Light-energized oxidation of organic wastes
by Jerome Wadsworth Sargent

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Civil Engineering
Montana State University

Abstract:
Many organic substances, including many complex organic compounds which are not biodegradable, can be oxidized in the presence of a photosensitizing dye, visible light and molecular oxygen. The dye absorbs energy from visible light and transfers it to the oxygen-substrate reaction system where photo-oxidation occurs. The dye can be recovered for reuse and only light energy and molecular oxygen are spent.

Basic science research has shown that many classes of organic compounds including phenols, amines, lignins, and nitriles are amenable to photo-oxidation; but application of the process to waste treatment has not been explored.

The purpose of this study was to do preliminary testing in determining if dye sensitized photo-oxidation can be applied to waste treatment. Several concentrations of methylene blue dye (.25 to 25 mg/l) were tested for effectiveness in sensitizing the photo-oxidation of cresol in water solution (10 to 300 mg/l). Temperature and pH changes were observed during the experimentation.

The results of the investigation indicate that cresol can be destroyed by methylene blue sensitized photo-oxidation. The rate of the process can be accurately described by the chemical kinetics equation first order in cresol (C = C0e^kt), but the mechanism of the reactions involved is probably not simply first order. The rate of the process varies with dye and substrate concentration and there are optimum values for both.

As cresol was photo-oxidized the pH of the reaction system decreased, indicating that the oxidation products were acidic. Temperature increased during the reaction due to heat emission by the light source.

This study indicated that dye sensitized photo-oxidation has potential as a waste treatment process and merits further investigation and development.

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Approved:

Head, Major Department

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ABSTRACT

Many organic substances, including many complex organic compounds which are not biodegradable, can be oxidized in the presence of a photosensitizing dye, visible light and molecular oxygen. The dye absorbs energy from visible light and transfers it to the oxygen-substrate reaction system where photo-oxidation occurs. The dye can be recovered for reuse and only light energy and molecular oxygen are spent.

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The results of the investigation indicate that cresol can be destroyed by methylene blue sensitized photo-oxidation. The rate of the process can be accurately described by the chemical kinetics equation first order in cresol ($C = C_o e^{kt}$), but the mechanism of the reactions involved is probably not simply first order. The rate of the process varies with dye and substrate concentration and there are optimum values for both.

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CHAPTER I

INTRODUCTION

Dye sensitized aerobic photo-oxidation is a process by which a photo-sensitive substrate can be chemically modified in the presence of a photo-sensitizing dye, visible light and molecular oxygen. Much scientific research has been done on dye sensitized photo-oxidation but engineering application of the process to water and waste treatment has received little attention. Kinny and Ivanuski (1969) did some work on photolysis of waste materials but very little on dye sensitization or mechanism analysis.

For photo-oxidation applied to waste treatment, the substrate would be waste molecules to be oxidized and the source of molecular oxygen would be dissolved oxygen in the waste stream. According to Foote (1968) and others, there are several mechanisms by which the process can occur, but Eggers et al (1964) state that the first step is almost always the absorption of light energy by sensitizer dye. The absorbed light energy electronically excites the dye to an excited singlet state (all electron spins paired and some bond electrons in energy orbitals higher than ground state). The singlet state is then spontaneously converted to a triplet state (electron spins parallel and with higher than ground state energy). Foote (1968) describes two general reaction pathways which can follow after formation of triplet state dye: (1) the triplet sensitizer interacts with ground state molecular oxygen, or (2) the triplet sensitizer reacts directly with the substrate present. In the first reaction pathway, on contact with a ground state oxygen molecule, triplet sensitizer passes its energy of light absorption on to the oxygen molecule to form excited singlet oxygen. The dye returns to ground state after the energy transfer and is capable of absorbing more light. Excited singlet oxygen is a strong oxidizing agent capable of quickly oxidizing photo-sensitive substrate molecules on contact. Since this reaction sequence results in net loss of only oxygen and light energy, it holds the greatest promise for waste treatment.

The second reaction pathway can result in permanent destruction of the sensitizer dye. Since the dyes are relatively expensive this process would likely prove uneconomical for waste treatment.

Which of the two above described pathways predominates in a photo-oxidation reaction system is a sensitive function of oxygen concentration, sensitizer concentration and reactivity with oxygen, substrate reactivity and concentration, and the rate of triplet sensitizer decay. Eggers et al (1964) state that the desired pathway can be selected by properly controlling reaction conditions.

According to Spikes and Straight (1967) many classes of organic compounds are sensitive to photo-oxidation, including: alcohols, nitrogen heterocyclics, organic acids, phenols, and benzenoid and aromatic heterocyclic compounds. Hence many of the substances found in domestic and industrial wastes, including refractory organics such as phenols, cresols, amines (from fish and beet sugar industries), lignins (from wood products), and unsaturated nitriles occurring in synthetic fiber industry waste, can be photo-oxidized. Bulla and Edgerley (1968) showed that 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), parathion, and IPC (isopropyl N-phenylcarbamate) can be photo-oxidized. The odor-causing sulfhydryl groups in mercaptans are readily photo-oxidized to non-odorous forms. Investigations by Mathews (1963), Oginsky et al (1959), and others show that most microorganisms, including viruses, can be killed by low concentrations of photo-sensitizing dyes in the presence of light and oxygen.

OBJECTIVES

The general purpose of this research is to make preliminary tests in the application of photo-oxidation to waste treatment. More specifically the objectives are to:

1. Test cresol for susceptibility to photo-oxidation.
2. Determine the dependence of the photo-oxidation reactions on dye concentration.
3. Determine how varying substrate concentration affects the photo-oxidation process.
4. Gather pH data from the photo-oxidation reactions for the purpose of determining how pH affects and is affected by photo-oxidation.

CHAPTER II

THEORY AND LITERATURE REVIEW

There are virtually no references to the application of dye sensitized photo-oxidation to water or waste treatment. Bulla and Edgerley (1968) investigated photo-oxidation of a few specific organic materials, mainly pesticides, but they used ultraviolet light and no sensitizer dye. Since engineering application of dye sensitized photo-oxidation has not been reported, it is necessary to try to extract usable information from reports of scientific research.

REACTION MECHANISM

The primary goal of past research in photo-oxidation has been to elucidate the mechanism by which the chemical reactions occur for any particular set of reaction conditions. But the evident conflict among the conclusions of the various investigators indicates that the goal has yet to be satisfactorily attained. One thing does seem clear, however. Dye-sensitized photo-oxidation can occur by many different mechanisms and reaction pathways depending on reaction conditions such as the relative concentrations of the reactants, characteristics of the light source, pH, and temperature. But it is seldom possible to predict the mechanism knowing just the reaction conditions.

As there are no general rules for predicting the mechanism of a photo-oxidation reaction, Coomber and Pitts (1970) describe analytical techniques such as flash photolysis or flash spectroscopy which must be employed to identify and measure the short-lived intermediates involved. Once the intermediates have been identified the reaction mechanism can be established. Most mechanism studies, however, have been made for reaction conditions much different from those in a water or waste treatment process and hence are not discussed in this report.

The following is a description of the mechanisms reported in the literature by which the photo-oxidation observed in this investigation might have occurred. To facilitate describing the different mechanisms, the process is arbitrarily divided into three steps: (1) the absorption of activating light energy, (2) the primary reaction of the energized species formed in (1) above, and (3) the subsequent reactions of any radicals or intermediates to form other intermediates or final products.

Absorption of Light Energy

Although formation of triplet sensitizer is usually the first step in dye sensitized photo-oxidation, Spikes and Straight (1967) indicate that the singlet state of the sensitizer can be involved. Since the singlet species is relatively short-lived, however, most reactions probably proceed by way of the triplet sensitizer.

Primary Reactions of Energized Sensitizer

The primary reactions of just triplet state sensitizer are discussed here.

If substrate molecules and molecular oxygen are present in the reaction system, most of the triplet sensitizer molecules have one of three destinies: (1) decay to ground state, (2) interaction with ground state molecular oxygen to form one of several possible radicals or intermediates, and (3) interaction with substrate to form one of several possible complexes or intermediates.

<u>Triplet Sensitizer Decay</u> If the triplet sensitizer decays directly to ground state no photo-oxidation reactions occur.

<u>Triplet Sensitizer-Oxygen Interaction</u> According to Grossweiner and Zwicker (1968) interaction of triplet sensitizer with ground state oxygen can involve simple energy transfer or electron transfer. Energy transfer from dye to oxygen produces either an active dye-oxygen complex or energized singlet oxygen plus ground state dye; and it is difficult to distinguish between them. Foote (1968) concluded that recent evidence favors the energized singlet oxygen plus ground state dye.

Foote (1968) and Pitts et al (1963) suggest that the two singlet oxygen species most likely involved in photo-oxidations are (Σg) and (Δg). (Δg) probably predominates in most instances because its energy of formation (22 kilocalories) is less than that of (Σg) (37 kilocalories).

Electron transfer from triplet sensitizer to ground state oxygen results in oxidative bleaching of the dye and production of a semi-reduced radical of molecular oxygen. Oxidative bleaching is loss of color due to loss of an electron or electrons by dye molecules. The dye can then be called "semi-oxidized sensitizer". The semi-oxidized oxygen molecules which gain electrons as a result of transfer from the dye are said to be semi-reduced.

Triplet Sensitizer-Substrate Interaction Little is known about the mechanism involved or the intermediates formed when triplet sensitizer interacts directly with substrate. Foote (1968) points out that simple energy transfer between the triplet sensitizer and substrate is unlikely in most instances because the triplet state of the sensitizer is usually lower in energy than the triplet state of the substrate. Foote (1968) and Grossweiner and Zwicker (1968) suggest that a more probable route involves formation of hydrogen atom or electron transfer complexes; but it is difficult to distinguish between hydrogen atom and electron transfer interactions. Hydrogen atom and electron transfer complexes can lead to: (1) irreversible complexing, (2) reversible complexing wherein the reverse reaction regenerates ground state sensitizer plus altered or unaltered substrate, and (3) complex formation followed by fragmentation of the complex into several ion radicals or molecular intermediates.

Secondary Reactions of Intermediates

Several kinds of intermediates might result from the primary reactions described earlier. They are: (1) semi-oxidized molecules of sensitizer or substrate, (2) semi-reduced molecules of sensitizer, molecular oxygen, or substrate, (3) energized singlet oxygen, and (4) complexes made up of different combinations of dye, oxygen and substrate.

The complexes might be either semi-reduced or semi-oxidized.

The following secondary reactions might be ovserved in an aerobic dye sensitized photo-oxidation system.

O-D = G-D (decay) (1)
O-D + R-O = G-D + G-O (2)
O-D + G-S = G-D + O-S (3)
O-D + R-S = G-S + G-S (4)
O-D + R-S = G-S + O-S (5)
SO + G-S = O-S (6)
T-D + R-S = G-D + O-S (7)

where O-D is semi-oxidized dye, G-D is ground state dye, R-O is semi-reduced oxygen, O-S is semi-oxidized substrate, R-S is semi-reduced substrate, G-S is ground state substrate, SO is singlet oxygen, and T-D is triplet dye sensitizer.

Any semi-reduced or semi-oxidized intermediate complexes might be expected to separate into the original ground state molecules from which they were formed, break down into new radical species, or react with other oxidized or reduced species to produce final products.

Fig. 1 is a graphic summary of the possible mechanisms for aerobic dye sensitized photo-oxidation. The superscripts o and 3 indicate ground state and triplet state respectively. The subscripts ox and red mean oxidized and reduced. Sing O_2 refers to singlet oxygen, Sub indicates substrate, and Sens means sensitizer dye.

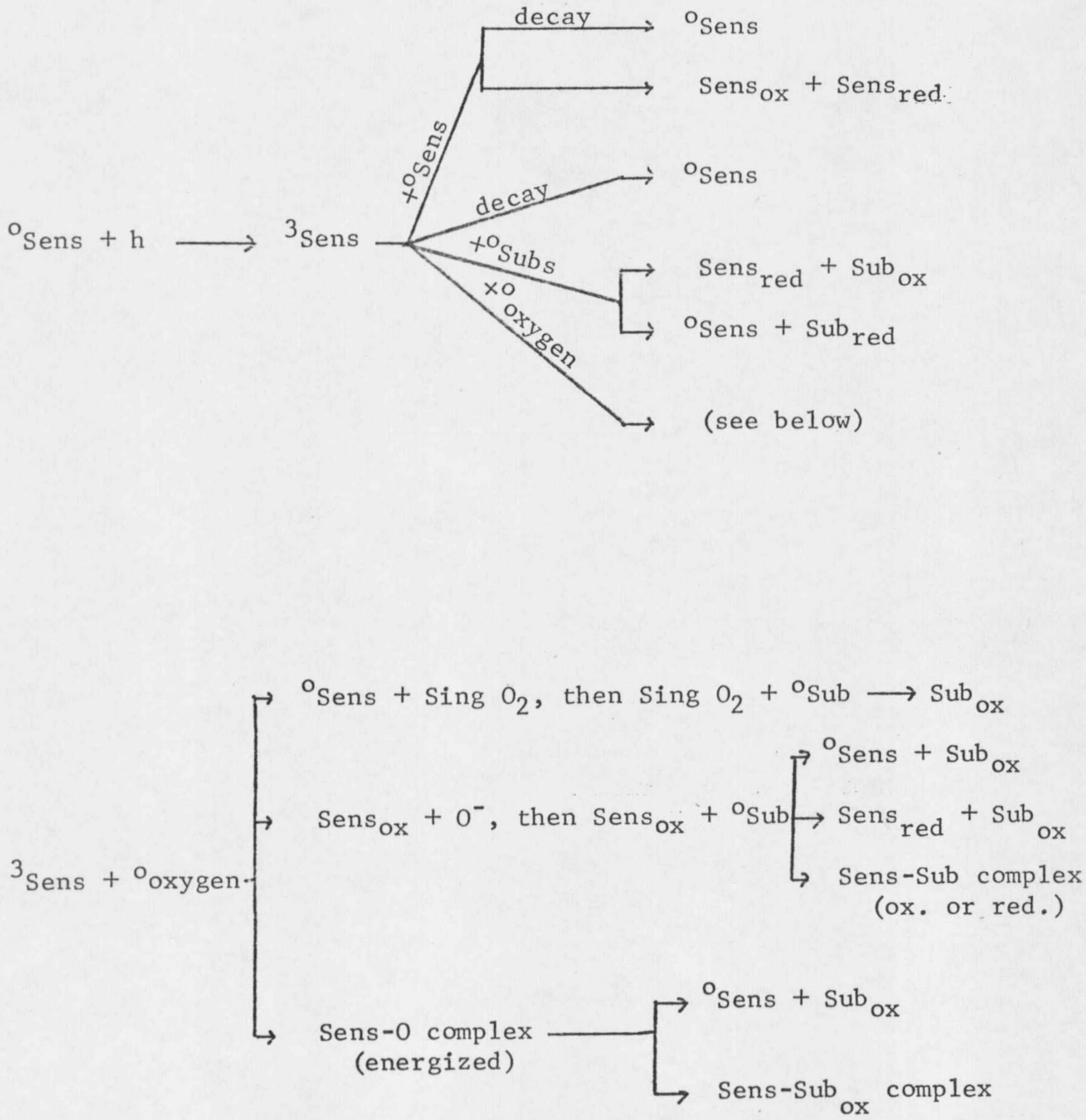


Fig. 1 SUMMARY OF AEROBIC DYE SENSITIZED PHOTO-OXIDATION REACTIONS

SUBSTRATE

Spikes and Straight (1967) list the following substances as being sensitive to photo-oxidation: alcohols, aldehydes, amines, amino acids, carbohydrates, esters, indoles, ketones, olefins, nucleic acids, organic acids, phenols, proteins, purines, pyrimidines, pyrroles, and benzenoid compounds.

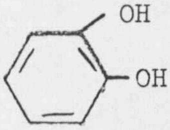
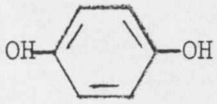
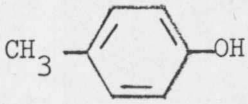
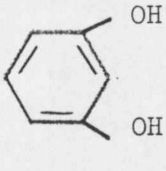
Kolesnikov (1958) determined the relative susceptibility of several phenolic and other substances to riboflavin-sensitized photo-oxidation. In Table 1, for several of those compounds the oxygen absorption during photo-oxidation is listed. One of Kolesnikov's conclusions was that para and ortho diphenols and their derivatives are not sensitive to photo-oxidation, but derivatives of monophenol are sensitive to the reaction.

SENSITIZER DYES

According to Kinney and Ivanuski (1969) many organic compounds are capable of absorbing light energy to initiate photo-oxidation. Some will sensitize only very specific reactions while others are more general and will sensitize the photo-oxidation of many substrates. The investigations of Bellin and Oster (1960) and Yamamoto (1958) indicate that the common dyes methylene blue, toluidine blue, rose bengal, neutral red and others are good non-specific sensitizers for photo-oxidation.

TABLE 1

OXYGEN ABSORBED BY PHENOLS DURING RIBOFLAVIN SENSITIZED PHOTO-OXIDATION

Substance	Structural formula	Micro-liters of oxygen absorbed by 5 ml samples of equal molar strength
control (riboflavin in aqueous solution)		4.5
procatechol		16.8 to 18.4
hydroquinone		13.4 to 16.5
p-cresol		80.5 to 86.9
resorcinol		49.3 to 55.2
tannin from tea	numerous different compounds	85.0 to 101.5

CHAPTER III

MATERIALS AND EQUIPMENT

MATERIALS

Sensitizer

The sensitizer used in this investigation was methylene blue, a relatively cheap and readily available dye. Fig. 2 is the absorption spectrum for a 3 mg/1 water solution of methylene blue as presented by Holmes (1924). The dye has absorption peaks at about 6100 and 6600 A^o.

Substrate

Cresol in distilled water solution was the substrate photo-oxidized in this study.

EQUIPMENT

Reactor

Fig. 3 illustrates the reactor used. The light source was a Sylvania 2, DMS, 500 watt tungsten incandescent lamp which emits strongly in the visible spectrum (4200-6600 A^o). The reactor was lined with aluminum foil to provide for maximum light intensity on the solution.

Aeration

To provide mixing and oxygen for the photo-oxidation reactions, the 200 milliliters of dye-substrate solution in the reaction vessel

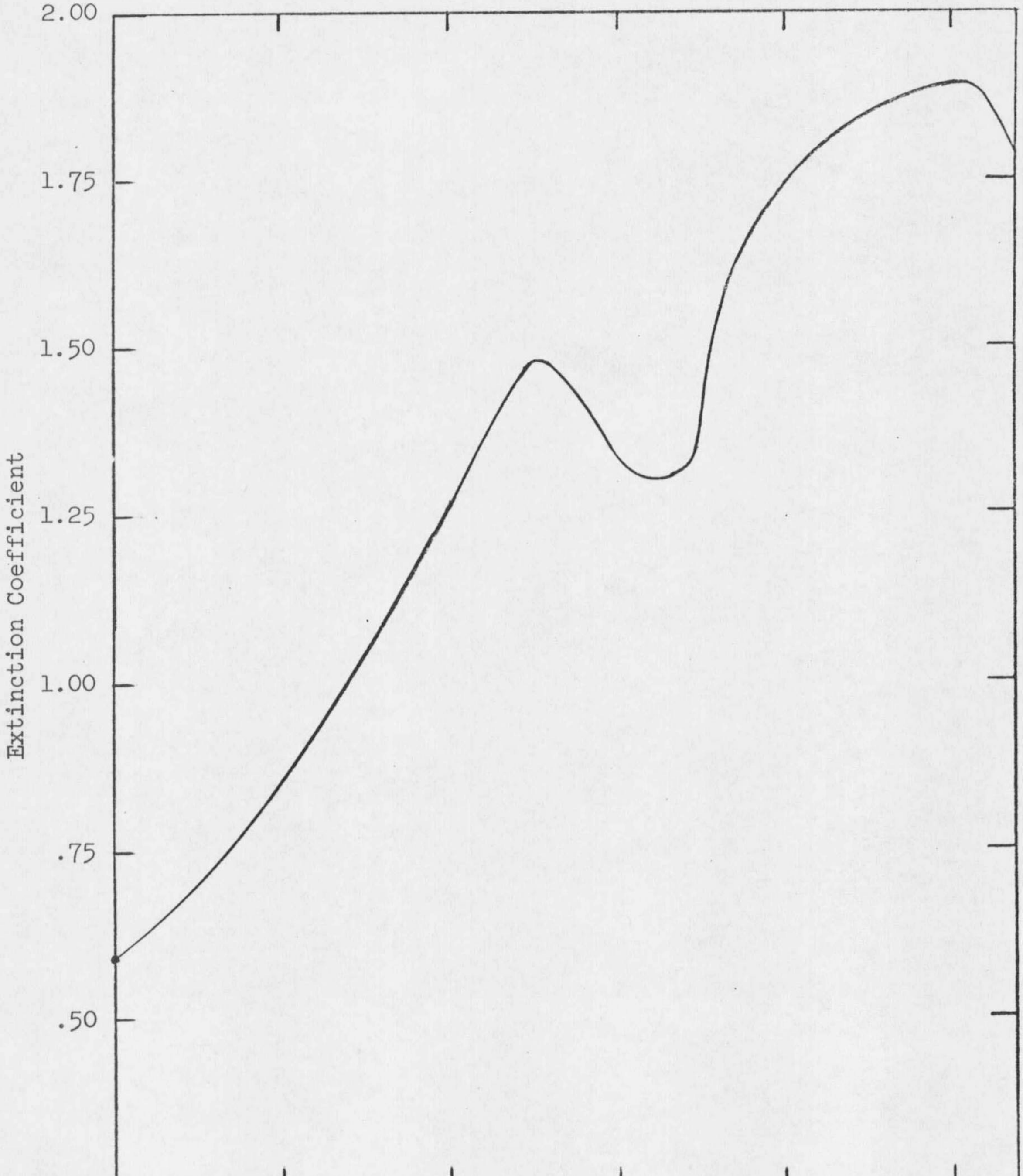


Fig. 2 . ABSORPTION SPECTRUM FOR 3 mg/l METHYLENE BLUE

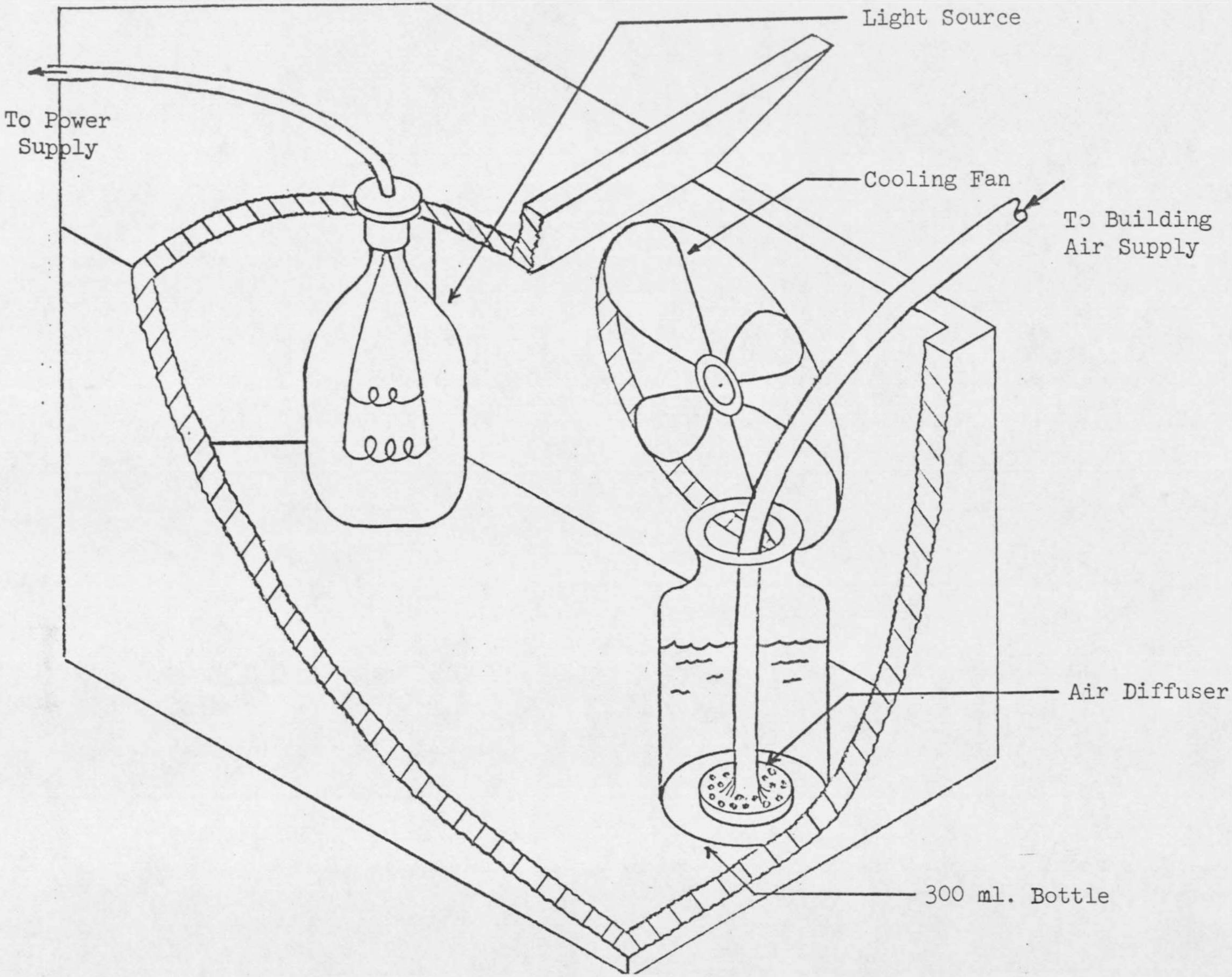


Fig. 3. PHOTO-OXIDATION REACTOR (to scale 1" = 3")

were aerated from an unfiltered, oil-pumped air supply. The diffuser was a Pyrex glass fritted disc 33 millimeters in diameter with a pore size range of 40 to 60 microns.

Analyzer

A Varian Aerograph model 204 1B dual-channel gas chromatograph with flame ionization detectors was used to monitor cresol concentration. Table 2 is a list of the operating parameters for the gas chromatographic measurement of cresol.

Recorder

A Sargent model DSRG dual channel recorder operating at 1 mv for full span recorded the output signal of the chromatograph.

Hydrogen Ion Concentration

pH measurements were made with an Orion model 404 specific ion meter using a Sargent combination glass electrode.

Temperature

Temperature measurements were made with a Curtin mercury expansion thermometer.

TABLE 2

OPERATING PARAMETERS FOR GAS CHROMATOGRAPHIC MEASUREMENT OF CRESOL IN AQUEOUS SOLUTION

Parameter	Description
Support material	Chromosorb W
Stationary phase (liquid)	FFAP (Free fatty acid phase)
Column -	
a) Material	a) stainless steel
b) Diameter	b) 1/8 inch
c) length	c) 5 feet
d) Temperature (isothermal operation)	d) 190°C
Injector temperature	232°C
Detector temperature	244°C
Sample size	2-5 micro-liters
Carrier gas	Helium @65 psig.
Carrier flow	38 ml/min.

CHAPTER IV

PROCEDURE

CONCENTRATIONS

Dye concentrations of .25, 1, 3, 5, 10, 15, and 25 mg/l were tested for effectiveness in sensitizing the photo-oxidation of 10, 50, 100, 150, 200, and 300 mg/l solutions of cresol. Two hundred milliliters of each possible combination of dye and substrate concentrations were placed in the reaction vessel shown in Fig. 3, aerated, and illuminated. The degree of aerobic photo-oxidation obtained was determined by measuring the decrease in cresol concentration.

AERATION

The aerobic reaction systems were aerated vigorously enough to make it visibly evident that air bubbles were distributed throughout the solution. Care was taken, however, to prevent solution from bubbling out of the reaction vessel. Dissolved oxygen concentration in the reaction system was not monitored.

ILLUMINATION

The aerated reaction system was illuminated for short time periods with intervals of no light between each illumination period to allow for recovery of dye bleached by addition of hydrogen atoms (reduction).

Organic substrates can be the source of hydrogen atoms which are added to dye molecules under the influence of light energy. Having intervals of darkness between illumination periods allows the dye to shed some of the excess hydrogen atoms and regain its color.

Illumination periods of 2, 5, and 10 minutes, separated by six-minute intervals of no light, were tested for relative effectiveness.

EXAMPLE EXPERIMENT

To illustrate the sequence of events for a single experiment, the procedure for testing photo-oxidation of a 100 mg/l cresol solution sensitized by 5 mg/l of methylene blue was as follows. The illumination period was two minutes. With the dye-substrate solution in the aerated reactor the lamp was turned on for two minutes. After illumination, the solution was removed from the reactor and a two micro-liter sample was injected into the gas chromatograph. The pH meter probe was placed in the solution for the six minutes it took for the cresol peak to appear on the chromatogram and the pH was read at about the same time the cresol peak appeared. Fig. 4 is a sample chromatogram for the injection of two microliters of a solution containing 5 mg/l methylene blue and 100 mg/l cresol before beginning illumination. Then the dye-substrate solution was placed back in the reactor, aerated, and illuminated again. The sequence was repeated 13 times. In all experiments the size of sample to inject depended on the amount necessary to obtain a satisfactory chromatogram.

TEMPERATURE

Temperature measurements were made after each illumination period for four selected experiments (two involving 2 minute illumination

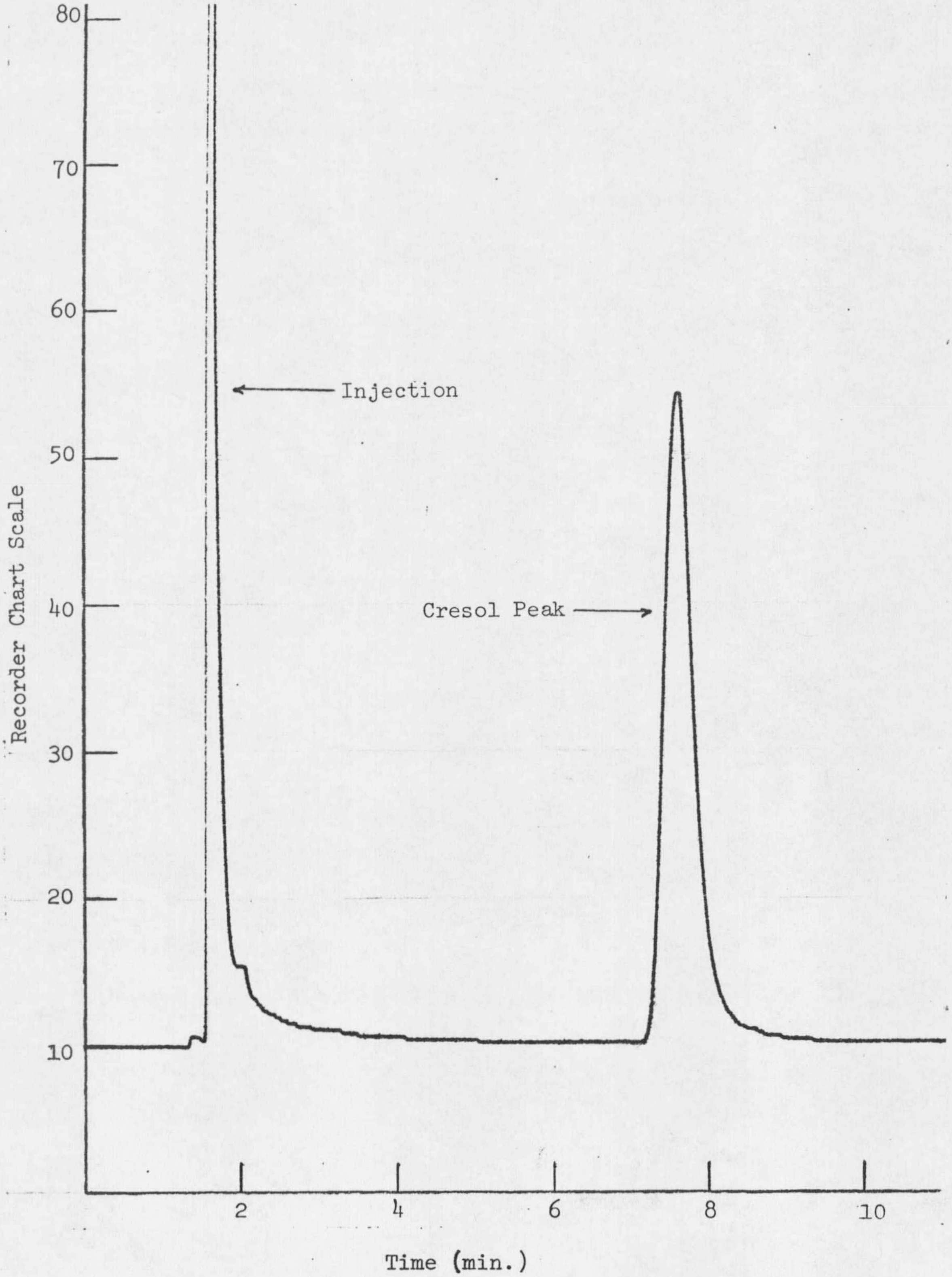


Fig. 4. SAMPLE CRESOL CHROMATOGRAM

periods, one with 5 minute illumination periods, and one with 10 minute illumination periods.

TESTS PERFORMED AND DATA REPRODUCIBILITY

A complete list of the tests performed is on page 52 of the Appendix. Several of the tests were performed in duplicate to test reproducibility of the experimental data.

To determine substrate loss not due to aerobic photo-oxidation cresol concentration was monitored in: (1) unilluminated dye-cresol solutions, (2) illuminated solutions of cresol only, and (3) dye-cresol solutions swept by nitrogen gas to make them anaerobic.

STANDARDS AND STOCK SOLUTIONS

At the beginning of each experiment, cresol standards were injected into the chromatograph until consistent peaks for each standard were obtained. Fresh standards were prepared each day from a one gram per liter stock solution which was made up one liter at a time.

The stock methylene blue solution was 100 milligrams per liter, prepared one liter at a time and stored in a foil covered flask to prevent bleaching.

METHOD OF DATA ANALYSIS

The area of the chromatogram peaks (peak height times peak width at ½ peak height) was correlated with cresol concentration by plotting calibration curves. As shown in Fig. 5, the calibration curve is a plot

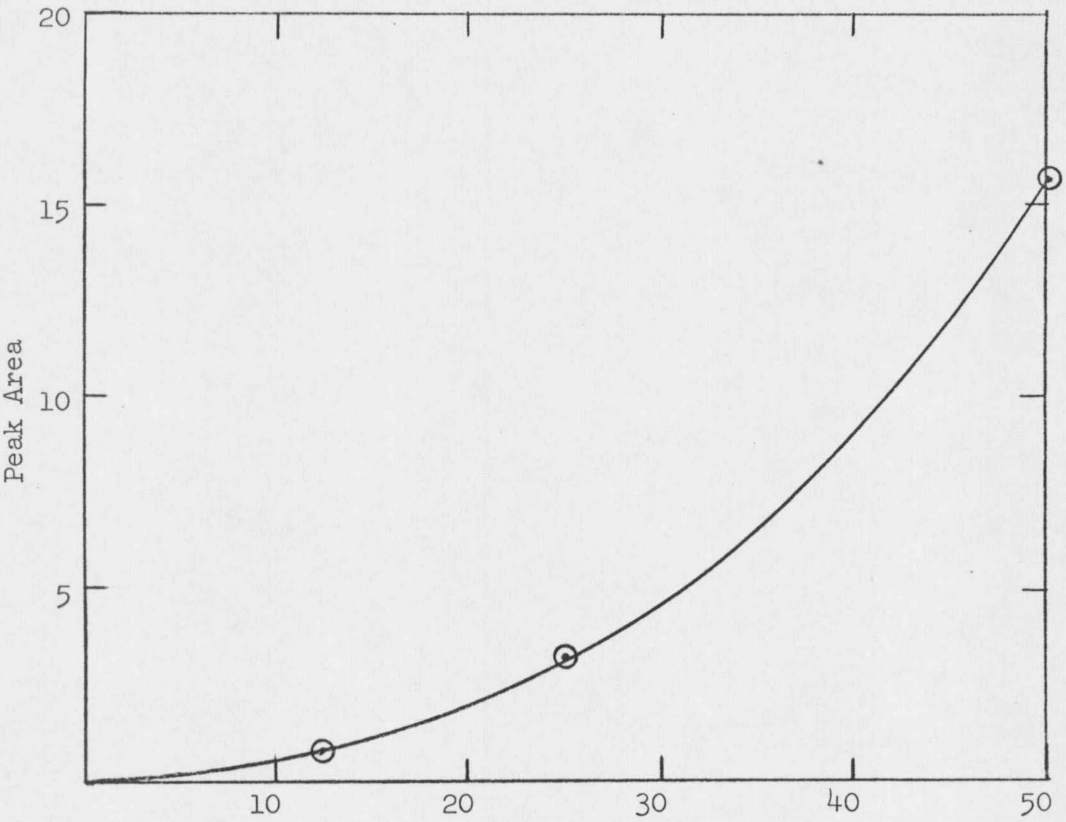


Fig. 5. CORRELATION CURVE FOR GAS CHROMATOGRAPHIC MEASUREMENT OF CRESOL

of the peak areas of cresol standard chromatograms versus their respective cresol concentrations.

The data for any one of the tests performed consisted of a cresol concentration and a pH value for each successive illumination period. Plots of cresol concentration and pH versus total illumination time were made to show the progression of cresol concentration and pH as cresol photolysis occurred. The cresol concentration and pH curves for each experiment were plotted on the same figure for the sake of comparison (Fig. 6 is an example).

The data for each experiment were fitted by the method of least squares to two equations:

(1) $C = C_o + bt^a$

where C = cresol concentration at time t

C_o = original cresol concentration at $t = 0$

b and a = constants

t = elapsed time

and

(2) $C = b + C_o e^{kt}$

where C = cresol concentration at time t

C_o = original cresol concentration at $t = 0$

b = constant

k = reaction rate constant

t = elapsed time

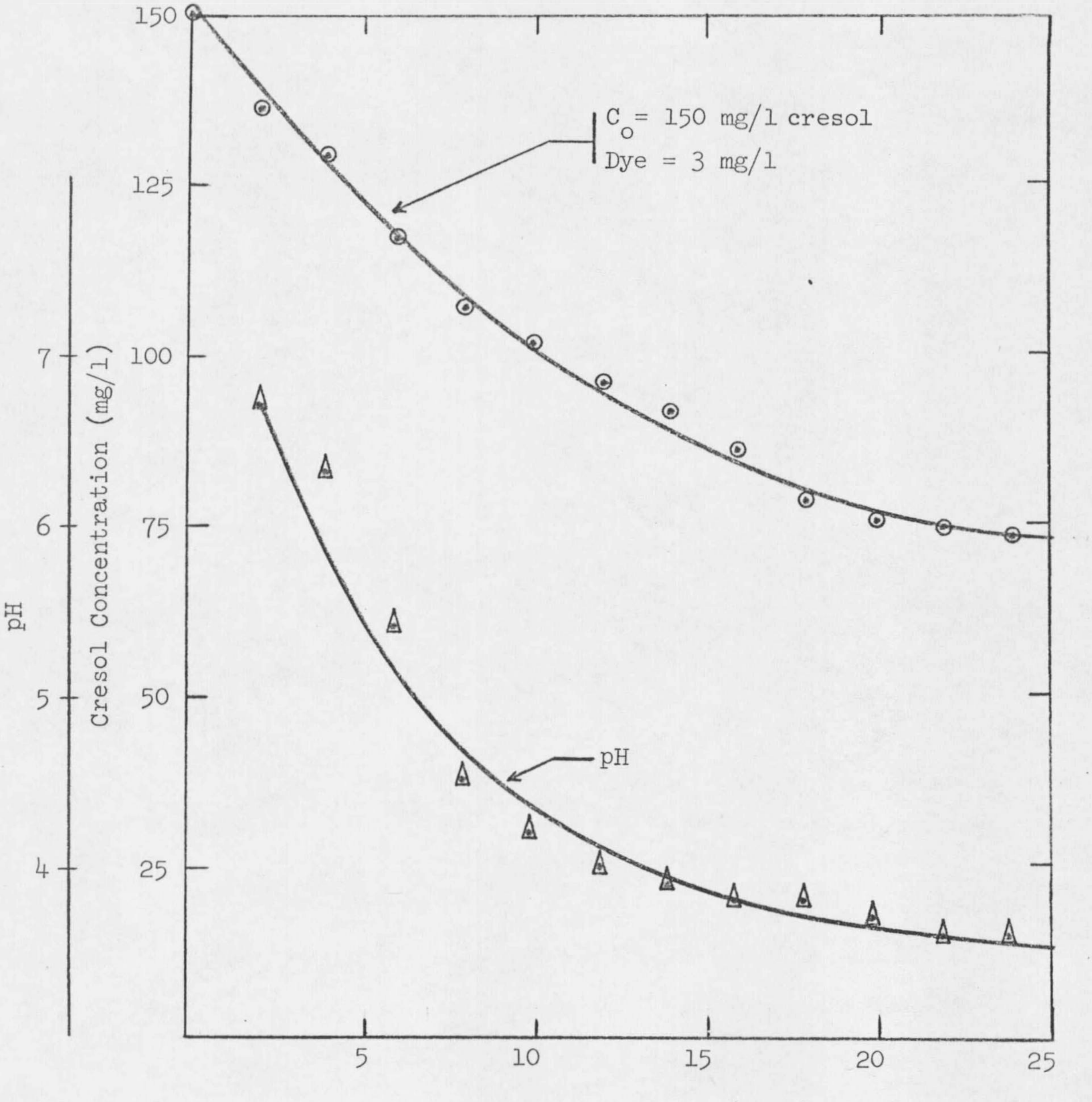


Fig. 6. CRESOL CONCENTRATION AND pH vs. ILLUMINATION TIME

The above two equations were chosen because they are graphically similar to the plots of data from this investigation.

A digital computer was programmed to perform the curve-fit procedure by the method of least squares. The computer output listed the equation constants for the two curves to which the data of each experiment were fitted. Also listed was the percent by which the data deviated from each of the fitted curves. A sample of the computer print-out is shown on page 54 of the appendix.

CHAPTER V

RESULTS

REACTION RATES

The methylene blue-cresol solutions which were not illuminated or aerated showed a slight decrease in cresol concentration (e.g. from 100 mg/1 to 95 mg/1) after one hour. The cresol solutions which were aerated and illuminated but contained no sensitizer dye showed no loss in cresol after twenty minutes of illumination.

For all tests wherein a dye-cresol solution was illuminated and aerated (see Appendix, page 52) the cresol concentration decreased exponentially with illumination time. Fig. 7 is a sample plot of cresol concentration vs. illumination time with the smooth curve fitted by the method of least squares to the mathematical expression $C = C_o e^{kt}$ (equation (2), page 22).

When anaerobic solutions of methylene blue and cresol were illuminated, cresol concentration decreased according to the first order kinetics equation (equation (2), page 22), but the rate was very much less than for the aerobic systems. Fig. 8 is a comparison of the reaction rates for anaerobic and aerobic systems.

For any individual experiment, the rate of disappearance of cresol can be described by the first order kinetics equation (equation (2), page 22). But the rate constant (k) varied with initial cresol concentration at constant dye concentrations (see Fig. 9).

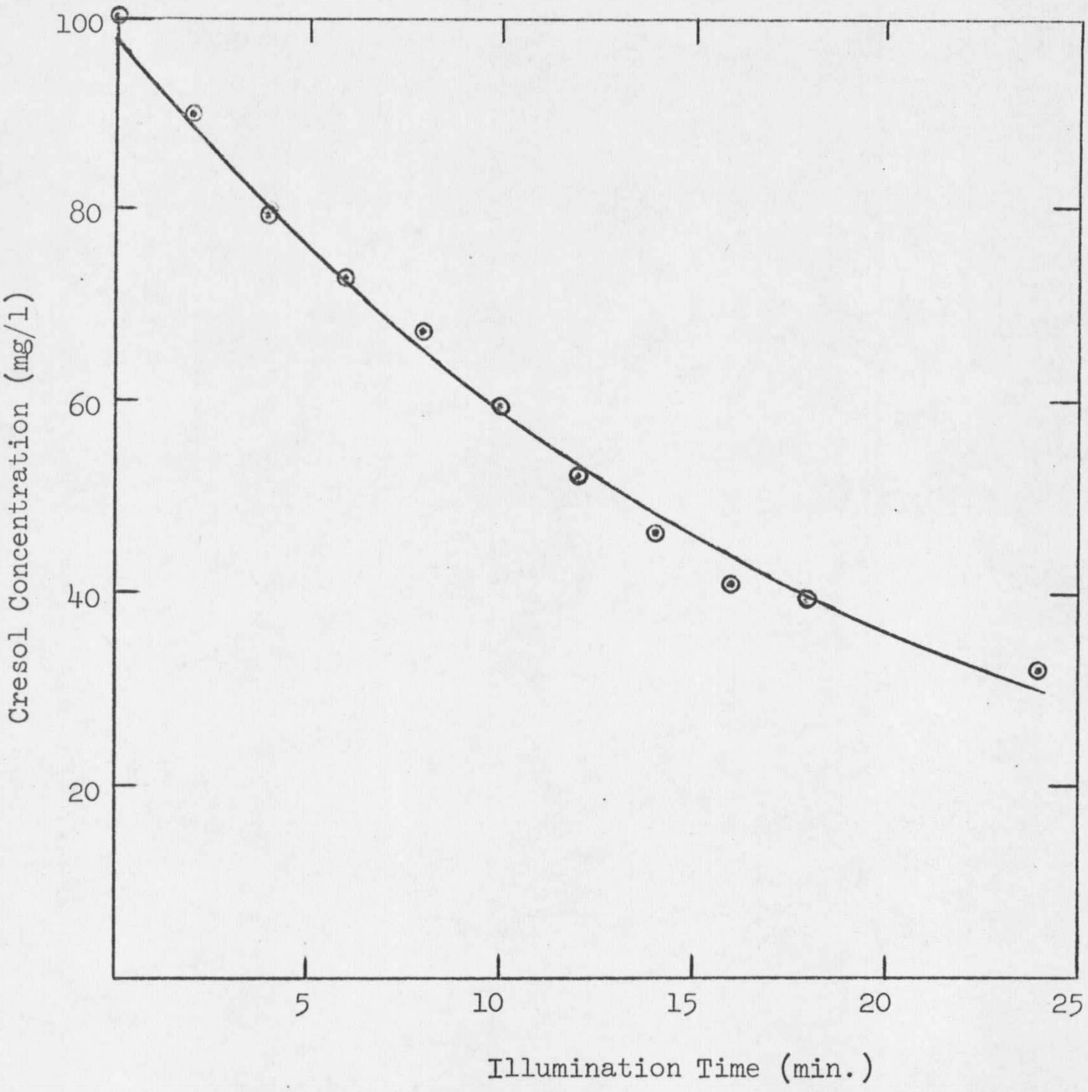


Fig. 7. CRESOL CONCENTRATION vs. ILLUMINATION TIME (curve fit by method of least squares)

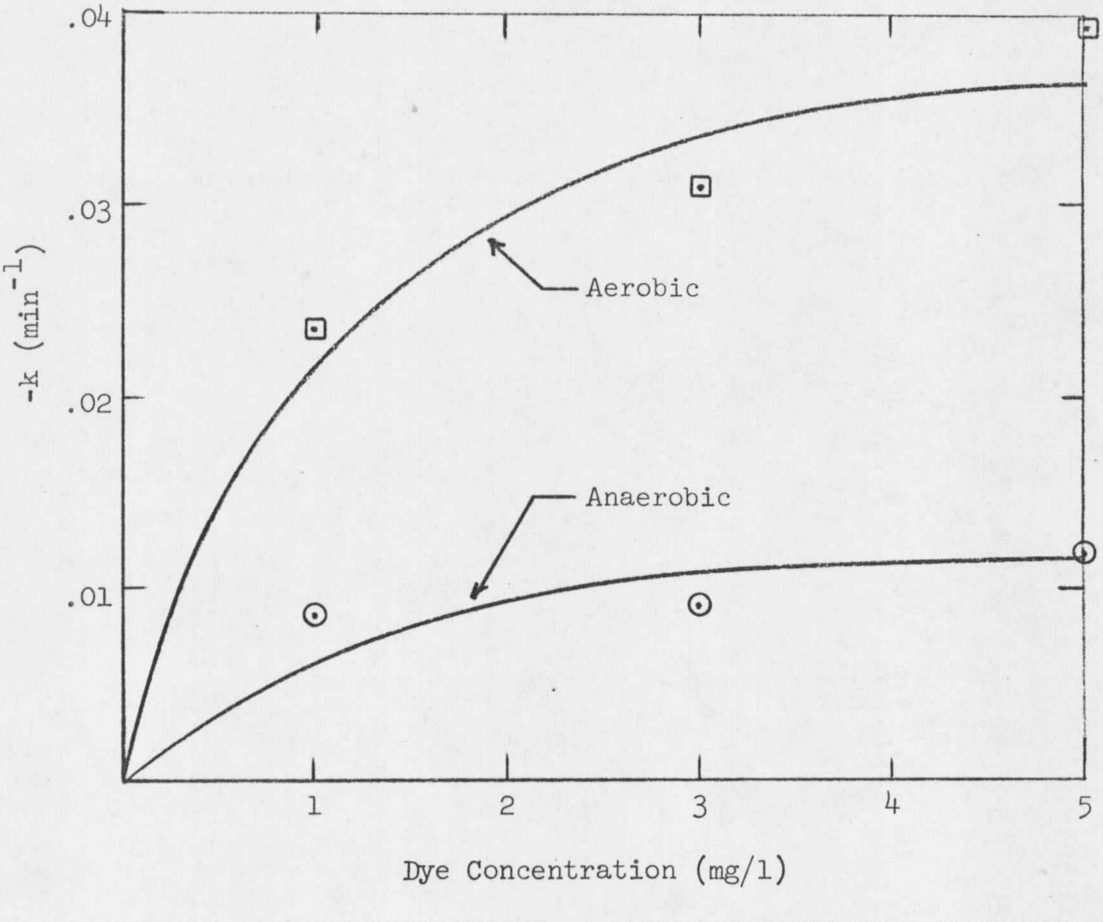


Fig. 8 . REACTION RATE vs. DYE CONCENTRATION. COMPARING AEROBIC AND ANAEROBIC RATES FOR C_o = 150 mg/l AND ILLUMINATION PERIOD = 2 min.

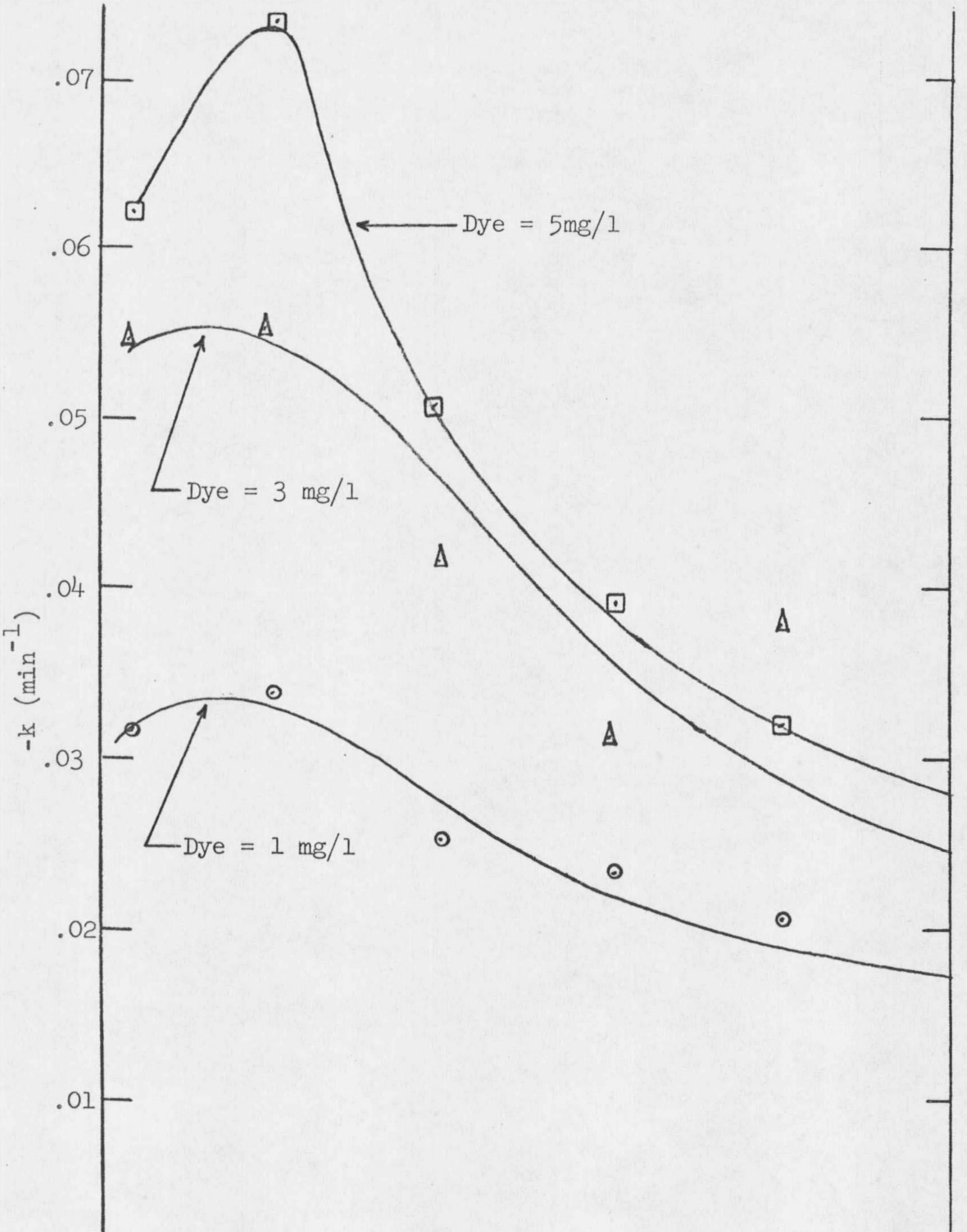


Fig. 9. REACTION RATE vs. CRESOL CONCENTRATION AT CONSTANT DYE CONCENTRATIONS

The rate constant exhibited a dependence on both dye and cresol concentrations. Figures 10 thru 13 show the variation of k with dye concentration for the various cresol solutions and illumination periods. The individual values of C_o and k for each experiment are summarized on pages 55 through 57 of the Appendix.

ACCURACY OF DATA ANALYSIS

The computerized curve fit and error analysis procedures showed that all the data were within ninety percent of the fitted first order curve. For about half the tests, all the data were within ninety-five percent of the fitted curve. None of the data fit the equation $C = C_o + bt^a$.

For all tests, the C_o computed from the equation of the fitted curve was within at least ninety percent of the actual initial cresol concentration.

DYE BLEACHING

There appeared to be a correlation between the amount of cresol photo-oxidized and the degree of dye bleaching observed. The dye solutions containing higher initial cresol concentrations bleached more than those with low initial cresol content. In no case, however, was any bleaching evident until after at least eight minutes of illumination.

The degree of bleaching was assessed simply by observation. Dye bleaching was not closely monitored since visible evidence was enough to indicate that a significant amount of bleaching was occurring.

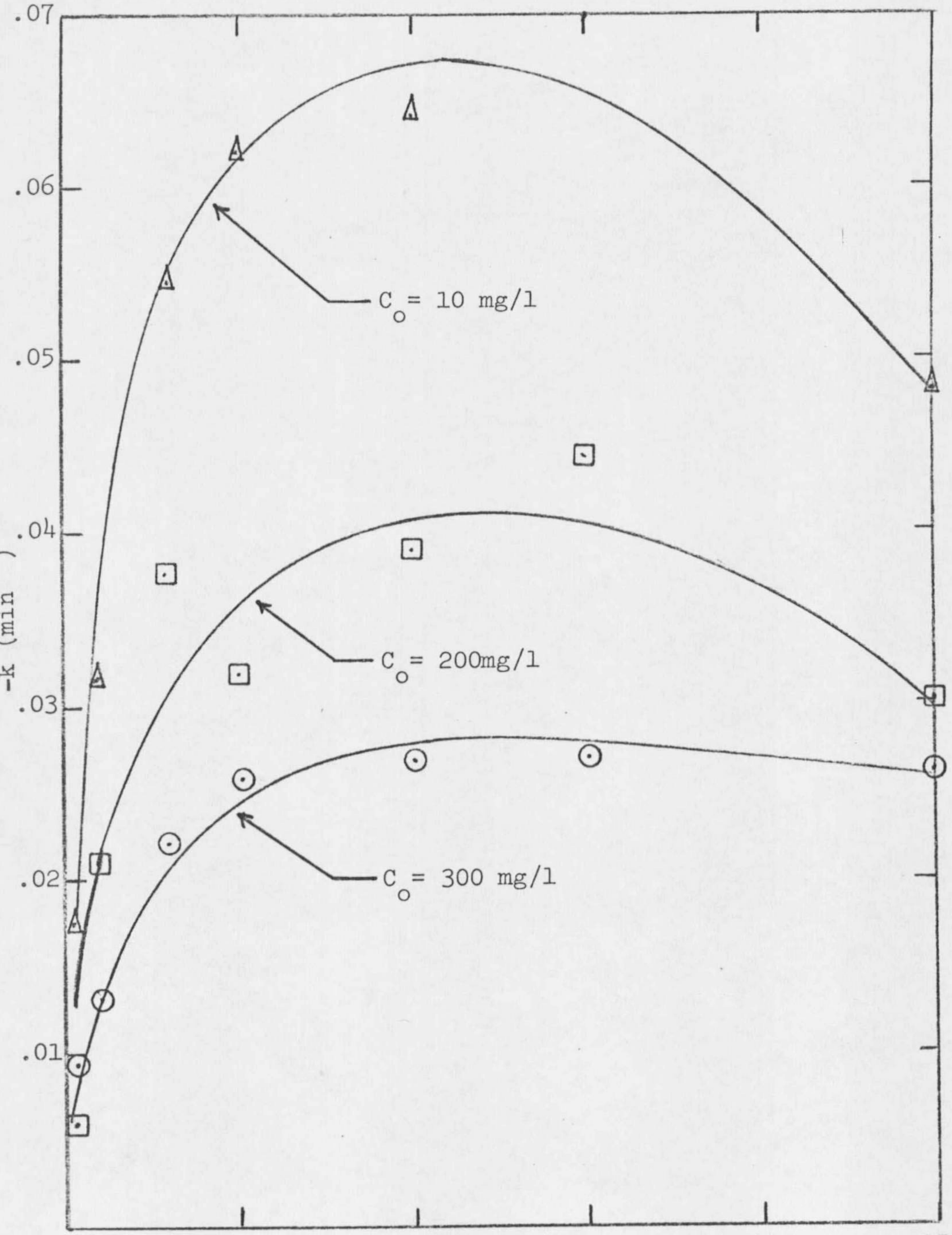


Fig. 10. REACTION RATE vs. DYE CONCENTRATION FOR TWO MINUTE ILLUMINATION PERIODS. C_o= 10, 200, AND 300 mg/l.

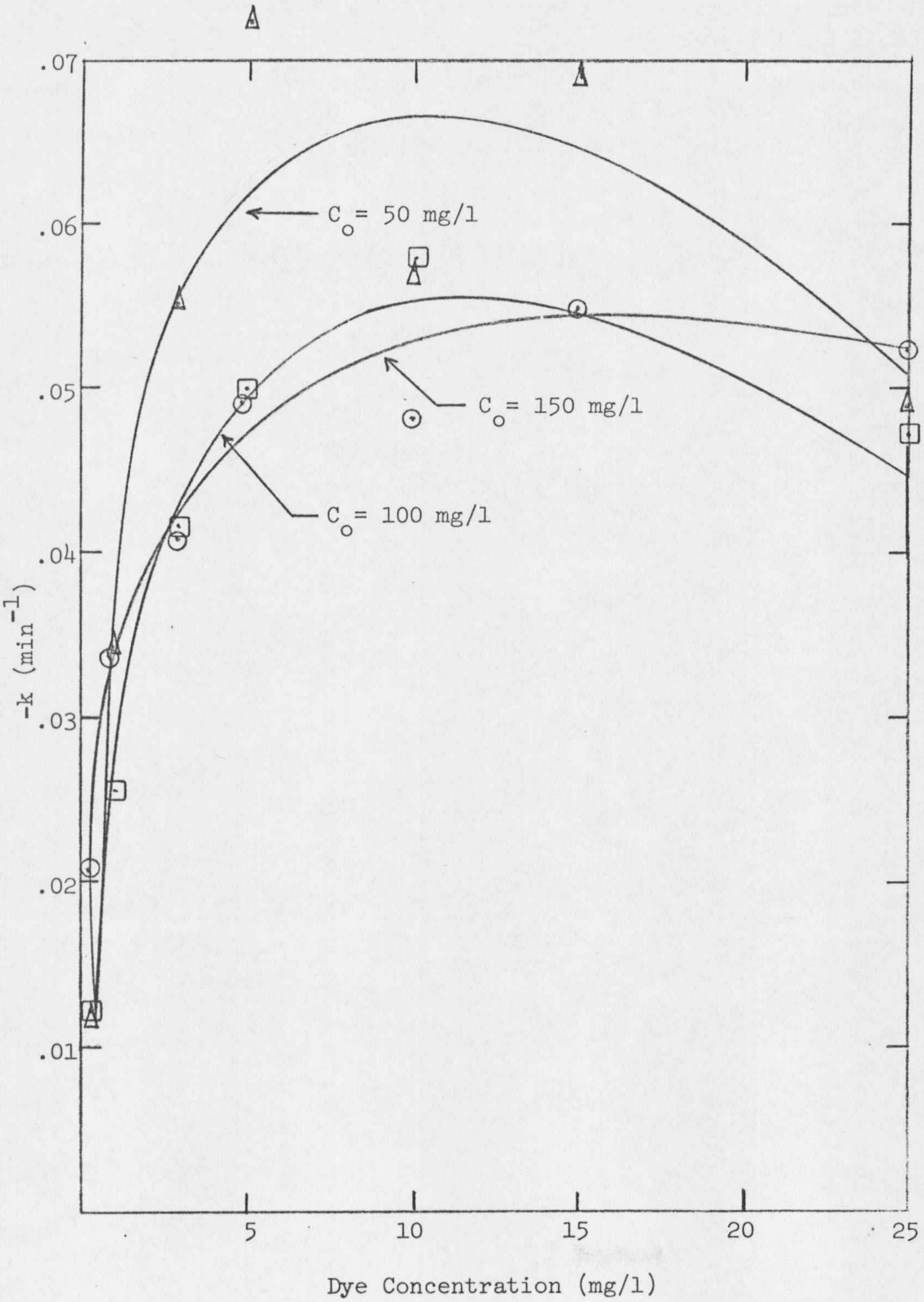


Fig. 11. REACTION RATE vs. DYE CONCENTRATION FOR TWO MINUTE ILLUMINATION PERIODS. C_o = 50, 100, AND 150 mg/l.

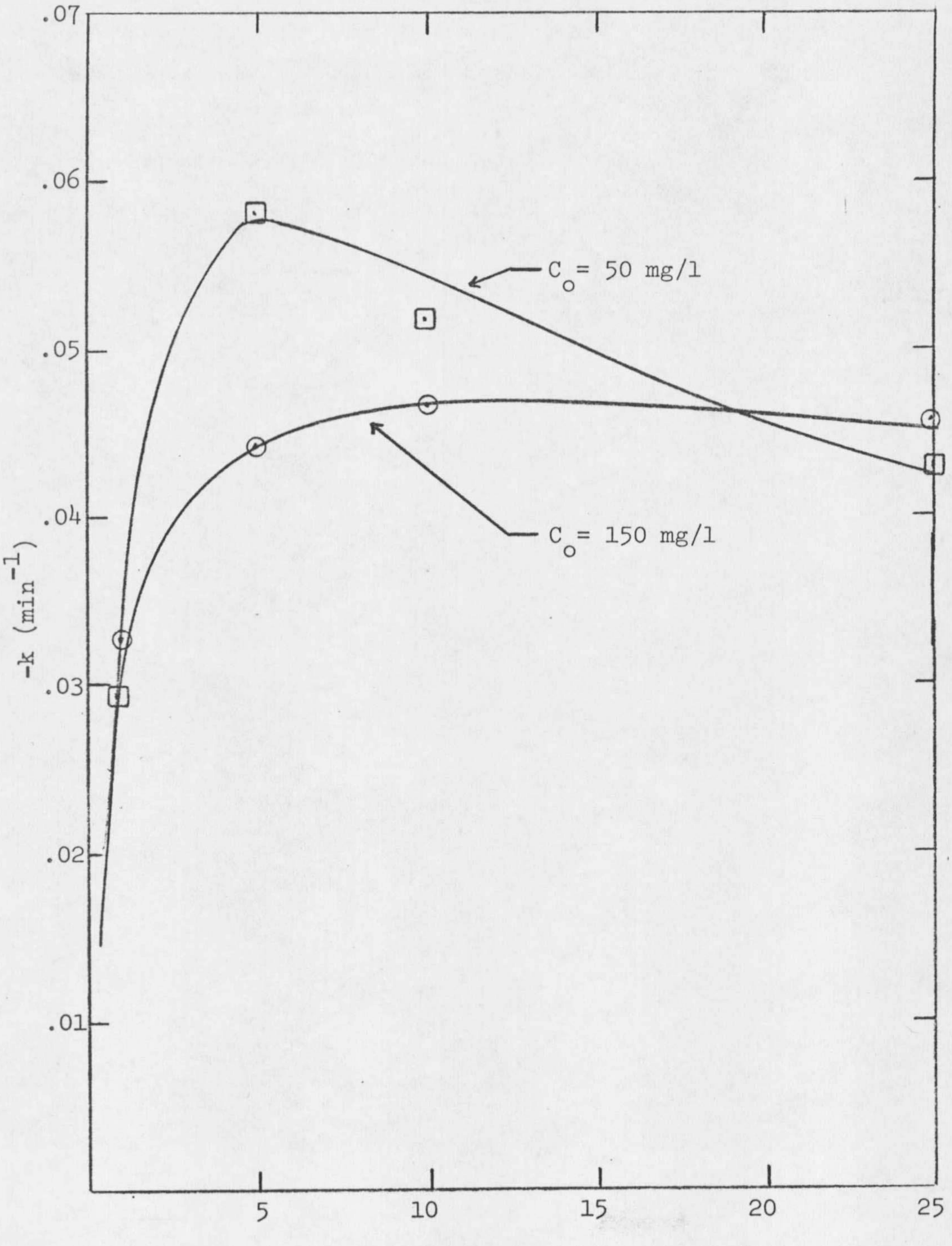


Fig. 12. REACTION RATE vs. DYE CONCENTRATION FOR FIVE MINUTE ILLUMINATION PERIODS.

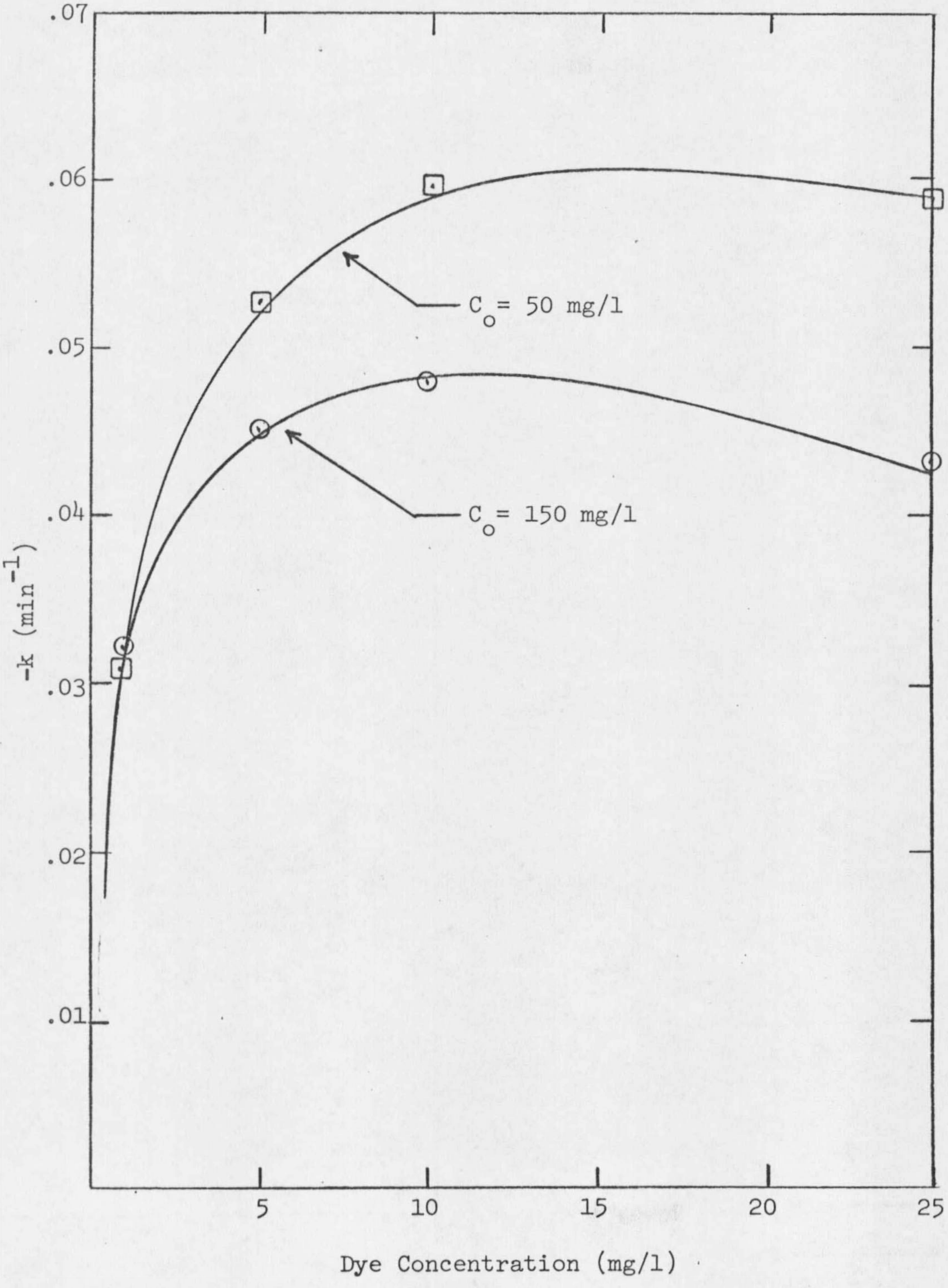


Fig. 13. REACTION RATE vs. DYE CONCENTRATION FOR TEN MINUTE ILLUMINATION PERIODS.

In all solutions where dye bleaching was apparent, the original unbleached color could not be recovered by aerating the solution in the dark. Hence the bleaching was not caused simply by hydrogen ion addition by the dye (i.e. reduction).

Since the sensitizer dye did not bleach detectably during the first eight minutes of illumination, the dye concentration during that time period might be considered constant. To determine the effect of changing dye concentration (through bleaching) on the reaction rate, a rate constant (k) was computed for the first eight minutes of data for each experiment. The k values for the first eight minutes of data did not vary in a systematic way from the k values for the full 26 minutes of data (see Fig. 14).

HYDROGEN ION CONCENTRATION

The pH data indicated generally that pH decreased as the amount of cresol photo-oxidized increased (see Fig. 6). For solutions in which comparatively little cresol photo-oxidation was observed (i.e. where cresol was 10 mg/1 and dye was .25 mg/1) the pH went down less than 1 pH unit. In solutions where more cresol was photo-oxidized, the pH decreased from its initial value of between 7 and 8 to as low as 2.

TEMPERATURE

In spite of the cooling fan in the reactor, the dye-cresol solution increased in temperature when the lamp was turned on. The greatest temperature increases occurred during the ten minute illumination

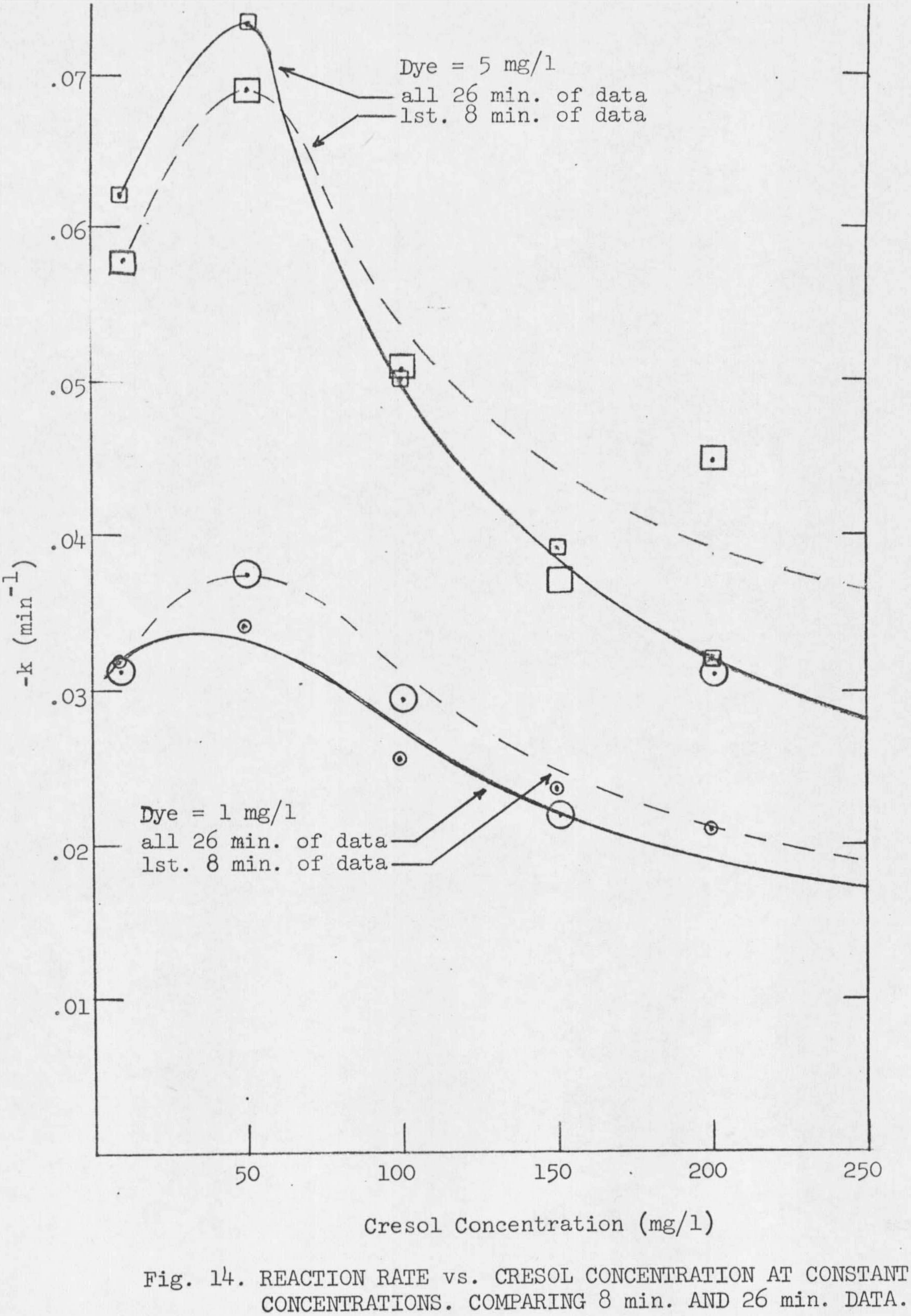


Fig. 14. REACTION RATE vs. CRESOL CONCENTRATION AT CONSTANT DYE CONCENTRATIONS. COMPARING 8 min. AND 26 min. DATA.

periods. Immediately after ten minutes of steady light the temperature of the solution was observed to be as high as 60°C compared to an initial temperature of 24°C. The temperature change was not nearly so pronounced (ΔT of from 12 to 15°C) for experiments involving two minute illumination periods. Fig. 15 shows the change in temperature with time for an experiment involving two minute illumination periods.

OTHER OBSERVATIONS

A flaky small particle floc appeared in the reaction vessel when a considerable amount of cresol had been photo-oxidized and the dye appreciably bleached (i.e. after about ten minutes of illumination of a solution containing at least 1 mg/l dye and 100 mg/l cresol). The floc was very light, did not settle, and appeared white in the blue colored solution. The rate and total amount of floc formation were not monitored because there was very little present and it could not be filtered out without the filter paper taking up dye. The dye taken up by the filter paper interfered with weighing the floc.

In addition to the floc, a thin oily film formed on the surface of the solution in the reaction vessel after several minutes of illumination. The film was most evident in solutions of high dye concentration (10 mg/l and above).

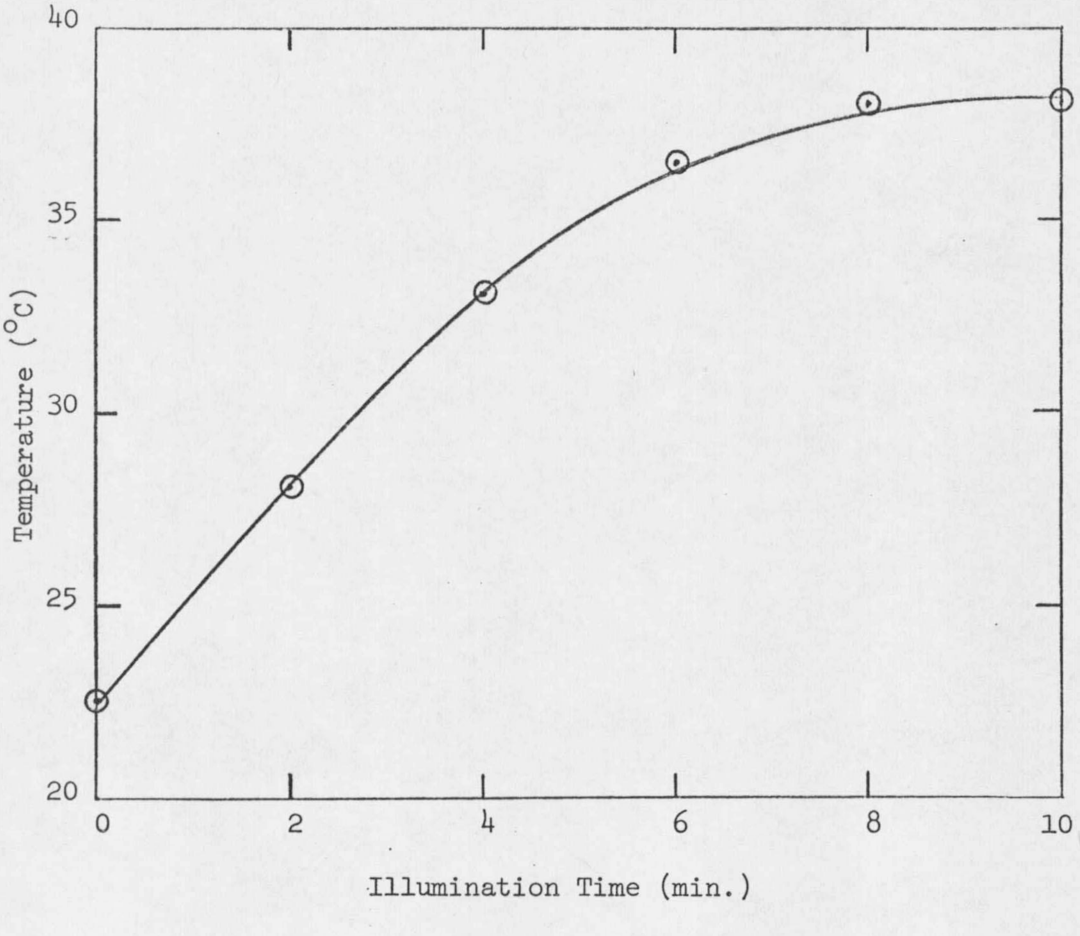


Fig. 15. TEMPERATURE vs ILLUMINATION TIME

CHAPTER VI

DISCUSSION

PROCEDURE, EQUIPMENT, AND MATERIALS

Sensitizer

Methylene blue was chosen as the sensitizer for this study because it has proved capable of sensitizing the photo-oxidation of many classes of organic compounds. It is also considerably cheaper than most of the other sensitizer dyes and readily available.

Substrate

Cresol occurs in petro-chemical and other waste effluents and is, according to Sawyer and McCarty (1967), refractory to the common waste treatment processes. As shown in Table 1, however, cresol is quite sensitive to dye sensitized photo-oxidation. Hence, it was chosen as the test substrate for this investigation.

Reaction System

The essential ingredients of an aerobic dye sensitized photo-oxidation system are sensitizer dye, photo-sensitive substrate, and molecular oxygen; all in solution in an appropriate solvent and exposed to the proper wavelength(s) of sufficiently intense light. Water was the solvent used, primarily because it is the carrier fluid for most waste effluents. Also, water does not interfere with the photo-oxidation reactions and is not opaque to the required light energy.

In all experiments, the solution in the reaction vessel was aerated as vigorously as possible so that the oxygen supply rate could be considered constant for all tests. It was assumed that the oxygen content in the air supply was constant. The intent was to eliminate oxygen concentration as an experiment variable.

The reaction systems were illuminated in short time intervals to avoid excessive bleaching of the sensitizer dye. Bleaching of methylene blue might be expected when the dye is exposed to high intensity light for several minutes, and bleached dye is not effective as a photosensitizer.

RESULTS

The primary intent of past research on photo-oxidation has been to elucidate the physical chemistry of the reactions. Little or no information is available on the effects of varying dye and substrate concentrations, and those parameters are of vital concern in application of photo-oxidation to water or waste treatment.

Dye Concentration

Figures 10 through 13 indicate that there is an optimum value of dye concentration in the dye sensitized photo-oxidation system. It lies between 5 and 10 mg/1 for cresol concentrations ranging from 10 to 300 mg/1. The optimum dye concentration does not, however, seem to vary in a significantly systematic way with initial cresol concentration.

Substrate Concentration

Fig. 9 indicates that aerobic photo-oxidation of cresol, photosensitized by 1 to 5 mg/l of methylene blue, proceeds most rapidly when the initial cresol concentration is about 50 mg/l. The optimum initial cresol concentration appears to increase as dye concentration increases.

Reaction Rate

The time rate of cresol photolysis in any one experiment of this investigation can be accurately described by the kinetics equation first order in cresol ($C = C_o e^{kt}$). In the first order equation, the values of the initial cresol concentration (C_o) and the reaction rate constant (k) determine the time rate of change in cresol concentration. But there are two factors which indicate that the actual reaction mechanism operating in this study is not first order in cresol. First, the investigations of Blum (1935 and 1941) and Foote (1968) indicate that the rate of the photo-oxidation process is a sensitive function of at least substrate concentration, dye concentration and oxygen concentration; and temperature, pH, and light intensity might also be important factors. In fact, many investigators have concluded that there are optimum values for the concentrations of substrate, dye and oxygen. Secondly, Fig. 9 shows that the rate constant k varies with initial cresol concentration at constant dye concentration. If the reaction were truly first order in cresol the rate constant at a constant dye concentration would remain the same for any initial cresol concentration. It is important to recognize that the photolysis reaction mechanisms involved in this investigation are probably not simply first order in cresol even though the first order kinetics equation is used to described the time rate at which the process proceeds.

Reaction Mechanism and Kinetics

It is safe to say that cresol was being altered by photolysis in the illuminated reaction systems because very little cresol disappearance was observed in unilluminated dye-cresol solutions. Furthermore, since both methylene blue and oxygen were necessary ingredients of reaction systems wherein cresol concentration decreased appreciably, the chemical process involved was dye sensitized photolysis.

Cresol disappearance was observed in illuminated anaerobic solutions of dye and cresol, indicating that some triplet sensitizer was reacting directly with substrate (cresol). That observation agrees with previous observations by Grossweiner and Zwicker (1968) that cresol is a relatively reactive substrate with triplet sensitizer. The half-life of cresol in the anaerobic photo-oxidation system with 3 mg/l dye and 150 mg/l cresol was 77.6 minutes. In the aerobic reaction of 3 mg/l dye and 150 mg/l cresol, however, the half-life of cresol was 22.6 minutes. Hence in the aerobic system, a reaction mechanism involving oxygen was operating and the mechanism was faster than the triplet sensitizer-substrate mechanism of the anaerobic reaction (see Fig. 8).

It is quite probable that both of the mechanisms described above are involved and competing in the aerobic reaction system, with the faster mechanism involving oxygen predominating.

Dye bleaching was not observed in the anaerobic methylene blue-cresol solutions which were illuminated. Therefore, either the triplet sensitizer-substrate reaction was occurring by a mechanism which conserved ground state dye or there was not enough reaction to cause an observable amount of dye bleaching.

The significant amount of dye bleaching observed in the aerobic reaction system indicated that aerobic photolysis of cresol for the conditions of this investigation proceeds by a mechanism which results in permanent destruction of part of the sensitizer. There is likely a sensitizer-oxygen-substrate complex involved since illumination of aerobic solutions of methylene blue without substrate did not result in visibly evident dye bleaching. Evidence of a reaction route involving a sensitizer-oxygen-substrate complex does not, however, belie the existance of a free singlet oxygen mechanism. In fact it should be possible to select different routes to predominate by proper control of light wave length and intensity, choice of sensitizer, and other means. Another possible explanation for the dye bleaching in the aerobic reactions might be the secondary reaction of either ground state or triplet sensitizer with products of cresol photolysis; and the cresol photolysis might have occurred by the singlet oxygen or some primary reaction mechanism.

Hydrogen Ion Concentration

The observed lowering of pH during aerobic photolysis of cresol is consistent with the expected production of acid groups during oxidation of cresol. Just interaction of light with certain photo-sensitizers can also influence pH by causing the dyes to break up into basic or acidic components. But since illuminated aerobic solutions of just methylene blue showed no change in pH, the pH changes in the dye-cresol solutions were caused primarily by acidic products of cresol photo-oxidation.

Reaction Products

No attempt was made during this investigation to collect, identify, or quantify the products of cresol photolysis. Also, no additions or deletions were made to the reaction vessel after illumination of a dye-cresol solution was begun. Hence all reactants and products stayed in the solution through each successive illumination period. The accumulation of reaction products may have had an effect on the reaction rate and influenced the value of the rate constant.

Temperature

It is likely that the rise in temperature during each experiment affected the rate constant. The absorption and transfer of energy by sensitizer is not temperature dependent but collision rate controls the secondary photo-oxidation reactions, so temperature probably has an overall effect.

Other Observations

The small particle floc and the oily surface film observed during some of the experiments were not identified in this investigation. Identification of them may provide significant evidence in establishing the mechanism of the reactions involved.

The values of the rate constants for the experiments done in duplicate differed by less than five percent, indicating that the experimental data were satisfactorily reproducible.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The physical chemistry of the dye sensitized photo-oxidation process is difficult to discern without the use of sophisticated analytical techniques and equipment. Furthermore, the mechanisms involved in a photo-oxidation reaction can be very complex and a sensitive function of reaction conditions. Hence, it is difficult to describe reaction mechanisms and reaction products for an investigation like the one herein reported.

The following general conclusions can be drawn about methylene blue sensitized photo-oxidation of cresol and the application of the photo-oxidation process to waste treatment:

1. A waste product (cresol) in aqueous solution can be destroyed by photo-oxidation -- a process which uses only visible light as the energy source. The process can successfully employ the conventional engineering methods of aeration, mixing, and handling of waste streams. The conditions necessary to achieve photo-oxidation are not so unusual as to be obtainable only in the laboratory.
2. Methylene blue, a readily available dye, is an effective sensitizer for cresol photo-oxidation and would likely sensitize photo-oxidation of other substrates (i.e. waste molecules).

3. There is an optimum dye concentration in an aerobic dye sensitized photo-oxidation system. For cresol solutions of from 10 to 300 mg/1 the optimum dye concentration is between 5 and 10 mg/1.

4. There is an optimum initial cresol concentration (i.e. cresol concentration before treatment begins) to achieve photo-oxidation of cresol under the conditions of this investigation. The optimum concentration is about 40 mg/1 for a dye concentration of 1 mg/1 and increases to about 70 mg/1 for a dye concentration 5 mg/1.

5. The first order chemical kinetics equation ($C = C_o e^{kt}$) accurately describes the rate at which cresol was photo-oxidized in this study; but the reaction mechanism is probably not simply first order in cresol.

6. Methlyene blue sensitized photolysis of cresol occurs as much as three times faster in an aerobic system than in an anaerobic system.

7. Some or all of the reaction products of dye sensitized cresol photo-oxidation are acidic and cause a pH drop of as much as 6 points on the pH scale for the conditions of this investigation.

8. The significant amount of cresol photo-oxidation achieved under the conditions of this investigation indicates that photo-oxidation has potential as a waste treatment process and merits

further study and development.

APPENDIX

TESTS PERFORMED

ILLUMINATION PERIOD (min.)	DYE CONCENTRATION (mg/1)	CRESOL CONCENTRATION (mg/1)
2	.25	10
2	1.0	10
2	3.0	10
2	5.0	10
2	10.0	10
2	15.0	10
2	25.0	10
2	.25	50
2*	1.0	50
2	3.0	50
2	5.0	50
2	10.0	50
2	15.0	50
2	25.0	50
2	.25	100
2	1.0	100
2	3.0	100
2*	5.0	100
2	10.0	100
2	15.0	100
2	25.0	100
2	.25	150
2	1.0	150
2	3.0	150
2*	5.0	150
2	10.0	150
2	15.0	150
2	25.0	150
2	.25	200
2	1.0	200
2	3.0	200
2	5.0	200
2	10.0	200
2	15.0	200
2	25.0	200
2	.25	300
2	1.0	300
2	3.0	300
2	5.0	300

ILLUMINATION PERIOD (min.)	DYE CONCENTRATION (mg/l)	CRESOL CONCENTRATION (mg/l)
2	10.0	300
2	15.0	300
2	25.0	300
5	1.0	50
5	5.0	50
5	10.0	50
5	25.0	50
5	1.0	150
5	5.0	150
5	10.0	150
5	25.0	150
10	1.0	50
10	5.0	50
10	10.0	50
10	25.0	50
10	1.0	150
10	5.0	150
10	10.0	150
10	25.0	150

* = done in duplicate

```
DYE-CØNCENTRATIØN =   3.00000

CURVEFIT NØ. 1 -Y=C+B*EXPAX

ENTRY INTØ LSCF

CØEFFICIENT ØF VARIABLE   1  IS                       -.41608043E-01

CØEFFICIENT ØF VARIABLE   2  IS                        .45753431E 01

ENTRY INTØ ERRØR

      Y-MEAS           Y-CALC           DEV              PERCENT              X
    100.000000       97.011017        2.988983          2.988982           .001000
     84.000000       89.265717       -5.265717         -6.268709          2.000999
     80.000000       82.138748       -2.138748         -2.673435          4.000999
     78.000000       75.580780        2.419220          3.101563          6.000999
     70.000000       69.546432         .453568           .647954          8.000999
     66.000000       63.993927        2.006073          3.039504         10.000999
     61.000000       58.884628        2.115372          3.467822         12.000999
     54.000000       54.183273        -.183273          -.339395         14.000999
     50.000000       49.857315         .142685           .285370         16.000992
     44.000000       45.876755       -1.876755         -4.265351         18.000992
     41.000000       42.213989       -1.213989         -2.960949         20.000992
     40.000000       38.843582        1.156418          2.891044         22.000992

STANDARD DEVIATIØN EQUALS    2.378

AVERAGE PERCENT DEVIATIØN EQUALS          -.00713

  91.667  PERCENT ØF DATA PØINTS WITHIN   5.000  PERCENT ØF THE EQUATIØN

 100.000  PERCENT ØF DATA PØINTS WITHIN  10.000  PERCENT ØF THE EQUATIØN

 100.000  PERCENT ØF DATA PØINTS WITHIN  15.000  PERCENT ØF THE EQUATIØN

 100.000  PERCENT ØF DATA PØINTS WITHIN  20.000  PERCENT ØF THE EQUATIØN
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SAMPLE COMPUTER OUTPUT

RESULTS OF EACH EXPERIMENT

Using all 26 minutes of data:

Cresol (mg/1)	Dye (mg/1)	C_o (mg/1)	k (min^{-1})
300 (t=2)	.25	302.9	-.0094
	1	289.8	-.0132
	3	282.6	-.0221
	5	283.9	-.0258
	10	276.5	-.0266
	15	282.9	-.0268
	25	293.9	-.0260
200 (t=2)	.25	199.0	-.0059
	1	182.9	-.0208
	3	202.4	-.0376
	5	201.0	-.0319
	10	193.2	-.0389
	15	192.0	-.0443
	25	196.1	-.0300
150 (t=2)	.25	149.8	-.0102
	1	145.4	-.0236
	3	142.3	-.0307
	5	147.5	-.0390
	10	147.4	-.0380
	15	150.1	-.0451
	25	153.5	-.0425
150 (t=5)	1	150.2	-.0221
	5	149.4	-.0353
	10	151.2	-.0380
	25	149.2	-.0337
150 (t=10)	1	144.7	-.0227
	5	142.7	-.0342
	10	142.1	-.0364
	25	142.6	-.0357
100 (t=2)	.25	98.9	-.0121
	1	97.9	-.0254
	3	97.0	-.0416
	5	97.4	-.0500
	10	104.8	-.0577

Cresol	Dye	C_o	k
	15	98.3	-.0475
	25	108.8	-.0472
50 (t=2)	.25	47.9	-.0120
	1	50.5	-.0340
	3	50.0	-.0549
	5	52.5	-.0723
	10	54.1	-.0572
	15	53.1	-.0693
	25	49.3	-.0488
50 (t=5)	1	46.1	-.0296
	5	48.3	-.0581
	10	47.7	-.0519
	25	44.3	-.0429
50 (t=10)	1	48.0	-.0306
	5	49.4	-.0527
	10	50.6	-.0596
	25	50.1	-.0587
10 (t=2)	.25	9.2	-.0175
	1	9.6	-.0318
	3	10.0	-.0545
	5	10.2	-.0620
	10	9.6	-.0642
	15	10.6	-.0705
	25	10.6	-.0480
Anaerobic - swept by N_2			
150 (t=2)	1	147.1	-.00848
	3	145.1	-.00893
	5	142.2	-.0117
Using first eight minutes of data:			
300 (t=2)	.25	301.3	-.00752
	1	297.0	-.0162
	3	292.9	-.0295
	5	291.8	-.0340
	10	293.9	-.0334

Cresol	Dye	C_o	k
	15	297.7	-.0346
	25	302.6	-.0306
200 (t=2)	.25	199.0	-.00586
	1	194.9	-.0304
	3	201.3	-.0322
	5	197.3	-.0448
	10	200.1	-.0435
	15	194.9	-.0488
	25	198.7	-.0315
150	.25	151.5	-.0142
	1	146.0	-.0218
	3	149.7	-.0413
	5	147.1	-.0367
	10	150.9	-.0445
	15	151.7	-.0476
	25	150.8	-.0371
100	.25	97.5	-.00781
	1	100.0	-.0291
	3	95.7	-.0394
	5	99.0	-.0505
	10	101.2	-.0499
	15	104.0	-.0587
	25	98.8	-.0295
50 (t=2)	.25	49.4	-.0219
	1	51.2	-.0374
	3		
	5	53.2	-.0689
	10	53.0	-.0481
	15	51.7	-.0649
	25	50.0	-.0519
10 (t=2)	.25	9.7	-.0276
	1	9.7	-.0311
	3	10.0	-.0569
	5	10.0	-.0574
	10	10.4	-.0801
	15	10.1	-.0580
	25	10.1	-.0413

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