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The degradation of trace pollutants in wastewater

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Title of Thesis: The Degradation of Trace Pollutants
in Wastewater
Christine M. Cheng, Master of Science, 1987
Thesis directed by: Dr. Richard Parker,
Professor of Chemistry

ABSTRACT

The effect of different treatments on the degradation of chlorinated organic pollutants in wastewater has been studied. The model compound investigated was para-chlorophenol. The different treatments used were ozone, UV irradiation, ultrasound, air flow and pure oxygen.

It is concluded that ozone has the greatest effect, ozone-UV irradiation follows closely behind, and UV irradiation has much less of an effect in degrading the p-chlorophenol.

P-chlorophenol was found to have an immeasurably slow degradation rate when treated with air even at an elevated temperature of 55⁰C.

The oxygen, at room temperature, showed a degradation of p-chlorophenol which, although small, was much greater than that of air at the higher temperature.

THE DEGRADATION OF TRACE POLLUTANTS IN WASTEWATER

BY

CHRISTINE M. CHENG

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Environmental Science/Toxicology Option.

1987

APPROVAL SHEET

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This thesis is dedicated to my sister Theresa and my parents with love.

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Chapter 1 Theory

Wastewaters derived from industrial processing facilities are often found to contain a wide variety of organic compounds of great complexity and stability. These wastewaters have placed a severe burden on present water treatment plants which are often inadequate for toxic substances such as phenols, cyanides, amines, chlorinated hydrocarbons, etc.

Wastewater from coal tar processing, phenol recovery, and coking operations, for example, usually contains a large amount of phenols as well as other components.

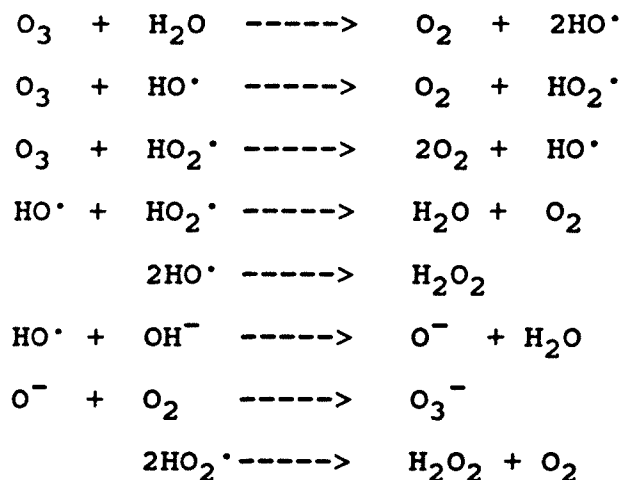
Chemical oxidation is one of the methods of treating wastewater pollutants. However, not all pollutants are removed by oxidants alone. Some compounds may not oxidize to completion but reach a residual equilibrium concentration. Conventional wastewater treatment processes can be augmented by tertiary treatment processes such as carbon adsorption, ion exchange, reverse osmosis, etc. Such concomitant treatments can be expected to provide effluents which meet projected zero discharge standards. Unfortunately, results indicate that tertiary processes in

a number of cases have not removed all the undesirable, difficult to oxidize wastewater species. Some of the species when chlorinated, in fact, produce even more highly undesirable discharge species¹. There is a definite need for a process which either takes these difficult-to-oxidize species to complete oxidation or converts them to biodegradable products.

Ozone, chlorine, chlorine dioxide, permanganate ion, and chloramine are the commonly used chemical oxidants in the United States. Use of any one of these does not necessarily result in complete oxidation of the pollutants. Further, as stated above, in some cases undesirable by-products are obtained in the oxidation process. For example, chlorine with an oxidation potential of 1.36 volts is a powerful disinfectant that has been used extensively for water treatment. Beller et. al. have reported the formation of trichloromethane which makes chlorination an undesirable oxidation². Ozonation is a good alternative to chlorination since ozone readily decomposes to oxygen in water leaving no by-products that need to be removed.

The decomposition of ozone in water occurs with a half life on the order of a few minutes and is favored by alkaline pH's.

A comprehensive review of the chemistry of ozone in the treatment of water has been reported by Peley³. Although the kinetics of decomposition of ozone in aqueous solution are uncertain, Peley has suggested the following mechanism:



In this mechanism the hydroxyl radical is believed to be the most important reactive intermediate in the decomposition of ozone.

Table I presents the oxidation potentials of ozone and its decomposition species for comparison purposes⁴. The hydroxyl radical with an oxidation potential of -2.80 volts is a more powerful oxidizing agent than ozone, oxygen, hydroxyl radical, hydrogen peroxide, or perhydroxyl

radical. Optimizing the conditions for the decomposition of ozone should facilitate the production of hydroxyl radicals and this in turn would facilitate the degradation of organic molecules. This direct relationship between the rate of decomposition of ozone and the rate of organic oxidation has been demonstrated experimentally by Hewes and Davison⁵.

Table I. Oxidation Potential of Ozone and its Decomposition Species.

Species		Oxidation Potential
Name	Formula	(Volts)
Ozone	O ₃	-2.07
Hydroxyl Radical	HO [•]	-2.80
Hydrogen Peroxide	H ₂ O ₂	-1.77
Perhydroxyl Radical	HO ₂ [•]	-1.50
Oxygen	O ₂	+0.41

Temperature and pH are factors which affect the decomposition of ozone in aqueous solution. A high pH favors the formation of the hydroxyl radical⁶. However, higher pH disfavors the complete removal of the organic

pollutants. One might expect that high temperature would facilitate the oxidation process. For degradation by ozone this is impractical because of the decreased solubility of ozone at elevated temperatures⁷.

Another possibility to accelerate ozone decomposition would be the use of ultraviolet radiation. This is a very effective method since ozone absorbs radiation of 254 nm wavelength and decomposes very rapidly in water⁸.

The use of free radicals in the degradation of pollutants such as phenols has been shown to be a viable system for treatment of industrial wastewaters as well as biological sludges⁹.

Oxidation of organics can be accomplished in a brief time via UV exposure. The combined use of ultrasonic cavitation and UV radiation in the presence of H_2O_2 and a catalyst is the basis of the Enercol Process⁹.

Ultrasound is another possibility to be explored to affect the degradation of trace pollutants in water. When the ultrasound waves are applied to liquids a process called "cavitation" occurs. Cavitation is the rapid

formation, growth, and subsequent implosive collapse of gas vacuoles. The result can be an extremely large increase in the rates of reaction processes.

The chemical reaction caused by ultrasound can be described as composed of three phenomena. Firstly, there is a rapid movement of fluids caused by variation of sonic pressure. Secondly, also the most important, is cavitation. Thirdly, there is microstreaming where a large amount of vibrational energy is put into small volumes with little heating.

It has been demonstrated that ultrasound can facilitate organic chemical processes in a wide variety of situations. For example, ultrasound has been shown to cause cleavage of substituted benzenes, thiophenes, and furanes¹⁰; to depolymerize polymethylsiloxane¹¹; to enhance acid hydrolysis of methylacetate¹²; to cause degradation of aspirins¹³, and amino acids¹⁴. The use of ultrasound can enhance the chemical reaction.^{15,16,17}

Based upon these successes, it might be expected that ultrasound can be used to enhance the degradation of organic molecules in water.

In this work para-chlorophenol has been selected as a model compound to study the degradation of trace organic pollutants in water. The object is to study the enhancement of the degradation of the model organic molecule using oxidants, ultraviolet radiation, and ultrasound. Temperature and pH effects will also be studied.

Chapter 2 Experimental Apparatus and Procedures

Para-chlorophenol Experiments

The reagent used was 99% pure para-chlorophenol which was obtained from Aldrich Chemical Company, Inc., Milwaukee, WIS. The sodium phosphate dibasic obtained from Matheson Coleman and Bell, East Rutherford, NJ was used to buffer the p-chlorophenol. The concentration of sodium phosphate dibasic was 0.2 M.

The properties and hazards of chemicals used in this experiment are listed in Table II. Gloves, facemasks, etc were used as required when working with the pure chemicals.

Samples of reaction mixtures were collected periodically. In all cases the first few milliliters were used for rinsing the pipets and then discarded.

Sample collection tubes were rinsed with distilled water and dried before use. The temperatures and pH values were monitored throughout the experiments. For the

different experimental runs, control runs were also performed for comparison.

Table II. Chemicals properties and Hazards

Names	Formula	Molecular Weight	Appearance	Hazards
p-chlorophenol	$\text{ClC}_6\text{H}_4\text{OH}$	128.56	White to off-white crystalline solid	Causes severe eye burns harmful if inhaled, harmful if absorbed
Sodium Phosphate, Dibasic	Na_2HPO_4	141.96	White crystals	Low hazard for usual industrial handling
Hydrochloric Acid	HCl	36.46	Clear solution	Causes skin and eye burns
Sodium Hydroxide	NaOH	40.00	White pellets	Causes severe skin and eye burns, harmful if inhaled

A. Ozone Degradation Experiments

The model T-816 Ozone Generator was obtained from Wilsbach Ozone Systems Corp. It can produce a minimum of 16 g of ozone per hour. The oxygen pressure was maintained at 8-9 psig.

The 200 mL of buffered p-chlorophenol were introduced into a 250 mL flask. Tygon tubing was used to connect the outflow of the ozone generator to the flask. Aliquots of reaction samples were taken from the same sample point at different time intervals and were stored in a refrigerator overnight.

The concentrations of p-chlorophenol were varied from 1.0×10^{-4} M to 2.0×10^{-3} M. The pH values of p-chlorophenol were varied from 5.00 to 10.00. The model 601A pH meter from Orion Research Inc. was used to adjust pH values.

In most cases the Gilford RESPONSE Spectrophotometer was used for absorbance analysis. In some cases the model Coleman 571 Perkin-Elmer Spectrophotometer was used. The samples were warmed back to room temperature before analysis.

B. Ultraviolet Light Degradation Experiments

The Sperti Sunlamp used as the ultraviolet light source was obtained from Cooper Hewitt Electric Co., KY.

200 mL of p-chlorophenol solution buffered in 0.2 M Na_2HPO_4 was introduced into a 250 mL beaker and then exposed to the UV lamp placed 10 inches above the sample flask. Aliquots were taken from the same sample point at different time intervals and then stored in a refrigerator overnight.

The RESPONSE Spectrophotometer obtained from Gilford Instrument Laboratories, Oberlin, OH. was used for absorbance analysis. The samples were warmed back to room temperature before analysis.

The concentrations of p-chlorophenol were varied from 2.0×10^{-4} M to 2.0×10^{-3} M. The pH values were varied from 8.00 to 10.00.

C. Ultrasound and Ozone Degradation Experiments

The model W-375 Sonicator from Heat Systems - Ultrasonics, Inc. was used. The power output control was kept at 8.0 (range from 1 to 10) and the duty cycle was kept at 80% " on ".

An ozone supply was maintained at the same time by means of a tube connected to an ozone generator.

The concentration of p-chlorophenol was $4.0 * 10^{-4}$ M. The pH values were 6.00 and 8.00. Runs were made at room temperature. Samples were withdrawn every hour and stored in the refrigerator overnight.

D. Other Experiments

In a similar manner, the experiments below were carried out.

1) Air Experiments

The concentration of p-chlorophenol was $2.0 * 10^{-4}$ M. The pH values were varied from 8.00 to 10.00. Temperatures were kept at 55°C. Air from the house airline was bubbled through the solution in the reaction vessel at a steady flow rate throughout the runs.

2) Ozone and U.V. Light Experiments

The concentrations of p-chlorophenol were $1.0 * 10^{-3}$ M and $2.0 * 10^{-3}$ M. The pH values were 8.00 to 10.00.

3) U.V. Light and Oxygen Experiments

The concentration of p-chlorophenol was $1.0 * 10^{-3}$ M. The pH value was 8.00. 99.9% pure oxygen from a cylinder was bubbled through the buffered para-chlorophenol solution.

Chapter 3 Results and Discussion

A. Effect of Ozone on Degradability of p-Chlorophenol

The spectrum of 1.0×10^{-3} M p-chlorophenol was run at pH 9.00 and room temperature (Figure A). An absorption peak appeared at 281 nm wavelength. Thus 281 nm was selected as the wavelength to monitor in the kinetic experiments. By examining the decrease of absorption at λ_{\max} as a function of time, the degradability of p-chlorophenol can be determined. By doing linear regression analysis, the slope, which represents the change in absorption per unit time, can be calculated; this is used as a measure of the rate of degradation.

A series of various concentrations of p-chlorophenol was treated by ozone to determine the effect of ozone on the degradability of p-chlorophenol. The runs were performed at pH 9.00 and room temperature. Table III represents the absorbance of p-chlorophenol as a function of time for several initial concentrations of p-chlorophenol. The effect of ozone on the degradability of p-chlorophenol with various concentrations is shown in

Figure B. The figure was prepared by use of the computer software package "Sigmaplot." The data is seen to fit the equation of a straight line, and the slope represents the rate of degradation. The rates thus obtained are given in Tables III and IV.

Table III. The Absorbance of p-chlorophenol vs Time

(PCP) ₀ M	T= 0	OD			Linear Regression		
		0	5	10(min)	Slope	Intcp	C.C.
0.0020	1.670	1.162	0.702	-0.0968	1.662	-0.999	
0.0010	0.741	0.349	0.146	-0.0595	0.710	-0.984	
0.0005	0.407	0.145	0.044	-0.0363	0.380	-0.969	
0.0002	0.145	0.029	0.000	-0.0232	0.145	-1.000	
0.0001	0.058	0.000	0.000	-0.0160	0.058	-1.000	

These are the experiments where p-chlorophenol was treated with ozone; absorbances are at $\lambda_{\max} = 281$ nm.

Table IV. Degradation Rate of p-chlorophenol by Ozone at pH 9.00

(PCP) M	R _o (Slope)	$\frac{R_o}{(PCP)_o}$	$\frac{R_o}{[(PCP)_o]^2}$	$\frac{R_o}{[(PCP)_o]^{0.68}}$
0.0020	-0.0968	48.4	24200	6.6
0.0010	-0.0595	59.5	59500	6.5
0.0005	-0.0363	72.6	145200	6.4
0.0002	-0.0232	116.0	580000	7.6
0.0001	-0.0160	116.0	1160000	6.1

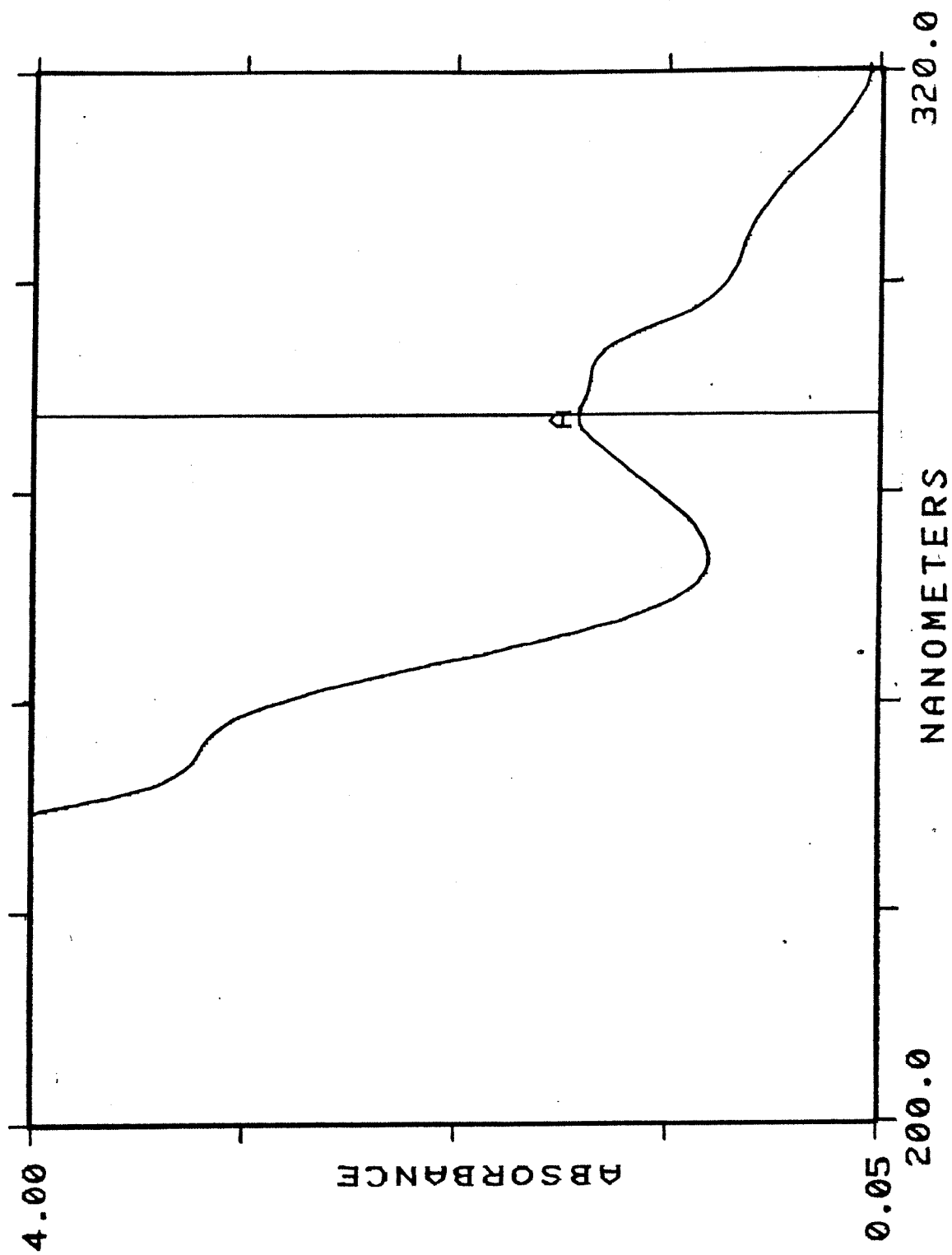
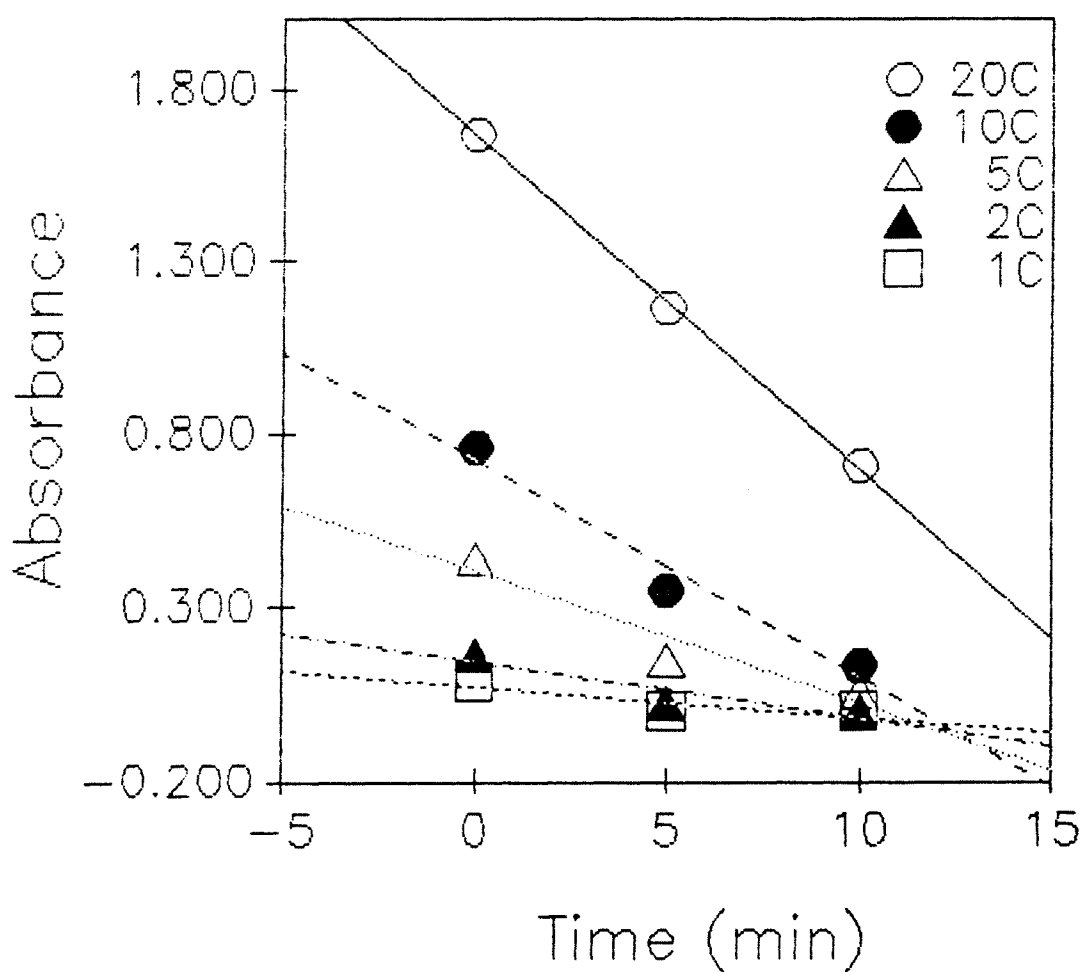


Figure A. Spectrum of p-chlorophenol

Figure B. The Effect of Ozone on the degradability of PCP With Concentration



$C=1 \cdot E-04M$

Assuming the kinetics fits a simple order rate law, then the experimental data would fit the equation

$$\text{Rate}_0 = k * [(\text{PCP})_0]^n \quad \text{EQN1}$$

where Rate_0 is the initial rate of degradation of p-chlorophenol,

$(\text{PCP})_0$ is the concentration at time zero,

k is the reaction rate constant,

and n is the order of reaction.

The values of $\text{Rate}_0/(\text{PCP})_0$ and $\text{Rate}_0/[(\text{PCP})_0]^2$ have been calculated to check if the data fit simple first or second order kinetics. The results presented in Table IV indicate the values in each case are not constant and thus the data does not fit the simple first or second order kinetic rate plot.

To determine the order which best describes the data, EQN1 is put in the form

$$\log \text{Rate}_0 = \log k + n \log (\text{PCP})_0 \quad \text{EQN2}$$

By doing linear regression analysis of $\log \text{Rate}_0$ vs $\log (\text{PCP})_0$, the parameters below are obtained

Correlation Coefficient = -0.995

Intercept = 0.821 = $\log k$, and $k = 6.62$

$$\text{slope} = 0.68 = n$$

Table IV presents the values of $R_0/[(\text{PCP})_0]^{0.68}$ for comparison purposes. Within the experimental error of ± 0.4 the calculated values of the rate constants are consistent, with the exception of the 0.0002 M reaction which appears to be spurious.

Apparently the reaction order is complex. But the order is really of little importance as far as this work is concerned. The intent is to study enhancement of the degradation and not get involved with the intricacies of mechanisms.

To examine the effect of pH on degradation of p-chlorophenol, a series of solutions of $1.0 \times 10^{-3} \text{M}$ p-chlorophenol at various pHs were treated with ozone. Table V represents the initial rate at each pH reported in absorption/min. However, the absorption of p-chlorophenol may change with pH, therefore the data must be corrected with absorption coefficient, ϵ , in $\text{OD cm}^{-1} \text{M}^{-1}$. The experimentally determined values of ϵ are presented in Table V. Thus, the absorptions/min are converted to $[(\text{mole/L})/\text{min}] = \text{Degradation Rate}$ which are also presented in Table V. A plot of degradation rate vs pH is shown in Figure C. There is no observable trend and it is

concluded that pH has little effect on rate of degradation over the range 8.20 to 10.00.

Table V. Degradation Rate of p-chlorophenol with ozone at various pH's

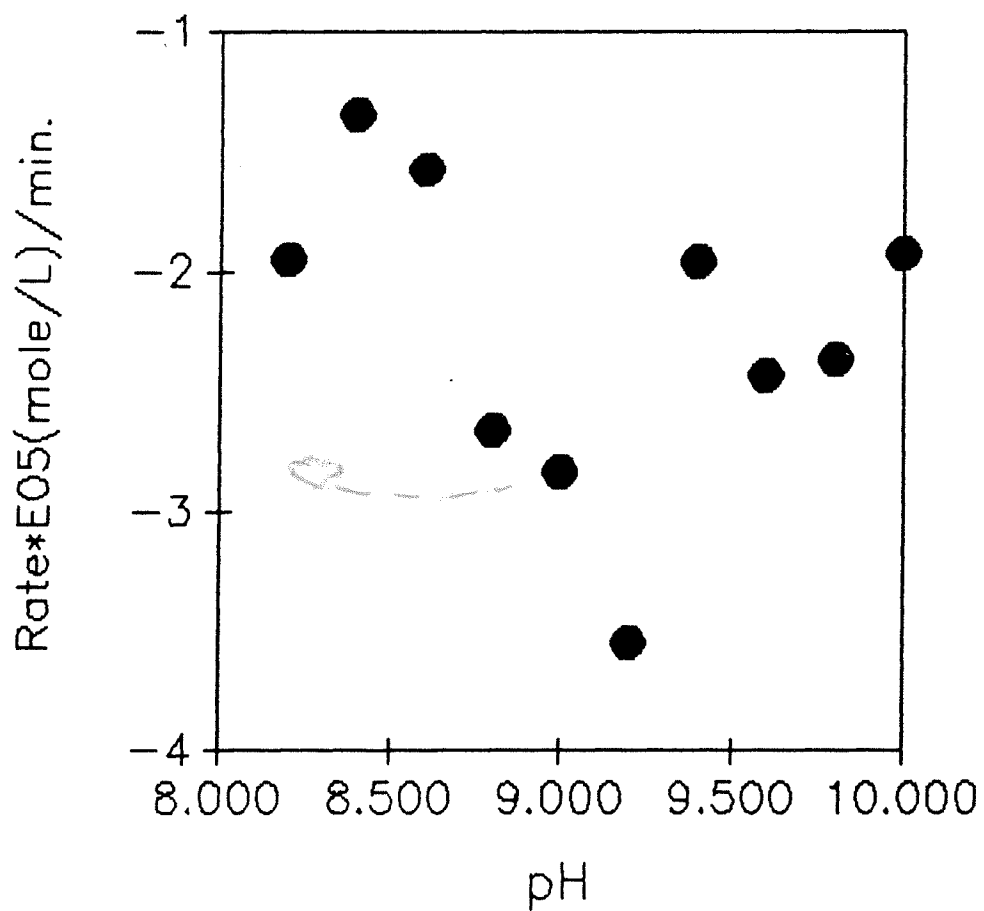
pH	Absorption (OD)	ϵ	Slope (OD/min)* 10^2	Degrad.R. (M/min)* 10^5
8.20	1.5164	1516.4	-2.95	-1.945
8.40	1.4756	1475.6	-1.99	-1.349
8.60	1.5312	1531.2	-2.41	-1.574
8.80	1.5108	1510.8	-4.02	-2.669
9.00	1.4560	1456.0	-4.12	-2.830
9.20	1.4515	1451.5	-5.15	-3.548
9.40	1.3719	1371.9	-2.68	-1.953
9.60	1.3318	1331.8	-3.23	-2.425
9.80	1.3080	1308.0	-3.09	-2.362
10.00	1.4138	1413.8	-2.76	-1.952

The concentrations of p-chlorophenol were 0.0010 M. The absorptions at each pH were at time zero.

B. Effect of UV on Degradability of p-chlorophenol

To determine the effect of UV on the degradability of p-chlorophenol, the same series of various concentrations of p-chlorophenol as were used in the ozone experiments were treated with UV radiation. The experiments were conducted at pH 9.00 and the temperature never exceeded 30°C.

Figure C. Effect of Ozone on the Degradability of PCP at various pH's



The degradation rates of p-chlorophenol by UV are shown in Table VI. In a manner similar to that of the ozone analysis the order which best describes the data can be obtained. The order is 0.73. The results of $R_0/[(PCP)_0]^{0.73}$ are presented in Table VI.

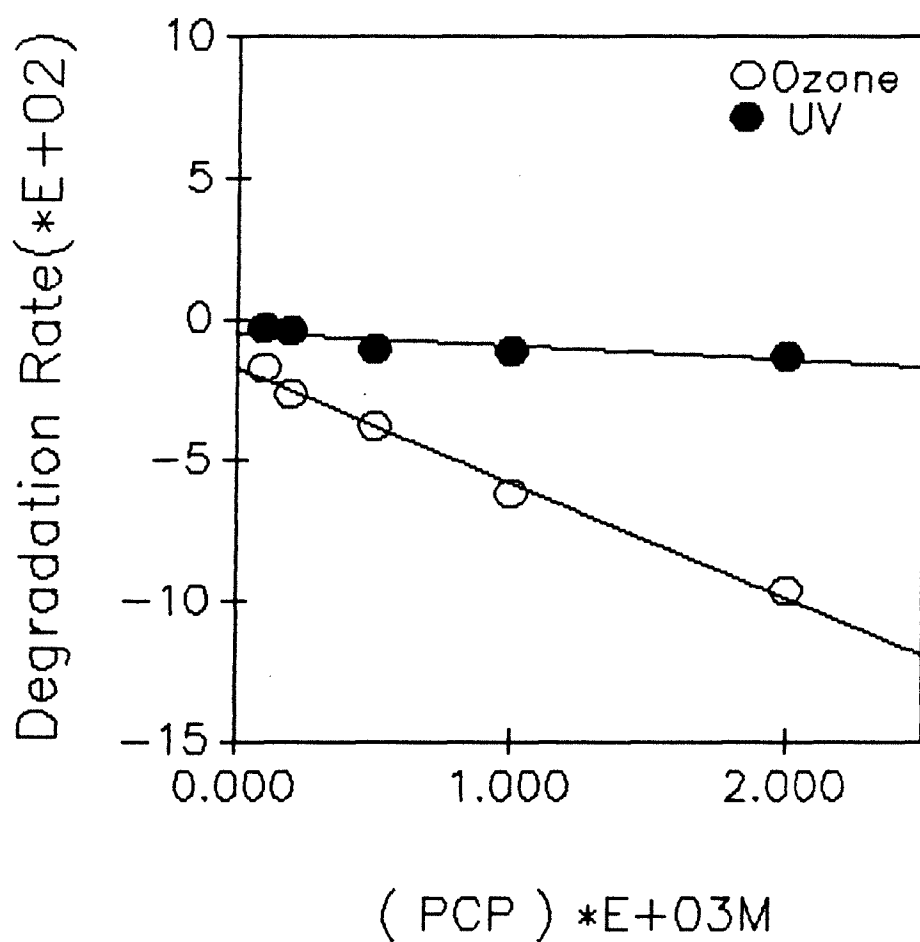
Table VI. Degradation Rate of p-chlorophenol by UV at pH

9.00				
(PCP)	R	$\frac{R}{(PCP)}$	$\frac{R}{[(PCP)]^2}$	$\frac{R}{[(PCP)]^{0.73}}$
M	$\times 10^3$			
0.0020	-13.10	6.55	3275	1.22
0.0010	-8.70	8.70	8700	1.35
0.0005	-5.90	11.80	23600	1.52
0.0002	-2.90	14.50	72500	1.45
0.0001	-1.45	14.50	145000	1.21

For comparison purposes Figure D presents the effect of ozone or U.V. on the degradability of p-chlorophenol with various concentrations. Thus, from Tables IV and VI, and Figure D, it is concluded that UV has less effect on degradability of p-chlorophenol than does ozone.

C. Effect of Ozone and UV on the Degradability of p-chlorophenol

Figure D. Effect of Ozone or UV on the Degradability of PCP with Concentration



In addition to treating the p-chlorophenol with ozone by itself or UV radiation by itself, the same series of various concentrations of p-chlorophenol were treated with both ozone and UV radiation. The experiments were performed at pH 9.00 and the temperature never exceeded 30°C.

Table VII presents the degradation rates of p-chlorophenol by ozone and UV radiation.

Table VII. Degradation Rate of p-chlorophenol by Ozone and UV at pH 9.00

$(PCP)_0$ M	R_0 (OD/min)	$R_0/[(PCP)_0]^{0.71}$
0.0020	-0.0807	6.65
0.0010	-0.0595	8.03
0.0005	-0.0349	7.70
0.0002	-0.0138	5.84
0.0001	-0.0116	8.03

As in the previous kinetic analysis, the data is fit to the equation

$$\text{Rate}_0 = k * [(PCP)_0]^n \quad \text{EQN 1}$$

A regression analysis fit of the data to EQN 1 yields an order of $n = 0.71$ for the ozone-UV light experiments.

Figure E. The Degradation Rates of PCP by different treatments with concentrations

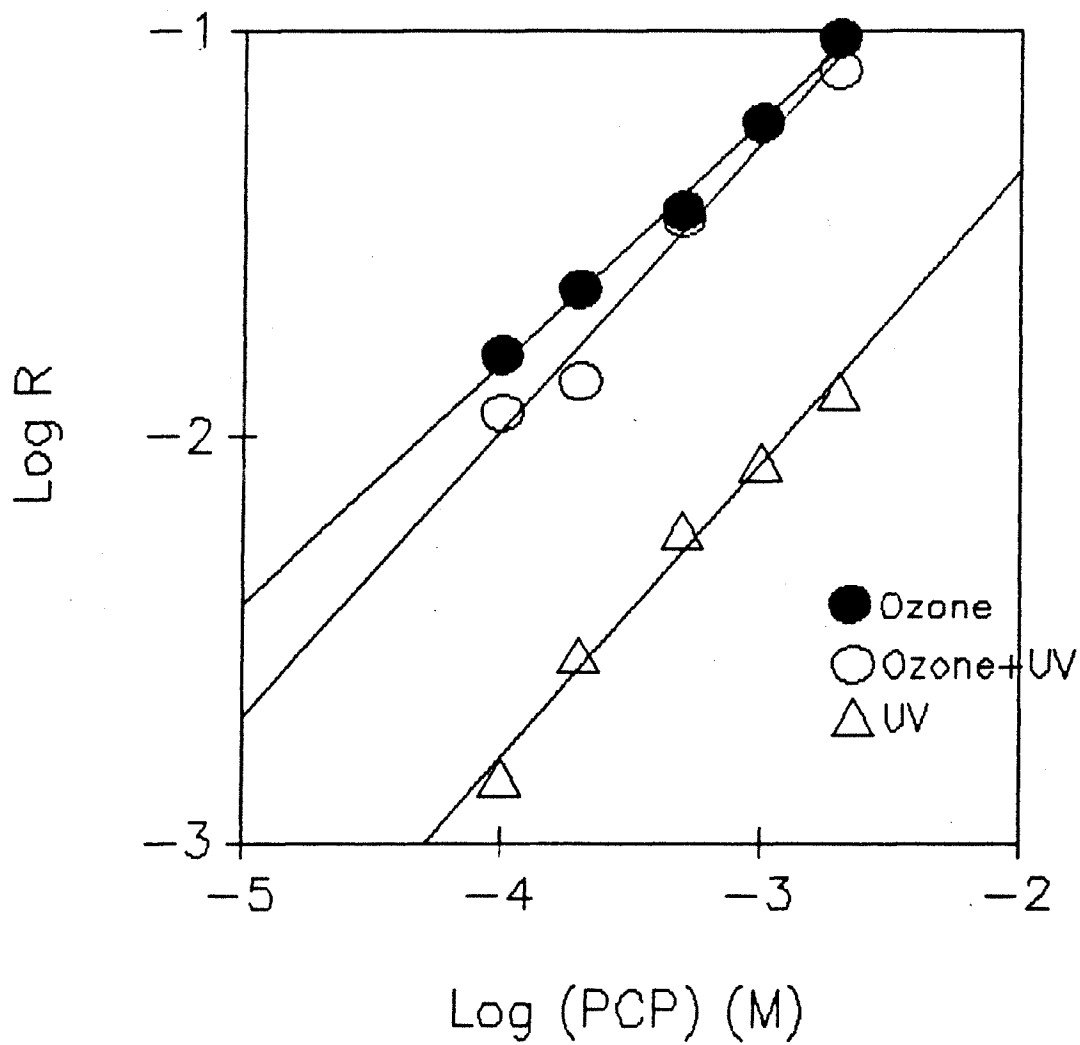


Figure E gives a plot of $\log R_0$ vs $\log(\text{PCP})_0$ for the different treatments and the straight line shows the best fit of the data which yields the order n in each case. The values of k for each treatment are presented in the last three columns of Table VIII for the ozone, UV light, and ozone-UV light respectively.

Table VIII. Experimental Values of Reaction Rate Constant (K) for Different Treatments.

(PCP) M	$\frac{R}{(\text{PCP})^{0.7}}$		
	O ₃	UV	O ₃ +UV
0.0020	7.50	1.02	6.25
0.0010	7.49	1.10	7.49
0.0005	7.42	1.21	7.14
0.0002	9.01	1.13	5.36
0.0001	7.32	0.92	7.32
Avg.	7.75	1.08	6.71

By comparing the rates of degradation of p-chlorophenol given in Table IV, VI, and VII, it is seen that the greatest effect on the degradation of p-chlorophenol is produced by ozone alone. The combination of ozone and UV has an effect just a little less than that of ozone by itself and UV alone has the smallest effect.

D. Effect of Other Treatments on the Degradability of p-chlorophenol

The effect of ultrasound on the degradability of p-chlorophenol was investigated. The results are summarized in Table IX. For the 4×10^{-4} M p-chlorophenol at pH 6.00 and 8.00, the ultrasound has an inhibitory effect on the degradability of p-chlorophenol by ozone. This result was surprising. It had been anticipated that a synergistic effect would be produced when ultrasound was applied to an ozonolysis of a chlorinated phenol, since ultrasound itself has been established to be capable of breaking covalent bonds.

Air was observed to have an immeasurably slow reaction rate with p-chlorophenol even at elevated temperature of 55°C (see Table IX). When this observation was made we turned to 99.99% oxygen as our reagent.

The oxygen, at room temperature, displayed a degradation of p-chlorophenol, although small, significantly greater than air at the higher temperature.

Reaction of p-chlorophenol with ozone and UV light was attempted next in order to enhance the decomposition

rate. Indeed, the reaction rate increased dramatically at room temperature. This was our first significant display of degradation of a toxic organic compound, and led us to examine the possibility of using ozone and ozone with UV light which were even more successful (as described above).

Table IX. The Effect of Different Treatments on the Degradability of p-chlorophenol

(PCP) ₀ M	Treatments					Temp °C	pH	Slope*10 ³ (degra. rate)
	O ₃	UV	O ₂	US	Air			
0.0004	x					RT	6.00	-5.90
0.0004	x			x		RT	6.00	-0.50
0.0004	x					RT	8.00	-6.21
0.0004	x			x		RT	8.00	-3.35
0.0002					x	55	8.00	~0.00*
0.0002					x	55	9.00	0.21
0.0002					x	55	10.00	~0.00*
0.0010		x				RT	8.00	-5.54
0.0010			x			RT	8.00	-0.50
0.0010		x	x			RT	8.00	-5.76

RT means room temperature

* the reaction rate immeasurably small

Chapter 4 Conclusions and Recommendations

Ozone application to municipal wastewater effluents has been demonstrated to be an effective disinfection method¹⁸. The disinfection with ozone is a function of the adsorbed dose and the effluent's ozone demand. It has also been proven that ozone can oxidize polychlorinated organic pollutants in wastewater discharge.

The disinfection of wastewater effluents by UV light is a viable alternative to chlorination^{19,20}.

It is documented that ozone/UV technology has effectively oxidized halogenated organics, benzene derivatives and various aliphatics²¹. The oxidation of toxic organic contaminants was at a rate which was many times faster than that obtained from applying ozone or UV light alone. For the degradation of p-chlorophenol, the effectiveness of ozone/UV is not additive when compared with UV or ozone when applied alone. One possible explanation is that ozone absorbs UV light at 254 nm, so that some of the ozone is converted to molecular oxygen in the presence of UV light²².

In this experiment, the reaction orders were found to be: 0.68 for ozone, 0.73 for UV light, and 0.71 for ozone-UV light. Assuming an average order of 0.7 for each of the cases, rate constants for the ozone, UV light, and ozone-UV light were determined to be 7.75, 1.08, and 6.71 respectively. This result just verifies the conclusion that ozone has the greatest effect, ozone-UV light follows closely behind, and UV light is much less effective in degrading the para-chlorophenol.

Further study on this system is recommended in order to completely optimize the conditions for enhancement of degradation of para-chlorophenol. The observed negative effect of ultrasound at pH's 6 and 8 was completely unexpected. Extending the ultrasound study into the alkaline region may well have the opposite effect.

Oxidants other than oxygen and ozone could be used. Hydrogen peroxide is a good possibility.

Finally, organic compounds other than para-chlorophenol could be used as models for trace pollutants. Possibilities are cresols, xylenes, and dichloro- or trichloro ethylene.

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