C only

Figure 4



Comparision of C/O3/UV & O3/UV Process

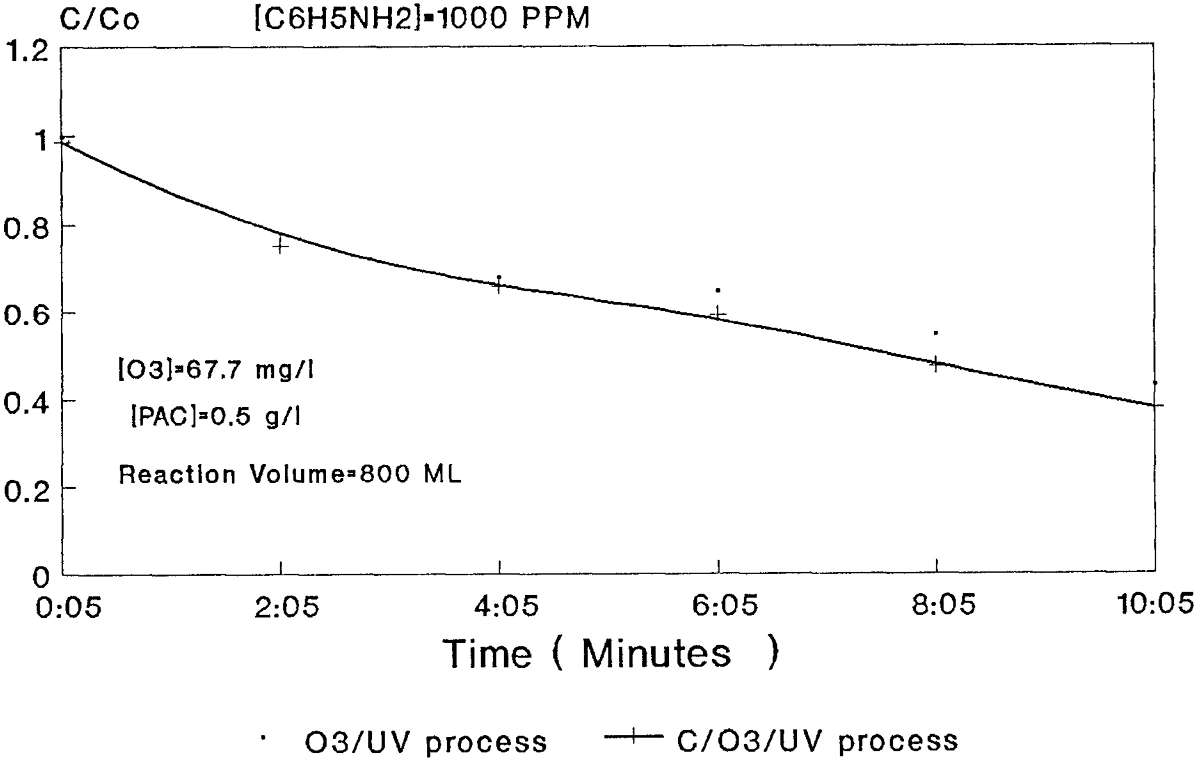
Figure 5



Comparision of C/O3/UV & O3/UV process

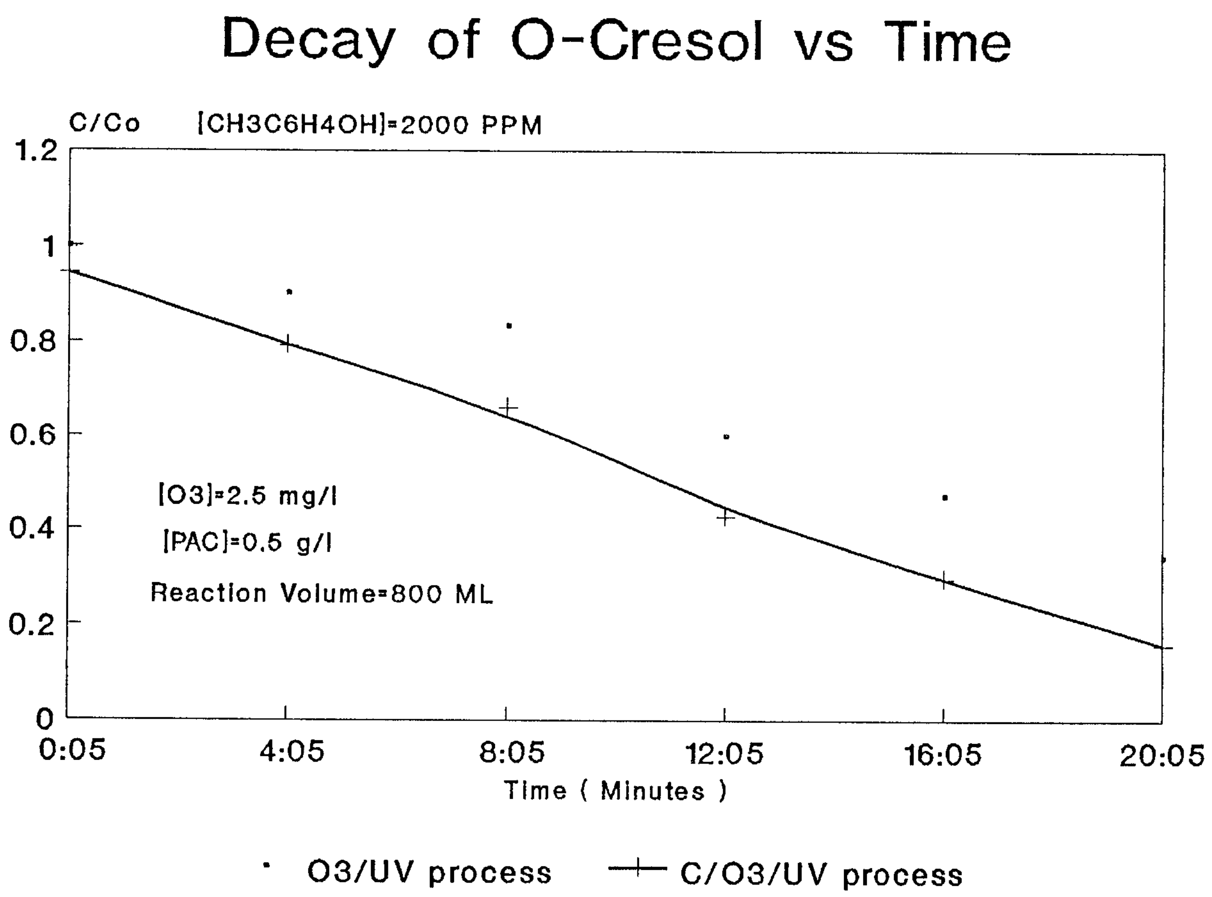
Figure 6

Decay of Aniline vs Time



Comparision of O3/UV & C/O3/UV process

Figure 7



Comparision of C/O3/UV & O3/UV process

Figure 8

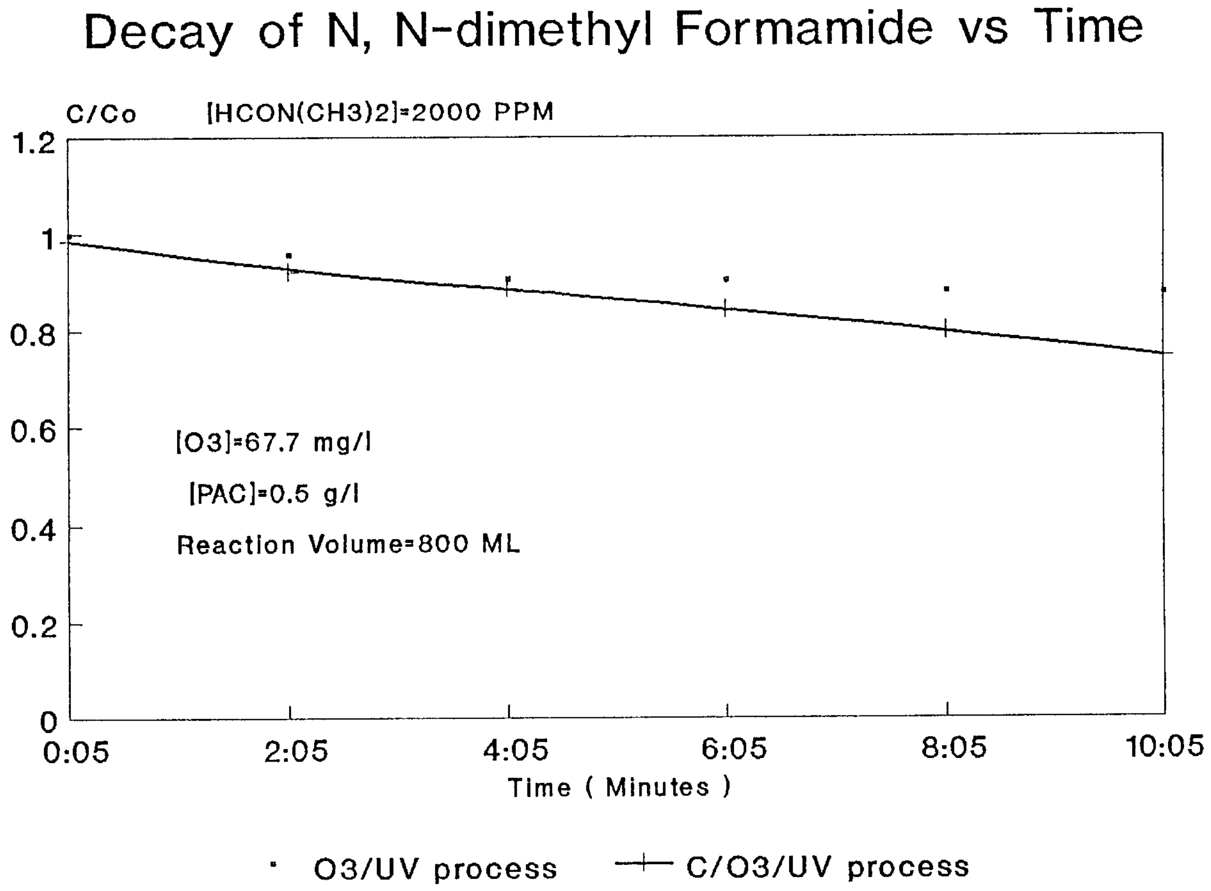


Figure 9

Comparision of C/O3/UV & O3/UV proceses

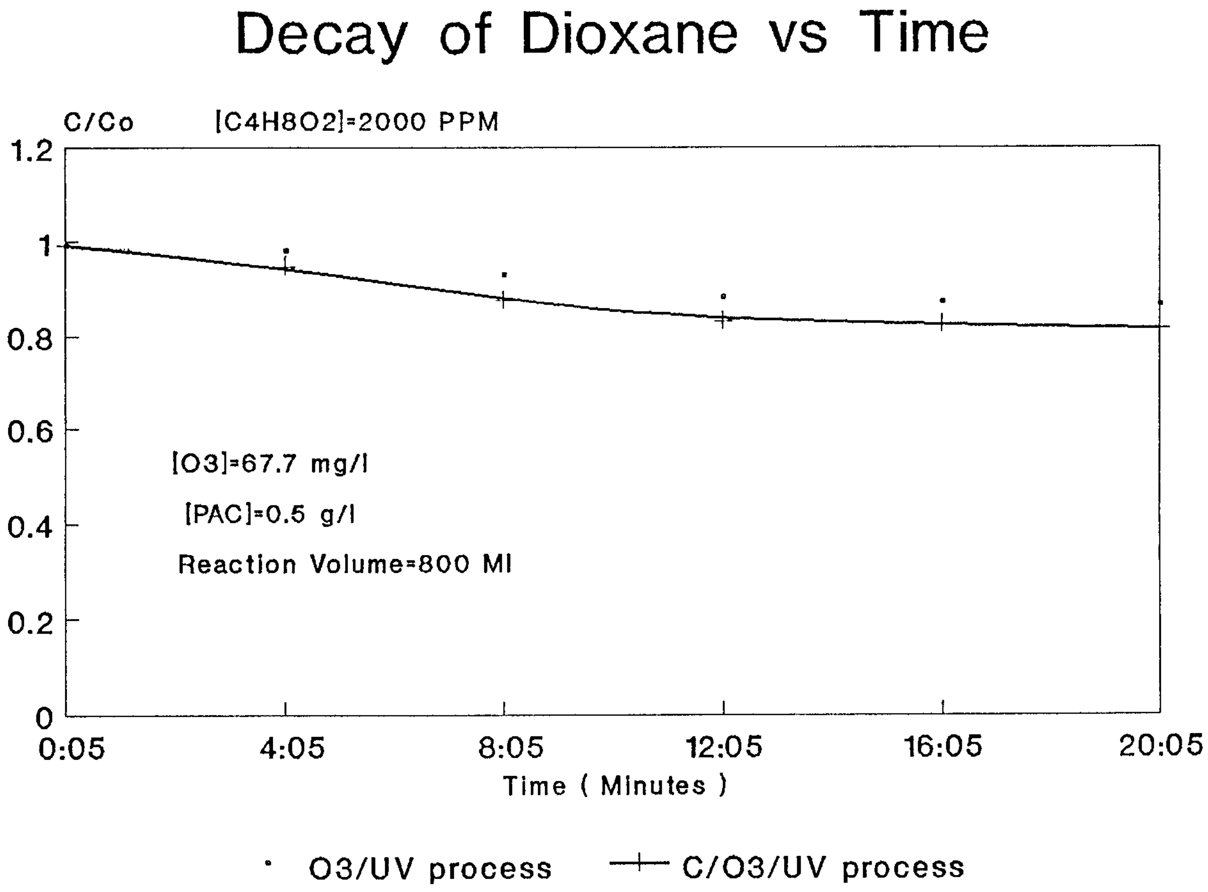
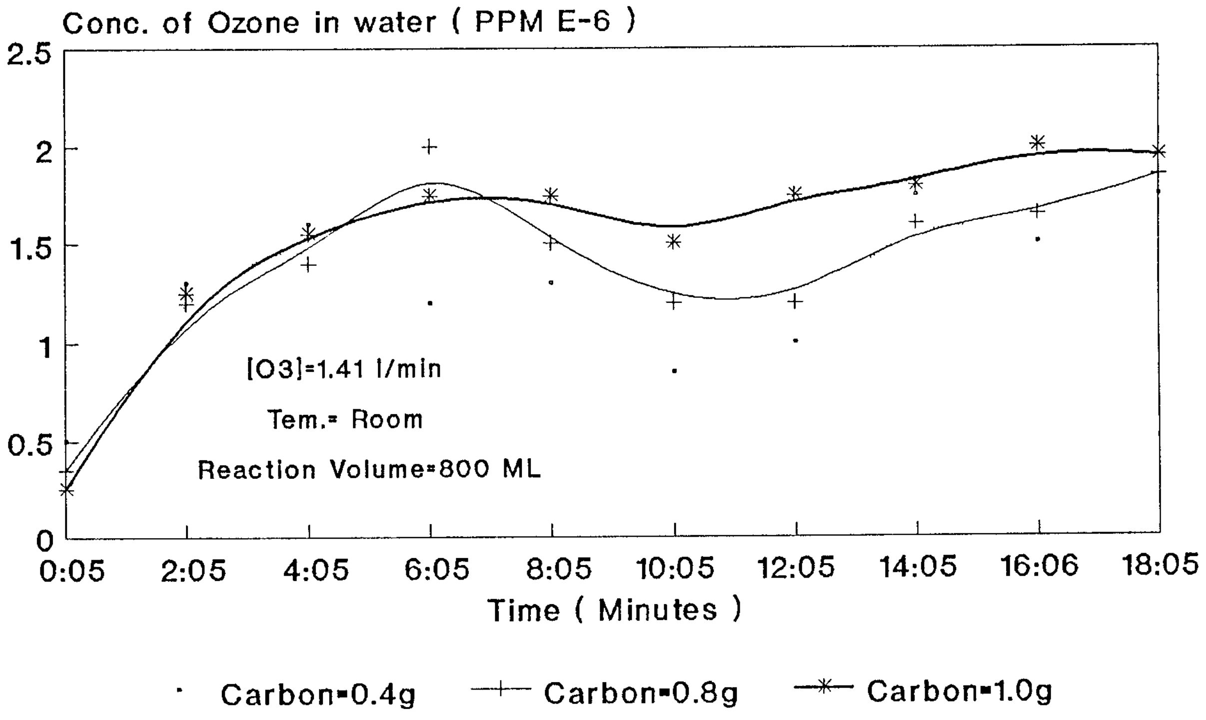


Figure 10

Comparision of C/O3/UV & O3/UV process

Ozone Solubility Under Differ Conditions
Case 1: Solubility vs Time/PAC Dosage

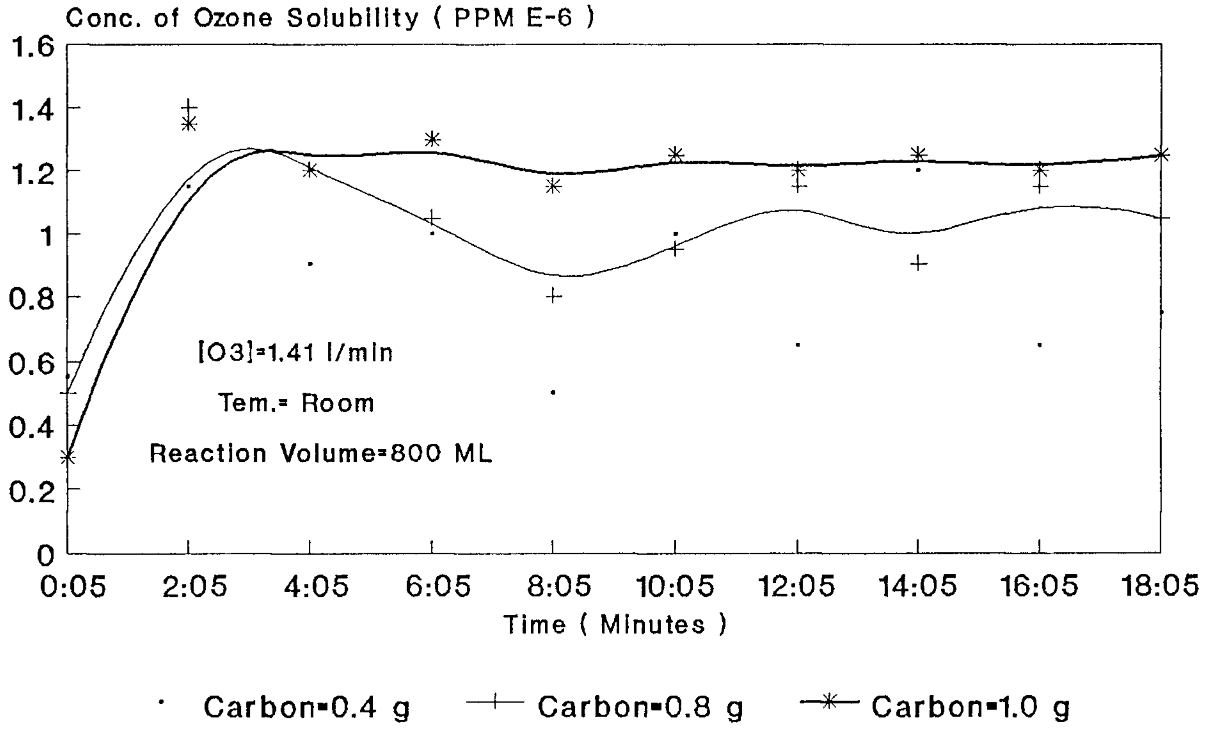


Carbon only (No UV radiation)

Figure 11

Ozone Solubility Under Differ Condition:

Case 2: Solubility vs Time/PAC dosage

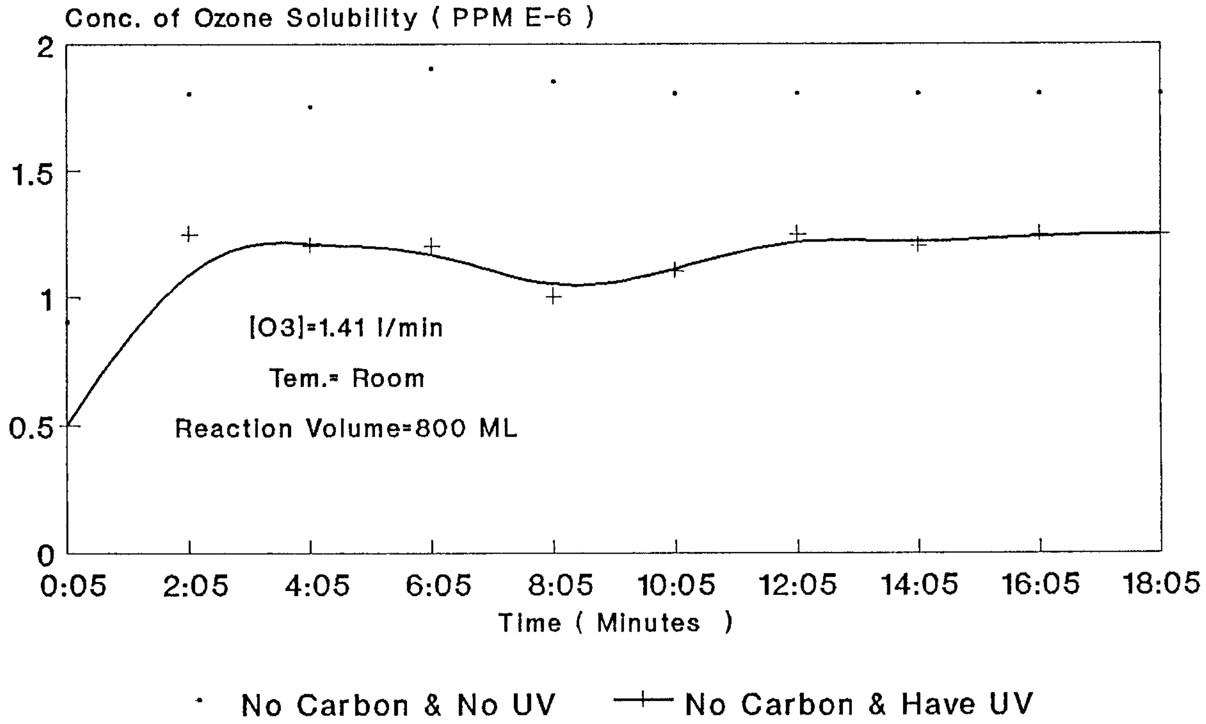


Integrated C/O3/UV process

Figure 12

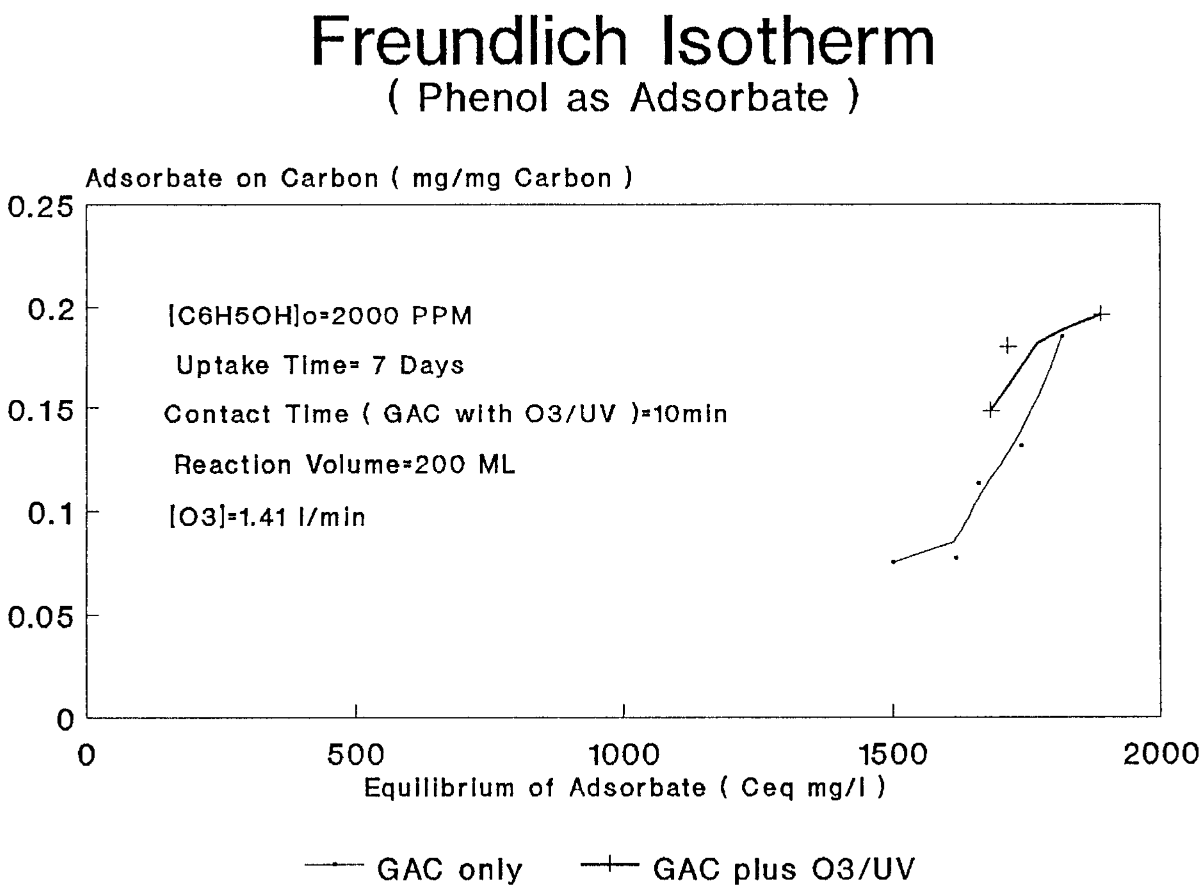
Ozone Solubility Under Differ Condition:

Case 3: Solubility vs Time/UV Radiation



Comparision of O3 & O3 + UV Process

Figure 13



Comparision of GAC only & O3/UV Cond.

Figure 14

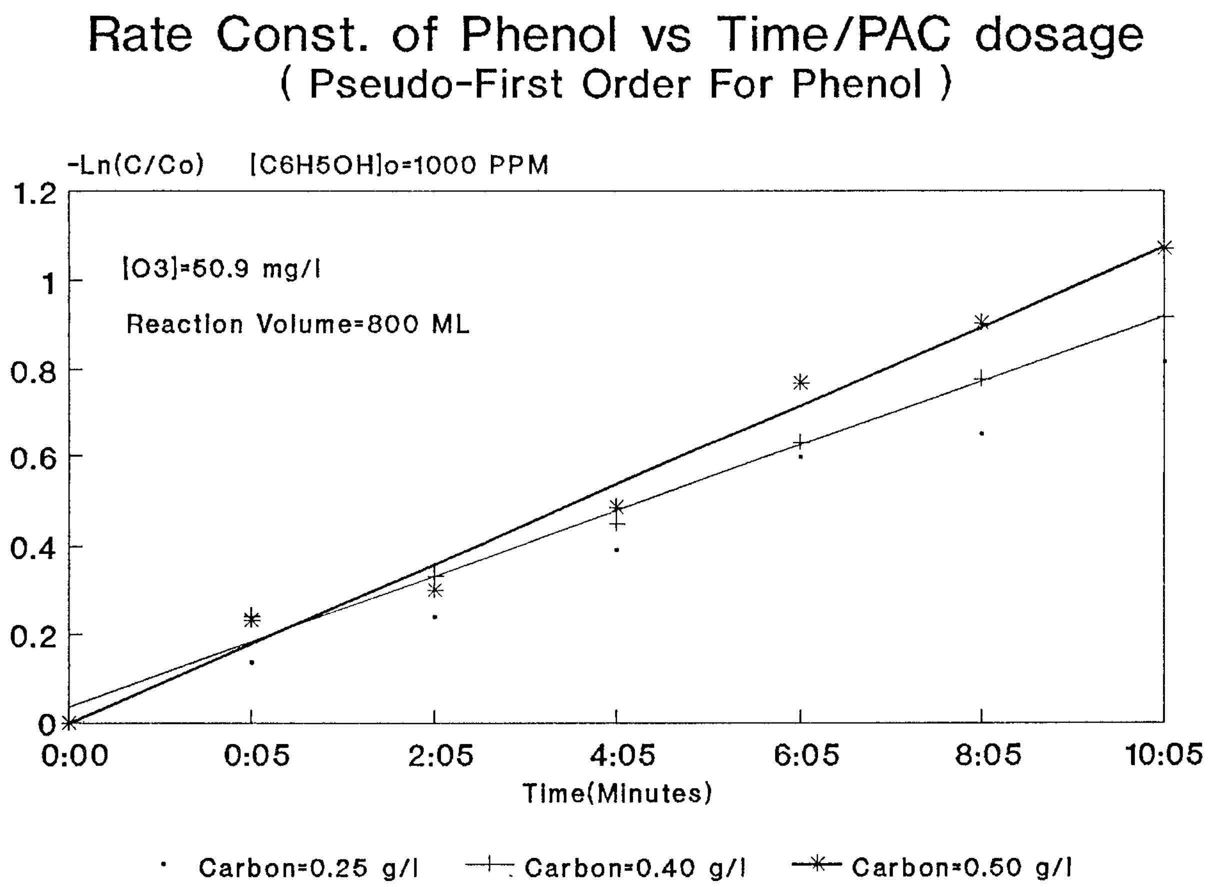


Figure 15

Integrated Charcoal/Ozonation/UV

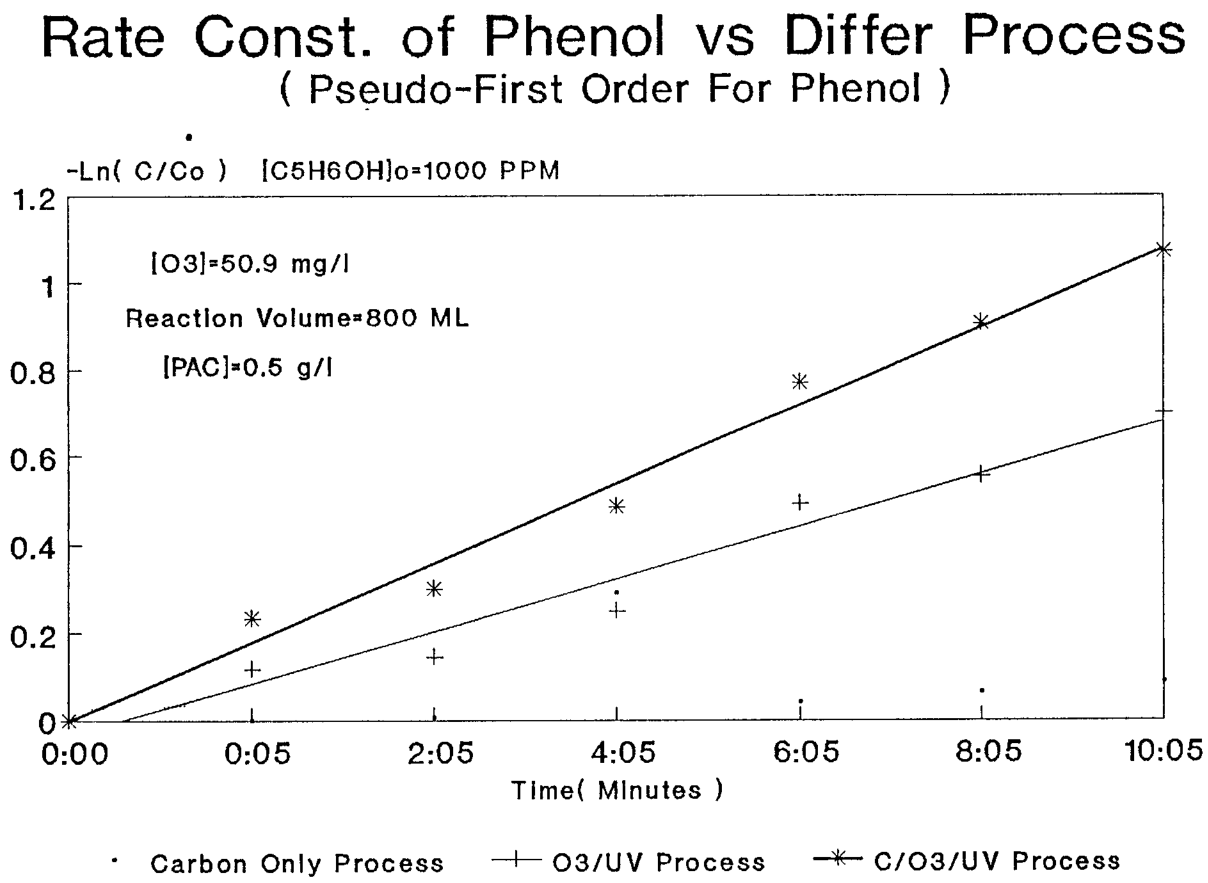


Figure 16

Comparision of C only & O3/UV & C/O3/UV

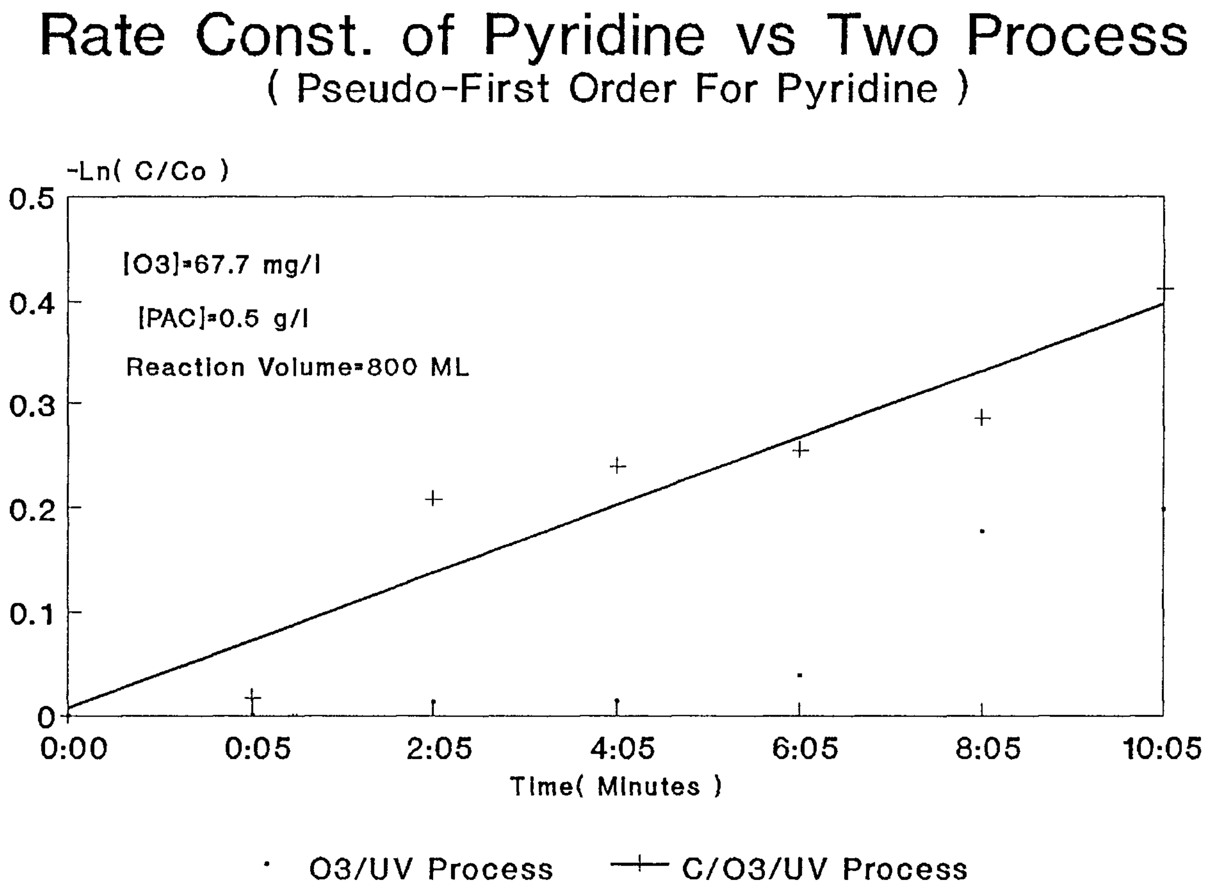


Figure 17

Comparision of O3/UV & C/O3/UV

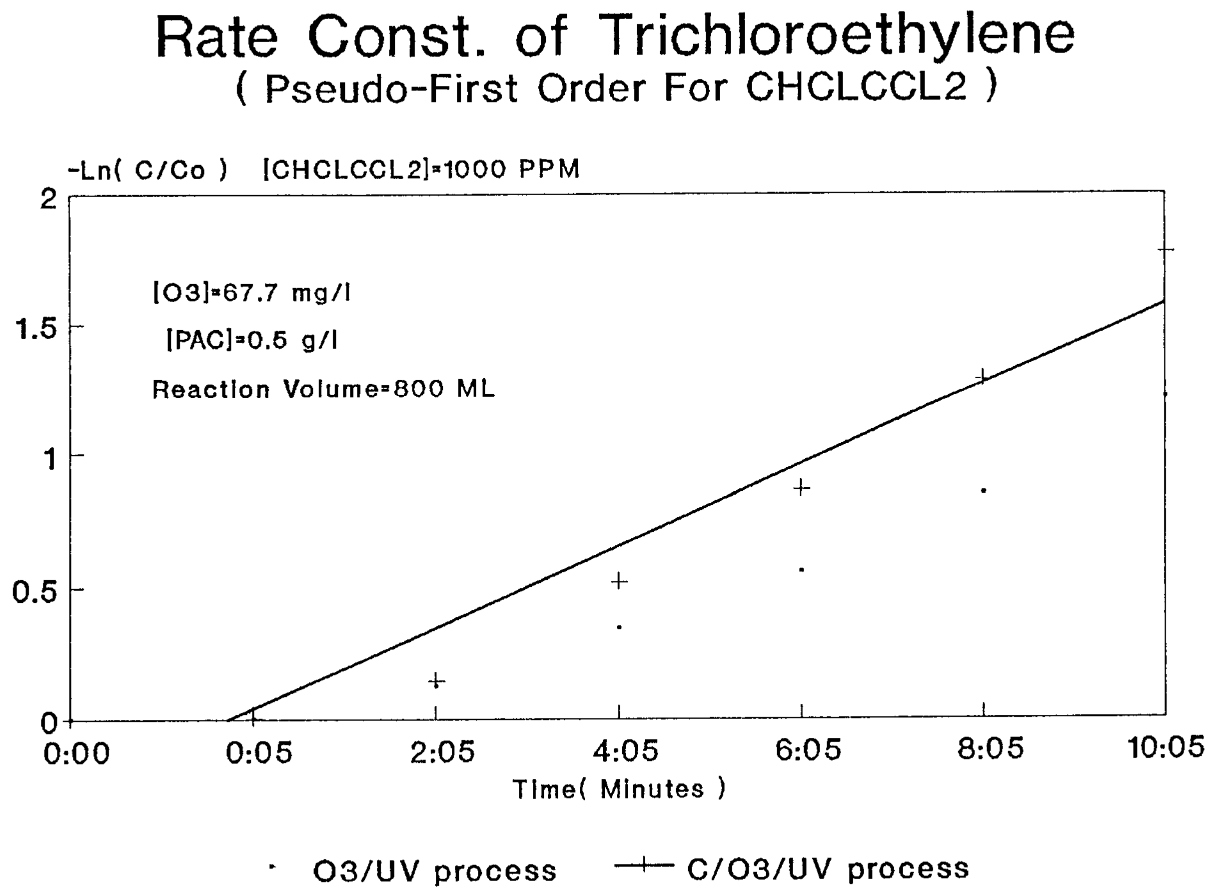


Figure 18

Comparison of O3/UV & C/O3/UV

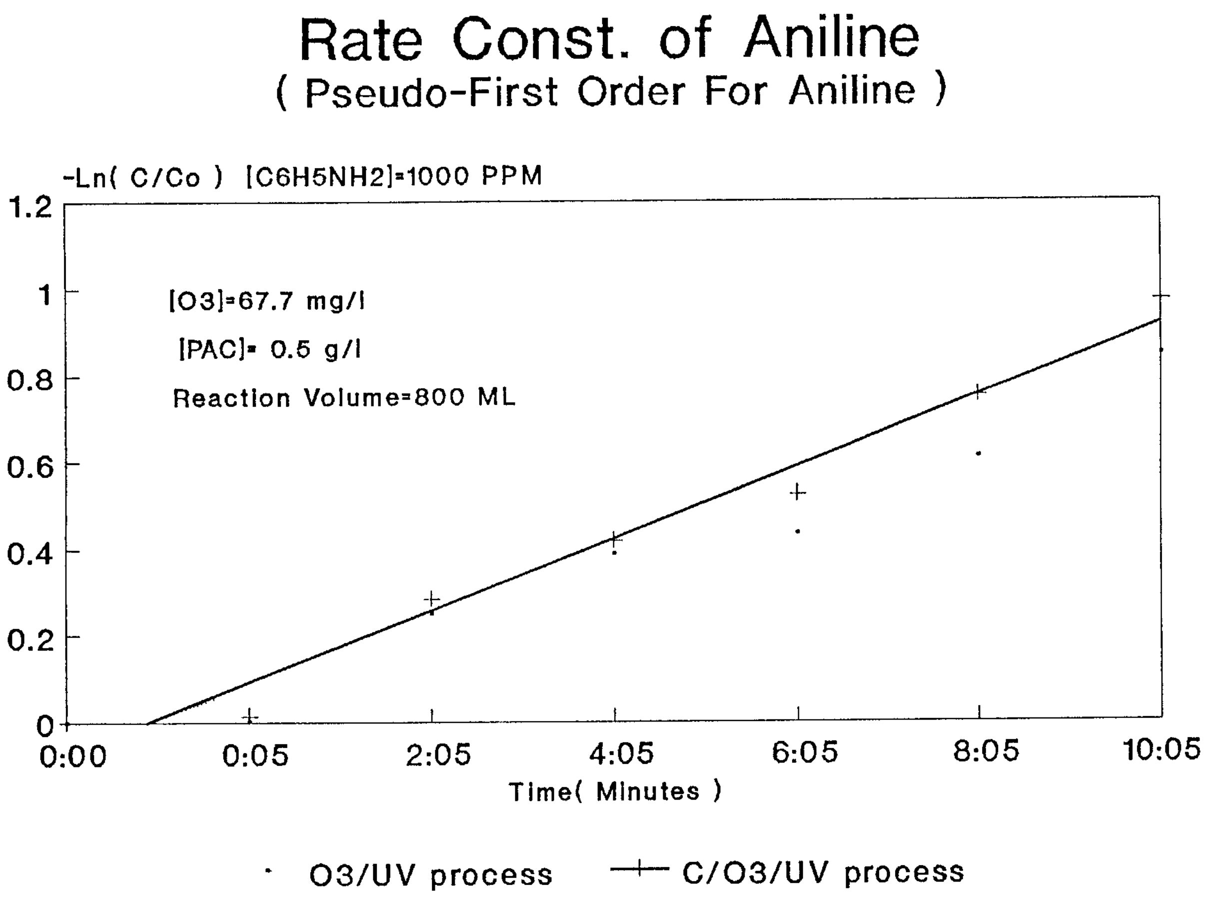
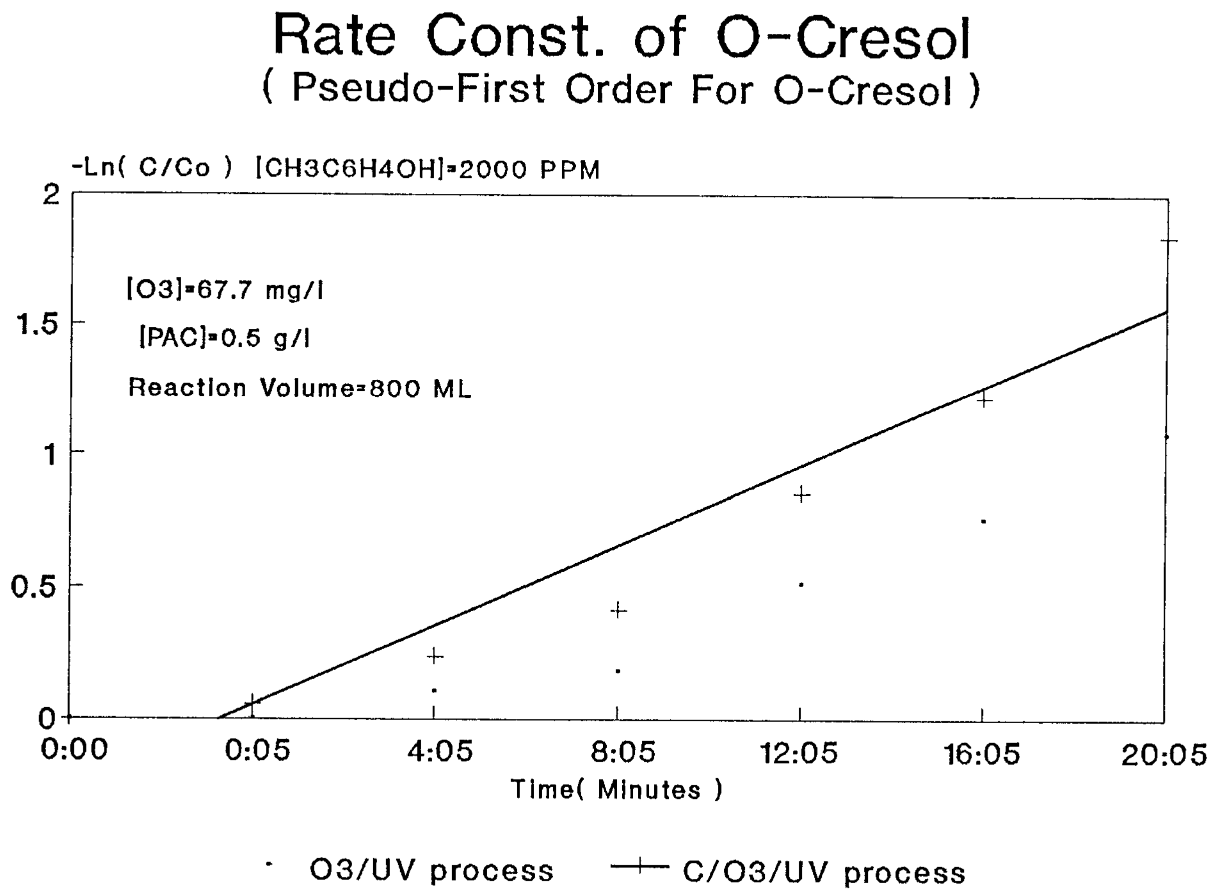


Figure 19

Comparison of O3/UV & C/O3/UV



Comparison of O3/UV & C/O3/UV

Figure 20

Rate Const. of N,N-Dimethyl Formamide ^{2}

(Pseudo-First Order For HCON(CH3)2)

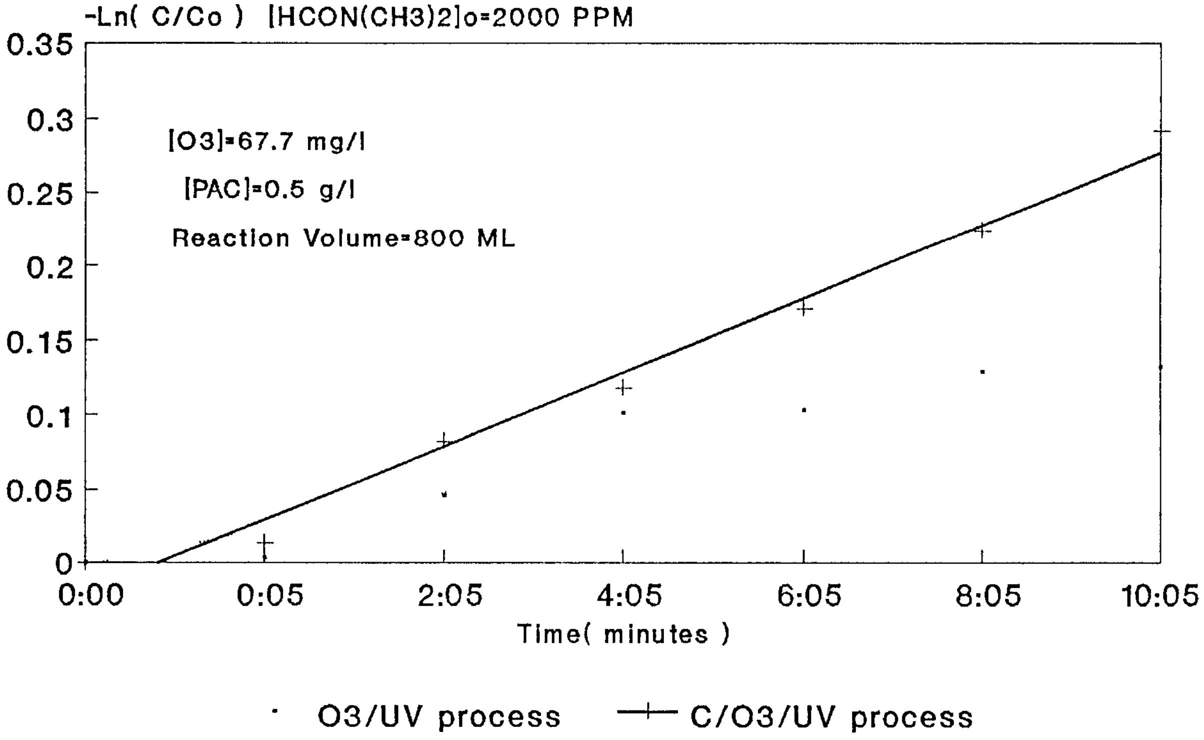


Figure 21

Comparison Of O3/UV & C/O3/UV

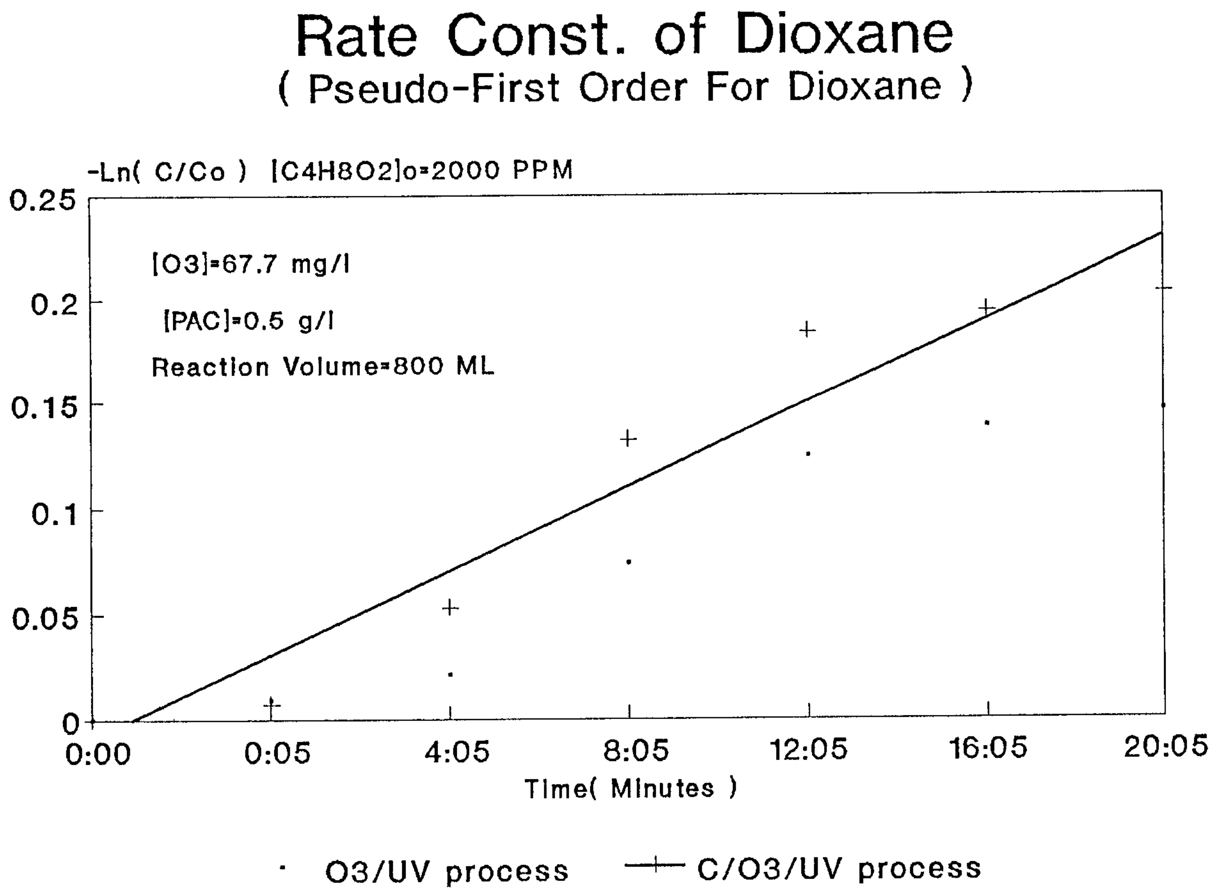


Figure 22

Comparison of O3/UV & C/O3/UV

BIBLIOGRAPHY

1. Chemisinoff, P.N., and Morresi, A.C. "Carbon Adsorption Applications." *Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc.* (1978)

2. Birdsalt, Jenkins, and Spadinger. "Analytical Chemistry." Vol.24 (1952): 662.

3. Staehelin, J. and Hoigne, J. "Decomposition of Ozone in water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide." *Environ. Sci. Technol.* 16 (1982): 676-810.

4. Glaze, W.H. "Drinking Water Treatment with Ozone." Envir*on. Sci. Technol.* 21 (1987): 224-230.

5. Hoigne, J., and Bader H. "Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water." *Water Res.* 17 (1983): 173-183.

6. Levenspiel. "Chemical Reaction Engineering, 2nd Ed." *John Wiley & Sons, Inc.* (1972)

7. Rice, R.G. "Ozone Oxidation Products -- Implications for Drinking Water Treatment." *Biohazardous of Drinking Water Treatment, Lewis Publishers.* (1989)

8. Singer, P. "American Water Works Association Journal." Vol.82, No.10 (1990): 78-88.

9. Stopka. "Ozone Is Primary Disinfectant." *Water Engineering & Management. Vol.*137, No.6. (1990): 19.

10. Wang, Y. "Ozone Technology Removes Organics from Groundwater." *American Water Works Association Journal. Vol.*81, No.6. (1989): 124.

11. Oehlshlaeger, H.F. "Reactions of Ozone with Organic Compounds, Ozone/Chlorine Dioxide Oxidation Products of Organic Materials." (1978)

12. Rice, R.G. "Ozone for the Treatment of Hazardous Materials." *AICHE Symposium Series, Water.* (1980)

13. Maloney, S.W., Suffet, T.H., and Bancroft, K. "Ozone-GAC Following Conventional US Drinking Water Treatment." *American Water Works Association Jour.* 77 (1985): 66-73.

14. Skoog, D. "Principles of Instrumentral Analysis, 3rd Ed." *Saunders College Publishing.* (1985)

15. Battino, R., Rettich, and Tominage, T. "The Solubility of Oxygen and Ozone in Liquids." *J. Phys. Chem. Ref. Data.* 12 (1983): No.2.

16. "Standard Methods for the Examination of Water and Wastewater." *15th Ed., APHA, Washington, D.C.* (1980)

17. Bader, H., and Hoigne, J. "Determination of Ozone in Water by the Indigo Method." *Water Res.* 15 (1981):449.

18. Taube, H., and Bray, W.C. "Chain Reactions in Aqueous Solutions Containing Ozone, Hydrogen Peroxide and Acid." *Jour. of Am. Chem. Soc.* 62 (1940): 3555-3577.

19. Fogler, H.S. "Elements of Chemical Reaction Engineering." *Prentice-Hall, Inc., New Jersey.* (1986)

20. Khan, S.R., Huang, C.R., and Bozzelli, J.W. "Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation." (1987)

21. Jain, K.K., and Bryce, A.J. "Feasibility of Munitions Wastewater Treatment by Adsorption-Oxidation." *Carbon Adsorption Handbook, Ed. Ann Arbor Science Publishers, Inc.* (1978)

22. Hoigne, J. "Mechanisms, Rates and Selectivities of Oxidations of Organic Compounds Initiated by the Ozonation of Water." *Hankbook of Ozone Technology and Application. Ann Arbor Science, Ann Arbor, MI.* (1982)

23. Davis, Allen P., and Wang, C.P. "The Photocatalytic Oxidation of Toxic Organic Compounds." *University of Delaware, Newark, Delaware.* (1990)

24. Sundstorm, D.W., Weir, B.A., and Klei, H.E. "Destruction of Aromatic Pollutants by UV light Catalyzed Oxidation with Hydrogen Peroxide." *The Unversity of Connecticut Storrs, Connecticut.* (1991)

25. Peyton, Gray R., Huang, Francls Y., Jimmle, L. Burleson, and Glaze, William H. "Destruction of Pollutants in Water with Ozone in Combination with Ultra violet Radiation. 1. General Principles and Oxidation of Tetrichloro ethylene." *Environ. Scl. Technol.* 16 (1982): 448-453.

26. Glaze, William H., Peyton, Gray R., Lin, Simon, Huang, R.Y., and Jimmle, L. Burleson. "Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. 2. Natural Trihalomethane Precursors." *Environ. Sci. Technol.* 16 (1982): No.8.

27. Peyton, Gray R. "Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. 3. Photolysis of Aqueous Ozone." *Environ. Sci. Technol.* 22 (1988): 761-767.

28. Peyton, Gray R. "Understanding and Optimizing Ozone/UV Treatment for the Destruction of Hazardous Organic Compounds in water: Mechanism efficiency and by products." *Illinois Stata Water Survey Champaign.* (1990)

29. Wentz, C.A., Jr. "Hazardous Waste Management." *McGrawHill, New York* (1989)

30. Ho, Kin. "Charcoal Catalyzed Ozone Decomposition of Organic Pollutants in Water." *Master Thesis, NJIT.* (1991)

31. David A. Vaccari, Joseph W.Bozzelli, and Dominiz Grasso."Integrated Adsorption/Oxidation Process: Bench-Scale Feasibility Study with Actual Industrial Wastes." (1991)

32. Weber, W., and O. Corpaciogln. "Catalytic Oxidation of Cyanide." *36th Purdue*

Industrial Waste Conference, Purdue Univ., West Lafyette, In. (1981)

33. Bernardin, F. "Cyanide Detoxification Using Adsorption and Catalytic Oxidation on Granular Activated Carbon." *Jou. Water Poll. Control Fed.* 45 (1973): No.2.