



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  
© Copyright by Jerome Wadsworth Sargent (1971)

**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 ( $C = C_0 e^{-kt}$ ), 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.

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.

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature

*Jerome W. Sargent*

Date

*8/9/77*

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

Approved:

  
\_\_\_\_\_  
Head, Major Department

  
\_\_\_\_\_  
Chairman, Examining Committee

  
\_\_\_\_\_  
Graduate Dean

MONTANA STATE UNIVERSITY  
Bozeman, Montana

August, 1971

ACKNOWLEDGEMENT

Financial support for this investigation was provided by the Water Quality Office of the Environmental Protection Agency. Facilities were provided by the Civil Engineering Department of Montana State University.

Special thanks are due Dr. S. J. Rogers of the MSU Chemistry Department for suggesting the subject of this study and for his continuous advice and suggestions.

Also gratefully acknowledged are the advice and guidance provided by the author's graduate committee; Dr. R. L. Sanks, Chairman, and Mr. T. T. Williams of the MSU Civil Engineering Department, and Dr. J. E. Robbins from the Department of Chemistry.

## TABLE OF CONTENTS

Chapter	Page
I. <u>INTRODUCTION</u> -----	1
OBJECTIVES -----	3
II. <u>THEORY AND LITERATURE REVIEW</u> -----	4
REACTION MECHANISM -----	4
Absorption of Light Energy -----	5
Primary Reactions of Energized Sensitizer -----	5
Triplet Sensitizer Decay -----	6
Triplet Sensitizer-Oxygen Interaction -----	6
Triplet Sensitizer-Substrate Interaction -----	7
Secondary Reactions of Intermediates -----	7
SUBSTRATE -----	10
SENSITIZER DYES -----	10
III. <u>EQUIPMENT AND MATERIALS</u> -----	12
MATERIALS -----	12
Sensitizer -----	12
Substrate -----	12
EQUIPMENT -----	12
Reactor -----	12
Aeration -----	12
Analyzer -----	15
Recorder -----	15
Hydrogen Ion Concentration -----	15
Temperature -----	15
IV. <u>PROCEDURE</u> -----	17
CONCENTRATIONS -----	17
AERATION -----	17
ILLUMINATION -----	17
EXAMPLE EXPERIMENT -----	18
TESTS PERFORMED AND DATA REPRODUCIBILITY -----	20
STANDARDS AND STOCK SOLUTIONS -----	20
METHOD OF DATA ANALYSIS -----	20
V. <u>RESULTS</u> -----	25
REACTION RATES -----	25
ACCURACY OF DATA ANALYSIS -----	29

TABLE OF CONTENTS  
(Continued)

Chapter	Page
DYE BLEACHING -----	29
HYDROGEN ION CONCENTRATION -----	34
TEMPERATURE -----	34
OTHER OBSERVATIONS -----	36
IV. <u>DISCUSSION</u> -----	38
PROCEDURE, EQUIPMENT, AND MATERIALS -----	38
Sensitizer -----	38
Substrate -----	38
Reaction System -----	38
RESULTS -----	39
Dye Concentration -----	39
Substrate Concentration -----	40
Reaction Rate -----	40
Reaction Mechanism and Kinetics -----	41
Hydrogen Ion Concentration -----	43
Reaction Products -----	43
Temperature -----	43
Other Observations -----	44
VII. <u>CONCLUSIONS AND RECOMMENDATIONS</u> -----	45
LITERATURE CITED -----	48
APPENDIX -----	51

## LIST OF TABLES

Table	Page
1. Oxygen Absorbed by Phenols During Riboflavin Sensitized Photo-Oxidation -----	11
2. Operating Parameters for Gas Chromatographic Measurement of Cresol in Aqueous Solution -----	16

## LIST OF FIGURES

Figure	Page
1. Summary of Aerobic Dye Sensitized Photo-Oxidation Reactions -----	9
2. Absorption Spectrum for 3 mg/l Methylene Blue -----	14
3. Photo-Oxidation Reactor -----	13
4. Sample Cresol Chromatogram -----	19
5. Correlation Curve for Gas Chromatographic Measurement of Cresol -----	21
6. Cresol Concentration and pH vs. Illumination Time -----	23
7. Cresol Concentration vs. Illumination Time -----	26
8. Reaction Rate vs. Dye Concentration. Comparing Aerobic and Anaerobic Rates for $C_0 = 150$ mg/l and Illumination Period = 2 min. -----	27
9. Reaction Rate vs. Cresol Concentration at Constant Dye Concentrations -----	28
10. Reaction Rate vs. Dye Concentration for Two Minute Illumination Periods. $C_0=10, 200$ and $300$ mg/l --	30
11. Reaction Rate vs. Dye Concentration for Two Minute Illumination Periods. $C_0=50, 100$ and $200$ mg/l --	31
12. Reaction Rate vs. Dye Concentration for Five Minute Illumination Periods -----	32
13. Reaction Rate vs. Dye Concentration for Ten Minute Illumination Periods -----	33
14. Reaction Rate vs. Cresol Concentration at Constant Dye Concentrations. Comparing Eight Minute and Two Minute Data -----	35

LIST OF FIGURES  
(Continued)

Figure	Page
15. Temperature vs. Illumination Time -----	37

## 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 ( $C = C_0 e^{-kt}$ ), 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.

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.

## 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.

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

Triplet Sensitizer-Oxygen Interaction 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 ( $\xi g$ ) and ( $\Delta g$ ). ( $\Delta g$ ) probably predominates in most instances because its energy of formation (22 kilocalories) is less than that of ( $\xi g$ ) (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.

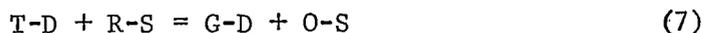
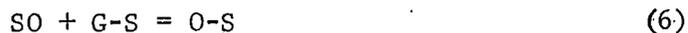
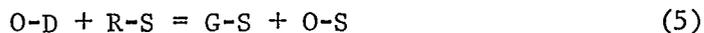
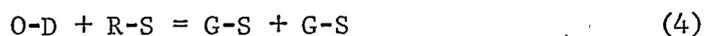
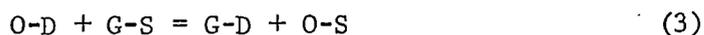
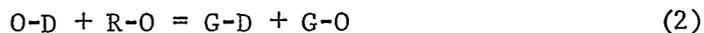
Triplet Sensitizer-Substrate Interaction Little is known about the mechanism involved or the intermediates formed when triplet sensitizer interacts directly with substrate. Foote (1968) points out that simple energy transfer between the triplet sensitizer and substrate is unlikely in most instances because 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 observed in an aerobic dye sensitized photo-oxidation system.



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 0 and 3 indicate ground state and triplet state respectively. The subscripts ox and red mean oxidized and reduced. Sing O<sub>2</sub> refers to singlet oxygen, Sub indicates substrate, and Sens means sensitizer dye.

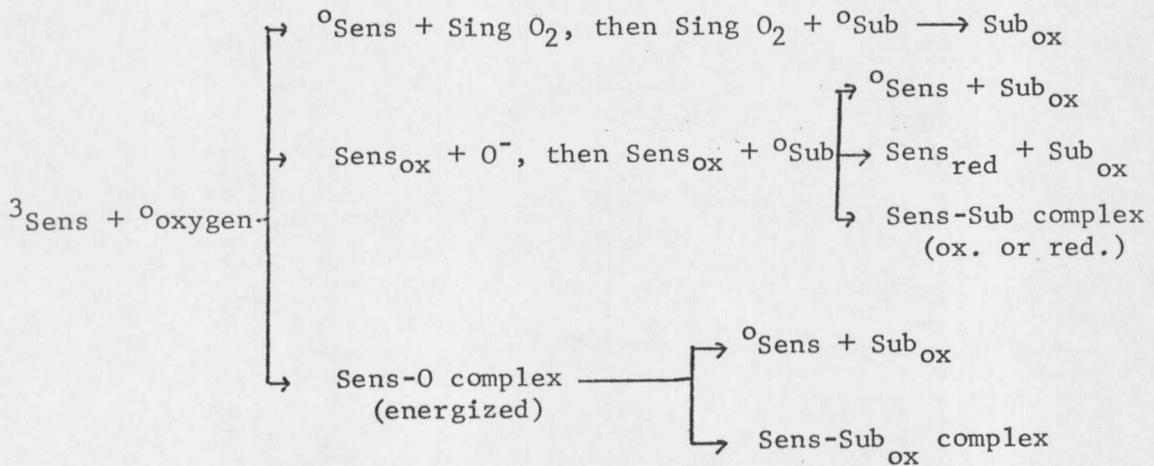
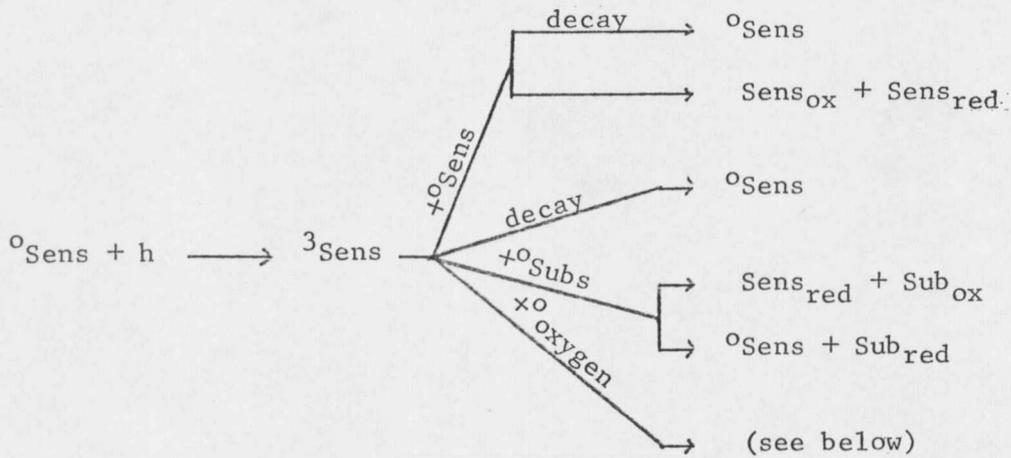


Fig. 1 SUMMARY OF AEROBIC DYE SENSITIZED PHOTO-OXIDATION REACTIONS

#### 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.

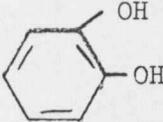
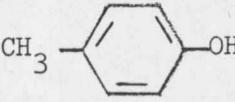
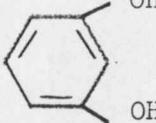
Kolesnikov (1958) determined the relative susceptibility of several phenolic and other substances to riboflavin-sensitized photo-oxidation. In Table 1, for several of those compounds the oxygen absorption during photo-oxidation is listed. One of Kolesnikov's conclusions was that para and ortho diphenols 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/l water solution of methylene blue as presented by Holmes (1924). The dye has absorption peaks at about 6100 and 6600  $\text{A}^\circ$ .

##### 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  $\text{A}^\circ$ ). 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



























































































