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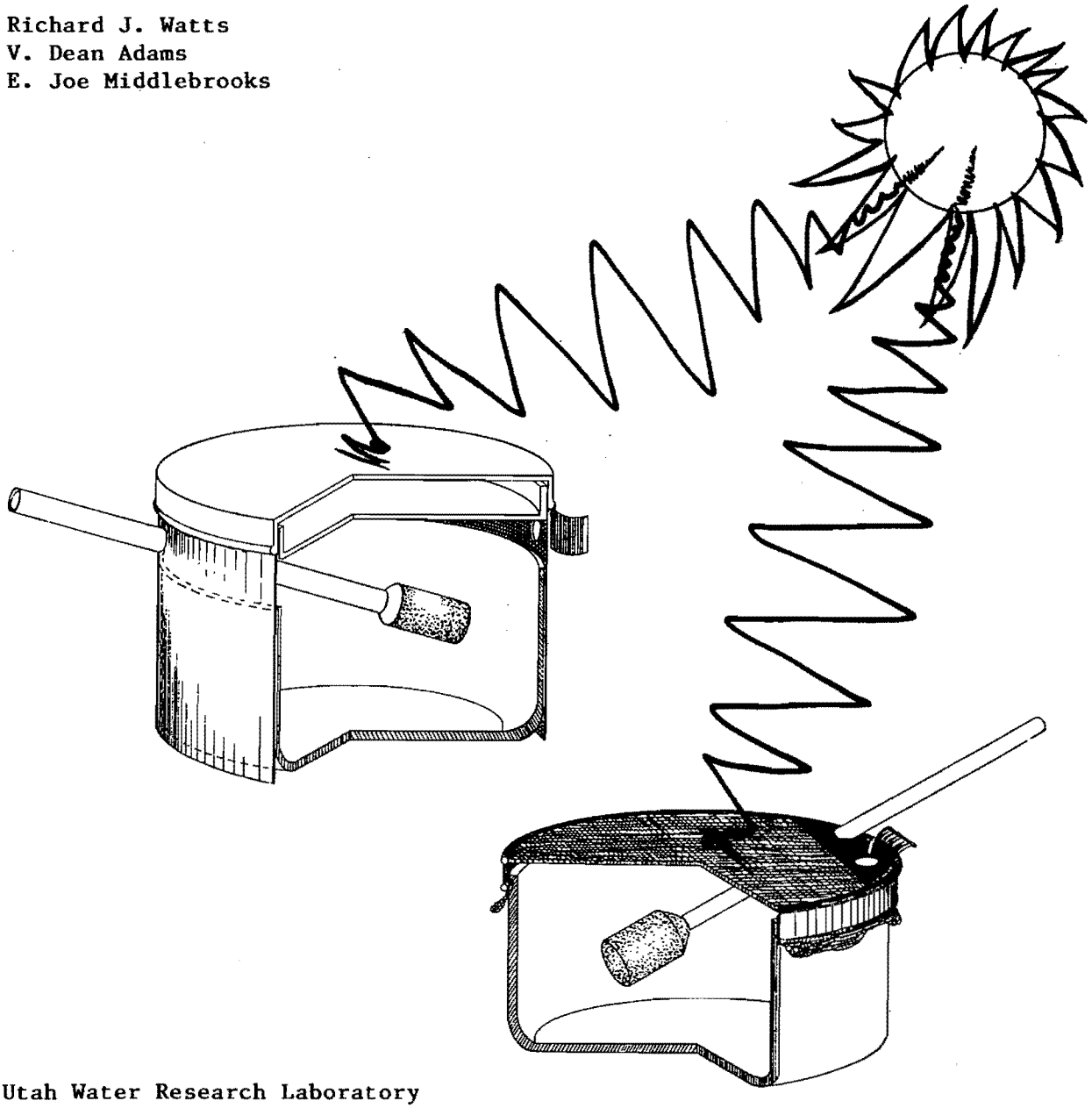

Utah Water Research Laboratory
Utah State University
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WATER QUALITY SERIES
UWRL/Q-85/02

DEVELOPMENT OF DESIGN CRITERIA FOR SENSITIZER PHOTOOXIDATION TREATMENT SYSTEMS

by

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ABSTRACT

Sensitized photooxidation is a physicochemical process that can degrade many toxic and refractory organic pollutants. A trace quantity of sensitizer added to the waste absorbs visible light; electronically excited intermediates then transfer the energy to decompose the waste.

Engineering design criteria were developed for industrial waste treatment lagoons that would use sensitized photooxidation. Design criteria were developed regarding optimum lagoon pH, optimum sensitizer concentration, depth and sizing of lagoons, dissolved oxygen requirements, and effect of temperature on photooxidation rate. Treatment of the refractory pesticides bromacil, terbacil, and fluometuron was investigated using methylene blue and riboflavin as sensitizers.

Methylene blue-sensitized photooxidation of the three pesticides was most efficient at basic pH. The optimum pH of riboflavin-sensitized photooxidation varied and was substrate-dependent.

A model was developed to predict sensitized photooxidation rate as a function of lagoon depth. The model is based on light intensity, sensitizer extinction coefficient, and an applied quantum yield, all of which are integrated over wavelengths of visible light. The model serves as the basis for sizing photooxidation lagoons.

A dissolved oxygen residual of 1 mg/l was required to maintain maximum methylene blue-sensitized photooxidation rate. At least 4 mg/l dissolved oxygen was necessary to maintain riboflavin-sensitized photooxidation at maximum levels. Oxygen uptake rates in sensitized photooxidation reactions were proportional to the concentration of substrate. Temperatures from 10° to 35°C had no significant effect on sensitized photooxidation rates.

Using the model developed, a methylene blue-sensitized photooxidation pilot lagoon was designed to treat a 30 mg/l bromacil influent concentration to 0.1 mg/l bromacil in the effluent. For an influent flow of 0.263 m^3/min (0.1 MGD) waste, a 0.1 mg/l methylene blue concentration, 36 cm depth, and 1870 m^2 surface area are required. A cost analysis was performed which indicated that sensitized photooxidation lagoons appear to be cost-competitive with other industrial waste treatment systems.

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INTRODUCTION

The American chemical industry spent approximately $622 million in 1982 in order to comply with U.S. Environmental Protection Agency pollution control regulations. This amount was a 31.5 percent increase over 1981 spending (Siegrist 1983). The high levels of expenditure are expected to continue. Chemical industries are projected to spend an average of $701 million annually for waste treatment from 1983 to 1985. The development of less costly processes to treat chemical wastes is therefore important.

Biological decomposition in waste stabilization ponds offers an inexpensive alternative, particularly where land costs are low (Eckenfelder 1966). However, the microorganisms that are generally efficient at assimilating organic matter are rendered less effective by toxic chemicals. Mammalian and microbial toxicity of organics range from a few mg/kg to over 10,000 mg/kg (Merck and Co. 1976). Furthermore, organic components in industrial waste streams which are carcinogenic or mutagenic, if present in even trace amounts, may pose a public health hazard.

Other chemicals resist microbial degradation (Nemerow 1978). Numerous classes of organic chemicals resist aerobic biological degradation. Resistances vary. Ketones have been found to be more resistant than alcohols, aldehydes, or acids, but less resistant than ethers (Ludzack and Ettinger 1960).

Biological waste treatment is therefore complicated by the toxicity and biological recalcitrance of some components of an organic chemical waste stream. Some of these compounds persist for long periods in the environment and may undergo biomagnification (Gomaa and Faust 1974). Many species are resistant or inhibitory to microbial oxidation. In addition to those noted above, Ludzack and Ettinger (1960) also add alkyl benzenes, diols, 2,4,5-trichlorophenol, and morpholenes with a nitrogen-containing heterocyclic ring. Phenols have been degraded effectively with adaptation by the microbial cultures (Tabak et al. 1981). The only phenol that was not significantly degraded was 4,6-dinitro-o-cresol. All phthalate esters and napthalenes showed significant degradation with rapid adaptation except for two phthalate esters that showed gradual adaptation. A number of dichlorobenzenes and 2,4-dinitrotoluene and 2,6-dinitrotoluene showed significant degradation with gradual adaptation, followed by toxicity in subsequent subcultures. Halogenated ethers, larger polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides were resistant to microbial degradation. In addition, polychlorinated biphenyls, phenolic wastes, halogenated aromatics, and refractory pesticides pose potential problems to biological industrial waste treatment (Nemerow 1978).

Some alternative to the standard biological decomposition processes may have to be used to deal with these problem chemicals. Acclimated cultures of microorganisms have been tried to treat some toxic and refractory wastes. Their use, however, can be costly and requires thorough operational guidance (Eckenfelder 1966). Environmental monitoring is important because biological treatment is sensitive to such factors as temperature, dissolved oxygen, and the synergistic toxicity of

chemicals which may result in the failure of the plant or lagoon. Furthermore, acclimated microbial cultures are not exempt from dose-response phenomena; a large enough dose of the substance will be toxic to the community of microorganisms (Loomis 1974). Acclimated cultures can be used to treat some wastes that could not otherwise be decomposed biologically; however, some organic waste streams are just not compatible with biological waste treatment (Little et al. 1980).

Physicochemical means of industrial waste treatment are increasingly used to deal with these problem wastes. Activated carbon is sometimes a cost effective treatment for removing toxic and refractory organic compounds from industrial wastes (Becker and Wilson 1978). Other physicochemical treatments such as chlorination, ozonation, and ultraviolet light treatment (Bauer 1972) and acid or alkaline hydrolysis (Hackman 1978; Ferguson 1975) have been effective under some circumstances. Incineration is a waste treatment process that is gaining widespread attention, particularly for extremely toxic and recalcitrant wastes such as polychlorodibenzo-p-dioxins and polychlorinated biphenyls (Hackman 1978). These methods are effective but often have high operation and maintenance costs and are therefore used on a limited basis (Siegrist 1983).

Photodegradation of toxic organic wastes may be both an effective and inexpensive process since the sunlight driving the decomposition reactions is available without cost.

Photodegradation of organic compounds may be achieved by two processes--direct photodegradation and sensitized photooxidation. In direct photodegradation, the molecules excited by the sunlight lose their absorbed light energy and are thus decomposed by dissociation, dehalogenation, isomerization, or other deactivation routes (Plimmer 1971). The problem with this method is that many organic pollutants absorb light primarily in the ultraviolet (UV) region. Because less energy reaches the earth's surface in the UV region than in the visible region, there is often insufficient sunlight for direct photodegradation (Thorington 1980).

This difficulty can be overcome by adding sensitizing molecules to absorb light in the energy-rich visible region of the solar spectrum. The electronically excited sensitizing molecule, or triplet sensitizer, may then return to ground state by transferring the absorbed energy to molecular oxygen or organic substrates (Spikes and Straight 1967). If molecular oxygen accepts energy from the triplet sensitizer, singlet oxygen is the pathway of oxidation. Singlet oxygen is a highly reactive species of oxygen with a lifetime of 2 μsec in water (Kearns 1971). It readily attacks a number of organic substrates, yielding oxidized products. Kasha and Khan (1970) stated that singlet molecular oxygen, even though it is a short-lived species, is proving to be an ubiquitous intermediate in oxidative systems that were once considered the exclusive domain of ground state molecular oxygen. If organic substrates accept energy from the triplet sensitizer, a number of mechanisms may cause substrate degradation. These include hydrogen abstraction, electron transfer, alkyl radical generation, and hydroxyl radical generation (Heelis et al. 1981).

Spikes and Straight (1967) found that many classes of organic compounds are susceptible to sensitized photooxidation. They listed alcohols, nitrogen heterocycles, organic acids, benzenoids, and aromatic heterocyclic compounds. Sargent and Sanks (1974) postulated that phenols, cresols, trinitrotoluene, and unsaturated nitriles should also be susceptible. If all of these compounds can indeed be successfully treated, the method offers considerable promise.

Nearly all of the environmental photodegradation research has been performed on pesticides, resulting in a wealth of knowledge of their photodegradation products. The treatment of pesticide wastes is a serious concern. The production of synthetic organic pesticides in the United States in 1978 amounted to 1.46 billion pounds. The average production for the years 1974 to 1978 was 1.44 billion pounds. Production of herbicides in 1978 was 664 million pounds (Fowler 1978). Pesticide manufacture and use is less intensive worldwide. Western Europe uses 56 percent of U.S. levels of pesticides, Japan 27 percent, and the remainder of the world uses but 40 percent of U.S. levels of pesticides (Cremlyn 1978).

The scope of this research, however, is more general. The purpose is to develop engineering design criteria for sensitized photooxidation lagoons to treat toxic and biologically recalcitrant organic wastes with regard to the following parameters:

1) Optimum pH of sensitized photooxidation reactions.

2) Maximum depth and optimum dye concentration of sensitized photooxidation lagoons.

3) Dissolved oxygen requirements for sensitized photooxidation reactions.

4) Effect of temperature on photooxidation rates.

5) Construction and operation and maintenance costs of sensitized photooxidation lagoons.

Through the use of these design criteria, sensitized photooxidation pilot lagoons may be sized based on incident radiation, temperature, and spectral quality of water in the influent stream.

With this information in hand, the chemical industry will be in a better position to assess the role for sensitized photooxidation waste stabilization ponds as an effective but inexpensive and low-maintenance alternative to traditional waste treatment. Where these ponds can do the job at less cost, they will reduce the cost to the industry of satisfying EPA requirements, provide them a more effective treatment, and thereby provide an incentive to the industry for more effective pollution control.

LITERATURE REVIEW

Light-induced oxidation of industrial wastes has its basis in organic photochemistry. The topics embraced by organic photochemistry are diverse, including quantum yield investigations, qualitative analysis of photoproducts, and elucidation of photochemical mechanisms. The following review will be limited to sensitized photooxidation theory, proposed mechanisms of sensitized photooxidation, studies concerned with the sensitized photooxidation of environmental pollutants, and attempts to apply the process to waste treatment.

Photooxidation reactions are dependent upon the energy received from the sun, or, if the reaction is carried out in a laboratory, upon the energy of the artificial light source. Generally, a duality for the description of the properties of light is used. The behavior of light may be expressed in terms of either wave or particle theory (Calvert and Pitts 1966). Light is a form of electromagnetic radiation, and its propagation and transmission may be most conveniently described in terms of wave theory. Quantum theory provides a framework for the description of many photochemical phenomena, and the absorption and emission of light are best explained by a particle-like nature. As electromagnetic radiation, light is a form of energy and the individual particles, or quanta, possess energy that depends on the wavelength of light. More energy is supplied by light quanta as the wavelength of the light decreases.

The Grotthus-Draper law states that light must be absorbed before any reaction can take place. However, it is not necessary that the absorption of radiant energy should result in the homolytic breaking of chemical bonds in the absorbing molecule. Light energy may be transferred from molecule to molecule via what are called sensitized reactions in which an electronically excited molecule (A*) returns to the ground state (A) by transferring its excess energy to a donor molecule (D). The donor molecule becomes electronically excited (D*) and may dissociate:

$$A + h\nu \rightarrow A^* \quad . \ . \ . \ . \ (1)$$

$$A^* + D \rightarrow D^* + A \quad . \ . \ . \ . \ (2)$$

$$D^* \rightarrow \text{products} \quad . \ . \ . \ . \ (3)$$

Sensitizing molecules may undergo a number of energy transformations upon absorption of light energy. These transformations are represented by the pathways shown in Figure 1. In this scheme, S_o represents the singlet ground state of the sensitizer, S_1 the first excited singlet state, and T_o the lowest energy triplet state. The singlet ground state is defined by all spin-paired electrons in the sensitizer. In the singlet excited state the electrons are raised to a higher energy molecular orbital, but the spins remain paired. A sensitizing molecule in the triplet state possesses electrons with their spins reversed (Spikes and Straight 1967). The transitions involved after the absorption of light energy as shown in Figure 1 include: (1) optical excitation, $S_o \rightarrow S_1$; (2) radiative deactivation, or fluorescence, $S_1 \rightarrow S_o$; (3) intersystem crossing, $S_1 \rightarrow T_o$; (4) intersystem crossing, $T_o \rightarrow S_1$; (5) radiationless deactivation of $S_1 \rightarrow S_o$; (6) radiationless deactivation of $T_o \rightarrow S_o$; and (7) radiative deactivation, or phosphorescence, $T_o \rightarrow S_o$ (Calvert and Pitts 1966).

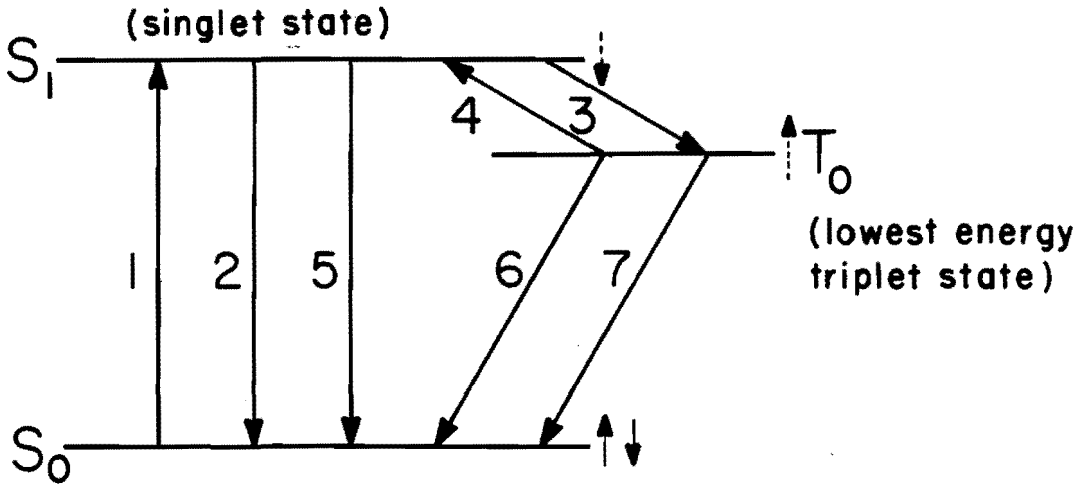


Figure 1. Schematic of the electronic states and transitions of sensitizers (from Spikes and Straight 1967), where:

1: $S_0 \rightarrow S_1$ = Optical excitation
2: $S_1 \rightarrow S_0$ = Radiative deactivation (fluorescence)
3: $S_1 \rightarrow T_0$ = Intersystem crossing
4: $T_0 \rightarrow S_1$ = Intersystem crossing
5: $S_1 \rightarrow S_0$ = Radiationless deactivation
6: $T_0 \rightarrow S_0$ = Radiationless deactivation
7: $T_0 \rightarrow S_0$ = Radiative deactivation (phosphorescence)

Sensitized photooxidation reactions transfer energy from either the excited singlet state or the triplet state of the sensitizer to reactants in the system. Sensitized photooxidation usually has a greater probability of occurring through the sensitizer triplet state than through the excited singlet state. This may be due to the short lifetime of the excited singlet state, rendering low probability of diffusion controlled reactions (Spikes and Straight 1967). For this reason and for simplicity, it will be assumed that the sensitized photooxidation reactions examined in this study are transferring energy from the triplet state.

The transfer of energy from the excited triplet sensitizer to reactants in the system may proceed by 1) initial energy transfer to the substrate or (2) initial energy transfer to molecular oxygen (Nilsson et al. 1972). The first process, termed Type I, usually involves a mechanism such as hydrogen abstraction, electron abstraction, or alkyl radical generation (Heelis et al. 1981). The second process, labeled Type II, involves energy transfer to molecular oxygen and results in excitation of the molecular oxygen to singlet oxygen (Kearns 1971). Whether Type I or Type II mechanisms are involved in a specific sensitized photooxidation reaction

depends on the sensitizer, substrate, pH, dissolved oxygen, and other physicochemical factors (Spikes and Straight 1967). A number of mechanistic studies have shown that methylene blue-sensitized photooxidation often occurs by Type II mechanisms, while riboflavin-sensitized photooxidation occurs by both Type I and Type II mechanisms.

Nilsson et al. (1972) applied a number of tests to the methylene blue-sensitized photooxidation of amino acids to distinguish between singlet oxygen and non-singlet oxygen mechanisms. The tests included using the singlet oxygen quenchers azide ion and tetramethylene and comparing photooxidation rates in water and deuterium oxide. The experiments provided evidence for the involvement of singlet oxygen in the methylene blue-sensitized photooxidation of amino acids.

Rehak and Poskocil (1978) used laser flash photolysis to study methylene blue excitation. They determined the rate constant describing energy transfer from methylene blue to oxygen to be in the order of 2×10^9 $M^{-1}sec^{-1}$. A slow absorption increase after methylene blue excitation affected by the presence of oxygen indicated the involvement of singlet oxygen.

A number of studies have found both Type I and Type II mechanisms occurring in flavin-sensitized photooxidation. Penzer and Radda (1968) in comparing flavin-sensitized mechanisms of amino acids, concluded that singlet oxygen was responsible for the photooxidation of adenosine and guanosine.

Riboflavin-sensitized photooxidation of histidine occurred by a hydrogen abstraction mechanism in addition to the singlet oxygen mechanism (Tomita et al. 1969).

The photooxidation of plastocyanin using flavin mononucleotide, flavin adenine dinucleotide, riboflavin, and lumiflavin as sensitizers was studied by O'Kelley and Hardman (1979). They postulated that the Type II singlet oxygen mechanism was most consistent with the data collected, since the photooxidation reaction was inhibited by potassium iodide.

Heelis et al. (1978) determined rate constants for the quenching of triplet flavin mononucleotide by eight amino acids. Hydrogen abstraction was responsible for quenching of the triplet flavin by the amino acids.

Other studies showing evidence for Type I mechanisms in flavin-sensitized reactions include those by Knowles and Mautner (1972), Lasser and Feitelson (1975), and Heelis et al. (1981). Riboflavin sensitization, therefore, is a complex process in which photooxidation may occur by a variety of mechanisms depending upon substrate and physicochemical conditions. This diversity in the photochemical mechanisms may allow numerous industrial waste substrates to be sensitive to riboflavin-sensitized photooxidation.

Sensitized photooxidation has been effective in treating and disinfecting wastewater. Gerba et al. (1977) found methylene blue-sensitized photooxidation could achieve high levels of viral inactivation. Similarly, dye-sensitized photooxidation reduced Escherichia coli by 1.3×10^7 coliform bacteria in 100 ml of sample containing 0.5 mg of methylene blue in 30 min (Acher and Juven 1977).

The photochemical oxidation of the wastewater sensitized by methylene blue resulted in decreases in fecal coliform bacteria, chemical oxygen demand, and methylene blue active substances by 100, 67, and 90 percent of their initial values, respectively (Acher and Juven 1977).

A number of studies investigated the reactivities of classes of organic chemicals to sensitized photoxidation.

Kopecky and Reich (1965) investigated the methylene blue-sensitized oxidation of alkenes ranging in size from four carbons to nine carbons. The compound 2,3-dimethyl-2-butene was found to be oxidized the fastest of the compounds studied while 1-nonene was the slowest. They also found that singlet oxygen was formed using five different sensitizers. The sensitized photooxidation of amines, using xanthone, fluorenone, p-amino-benzophenone, and methyl-β-naphthyl ketone as sensitizers, indicated that the reactions occurred by initial hydrogen abstraction from the amine by the excited ketone to give radicals of the amines, which subsequently reacted with oxygen to give products (Bartholomew et al. 1971). A mechanistic approach was used by Ando et al. (1973) in studying the reaction of alkylthiosubstituted ethylenes in acetone with singlet oxygen. They found that the reactions proceeded via the intermediates 1,2-dioxetane or perepoxide followed by preferential migration of the ethylthio group.

In the presence of dissolved oxygen and the sensitizers acetone or riboflavin, ethylenethiourea was rapidly photooxidized to ethylene urea and glycine sulfate (Ross and Crosby 1973). Several chloroanalines were effectively photooxidized when sensitized by using flavins (Rosen et al. 1970; Miller et al. 1980).

Acher and co-workers have recently studied the sensitized photooxidation of uracil derivatives. In the first of these publications, Acher and Dunkelblum (1979) investigated the methylene blue-sensitized photooxidation of bromacil under direct outdoor solar radiation. They found that the addition of methylene blue and oxygen caused a fast chemical transformation of bromacil. The major photooxidation products were identified as a mixture of diastereo-isomers of 3-sec-butyl-5-acetyl-5-hydroxy-hydantoin. Moilanen and Crosby (1974) investigated the direct sunlight photodecomposition of bromacil in water and found after four months a 2.2 percent yield of the only degradation product, 5-bromo-6-methyluracil.

Acher and Saltzman (1980) reported the oxidation kinetics of bromacil using the sensitizers riboflavin, methylene blue, rose bengal, humic acids, and chlorophyll. Under optimum experimental conditions, the photooxidation was complete after about 1 hour. The rate of reaction was found to be pH dependent, being faster at high pH and almost negligible in acidic solution.

Acher (1982a) also investigated the photodecomposition of two uracil derivatives, bromacil and terbacil, in sensitized, frozen, aqueous solutions. Frozen samples were covered with ice blocks up to 11 cm thick. The amount of incident light reaching them was attenuated, but the photodecomposition reaction rates remained high.

The most engineering-oriented approach to sensitized photooxidation was taken by Sargent and Sanks. In one publication, Sargent and Sanks (1974), used cresol as a substrate. They investigated optimum dye concentration, optimum substrate concentrations, and effect of pH in bench scale photooxidation experiments. The optimum concentration of methylene blue for bench-scale photooxidation of cresol was between 5 and 10 mg/l. Sensitized photooxidation rate was also found to vary with initial cresol concentration. For 1 mg/l methylene blue-sensitized photooxidation, 40 mg/l initial cresol concentration was optimum. For 5 mg/l methylene blue-sensitized photooxidation, 70 mg/l cresol was optimum.

Sargent and Sanks (1976) also investigated the efficiency of a number of sensitizers in the photooxidation of cresol and phenol. Out of eight sensitizers, methylene blue and rose bengal were the most effective.

In conclusion, light energy reaching the earth's surface is most abundant

between 400 and 700 nm, with the earth's ozone layer filtering nearly all of the light below 290 nm. The absorption spectrum of most organic pollutants is below the 290 nm cut off; thus, direct photolysis rates are relatively slow. Sensitized photolysis rates are often orders of magnitude greater than direct photolysis rates because most sensitizers absorb light in the energy-rich visible light region. Sensitized photooxidation reactions may proceed by two routes: Type I (radical mechanisms) and Type II (singlet oxygen mechanism). Research has shown that methylene blue sensitized photooxidation usually proceeds by a Type II mechanisms and riboflavin sensitized photooxidation may proceed by both Type I and Type II mechanisms. Sensitized photooxidation has been effective in rapidly degrading selected organic pollutants. The process has also been effective in disinfecting effluents and in lake restoration. The rapid degradation rates that proceed by sensitized photoreactions make the process an attractive means of waste treatment, especially if the process is conducted in reactors under sunlight. The resultant system, based on the research included herein, would provide low-cost waste treatment using solar energy to break the bonds of toxic and refractory organic pollutants.

METHODOLOGY

Effect of pH on Sensitized Photooxidation Rate

Experiments to study the sensitized photooxidation rate as a function of pH were performed under batch conditions using 200 ml of 30 mg/l aqueous herbicide solutions in 250 ml Pyrex™ beakers. The solutions were aerated with compressed air at a flow rate of 0.25 l/min (0.5 SCFH) to maintain the dissolved oxygen at saturation. Temperature was maintained at 25°C ± 3°C. Constant light was provided by Duro Test Vitalite™ lamps, which are 91 percent corrected to the quality of natural sunlight. Radiation impinging upon herbicide solutions was 47 W/m^2, as measured by a Lambda LI-185 Photometer/Radiometer/Quantum Sensor. Radiation of the Duro Test Vitalite™ lamps as a function of wavelength was measured by an Optronic 742 spectroradiometer and is shown in Figure 2.

The effect of pH on sensitized photooxidation rate was investigated using highly buffered aqueous samples to prevent pH drift during the experiments. Water from a Milli-Q™ deionizing system was used. Samples adjusted to pH 7 and lower received 1000 mg/l NaH_2PO_4 as a buffer. For samples adjusted to pH higher than 7, 500 mg/l NaH_2PO_4 and 500 mg/l Na_2CO_3 were added as buffers. Three herbicides were used as photooxidation substrates: two uracil derivatives, bromacil and terbacil; and one urea derivative, fluometuron. Sensitized photooxidation as a function of pH was generally studied in triplicate from pH 3 to pH 12 at 1-unit pH intervals using the sensitizers methylene blue (2 mg/l) and riboflavin (10 mg/l). Sensitized photooxidation of bromacil and terbacil solutions was also investigated using a methylene blue-riboflavin mixture (2 mg/l and 10 mg/l, respectively) over the same pH range. Two hundred ml of a solution containing 30 mg/l herbicide were placed in 250 ml beakers, the pH was appropriately adjusted with 5 N NaOH or 20 percent HCl, and the solution was placed under the previously described temperature, aeration, and light conditions. The experiment was started by adding the sensitizer to the solutions. Samples were collected for determination of dye concentration and substrate concentration at 15 minute intervals over a 90-minute period. The beakers were adjusted to their original pH with 3 N NaOH at 15-minute intervals. The pH after 15 minutes of reaction rarely drifted more than 0.1 pH unit before adjustment.

Sensitizer concentration was measured by reading optical density at 660 nm for methylene blue or 445 nm for riboflavin on a Bausch and Lomb Spectronic 70. Disappearance of substrate was monitored by gas chromatography using a Hewlett-Packard 5880A gas chromatograph after a 1:1 ethyl acetate extraction. A 61 cm x 2 mm (ID) glass column packed with 1 percent SP-2250 on 80/100 Supelcoport was used. Chromatographic conditions for bromacil and terbacil were injector port temperature 250°C, oven temperature initial value 170°C, program rate 20°C/min, detector temperature 300°C, and nitrogen carrier flow rate 40 ml/min. A flame ionization detector was used. For fluometuron analysis, the same column and detector were used, but oven temperature was 150°C (isothermal), injector port temperature 250°C, detector port temperature 300°C, and nitrogen carrier flow rate 30 ml/min.

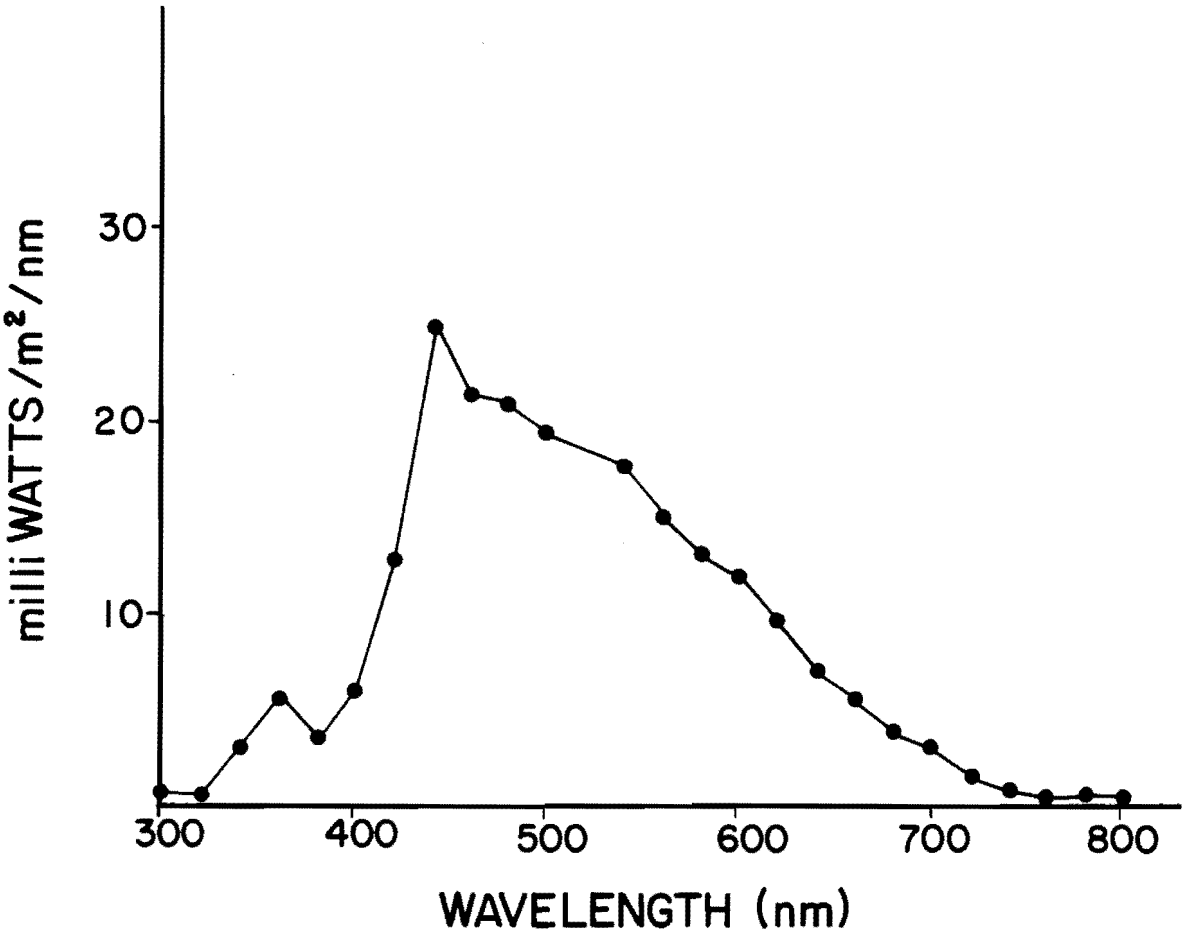


Figure 2. Radiation as a function of wavelength for Duro Test™ Vitalite lamps.

Sensitized Photooxidation Rate as a Function of Lagoon Depth

In a lagoon, the quantity of light decreases and the quality of light changes with increasing depth. The mechanistic approach involved in this study used a constant light source of 107 W/m^2 impinging on reaction chambers at temperature of 25°C ± 5°C with aeration of 0.5 l/min (1.0 $\overline{SCFH}$). Eight reaction chambers were used to simulate depths of a sensitized photooxidation lagoon. These chambers consisted of a 150 mm x 15 mm Pyrex glass petri dish with a 15 cm cylinder of tripled 6 mil black plastic taped to the lower section of the dish. The plastic supported the petri dish and allowed it to sit in a level position. Under the petri dish-plastic sleeve assembly sat the reaction vessel--a 15 cm diameters x 5.5 cm deep amber glass dish covered with black electrical tape. The plastic sleeve attached to the petri dish contained two ports: an air diffuser port and a sampling port. A schematic of a typical reaction chamber is presented in Figure 3. Depth was simulated by filling the petri dishes 1.0 cm deep with a concentrated solution of the sensitizer. The concentrations of dye in the eight petri dishes used in an experiment were chosen to simulate succeedingly deeper cross-sections of a lagoon. For instance, for a 1 mg/l methylene blue lagoon concentration to simulate a depth of 60 cm, a 60 mg/l

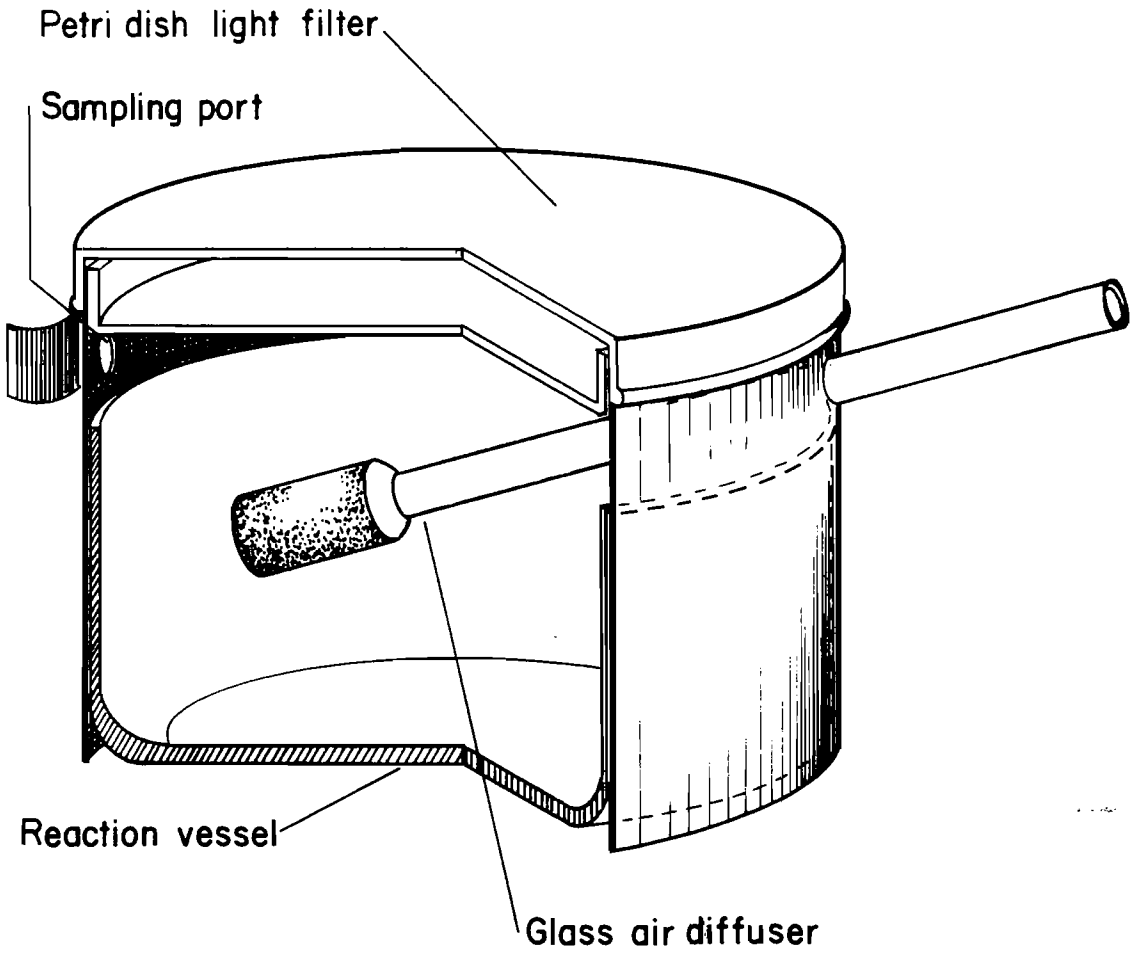


Figure 3. Reaction chamber used to measure sensitized photooxidation rate as a function of simulated depth.

solution 1 cm deep in the petri dish would be necessary. This 1 cm deep solution does not take into account the absorption of light by water. However, the absorption of light by water is minimal compared to that of the dye. For instance, at 660 nm the extinction coefficient of water is 1.6 percent of that of 1 mg/l methylene blue (0.0037 cm^{-1} for water; 0.218 cm^{-1} for methylene blue). At 600 nm the extinction coefficient of water is 1.5 percent that of 1 mg/l methylene blue (0.0021 cm^{-1} for water; 0.143 cm^{-1} for methylene blue). Sensitizer bleaching in the petri dish during experiments was negligible since NaN_3, a singlet oxygen quencher, was added to a final concentration of 25 mg/l. Lagoon sensitizer concentrations, simulated depths, and necessary sensitizer concentrations in the petri dishes are reported in Table 1.

Two sensitizers were studied--methylene blue and riboflavin. Methylene blue-sensitized experiments used bromacil as the substrate in deionized water buffered with 500 mg/l Na_2HPO_4 and 500 mg/l Na_2CO_3 adjusted to pH 10.5 with 3 N NaOH. Riboflavin-sensitized experiments employed terbacil as the substrate in deionized water buffered with 1000 mg/l Na_2HPO_4 adjusted to pH 3 with 20 percent HCl. These conditions were used in order to obtain the highest reaction rates possible under the relatively low

Table 1. Simulated lagoon sensitizer concentrations, depths, and necessary sensitizer concentrations in petri dishes for depth experiments.

Lagoon Sensitizer Concentration							
Methylene Blue							
0.1 mg/l		0.5 mg/l		1.0 mg/l		2.0 mg/l	
Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)
0	0	0	0	0	0	0	0
10	1	4	1	3	3	1.5	3
20	2	8	2	6	6	3	6
30	3	12	3	10	10	5	10
40	4	16	4	15	15	7.5	15
60	6	24	6	20	20	10	20
80	8	32	8	30	30	15	30
100	10	40	10	40	40	20	40
Riboflavin							
1.0 mg/l		2.5 mg/l		5.0 mg/l		10.0 mg/l	
Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)	Simulated Depth (cm)	Petri Dish Concentration (mg/l)
0	0	0	0	0	0	0	0
5	5	2	5	1	5	0.5	5
10	10	4	10	2	10	1	10
20	20	8	20	4	20	2	20
30	30	12	30	6	30	3	30
40	40	16	40	8	40	4	40
50	50	20	50	10	50	5	50
60	60	24	60	12	60	6	60

indoor light regime. Experiments using eight simulated depths were initiated by the addition of sensitizer to the reaction vessel and proceeded for two hours, with samples collected from the reaction vessels at 30 min intervals. All experiments were performed in triplicate. Disappearance of parent substrate was measured by gas chromatography using the same chromatographic conditions for bromacil and terbacil described previously. Sensitizer concentration in the reaction vessels was monitored concurrently by measurement of optical density (660 nm for methylene blue; 445 nm for riboflavin) using a Bausch and Lomb Spectronic 70.

Effect of Quantity of Radiation on Sensitized Photooxidation Rate

This study was performed outdoors under cloudless skies to examine the effect of quantity of solar radiation on sensitized photooxidation rates with light quantities greater than the indoor light regimes used. Quantity of total solar radiation was varied in these experiments from the levels used in indoor experiments (ca. 100 W/m^2) to that of maximum summer solar radiation under cloudless skies in Logan, Utah (ca. 2900 W/m^2). Temperature was difficult to control in these experiments since they were conducted outside, but generally averaged 25°C ± 5°C. Aeration was maintained at 0.5 l/min (1.0 SCFH).

The experiments were conducted in six 150 mm diameter x 25 mm amber glass vessels wrapped on the outside with black plastic tape. Layers of cheesecloth were placed over the mouth of each flask. Successively higher amounts of cheesecloth resulted in filtering the quantity of solar radiation impinging on the solution. The flask receiving the full quantity of solar radiation was not covered. The cheesecloth was held in place by an 18 cm diameter embroidery loop. Each cheesecloth filter contained a port for a glass air diffuser and a port for sampling. These ports were covered with black plastic tape so that no extraneous light could enter the vessel. A drawing of a typical reaction chamber is shown in Figure 4. The effect of cheesecloth thickness on quality of light filtered is shown in Figure 5. The percentage of total solar radiation reaching the solution in the vessel was measured by a Lambda LI-185 Photometer/Radiometer/Quantum Sensor. The six reaction chambers received 100 percent, 52 percent, 37 percent, 16 percent, 8.1 percent, and 3.3 percent of incident radiation.

Experiments were conducted with buffered methylene blue (2 mg/l) -bromacil (30 mg/l) solutions at pH 8.3 and riboflavin (10 mg/l)-terbacil (30 mg/l) solutions at pH 3 prepared as described for previous experiments. The buffered bromacil or terbacil solutions were placed in the reaction vessels with overlying cheesecloth filters under aeration and the reaction was started by adding the sensitizer. The experiment was conducted for 1 hr with sample collection occurring every 15 min. Total solar radiation was measured every 15 min during the experiments using a Lambda LI-185 Photometer/Radiometer/Quantum Sensor. Bromacil, terbacil and sensitizer concentrations were determined as previously described in this study.

Effect of Mean Velocity Gradient on Sensitized Photooxidation Rate

Thirty eight liter (10 gallon) aquaria were used to investigate the effect of mixing upon the sensitized-photooxidation rate. Experiments were conducted using three aquaria simultaneously; one with minimal mixing, the second with moderate mixing, and the third with turbulent mixing. Mixing was provided by three glass air diffusers mounted on the bottom of each aquarium along one side. The aquarium in which minimal mixing was established received

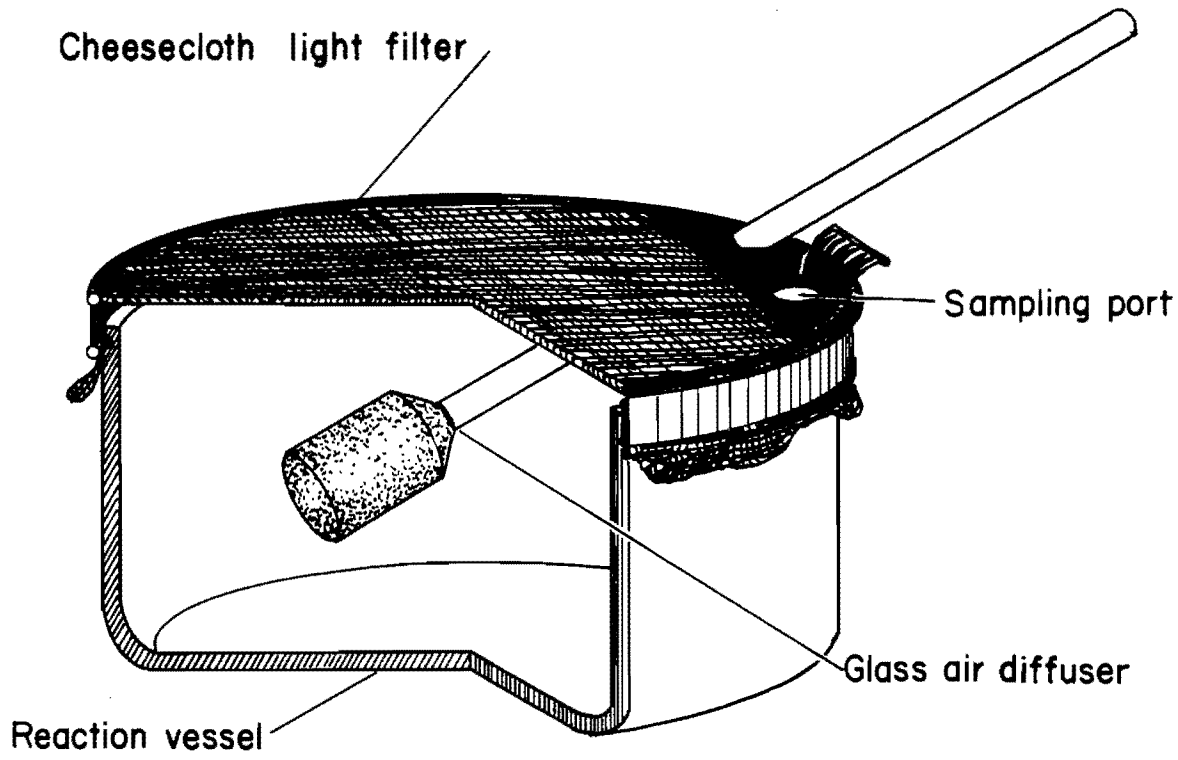


Figure 4. Reaction chamber used to measure sensitized photooxidation rate as a function of quantity of radiation.

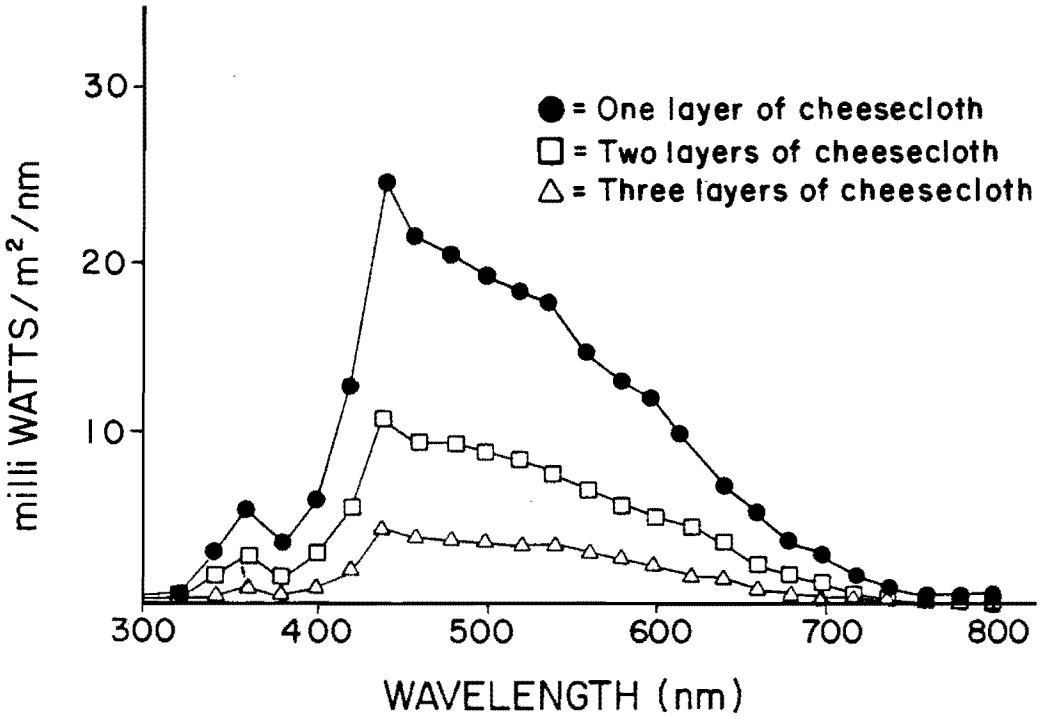


Figure 5. The effect of cheesecloth on the quality and quantity of light filtered under Duro Test™ Vitalite lamps.

approximately 0.1 l/min compressed air to maintain sufficient dissolved oxygen residual. The tank with moderate mixing was supplied with 1 l/min compressed air flow through each gas diffuser. The tank with maximum mixing received 5 l/min compressed air through each gas diffuser.

Mixing experiments were performed under Duro Test Vitalite™ lamps under radiation of 95 W/m^2. The experiments were conducted by filling the aquaria with 38 l of 20 mg/l bromacil or 20 mg/l terbacil with 1000 mg/l NaH_2PO_4 buffer. Methylene blue at concentrations of 2 mg/l and 0.75 mg/l was used as the sensitizer in experiments where bromacil was the substrate. Riboflavin at concentrations of 2.5 mg/l and 10 mg/l was used as sensitizer in the experiments where terbacil was employed as the substrate. Experiments were initiated by adding the appropriate concentration of sensitizer. Samples were collected over a one-day period. The sampling procedure consisted of turning off the light source, stirring the reactor to obtain a homogeneous sample, and collecting an aliquot. Each aliquot was analyzed for sensitizer concentration and remaining herbicide using the procedures previously described.

Dissolved Oxygen Requirements for Sensitized Photooxidation

Studies to determine the effects on sensitized photooxidation rates of dissolved oxygen were performed under Duro Test Vitalite™ lamps with a radiation of 107 W/m^2. Temperature was maintained at 25°C ± 5°C.

The experiments, conducted in triplicate, were performed in 250-ml Pyrex™ glass beakers. The two sensitizers used were methylene blue (2 mg/l) and riboflavin (10 mg/l). Methylene blue-sensitized experiments employed 30 mg/l and 250 mg/l bromacil as substrate in deionized water buffered with 500 mg/l Na_2HPO_4 and 500 mg/l Na_2CO_3 adjusted to pH 10.5 with 3 N NaOH. Riboflavin-sensitized experiments employed 30 mg/l and 250 mg/l terbacil as substrate in deionized water buffered with 1000 mg/l Na_2HPO_4 adjusted to pH 3 with 20 percent H_2SO_4. The pH values were chosen to obtain high reaction rates under the relatively low light regime.

Two hundred ml of bromacil-methylene blue or terbacil-riboflavin solutions were aerated with a total gas flow of 0.5 l/min (1.0 SCFH), regardless of the dissolved oxygen residual maintained. The desired dissolved oxygen level was obtained by mixing compressed air with compressed molecular nitrogen in the correct proportions. These tests were performed at dissolved oxygen levels ranging from 0.1 to 8.1 mg/l.

Experiments were conducted for 2 hours with samples collected at 30 min intervals. The samples were analyzed for residual bromacil or terbacil and sensitizer concentration as described previously. Chemical oxygen demand was also measured using the low-level ampule technique for 30 mg/l bromacil/terbacil samples and the high-level ampule technique for 250 mg/l bromacil/terbacil samples (APHA 1980).

Dissolved Oxygen Uptake of Sensitized Photooxidation

Oxygen uptake experiments were conducted under bench scale conditions in 250 ml Pyrex™ beakers. The experiments were performed under radiation of 107 W/m^2 under Duro Test Vitalite™ lamps and temperature of 25°C ± 2°C.

Experiments were conducted by placing 150 ml of aqueous bromacil or terbacil in 250 ml beakers. The experiments were performed using 0, 30 mg/l, 90 mg/l, and 150 mg/l bromacil and terbacil concentrations. All solutions received 1000 mg/l NaH_2PO_4 buffer. Bromacil solutions were adjusted to pH 10.5 with 3N NaOH. Terbacil solutions were adjusted to pH 3 with 20 percent

HCl. The solutions were aerated with compressed air for 20 min prior to the start of the experiment.

Experiments were initiated by adding 2 mg/l methylene blue to bromacil solutions or 10 mg/l riboflavin to terbacil solutions. Aliquots were collected at 10 min intervals and sensitizer concentration and bromacil/terbacil concentrations were measured using the methodology described previously. Dissolved oxygen residual was measured concurrently with sample collection at 10 min intervals using a Yellow Springs Instruments Model 54 dissolved oxygen meter. To prevent diffusion of oxygen into the herbicide solution during the experiment, a layer of argon gas was maintained in the top of the beaker above the solution by purging with a flow of approximately 250 ml/min of compressed argon gas.

Biochemical Oxygen Demand of Photooxidized Bromacil

The biochemical oxygen demand of photooxidation products of bromacil was determined to assess if the decomposition products may be treated biologically. This experiment used 1200 ml of 750 mg/l bromacil in a 2000 ml Pyrex™ erlenmeyer flask buffered with 1000 mg/l NaH_2PO_4 and adjusted to pH 9 with 3N NaOH. Methylene blue was added at a final concentration of 2 mg/l and the flask was placed under summer sunlight with radiation of 2200 W/m^2 $\pm$ 500 W/m^2. A stream of compressed air with a flowrate of 0.2 ℓ/min was passed through the solution. Temperature during the experiment was 25°C $\pm$ 5°C.

Two hundred ml aliquots were collected from the flask at 0, 1, 2, 3, 4, and 5 hr intervals. Twenty-day BOD analyses were performed on each aliquot by first diluting the samples with BOD dilution water (APHA 1980) at two concentrations: 0.0133 dilution (750 mg/l initial concentration of bromacil to 10 mg/l as bromacil); and 0.00767 (750 mg/l initial concentration of bromacil to 5 mg/l as bromacil). The BOD analysis was prepared with duplicate bottles on each bromacil dilution. Enough BOD bottles were prepared for seven dissolved oxygen readings over the 20-day BOD period. In summary, the following experimental matrix was prepared: 6 time exposures to photooxidation x 2 BOD dilutions x 7 dissolved oxygen readings over 20 days x 2 replicates, resulting in 168 BOD bottles. In addition, control BOD bottles were prepared for a BOD seed (settled Hyrum Wastewater Treatment Plant mixed liquor), seed with methylene blue, a BOD standard of glucose and glutamic acid (APHA 1980), and the glucose-glutamic acid standard plus methylene blue. Dissolved oxygen in the bottles was determined at days 0, 1, 3, 5, 10, 17, and 20 using a Yellow Springs Instruments Model 54 dissolved oxygen meter. Chemical oxygen demand analysis was performed on the undiluted photooxidation samples using the high-level ampule technique (APHA 1980).

Effect of Temperature on Sensitized Photooxidation Rate

The investigation of sensitized photooxidation rate as a function of temperature was conducted under controlled light and aeration conditions, with temperature varied from 11°C to 35°C. Light was supplied by Duro Test Vitalite™ lamps with radiation of 107 W/m^2. Aeration was maintained at 0.5 l/min (1.0 SCFH).

The experiments were performed in 250 ml Pyrex glass beakers. Buffered methylene blue (2 mg/l)-bromacil (30 mg/l and 250 mg/l) and riboflavin (10 mg/l)-terbacil (30 mg/l and 250 mg/l) solutions were used as described in previous experiments of this study.

The effect of temperature on sensitized photooxidation rate was investigated with measurements made at 11°, 16°, 21°, 31°, and 35°C. Sufficient time was allowed for the solutions to reach the temperature selected.

Triplicate experiments were performed for 2 hours and were initiated by adding the sensitizer to aerated solutions of bromacil or terbacil. Samples were collected at 30 min intervals and analyzed for bromacil or terbacil and sensitizer concentration as described for previous experiments in this study.

RESULTS AND DISCUSSION

Effect of pH on Sensitized Photooxidation Rate

The data obtained from the experiments investigating the effect of pH on sensitized photooxidation rate were plotted as the natural logarithm of concentration at time t divided by time zero concentration (i.e., ln (C_t/C_o)) as a function of time. The result was a straight line with the coefficient of determination, R^2, generally greater than 0.95. These kinetic reactions are either first order or pseudo-first order (Atkins 1977). The negative slope of the plotted line is defined as the first-order rate constant, k, in min^{-1} (Atkins 1977). Acher and Saltzman (1980) found sensitized photooxidation of bromacil to follow first order kinetics. Analyses of the data in this study for the sensitized photooxidation of terbacil and fluometuron show that these compounds also follow first order kinetics.

Riboflavin (10 mg/l), methylene blue (2 mg/l), and riboflavin-methylene blue (10 mg/l-2 mg/l) sensitized photooxidation rate constants for bromacil and terbacil as a function of pH are shown in Figures 6 and 7, respectively. The rate constants for the enhanced photooxidation of fluometuron using riboflavin (10 mg/l) and methylene blue (2 mg/l) as a function of pH are shown in Figure 8.

Control experiments using no sensitizer, conducted from pH 3 to pH 12, showed no measurable decomposition of the three substrates. This agrees with the results found by Moilanen and Crosby (1974), who monitored the direct photodegradation of bromacil under summer sunlight and found almost complete recovery of the parent material after four months of exposure, indicating that bromacil is stable toward sunlight. Bromacil is also biologically recalcitrant, with a biological half life of 5 to 6 months in agricultural soils (Sherman and Kaplan 1975). The direct photodecomposition rates and rates of biological decomposition for terbacil and fluometuron are similar to those for bromacil (Merck and Co. 1976), which substantiate the control results.

Figure 6 shows that the rate of methylene blue sensitized photooxidation of bromacil was low below pH 7. However, above pH 7 the rate climbed sharply until a maximum was attained at pH 10. Continued increases in pH from 10 to 12 produces a slight decrease in photooxidation rate. A similar situation is represented in Figure 7 for the methylene blue-sensitized photooxidation of terbacil--low photooxidation rates were computed below pH 7, with the rates rising to extremely high levels at pH 10 and pH 11. Methylene blue-sensitized photooxidation rates for fluometuron as substrate were very low. But even with the low photooxidation rates, the highest rate was maintained at pH 9 to pH 10. The consistency of these results, regardless of substrate, indicates that sensitized photooxidation with methylene blue is ineffective below pH 7, with the rate of photooxidation increasing sharply above pH 8.

The photochemical literature describes two mechanisms of sensitized photooxidation: Type I (radical mechanisms) and Type II (singlet oxygen mechanism) (Spikes and Straight 1967; Heelis et al. 1981). Type I mechanisms involve radical reactions. These may include hydrogen abstraction, electron

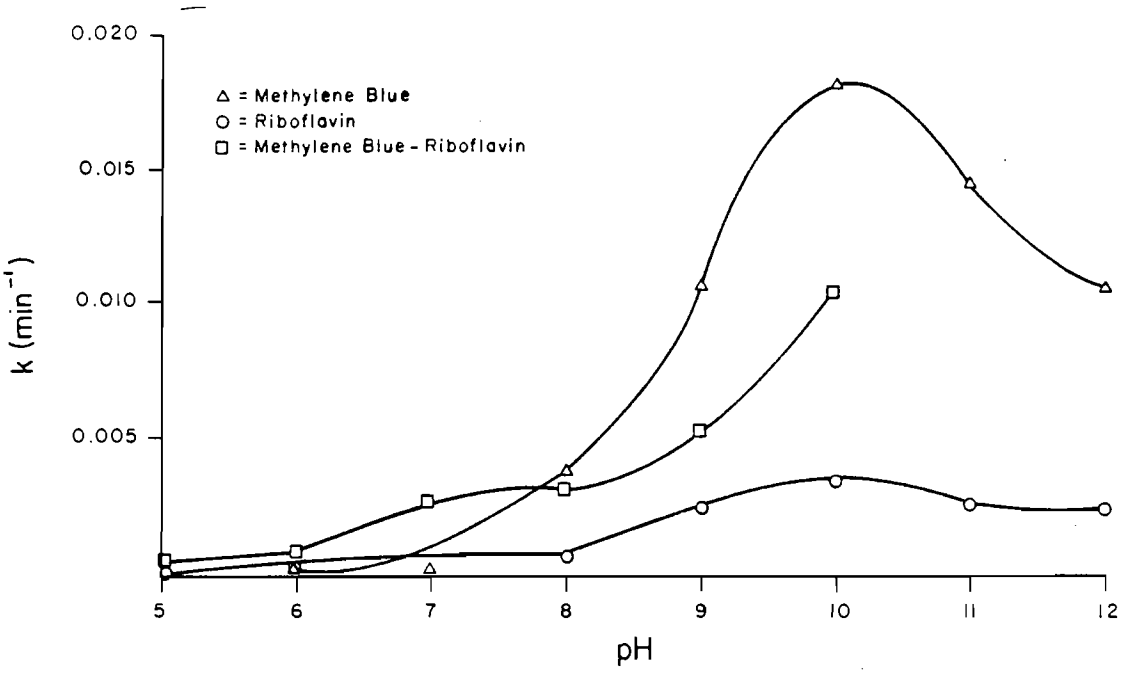


Figure 6. First-order rate constants for riboflavin (10 mg/l), methylene blue (2 mg/l), and riboflavin-methylene blue (10 mg/l - 2 mg/l) sensitized photooxidation of 30 mg/l bromacil as a function of pH.

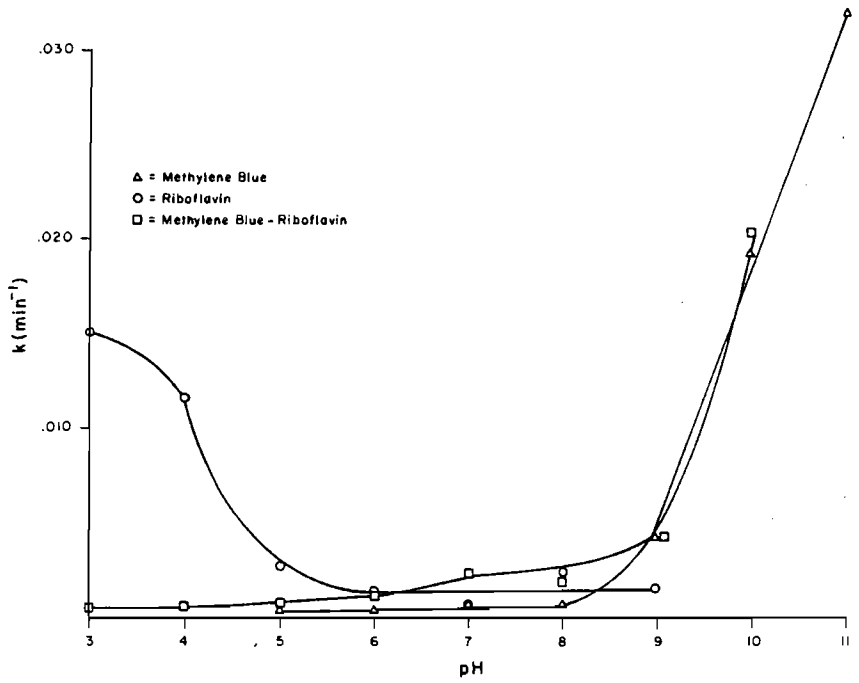


Figure 7. First-order rate constants for riboflavin (10 mg/l), methylene blue (2 mg/l), and riboflavin-methylene blue (10 mg/l - 2 mg/l) sensitized photooxidation of 30 mg/l terbacil as a function of pH.

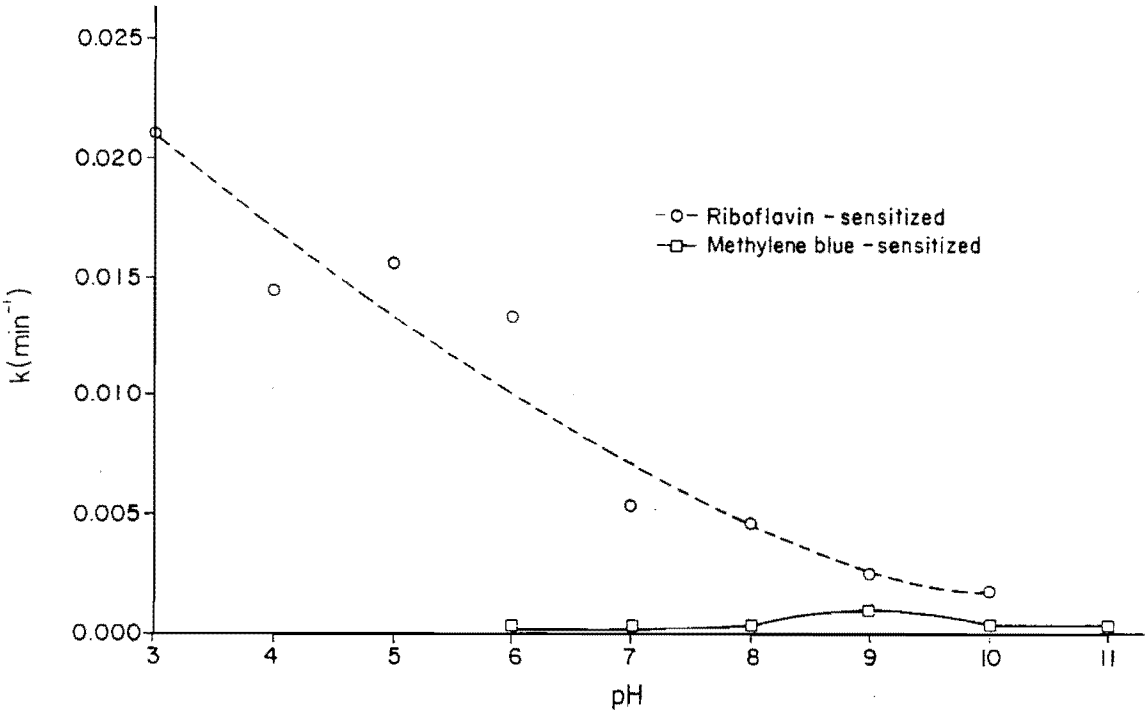


Figure 8. First-order constants for riboflavin (10 mg/1) and methylene blue (2 mg/1) sensitized photooxidation of 30 mg/1 fluometuron as a function of pH.

transfer, alkyl radical propagation, and hydroxyl radical generation (Heelis et al. 1981). The Type II mechanism is more specific and is related to the transfer of energy from the triplet sensitizer to ground state molecular oxygen, resulting in the formation of singlet oxygen (Foote 1968). Singlet oxygen, which is short-lived and highly reactive, oxidizes numerous classes of organic compounds. The mechanism that occurs in the sensitized photooxidation process may depend on the sensitizer, the substrate, the substrate concentration, the pH, and the dissolved oxygen concentration (Spikes and Straight 1967).

Methylene blue has been shown in numerous studies to be a generator of singlet oxygen (Nilsson et al. 1972; Halmann and Levy 1979). The Type II mechanism is probably prevalent in most methylene blue-sensitized photooxidation reactions. The generation of singlet oxygen is governed by the quantum yield of methylene blue triplet formation, which is related to the ionic nature of the sensitizer. Methylene blue is an organic cation at acidic and neutral pH, and exists in uncharged form at basic pH. The quantum yield of methylene blue triplet formation corresponds to the percentage of molecules existing in the uncharged form (Bonneau et al. 1975).

The quantum yield of methylene blue triplet formation is therefore highest at basic pH, and singlet oxygen production is highest at basic pH.

Methylene blue-sensitized photooxidation of bromacil, terbacil, and fluometuron was most efficient at basic pH. Methylene blue at basic pH in the presence of visible light and dissolved oxygen is an efficient system for the generation of singlet oxygen. It appears that this generation of singlet oxygen caused the degradation of the parent compounds. The Type II mechanism is therefore consistent with the results obtained for the methylene blue-sensitized photooxidation of bromacil, terbacil, and fluometuron.

Figure 8 indicates that fluometuron was decomposed at a slow rate compared to bromacil and terbacil. The optimum rate constant of fluometuron photooxidation was 0.00123 min^{-1}, 6.2 percent of the optimum rate constant for methylene blue-sensitized photooxidation of bromacil. The low efficiency of methylene blue-sensitized photooxidation of fluometuron may be related to quenching of singlet oxygen by a fluometuron functional group. Some carbonyl groups, such as the amide moiety, quench singlet oxygen (Kearns 1971). Acher (1982b) found that atrazine was resistant to methylene blue sensitized photooxidation. He attributed this resistance to quenching of singlet oxygen by the atrazine amide moiety. The possible quenching of singlet oxygen resulted in negligible decomposition of fluometuron. This phenomenon provides further evidence that the Type II mechanism was predominant in methylene blue-sensitized photooxidation.

Riboflavin-sensitized photooxidation of bromacil, terbacil, and fluometuron follows a less consistent pattern with pH than methylene blue-sensitized photooxidation. The rate of riboflavin-sensitized photooxidation of bromacil was low below pH 7, with increased rate at basic pH reaching a maximum at pH 9. The rates of riboflavin-sensitized photooxidation of terbacil and fluometuron were quite different, with the lowest rates of photooxidation at basic pH rising to high rates of photooxidation at low pH. Acher et al. (1981) observed a trend very different from that found in this study with the riboflavin-sensitized photooxidation of terbacil. They found low pH riboflavin-sensitized photooxidation of terbacil to be less efficient than photooxidation in basic solution. The difference between the results of Acher et al. (1981) and the results described in Figure 7 for the pH optimum of riboflavin-sensitized photooxidation of terbacil may be due to the differences in methodology used to monitor terbacil concentration. Acher et al. (1981) used ultraviolet spectrophotometry; whereas gas chromatography was used in this study. Also, the high concentration of buffers used in this study may have quenched the riboflavin triplet in some pH regimes, resulting in lower substrate degradation rates.

The results obtained in this study and the results of Acher and Saltzman (1980) and Acher et al. (1981) regarding the optimum pH of riboflavin-sensitized photooxidation are somewhat unexpected. Spikes and Straight (1967) reported that the quantum yield for riboflavin triplet state excitation is highest at neutral pH, and diminishes at the pH extremes. Based on the quantum yield for riboflavin triplet formation, the optimum pH of riboflavin-sensitized photooxidation would be expected near pH 7. An hypothesis for the pH optima at basic pH for bromacil and at acidic pH for terbacil and fluometuron is ionization of the substrate at the pH optimum, which may enhance singlet oxygen attack or favor hydrogen abstraction or electron transfer.

Riboflavin and methylene blue may not be acting by identical mechanisms, since riboflavin and methylene blue-sensitized photooxidation rates as a function of pH show no similarities with the three substrates. If riboflavin-sensitized and methylene blue-sensitized photooxidation mechanisms of the three substrates used in this study were the same, the curves describing methylene

blue-sensitized photooxidation and riboflavin-sensitized photooxidation would be similar.

Acher and Saltzman (1980) and Acher et al. (1981) concluded that the methylene-sensitized photooxidation of bromacil and terbacil and the riboflavin-sensitized photooxidation of bromacil occur via the singlet oxygen mechanism. However, Acher et al. (1981) proposed that radical mechanisms may be taking place in the riboflavin-sensitized photooxidation of terbacil at acidic pH; this lends support for the difference in the mechanisms of methylene blue and riboflavin-sensitized photooxidation of terbacil. The marked differences in the rates of methylene blue and riboflavin-sensitized photooxidation of fluometuron, particularly if a fluometuron functional group quenches singlet oxygen, suggests that radical mechanisms may be occurring in the low pH riboflavin-sensitized photooxidation of fluometuron.

The speculations on mechanisms involved in methylene blue and riboflavin-sensitized photooxidations are not conclusive. In order to substantiate them, photooxidation experiments would need to be repeated using competitive studies with the singlet oxygen quenchers sodium azide and DABCO (1,4-diazobicyclo (2,2,2) octane), and also repeating the experiments in D_2O rather than H_2O (Nilsson et al. 1972).

The effects of combined methylene blue and riboflavin sensitization of 30 mg/l bromacil and 30 mg/l terbacil solutions were also investigated. The results of these experiments are shown in Figures 6 and 7. A comparison with the results obtained using methylene blue and riboflavin separately showed the reaction rates using both sensitizers to be additive in the neutral pH ranges, with an antagonistic effect upon sensitized photooxidation rate at pH extremes. To treat a waste that enters a lagoon at near-neutral pH, there may be an advantage of using both dyes to attain higher photooxidation rates. The higher photooxidation rates at neutral pH characteristic of the methylene blue-riboflavin system may allow for lower detention times in the lagoon. Using the two sensitizers in the lagoon would also not require a more shallow lagoon, since riboflavin and methylene blue absorb in separate regions of the light spectrum, as noted in Figure 9, resulting in no competition for light by the two sensitizers.

Methylene blue concentration, measured at 15-min intervals over 90 min, was found to oscillate in all experiments. The oscillating methylene blue concentrations, measured by optical density at 660 nm using a Bausch and Lomb Spectronic 70, are shown in Figures 10a, b, and c for three replicates in an experiment in which bromacil was the substrate at initial pH of 8. The oscillations occurred at differing time intervals in all three replicates. The result for the mean of the three replicates was dampened oscillations, as shown in Figure 11.

The bleaching of methylene blue was not easily quantified, because of the oscillations in the plots of methylene blue concentration versus time as shown in Figures 10 and 11. Three quantitative expressions were used to evaluate methylene blue bleaching. These included:

1) Linear bleaching rate:

$$C_t = -kt + C_o \quad . \; . \; . \; . \; (4)$$

where

C_t = substrate concentration at time t (mg/l)

C_o = substrate concentration at time 0 (mg/l)

t = time (min)

k = constant (mg/l·time)

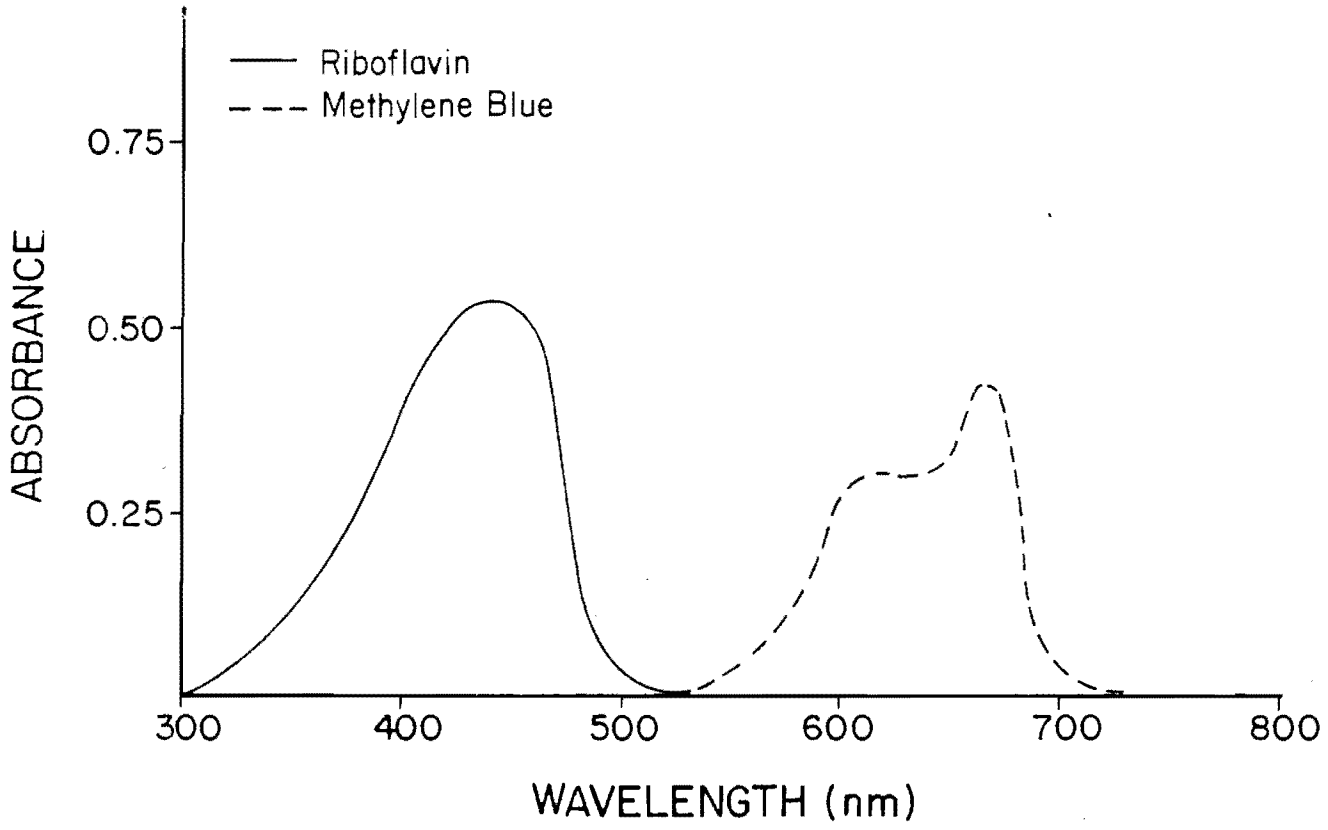


Figure 9. Absorbance as a function of wavelength for aqueous solutions of 10 mg/l riboflavin and 5 mg/l methylene blue.

2) Weighted average of methylene blue concentration during experiment:

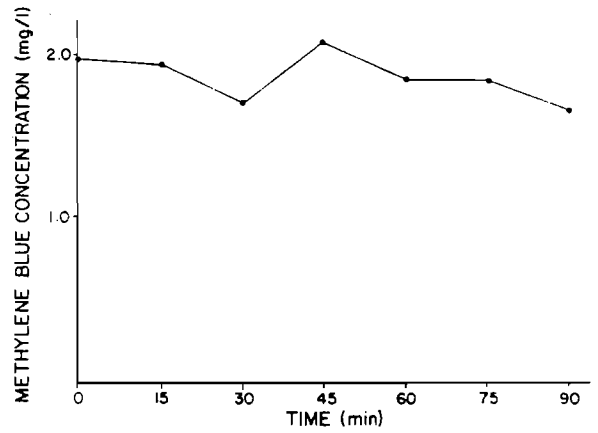
$$\text{Weighted Average of Methylene Blue Concentration During Experiment} = \frac{C_{15}\cdot 15+C_{30}\cdot 30+C_{45}\cdot 45+C_{60}\cdot 60+C_{75}\cdot 75+C_{90}\cdot 90}{15 + 30 + 45 + 60 + 75 + 90} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{Percent Methylene Blue Degradation} = 100 - \frac{\text{Weighted Methylene Blue Concentration}}{\text{Methylene Blue Concentration at } t = 0} \times 100 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

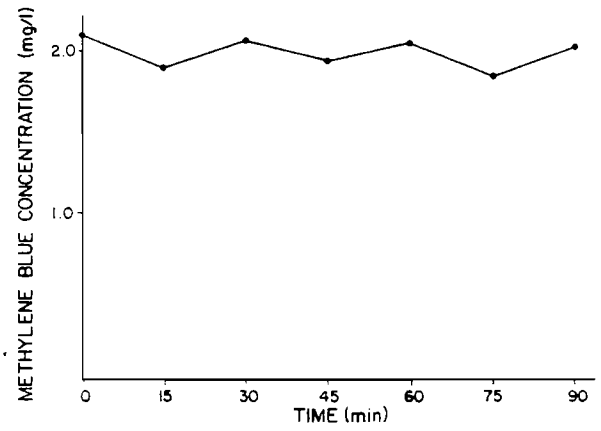
where

C_{15}, C_{30}, etc. = methylene blue concentration at time = 15 min, time = 30 min, etc.

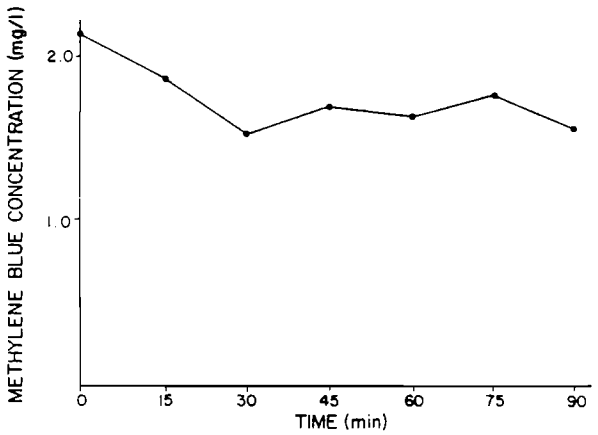
15, 30, ... 90 = time (min) samples were collected during experiment



(a)



(b)



(c)

Figure 10. Methylene blue bleaching pattern for three replicates of the sensitized photo-oxidation of bromacil at pH 8.

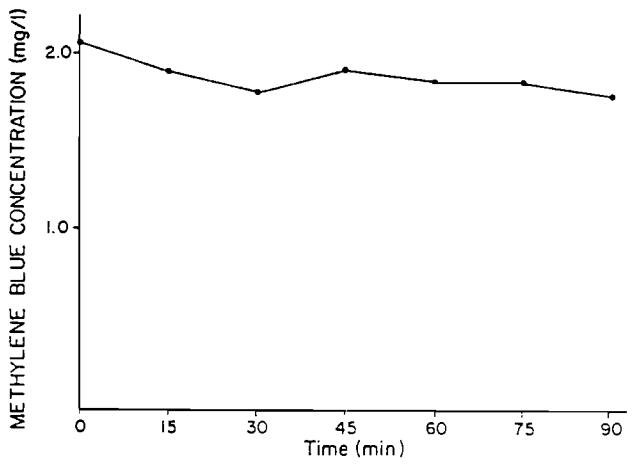


Figure 11. Dampening effect on methylene blue oscillating bleaching pattern resulting from averaging the three replicates of Figure 10.

3) Exponential bleaching rate:

$$C_t = C_o e^{-kt} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

C_t = methylene blue concentration at time t (mg/l)

C_o = methylene blue concentration at time 0 (mg/l)

t = time (min)

k = constant (min^{-1})

Data analyzed by the three methods were compared statistically by least squares curve fitting techniques. In almost all cases, methylene blue data were best quantified by exponential decay (Equation 7). Therefore, Equation 7 was used to describe methylene blue bleaching in this study. Although

Equation 7 was used to describe methylene blue bleaching, the coefficient of determination values, R^2, were generally 0.3 to 0.8. Quantification of methylene blue bleaching is, therefore, at best a compromise due to its oscillating bleaching pattern.

Figures 12, 13, and 14 represent first-order rate constants (k in Equation 7) for methylene blue bleaching as a function of pH using the substrates bromacil, terbacil, and fluometuron, respectively. Methylene blue was least stable at basic pH for all substrates investigated. The degradation of the methylene blue may be related to the production of singlet oxygen, which, when generated, attacks the sensitizer that originally generated it.

Riboflavin bleaching during the 90-minute experiments followed first-order kinetics, as demonstrated by a linear relationship of $\ln (C_t/C_o)$ as a function of time. First-order rate constants of riboflavin degradation as a function of pH are presented in Figures 15, 16, and 17 in association with the rate constants of bromacil, terbacil, and fluometuron, respectively. The degradation of riboflavin as a function of pH was consistent for all three substrates. Riboflavin decomposition was minimal at low and neutral pH, but increased markedly above pH 7. This degradation of the riboflavin appears to be substrate-independent, since it is consistent with all three substrates investigated. Possible hypotheses for the riboflavin bleaching mechanism include singlet oxygen attack on riboflavin or a radical mechanism between riboflavin molecules.

First-order rate constants for riboflavin and methylene blue bleaching as a function of pH for the experiments that were sensitized by both dyes are presented in Figures 18 and 19. Also included in Figures 18 and 19 are first-order rate constants for bromacil and terbacil, respectively. Degradation of riboflavin and methylene blue was substantial when the sensitizers were present together in solution. In addition, degradation of both sensitizers occurred throughout the pH ranges tested.

Bench scale studies undertaken to assess the effect of pH on sensitized photooxidation rate of an uncharacterized waste should also monitor sensitizer degradation. The degradation rates of riboflavin and methylene blue showed consistent degradation patterns--an increase in methylene blue degradation rates above pH 8 and an increase in riboflavin degradation rates above pH 7.5. However, sensitizers may degrade via different mechanisms under varying pH, dissolved oxygen, substrate concentration, and other physicochemical conditions, possibly rendering degradation rates as a function of pH different from those shown in this study.

The rate of sensitizer degradation to the rate of waste decomposition is important in terms of lagoon hydraulics. Most waste stabilization ponds that are not aerated follow plug flow hydraulics (Metcalf and Eddy 1979). Aerated lagoon hydraulics also closely follow plug flow hydraulics (Murphy and Wilson 1974). Regardless of the need for aeration in sensitized photooxidation lagoons, plug flow hydraulics will be an important consideration in lagoon design. Regarding sensitizer degradation in light of plug flow hydraulics, there seem to be two alternatives to maintain significant amounts of sensitizer along the entire plug flow regime: (1) feed a slug of dye of high concentration at the headworks of the lagoon. The concentration would need to be high enough so that there is still significant photooxidation rates at the end of the hydraulic regime of the lagoon, or (2) feed the required amount of dye as specified by design at the headworks followed by subsequent feeds along the plug flow regime. This option would keep the sensitizer concentration relatively constant in the lagoon. Option 1 has the advantage of needing

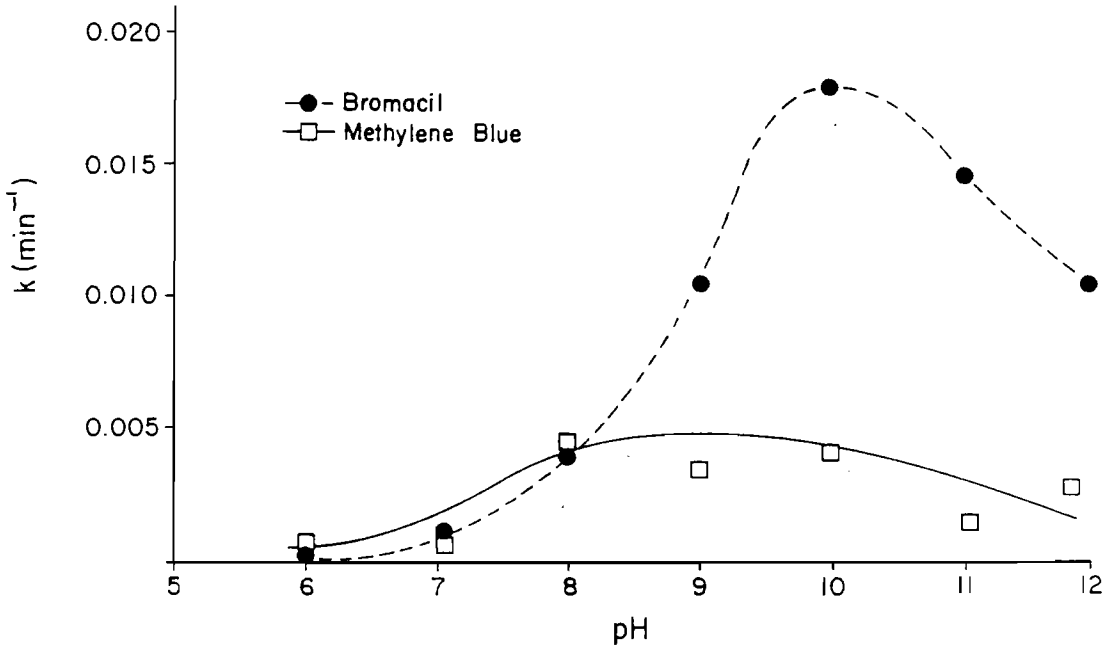


Figure 12. Effect of pH on first-order rate constants of methylene blue-sensitized photooxidation of bromacil and methylene blue bleaching. Initial bromacil concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

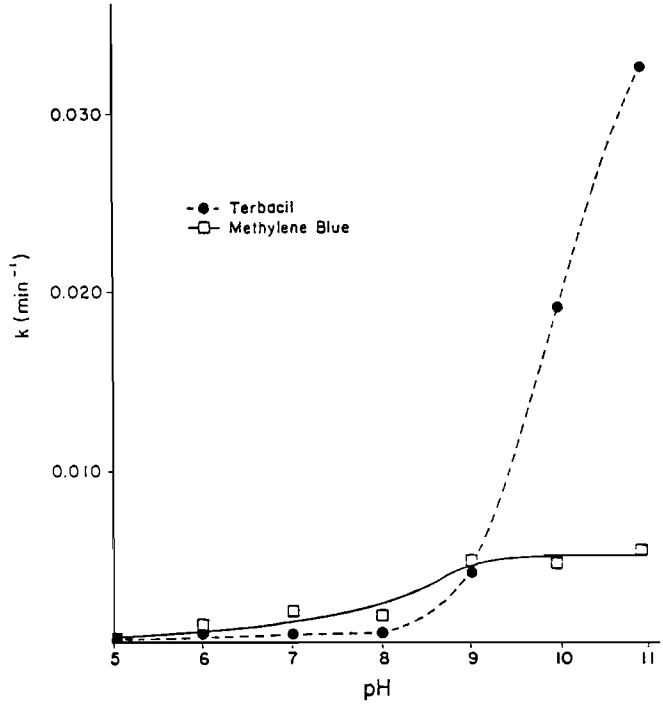


Figure 13. Effect of pH on first-order rate constants of methylene blue-sensitized photooxidation of terbacil and methylene blue bleaching. Initial terbacil concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

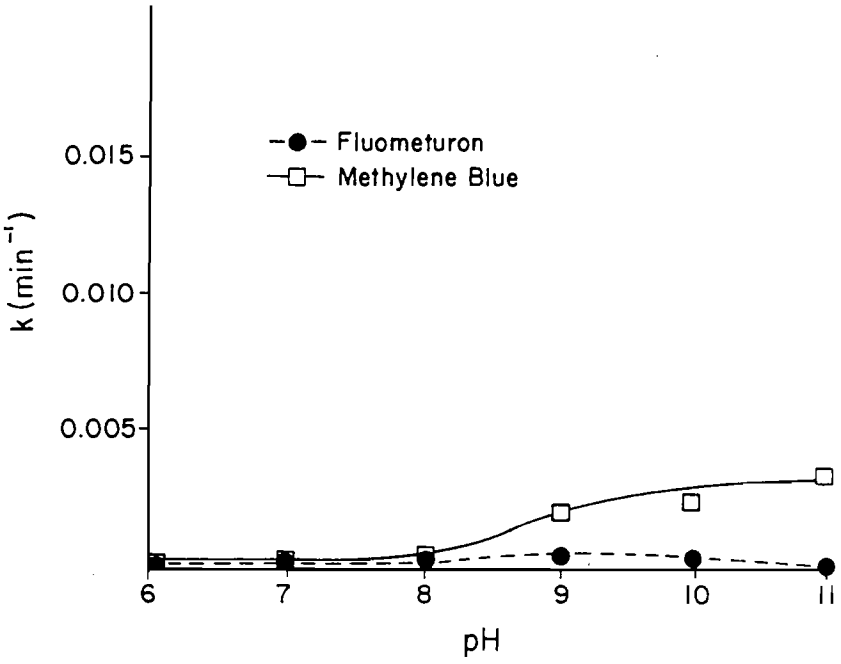


Figure 14. Effect of pH on first-order rate constants of methylene blue-sensitized photooxidation of fluometuron and methylene blue bleaching. Initial fluometuron concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

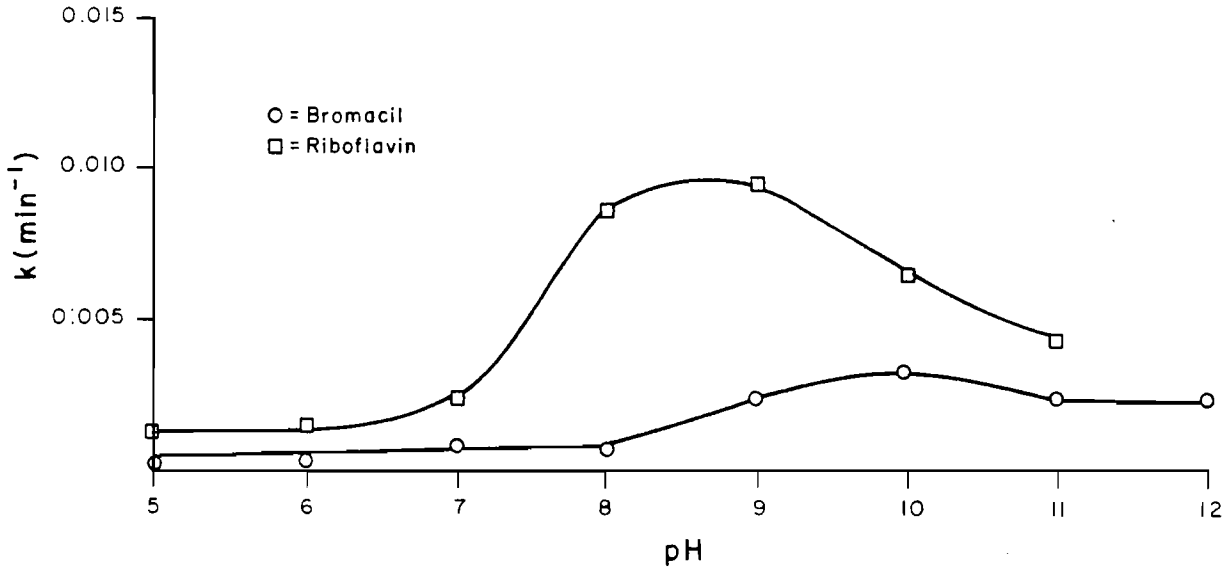


Figure 15. Effect of pH on the first-order rate constants of riboflavin-sensitized photooxidation of bromacil and riboflavin bleaching. Initial bromacil concentration was 30 mg/l; initial riboflavin concentration was 10 mg/l.

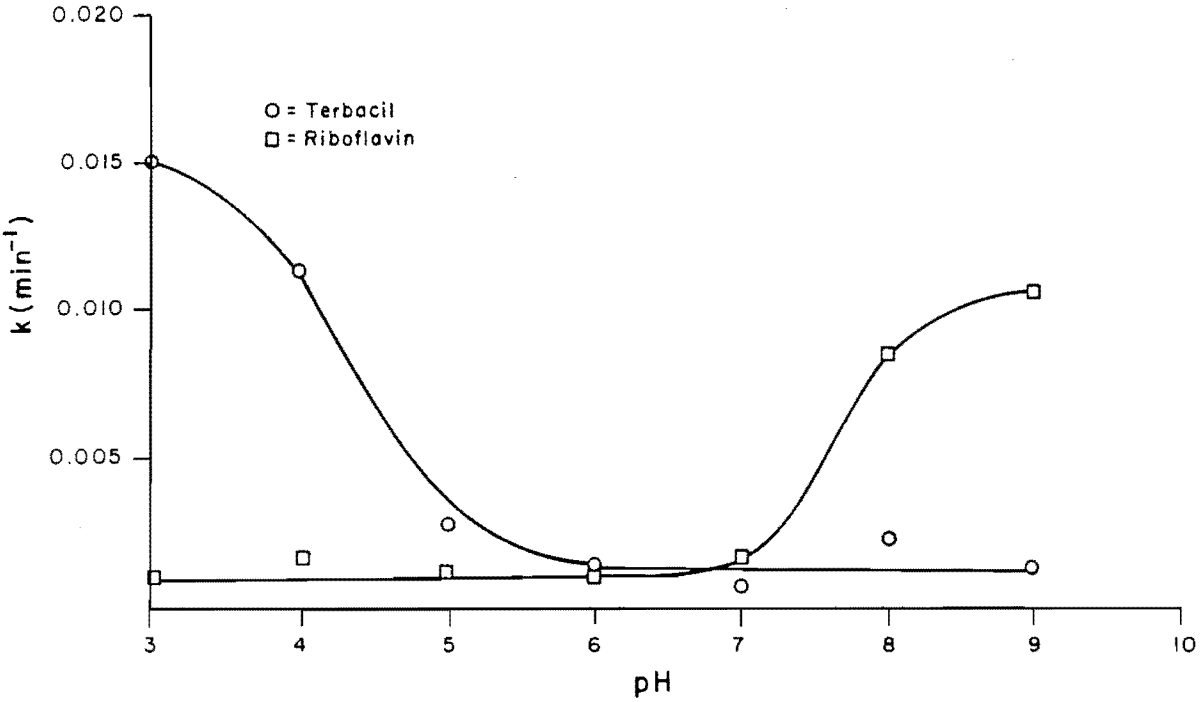


Figure 16. Effect of pH on the first-order rate constants of riboflavin-sensitized photooxidation of terbacil and riboflavin bleaching. Initial terbacil concentration was 30 mg/l; initial riboflavin concentration was 10 mg/l.

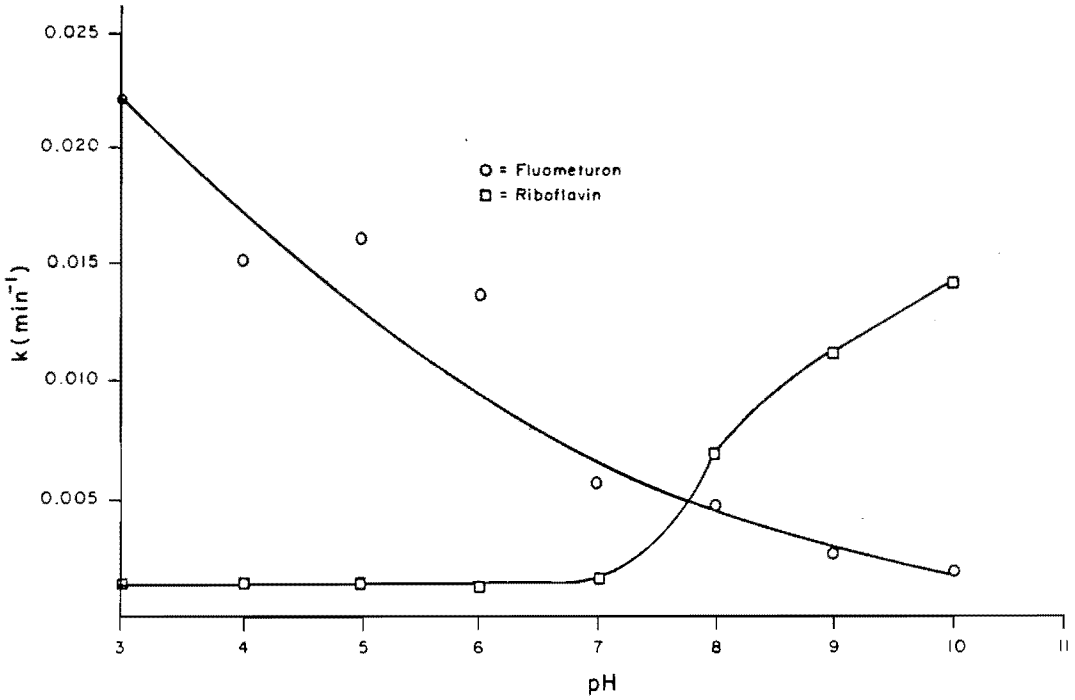


Figure 17. Effect of pH on first-order rate constants of riboflavin-sensitized photooxidation of fluometuron and riboflavin bleaching. Initial fluometuron concentration was 30 mg/l; initial riboflavin concentration was 10 mg/l.

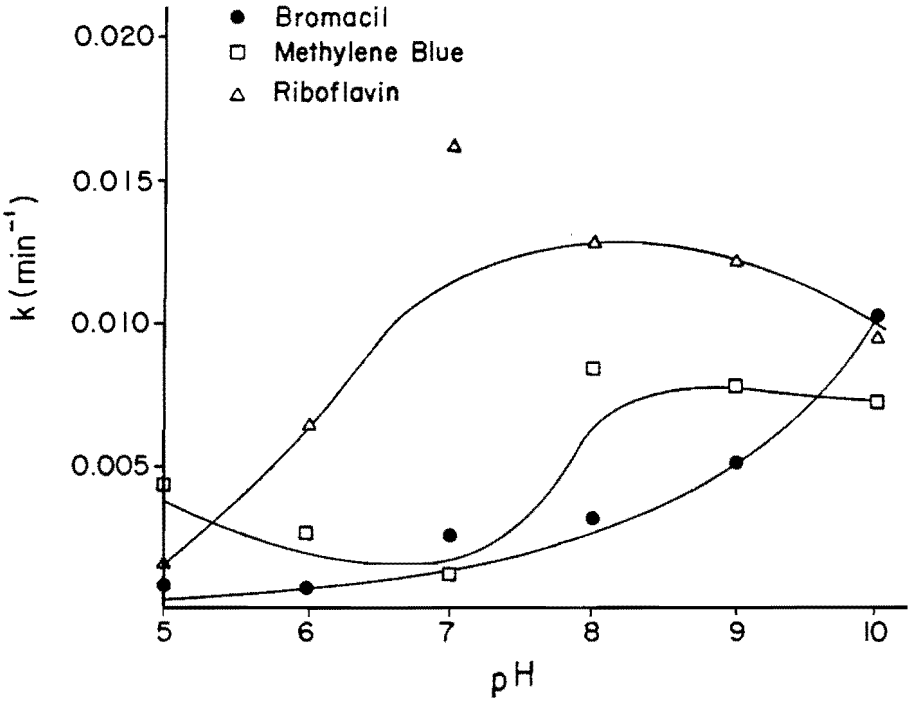


Figure 18. First-order rate constants for the degradation of 30 mg/1 bromacil and the bleaching of methylene blue (2 mg/1) and riboflavin (10 mg/1) as a function of pH for experiments sensitized by both compounds.

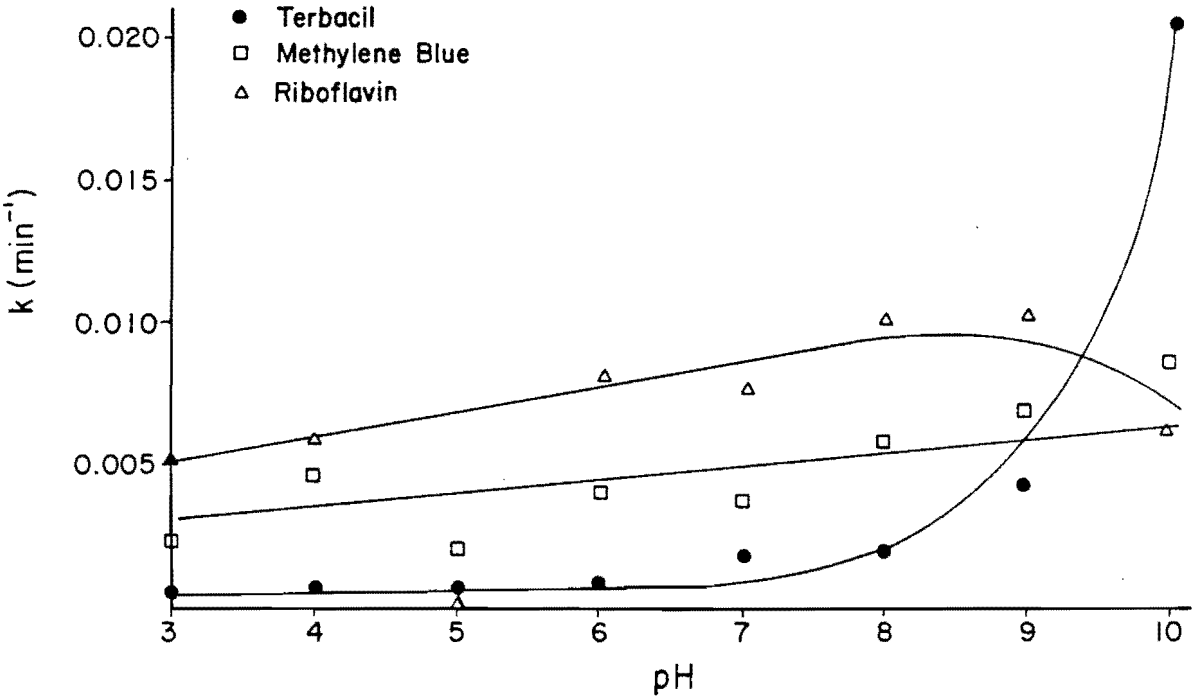


Figure 19. First-order rate constants for the degradation of 30 mg/1 terbacil and the bleaching of methylene blue (2 mg/1) and riboflavin (10 mg/1) as a function of pH for experiments sensitized by both compounds.

only one chemical feed. Disadvantages of Option 1 include the problem of a constantly decreasing dye concentration throughout the lagoon, which, due to increased light penetration, may require the depth of the lagoon to increase along the hydraulic regime of the lagoon. Other disadvantages of the single feed design include decreasing photooxidation rate as the dye is bleached and a need to overcompensate in the addition of the dye so that there is a residual left at the end of the hydraulic regime of the lagoon, resulting in higher dye costs. The primary disadvantage of Option 2, the multiple feed system, is the necessity of purchasing and operating numerous feeds along the hydraulic regime of the lagoon. The advantages of the multifeed option include the maintenance of a constant dye concentration in the lagoon and no need to overcompensate in dye addition, resulting in lower sensitizer costs for the lagoon.

Regardless of the sensitizer feed design, two criteria must be met at the end of the hydraulic regime of the lagoon. They are 1) the sensitized photooxidation rate must be significant as related to the remaining sensitizer residual and 2) the concentration of the dye in the discharge must be below toxic levels for discharge to aquatic or terrestrial environments. The toxicity of methylene blue is particularly critical, since low levels (> 0.1 mg/l) are phytotoxic and toxic to bacteria (Acher and Juven 1977; Acher and Rosenthal 1977).

Regardless of the dye feed system used, the operating cost of the lagoons would be greatly reduced if sensitizer bleaching is kept to a minimum. Sargent and Sanks (1974) emphasized minimizing sensitizer bleaching by controlling waste concentration, pH, and dissolved oxygen to inhibit dye bleaching, thereby making dye additions minimal.

A good example of efficient degradation of waste with minimal degradation of dye is the riboflavin-sensitized photooxidation of fluometuron at pH 7. From Figure 17, the k for fluometuron degradation was 0.055 min^{-1} and the k for riboflavin degradation was 0.013 min^{-1}. This type of waste could be efficiently treated in a sensitized lagoon since: (1) no pH adjustment would be required, assuming the waste enters the lagoon near neutral pH; (2) relatively fast photooxidation of fluometuron is available; and (3) the slow degradation rate of riboflavin would allow for high photooxidation rates throughout the plug flow regime of the lagoon.

On the other hand, an example of poor photooxidation conditions is the riboflavin-sensitized photooxidation of terbacil at pH 9, as shown in Figure 16. In this case the k for terbacil degradation was 0.0010 min^{-1}, whereas the k for riboflavin degradation was 0.012 min^{-1}. A lagoon designed to treat terbacil with these conditions would be of poor design, since the riboflavin would degrade much faster than the waste would be oxidized in the plug flow regime.

Sargent and Sanks (1974) emphasized using a completely mixed regime for sensitized photooxidation where the concentration of dye would be nearly equal throughout the system. In this case degradation of the dye is not as crucial as with a plug flow regime. Sargent and Sanks suggested that such a system would require an ion exchange recovery system for the dye, with subsequent recycle of the dye to the headworks of the lagoon. Such a dye recovery system and recycle may prove to be rather costly and troublesome. Furthermore, high aeration and blower costs would be required to maintain the complete mix system. In addition, high aeration may not be necessary for sensitized photooxidation, as it is for biological waste treatment.

Optimization of pH for maximum waste decomposition and minimum sensitizer

bleaching has some obvious advantages and disadvantages. The numerous sensitizer-substrate systems investigated in this study had varying optima of pH for maximum photooxidation. For methylene blue-sensitized systems, the optimum pH was generally above 8. For riboflavin-sensitized systems, the optimum pH was either very acidic or very basic. Neutral pH was never optimal. The pH of industrial waste streams, including waste streams from pesticide synthesis, varies substantially (Atkins 1972). For example, waste streams from the synthesis of bromacil are generally at pH 9 (U.S. EPA 1976). Low pH waste streams originate from the synthesis of DDT, parathion, and 2,4-D. High pH waste is generated from the synthesis of carboxyl (Atkins 1972). The optimum design would match selection of the sensitizer to the pH of the waste that is to be treated. Before making the selection, bench-scale experiments should be used to test methylene blue, riboflavin, and perhaps other sensitizers to determine the optimum pH of photooxidation for the waste to be treated. If one sensitizer performs better than the others at the pH of the waste, that sensitizer would be chosen. If neither sensitizer is efficient at the pH of the waste stream, pH adjustment may be necessary to lower the pH by the use of acid or to increase the pH by the addition of sodium hydroxide or lime. Even if moderate photooxidation rates can be accomplished at the pH of the waste stream using one of the sensitizers, the rate of photooxidation might be elevated to very high levels by a small pH adjustment. An example of this is methylene blue-sensitized photooxidation of terbacil at an original pH of 8 (Figure 13). If a terbacil-containing waste stream at pH 8 were adjusted to pH 10 prior to photooxidation, a 47-fold increase in reaction rate would be possible. The advantage of such a pH adjustment would be a lower detention time of the lagoon and therefore lower land requirement. The disadvantage would be significantly higher operating costs to make the pH adjustment. The decision for such a pH adjustment would be based on economic analysis.

The pH of a photooxidation lagoon, although important, is not as critical as is the pH of a biological waste treatment system. In a biological treatment system, a slug of acid or base entering the system can be toxic to the community of organisms and disrupt the steady state performance of the treatment facility. The situation is particularly critical when acclimated cultures are used. If the acclimated microorganisms of a lagoon are damaged by a pH shock, a new acclimated culture must be brought to steady state, a process which is time consuming (Eckenfelder 1966). In a sensitized photooxidation lagoon a sudden change in pH would, no doubt, change the photooxidation rate, but the system could be easily corrected. By correcting the pH with the addition of acid or lime, the desired photooxidation rates could be restored. One possibility of a pH shock to sensitized photooxidation lagoons is that the shock could actually increase the rate of photooxidation, making correction unnecessary. For example, if a caustic slug entered a methylene blue-sensitized photooxidation lagoon treating terbacil that was originally at pH 8 (Figure 13) and the resulting pH was 11, photooxidation rates would increase dramatically.

In sensitized photooxidation reactions, the pH usually decreases as the reaction proceeds. This phenomenon was noted in this study and by other authors (Acher and Saltzman 1980; Acher 1982a). Thus, as the waste proceeds through the plug flow regime of the lagoon, the pH will drop. The degree of pH drop depends on the alkalinity of the wastewater and the strength of the waste. If the pH drops substantially, the photooxidation rate may be affected. Chemical feeds containing lime would then be necessary along the hydraulic regime of the lagoon. In some cases a decrease in pH may increase the rate of photooxidation, as in the case of

riboflavin-sensitized photooxidation of terbacil (Figure 16). The use of lime feeds for pH stabilization as the photooxidation reaction progresses along the hydraulic regime of a lagoon design should be based on economic analysis.

Sensitized Photooxidation Rate as a Function of Lagoon Depth

First-order rate constants, $k(min^{-1})$, were calculated for the disappearance of parent herbicide at simulated depths in petri dish-reaction chambers by plotting $\ln C_t/C_o$ as a function of time. Rate constants, plotted as a function of simulated depth, are presented in Figures 20 and 21 for four concentrations of methylene blue and riboflavin, respectively. The data indicate that the photooxidation rate decreases with depth because of reduced radiation penetration. In a lagoon with a high sensitizer concentration (e.g., 2.0 mg/l methylene blue), a high reaction rate may be maintained at the surface, but there is a sharp decline in reaction rate with depth because the dye increases the rate of light extinction. With a small amount of dye present, the surface photooxidation rate would be lower, but the rate does not decrease so rapidly with depth due to less light extinction.

The data presented in Figures 20 and 21 took months to collect. Collection of such data to design a waste treatment system for an uncharacterized waste would require an inordinate amount of time. Moreover, if data are necessary for numerous surface light intensities, the time required for sizing the pilot lagoon would be out of the question. A more efficient approach to lagoon sizing is needed.

The approach used here was to describe the rate of photooxidation as a function of depth mathematically for design purposes. The generalized model predicts sensitized photooxidation rate as a function of depth based on the quantity and quality of light reaching the surface of the lagoon, the photooxidation rate at the surface of the lagoon, and the spectral quality of the waste entering the lagoon.

As light penetrates through successive horizontal sections of a lagoon, not only will the total quantity of light decrease, but the spectral quality of light will also change. The factor influencing the change in the quality of the light is the extinction coefficient of the dye, and this coefficient varies over the spectrum of light wave lengths. Therefore, for methylene blue which has maximum absorbance at 660 nm, the band from 650 to 670 nm is the region from which light is extinguished first. In contrast, from 400 to 410 nm, the extinction coefficient is very small, and little light is extinguished. This differential filtration of wavelengths of light with depth causes the change in light quality.

A model used to describe photooxidation rate must account for the decrease in quantity of light as well as the change in the quality of light in horizontal control volumes differentiated by depth. The decrease in quantity of light may be estimated by the use of the Beer-Lambert Law, which relates light intensity at depth z to surface light intensity:

$$I_z = I_o \, 10^{-\varepsilon C z} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

I_z = intensity at depth z ($\mu E/m^2$.sec)

I_o = surface intensity ($\mu E/m^2$.sec)

ε = extinction coefficient (cm^{-1} M^{-1})

C = concentration of solute (M)

z = depth through which light passes (cm)

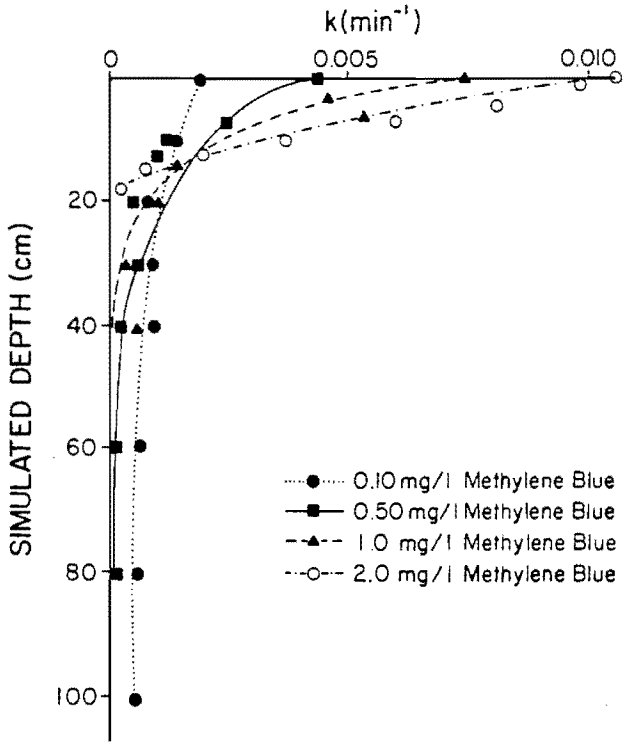


Figure 20. Methylene blue-sensitized first-order rate constants as a function of simulated depth for the photooxidation of 30 mg/l bromacil with four methylene blue concentrations.

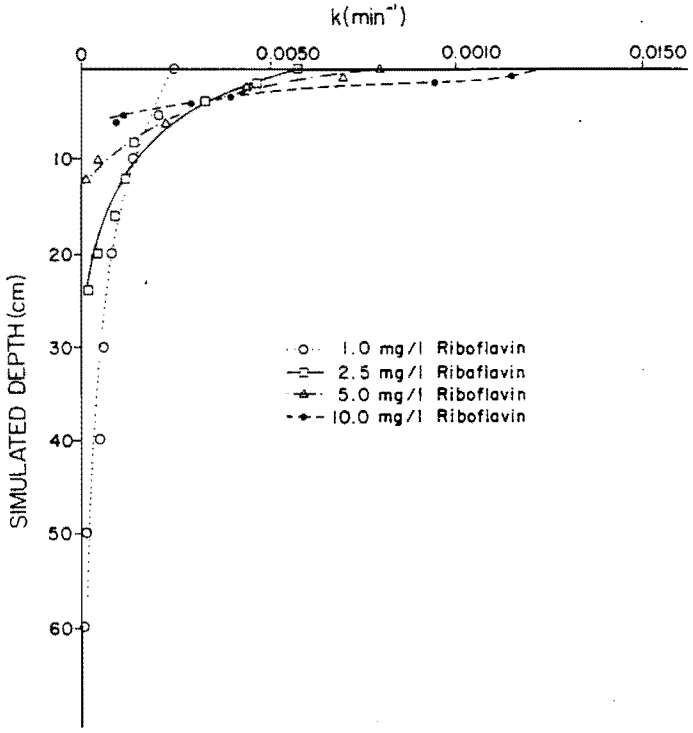


Figure 21. Riboflavin-sensitized first-order rate constants as a function of simulated depth for the photooxidation of 30 mg/l terbacil with four concentrations of riboflavin.

The change in quality of light may be quantified by the determination of the light intensity at wavelengths across the visible spectrum (400 to 700 nm) at depth z. The result is the term, $I_{z,\lambda}$, which is the light intensity in $\mu E/m^2 \cdot sec$ at 5 nm intervals at depth z. When riboflavin is used as sensitizer, $I_{z,\lambda}$ calculations must be monitored to 350 nm, since riboflavin absorbs light from 350 to 400 nm.

The First Law of Photochemistry states that light must be absorbed by a molecule before a photochemical reaction can take place (Calvert and Pitts 1966). A model must therefore include a measure of the amount of light absorbed by a known concentration of sensitizing molecules in solution. The extinction coefficient, ϕ, is a measure of light absorption by a sensitizer and is included in the model.

A model must also include a term that quantifies the efficiency of the photochemical reaction taking place. The quantum yield, ϕ, is defined by Calvert and Pitts (1966) as

$$\phi = \frac{\text{moles of molecules reacting}}{\text{moles of photons absorbed}} \quad . \quad . \quad . \quad . \quad (9)$$

In a more specific sense, the quantum yield for sensitizing molecules reaching the triplet state through intersystem crossing, ϕ_{isc}, is defined

$$\phi_{isc} = \frac{\text{moles of sensitizers excited to triplet state through intersystem crossing}}{\text{moles of photons absorbed}} \quad . \quad . \quad . \quad .(10)$$

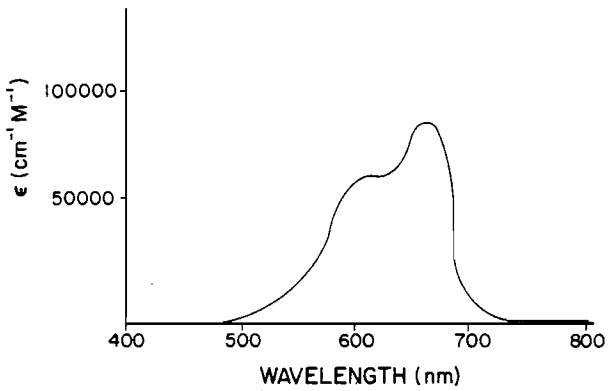
A model describing sensitized photooxidation rate as a function of depth is most easily synthesized for predicting the rate of sensitizer triplet formation followed by extrapolation to a more general model for waste degradation.

Quality of light may be interpreted as intensity in bands throughout the visible spectrum. Therefore, a model must include the term $I_{z,\lambda}$. The extinction coefficient is also a function of wavelength as shown in Figure 22a for methylene blue and Figure 22b for riboflavin. The extinction coefficient as a function of wavelength, ε_λ, is also included. The quantum yield of sensitizer triplet formation is assumed to be independent of wavelength. Quantum yields do not vary substantially as a function of wavelength over the visible spectrum (Calvert and Pitts 1966). Relating these terms in 5 nm intervals leads to the following integral describing the rate of sensitizer triplet formation:

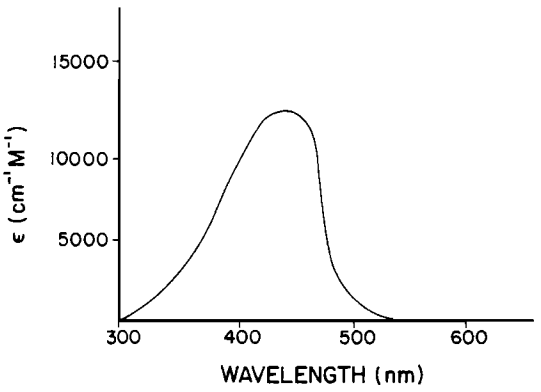
$$\text{Rate of Sensitizer Triplet Formation} = \int_{350\text{ nm, 5 nm}}^{800\text{ nm, 5 nm}} I_{z,\lambda} \cdot \varepsilon_\lambda \cdot \phi_{isc}\, d\lambda \quad . \quad . \quad . \quad . \quad .(11)$$

A check of equality of units on the left and right hand sides of the equation follows:

$$\text{Mole triplet sensitizer formed/min/mole sensitizer} = \left(\frac{I_{z,\lambda}}{\frac{\text{moles photons}}{dm^2 \cdot min}}\right) \cdot \left(\frac{\varepsilon_\lambda}{\frac{\text{moles photons absorbed}}{\text{moles photons} \cdot dm \cdot \frac{\text{moles sensitizer}}{dm^3}}}\right)$$



(a)



(b)

Figure 22. Molar extinction coefficients of methylene blue (a) and riboflavin (b) as a function of wavelength.

$$\cdot \left(\frac{\text{moles triplet sensitizer formed}}{\text{moles photons absorbed}} \right)^{\phi_{isc}} \quad . \quad . \quad . \quad . \quad .(12)$$

The model may be adapted to predict the sensitized photooxidation rate of a given substrate if physical and chemical conditions are held constant (e.g., light intensity, pH) or are present in excess (e.g., dissolved oxygen). In this case, the rate of triplet sensitizer formation is proportional to the pseudo first-order rate constant of the sensitized photooxidation reaction of a compound (e.g., bromacil) under the same physical and chemical conditions:

$$k \propto \text{specific rate of triplet sensitizer formation} \quad . \quad .(13)$$

or

$$k = \text{Constant} \cdot \text{specific rate of triplet sensitizer formation} \quad . \quad . \quad .(14)$$

The quantum yield of sensitizer triplet formation, ϕ_{isc}, may be related to a more general quantum yield of reaction, ϕ_{rxn}, by this constant:

$$\phi_{rxn} = \phi_{isc} \cdot \text{Constant} \quad . \quad . \quad .(15)$$

Substitution of Equation 15 into Equation 11 and cancelling the constant on each side of the model yields the pseudo first-order rate constant of sensitized photooxidation for a specific substrate:

$$k = \int_{350\text{ nm, 5 nm}}^{800\text{ nm, 5 nm}} I_{z,\lambda} \cdot \varepsilon_{\lambda} \cdot \phi_{rxn}\, d\lambda \quad . \quad . \quad .(16)$$

The following outline describes how the model may be used to predict photooxidation rate as a function of depth.

I) Convert spectroradiometer data for design light conditions from W/m^2 to $E/dm^2 \cdot min$, where $\mu E/m^2 \cdot sec \cdot nm = W/m^2/nm\ \lambda \times 8.36 \times 10^{-3}$

II) Integrate the 1 nm bands provided by the spectroradiometer to 5 nm bands using Simpson's integration (Rodin 1970)

III) Determine the extinction coefficient for the sensitizer over the visible range at 5 nm intervals from ε_{max} and the absorption spectrum of the sensitizer. The values are generally read from a spectrum such as Figure 22.

IV) Numerically integrate

$$k = \int_{350\text{ nm, 5 nm}}^{800\text{ nm, 5 nm}} I_{z,\lambda} \cdot \varepsilon_{\lambda} \cdot \phi_{rxn}\, d\lambda \quad \ldots (16)$$

where k, ε_{λ}, and I_{λ} are knowns, and ϕ_{rxn} is unknown. The first-order rate constant, k, is the zero-depth, or surface rate constant for substrate photooxidation under specific physical and chemical conditions (e.g., pH, aeration, etc.) to be used for design. The quantum yield of reaction calculated may then be used to calculate k at successive depths. Spikes and Straight (1967) reported that quantum yield is not a function of light intensity, so the ϕ_{rxn} calculated for the surface reaction can be used to calculate k at lower light intensities.

V) The intensity of light at successive depths in 5 nm intervals, $I_{z,\lambda}$, is calculated using the Beer-Lambert Law.

VI) Using ϕ_{rxn} calculated for the surface reaction and $I_{z,\lambda}$ calculated for the depth of interest, numerically integrate.

$$k = \int_{350\text{ nm, 5 nm}}^{800\text{ nm, 5 nm}} I_{z,\lambda} \cdot \varepsilon_{\lambda} \cdot \phi_{rxn}\, d\lambda \quad \ldots (16)$$

In this integration ϕ_{rxn}, ε_{λ}, and $I_{z,\lambda}$ are known and k is unknown.

Equation 16 was used to calculate photooxidation rate constants of bromacil and terbacil, as well as bleaching rate constants of methylene blue and riboflavin as a function of depth. Rate constants as a function of simulated depth calculated using Equation 16 related to the mean of three replicates for rate constants determined in the laboratory are presented in Figure 23. Methylene blue-sensitized photooxidation of bromacil shows the same data for the photooxidation of terbacil sensitized by riboflavin (Figure 24). Methylene blue and riboflavin bleaching rate constants as a function of simulated depth calculated using Equation 16 compared with laboratory bleaching rates are presented in Figures 25 and 26, respectively. No methylene blue bleaching was detected in the experiments conducted with 0.1 mg/l methylene blue lagoon concentration; therefore, these data are not included in Figure 25.

The accuracy of Equation 16 was verified by statistical analysis. Laboratory first-order rate constants as a function of simulated depth, measured in petri dish reaction chambers, were used to verify model simulations generated by Equation 16. Model data were generated using the zero depths of the laboratory data to initialize Equation 16. Using Equation 16, model rate constants were then calculated at the same depths for which laboratory rate constants were previously measured. For each sensitizer concentration studied, three rate constants versus simulated depth curves were generated using Equation 16, initialized by the three replicate zero-depth laboratory rate constants. The three model depth curves were then compared statistically to the three corresponding laboratory curves. An exception was statistical analysis of laboratory data versus model data for methylene blue bleaching rate as a function of simulated depth. For

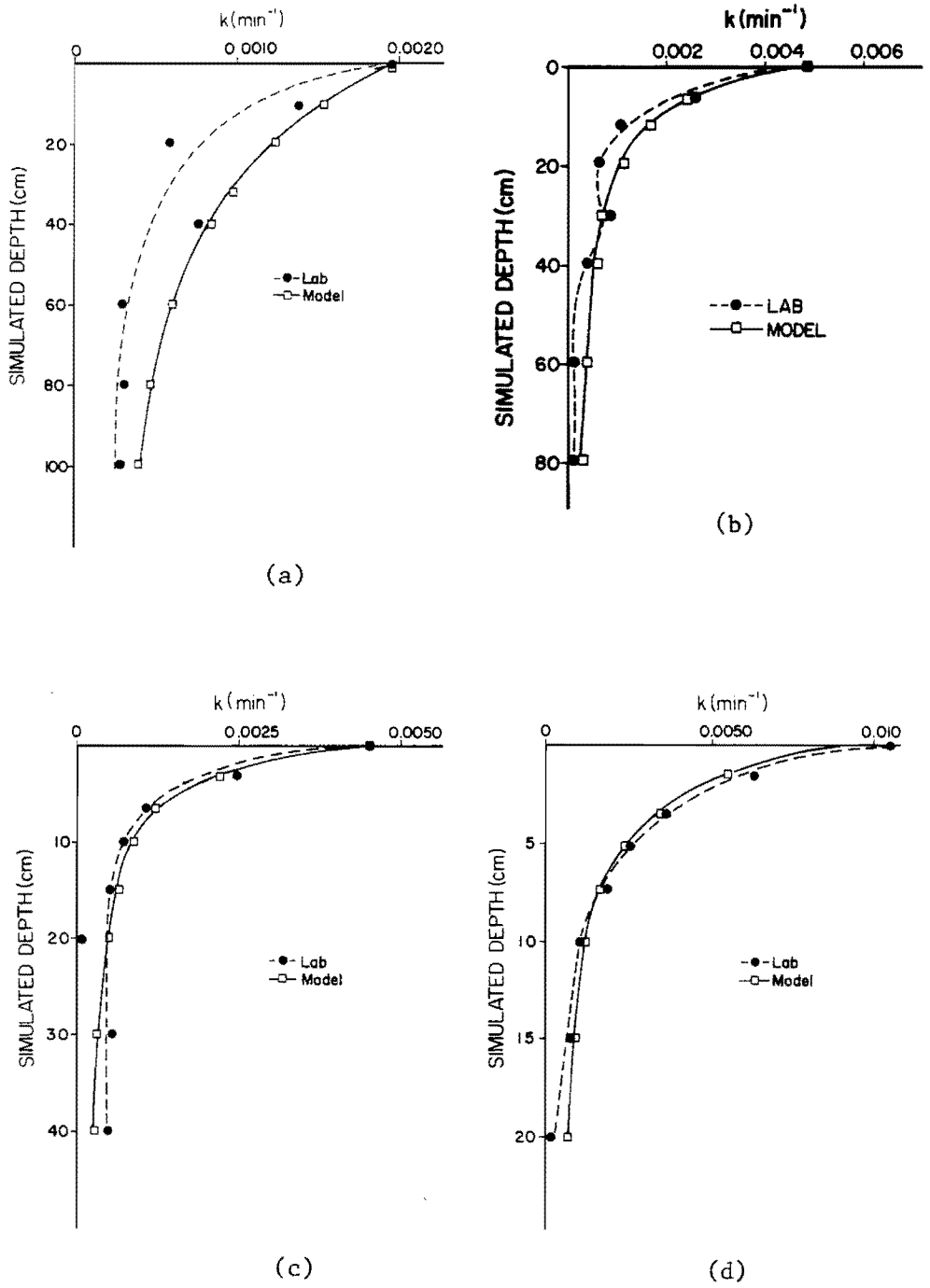


Figure 23. Comparison of mean of three replicates of laboratory data and the simulation generated by the depth model (Equation 16) for methylene blue-sensitized photooxidation of bromacil first-order rate constants as a function of depth for 0.1 mg/l methylene blue (a); 0.5 mg/l methylene blue (b); 1.0 mg/l methylene blue (c); and 2.0 mg/l methylene blue (d).

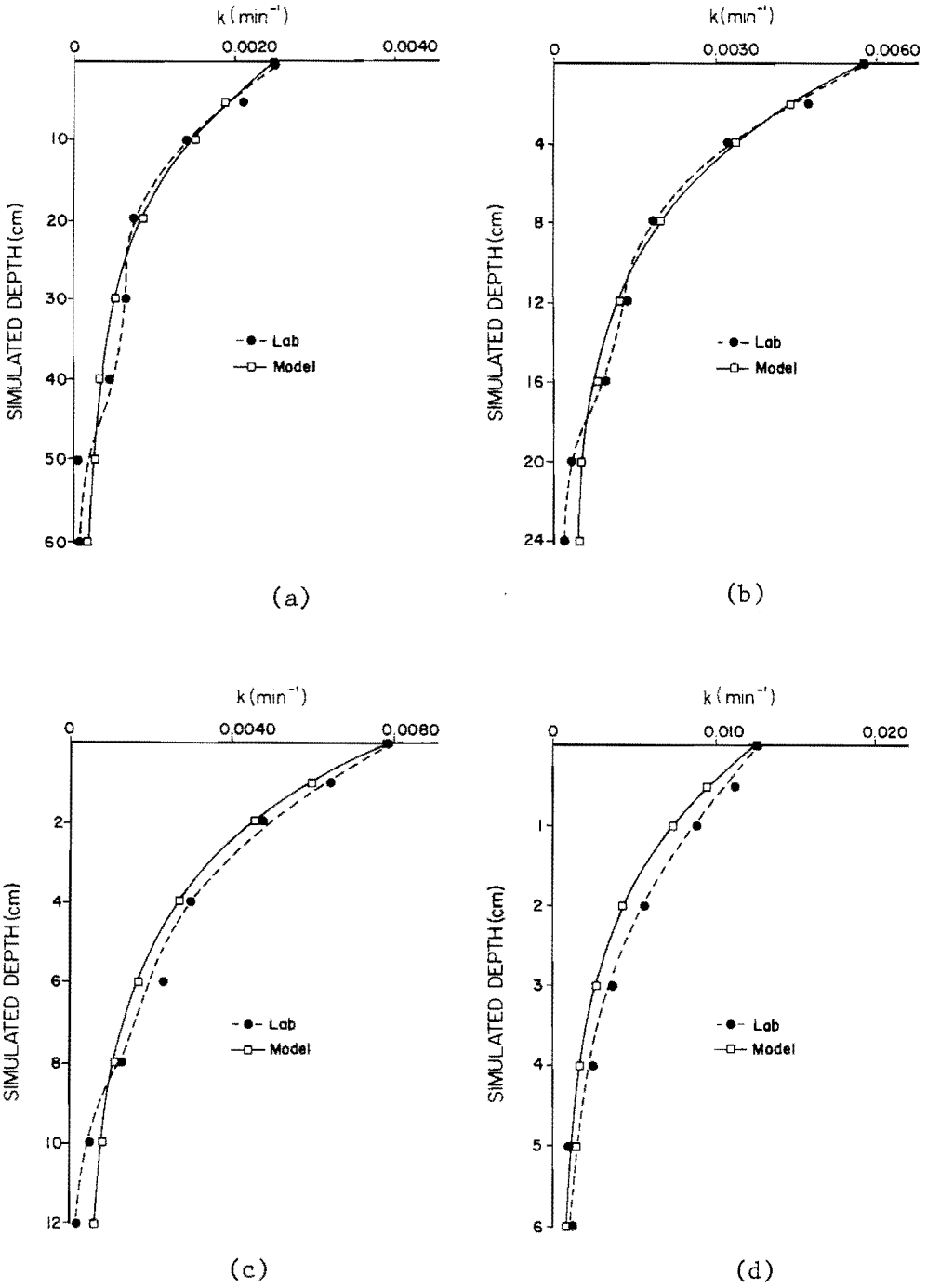


Figure 24. Comparison of mean of three replicates of laboratory data and the simulation generated by the depth model (Equation 16) for riboflavin-sensitized photooxidation of terbacil first-order rate constants as a function of depth for 1.0 mg/l riboflavin (a); 2.5 mg/l riboflavin (b); 5.0 mg/l riboflavin (c); and 10.0 mg/l riboflavin (d).

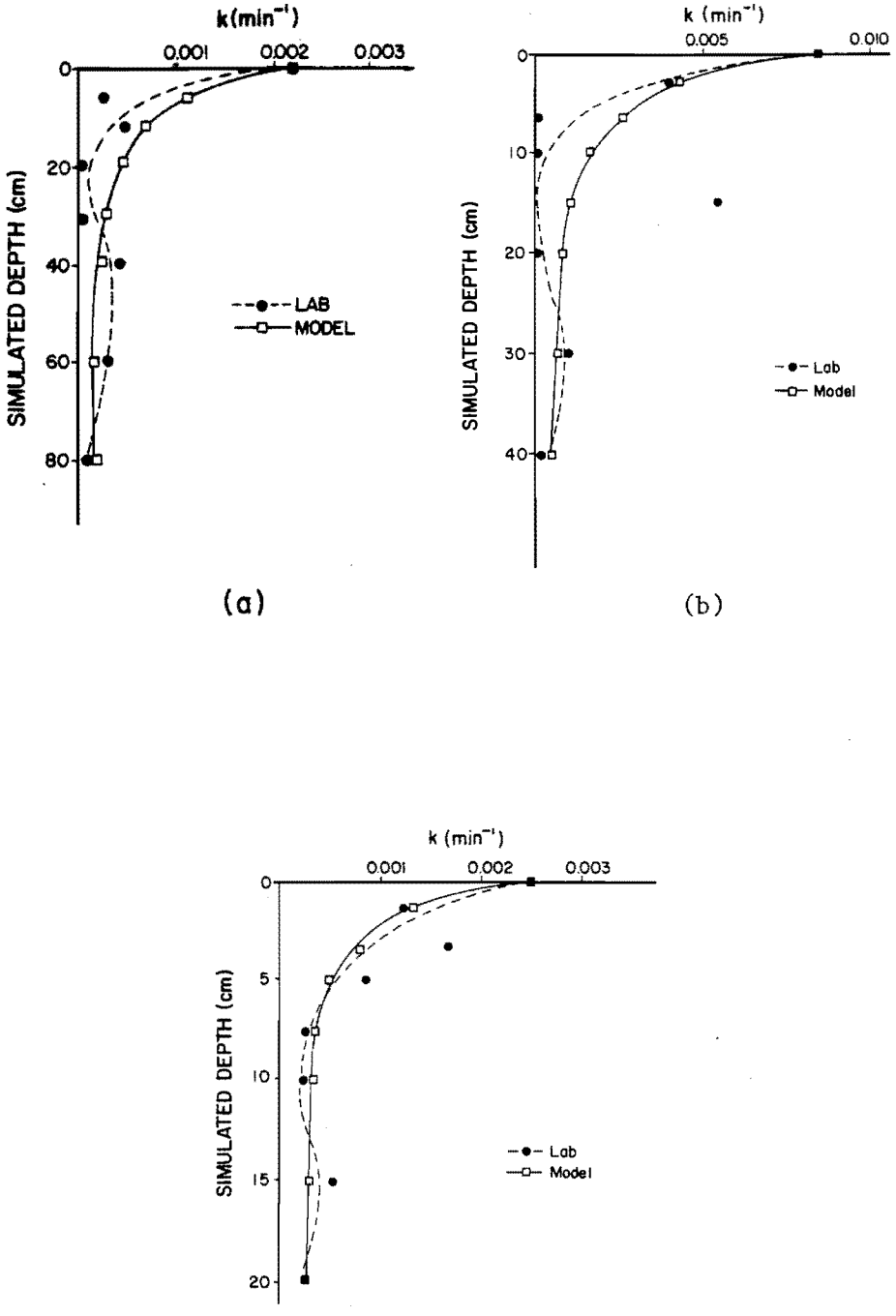


Figure 25. Comparison of laboratory data and the simulation generated by the depth model, Equation 16, for first-order constants of methylene blue bleaching rate in the photooxidation of 30 mg/l bromacil as a function of simulated depth for 0.5 mg/l methylene blue (a); 1.0 mg/l methylene blue (b); and 2.0 mg/l methylene blue (c).

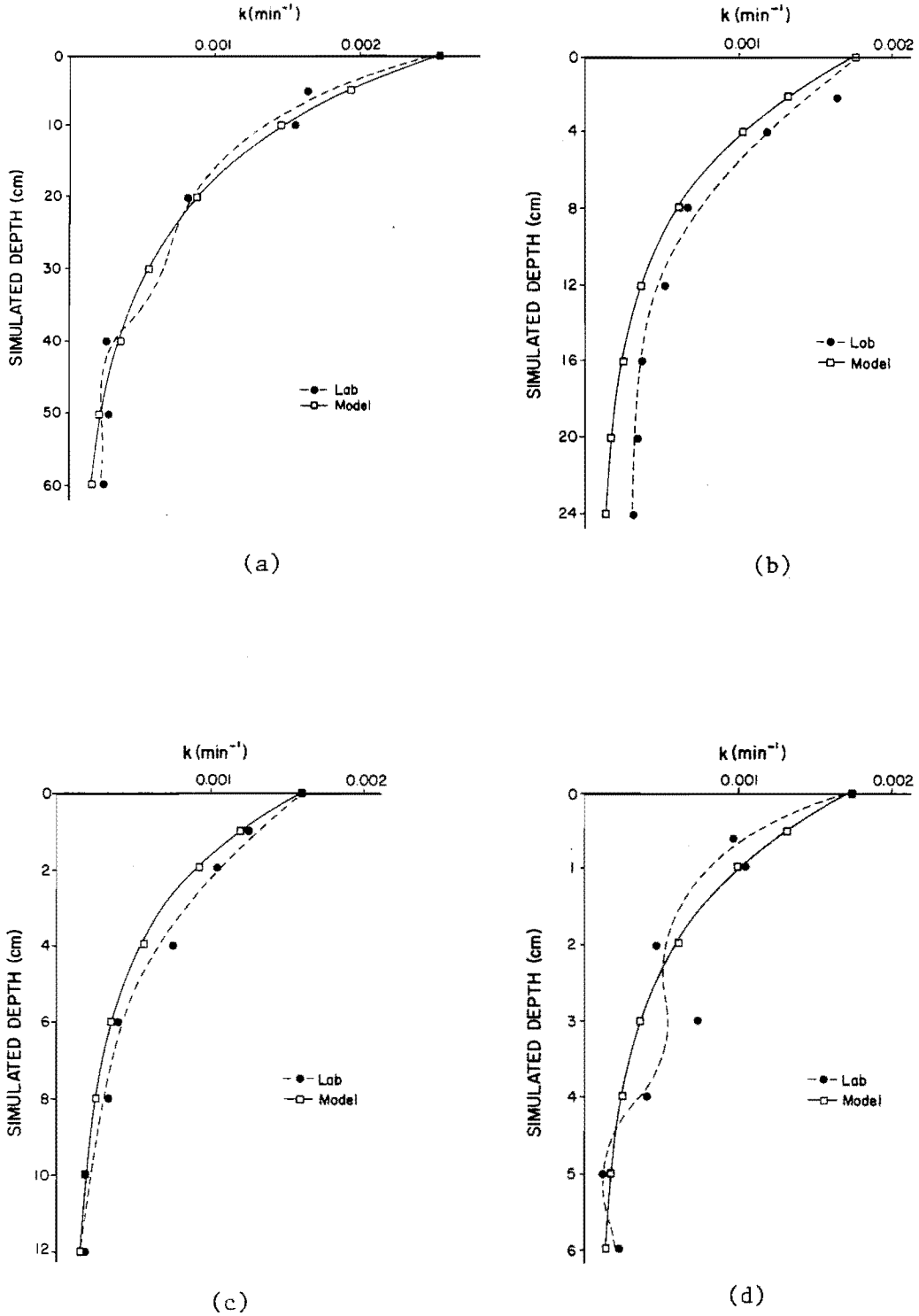


Figure 26. Comparison of mean of three replicates of laboratory data and the simulation generated by the depth model, Equation 16, for the first-order rate constants of riboflavin bleaching in the photooxidation of 30 mg/l bromacil as a function of simulated depth for 1.0 mg/l riboflavin (a); 2.5 mg/l riboflavin (b); 5.0 mg/l riboflavin (c); and 10.0 mg/l riboflavin (d).

methylene blue bleaching, all three replicates were necessary to determine one meaningful rate constant at each depth, due to the reversible methylene blue bleaching shown in Figure 10. In this case only one replicate model curve could be generated, since only one replicate laboratory curve was available. Resultingly, one replicate was available for statistical analysis of methylene blue bleaching rate as a function of simulated depth.

Randomized block design analysis of variance was used to determine if model simulations were not significantly different ($\alpha \leq 0.05$) from laboratory data. A 2 x 8 factorial design was analyzed blocked with replicates. The factorial design had two treatments (Equation 16 versus laboratory data) and eight simulated depths. Results of the statistical analyses are presented in the analysis of variance tables (Tables 2, 3, 4, and 5). Model simulations were not significantly different from laboratory data at the 95 percent confidence level for sensitized photooxidation of bromacil and terbacil, and for methylene blue and riboflavin bleaching. The depth model, Equation 16, was an accurate means of predicting sensitized photooxidation rate as a function of depth, and can be used for sensitized photooxidation lagoon design.

Equation 16 can be used to predict sensitized photooxidation rate as a function of lagoon depth for any quantity and quality of light that is expected to fall on the lagoon. Equation 16 can also be used to design for a waste of any spectral quality. Design for an uncharacterized waste involves determination of ε_λ for the waste. Determination of ε_λ involves relating the optical density of the waste to the optical density of a known concentration of compound at a wavelength for which the extinction coefficient is known. For example, if a 5 mg/l (6.77×10^{-5} M) solution of methylene blue reads 0.89 absorbance units at 660 nm, sufficient information is present to calculate the extinction coefficient of an unknown sample at any wavelength. The extinction coefficient of methylene blue at 660 nm is 84000 $M^{-1}cm^{-1}$. The extinction coefficient of a waste sample at any wavelength therefore may be calculated by a simple ratio:

$$\frac{\varepsilon_{MB,\ 660\ nm}}{O.D._{MB,\ 660\ nm}} = \frac{\varepsilon_{sample,\ \lambda}}{O.D._{sample,\ \lambda}} \quad . \ . \ . \ .(17)$$

where

O.D. = optical density

As a practical example, to calculate ε_λ of an industrial wastewater sample at 510 nm when the optical density is 0.10 for the waste and 0.89 for methylene blue at 660 nm, the following calculation is made:

$$\frac{84{,}000}{0.89} = \frac{\varepsilon_{sample,\ 510\ nm}}{0.10} \quad . \ . \ .(18)$$

$$\varepsilon_{sample,\ 510\ nm} = 9{,}440\ M^{-1}\ cm^{-1} \quad . \ . \ . \ .(19)$$

Using calculations such as Equation 18 to determine ε_λ at 5 nm intervals, the spectral quality of the waste entering the lagoon may be obtained. The extinction coefficients, ε_λ, may then be used in the Beer-Lambert Law calculations, Equation 8, to determine light intensity at depth z in 5 nm intervals ($I_{z,\lambda}$). Extinction coefficients of the waste are used only in Equation 8, the Beer-Lambert Law, but not in the depth model, Equation 16. The extinction coefficient of the sensitizer is used in the depth model, since ε_λ of the sensitizer is a measure of the light energy absorbed by the sensitizer for subsequent photooxidation reactions.

Table 2. Analysis of variance tables relating two treatments, laboratory data and the model simulation data, for sensitized photooxidation rate of bromacil as a function of simulated lagoon depth.

Bromacil degradation sensitized by 0.1 mg/l methylene blue

Source	df	SS	MS	F
Replicates	2	1.99×10^{-6}	9.93×10^{-7}	
Treatments	1	5.26×10^{-7}	5.26×10^{-7}	
Error Replicates	2	1.71×10^{-7}	8.56×10^{-8}	6.14*
Depth	7	1.38×10^{-5}	1.97×10^{-6}	
Depth x Treatments	7	3.97×10^{-7}	5.67×10^{-8}	0.704*
Error Treatments	28	2.25×10^{-6}	8.05×10^{-8}	
Total	47	1.19×10^{-5}	4.07×10^{-7}	

Bromacil degradation sensitized by 0.5 mg/l methylene blue

Source	df	SS	MS	F
Replicates	2	1.38×10^{-7}	6.95×10^{-8}	
Treatments	1	2.02×10^{-8}	2.02×10^{-8}	0.0241*
Error Replicates	2	1.67×10^{-6}	8.37×10^{-7}	
Depth	7	1.49×10^{-5}	2.14×10^{-6}	
Depth x Treatments	7	7.54×10^{-7}	1.08×10^{-7}	0.597*
Error Treatments	28	5.09×10^{-6}	1.81×10^{-7}	
Total	47	2.26×10^{-5}	4.81×10^{-7}	

Bromacil degradation sensitized by 1.0 mg/l methylene blue

Source	df	SS	MS	F
Replicates	2	8.68×10^{-6}	4.34×10^{-6}	
Treatments	1	1.23×10^{-6}	1.23×10^{-6}	1.48*
Error Replicates	2	1.67×10^{-6}	8.33×10^{-7}	
Depth	7	1.61×10^{-4}	2.29×10^{-5}	
Depth x Treatments	7	3.85×10^{-6}	5.49×10^{-7}	2.39*
Error Treatments	28	6.45×10^{-6}	2.30×10^{-7}	
Total	47	1.82×10^{-4}	3.88×10^{-6}	

Bromacil degradation sensitized by 2.0 mg/l methylene blue

Source	df	SS	MS	F
Replicates	2	8.13×10^{-6}	4.06×10^{-6}	
Treatments	1	9.80×10^{-7}	9.80×10^{-7}	2.59*
Error Replicates	2	7.59×10^{-7}	3.79×10^{-7}	
Depth	7	9.64×10^{-5}	1.38×10^{-5}	
Depth x Treatments	7	2.01×10^{-5}	2.87×10^{-6}	1.41*
Error Treatments	28	5.72×10^{-5}	2.04×10^{-6}	
Total	47	1.84×10^{-4}	3.91×10^{-6}	

*Not significant at $\alpha \leq 0.05$.
Note: df = Degrees of Freedom, SS = Sum of Squares, MS = Mean Squares

Table 3. Analysis of variance tables relating two treatments, laboratory data and the model simulation data, for rate of bleaching of methylene blue as a function of simulated lagoon depth.

Bleaching of 0.5 mg/l methylene blue

Source	df	SS	MS	F
Treatments	1	9.63×10^{-8}	9.63×10^{-8}	0.908*
Depth	7	1.21×10^{-6}	1.72×10^{-7}	
Depth x Treatments	7	7.44×10^{-7}	1.06×10^{-7}	
Total	15	2.05×10^{-6}	1.36×10^{-7}	

Bleaching of 1.0 mg/l methylene blue

Source	df	SS	MS	F
Treatments	1	2.31×10^{-6}	2.31×10^{-6}	6.11*
Depth	7	6.09×10^{-6}	8.70×10^{-7}	
Depth x Treatments	7	2.65×10^{-6}	3.78×10^{-7}	
Total	15	1.10×10^{-5}	7.36×10^{-7}	

Bleaching of 2.0 mg/l methylene blue

Source	df	SS	MS	F
Treatments	1	1.69×10^{-6}	1.69×10^{-6}	1.54*
Depth	7	1.57×10^{-5}	2.24×10^{-6}	
Depth x Treatments	7	7.68×10^{-6}	1.10×10^{-6}	
Total	15	2.51×10^{-5}	1.67×10^{-6}	

*Not significant at $\alpha \leq 0.05$.
Note: df = Degrees of Freedom, SS = Sum of Squares, MS = Mean Squares

One weakness of the Beer-Lambert Law for calculating light intensity at depth z is the inaccuracy of the equation under some circumstances (Sawyer and McCarty 1978). Under high solute concentration, the law is not an accurate measure of light extinction. This inaccuracy, however, can be compensated by the use of engineering safety factors.

In summary, the design quantity and quality of light impinging on the lagoon to be built would be supplied by spectroradiometer data. The lagoon design would use a sample of waste that would enter the lagoon. A waste sample with sensitizer addition would be placed in a spectrophotometer and compared with known solutions to estimate ε_λ of the waste. These ε_λ values could then be used in Beer-Lambert Law calculations to determine $I_{z,\lambda}$, which is used in the depth model to predict k as a function of depth.

Effect of Quantity of Radiation on Sensitized Photooxidation Rate

The laboratory data for photooxidation rate as a function of simulated

Table 4. Analysis of variance tables relating two treatments, laboratory data and the model simulation data, for sensitized photooxidation rate of terbacil as a function of simulated lagoon depth.

Terbacil degradation sensitized by 1.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	4.80×10^{-7}	2.40×10^{-7}	
Treatments	1	1.17×10^{-9}	1.17×10^{-9}	0.0515*
Error Replicates	2	4.54×10^{-8}	2.27×10^{-8}	
Depth	7	3.55×10^{-5}	5.07×10^{-6}	
Depth x Treatments	7	1.32×10^{-7}	1.88×10^{-8}	0.625*
Error Treatments	28	8.43×10^{-7}	3.01×10^{-8}	
Total	47	3.70×10^{-5}	7.87×10^{-7}	

Terbacil degradation sensitized by 2.5 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	8.44×10^{-6}	4.22×10^{-6}	
Treatments	1	2.43×10^{-7}	2.42×10^{-7}	4.06*
Error Replicates	2	1.20×10^{-7}	5.98×10^{-8}	
Depth	7	1.45×10^{-4}	2.07×10^{-5}	
Depth x Treatments	7	2.42×10^{-7}	3.45×10^{-8}	0.138*
Error Treatments	28	6.97×10^{-6}	2.49×10^{-7}	
Total	47	1.61×10^{-4}	3.42×10^{-6}	

Terbacil degradation sensitized by 5.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	3.48×10^{-5}	1.74×10^{-5}	
Treatments	1	1.95×10^{-7}	1.95×10^{-7}	0.859*
Error Replicates	2	4.55×10^{-7}	2.27×10^{-7}	
Depth	7	3.20×10^{-4}	4.57×10^{-5}	
Depth x Treatments	7	1.41×10^{-6}	2.02×10^{-7}	0.227*
Error Treatments	28	2.49×10^{-5}	8.90×10^{-7}	
Total	47	3.82×10^{-4}	8.12×10^{-6}	

Terbacil degradation sensitized by 10.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	9.54×10^{-6}	4.77×10^{-6}	
Treatments	1	1.25×10^{-6}	1.25×10^{-6}	3.04*
Error Replicates	2	8.23×10^{-7}	4.11×10^{-7}	
Depth	7	8.24×10^{-4}	1.18×10^{-4}	
Depth x Treatments	7	1.75×10^{-5}	2.50×10^{-6}	1.19*
Error Treatments	28	5.89×10^{-5}	2.10×10^{-6}	
Total	47	9.12×10^{-5}	1.94×10^{-5}	

Not significant at $\alpha \leq 0.05$.
Note: df = Degrees of Freedom, SS = Sum of Squares, MS = Mean Squares

Table 5. Analysis of variance tables relating two treatments, laboratory data and the model simulation data, for rate of bleaching of riboflavin as a function of simulated lagoon depth.

Bleaching of 1.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	1.81×10^{-5}	9.07×10^{-6}	
Treatments	1	8.29×10^{-10}	8.29×10^{-10}	0.00220*
Error Replicates	2	7.54×10^{-7}	3.77×10^{-7}	
Depth	7	2.98×10^{-5}	4.26×10^{-6}	
Depth x Treatments	7	2.73×10^{-7}	3.90×10^{-8}	0.0574*
Error Treatments	28	1.90×10^{-5}	6.80×10^{-7}	
Total	47	6.80×10^{-5}	1.45×10^{-6}	

Bleaching of 2.5 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	1.31×10^{-7}	6.53×10^{-8}	
Treatments	1	1.08×10^{-7}	1.08×10^{-7}	0.246*
Error Replicates	2	8.75×10^{-7}	4.38×10^{-7}	
Depth	7	1.81×10^{-5}	2.59×10^{-6}	
Depth x Treatments	7	9.45×10^{-7}	1.35×10^{-7}	1.34*
Error Treatments	28	2.83×10^{-6}	1.01×10^{-7}	
Total	47	2.30×10^{-5}	4.89×10^{-7}	

Bleaching of 5.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	2.04×10^{-6}	1.02×10^{-6}	
Treatments	1	5.86×10^{-8}	5.86×10^{-8}	13.2*
Error Replicates	2	8.86×10^{-9}	4.43×10^{-9}	
Depth	7	1.22×10^{-5}	1.74×10^{-6}	
Depth x Treatments	7	6.05×10^{-8}	8.64×10^{-9}	0.152*
Error Treatments	28	1.59×10^{-6}	5.67×10^{-8}	
Total	47	1.59×10^{-5}	3.39×10^{-7}	

Bleaching of 10.0 mg/l riboflavin

Source	df	SS	MS	F
Replicates	2	4.63×10^{-7}	2.31×10^{-7}	
Treatments	1	2.85×10^{-9}	2.85×10^{-9}	0.0345*
Error Replicates	2	1.65×10^{-7}	8.27×10^{-8}	
Depth	7	1.26×10^{-5}	1.80×10^{-6}	
Depth x Treatments	7	4.52×10^{-7}	6.45×10^{-8}	
Error Treatments	28	1.38×10^{-6}	4.93×10^{-8}	1.31*
Total	47	1.51×10^{-5}	3.21×10^{-7}	

*Not significant at $\alpha \leq 0.05$
Note: df = Degrees of Freedom, SS = Sum of Squares, MS = Mean Squares

depth were collected at relatively low radiation--28 W/m^2--compared to up to 3000 W/m^2 of a bright summer day. Rate constants for design light intensities other than the intensity for which bench scale tests are performed must be determined if the depth model, Equation 16, is to be initialized at other design intensities. Figure 27 and Figure 28 represent first-order photooxidation rate constants as a function of light quantity for methylene blue-sensitized photooxidation of bromacil and methylene blue bleaching, and riboflavin-sensitized photooxidation of terbacil and riboflavin bleaching, respectively. Sensitized photooxidation as a function of light quantity was linear. The linear equations and R^2 associated with the rate constants as a function of quantity of radiation in Figures 27 and 28 are presented in Table 6. The linear relationship between sensitized photooxidation rate and quantity of radiation is compatible with the First Law of Photochemistry, which states that light must be absorbed before a photochemical reaction can occur (Calvert and Pitts 1966). Sargent and Sanks (1976) found an exponential increase in methylene blue-sensitized photooxidation rate of cresol as a function of increasing light intensity.

Nonetheless, the present study showed a linear relationship between total light intensity and first-order sensitized photooxidation rate. This linear relationship is valid, however, only if the quality of the light is constant as a function of intensity. The linear scale-up factor allows simple initializing of the depth model. For example, if bench scale, zero-depth reactions are conducted at 500 W/m^2 total radiation but the design engineer wishes to generate a rate versus depth curve for a total radiation of 1500 W/m^2, the rate constant at 500 W/m^2 would be multiplied by 3 for the zero-depth k to initialize the model. Due to the simplicity of a linear relationship between photooxidation rate and light quantity, the depth model may be used for any light intensity once the bench scale k is determined under known quality and quantity of light.

Effect of Mean Velocity Gradient on Sensitized Photooxidation Rate

The depth model, Equation 16, was developed for a lagoon in which horizontal control volumes do not interact with one another. Mixing experiments were developed to determine if a higher mean photooxidation rate could be achieved with additional energy input of turbulence and aeration compared to a static lagoon system.

The rate of mixing in the 38 ℓ (10 gal) reactors was quantified by calculating the mean velocity gradient for each reactor. The mean velocity gradient, $\bar{G}$, is defined as

$$\bar{G} = \sqrt{\frac{P/V}{u}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where

$\bar{G}$ = mean velocity gradient (sec^{-1})
P = power input to reaction ($N \cdot m/sec$)
V = volume of reactor (m^3)
u = dynamic viscosity of fluid ($N \cdot sec/m^2$)

The $\bar{G}$ value describes the amount of mixing that is provided by hydraulic or mechanical means (Weber 1972, Metcalf and Eddy 1979).

The first step in calculating $\bar{G}$ is the determination of power supplied to the reactors by aeration:

$$P = P_1 S \ln (P_2/P_1) \quad . \quad . \quad . \quad . \quad (21)$$

where

P = power input
P_1 = atmospheric pressure
P_2 = pressure at depth gas release

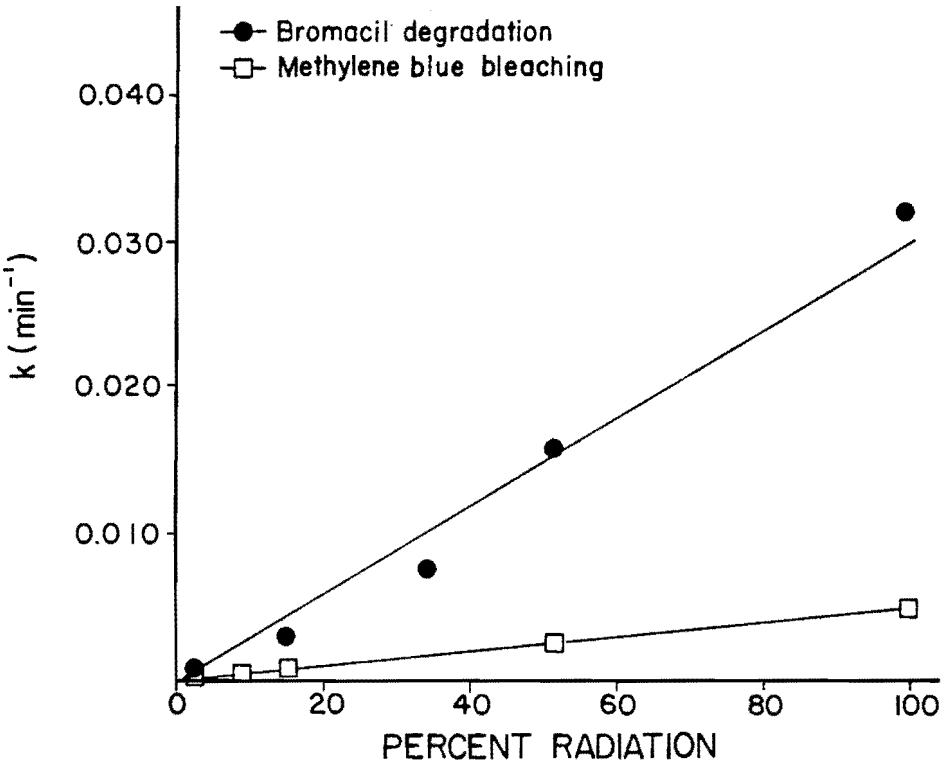


Figure 27. First-order rate constants for sensitized photooxidation of bromacil and methylene blue bleaching as a function of quantity of radiation.

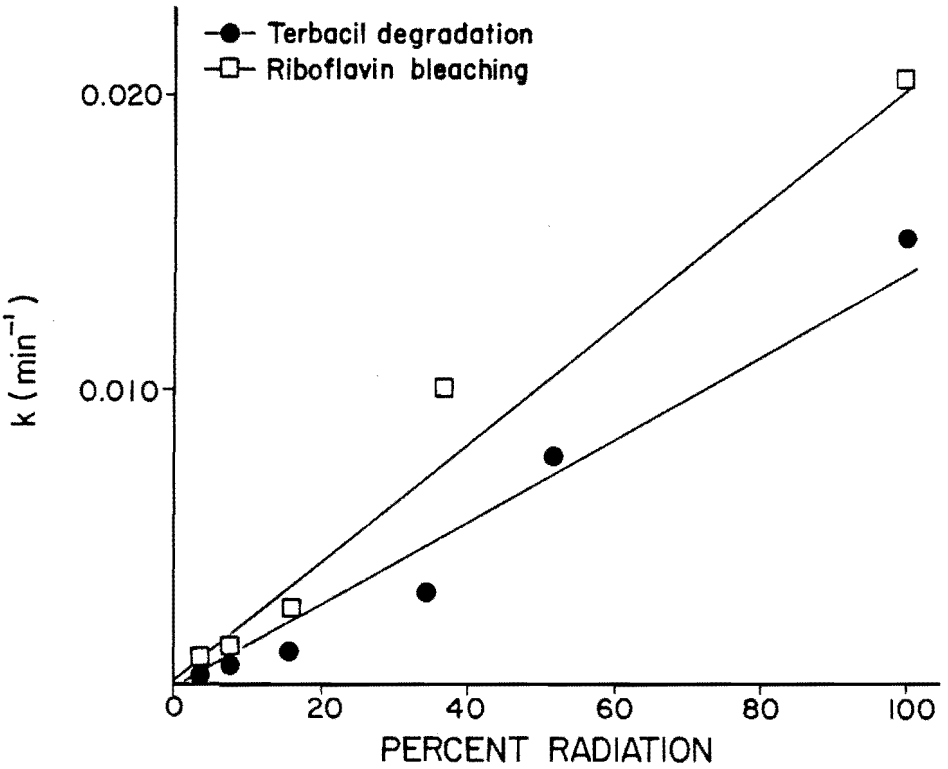


Figure 28. First-order rate constants for sensitized photooxidation of terbacil and riboflavin bleaching as a function of quantity of radiation.

Table 6. Linear equations and correlation for rate constants as a function of percent of solar radiation for photooxidation of bromacil and terbacil, and bleaching of riboflavin and methylene blue.

k as Function of Percent of Radiation (min^{-1})	Linear Equation	Coefficient of Determination R^2
$k_{Bromacil\ degradation}$	$y = 0.000323x - 0.00115$	0.985
$k_{Terbacil\ degradation}$	$y = 0.000152x - 0.000870$	0.971
$k_{Methylene\ blue\ bleaching}$	$y = 0.0000239x + 9.63 \times 10^{-5}$	0.983
$k_{Riboflavin\ bleaching}$	$y = 0.00210x + 5.43 \times 10^{-5}$	0.980

S = aeration flow rate

Mean velocity gradient, $\bar{G}$, was then calculated based on the power input, the volume of the reactor, and the dynamic viscosity of water at 25°C.

Mean velocity gradient, $\bar{G}$, for three hydraulic regimes are presented in Table 7. Reactor 1 was supplied with aeration only to maintain saturated dissolved oxygen. There was minimal mixing as noted by the small $\bar{G}$ of 29.1 sec^{-1}. Reactor 2 was characterized by moderate mixing with a $\bar{G}$ of 244 sec^{-1}. The approximate time for the water to turn over in Reactor 2, as measured by the timing of a slug of dye, was 17 sec. Reactor 3 was characterized by turbulent mixing and $\bar{G}$ of 668 sec^{-1}. Seven sec was required for a complete turnover of water in Reactor 3.

Mean first-order sensitized photooxidation rate constants, k_{mean}, were determined experimentally by stirring the 38 ℓ reactor prior to collecting samples for determination of substrate and sensitizer concentration. Mean first-order rate constants, k_{mean}, as a function of $\bar{G}$ are shown in Figure 29 for 0.75 mg/l and 2 mg/l methylene blue-sensitized photooxidation of bromacil. Figure 30 shows k_{mean} as a function of $\bar{G}$ for 2.5 mg/l and 10 mg/l riboflavin-sensitized photooxidation of terbacil. Mean first-order rate constants for bleaching of 0.75 mg/l and 2.0 mg/l methylene blue as a function of $\bar{G}$ are presented in Figure 31. Mean first order rate constants for bleaching of 2.5 mg/l and 10.0 mg/l riboflavin as a function of $\bar{G}$ are presented in Figure 32. The values of k_{mean} generated for the three mean velocity gradients with each sensitizer concentration were evaluated for equivalence of population means using split plot randomized block design analysis of variance. The statistical factorial design was two levels (two sensitizer concentrations) x three mean velocity gradients x two replicates. The results of the statistical analysis are presented in Table 8. The k_{mean} values of the three mixing regimes were not significantly different at the 95 percent confidence level with methylene blue and riboflavin used as sensitizers. Therefore, the increased energy of high aeration and mean velocity gradient does not appear to increase sensitized photooxidation rate or sensitizer bleaching rate.

The failure of a larger velocity gradient to increase the sensitized

Table 7. Aeration characteristics and mean velocity gradients used to describe liquid mixing in 38 ℓ photooxidation reactors.

Reactor	Aerators	Total Aeration (ℓ min^{-1})	G (sec^{-1})
1	3 fritted glass air diffusers mounted longitudinally	0.03	29.1
2	3 fritted glass air diffusers mounted longitudinally	3.00	244
3	3 fritted glass air diffusers mounted longitudinally	15.00	668

photooxidation rate is reasonable for the photochemical mechanisms taking place. The rate of sensitizer triplet formation is rapid. The average lifetime of the methylene blue triplet is 4.2×10^{-5} sec (Matsumoto 1962). The average lifetime of the riboflavin triplet is approximately 10^{-4} sec (Fife 1978). Singlet oxygen has an average lifetime in water of 2 μsec (Kearns 1971). Based on the short lifetimes of these species, the sensitized photochemical reactions are likely to take place close to the point of excitation. For a methylene blue molecule excited at the surface of a lagoon in which there is minimal water movement, the triplet methylene blue molecule will transfer its energy to singlet oxygen and the singlet oxygen will attack the organic substrate all at the surface. For a lagoon that is rapidly mixed with high $\bar{G}$, a methylene blue molecule excited to the triplet state at the surface will release its energy and result in oxidation of the substrate in essentially the same location as the system with no water movement. This is due to the difference in the relative speeds of two processes. The photochemical reactions take place in a matter of microseconds. The significant transport of water in a lagoon requires seconds to tens of seconds. In the reactor with the highest $\bar{G}$ of 668 sec^{-1}, the photochemical reactions are completed in approximately 40 μsec. The perimeter of the reactor is 88 cm, and the approximate time for the turnover of water is 7 sec. The distance an excited methylene blue molecule can travel is therefore 88 cm/7 sec · 4.0×10^{-5} sec = 5.0×10^{-4} cm, a negligible distance. If the photochemical reactions took place over a period of seconds rather than microseconds, mixing could increase k_{mean} of a lagoon, since the energy captured by a sensitizing molecule at the surface of the lagoon could be carried to an area that receives no light.

Since the reactors utilizing high aeration showed no increase in reaction rate, the mechanical energy of turbulence and mixing appear not to increase sensitized photooxidation rates. Since light energy is the primary driving force in sensitized photooxidation reactions, there does not appear to be a mechanism by which turbulence enhanced the rate of methylene blue-sensitized photooxidation of bromacil or riboflavin-sensitized photooxidation of terbacil.

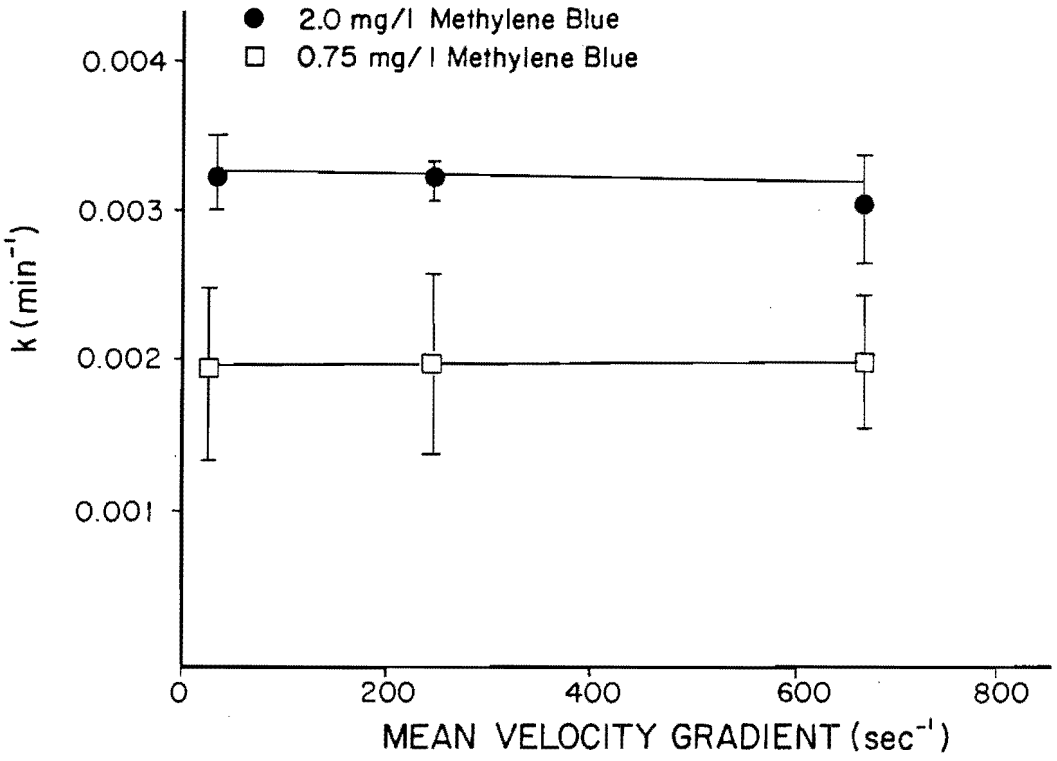


Figure 29. Effect of mean velocity gradient on methylene blue-sensitized photooxidation of 20 mg/l bromacil solutions in 38 ℓ reactors.

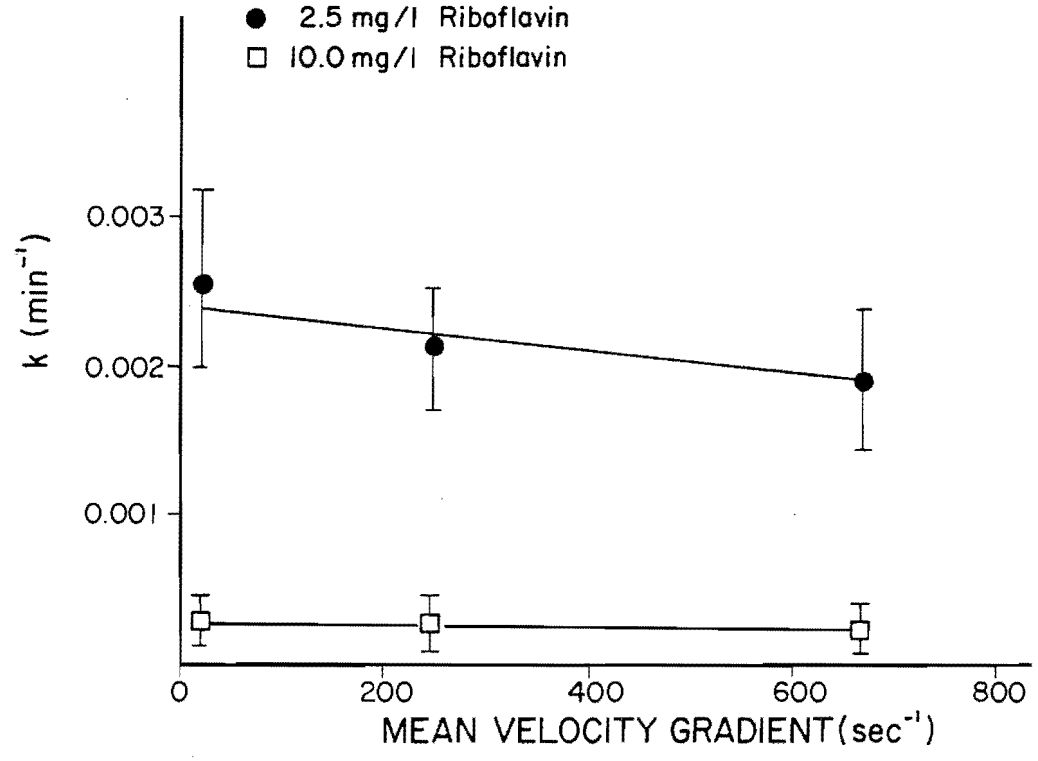


Figure 30. Effect of mean velocity gradient on riboflavin-sensitized photooxidation of 20 mg/l terbacil solutions in 38 ℓ reactors.

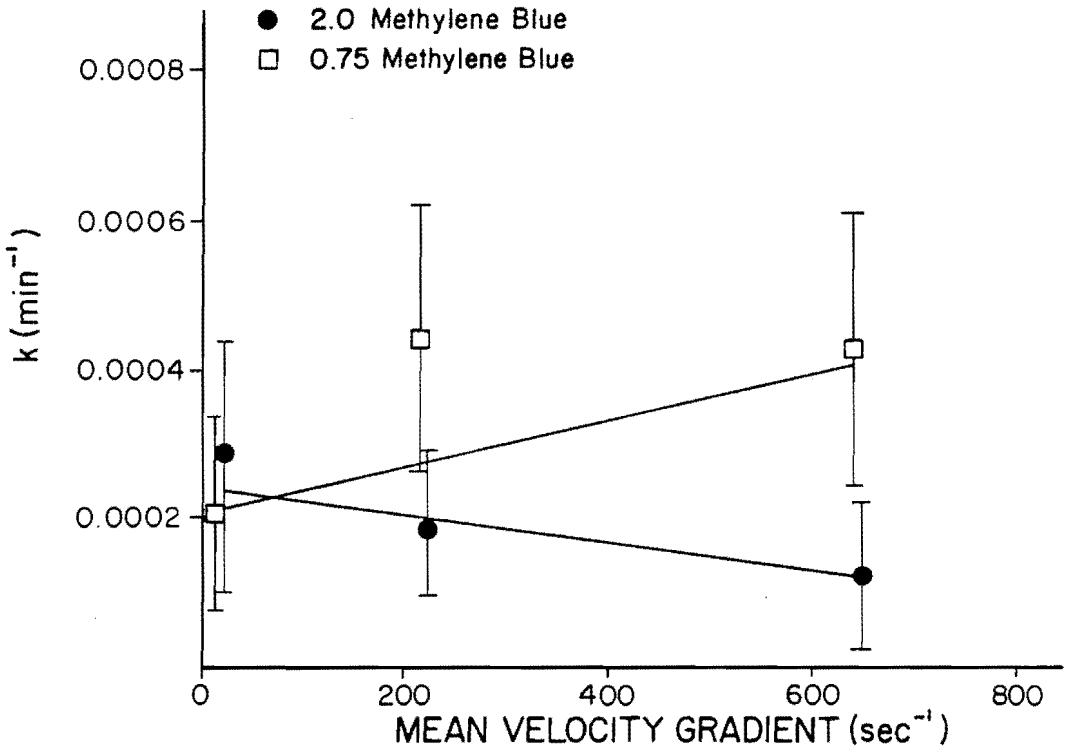


Figure 31. Effect of mean velocity gradient on methylene blue bleaching in the photooxidation of 20 mg/l bromacil solutions in 38 ℓ reactors.

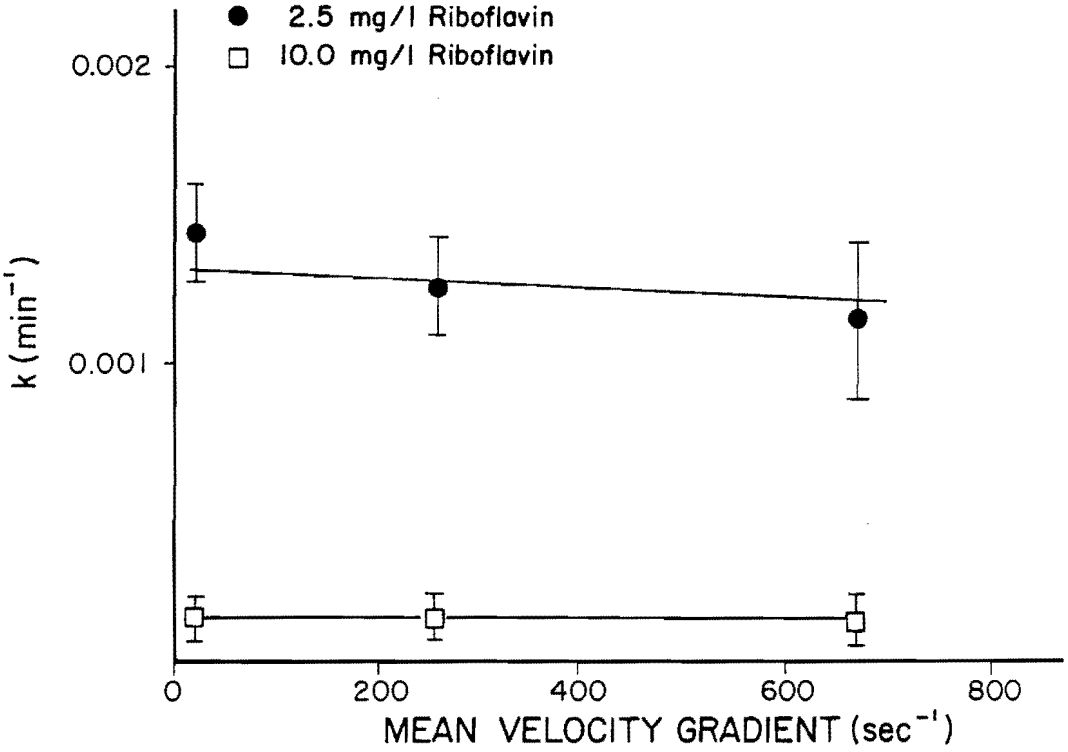


Figure 32. Effect of mean velocity gradient on riboflavin bleaching in the photooxidation of 20 mg/l terbacil solutions in 38 ℓ reactors.

Table 8. Analysis of variance tables relating three treatments (three mixing regimes measured by mean velocity gradient in 38 ℓ reactors for bromacil degradation, methylene blue bleaching, terbacil degradation, and riboflavin bleaching.

Bromacil Degradation

Source	df	SS	MS	F
Replicates	1	2.85×10^{-7}	2.85×10^{-7}	
Treatments	2	3.66×10^{-8}	1.83×10^{-8}	0.541*
Error Level	2	6.76×10^{-8}	3.38×10^{-8}	
Levels	1	4.07×10^{-6}	4.07×10^{-6}	
Treatment x Levels	2	3.19×10^{-8}	1.59×10^{-8}	0.0514*
Error Treatments	3	9.27×10^{-7}	3.09×10^{-7}	
Total	11	5.42×10^{-6}	4.93×10^{-7}	

Methylene Blue Bleaching

Source	df	SS	MS	F
Replicates	1	3.12×10^{-7}	3.12×10^{-7}	
Treatments	2	6.54×10^{-8}	3.27×10^{-8}	1.75*
Error Level	2	3.74×10^{-8}	1.87×10^{-8}	
Levels	1	3.69×10^{-7}	3.69×10^{-7}	
Treatment x Levels	2	1.48×10^{-9}	7.41×10^{-10}	0.0182*
Error Treatments	3	1.22×10^{-7}	4.08×10^{-8}	
Total	11	9.08×10^{-7}	8.25×10^{-8}	

Terbacil Degradation

Source	df	SS	MS	F
Replicates	1	1.17×10^{-6}	1.17×10^{-6}	
Treatments	2	3.01×10^{-7}	1.50×10^{-7}	0.598*
Error Level	2	5.03×10^{-7}	2.51×10^{-7}	
Levels	1	8.04×10^{-6}	8.04×10^{-6}	
Treatment x Levels	2	3.52×10^{-7}	1.76×10^{-7}	0.289*
Error Treatments	3	1.83×10^{-6}	6.09×10^{-7}	
Total	11	1.22×10^{-5}	1.11×10^{-6}	

Riboflavin Bleaching

Source	df	SS	MS	F
Replicates	1	5.98×10^{-8}	5.98×10^{-8}	
Treatments	2	1.11×10^{-7}	5.56×10^{-8}	4.09*
Error Level	2	2.72×10^{-8}	1.36×10^{-8}	
Levels	1	2.88×10^{-6}	2.88×10^{-6}	
Treatment x Levels	2	4.46×10^{-8}	2.23×10^{-8}	0.699*
Error Treatments	3	9.55×10^{-8}	3.19×10^{-8}	
Total	11	3.22×10^{-6}	2.92×10^{-7}	

*Not significant at $\alpha \leq 0.05$.
Note: df = Degrees of Freedom, SS = Sum of Squares, MS = Mean Squares

If mixing and turbulence do not enhance the photooxidation rate, there is no need to design for high aeration; and the depth model (Equation 16) describes the photooxidation rate in a lagoon. One way to check whether or not this is so is to compare the k_{mean} from the mixing experiments with the k_{mean} calculated from the k versus depth curve generated from Equation 16. Using bench scale data under the same physical and chemical conditions as the mixing chambers for the zero-depth conditions to initialize Equation 16, the rate constant versus depth curves for 0.75 mg/l and 2 mg/l methylene blue-sensitized photooxidation of bromacil and 2.5 mg/l and 10 mg/l riboflavin-sensitized photooxidation of terbacil were generated and were presented in Figures 33 and 34, respectively. By selecting horizontal control volumes of 2 cm width, the k_{mean} may be calculated by using an average weighted by the width of the control volume:

$$k_{mean} = k_1 \cdot 2\text{ cm} + k_3 \cdot 2\text{ cm} + k_5 \cdot 2\text{ cm} + k_7 \cdot 2\text{ cm} + k_9 \cdot 2\text{ cm} + k_{11} \cdot 2\text{ cm} + k_{13} \cdot 2\text{ cm} + k_{15} \cdot 2\text{ cm} + k_{17} \cdot 2\text{ cm} + k_{19} \cdot 2\text{ cm} + k_{21} \cdot 2\text{ cm} + k_{23} \cdot 2\text{ cm} + k_{25} \cdot 2\text{ cm}/26\text{ cm} \quad . \quad .(22)$$

The following example illustrates the use of Equation 22 using data generated by Equation 16 for 0.75 mg/l methylene blue in a 38 ℓ reactor 26 cm deep:

$$k_{mean} = 0.006(2) + 0.00353(2) + 0.00263(2) + 0.00205(2) + 0.00166(2) + 0.00138(2) + 0.00119(2) + 0.00104(2) + 0.000934(2) + 0.000846(2) + 0.000776(2) + 0.000718(2) + 0.000669(2)/26 \quad . \quad .(23)$$

$$k_{mean} = 0.00172\ min^{-1} \quad . \quad . \quad .(24)$$

The k_{mean} values generated by Equation 22 and k_{mean} values for laboratory data are shown in Table 9. Regardless of the mixing rate, k_{mean} values generated by Equation 22 agree with laboratory k_{mean} values. This is further evidence that the depth model is sufficient for prediction of the rate of waste decomposition in a sensitized photooxidation lagoon and satisfactory for lagoon design.

An assumption in using Equation 16, however, is that the lagoon does not stratify, i.e., it is polymictic. It is difficult to assess the depth at which a body of water will thermally stratify. Wetzel (1975) stated that the depth required for a pond to stratify thermally varies with the surface area, basin orientation in relation to prevailing wind, depth-volume relations, and protection by surrounding topography and vegetation. Wetzel (1975) emphasized that the generalizations used for predicting lake stratification are often misleading. Therefore, assessment of the stratification problem requires data collected from a pilot photooxidation lagoon.

Dissolved Oxygen Requirements for Sensitized Photooxidation

Relationships of methylene blue-sensitized photooxidation rate constants to residual dissolved oxygen content are presented in Figure 35 for 30 mg/l and 250 mg/l bromacil solutions. Figure 36 shows riboflavin-sensitized photooxidation rate constants for 30 and 250 mg/l terbacil as functions of dissolved oxygen concentration. These figures show that the data collected fit saturation curves. For 30 mg/l bromacil, the reaction rate reached the saturation value of 0.038 min^{-1} at 0.9 mg/l dissolved oxygen. For the 250 mg/l bromacil solutions, the reaction rate achieved the maximum of 0.032 min^{-1} at 2.0 mg/l dissolved oxygen. For the 30 mg/l terbacil solutions, the maximum reaction rate of 0.012 min^{-1} was reached at approximately 4 mg/l terbacil. The

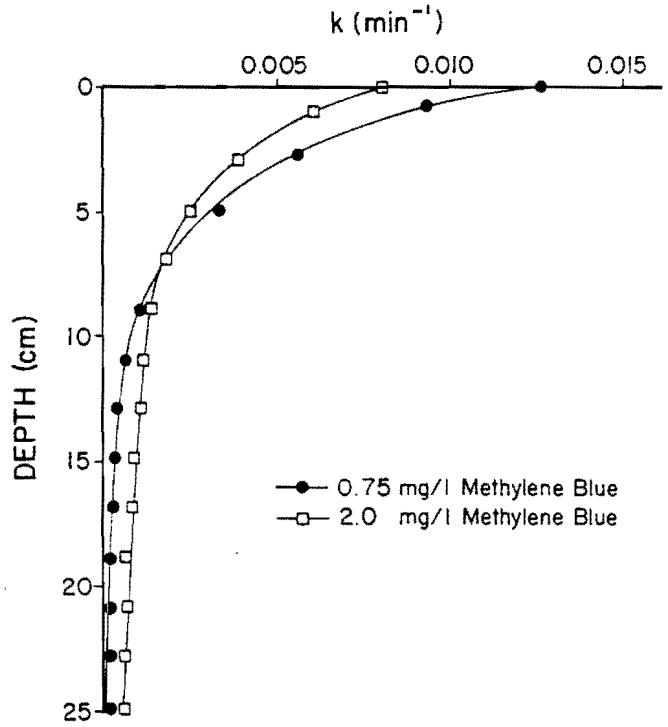


Figure 33. First-order photooxidation rate constants as a function of depth for bromacil degradation in 38 ℓ reaction chambers sensitized by 0.75 mg/l methylene blue and 2.0 mg/l methylene blue.

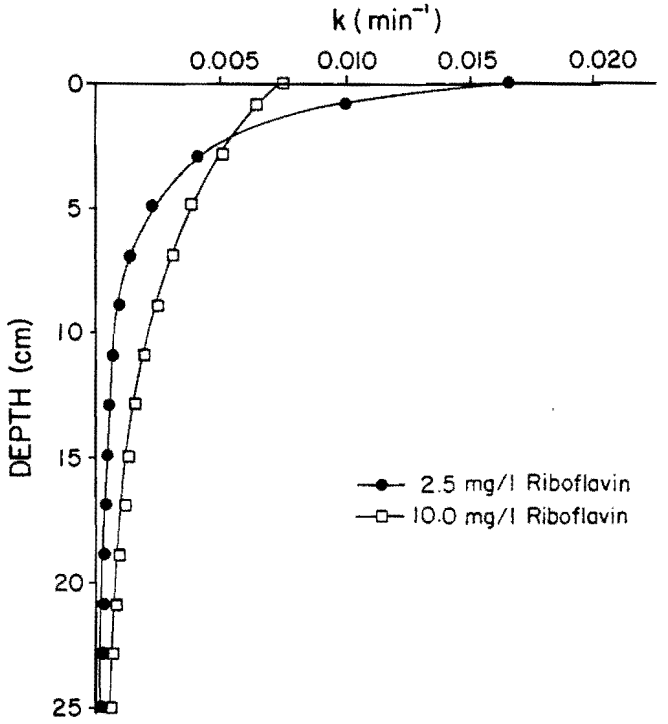
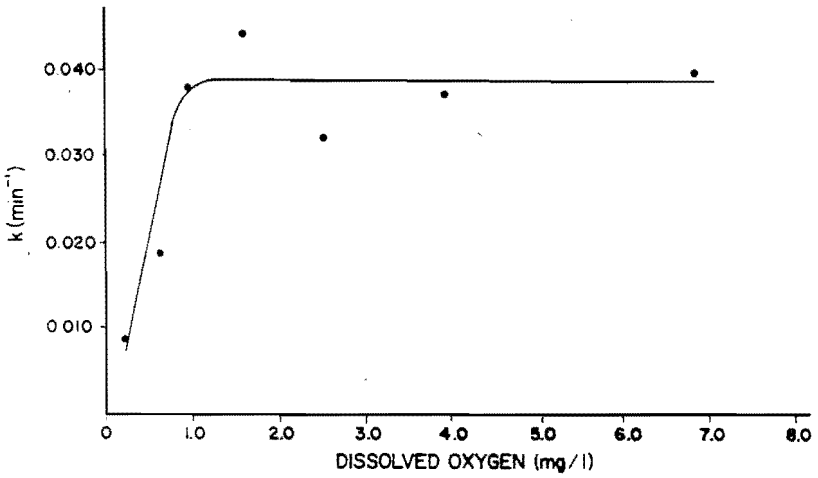


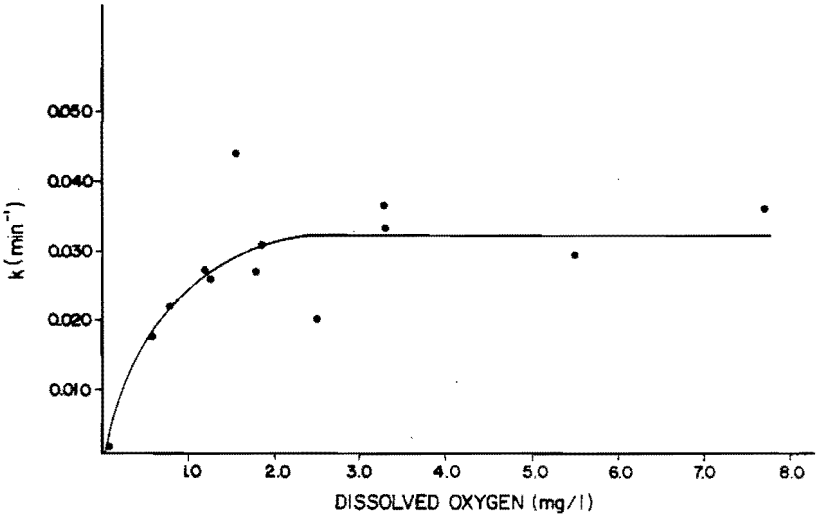
Figure 34. First-order photooxidation rate constants as a function of depth for terbacil degradation in 38 ℓ reactors sensitized by 2.5 mg/l riboflavin and 10.0 mg/l riboflavin.

Table 9. Laboratory data for composite sensitized photooxidation rate constants for experiments conducted in 38 ℓ reactors and corresponding predictive rate constants generated by depth model, Equation 16.

Substrate	Sensitizer and Concentration	k_{mean} Laboratory (min^{-1})	k_{mean} Model (min^{-1})
Bromacil	0.75 mg/l Methylene Blue	0.00213	0.00172
Bromacil	2.0 mg/l Methylene Blue	0.00320	0.00297
Terbacil	2.5 mg/l Riboflavin	0.00197	0.00227
Terbacil	10.0 mg/l Riboflavin	0.000478	0.000446



(a)



(b)

Figure 35. First-order rate constants for methylene blue-sensitized photooxidation of bromacil as a function of dissolved oxygen residual.

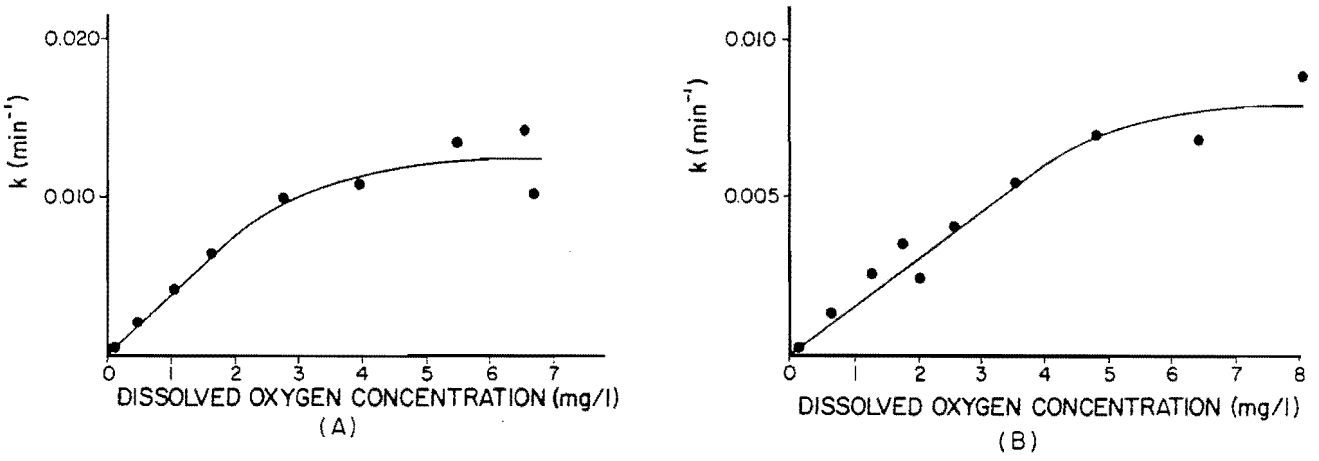


Figure 36. First-order rate constants for riboflavin-sensitized photooxidation of terbacil as a function of dissolved oxygen residual.

250 mg/l terbacil solutions achieved the saturation rate constant of 0.0075 min^{-1} at approximately 5 mg/l dissolved oxygen.

The common shape of these curves may be explained by the photochemical reactions taking place as presented by Spikes and Straight (1967) and Nilsson et al. (1972):

$$1)\quad \text{Sens} + h\nu \xrightarrow{k_1} {}^3\text{Sens} \quad . \quad . \quad .(25)$$

$$2)\quad {}^3\text{Sens} + O_2 \xrightarrow{k_2} \text{Sens} + O_2(^1\Delta) \quad . \quad . \quad .(26)$$

$$3)\quad {}^3\text{Sens} \xrightarrow{k_3} \text{Sens} + \text{heat} \quad . \quad .(27)$$

$$4)\quad {}^3\text{Sens} + \text{Substrate} \xrightarrow{k_4} \text{Sens} + \text{Substrate} + \text{heat} \quad . \quad . \quad .(28)$$

$$5)\quad \text{Substrate} + O_2(^1\Delta) \xrightarrow{k_5} \text{Oxidized Substrate} \quad . \quad . \quad .(29)$$

$$6)\quad O_2(^1\Delta) \xrightarrow{k_6} O_2 + \text{heat} \quad . \quad .(30)$$

The steps in this mechanism may be transformed to rate expressions. The rate of triplet sensitizer formation may be described as:

$$\text{Rate}_{^3\text{Sens}} = I_a \cdot \phi_{isc}$$

$$= \int_{400\ nm}^{700\ nm} I_\lambda \cdot \varepsilon_\lambda \cdot \ell \cdot (\text{Sens}) \cdot \phi_{isc}\, d\lambda \quad . \quad . \quad . \quad . \quad .(31)$$

where ℓ is light path length, (Sens) is sensitizer concentration, and is the quantum yield of intersystem crossing.

$$\frac{d(^3\text{Sens})}{dt} = \text{Rate}_{^3\text{Sens}} - (^3\text{Sens})(k_2(O_2) + k_3 + k_4\,(\text{Substrate})) \quad . \quad . \quad . \quad . \quad .(32)$$

assuming steady state, (ss)

$$(^3\text{Sens})_{ss} = \frac{\text{Rate}_{^3\text{Sens}}}{(k_2(O_2) + k_3 + k_4\,(\text{Substrate}))} \quad . \quad . \quad . \quad . \quad .(33)$$

The rate of change in singlet oxygen concentration may be described by the following rate equation:

$$\frac{d(O_2(^1\Delta))}{dt} = k_2(O_2)(^3\text{Sens}) - k_5(O_2(^1\Delta))(\text{Substrate}) - k_6(O_2(^1\Delta)) \quad . \quad . \quad . \quad . \quad .(34)$$

assuming steady state, (ss)

$$(O_2(^1\Delta))_{ss} = \frac{k_2(O_2)(^3\text{Sens})}{k_5(\text{Substrate}) + k_6} \quad . \quad . \quad . \quad . \quad .(35)$$

The rate of disappearance of substrate may be described as follows:

$$\frac{-d(\text{Substrate})}{dt} = k_5(O_2(^1\Delta))(\text{Substrate}) \quad . \quad . \quad .(36)$$

Substituting Equation 33 for $[O_2(^1\Delta)]$ yields

$$\frac{-d(\text{Substrate})}{dt} = \frac{k_5 k_2 (\text{Substrate})(^3\text{Sens})(O_2)}{k_5(\text{Substrate}) + k_6} \quad . \quad .(37)$$

Defining $\text{Rate}_{^3\text{sens}} = k_1[\text{Sens}]$ yields

$$(^3\text{Sens})_{ss} = \frac{k_1\ (\text{Sens})}{(O_2)\ k_2 + k_3} \quad . \quad .(38)$$

Substituting Equation 38 into Equation 36 yields

$$\frac{-d(\text{Substrate})}{dt} = \frac{k_1\ k_2\ k_5\ (O_2)(\text{Substrate})(\text{Sens})}{(k_2(O_2) + k_3 + k_4(\text{Substrate}))(k_5(\text{Substrate}) + k_6)} \quad . \quad . \quad .(39)$$

Additional insight on the curves shown in Figures 35 and 36 may be obtained by examining the rate constants involved. The value of k_2, the rate of transfer of energy from the triplet sensitizer to ground state molecular oxygen, has been reported at 2×10^9 $M^{-1}sec^{-1}$ for methylene blue (Nilsson et al. 1972) and 2.65×10^9 $M^{-1}sec^{-1}$ for triplet flavin (Knowles and Mautner 1972). The fact that these k_2 values are much larger than the values reported

for k_3 and k_6 of 10^3 to 10^6 sec^{-1} indicates that the transfer of energy from the triplet sensitizer to molecular oxygen proceeds at a fast rate and is the prevalent pathway of energy transfer relative to the quenching reactions described by k_3 and k_6. Figures 35 and 36 show that methylene blue-sensitized photooxidation reached saturation at lower dissolved oxygen concentration than riboflavin-sensitized photooxidation. This may be due to a low value of k_4 for the methylene blue-bromacil system. However, the value of k_4 for the riboflavin-terbacil system may be relatively high ($\sim 10^9$ M^{-1} sec^{-1}). The high k_4 value may cause the riboflavin-sensitized system to reach saturation at high dissolved oxygen concentrations by competing with k_2. In other words, more dissolved oxygen may be required to reach saturation in riboflavin-sensitized photooxidation due to terbacil quenching of the riboflavin triplet state (described by k_4), competing with energy transfer from triplet riboflavin to molecular oxygen (described by k_2).

The data obtained in the dissolved oxygen residual curves may also be explained using Equation 39 with manipulation of rate constants depending upon the physicochemical conditions. The 250 mg/l initial substrate concentrations showed lower photooxidation rates probably due to increased quenching of the triplet sensitizer by the substrate. With high dissolved oxygen concentration, the rate constants in Equation 37 for quenching of the triplet sensitizer (k_3) and singlet oxygen (k_6) become negligible, but k_4, the rate constant for quenching of the triplet sensitizer by the substrate, is still important. Eliminating k_3 and k_6 from Equation 36 yields

$$\frac{-d(Substrate)}{dt} = \frac{k_1(O_2)(Sens)}{k_2(O_2)+k_4(Substrate)} \quad . \quad . \quad . \quad .(40)$$

Equation 38 indicates that photooxidation rate is inversely proportional to the concentration of substrate. This is in agreement with laboratory data; 250 mg/l substrate concentrations were photooxidized more slowly than 30 mg/l substrate concentrations. Sargent and Sanks (1976) found similar results in the methylene blue-sensitized photooxidation of cresol. For a 1 mg/l methylene blue concentration, maximum rate of photooxidation was found at 50 mg/l cresol. The rate decreased with increasing concentration of cresol.

With dissolved oxygen at saturation resulting in low sensitizer triplet quenching, k_4 becomes negligible, leading to the expression

$$\frac{d(Substrate)}{dt} = \frac{k_1(Sens)}{k_2} \quad . \quad . \quad .(41)$$

Therefore, with all parameters constant, the sensitized photooxidation rate is directly proportional to the concentration of sensitizer. The k_1 term is a function of photons absorbed by the sensitizer. As the sensitizer increases in concentration, unless an infinitesimally thin solution is being studied, the attenuation of light by the sensitizer results in less photons absorbed. Increasing sensitizer concentration therefore eventually decreases the rate of photooxidation. Acher and Saltzman (1980) found 2 to 5 mg/l methylene blue to be optimum for photooxidation of bromacil. Sargent and Sanks (1974) concluded that optimum sensitized photooxidation rate for cresol was 5 to 10 mg/l methylene blue. The differences in these studies probably results from differences in light path length or quantity of radiation able to penetrate the solutions in the reaction vessels. A study working with, for instance, 10 ℓ volumes would probably find optimum methylene blue concentration much less than 2 mg/l, since more light would need to be available for absorption throughout the solution.

Methylene blue bleaching rates in the photooxidation of 30 mg/l and 250 mg/l bromacil are presented in Figure 37. Riboflavin bleaching rates in the photooxidation of 30 mg/l and 250 mg/l terbacil are presented in Figure 38.

Figure 37 shows that methylene blue bleaching rates were higher for 30 mg/l bromacil than for 250 mg/l bromacil. Bleaching rates climbed exponentially for dissolved oxygen concentrations less than 0.9 mg/l for 30 mg/l bromacil. A similar increase in bleaching rates was noted below 2 mg/l for 250 mg/l bromacil. These data may be explained in terms of the photochemical mechanisms that are occurring. With high dissolved oxygen, a bleaching saturation phenomenon is present, since the mechanism resulting in methylene blue bleaching is precluded by the high rate constant favoring energy transfer by triplet methylene blue to molecular oxygen. This saturation level bleaching rate is lower for the 250 mg/l initial concentration of bromacil than for the 30 mg/l initial bromacil concentration, due possibly to quenching of the bleaching process by the higher bromacil concentration. At low dissolved oxygen concentrations there is not a significant quantity of oxygen for energy transfer from triplet methylene blue to oxygen, so the sensitizer bleaching process is favored.

The methylene blue bleaching data confirmed the results found in Figure 35 regarding the dissolved oxygen concentration necessary for zero order bromacil degradation rates. With 30 mg/l bromacil, photooxidation rates reached zero order at 1.0 mg/l dissolved oxygen. In the same experiments, the methylene blue bleaching rate reached zero order at 0.9 mg/l dissolved oxygen. A similar close relationship was noted with 250 mg/l bromacil. Bromacil photooxidation rate reached saturation at 2 mg/l dissolved oxygen. Methylene blue bleaching rate also reached saturation with respect to dissolved oxygen at 2 mg/l. The correspondence between the point where rates became zero order with respect to dissolved oxygen for methylene blue bleaching and bromacil oxidation supports the proposition that dissolved oxygen plays a critical role in the transfer of energy from triplet methylene blue to dissolved oxygen. The absence of dissolved oxygen below the points at which the systems become zero order probably resulted in increased bleaching of methylene blue since the photochemical energy could not be transferred to molecular oxygen.

The data in Figure 38 show that riboflavin bleaching was zero order with respect to oxygen throughout the range of dissolved oxygen concentrations for 30 mg/l and 250 mg/l terbacil. The zero order nature of riboflavin bleaching throughout the dissolved oxygen regime may have been due to terbacil quenching, regardless of the level of dissolved oxygen. In other words, quenching of the riboflavin bleaching processes by terbacil may have overshadowed the importance of energy transfer from the triplet riboflavin via Type I or singlet oxygen mechanisms. The rate of bleaching of riboflavin in the 30 mg/l terbacil solutions was higher than in 250 mg/l terbacil solutions. This indicates that the terbacil may have played a significant role in quenching the riboflavin bleaching process.

The engineering application of the data presented in Figures 35, 36, 37, and 38 is that for optimum lagoon design, dissolved oxygen should be maintained in the area of zero-order kinetics with respect to dissolved oxygen. The reasons for this are: (1) the highest possible photooxidation rates as a function of dissolved oxygen may be maintained; (2) for methylene blue the rate of bleaching is lower, requiring fewer sensitizer feeds and less sensitizer to be added in the plug flow regime of the lagoon. From an engineering cost standpoint, it would be most efficient to maintain the dissolved oxygen concentration slightly above the dissolved oxygen concentration where

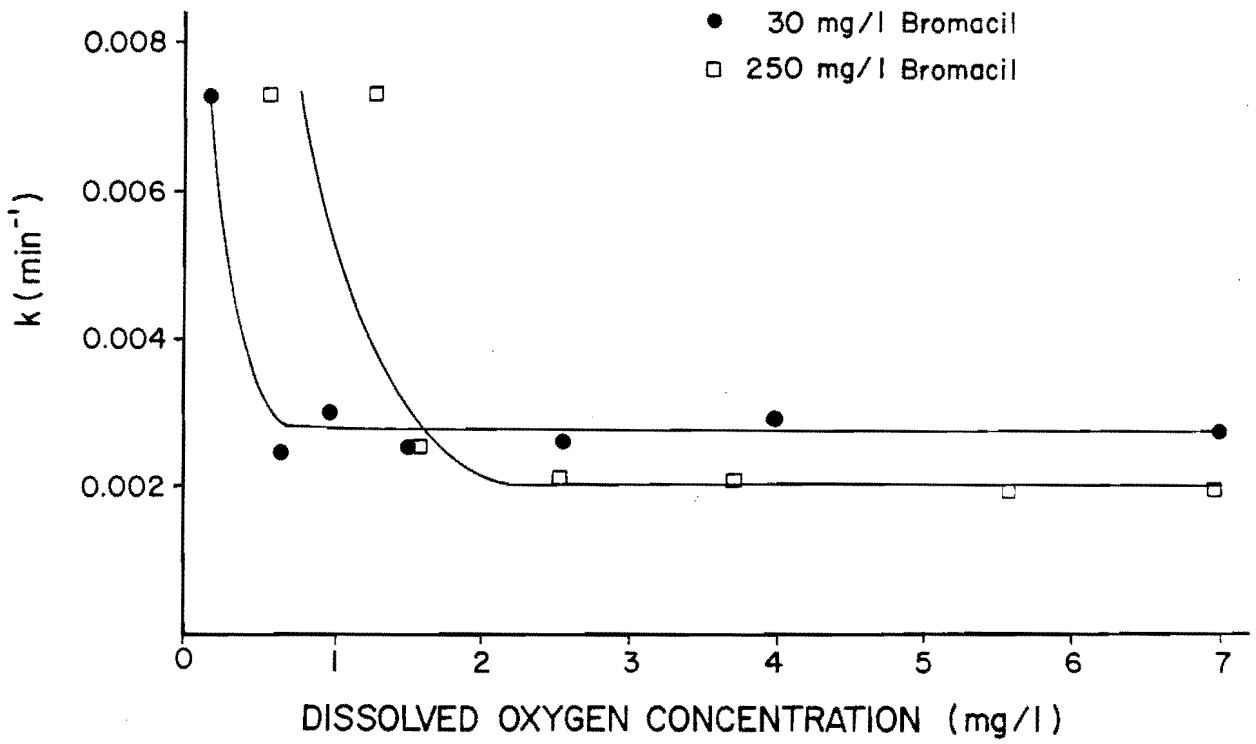


Figure 37. First-order rate constants for the bleaching of 2 mg/l methylene blue used as sensitizer in the photooxidation of bromacil as a function of dissolved oxygen concentration.

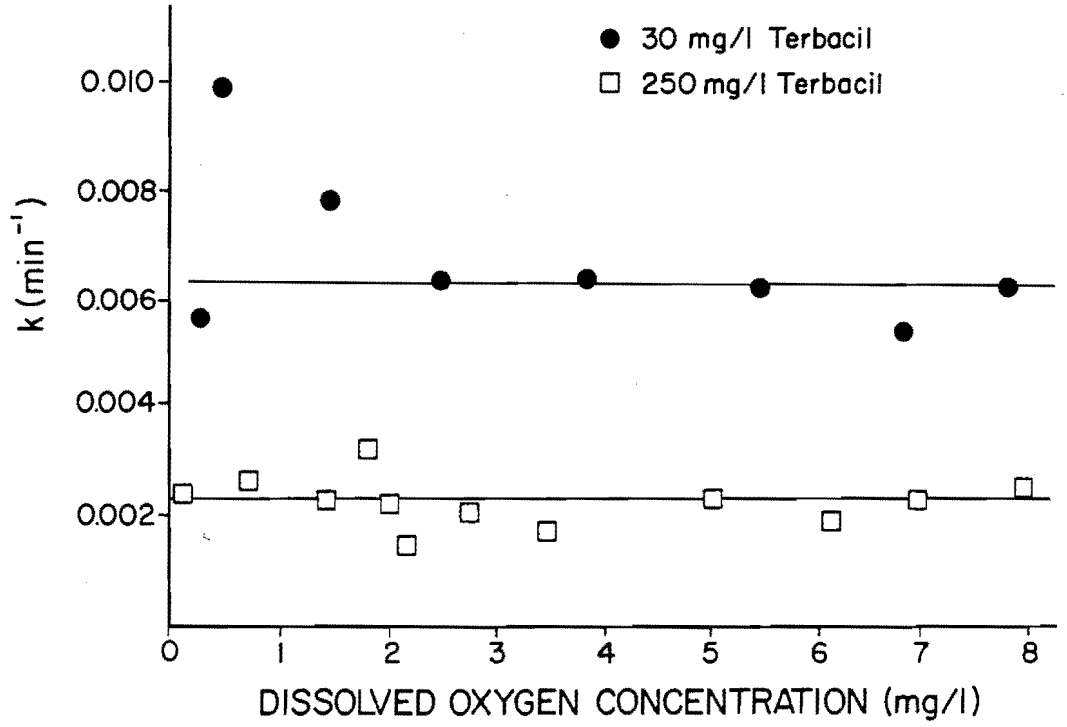


Figure 38. First-order rate constants for the bleaching of 10 mg/l solutions of riboflavin used as sensitizer in the photooxidation of terbacil as a function of dissolved oxygen concentration.

zero order kinetics is established. As an example, if the photooxidation lagoon is to treat 30 mg/l bromacil using 2 mg/l methylene blue, 1 to 2 mg/l dissolved oxygen should be maintained in the lagoon.

Dissolved Oxygen Uptake of Sensitized Photooxidation

The oxygen utilization rate in the photooxidation process was quantified to determine the aeration requirements for a sensitized photooxidation lagoon. The rate of oxygen uptake was shown to follow first-order kinetics by a plot of $\ln [O_2]_t/[O_2]_o$ as a function of time. First-order rate constants for dissolved oxygen uptake as a function of bromacil concentration sensitized by 2 mg/l methylene blue are presented in Figure 39. Oxygen uptake rate constants as a function of terbacil concentration sensitized by 10 mg/l riboflavin are presented in Figure 40. Oxygen uptake rate followed a linear relationship with initial substrate concentration. Therefore, oxygen was consumed in the decomposition of the substrate.

Although it can be quantified as first order for engineering purposes, dissolved oxygen uptake was probably not first order with respect to oxygen. Dissolved oxygen disappearance in these experiments closely followed substrate degradation. Moreover, Figures 39 and 40 showed that the rate of dissolved oxygen uptake is directly proportional to the substrate concentration. The rate of dissolved oxygen uptake was therefore probably proportional to the concentration of substrate present at any time. This may be represented

$$d(O_2) = k_{uptake} \cdot d(\text{Substrate}) \quad .(42)$$

Equation 39 may be integrated in the following manner:

$$\int_{O_{2to}}^{O_{2t}} dO_2 = k_{uptake} \int_{O_{2to}}^{O_{2t}} (\text{Substrate}) \quad . \; . \; .(43)$$

which yields

$$\frac{O_{2_o} - O_{2_t}}{\text{Substrate}_o - \text{Substrate}_t} = k_{uptake} \quad . \; . \; .(44)$$

where k_{uptake} is a dimensionless term related to the quantity of oxygen consumed per quantity of substrate decomposed.

Acher and Dunkelblum (1979) investigated the sensitized photooxidation of bromacil with the scheme shown in Figure 41. Oxygen would be primarily consumed by the formation of the carbonyl oxygen on the acetyl group of the number 2 carbon of 3-sec-butyl-2-acetyl-2-hydroxy-hydantoin. The hydroxide added to the number five hydantoin carbon probably originated from water molecules. The following equation relates oxygen uptake by bromacil to form 3-sec-butyl-2-acetyl-2-hydroxyhydantoin:

$$C_9H_{13}BrN_2O_2 + 3/4O_2 + 1/2H_2O \rightarrow C_9H_{14}N_2O_4 + Br^- \quad . \; . \; . \; .(45)$$

By molar stoichiometry the quantity of dissolved oxygen required to oxidize 1 mg/l of bromacil to the hydantoin is 0.092 mg/l. The theoretical k_{uptake} for methylene blue-sensitized photooxidation of bromacil is therefore 0.092.

Acher et al. (1981) determined the sensitized photooxidation products of terbacil. The primary degradation product of riboflavin-sensitized photooxidation of terbacil at low pH is presented in Figure 42. Acher et al. (1981) found two other terbacil degradation products at low pH. One, a uracil dimer was formed in small quantities. The oxygen uptake influence of this compound was probably negligible

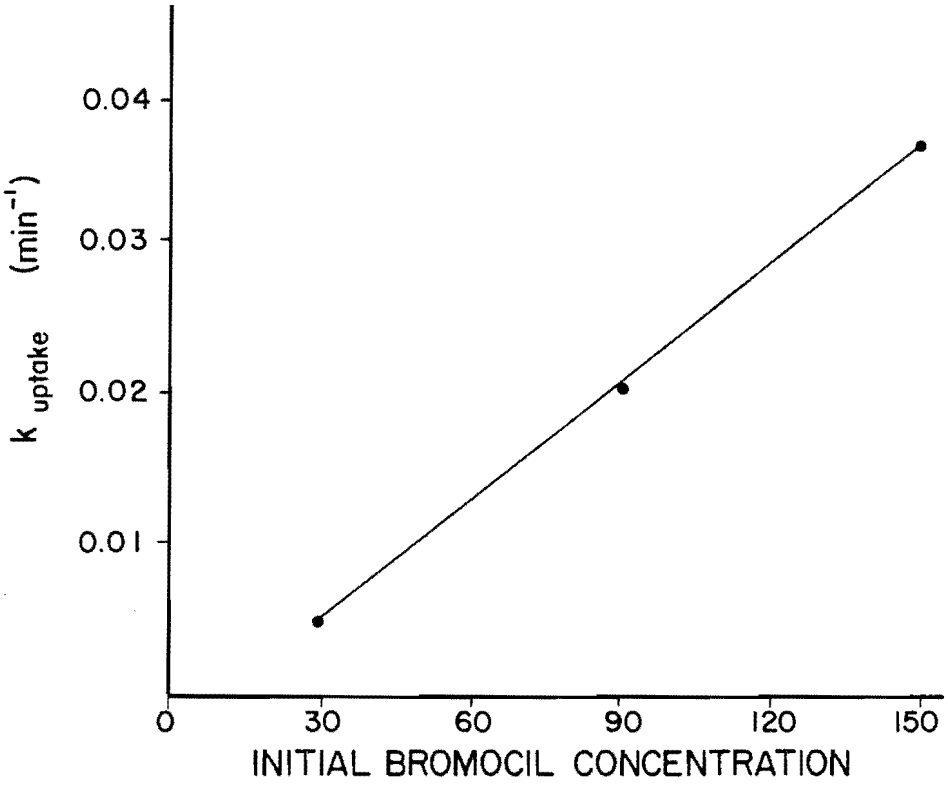


Figure 39. Effect of initial bromacil concentration on first-order rate constants of dissolved oxygen uptake in methylene blue-sensitized photooxidation.

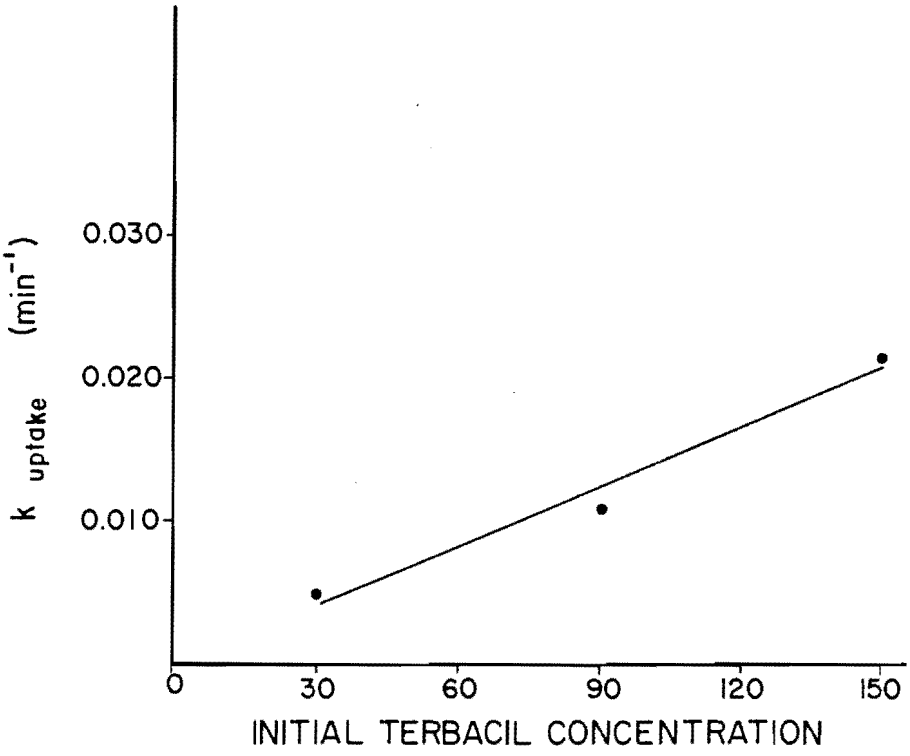
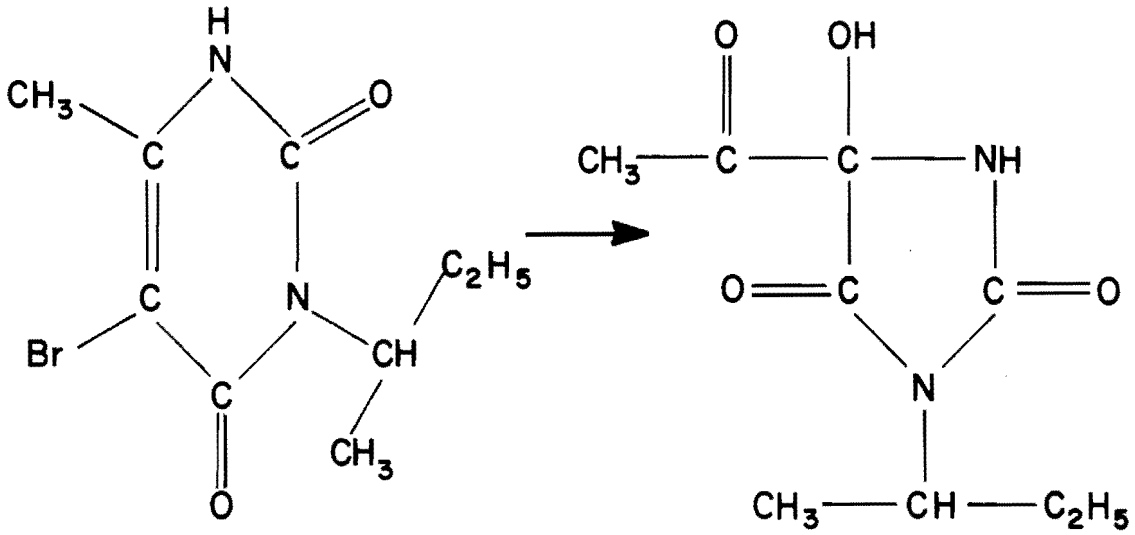


Figure 40. Effect of initial terbacil concentration on first-order rate constants of dissolved oxygen uptake in riboflavin-sensitized photooxidation.

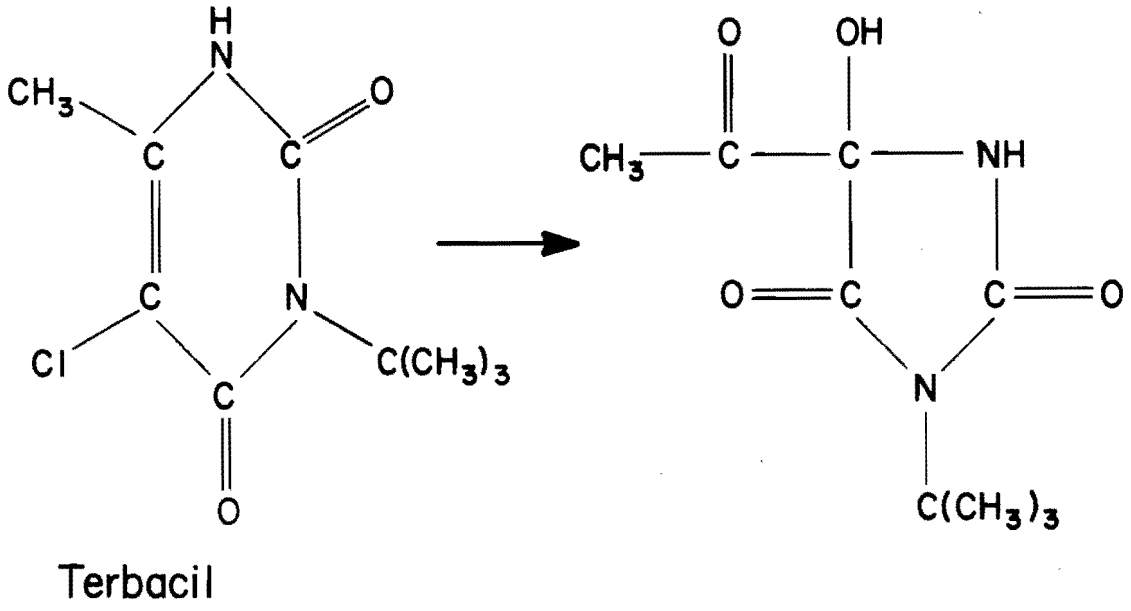


Bromacil

5-bromo-3-sec-butyl-6-methyluracil

3-sec-butyl-5-acetyl-5-hydroxyhydantoin

Figure 41. The structure of bromacil and the primary product of sensitized photo-oxidation of bromacil found in 86 percent yield (after Acher and Dunkelblum 1979).



Terbacil

3-Tert-butyl-5-Chloro-6-methyluracil

3-Tert-butyl-5-acetyl-5-hydroxyhydantoin

Figure 42. The structure of terbacil and the primary product of sensitized photo-oxidation of terbacil at low and neutral pH (after Acher et al. 1981).

since it was found in small quantities. The other, an unidentified compound of polymeric character, did not appear in the first 30 minutes of the experiments. Since the oxygen uptake experiments were conducted in a time period of less than 30 minutes, the influence of the polymeric compound was probably negligible.

Oxygen would be consumed in the oxidation of terbacil by the addition of the carbonyl oxygen on the acetyl group of 3-tert-butyl-5-acetyl-5-hydroxyhydantoin. In an analogous manner to bromacil photooxidation, the hydroxide on the number five hydantoin carbon was attributed to hydroxide addition, so the origin of this oxygen may be traced to water molecules. The following equation relates oxygen uptake by bromacil to form 3-tert-butyl-5-acetyl-5-hydroxyhydantoin:

$$C_9H_{13}C_1N_2O_2 + 3/4O_2 + 1/2H_2O \rightarrow$$

$$C_9H_{14}N_2O_4 + Cl^- \quad . \quad . \quad . \quad .(46)$$

By molar stoichiometry the quantity of dissolved oxygen required to oxidize 1 mg of bromacil to the hydantoin derivative is 0.111 mg. The theoretical k_{uptake} for riboflavin-sensitized photooxidation of terbacil is therefore 0.111.

Oxygen uptake rate constants, k_{uptake}, were determined from laboratory data. Dissolved oxygen at time zero minus dissolved oxygen at time t ($[O_2]_o - [O_2]_t$) was plotted as a function of substrate concentration at time zero minus substrate concentration at time t ($[Substrate]_o - [Substrate]_t$) for data from oxygen uptake experiments. The results were a linear with R^2 generally greater than 0.95. Laboratory k_{uptake} values and theoretical k_{uptake} values are presented in Table 10. The laboratory k_{uptake} values were in agreement with corresponding theoretical values, but were generally lower. The lower laboratory values obtained are probably due to experimental error. Oxygen uptake data were obtained in beakers with a stream of argon gas passed over the mouth of the beaker to prevent diffusion of oxygen into the solution in the beaker. However, with the placement of an oxygen probe in the solution every few minutes and agitation of the probe while in the solution, which is necessary for its use, there was probably diffusion of atmospheric oxygen into the solution. Dissolved oxygen may also have diffused through the layer of argon. It appears that oxygen uptake in sensitized photooxidation may be accounted for by the addition of oxygen to the substrates involved.

Kearns (1971) reviewed the reactions that singlet oxygen undergoes with numerous classes of organic compounds. In many of these reactions molecular oxygen is added to the organic substrate. The rate at which the oxygen is added to the substrate will result in the oxygen uptake rate for the particular compound.

The dissolved oxygen residual required for methylene blue-sensitized photooxidation lagoons of 1 to 2 mg/l is similar to that required for biological waste treatment (Metcalf and Eddy 1979). The oxygen utilization rate of the waste in the photooxidation lagoon, however, will vary with the strength of the waste. For a weak waste entering the lagoon there will be a low oxygen utilization rate. A higher strength waste will have a proportionally higher oxygen uptake rate.

The need for aeration in the sensitized photooxidation lagoon may be calculated using equations provided by Weber (1972) for performing a mass balance about a plug flow reactor:

$$V_x \cdot \frac{d(Substrate)}{dx} = -k(Substrate)$$

$$. \quad . \quad .(47)$$

Table 10. Theoretical and laboratory values for dissolved oxygen uptake coefficient, k_{uptake}, for three concentrations of bromacil sensitized by methylene blue and three concentrations of terbacil sensitized by riboflavin.

Substrate and Concentration	Sensitizer	Theoretical k_{uptake}	Laboratory k_{uptake}
30 mg/l Bromacil	2 mg/l Methylene Blue	0.0919	0.0727
90 mg/l Bromacil	2 mg/l Methylene Blue	0.0919	0.0694
150 mg/l Bromacil	2 mg/l Methylene Blue	0.0919	0.0756
30 mg/l Terbacil	10 mg/l Riboflavin	0.111	0.845
90 mg/l Terbacil	10 mg/l Riboflavin	0.111	0.936
150 mg/l Terbacil	10 mg/l Riboflavin	0.111	0.104

$$V_x \cdot \frac{dC}{dx} = k(C_s - C) - k(\text{Substrate}) \quad \ldots (48)$$

where

C = concentration of dissolved oxygen (M/L^3)

C_s = saturation concentration of dissolved oxygen (M/L^3)

V_x = velocity of wastewater in reactor (L/T)

where (Substrate) is the steady state concentration of the waste undergoing the photooxidation process. Integration of Equation 47 yields

$$(\text{Substrate}) = (\text{Substrate})_o \, e^{-kx/V_x} \quad \ldots (49)$$

where

k = first-order rate constant of oxygen uptake

x = length of reactor (L)

Substituting Equation 49 into Equation 48 and integrating yields

$$(C_s - C) = (C_s - C)_o \, e^{-\hat{k}x/v_x} + \frac{(\text{Substrate})_o \, k}{\hat{k} - k} \left(e^{-kx/v_x} - e^{-\hat{k}x/v_x}\right) \quad \ldots (50)$$

where

$\hat{k}$ = first-order rate constant of oxygen absorption from the atmosphere

To determine if diffusion will supply the needed oxygen in the lagoon, the rate of absorption of oxygen may be calculated using the O'Connor-Dobbins equation (Weber 1972)

$$\hat{k} = (DV/h^3)^{0.5} \quad . \quad . \quad . \quad . \quad . \quad .(51)$$

where

D = diffusivity of oxygen (m^2/day)

V = mean velocity of water through the lagoon (m/day)

h = depth of lagoon (m)

The values for the oxygen uptake constant, the initial substrate concentration, and the lagoon dimensions are entered into Equation 48, and the solution for dissolved oxygen concentration, C, is obtained. If C is less than 1 to 2 mg/l for a lagoon using methylene blue, aeration must be supplied.

Aeration requirements are calculated based on the oxygen deficit in the lagoon. This deficit is a function of strength of waste and resulting rate of oxygen uptake, depth of lagoon, and amount of treatment desired. An example of the use of Equations 45 through 49 in lagoon design will be presented in the design of a sensitized photooxidation pilot lagoon.

Decrease of chemical oxygen demand (COD) followed first-order kinetics for samples collected in the experiments measuring substrate degradation rate as a function of dissolved oxygen residual. Chemical oxygen demand as a function of dissolved oxygen residual for 30 mg/l and 250 mg/l bromacil and for 30 mg/l and 250 mg/l terbacil are presented in Figures 43 and 44, respectively. The saturation curves in these figures show that COD removal is nearly proportional to the rate of photooxidation of substrate shown in Figures 35 and 36. This is expected since substrate decomposition by sensitized photooxidation is an oxidative process. The ratios of rate of COD removal to rate of substrate removal in the zero-order areas of Figures 43 and 44 and Figures 35 and 36 are presented in Table 11. The average k_{COD} is approximately 10 percent of $k_{substrate}$. Therefore, sensitized photooxidation appears to be a relatively poor means for COD removal. Assuming the same ratio of k_{COD} to $k_{substrate}$, if k_{mean} for substrate removal of bromacil in a lagoon was 0.008 min^{-1}, the k_{COD} would be 0.0008 min^{-1}. If 95 percent COD removal is desired, the required detention time of a lagoon could be calculated by the first-order rate equation

$$\ln 5/100 = -0.0008 \text{ min}^{-1}(t) \quad .(52)$$

$$t = 3745 \text{ min} = 2.6 \text{ days} \quad . \quad . \quad .(53)$$

A 2.6 day detention time is less than a facultative lagoon (Metcalf and Eddy 1979, Middlebrooks et al. 1983). However, for a sensitized photooxidation lagoon the sensitizer concentration must be maintained throughout the plug flow regime of the lagoon. Therefore, designing a photooxidation lagoon with a detention time of 2.6 days may prove to be expensive due to sensitizer costs.

Since the rate of substrate decomposition is rapid compared to the rate of COD removal, sensitized photooxidation lagoons may prove to be an effective means of detoxification or removal of biologically recalcitrant species in industrial waste prior to biochemical oxygen demand (BOD) polishing by biological waste treatment.

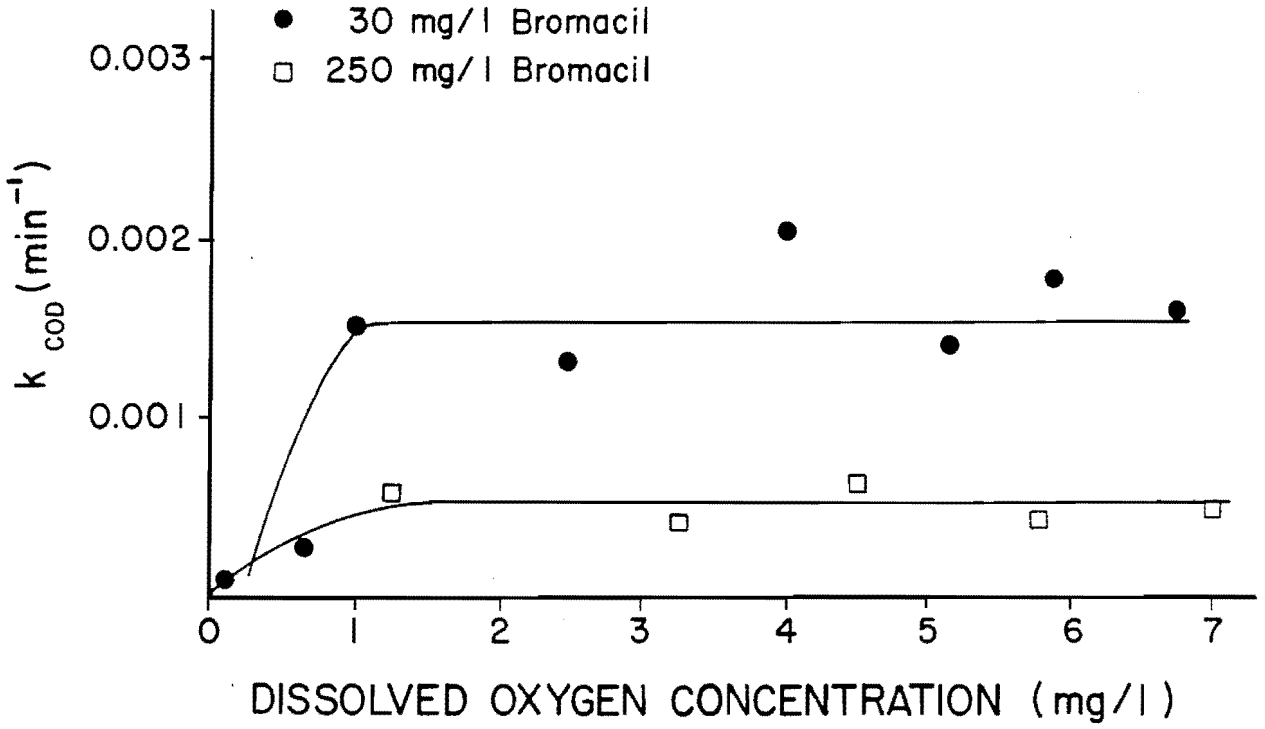


Figure 43. Effect of dissolved oxygen concentration on the first-order rate constants of COD removal of bromacil in the sensitized photooxidation by 2 mg/l methylene blue.

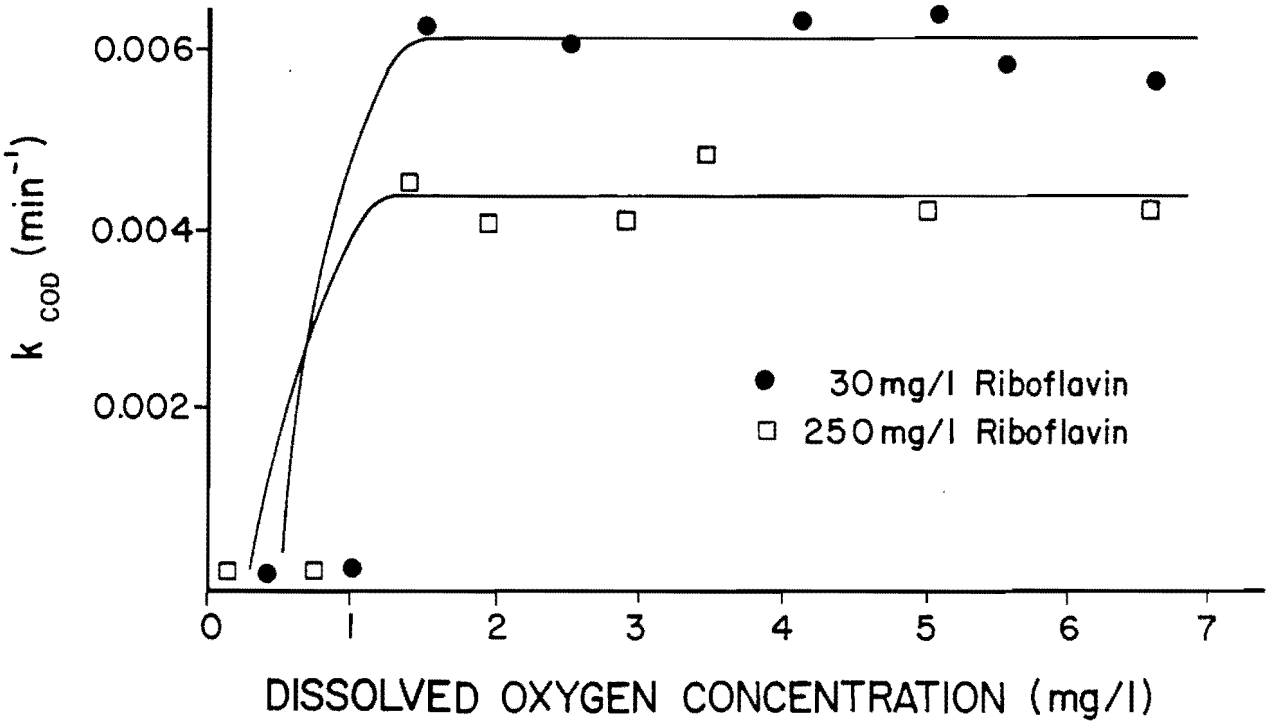


Figure 44. Effect of dissolved oxygen concentration on the first-order rate constants of COD removal of terbacil in the sensitized photooxidation by 10 mg/l riboflavin.

Table 11. Comparison of zero-order rate constants of substrate degradation and zero-order rate constants for COD removal in experiments involving sensitized photooxidation as a function of dissolved oxygen.

Substrate	Concentration	$k_{substrate}$ (min^{-1})	k_{COD}	$\frac{k_{COD}}{k_{substrate}}$
Bromacil	30 mg/1	0.038	0.0061	0.16
Bromacil	250 mg/1	0.032	0.0043	0.13
Terbacil	30 mg/1	0.013	0.0015	0.12
Terbacil	250 mg/1	0.011	0.0006	0.06

The use of sensitized photooxidation lagoons for detoxification or for the removal of biologically recalcitrant chemicals has some advantages. Among these advantages are: (1) a shock load of toxic materials would not cause plant failure; and (2) a pH shock would not disable the system, and could be easily corrected for almost instantaneous reestablishment of normal plant function by the addition of acid or base. If detoxification and pretreatment are the role desired for sensitized photooxidation lagoons, then the lagoon must be designed for a detention time to reach photooxidation products that are nontoxic or not biologically recalcitrant.

Biochemical Oxygen Demand of Photooxidized Bromacil

Biodegradability of bromacil solutions subjected to six time exposures of methylene blue-sensitized photooxidation was investigated to determine their toxicity and biological recalcitrance. The detention time in a pilot lagoon could be varied with the time of solar exposure necessary to reach nontoxic or biologically labile degradation products. Biodegradability was measured using the biochemical oxygen demand (BOD) analysis on samples with original concentrations of 5 and 10 mg/1 bromacil at six photooxidation exposures. These samples were diluted from 750 mg/1 original bromacil concentration to 5 mg/1 and 10 mg/1. The six samples were first exposed to 0, 1, 2, 3, 4, and 5 hrs of methylene blue-sensitized photooxidation under radiation of 2000 W/m^2. The results of the 20-day BOD analyses for the bromacil solutions and a 3 mg/1 glucose-3 mg/1 glutamic acid BOD standard are plotted in Figure 45 for samples diluted to 5 mg/1 as initial bromacil and in Figure 46 for samples diluted to 10 mg/1 as initial bromacil. The data in these figures are typical for BOD_{20} tests in that they are first-order with nearly all oxygen consumption complete after 20 days (Sawyer and McCarty 1978). The BOD_{20} of bromacil solutions not subjected to photooxidation was approximately 0.2 to 0.3 mg/1 BOD. These data are in agreement with the results of Sherman and Kaplan (1975) and E. I. duPont de Nemours and Co. (1979a) that bromacil is biologically recalcitrant with a biological half-life of 5 to 6 months. The BOD of samples subjected to 1, 2, 3, 4, and 5 hrs of sensitized photooxidation were similar, as evidenced by the grouped nature of the curves in both Figures 45 and 46. The BOD_{20} of the 10 mg/1 samples was generally about 3 mg/1 and generally about 2.5 mg/1 for the 5 mg/1 samples. The glucose-glutamic acid BOD standard exerted a BOD typical for its concentration of organic matter, confirming that the BOD seed and dilution water were satisfactory. The BOD standard

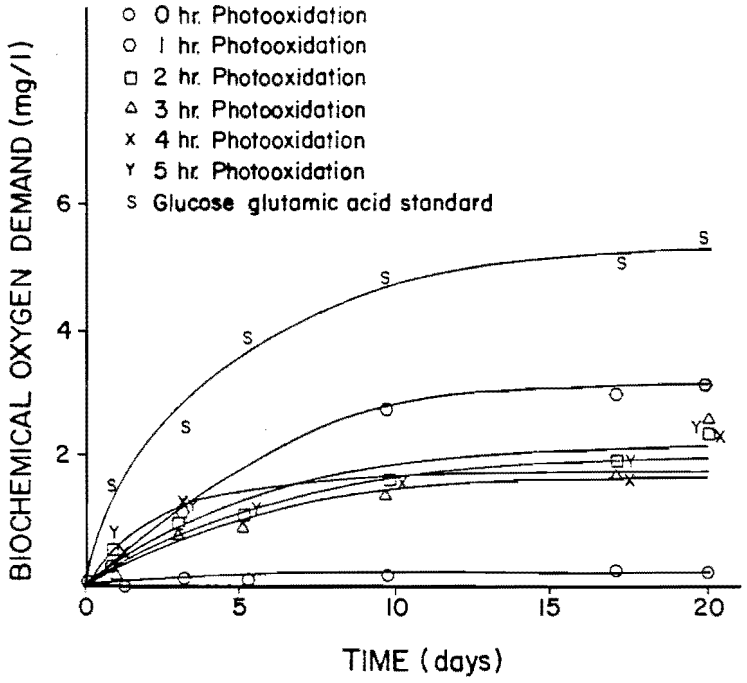


Figure 45. Biochemical oxygen demand over 20 day period for bromacil samples subjected to methylene blue-sensitized photooxidation ranging from 0 to 5 hours under solar radiation. Concentration of substrate was 5 mg/l bromacil prior to photooxidation.

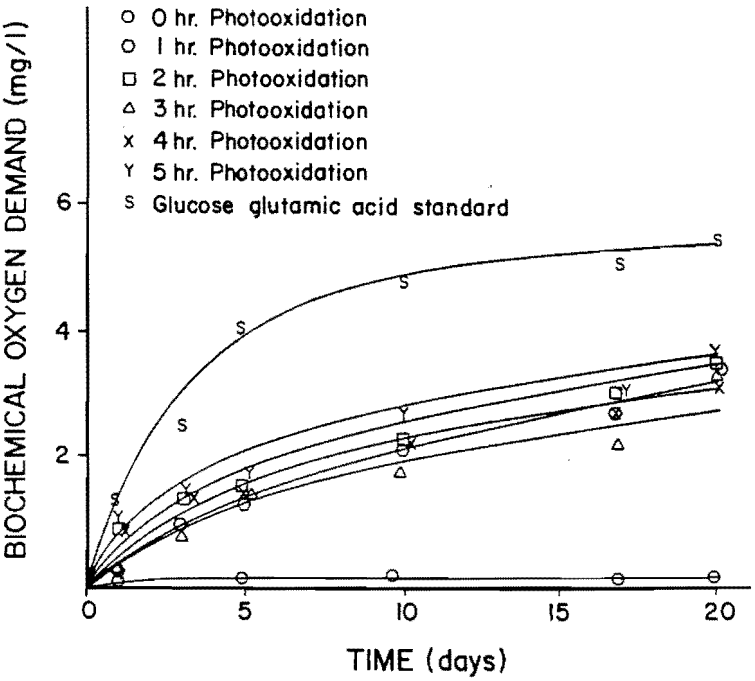


Figure 46. Biochemical oxygen demand over 20 day period for bromacil samples subjected to methylene blue-sensitized photooxidation ranging from 0 to 5 hours under solar radiation. Concentration of substrate was 10 mg/l bromacil prior to photooxidation.

containing the same concentration of methylene blue as the 10 mg/l bromacil sample showed results similar to the BOD standard, negating any methylene blue toxicity.

Figures 47 and 48 represent BOD_{20} and COD of the six photooxidation treatments for samples diluted to 5 mg/l and 10 mg/l initial bromacil, respectively. Sensitized photooxidation removed 18 percent of the COD from the 10 mg/l samples and 14 percent from the 5 mg/l samples after 5 hrs of irradiation. BOD_{20} for 5 mg/l and 10 mg/l samples increased sharply from the 0 hr photooxidation sample to the 1 hr photooxidation sample and increased only slightly thereafter.

Medley and Stover (1983) recommended the BOD_{20}/COD ratio as an index of the biodegradability of refractory organic chemicals. Percent biodegradability, BOD_{20}/COD x 100, for the bromacil samples exposed to six photooxidation times is presented in Figure 49 for the bromacil samples exposed to six sensitized photooxidation times. Samples diluted to 5 mg/l initial bromacil concentration reached over 30 percent biodegradability after 1 hr of sensitized photooxidation, but the biodegradability did not increase significantly with up to 5 hrs of photooxidation. The 10 mg/l samples were similar; 21 percent biodegradability was achieved after 1 hr of sensitized photooxidation, increasing to 23 percent after 5 hrs of photooxidation.

Figures 47 and 48 show that the BOD_{20} of bromacil solutions increased after 1 hr of sensitized photooxidation. There was negligible BOD increase in the bromacil samples exposed to 2 to 5 hrs of photooxidation. Figures 48 and 49 also show that the COD of bromacil solutions decreased for the first 1 to 2 hrs of photooxidation, with little COD removal thereafter. A possible explanation for these data may be that the photooxidation of bromacil ceased after 1 to 2 hrs of photooxidation. This may be due to the formation of a degradation product that is resistant to sensitized photooxidation, or that quenches singlet oxygen or the methylene blue excited state. With little photooxidation occurring after 1 to 2 hours of solar exposure, the BOD_{20}, COD, and biodegradability (BOD_{20}/COD x 100) would not change for samples exposed for 2 to 5 hrs, as shown in Figures 47, 48, and 49. If photooxidation of bromacil ceased after 1 to 2 hrs, the BOD_{20} and COD analyses for samples exposed to 2 to 5 hrs of photooxidation would have been performed on almost identical photooxidation products.

Percent biodegradability, measured by BOD_{20}/COD x 100, of 5 mg/l initial bromacil samples was 50 percent greater than for 10 mg/l samples. Increased BOD as a function of dilution of substrate is normally attributed to toxicity or cellular inhibition. The bromacil photooxidation products may therefore be toxic or inhibitory to bacterial metabolism. Acher and Dunkelblum (1979) found that bromacil, when subjected to methylene blue-sensitized photooxidation is debrominated to 3-sec-butyl-5-acetyl-5-hydroxyhydantoin in yields of 86 percent. The hydantoin is less polar than bromacil due to the loss of bromine, and may serve as a possible explanation for toxicity of the bromacil photooxidation products. Since the hydantoin is less polar than bromacil, it may be more easily absorbed through bacterial cell membranes, resulting in toxicity or inhibition of cellular metabolism (Loomis 1974).

The fact that BOD tests are sensitive to the nature and strength of the seed used may be a cause of error in the biodegradability tests. The seed used in the BOD analysis was obtained from the oxidation ditch of the Hyrum, Utah, Wastewater Treatment Plant. The wastewater entering the Hyrum Wastewater Treatment Plant comes almost exclusively from domestic sources and is diluted by infiltration and inflow into the

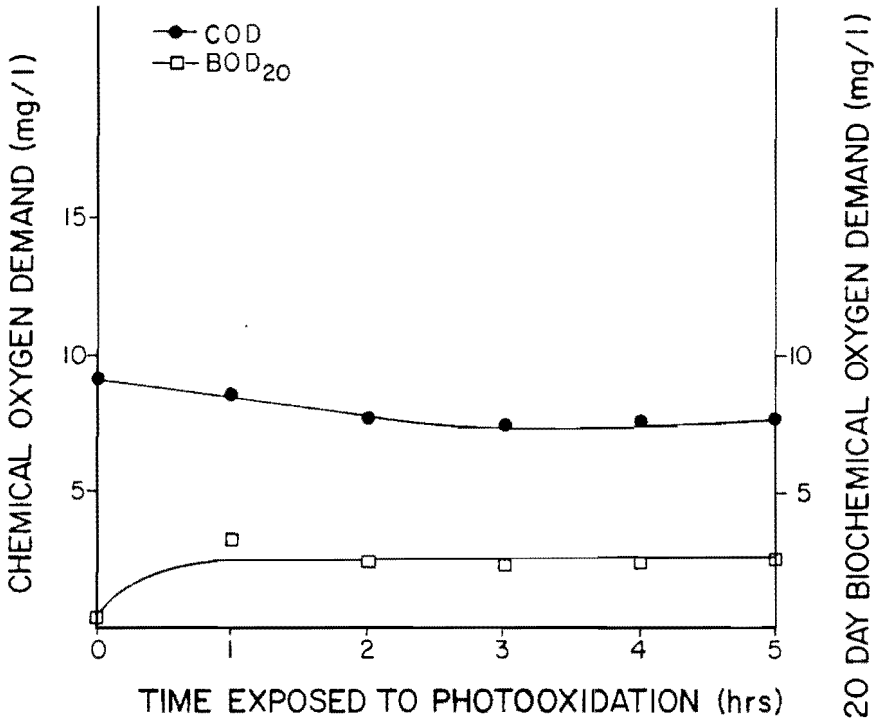


Figure 47. Chemical oxygen demand and 20-day biochemical oxygen demand of bromacil exposed to photooxidation. Bromacil concentration was 5 mg/l prior to photooxidation.

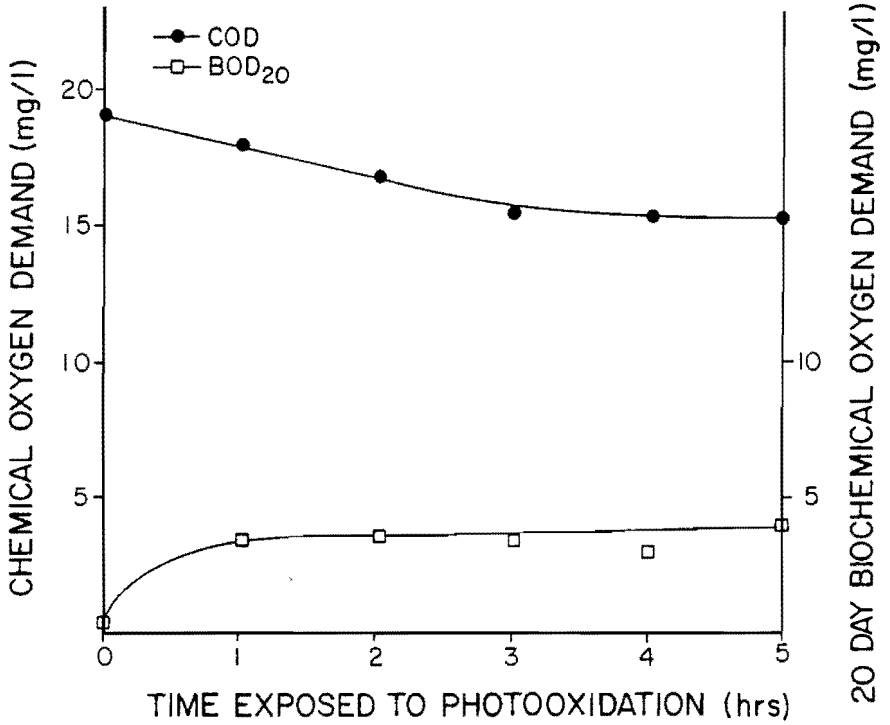


Figure 48. Chemical oxygen demand and 20-day biochemical oxygen demand of bromacil exposed to methylene blue-sensitized photooxidation. Bromacil concentration was 10 mg/l prior to photooxidation.

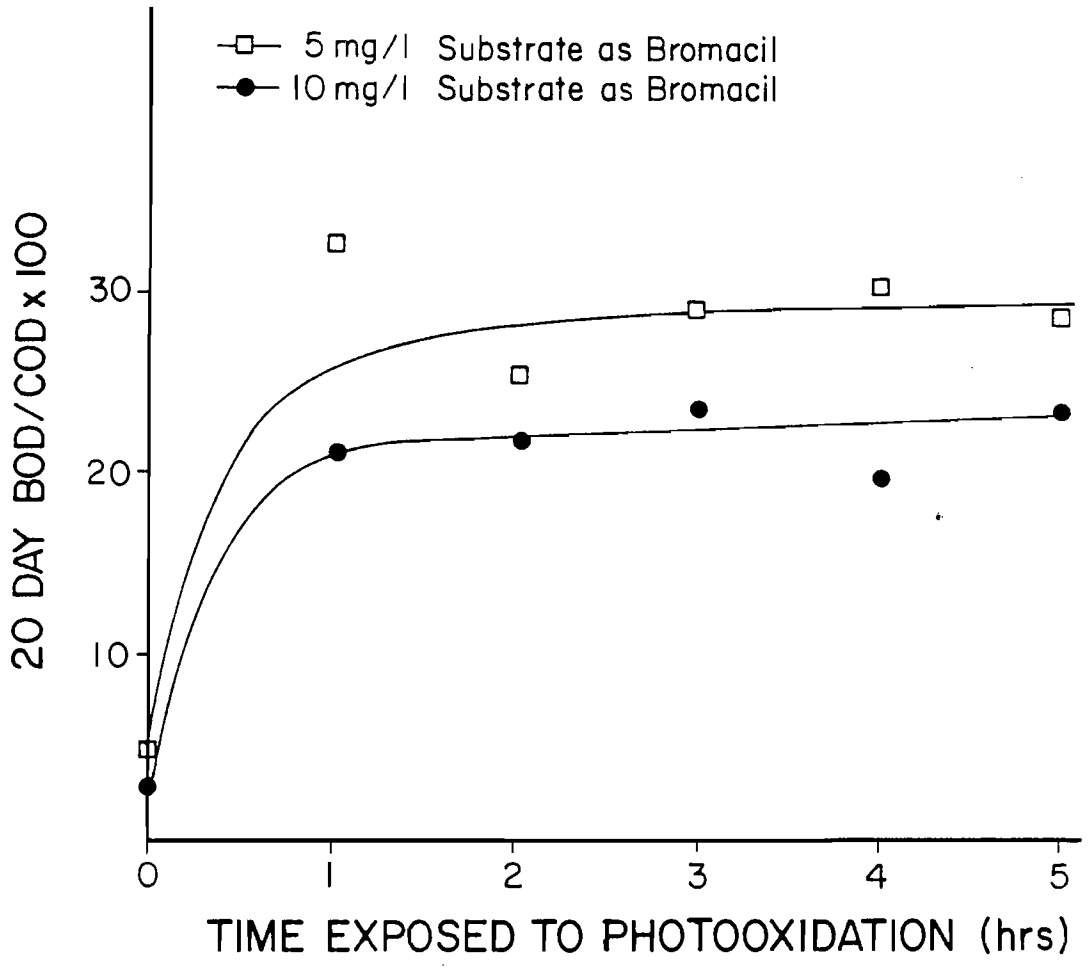


Figure 49. Biodegradability of photooxidized bromacil measured by BOD_{20}/COD x 100.

collection system (Upton 1982). These two factors could result in a bacterial seed that does not have the metabolic capabilities to degrade synthetic organic compounds. Medley and Stover (1983) used an acclimated seed developed in batch activated sludge systems for studying the BOD of three synthetic organic compounds exposed to ozonation. The seeds were developed in activated sludge systems containing the compound and the oxidized compound resulting from ozonation. If a seed acclimated to bromacil and bromacil photooxidation products was used, enzymes to catalyze the degradation of the photooxidation products, if present in the bacterial genomes, would have been induced prior to the BOD analysis. There is evidence in Figures 45 and 46 that the bacterial seed became acclimated near the end of the 20-day BOD analysis. The BOD for many of the five samples containing bromacil photooxidation products showed marked increase in BOD from day 17 to day 20. This BOD increase may be due to microbial acclimation during the 20-day BOD analysis. Few compounds are as susceptible to biological degradation as the carbohydrates and proteins of municipal wastewater which are easily assessed by the BOD test. More complex compounds may not exhibit BOD, but may be treated practically by efficient biological processes such as activated sludge (Eckenfelder 1966).

In summary, bromacil photooxidation products appear toxic in the BOD analysis. The BOD_{20} of bromacil solutions increased after 1 hr of sensitized photooxidation. Increased BOD was not achieved with 2 to 5 hrs of sensitized photooxidation. The COD of bromacil solutions decreased for 1 to 2 hrs of sensitized photooxidation, with little subsequent COD removal. Photooxidation of the bromacil solutions may have ceased after 1 to 2 hrs, resulting in no further decrease of COD and minimal increase in biodegradability of solutions exposed to 2 to 5 hrs of photooxidation. Higher biodegradability of photooxidized bromacil may have been achieved if an acclimated seed had been used.

Biological treatment is an efficient means of treating wastes that are nontoxic and not biologically recalcitrant (Metcalf and Eddy 1979). The most economical use of sensitized photooxidation may be to utilize photooxidation to detoxify the waste and make refractory wastes biologically labile prior to biological treatment. Facultative lagoons or activated sludge could then follow photooxidation lagoons for BOD removal and polishing. With the data of Figures 45 through 49, it may be concluded that bromacil photooxidation products were not as biologically labile as glucose and glutamic acid. It is difficult to predict how the bromacil degradation products may behave in an activated sludge system with a high MLVSS and an acclimated population of microorganisms. Bench-scale activated sludge units should be used to study the photooxidation products of bromacil.

If sensitized photooxidation is to be used to pre-treat an uncharacterized waste prior to biological treatment, the waste photooxidation products should be analyzed for biodegradability prior to photooxidation lagoon design. The photooxidation lagoon can then be sized based on the detention time required to obtain biologically labile photooxidation products.

Effect of Temperature on Sensitized Photooxidation Rate

Sensitized photooxidation rate constants as a function of temperature for 30 mg/l and 250 mg/l bromacil and 30 mg/l and 250 mg/l terbacil are presented in Figures 50 and 51, respectively. The rate constants for the methylene blue bleaching and for riboflavin bleaching as a function of temperature are presented in Figures 52 and 53, respectively. Ambient temperatures from 10°C through 35°C had little effect on the sensitized photooxidation rate. The results show that the methylene blue-sensitized photooxidation of bromacil and riboflavin-sensitized photooxidation of terbacil do not follow the Van't Hoff rule of a twofold increase in reaction rate for every 10°C rise in temperature. Spikes and Straight (1967) had similar findings when they reported that the temperature dependence of sensitized photooxidation of amino acids is small with experimental activation energies changing by only 3 to 5 kcal/mole over a wide temperature range.

Acher (1982a) investigated the rates of methylene blue- and riboflavin-sensitized photooxidation of bromacil and terbacil in frozen films and under ice cover. Acher did not attribute the decreased photooxidation rates to below-freezing temperatures. He explained the low photooxidation rates relative to summer conditions by light attenuation by the ice. Boodagheans and Burrell (1982) presented some thermodynamic data for singlet oxygen. The H_f^o of $O_2(^1)$ at 298°K and 373°K was reported at 94.14 kJ mol^{-1} and 94.16 kJ mol^{-1}, respectively. These values are not significantly different. Light absorption by the sensitizer and energy transfer to oxygen do not depend on temperature (Sargent and Sanks 1976). The collision rate, which limits the secondary photooxidation, however, is a function of temperature. Such a temperature effect was not noted for the data

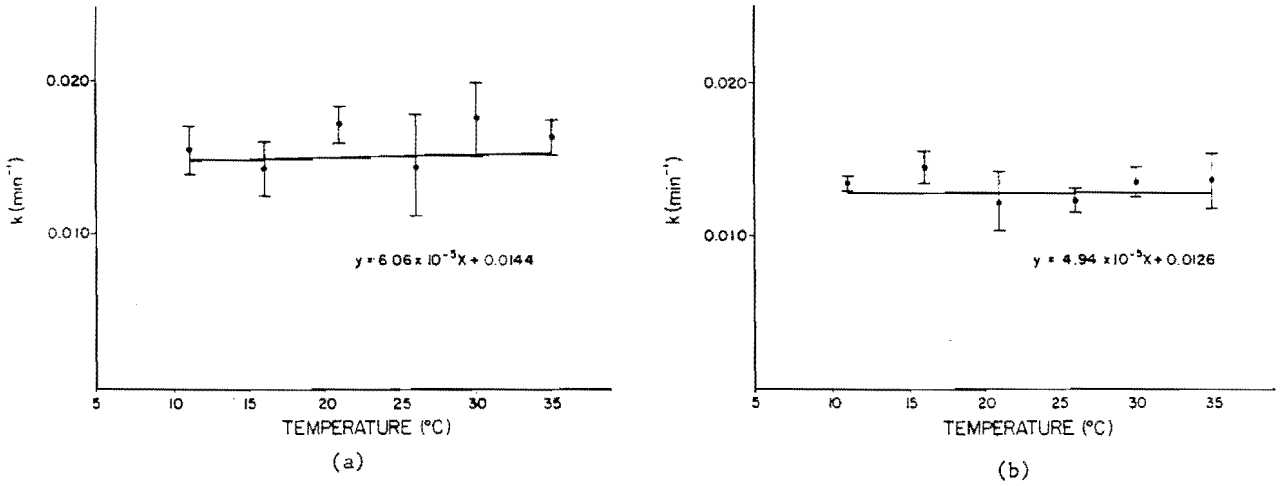


Figure 50. First-order rate constants for methylene blue-sensitized photooxidation of 30 mg/l bromacil (a) and 250 mg/l bromacil (b) as a function of temperature. Initial methylene blue concentration was 2 mg/l. Vertical bars represent standard deviation for three replicates.

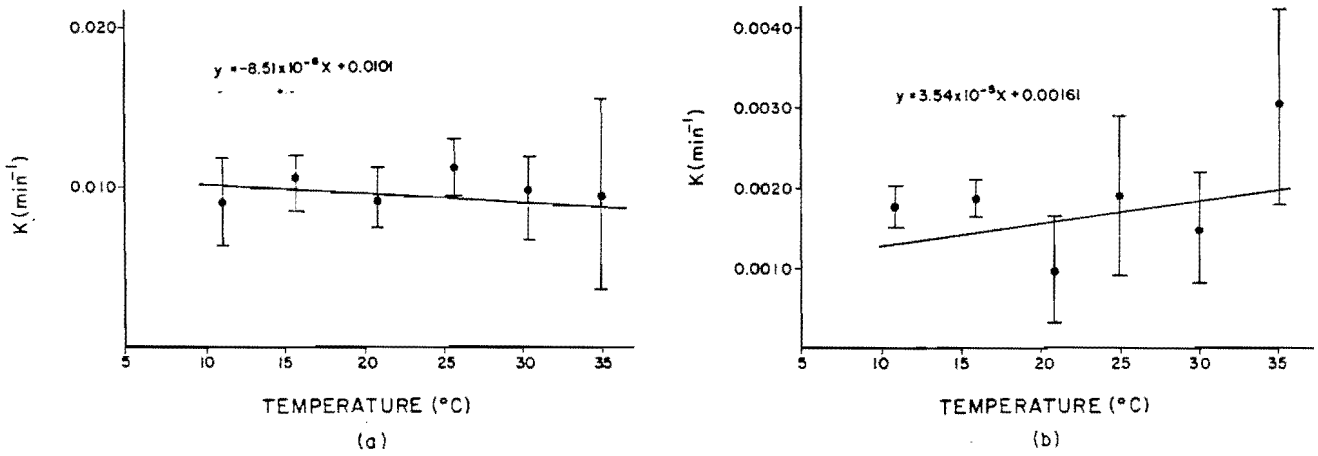


Figure 51. First-order rate constants for riboflavin-sensitized photooxidation of 30 mg/l terbacil (a) and 250 mg/l terbacil (b) as a function of temperature. Riboflavin concentration was 10 mg/l. Vertical bars represent standard deviation for three replicates.

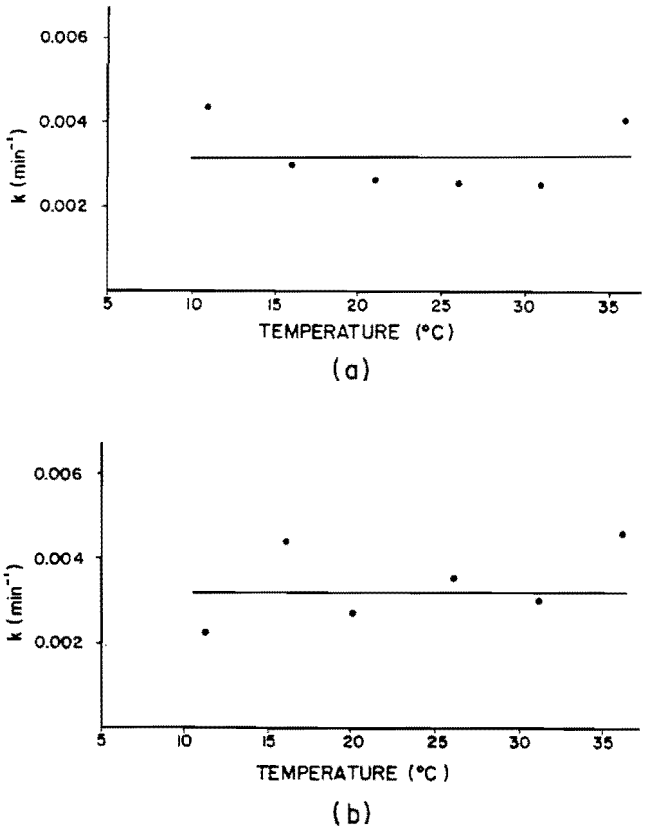


Figure 52. Effect of temperature on the first-order rate constants of methylene blue bleaching in the photooxidation of 30 mg/l bromacil (a) and 250 mg/l bromacil (b).

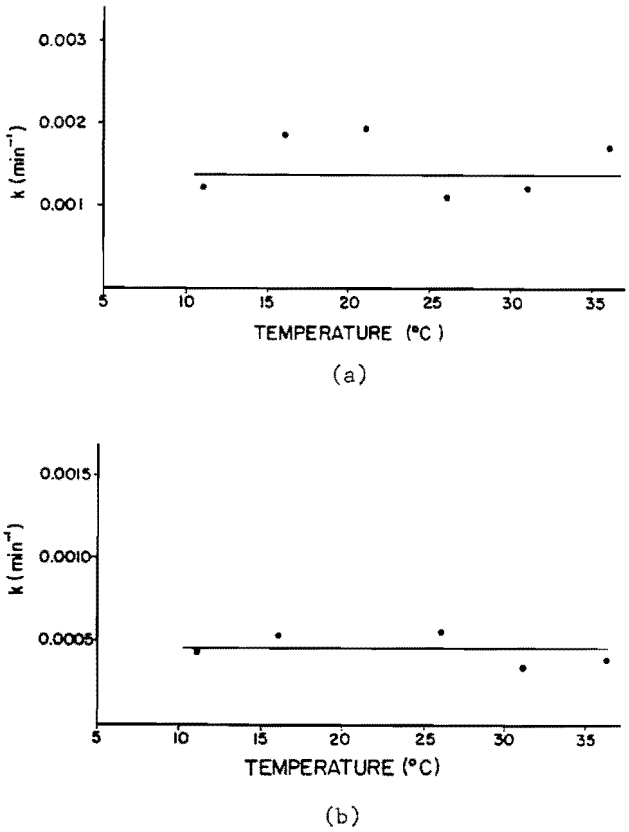


Figure 53. Effect of temperature on the first-order rate constants of riboflavin bleaching in the photooxidation of 30 mg/l terbacil (a) and 250 mg/l terbacil (b).

shown in Figures 50 through 53. A possible explanation for the minimal effect of temperature on the photooxidation rate may be that the singlet oxygen and radical species are so reactive, and occur in such a small sphere from the point of excitation, that the collision rate is negligible.

The engineering aspects of these data indicate that there is no need for temperature correction in the design of sensitized photooxidation lagoons. Winter temperatures will not have a significant effect on the design of sensitized photooxidation lagoons. In biological treatment, the reduced enzymatic rates in winter temperatures result in significantly larger design of plants (Metcalf and Eddy 1979). Though temperature will not dictate larger lagoon design, the significant decrease in ambient light during the winter will likely be the most significant factor in winter lagoon design.

DESIGN OF A SENSITIZED PHOTOOXIDATION LAGOON

The design criteria developed through this research may be used to design a sensitized photooxidation pilot system. The following section will present a preliminary, hypothetical photooxidation system design for a 0.263 m^3/min (0.1 MGD) bromacil waste. Some of the guidelines proposed are assumptive in nature; this is due to the lack of available information on such a new treatment system. This chapter represents the first attempt at the design of a sensitized photooxidation system and many of the practical considerations associated with such a system are unknown. Therefore, some of the design parameters are somewhat speculative.

A sensitized photooxidation lagoon should be sized according to the quantity of light impinging on the lagoon, since light energy is the driving force in the photochemical reactions. A step-by-step procedure for the design of a sensitized photooxidation pilot lagoon follows.

1. Using bench scale equipment (e.g., beakers), measure the photooxidation rate of the waste to be treated using numerous sensitizer concentrations. In the design to be performed for the treatment of a 30 mg/l bromacil waste, seven bench scale methylene blue concentrations were evaluated: 0.05, 0.075, 0.1, 0.25, 0.5, 1.0, and 2.0 mg/l methylene blue. If the pH of the waste is not compatible with sensitized photooxidation, a number of pH values may be evaluated. The cost of pH adjustment of the waste would then be considered in the design. For instance, if a waste to be sensitized with methylene blue enters the lagoon at pH 6, the bench scale experiments may be performed at pH 6, 7, 8, and 9, each at seven methylene blue concentrations, i.e., a matrix of four pH values x seven sensitizer concentrations. The lagoons would be designed for the least-cost option of the 28 points on the matrix.

2. Spectroradiometer data and the bench-scale rate constant are used to initialize Equation 16. Using Equation 16, a k vs. depth curve is generated for each design criterion of the matrix.

3. Using Equation 22, k_{mean} is calculated for successive depths of 2 cm intervals.

4. Using the calculated k_{mean} values, lagoon volume and area determine the plug flow design equation:

$$\ln \frac{C}{C_o} = -k_{mean} \left(\frac{V}{Q}\right) \quad . \quad .(54)$$

The optimum depth is chosen where minimum area is achieved, ensuring minimal land purchase.

5. Based on land required, construction costs, and chemical costs for each point on the bench scale matrix, design for the least-cost dye concentration, pH, and depth of the lagoon.

The design of a sensitized photooxidation pilot lagoon should be based on samples from the waste stream to be treated. Attempts to obtain pesticide waste samples in the United States were unsuccessful, since the waste characteristics are proprietary. The waste from industrial bromacil synthesis was described by Acher (1982b), who obtained a sample in Israel. The description was high total dissolved solids, pH 9, 30 mg/l bromacil, and a red color. This exemplary design will use a synthetic waste, since an industrial waste sample could not be obtained. The synthetic bromacil waste was prepared to match Acher's description. The waste, with characteristics shown in Table 12, was compared to methylene blue in spectral quality for Beer-Lambert Law (Equation 8) calculations. The spectral quality of the synthetic waste is shown in Figure 54.

Design parameters, including desired bromacil effluent concentration, hydraulic loading, and solar radiation, are shown in Table 13. Two design options were investigated; the design of a sensitized photooxidation lagoon based on a cloudy winter day (Option I) and a design based on a cloudless winter day with flow equalization for cloudy days (Option II). Both designs provided flow equalization for waste generated at night. A sensitivity analysis was performed on each design, optimizing for seven sensitizer concentrations and six time exposures of solar radiation. Prior to the design of the two options, flow equalization and rapid sand filtration were considered.

The size of the flow equalization basin depends on the time exposure of solar radiation for which the lagoon is designed and whether the lagoon is designed for Option I (cloudy day) or Option II (cloudless day). The flow equalization basin should be constructed according to the guidelines of Metcalf and Eddy (1979), including earthen construction liner to prevent seepage, side slopes of 3:1 to 2:1 slope stabilization, and depth of 2 m. Cost estimates were determined according to U.S. EPA (1980).

Table 12. Synthetic industrial bromacil waste used to design sensitized photooxidation pilot lagoon.

Constituent	Concentration
Bromacil	30 mg/l
Sodium chloride (TDS)	10,000 mg/l
Rose bengal (red color)	5 mg/l
Suspended solids (SS)	100 mg/l

Suspended solids, such as clays and colloids, can adsorb and bind sensitizers. Acher and Saltzman (1980) found that clays and other solids that bind sensitizers significantly reduce the rate of sensitized photooxidation. Suspended solids can also reduce light penetration (Wetzel 1975). Fortunately, pesticide wastes are usually low in suspended solids. Values range from 0 to 100 mg/l (Atkins 1972). Where suspended solids are high enough to interfere with sensitized photooxidation, a physical roughing filter may be necessary to remove particles. Intermittent or rapid, high permeability sand filters may be the most efficient design. A schematic of the proposed photooxidation is shown in Figure 55.

Design Option I: Design for cloudy winter day

The design conditions listed in Table 13 were used in the design of a sensitized photooxidation pilot lagoon to treat the synthetic waste described in Table 12 with the spectral quality shown in Figure 54. Solar radiation as a function of time of day for a cloudy winter day for Logan, Utah,

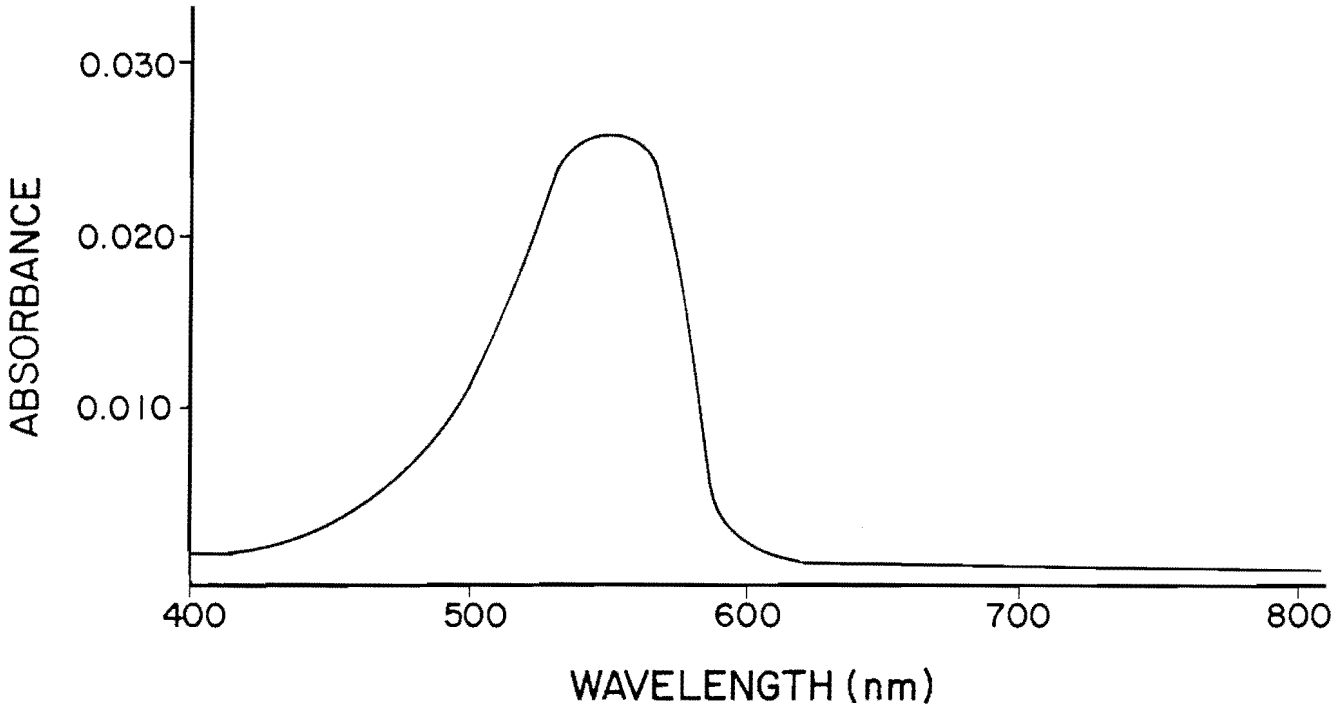


Figure 54. Spectral quality of synthetic bromacil waste used to design sensitized photooxidation pilot lagoon.

Table 13. Design conditions for sensitized photooxidation pilot lagoon.

Influent bromacil concentration: 30 mg/l
Desired effluent bromacil concentration: 0.1 mg/l
Waste flow rate: 0.1 mgd (0.263 m^3/min) steady flow
Solar radiation: As shown in Figure 56 for a cloudy winter day and Figure 59 for a cloudless winter day
Maximum duration of successive cloudy days: 5 days
Minimum duration of successive cloudless days: 3 days
Dissolved oxygen: 6.0 mg/l

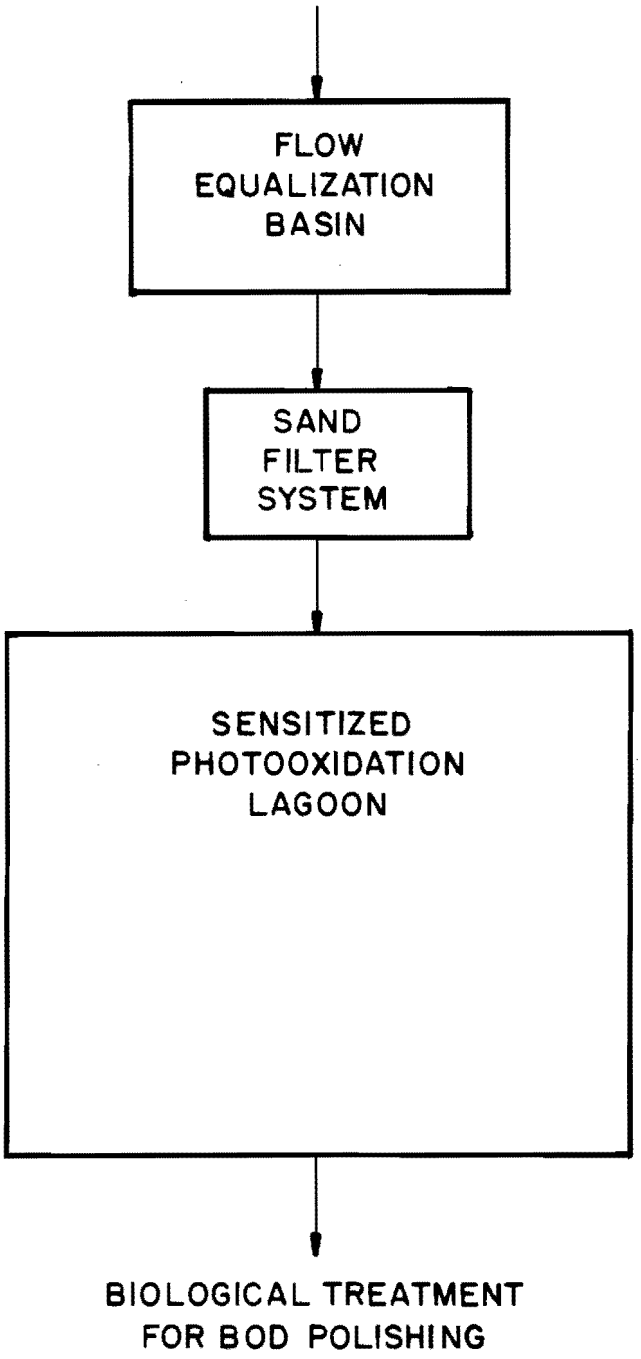


Figure 55. Schematic of design options I and II.

is shown in Figure 56. Six time exposures to solar radiation were chosen ranging from 2 hours to 7 hours. The minimum solar radiation associated with each time exposure was read from Figure 56. These time exposures and corresponding minimum solar radiation are shown in the design matrix, Table 14. Seven methylene blue concentrations were used in the design matrix. These concentrations are also listed in Table 14. Zero-depth first-order rate constants for the methylene blue-sensitized photooxidation provided by bench scale data are presented in Table 14 for the six solar radiation time exposures times seven sensitizer concentration factorial design.

The daily time exposure used for lagoon design determines the size of the flow equalization basin. For example, a design for 7-hr lagoon radiation exposure time would require a flow equalization capacity for 17 hrs of flow. During the 7 hrs of photooxidation treatment, the flow into the lagoon would include flow from 17 hrs of flow equalization plus base flow. The need for flow equalization may be described by:

$$V = Q \cdot t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

where

V = volume of flow equalization basin (m^3)

Q = steady flow rate of influent wastewater (m^3/min)

t = daily time requirement for flow equalization (min)

The area of the flow equalization basin is

$$\text{Area } (m^2) = V\ (m^3)\ /2(m) \quad . \quad . \quad (56)$$

A depth of 2m was assumed.

The volume of wastewater entering the photooxidation lagoon may be calculated by summing the flow from the equalization basin plus the base flow. One entire volume contained in the equalization basin will be discharged during $t_{exposure}$.

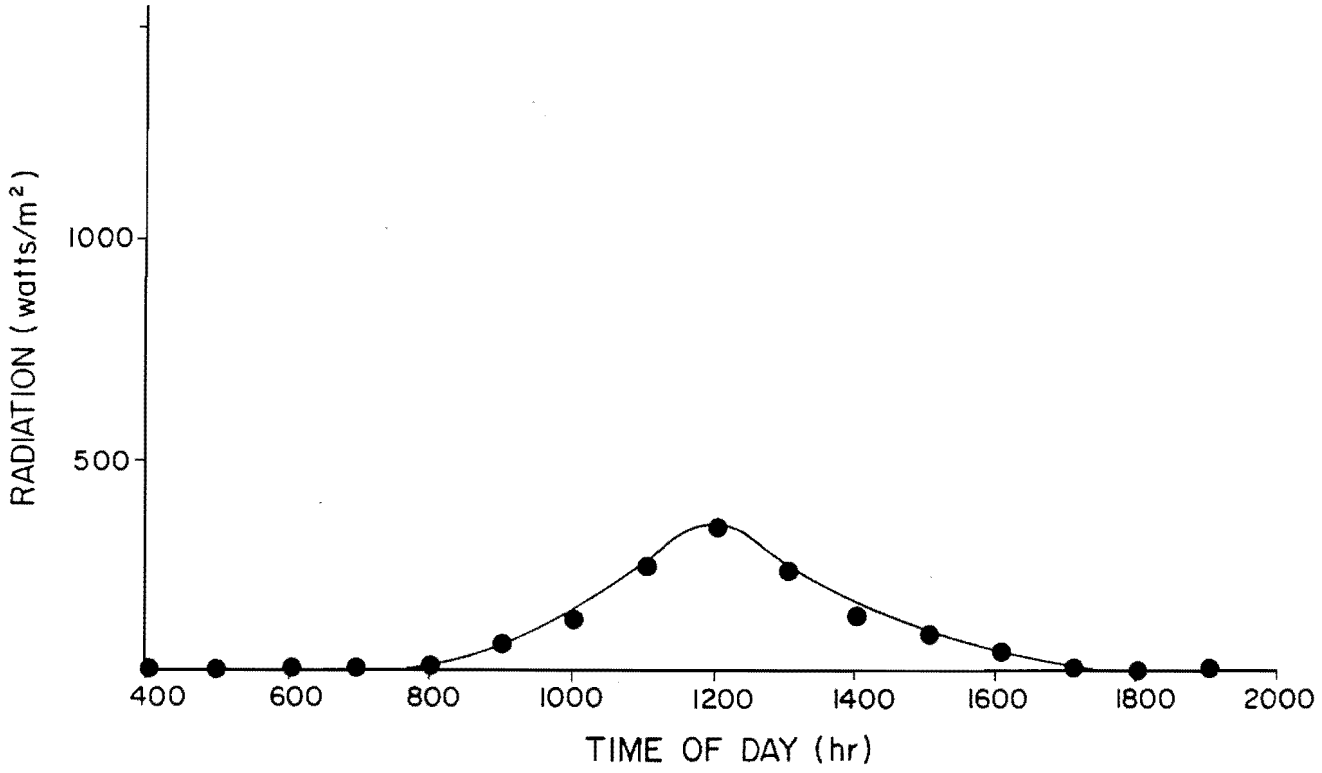


Figure 56. Solar radiation as a function of time of day for November 22, 1981, a cloudy winter day, Logan, Utah (Latitude 42° North).

$$Q_{influent} = V/t_{exposure} + Q_{base} \quad . \; . \; .(57)$$

where

$Q_{influent}$ = flow rate of wastewater entering the photo-oxidation lagoon (m^3/min)

V = volume of flow equalization basin (m^3)

$t_{exposure}$ = design time of solar exposure for photo-oxidation lagoon (min)

Q_{base} = steady base flow rate (m^3/min)

For example, if a 7 hr solar time exposure is chosen for design with a 0.263 m^3/min (0.1 MGD) steady wastewater flow rate, the time period required for flow equalization would be 17 hrs or 1020 min. The required volume for flow equalization is:

$$V = 0.263 \text{ m}^3/\text{min} \cdot 1020 \text{ min} \quad . \; .(58)$$

$$V = 268 \text{ m}^3 \quad . \; . \; . \; . \; . \; . \; .(59)$$

The corresponding area is:

$$\text{Area} = 268 \text{ m}^3/2\text{m} \quad . \; . \; . \; . \; .(60)$$

$$\text{Area} = 134 \text{ m}^2 \quad . \; . \; . \; . \; .(61)$$

The resultant wastewater flow rate entering the lagoon during the 7 hr period of solar exposure is

Table 14. Zero-depth sensitized photooxidation rate constants for Design Option I sensitivity analysis based on seven methylene blue concentrations and six solar radiation exposure times.

Solar Radiation Exposure Time Criteria / Sensitizer Concentration (mg/l)	zero depth $k(min^{-1})$						
	0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=60W/m^2 Q=0.901 m^3/min	0.0000334	0.0000580	0.00418	0.00634	0.0112	0.0155	0.0232
t=6 hr Rad=80 W/m^2 Q=1.05 m^3/min	0.0000449	0.0000773	0.00557	0.00843	0.0149	0.0207	0.0309
t=5 hr Rad=100 W/m^2 Q=1.26 m^3/min	0.0000556	0.0000967	0.00696	0.0105	0.0186	0.0258	0.0386
t=4 hr Rad=130 W/m^2 Q=1.57 m^3/min	0.0000741	0.000129	0.00926	0.140	0.0247	0.0343	0.0513
t=3 hr Rad=180 W/m^2 Q=2.10 m^3/min	0.000102	0.000177	0.0127	0.0193	0.0340	0.0472	0.0705
t=2 hr Rad=230 W/m^2 Q=3.15 m^3/min	0.000129	0.000226	0.0162	0.0208	0.0434	0.0602	0.0900

$$Q_{influent} = \frac{268\ (m^3)}{420\ (min)} + 263\ m^3/min$$

$$Q_{influent} = 0.901\ m^3/min \quad . \quad .(63)$$

Design solar exposure times with corresponding $Q_{influent}$, minimum solar radiation, and zero-depth methylene blue-sensitized photooxidation rate constants for seven methylene blue concentrations are presented in Table 14.

An example of lagoon sizing will be provided for illustrative purposes. After the example is given, only final design dimensions will be given for design parameters. The example involves lagoon sizing for 0.1 mg/l methylene blue at 20 cm depth with 7 hrs exposure of solar radiation. Using the zero-depth k value of 0.0418 min^{-1} for photooxidation of bromacil sensitized by 0.1 mg/l methylene blue with radiation of 60 W/m^2 (minimum radiation for 7 hrs of solar radiation from Figure 56), the k vs. depth curve, generated by Equation 16, is shown in Figure 57. The composite rate constant, k_{mean}, may be determined with Equation 22 using 2 cm horizontal control volumes.

$$k_{mean} = 2(0.00386) + 2(0.00341) + 2(0.00308) + 2(0.00281) + 2(0.00258) + 2(0.00237) + 2(0.00219) + 2(0.000202) + 2(0.00188) + 2(0.00174)/20 \quad . \quad . \quad .(64)$$

$$k_{mean} = 0.00260\ min^{-1} \quad . \quad . \quad .(65)$$

Using the appropriate design criteria of Table 13 and the plug flow design equation (Equation 54), solve for volume of the pilot lagoon.

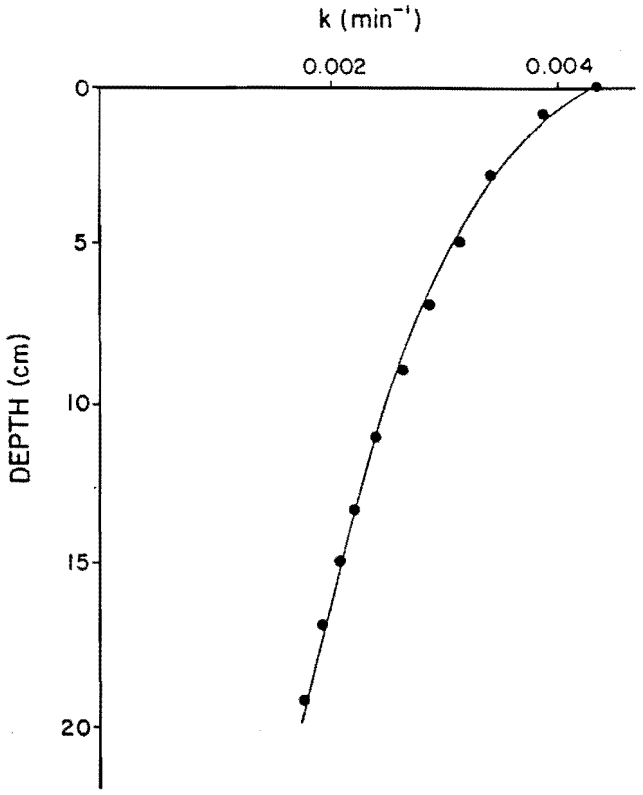


Figure 57. First-order rate constants as a function of lagoon depth for the photooxidation of bromacil in a synthetic waste sensitized by 0.1 mg/l methylene blue under 60 W/m^2 solar radiation.

$$\frac{C}{C_o} = e^{-k_{mean}\left(\frac{Vol}{Q}\right)} \quad . \quad . \quad . \quad .(66)$$

where

C_o = influent waste concentration (mg/l)

C = desired effluent waste concentration (mg/l)

k_{mean} = mean first-order rate constant for waste degradation (min^{-1})

Q = wastewater flow rate entering lagoon (m^3/min)

Vol = volume of lagoon (m^3)

Substituting the appropriate design criteria from Table 13, the k_{mean} of 0.00260 min^{-1}, and the corresponding $Q_{influent}$ of 0.901 m^3/min associated with 7 hrs of solar radiation, the volume of the lagoon is 2560 m^3. Dividing by the design depth, 0.20 m, results in a lagoon area of 12800 m^2.

The design was performed for 25 depths (2 cm intervals to a depth of 50 cm) for every datum of the factorial design matrix in Table 14. The lagoon area requirements were calculated as a function of the lagoon depth with the results shown in Figure 58 for 0.1, 0.25, 0.5, and 2.0 mg/l methylene blue for 7 hr solar radiation exposure. The four curves indicate that a large area is required for very shallow depths and a substantial decrease in area with added depth up to depths of about 25 cm. The asymptotic section of the curve is related to decreasing reaction rate as a function of depth balanced by the increase in volume. In other words, with increasing depth the composite first-order rate constant decreases, but the detention time of the lagoon, Vol/Q, increases, resulting in a near-constant change in area with depth.

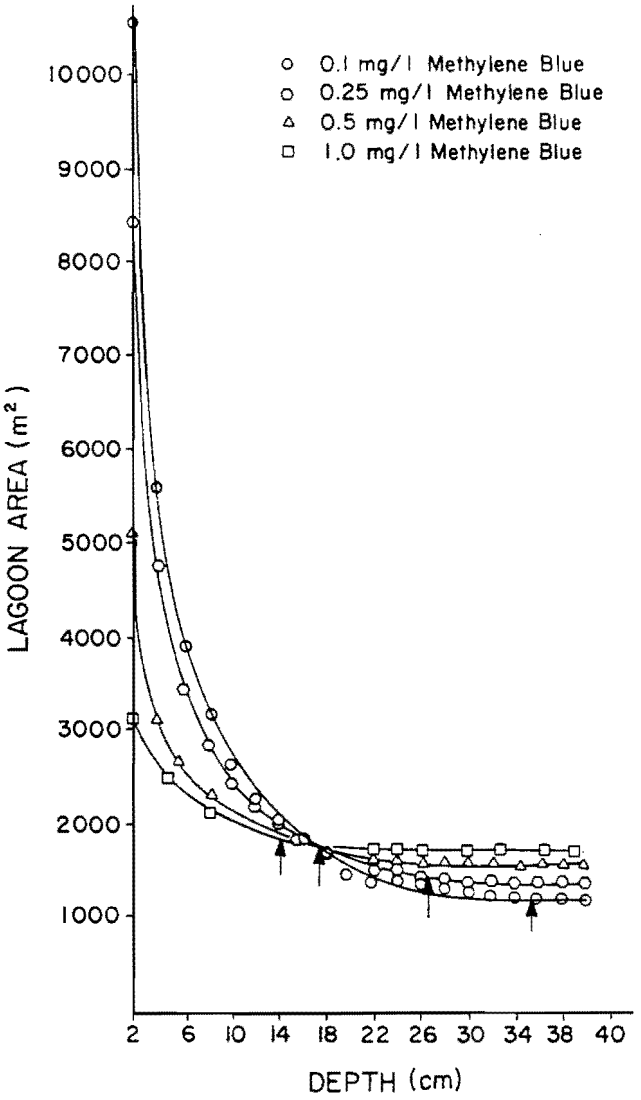


Figure 58. Lagoon area requirements as a function of lagoon depth for four methylene blue concentrations.

A reasonable design criterion is to set the lagoon depth so that less than a 2.5 percent decrease in area results from a 2 cm increase in depth. This point is indicated by an arrow on the four curves in Figure 58. At this point, land requirements are at a practical minimum. The depth is still shallow enough for sufficient mixing and diffusion so that aeration and mechanical mixing to prevent stratification (Wetzel 1975) would not be necessary. Equation 16, the depth model, can be used for lagoon design only if the lagoon does not stratify during operation. Short detention time also reduces stratification since the water is not in the lagoon long enough to absorb heat and stratify. Also, the sediments in a shallow lagoon play an important role in inhibiting stratification by releasing heat to the water stored near the bottom of the lagoon. Hutchinson (1957) showed that for 1.7 m deep Hula Lake, Israel, the sediments

contributed 37.9 percent of the heat. Sediments of 12 m deep Lake Mendota, Wisconsin, contributed only 7.8 percent. Sediments in a 30-cm deep lagoon would probably play a key role in absorbing solar infrared radiation and releasing it to the lagoon, resulting in eddy diffusion and inhibition of stratification. Wetzel (1975) presented data for temperature and percent solar radiation as a function of depth for Crooked Lake and Little Crooked Lake, Indiana. The circulating epilimnion of Crooked Lake was 4 m deep. Approximately 84 percent of the total solar radiation had been attenuated at the bottom of the epilimnion. For Little Crooked Lake, 95 percent of the total solar radiation was attenuated at the bottom of the 2.5 m deep epilimnion. Approximately 70 percent of the total solar radiation is attenuated at a 30-cm depth in a photooxidation lagoon. The sediments would also contribute significantly to the heat budget, result in eddy diffusion, and enhance circulation. At 30-cm depth, a photooxidation lagoon is unlikely to stratify. This tenet, however, must be tested using a photooxidation pilot lagoon.

A lagoon with a high composite first-order reaction rate and low detention time will guard against algal and bacterial growth, negating dye adsorption and light attenuation associated with suspended solids. The consequent lagoon design is a shallow lagoon with short detention time rather than a deep lagoon with long detention time.

Photooxidation lagoon area requirements for the six solar exposure time times seven methylene blue concentration design matrix are shown in Table 15. A minimum photooxidation lagoon area of 5470 m^2 resulted from design with 0.1 mg/l methylene blue and 3 hr solar exposure time. The two opposing factors in optimum solar exposure time were high zero-depth photooxidation rate constant associated with the higher light intensity at midday vs. increasing $Q_{influent}$ that increased dramatically as the solar exposure time of the lagoon was shortened. This increasingly high $Q_{influent}$ associated with shorter lagoon solar exposure times overrides the importance of the high k associated with the more abundant light intensity of midday at a solar exposure time between 2 and 3 hrs.

The minimum land requirement was associated with addition of 0.1 mg/l of methylene blue when the high composite first-order rate constant was averaged over depth. In lagoon design, successive depth layers should be used to determine the optimum sensitizer concentration and minimum land requirement. Acher and Saltzman (1980) found maximum sensitized photooxidation of bromacil at 5 mg/l methylene blue concentration.

A low concentration of methylene blue provided optimum design because of the low light attenuation associated with the low concentration of dye. A 5 mg/l methylene blue concentration gives a higher photooxidation rate at the surface but almost none at any depth. A low concentration of methylene blue, however, will maintain the highest possible composite photooxidation rate.

Design Option II: Design for cloudless winter day with flow equalization for cloudy days.

The second setting checked was to base the design on a cloudless day with provision to hold the water through overcast periods. In order to illustrate this method, a sensitized photooxidation pilot lagoon to treat the synthetic waste described in Table 12 and Figure 54, and the design conditions shown in Table 13. The design assumed that the maximum number of consecutive cloudy days is five, and that the flow equalization basin, which would fill during the five consecutive cloudy days, could be emptied by three consecutive cloudless days following the cloudy days. Solar radiation as a function of

Table 15. Lagoon dimensions for Design Option I sensitivity analyses based on seven methylene blue concentrations and six solar radiation exposure times.

Solar Radiation Exposure Time Criteria \ Sensitizer Concentration (mg/l)	lagoon dimensions (mxm^2) 0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=60W/m^2 Q=0.901 m^3/min	0.44 x 641000	0.40 x 439000	0.36 x 7100	0.26 x 8190	0.18 x 8770	0.14 x 9360	0.12 x 10700
t=6 hr Rad=80 W/m^2 Q=1.05 m^3/min	0.44 x 556000	0.40 x 384000	0.36 x 6230	0.26 x 7190	0.18 x 7780	0.14 x 8170	0.12 x 9360
t=5 hr Rad=100 W/m^2 Q=1.26 m^3/min	0.44 x 539000	0.40 x 369000	0.36 x 5990	0.26 x 6920	0.18 x 7522	0.14 x 7870	0.12 x 8990
t=4 hr Rad=130 W/m^2 Q=1.57 m^3/min	0.44 x 506000	0.40 x 346000	0.36 x 5630	0.26 x 6490	0.18 x 6940	0.14 x 7400	0.12 x 8460
t=3 hr Rad=180 W/m^2 Q=2.10 m^3/min	0.44 x 491000	0.40 x 337000	0.36 x 5470	0.26 x 6280	0.18 x 6740	0.14 x 7170	0.12 x 8200
t=2 hr Rad=230 W/m^2 Q=3.15 m^3/min	0.44 x 576000	0.40 x 394032	0.36 x 6420	0.26 x 8730	0.18 x 7980	0.14 x 8420	0.12 x 9630

time of day for a cloudless winter day for Logan, Utah, is shown in Figure 59. As with Design Option I, six solar exposure times were chosen from this curve. Zero-depth first-order photo-oxidation rate constants as a function of seven methylene blue concentrations and six solar exposure times are shown in Table 16.

Flow equalization basin area requirements were calculated based on the need to hold five days of wastewater from cloudy days. Flow equalization basin volume for the design options in Table 16 are

$$V = 0.263\ m^3/min \cdot 5\ days \cdot 1440\ min/day \quad . . . . . (67)$$

$$Vol = 1{,}894\ m^3 \quad . . . . . (68)$$

The area of the flow equalization basin, using the 2 m recommended depth of Metcalf and Eddy (1979) is

$$Area = 1849 m^3/2m \quad . . . . . (69)$$

$$Area = 947\ m^2 \quad . . . . . (70)$$

The maximum $Q_{influent}$ may be calculated based on the solar exposure time and the assumption that the flow equalization basin should be emptied in three consecutive cloudless days.

$$Q_{influent} = \left(\frac{V}{t_{exposure} \cdot \frac{60\ min}{hr}}\right)/3\ days + Q_{base} \quad . . . . (71)$$

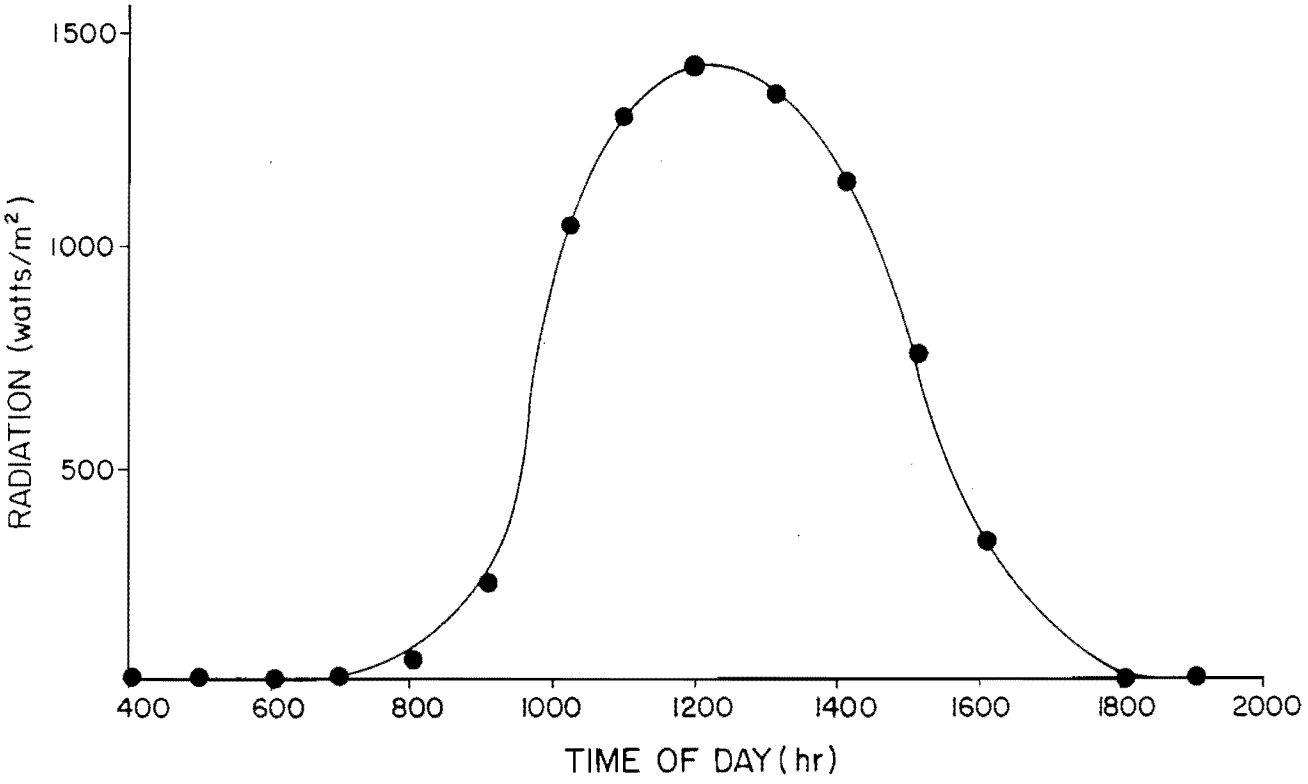


Figure 59. Solar radiation as a function of time of day for December 8, 1981, a cloudless winter day, Logan, Utah (Latitude 42° North).

Table 16. Zero-depth sensitized photooxidation rate constants for Design Option II sensitivity analysis based on seven methylene blue concentrations and six solar radiation exposure times.

Solar Radiation Exposure Time Criteria / Sensitizer Concentration (mg/l)	Zero-depth $k(min^{-1})$						
	0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=250 W/m^2 Q=2.40 m^3/min	0.000140	0.000244	0.0174	0.0223	0.0646	0.0964	
t=6 hr Rad=500 W/m^2 Q=2.80 m^3/min	0.000280	0.000487	0.0348	0.0446	0.129	0.193	
t=5 hr Rad=830 W/m^2 Q=3.36 m^3/min	0.000467	0.000812	0.0580	0.0774	0.215	0.321	
t=4 hr Rad=1070 W/m^2 Q=4.21 m^3/min	0.000598	0.00104	0.0743	0.0952	0.275	0.411	
t=3 hr Rad=1250 W/m^2 Q=5.61 m^3/min	0.000701	0.00122	0.0870	0.112	0.323	0.482	
t=2 hr Rad=1340 W/m^2 Q=8.41 m^3/min	0.000747	0.00130	0.0928	0.119	0.344	0.514	

where

$t_{exposure}$ = time of solar exposure for lagoon design (hr)

V = volume of flow equalization basin (m^3)

Q_{base} = steady base wastewater flow (m^3/min)

$Q_{influent}$ = maximum influent wastewater flow during time of solar exposure

Maximum $Q_{influent}$, with corresponding solar exposure times and zero-depth first-order photooxidation rate constants as a function of seven methylene blue concentrations, is shown in Table 16.

Results of photooxidation lagoon design based on minimum practical area (less than 2.5 percent decrease in lagoon area per 2 cm increase in depth) are shown in Table 17 for the data in the six solar exposure times x seven methylene blue concentration design matrix. Minimum lagoon area requirement was for the 4 hr solar exposure time with 0.1 mg/l methylene blue. The minimum land requirement was 1870 m^2 with a depth of 0.36 m.

To determine if aeration is necessary in the photooxidation lagoon, Equations 47 and 48 were used to calculate the dissolved oxygen concentration at the end of the plug flow regime in the lagoon:

$$(C_s-C) = (C_s-C)_o\, e^{-\hat{k}x/v_x} + \frac{(\text{Substrate})_o\, k}{\hat{k}-k}\left(e^{-kx/v_x} - e^{-\hat{k}x/v_x}\right) \quad . \quad . \quad . \quad .(50)$$

and

$$\hat{k} = (DV/h^3)^{0.5} \quad . \quad . \quad . \quad . \quad . \quad .(51)$$

where symbols were defined previously.

Substituting all these coefficients into Equation 50 gives a dissolved oxygen deficit of 3.1 mg/l. Consequently, the amount of dissolved oxygen remaining at the end of the plug flow regime is 6.0 - 3.1 = 2.9 mg/l. Since 1 mg/l dissolved oxygen is sufficient to support the maximum sensitized photooxidation rate, no aeration is necessary. Dissolved oxygen deficits were calculated for the other lagoon designs in Tables 15 and 17. None of the dissolved oxygen levels dropped below 1 mg/l; therefore, for this waste and photooxidation lagoon design, no aeration is necessary. Treatment of a more concentrated waste would necessarily have a higher oxygen uptake rate constant, as shown in Figures 39 and 40, and aeration may be required.

Economics

The selection of the optimal lagoon design from among these possibilities should be based on minimum cost. The costs may be classified between capital costs and operation and maintenance costs (Targuin and Blank 1976). Capital costs for photooxidation lagoons include construction costs, land costs, and appurtenance costs. A lagoon construction cost of $5.00 per m^2 was assumed since no costing figures are available for shallow (e.g., 0.3 m to 0.4 m depth) lagoons. Facultative lagoon cost estimates reported by U. S. EPA (1980) are inappropriate, since facultative lagoons are constructed at a depth of 2 to 3 m. Flow equalization and sand filter construction costs were estimated from U.S. EPA (1980). Land costs were approximated at $6,000 per acre. Land costs would vary according to geographic location. Appurtenances include chemical feeds ($400, Conley Co., Salt Lake City, Utah), pumps, piping, wiers, and structures. Total capital cost was calculated using the format of U.S. EPA (1980) shown in Table 18.

Table 17. Lagoon dimensions for Design Option II sensitivity analysis based on seven methylene blue concentrations and six solar radiation exposure times.

Solar Radiation Exposure Time Criteria \ Sensitizer Concentration (mg/l)	Lagoon Dimensions (mxm^2)						
	0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=250 W/m^2 Q=2.40 m^3/min	0.44 x 408000	0.40 x 278000	0.36 x 4560	0.26 x 6110	0.18 x 4970	0.14 x 5990	0.12 x 6860
t=6 hr Rad=500 W/m^2 Q=2.80 m^3/min	0.44 x 238000	0.40 x 162700	0.36 x 2660	0.26 x 3620	0.18 x 2900	0.14 x 3500	0.12 x 4000
t=5 hr Rad=830 W/m^2 Q=3.36 m^3/min	0.44 x 171000	0.40 x 117000	0.36 x 1920	0.26 x 2610	0.18 x 2090	0.14 x 2520	0.12 x 2880
t=4 hr Rad=1070 W/m^2 Q=4.21 m^3/min	0.44 x 167056	0.40 x 114000	0.36 x 1870	0.26 x 2550	0.18 x 2040	0.14 x 2460	0.12 x 2820
t=3 hr Rad=1250 W/m^2 Q=5.61 m^3/min	0.44 x 190000	0.40 x 152000	0.36 x 2130	0.26 x 2880	0.18 x 2310	0.14 x 2790	0.12 x 3200
t=2 hr Rad=1340 W/m^2 Q=8.41 m^3/min	0.44 x 267000	0.40 x 183000	0.36 x 2990	0.26 x 4070	0.18 x 3260	0.14 x 3930	0.12 x 4500

Table 18. Guidelines used for computing total capital costs of lagoon construction (from U.S. EPA 1976).

I. Component Construction Costs		$
	Subtotal 1	$
II. Non-component Costs		
Piping (5-15% of Subtotal 1)		$
Electrical (6-10% of Subtotal 1)		$
Instrumentation (5-8% of Subtotal 1)		$
Site Preparation (5% of Subtotal 1)		$
	Subtotal 2	$
III. Non-construction Costs		
Engineering and Construction Supervision (15% of Subtotal 1 + Subtotal 2)		$
Contingencies (15% of Subtotal 1 + Subtotal 2)		$
Land Cost		$
	Subtotal	$
Total Capital Cost = Subtotal 1 + Subtotal 2 + Subtotal 3		

Operation and maintenance costs include aeration required for the flow equalization basin, backwashing and maintenance of sand filters, pumping, and sensitizer costs. Operation and maintenance costs for flow equalization and rapid sand filtration were from U.S. EPA (1980). Methylene blue costs were based on a cost estimate of $13.00/kg supplied by a manufacturer in Europe (LeBaron 1982). For calculation of methylene blue requirements, it was assumed that one feed at the headworks of the lagoon would add the required concentration of methylene blue, and two additional feeds along the plug flow regime of the lagoon would each add 50 percent of the original methylene dose to account for sensitizer bleaching. No aeration costs were included in operation and maintenance costs since diffusion and dissolved oxygen residual entering the lagoon were calculated to be sufficient to maintain dissolved oxygen concentrations above the required level of 1 mg/l.

Capital and operation and maintenance costs were converted to equivalent uniform annual cost (EUAC) over a 20 year period using an annual interest rate of 10 percent. For illustrative purposes, a 20 year EUAC cost estimate of the Option I design for 7 hour solar exposure time with 0.1 mg/l methylene blue follows:

Component Construction Costs

Lagoon construction (including liner) 7100 m^2 x $5/$m^2$	$35,500
Flow equalization basin construction (from U.S. EPA 1980)	$70,000
Intermittent sand filter construction (from U.S. EPA 1980)	$11,000
Subtotal 1:	$116,500

Non-Component Costs

Piping (10% x $116,500)	$11,650
Electrical (8% x $116,500)	$9,320

Instrumentation (includes chemical feeds - 5% x $116,500)	$ 5,825
Site preparation (5% x $116,500)	$ 5,825
Subtotal 2:	$32,620

Non-Construction Costs

Engineering and construction supervision	
15% x ($116,500 + $32,620)	$22,368
Contingencies 15% x ($116,500 + $32,620)	$22,368
Land for lagoon (7100 m^2 = 1.75 acre x $6,000/acre)	$10,500
Land for flow equalization (134 m^2 = 0.034 acre x $6,000/acre)	$ 204
Miscellaneous land (0.5 acre x $6,000/acre)	$ 3,000
Subtotal 3:	$58,440
Total Capital Costs	$207,560

Operation and maintenance (O&M) costs

Lagoon sensitizer costs:

Sensitizer addition: 0.1 g/m^3 - initial dose + 2 doses of 0.05 g/m^3 = 0.2 g/m^3

Total sensitizer = 27,600 g	$ 359/year
Flow equalization O&M (from U.S. EPA 1980)	$ 1,800
Sand filtration O&M (from U.S. EPA 1980)	$ 900
Total O&M	$ 3,059

Treating capital costs as initial costs and O&M costs as yearly, recurring costs, the EUAC over 20 years may be calculated using an interest rate of 10 percent and tables from Targuin and Blank (1976)

$$EUAC = [P - SV(P/F, 1\%, n)] (A/P, i\%, n) + \text{annual cost} \quad . \quad . \quad . \quad . \quad . \quad .(72)$$

where

EUAC = equivalent uniform annual cost ($/year)

P = present cost ($)

(A/P, i%, n) = an equivalency factor for known interest rate (i) and engineering lifetime (n)

Assuming a salvage value for land and equipment to be 50 percent of the capital cost

$$EUAC = [(\$207,560) - (\$103,780)\ (.1486)]\ (.11746) + \$3059 \quad . \quad . \quad . \quad . \quad .(73)$$

$$EUAC = \$25,500/year \quad . \quad . \quad .(74)$$

Estimates of the yearly operation and maintenance cost and 20-year EUAC cost are presented in Table 19 for the Design Option I sensitivity analysis matrix and in Table 20 for the Design Option II sensitivity analysis matrix. The lowest EUAC on either table ($20,100) and therefore the design of choice is for a 0.1 mg/l methylene blue concentration with a 4-hour solar radiation exposure time and the Design Option II criterion of a cloudless day. For comparative purposes, it is useful to convert the cost of this design to an amount per million gallons (MG) of treated waste (Nemerow 1978). Since the amount of wastewater treated in one year at a rate of 0.1 MGD is 3.65×10^7

Table 19. Equivalent uniform annual cost (EUAC) for 20 years and annual operation and maintenance (O&M) costs for the Design Option I sensitivity analysis.

Solar Radiation Exposure Time Criteria \ Sensitizer Concentration (mg/l)	Lagoon costs (EUAC ($/yr))/(O&M ($/yr))						
	0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=60W/m^2 Q=0.901 m^3/min	701000 2880	486000 2969	25500 3059	26800 3598	27900 4495	29500 6290	32700 9880
t=6 hr Rad=80 W/m^2 Q=1.05 m^3/min	610000 2880	427000 2969	24600 3059	25700 3598	26900 4495	28200 6295	31300 9880
t=5 hr Rad=100 W/m^2 Q=1.26 m^3/min	592000 2880	411000 2969	24400 3059	25400 3598	26600 4495	27900 6295	30900 9880
t=4 hr Rad=130 W/m^2 Q=1.57 m^3/min	557000 2880	386000 2969	24000 3059	25500 3598	26000 4495	27400 6295	30300 9880
t=3 hr Rad=180 W/m^2 Q=2.10 m^3/min	541000 2880	377000 2969	23900 3059	25300 3598	26700 4495	27100 6295	30000 9880
t=2 hr Rad=230 W/m^2 Q=3.15 m^3/min	632000 2880	438000 2969	24900 3059	27900 3598	28000 4495	30300 6295	31600 9880

Table 20. Equivalent uniform annual cost (EUAC) for 20 years and annual operation and maintenance (O&M) costs for the Design Option II sensitivity analysis.

Solar Radiation Exposure Time Criteria \ Sensitizer Concentration (mg/l)	Lagoon costs (EUAC ($/yr))/(O&M ($/yr))						
	0.05	0.075	0.1	0.25	0.5	1.0	2.0
t=7 hr Rad=250 W/m^2 Q=2.40 m^3/min	453000 2880	314000 2969	23000 3059	24700 3598	24000 4495	26000 6295	28700 9880
t=6 hr Rad=500 W/m^2 Q=2.80 m^3/min	272000 2880	191000 2969	20900 3059	22100 3598	21800 4495	23400 6295	25700 9880
t=5 hr Rad=830 W/m^2 Q=3.36 m^3/min	200000 2880	143000 2969	20200 3059	21000 3598	21000 4495	22300 6295	24500 9880
t=4 hr Rad=1070 W/m^2 Q=4.21 m^3/min	196000 2880	140000 2969	20100 3059	21500 3598	20900 4495	22300 6295	24400 9880
t=3 hr Rad=1250 W/m^2 Q=5.61 m^3/min	220000 2880	180000 2969	20500 3059	21800 3598	22100 4495	22600 6295	24800 9880
t=2 hr Rad=1340 W/m^2 Q=8.41 m^3/min	303000 2880	213000 2969	21400 3059	23100 3598	23100 4495	25600 6295	26200 9880

gallons, the cost per million gallons is $\$20,100 \times 10^6/3.65 \times 10^7 = \$551/MG$.

Industrial waste cost figures were reported by Nemerow in 1975 dollars. These cost estimates adjusted to present worth in 1983 by using an 8-percent inflation rate (Targuin and Blank 1976) for selected industrial waste treatment technologies are shown in Table 21. It is difficult to know how the cost estimates reported by Nemerow were calculated. They were apparently collected from a number of sources; hence the great variability in the estimates. The variability may also be due to the nature and strength of the waste. For example, the cost estimate supplied by Nemerow (1978) for treatment of a pesticide waste by activated carbon is relatively low compared to the other types of industrial waste treatment listed. This treatment may be for a weak waste in which carbon regeneration was not a major expense. Nonetheless, the cost estimate for sensitized photooxidation is lower than that given for many of the waste treatment schemes listed in Table 21.

U.S. EPA (1976) reported on the BPT (best possible treatment) technology for three classes of pesticide wastes. These treatment processes and associated costs are listed in Table 22. The operation and maintenance costs per 0.1 MG are $192,000, $254,000, and $217,000 for the three processes. These values are substantially greater than the $3,059 required for the yearly operation of a 0.1 MGD sensitized photooxidation lagoon. The low-cost of sensitized photooxidation comes because there is no need for aeration, low dye cost, and the low-technology and low-cost advantages characteristic of lagoons, such as little need for instrumentation and operator supervision. The largest cost component for the lagoon designed in this study was for flow equalization. Without flow equalization the annual O&M costs for the 0.1 MGD photooxidation lagoon would be ($3,059 - $1,800) = $1,259. This EUAC cost converted per volume of wastewater without flow equalization is $3,860, which is reasonable. A sensitized photooxidation lagoon could be built without flow equalization if the industry discharged primarily during the day. The need for flow equalization would therefore depend on the discharge quantity and quality characteristics of the particular waste.

The above comparisons show sensitized photooxidation lagoon treatment to be economically competitive with the other processes listed in Tables 21 and 22. Photooxidation lagoons would be particularly cost effective if the effluent could be discharged to a municipal system for BOD polishing. This should be permissible as long as the photooxidation products are nontoxic and biologically labile.

Waste treatment costs are difficult to estimate, particularly when a waste treatment process is as new and undeveloped as sensitized photooxidation. In addition, the cost is sensitive to the particular waste. An example is the need for pH adjustment. Industrial wastes can vary in pH from very acidic to very basic (Atkins 1972). The need for pH adjustment would depend on the distance of the waste from neutrality and the alkalinity of the waste. This can result in a wide range of costs necessary for pH adjustment and treatment. A second variable affecting cost is the spectral quality of the waste. A turbid waste requires a shallow lagoon and a large area, further increasing the costs. Conversely, a waste with few dyes that absorb light in the visible region will allow for deep lagoon design and lower land costs. McKay et al. (1980) found that silica has the capability for removing color from water and wastewater. The sand filter placed at the headworks of the lagoon may remove some of the soluble turbidity from the waste, enhancing light penetration and lagoon efficiency. Numerous other factors can cause variability in costs. These include the time required for

Table 21. Estimates of capital and operation and maintenance costs for typical industrial waste treatment processes (from Nemerow 1978).

Industry	Type of Treatment	Cost Per MG (1983 Cost)
Textile - synthetic weaving mill	Secondary	$8813
Textile - cotton finishing plant	Secondary	$120-$315
Textile - woven carpets and rugs	Chemicals and settling basin	$3128
Metal plating	Gas chlorination	$7870
Metal plating	NaOCl	$13,894
Metal plating	Neutralization and settling	$2587
Fuel oil waste	Reverse osmosis	$26-$1222
Fuel oil waste	Centrifugation	$68-$2258
Organic chemical waste	Secondary	$1364
Pesticides	Activated Carbon	$65

Table 22. Best Possible Treatment (BPT) technology for three major categories of pesticide waste streams and associated costs (from U.S. EPA 1976).

Pesticide Waste	Unit Processes	Waste-water Flow Rate (MGD)	Capital Cost	Operation and Maintenance Costs
Halogenated Organics	Flow equalization pH adjustment Filtration Carbon adsorption Biological treatment	0.798	$5,190,000	$1,536,000
Organo-phosphorus	Alkaline hydrolysis Flow equalization pH adjustment Biological treatment	0.835	$6,666,700	$2,116,700
Organo-nitrogen	Hydrolysis pH adjustment Flow equalization Biological treatment	1.08	$6,693,600	$2,187,000

photooxidation to yield products that are biologically labile and the variability in land costs.

In summary, sensitized photooxidation was found to be a process that competes cost-wise with physicochemical methods for detoxification prior to polishing by biological treatment. The objective of this study was to develop design methods and engineering criteria for sensitized photooxidation lagoons. The effects of pH and temperature incorporated in a rational model developed for sizing sensitized photooxidation lagoons. Investigation of the oxygen uptake rate and effect of dissolved oxygen residual on sensitized photooxidation rate provided data for calculation of aeration requirements. Based on the results of this research, a sensitized photooxidation pilot lagoon was designed to treat a bromacil waste. The guidelines established in this study may be used to design a sensitized photooxidation pilot lagoon from bench scale data for any toxic or refractory industrial waste. The cost estimates for the treatment of industrial waste using sensitized photooxidation seem reasonable, but the cost estimates and pilot plant performance data deserve further verification. Refinement of a treatment process requires years of investigation. This research provides initial design criteria for sensitized photooxidation lagoons and thereby gives the engineer the capability, given bench scale data, to design an efficient sensitized photooxidation lagoon to treat industrial wastes.

ENGINEERING SIGNIFICANCE

The previous 20 years have provided a wealth of information on the theoretical aspects of sensitizer-mediated photochemistry. However, there have been few investigations dealing with the application of sensitized photooxidation to waste treatment. Sargent and Sanks (1974, 1976) provided the most engineering-oriented approach in the application of sensitized photooxidation to waste treatment. Their studies, however, did not provide sensitized photooxidation lagoon design criteria.

This dissertation provides quantitative criteria for sizing sensitized photooxidation lagoons based on bench-scale laboratory data for any type of waste and known light quantity and quality. Secondly, the need for pH adjustment, optimum sensitizer concentration, and aeration requirements may be determined from information presented in this research. Pilot photooxidation lagoons may be designed using the criteria presented in this study without the trial-and-error approach often used in the empirical design of new unit processes. Less time and effort may be required to optimize the photooxidation pilot lagoon if the photochemical mechanisms are followed as presented in this dissertation. An industry should be able to design and construct a sensitized photooxidation pilot lagoon to treat their waste based on bench-scale laboratory data and computer solutions of the depth model provided.

The use of rational design for the biological treatment of wastes is now coming of age after decades of empirical design. This is leading to improvements in the design, operation and maintenance, and troubleshooting capabilities of biological waste treatment facilities. A rational approach to design based on fundamental principles and mechanisms may allow rapid development and improvement in sensitized photooxidation lagoon treatment of toxic and biologically recalcitrant wastes.

SUMMARY AND CONCLUSIONS

Engineering design criteria were developed for sensitized photooxidation lagoons. Treatment of the refractory pesticides bromacil, terbacil, and fluometuron was investigated using methylene blue and riboflavin as sensitizers. The effects of pH and temperature on sensitized photooxidation rates were investigated. A model was developed to predict sensitized photooxidation as a function of lagoon depth. Aeration requirements for sensitized photooxidation were calculated based on oxygen uptake rate and the effect of dissolved oxygen residual on sensitized photooxidation rate. A sensitized photooxidation pilot lagoon to treat waste from the industrial synthesis of bromacil was designed. Cost estimates showed that sensitized photooxidation lagoons may provide an inexpensive means of treating industrial wastes that are not compatible with biological treatment.

The quantitative information developed for this analysis suggests the following conclusions:

1. Methylene blue-sensitized photooxidation of bromacil, terbacil, and fluometuron was most efficient at high pH, but practical rates of photooxidation can be maintained at neutral pH. The rate of bleaching of methylene blue was highest above pH 8.

2. The optimum pH of riboflavin-sensitized photooxidation depended on the substrate and therefore on the waste being treated. The rate of riboflavin bleaching was highest above pH 7.

3. Sensitized photooxidation rate as a function of depth is mathematically described by a first order kinetic model. The model is based on light intensity, extinction coefficient, and quantum yield integrated over wavelengths across the visible spectrum; it provided excellent correlation with laboratory data. The model can be used to design and size sensitized photooxidation lagoons as functions of incident light quantity and quality, spectral quality of the waste, and sensitizer concentration.

4. A dissolved oxygen residual of 1 to 2 mg/l was required for maximum rates of methylene blue-sensitized photooxidation. Riboflavin-sensitized photooxidation required higher dissolved oxygen concentrations for maximum sensitized photooxidation rate. High substrate concentration necessitates a higher dissolved oxygen residual to maintain maximum photooxidation rate.

5. Turbulent mixing (G values $\geq$ 29.1) associated with high aeration had no effect on sensitized photooxidation rate relative to a system under static hydraulic conditions.

6. A dissolved oxygen residual below 1 mg/l leads to increased methylene blue bleaching due to transfer of energy in sensitizer-sensitizer interactions rather than transfer of methylene blue triplet energy to molecular oxygen or substrate.

7. Dissolved oxygen uptake in sensitized photooxidation is proportional to the concentration of substrate. Treatment of dilute wastes may not require aeration, whereas strong industrial wastes may require aeration in proportion to the concentration of the waste.

8. Temperature from 10°C to 35°C appears to have little effect on sensitized photooxidation rates or rates of sensitizer bleaching.

9. Products of sensitized photooxidation of bromacil were more biologically labile than bromacil. They were also toxic to microorganisms in the BOD analysis. The degradation products were not as susceptible to microbial degradation as glucose and glutamic acid under the conditions of the 20-day BOD test.

10. A sensitized photooxidation lagoon system is potentially more economically efficient than conventional treatment processes.

RECOMMENDATIONS FOR FURTHER STUDY

1. The design criteria developed in this dissertation, using a sensitized photooxidation pilot lagoon, should be verified for more general application.

2. The capability of sensitized photooxidation lagoons to treat a larger variety of actual industrial wastes should be studied.

3. Deviations from the Beer-Lambert Law and the effects of light scattering on sensitized photooxidation should be investigated, since it may enhance photooxidation lagoon efficiency and decrease lagoon detention time.

4. This study assumed that wind action, eddy diffusion, and the relatively high lagoon wastewater velocity associated with low detention time would create sufficient mixing in a 36 cm deep lagoon to occasionally bring wastewater from the deeper part of the lagoon to the surface. This assumption should be evaluated by a pilot lagoon study.

5. The growth of microorganisms in sensitized photooxidation lagoons and effect on lagoon efficiency should be documented.

6. A rapid sand filter was deemed necessary for lagoon optimization. The need for rapid sand filters for suspended solids removal of lagoon influent should be investigated.

7. The biological recalcitrance of sensitized photooxidation degradation products should be studied further to determine the feasibility of photooxidation lagoons as an industrial pretreatment process.

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