



Dye catalyzed oxidation of refractory organic wastes using visible light energy
by Jerome Wadsworth Sargent

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Civil Engineering
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Abstract:

Dye sensitized aerobic photo-oxidation is a photo-chemical process by which some organics refractory to conventional waste treatment can be oxidized. Sensitizer dye absorbs visible light energy and transfers it to dissolved oxygen to form singlet oxygen. Singlet oxygen is a strong oxidizing agent capable of oxidizing various refractory organics including heterocyclic aromatics like cresol and phenol. The oxidation products are likely to be nonaromatic compounds tractable to biological oxidation. With sunlight as the light source only oxygen and energy for aeration are consumed.

The sensitizer can be reused many times if a method of dye application and recovery is developed. Some dyes might serve as sensitizers while irreversibly bound to polymers like ion exchange resins, polysaccharides, or polymeric gels. After substrate photo-oxidation, polymer and dye could be removed by sedimentation, screening, or some other method.

Methylene blue and Rose Bengal are effective sensitizers of aerobic photo-oxidation of phenol and cresol. Minimum cresol half-life is 2.45 minutes with methylene blue and 2.74 minutes with Rose Bengal. Phenol half-life is 6.9 minutes with methylene blue and 7.5 minutes with Rose Bengal.

High pH (9 to 10) favors dye sensitized aerobic photo-oxidation. Reaction rate increases with increasing light intensity from tungsten incandescent lamps. Light from commercially available fluorescent lamps is not sufficiently intense to energize the process. Substrate oxidation can be achieved in liquid layers up to 1 3/4 inches thick.

Optimum methylene blue concentration to sensitize aerobic photooxidation of cresol and phenol is 1.56 10^{-5} M. Optimum initial substrate concentration is about 4.5×10^{-4} M.

Attaching methylene blue to various commercially available cation exchange resins significantly reduces the dye's ability to sensitize singlet oxygen production. Further testing is necessary to develop a method by which dye can be applied and recovered for reuse without detracting from its ability to absorb visible light and generate singlet oxygen.

For the technologic and economic feasibility of dye sensitized aerobic photo-oxidation applied to waste treatment to be assessed, the process must be tested with sunlight and actual waste streams.

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WASTES USING VISIBLE LIGHT ENERGY

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JEROME WADSWORTH SARGENT

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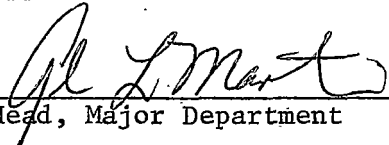
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ABSTRACT

Dye sensitized aerobic photo-oxidation is a photo-chemical process by which some organics refractory to conventional waste treatment can be oxidized. Sensitizer dye absorbs visible light energy and transfers it to dissolved oxygen to form singlet oxygen. Singlet oxygen is a strong oxidizing agent capable of oxidizing various refractory organics, including heterocyclic aromatics like cresol and phenol. The oxidation products are likely to be nonaromatic compounds tractable to biological oxidation. With sunlight as the light source only oxygen and energy for aeration are consumed.

The sensitizer can be reused many times if a method of dye application and recovery is developed. Some dyes might serve as sensitizers while irreversibly bound to polymers like ion exchange resins, polysaccharides, or polymeric gels. After substrate photo-oxidation, polymer and dye could be removed by sedimentation, screening, or some other method.

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High pH (9 to 10) favors dye sensitized aerobic photo-oxidation. Reaction rate increases with increasing light intensity from tungsten incandescent lamps. Light from commercially available fluorescent lamps is not sufficiently intense to energize the process. Substrate oxidation can be achieved in liquid layers up to 1 3/4 inches thick.

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CHAPTER I

INTRODUCTION

Photo-oxidation is the oxidation of a substrate by means of a series of chemical reactions involving light energy. The various different kinds of photo-oxidation processes are legion so it is necessary to describe carefully and completely a particular photo-oxidation sequence being discussed. The process which is the subject of this report, dye sensitized aerobic photo-oxidation, is described in an earlier paper by Sargent (1971).

The literature is replete with reports of scientific research on photo-oxidation and its almost unlimited applications. Less numerous but still extensive are references concerning application of various photo-oxidation processes to water and wastewater treatment. Virtually all of the latter deal with destruction of waste molecules or micro-organisms either directly or indirectly by ultraviolet light. Examples are the investigation by Bulla and Edgerley (1968) of photolysis of pesticides by ultraviolet light, the studies by Matsuura and Smith (1970) of UV energized photo-decomposition of formic acid and detergents, and testing of photochemical oxidation of soluble organics in municipal wastewater by Hancil and Smith (1971). Kinney and Ivanuski (1969) refer only incidentally to dye sensitized photolysis of waste materials.

Water or wastewater treatment processes which require ultraviolet light often prove uneconomical because of energy requirements. That disadvantage will only be aggravated as energy becomes an ever more scarce commodity. Dye sensitized aerobic photo-oxidation, however, is energized by visible light which suggests the possibility of using sunlight.

Most organic waste molecules are not destroyed by direct absorption of visible light. But, according to Kautsky (1938) and Foote (1968), many dyes like methylene blue and Rose Bengal will absorb visible light energy in water solution and selectively transfer that energy to dissolved oxygen. The oxygen is excited to a singlet state and becomes a strong oxidizing agent capable of oxidizing many ordinarily refractory organic molecules. After energy transfer to oxygen the dye is available to absorb more light energy. With sunlight as the energy source only oxygen and energy for aeration are spent.

Earlier studies by Sargent (1971) and Kolesnikov (1958), and unreported preliminary testing by Seely (1973) show that some organic materials which appear in some waste streams and are refractory to ordinary treatment processes can be destroyed by dye-sensitized aerobic photo-oxidation. Many investigators including Mathews (1963), Blum (1935), and Wallis et al (1972) have shown bacteria and viruses can be killed by the same method. But an engineering process to employ dye sensitized aerobic photo-oxidation in water or wastewater

treatment has yet to be developed. One reason is that photo-chemistry is foreign to sanitary engineers and the gap between scientific research and engineering application has never been bridged.

For dye sensitized aerobic photo-oxidation to be successfully employed as a treatment process a means of applying, recovering, and reusing the sensitizer dye must be developed. Only a very low concentration of dye is required [1.5×10^{-5} molar (M)] but dyes are relatively expensive and consumptive use of dye should be avoided. One possible method of dye application and recovery is to bind the dye irreversibly to larger particles like ion exchange resins or polymeric gels. The dye can serve as a sensitizer while attached to the polymer and the polymer-dye complex can be removed for reuse by sedimentation, screening, or some other process. Several investigators have studied dye binding to polymers including Bellin and Yankus (1968), Bellin (1968), Vitagliano and Costantino (1969), and Bradley and Wolf (1959). With their work as guide, it is likely a dye sensitized aerobic photo-oxidation treatment process with little consumptive use of dye can be developed.

Dye might also be applied in solution to sensitize substrate oxidation followed by removal of the dye by ion exchange. But ion exchange resins are very selective for most dyes. Hence dye elution from the resin for reuse would probably be impractical, and both dye and resin could only be used once.

OBJECTIVES

The general purpose of this research is to analyze and optimize the important parameters of dye sensitized aerobic photo-oxidation as applied to water and wastewater treatment. Specific objectives are to:

1. Test fluorescent and tungsten incandescent lamps as energy sources for dye sensitized aerobic photo-oxidation.
2. Develop a reactor for testing dye sensitized aerobic photo-oxidation both in batch and flow-thru process as a water and wastewater treatment method.
3. Test several dyes for effectiveness as photo-sensitizers.
4. Determine the extent to which phenol and cresol can be photo-oxidized in a dye sensitized process using visible light.
5. Optimize substrate concentration, dye concentration, light intensity, and pH as parameters of dye sensitized aerobic photo-oxidation.
6. Determine the liquid layer thickness to achieve optimum photo-oxidation under the conditions of this investigation.
7. Compare reaction rates in batch and flow-thru processes.
8. Determine if dye attached to various different commercial ion exchange resins can sensitize aerobic photo-oxidation of substrate.

9. Test an ion exchange resin for capacity to remove sensitizer dye from aqueous solution.

LIMITATIONS

All experiments in this study were performed in the laboratory using a small reactor. No testing was done with sunlight or actual waste streams.

Of the great number of dyes with potential as sensitizers for aerobic photo-oxidation, nine were used in this study. Two substrates (phenol and cresol) representative of aromatic, heterocyclic waste materials were tested.

The reaction mechanisms involved in dye sensitized aerobic photo-oxidation are complex and not completely understood. Hence all parameters important to the process have not been defined. Several parameters of probable importance were studied in this investigation.

CHAPTER II

THEORY

GENERAL PHOTO-OXIDATION

Any chemical reaction or series of reactions which requires light energy and results in oxidation of some material can be called photo-oxidation. An almost unlimited number of different photo-oxidations are possible. One reason is many atoms and molecules can absorb light of proper wavelengths and be excited to energy states above their normal ground state. An atom or molecule thus excited or energized is a stronger oxidizing and reducing agent than its ground state. Hence absorption of light energy can cause oxidation which would not otherwise occur.

Greatly enlarging the number of possible photo-oxidation reactions is the fact that a given photo-chemical sequence can involve from one to several constituents as direct reactants, reaction intermediates, or catalysts. In fact a given set of primary reactants can react by many different pathways depending on such factors as temperature, pH, relative reactivity and concentration of reactants, and properties of the light source.

DYE SENSITIZED AEROBIC PHOTO-OXIDATION

REACTION SEQUENCE

Dye sensitized aerobic photo-oxidation is this writer's choice of a term to describe a particular photo-oxidation reaction, primary features of which are: (1) it is energized by visible light, (2) dye serves as the light absorber, (3) oxygen is required and consumed in a singlet state, and (4) a chosen substrate is irreversibly oxidized.

Energy Absorption

Most organic molecules which appear in wastewater streams are not destroyed by direct absorption of visible light. But dyes can be added which will absorb visible light to start a sequence of events resulting in oxidation of certain organics.

The ground state of dyes and most other molecules is a singlet. A singlet molecule is one which has all electron spins paired. Light absorption energizes the dye from ground state to an excited singlet state. An excited singlet still has paired electron spins but some electrons have been raised to higher energy orbitals. Excited singlet dye is very short-lived and either decays directly back to ground state singlet, which is fluorescence, or converts to a triplet state.

Triplet dye is a relatively long-lived species and has two electrons with unpaired spins. Kato et al (1963) observed triplet dye lifetimes of about thirty microseconds and Grossweiner and Zwicker

(1961) reported ten microsecond survival times. Triplet state dye either decays directly back to ground state, which is phosphorescence, or returns to ground state after transferring its energy to some other molecule. Figure 1 is a diagram of possible electronic states and transitions after light absorption by sensitizer dye.

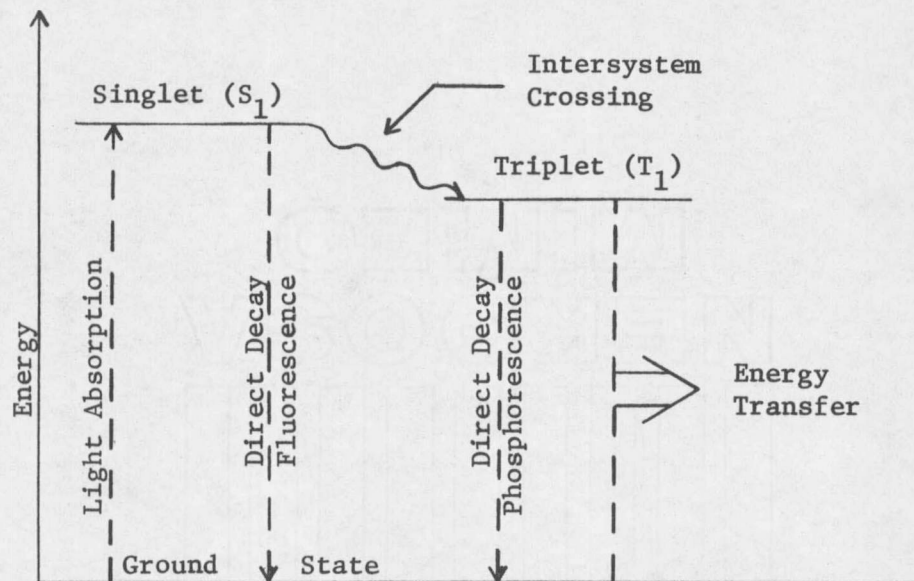


Fig. 1. ENERGY STATES AND TRANSITIONS OF SENSITIZER DYE

Energy Transfer

Final disposition of the absorbed energy of triplet dye depends on environmental conditions such as kind of solvent, type and concentration of other molecules in solution, and temperature. For energy transfer to another molecule to occur, the energy gap between ground state and the first excited state of that molecule must be less than the absorbed energy of triplet dye, which is on the order of 40 kilocalories per mole (Kcal/M) for dyes of interest as sensitizers. Most organics require much more energy to be excited than is available from triplet dye. Oxygen, however, is unusual because its ground state is a triplet and the energy gap between ground state and the first excited state, which is a singlet, is unusually low (22 Kcal/M). Hence if dissolved oxygen is present even in trace amounts triplet dye will selectively transfer its energy to oxygen. Merkel and Kearns (1972) measured quantum yields of 0.9 ± 0.1 for formation of singlet oxygen from quenching of triplet state methylene blue.

Energy transfer from triplet dye to oxygen to generate singlet oxygen is the mechanism essential to dye sensitized aerobic photo-oxidation. But other mechanisms can compete with and even preempt the triplet dye to oxygen energy transfer. Kepka and Grossweiner (1971) observed direct reaction between triplet eosin dye and substrate at high substrate concentration. At lower substrate concentration they found electron transfer from triplet dye to oxygen. Sargent (1971)

gave a summary of other possible reaction pathways for triplet dye. Which pathway predominates is a sensitive function of at least dye concentration, electronic properties of the dye, oxygen concentration, pH, substrate concentration, and substrate reactivity.

The relative excitation energies of sensitizer dye, oxygen, and other molecules present are critical in determining the pathway of energy transfer in a dye sensitized photo-oxidation system.

Triplet Dye Energy. The triplet energy of a dye is a function of the wavelength at which the dye phosphoresces. The relationship is:

$$\lambda \times E_T = 28,600 \quad (1)$$

where λ is the dye's wavelength of phosphorescence and E_T is the dye's triplet energy. From measurements of the phosphorescence wave band of a dye, its triplet energy can be calculated.

For efficient energy transfer from triplet dye to ground state oxygen, triplet dye energy should be at least 5 Kcal/M greater than the energy gap between ground state oxygen and its first singlet state (22 Kcal/M). Hence triplet dye energy should be about 27 Kcal/M or more for the dye to be capable of sensitizing singlet oxygen formation.

Energized Oxygen. Two singlet states of oxygen have been observed in aqueous dye sensitized photo-oxidation systems. The first excited state has excitation energy of 22 Kcal/M and is labeled ($^1\Delta_g$). The

second excited state, called ($^1\Sigma_g$), has an excitation energy of 37 Kcal/M. According to Merkel and Kearns (1972) ($^1\Sigma_g$) is very short-lived with an estimated lifetime of less than 10^{-4} microseconds in water. On the other hand those same investigators, in agreement with Foote (1968), estimate the lifetime of ($^1\Delta_g$) to be nearly two microseconds in water. Hence ($^1\Delta_g$) is probably the oxygen species involved in oxidation of substrate.

The bond electrons of ($^1\Delta_g$) possess absorbed energy which has raised them to energy levels relatively more removed from the oxygen nucleus than the ground state energy levels. As a consequence those electrons, being held less tightly to the molecule, are more available for transfer to other materials. This makes the singlet state a stronger reducing agent than ground state oxygen. Conversely, since the bond electrons are relatively far from the nucleus the oxygen molecule's attraction for electrons is increased and it becomes a stronger oxidizing agent. In most reactions singlet oxygen is more likely to serve as an oxidizing agent than as a reducing agent.

Reactions of Energized Oxygen

The fate of singlet oxygen depends on the environment of the reaction system. It can be quenched by solvent, decay spontaneously to ground state, be quenched by dye or other molecules in solution, or react with substrate. The extent to which each pathway occurs is determined by such factors as sensitizer type and concentration,

oxygen concentration, properties of the activating light energy, and reactivity and concentration of other molecules in solution.

Reaction between singlet oxygen and substrate is a diffusion controlled process with the rate dependent mainly on the viscosity of the solvent. According to Pitts and Calvert (1966) the rate constants for diffusion controlled bimolecular reactions are typically from 10^9 to 10^{10} liters per mole second. Quenching of singlet oxygen by dye or ground state oxygen was observed by Merkel and Kearns (1972) to be insignificant compared to quenching by water which allows a two micro-second lifetime for ($^1\Delta_g$). Hence if a reactive substrate is present the singlet oxygen-substrate reaction will likely be competitive with quenching reactions.

PROCESS PARAMETERS

Mechanisms and Reaction Conditions

There has been a great deal of controversy in the literature about reaction mechanisms which occur in a dye sensitized aerobic photo-oxidation system. Some investigators claim oxidation is by singlet oxygen. Others argue a dye-oxygen complex is the oxidizing agent. Still others are convinced ground state oxygen-substrate complex formation precedes energy transfer and oxidation. The root of controversy seems to lie in attempts by investigators to assign to all dye sensitized aerobic photo-oxidations the mechanism observed in their

particular studies. More likely many mechanisms are possible depending on a multitude of parameters such as kind of sensitizer dye, properties of the light source, oxygen concentration, sensitizer concentration, pH, temperature, and concentration and reactivity of substrate. In fact a particular mechanism might be selected by proper adjustment of process parameters.

Parameter Values

A complete understanding of all parameters important in dye sensitized aerobic photo-oxidation has yet to be achieved. But there is evidence that at least pH, dye concentration, substrate concentration, properties of light source, oxygen concentration, and substrate reactivity are important.

pH. Many investigators including Weil et al (1951), Bellin and Yankus (1968), and Sargent (1971) have concluded high pH (8 to 10) favors dye sensitized aerobic photo-oxidation. Acid ionization of substrates like phenol and cresol increases electron density at the ionization site, thus enhancing attack by singlet oxygen. Also, any protons which might be liberated when substrate is oxidized are taken up by excess hydroxyl ions.

Dye Concentration. Absorption of light increases with dye concentration to the limit of available light energy. At high dye concentra-

tion, however, quenching of triplet dye by its ground state becomes important and direct reaction between sensitizer and substrate might be enhanced. Sargent (1971) concluded optimum dye concentration is on the order of 1.5×10^{-5} M for sensitizing aerobic photo-oxidation.

Substrate Concentration. Since the substrate-singlet oxygen reaction is a diffusion controlled process, increasing substrate concentration should increase reaction rate. On the other hand direct reaction between triplet dye and substrate also increases with substrate concentration. Sargent (1971) observed a cresol concentration of about 5×10^{-4} M to be optimum for methylene blue sensitized aerobic photo-oxidation.

Substrate Reactivity. Only materials reactive with singlet oxygen can be substrate for dye sensitized aerobic photo-oxidation. Substrate reactivity with triplet dye is undesirable because that reaction can result in irreversible dye destruction.

Properties of Light Source. The energy of only those light wavelengths absorbed by sensitizer dye serves to generate triplet dye and in turn singlet oxygen. The degree to which the light source emission spectrum and the sensitizer absorption spectrum overlap is a measure of total energy absorbed. For efficient use of available light energy a

sensitizer should be selected to absorb as much of the light's emission spectrum as possible.

Oxygen Concentration. The relationship between triplet dye energy and the energy gap from ground state oxygen to its first singlet favors energy transfer from triplet dye to dissolved oxygen. According to Foote (1968) even trace amounts of oxygen can successfully compete for triplet dye energy.

Concentration of dissolved oxygen in water is temperature dependent and limited to about 5×10^{-4} M. If the oxygen required to oxidize substrate exceeds that value aeration is necessary. Neither oxygen concentration above trace amounts nor rate of oxygen transfer by aeration has been reported as limiting in dye sensitized aerobic photo-oxidation.

SUBSTRATE

Compounds Photo-Oxidized

According to Spikes and Straight (1967) many organic compounds including alcohols, aldehydes, amines, esters, indoles, olefins, carbohydrates, and nucleic acids can undergo sensitized photo-oxidation. Glad and Spikes (1966), Weil et al (1951) and many others have reported sensitized photo-oxidation of aromatic amino acids. Evidence that phenols and cresols can be photo-oxidized has been presented by

Grossweiner and Zwicker (1961 and 1963), Kolesnikov (1958) and Sargent (1971).

Although a wide range of compounds can be oxidized by one or another of the many photo-chemical processes, relatively few are sensitive to dye sensitized aerobic photo-oxidation. In fact Foote (1968) refers to singlet oxygen as a very selective intermediate which fails to react with most compounds. Fortunately some refractory materials like phenol, cresol, and pesticides which appear in waste streams are among those compounds reactive with singlet oxygen.

According to Craig (1972) singlet oxygen is most reactive with molecules of high electron density possessing high energy electrons. In organic compounds, unsaturated covalent bonds are sites of high electron density. But being unsaturated is not a sufficient condition for reactivity with singlet oxygen. For example benzene, with three double (π) bonds, is electron rich but the π bonds are evenly distributed among the carbon atoms, making the electrons quite stable. Substitution of electron withdrawing groups like nitro, sulfo, or cyano groups reduces the π bond density in the benzene ring and makes the aromatic even more difficult to oxidize. On the other hand if electron donating groups like hydroxyl or methyl groups are substituted, the π bond density at the ring carbon atoms increases and the resulting aromatic is more susceptible to oxidation.

Cresol, with one hydroxyl and one methyl group substituted on a benzene ring, should be reactive with singlet oxygen. Sargent (1971) observed a cresol half-life of less than ten minutes in a dye sensitized aerobic photo-oxidation system. Similarly phenol and the aromatic amino acids have proved sensitive to oxidation by singlet oxygen.

The aromatic ring is the structure in many organics which makes them refractory to most wastewater treatment processes, especially biological oxidation. Since singlet oxygen will readily react with many substituted aromatic molecules, dye sensitized aerobic photo-oxidation might be applied to waste treatment.

Oxidation Products

The greatest potential for dye sensitized aerobic photo-oxidation applied to waste treatment probably lies in destruction of unsaturated heterocyclic compounds. Therefore only products of reaction between singlet oxygen and aromatic ring structures are discussed here.

Craig (1973) suggests three possible pathways by which singlet oxygen might react with unsaturated heterocyclic compounds. For convenience they are labeled Diels-Alder reaction, dioxetane ring mechanism, and ene reaction. The three pathways are illustrated in Figure 2 for the reaction of singlet oxygen with cresol. The superoxide reaction shown in Figure 2 is an alternate of the dioxetane ring mechanism wherein only one atom of the oxygen molecule bonds to two adjacent carbon atoms in cresol's benzene ring. Which pathway

