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FINAL REPORT

PROJECT No. I-171-80

**Use of Solar Energy for the
Detoxification Of Organic Pesticides in
Water**

A.J. Acher, E.J. Middlebrooks, V.D. Adams

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- 1) Pesticides - Biodegradation 2) Pesticides - Toxicology
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Abstract

The use of the sunlight or artificial light and dye-sensitizer for detoxification of organic pesticides in water was investigated.

The pesticides studied were uracil (terbacil), s-triazine (atrazine, ametryne, atraton) and amide (propachlor) herbicide derivatives.

Different factors controlling the photochemical degradation rate of above herbicides into polluted water sources and sewage effluents (light intensity, pH, concentration, temperature, sensitizer, chemical structure, suspended solids, etc.) were taken into consideration.

The photodegradation products were isolated and their chemical structure determined by combined spectroscopical methods. Their phytotoxicity and the phytotoxicity of the treated water towards sensitive test plants were checked.

A mathematical model, based on light intensity, extinction coefficient, quantum yield over wavelengths across visible spectrum and constant rate of reactions, provided excellent correlation with laboratory data and can be used for the design of photooxidation lagoon.

The laboratory experience data, included in the six annexed papers and in the Ph.D dissertation thesis, enable the design and the operation of a pilot photooxidation lagoon for reusing of the treated water for agricultural purposes.

Description of the research results

The major objectives of this research, as they are presented in page IV of the research proposal, and the results obtained during 26 months of elaborate work of both Israeli and American teams, are given in this final report.

Objectives:

The major objectives of this research were:

- a. To study the factors controlling the photochemical degradation rate of organic contaminants of various chemical structures (e.g. uracils, triazines, urea derivatives) in polluted water sources and sewage effluents.
- b. To separate and identify the degradation products resulting from the photooxidation process, and to compare them with possible natural metabolites of organic agrochemicals.
- c. To study the phytotoxic properties of the photodegradation products.
- d. To develop an effective method for the detoxification of organic pollutants which could be applicable for both polluted natural water and domestic and industrial wastewater.

Results:

The pertinent results obtained in the laboratory research following the aims of the above objectives are included in five reviewed publications (two still in press), in a paper presented at "The Fifth International Congress of Pesticide Chemistry (IUPAC), September 1982, Kyoto, and in a Ph.D. Dissertation Thesis (Utah State University):

1. Photosensitized decomposition of Terbacil in aqueous solution.
J. Agric. Food Chem., 29, 707-711 (1981)

2. Removal of phytotoxicity of uracil herbicides in water by photodecomposition. Pesticide Science, 13, 211-217 (1982)
3. Identification of sensitized photooxidation products of s-triazine herbicides in water. J. Agric. Food Chem., 31, 138-142 (1983).
4. Factors affecting the photosensitized degradation of s-triazine herbicides in water. J. Environ. Quality, 12, in press (1983).
5. The photodecomposition of Propachlor. J. Agric. Food Chem., sent for publication (1983)
6. Sunlight photosensitized degradation of herbicides in water. Conference presented at: "The Fifth International Congress of Pesticide Chemistry (IUPAC), August 29-September 4, 1982, Kyoto, Japan. Abstracts Vb-2.
7. The development and design of dye-sensitized photooxidation water stabilization ponds for the treatment of industrial waste (Ph.D. dissertation thesis). R.J. Watts, Ph.D. candidate, Div. of Environ. Eng., Utah State University, 1983).

Conclusions and Suggestions

The expected contribution of this work was described in pages 4 and 5 of the research proposal:

- a. The elucidation of the chemical processes involved in the dye-sensitized photooxidation of various organic pollutants in water.
- b. The identification and characterization of the photodegradation products will contribute to the clarification of the effectiveness of the dye-sensitized photooxidation method in detoxifying contaminated water.

c. The development of a simple, economical and effective method of water detoxification which will enable the reuse of treated water for agricultural purposes.

The results and data included in papers (1-7) attached to this final report show that the expected contributions from this research were thoroughly fulfilled.

Papers 1 to 6 describe and discuss results and data connected to the above a and b paragraphs; the Ph.D. dissertation thesis describes and discusses results and data connected with paragraph c.

The study of the behavior of the uracil, s-triazine and amide herbicide derivatives, toward sensitized photooxidation, together with the work done on the phytotoxicity of the photooxidated waters on sensitive test plants, gave scientific support for the practical use of this method for sunlight-dye-detoxification of waters containing these pesticides.

The research undertaken at Utah Water Research Laboratory showed that photooxidation lagoons for waste detoxification treatment look promising from an engineering and economic standpoint. A mathematical model based on light intensity, extinction coefficient and quantum yield, integrated over wavelengths across visible spectrum provided excellent correlation with laboratory data.

This model can be used to design and size sensitized photo-oxidation lagoons as functions of incident light quantity and quality, spectral quality of the waste, dye concentration and rate of the photooxidation reactions.

In order to use all the data and the experience accumulated during this research by Israeli and American teams, and to develop a simple,

economical and effective method of water detoxification, pilot scale facilities must be developed. This will enable to investigate the

- practical design and operation of the photooxidation lagoon for reusing the treated water for agricultural purposes.

Table 1: The effect of suspended solids on the photodegradation of I^{*}

Suspended material		Reaction products		
Type	mg L ⁻¹	I μM	I _A	I _A yield ^{**} %
Kaolinite	50	8.4	69.3	87.0
	500	5.6	46.7	56.6
Bentonite	50	8.6	45.3	57.0
	500	55.9	30.1	93.3
Lake Kinneret	400	33.8	53.4	98.5
None	-	9.5	68.7	87.5

* Initial I concentration, 88 μM (20 mg L⁻¹); RF:1 molar ratio, 0.3; pH, 6; irradiation time, 3 h.

** Based on I decomposed

Table 2: The effect of dissolved organic matter on the photodegradation of I^{*}.

Organic Material mg L ⁻¹	RF μM	Reaction products		
		I μM	IA μM	IA yield %
80	0	88.0	0.0	0.0
400	0	81.5	1.3	20.0
400	26.6	66.4	8.0	37.0
none	26.6	9.5	61.6	78.5

* Initial I concentration: 88 μM (20 mg L⁻¹); RF:I molecular ratio 0.3; pH 6; irradiation time 3 h.

** Based on I decomposed.

Table 3: Response of oat seedlings to s-triazine solutions^{*}.

mg L ⁻¹	s-triazine solutions		
	I	II	III
1	6	7	7
5	5	4	5
10	2	3	1
15 (irradiated)	10	10	7
Distilled water	10	10	10

* Grades: 10 = no injury; 0 = total necrosis

Fig. 1 - The structure of s-triazines

Compound	Substituent group		
	R ₁	R ₂	R ₃
I	SCH ₃	CH(CH ₃) ₂	CH ₂ CH ₃
II	Cl	CH(CH ₃) ₂	CH ₂ CH ₃
III	OCH ₃	CH(CH ₃) ₂	CH ₂ CH ₃
IV	Cl	CH ₂ CH ₃	CH ₂ CH ₃
V	Cl	CH(CH ₃) ₂	CH(CH ₃) ₂

Fig. 2 - The effect of s-triazazine substituents on the photodegradation reaction.

Initial concentration 5 mg L⁻¹; herbicide:RF mole ratio 1;
initial pH 5.8-6.0.

Fig. 3 - The effect of the initial pH on the composition of the irradiated solutions.

Initial concentration 20 mg L^{-1} ; herbicide:RF mole ratio 0.3; irradiation time 60 min.

Fig. 4 - The effect of the initial RF:herbicide ratio on the photodegradation reaction.

Initial concentration 20 mg L^{-1} ; initial pH 5.8-6.0; irradiation time 100 min.

Fig. 5 - The effect of preirradiation of RF on its sensitizing activity.

Initial concentrations :RF 10 mg L^{-1} ; I 10 mg L^{-1} ;
initial pH 6.2; preirradiation time 60 min.

Solid lines - fresh RF; broken lines - bleached RF.

Fig. 6 - The effect of RF irradiation on its UV-VIS spectra.

RF concentration 10 mg L^{-1} .

THE PHOTODECOMPOSITION OF PROPACHLOR*

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Abstract

The photolysis of solutions of propachlor (I) was investigated. Photolysis carried out under UV-light (5h) led to about 80% decomposition of I. The three photodegradation products isolated were: N-isopropyl-oxindol (II), N-isopropyl-3-hydroxy-oxindol (III), and a product (IV) not completely identified.

Photolysis performed under visible light (12h) of the solution of I containing riboflavin led to the almost complete photodegradation of the title compound. From the irradiated solutions, only minute amounts of one photodegradation product were isolated and identified: *m*-hydroxypropachlor (V).

The chemical structures of the photodegradation products were determined by spectroscopic methods. The structures of II and V were also confirmed by comparison with the authentic samples prepared by chemical methods. The photodegradation products and the reaction mixture from visible light experiments were checked for phytotoxicity and found to be nontoxic to the test plants.

* Contribution from the Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel. No.668-E, 1983 series.

Introduction

Propachlor (2-chloro-N-isopropylacetanilide, I) is a pre-emergence herbicide effective against annual grasses and certain broad-leaved weeds (Martin, 1972). It was selected as a representative of the anilide herbicide group for photodecomposition studies aimed at finding a photochemical method of detoxification of water from organic pollutants. Such studies have already been carried out with uracil (Acher and Dunkelblum, 1979; Acher and Saltzman, 1980; Acher et al., 1981; Saltzman et al., 1982) and with s-triazine herbicides (Rejtő et al., 1983).

Herbicides from the anilide group are known as general growth inhibitors of young seedlings, or inhibitors of root growth. Studies of the specific mode of action of I showed that it causes a reduction in cell elongation and cell division rate, by inhibiting protein synthesis in root tips (Ashton and Crafts, 1973). The degradation of I in corn and soybeans has been reported (Jaworski, 1969), but the structure of the metabolite has not been defined. It was suggested that the chlorine atom of I has been displaced by a nucleophilic substrate in the plants.

Anilide compounds were found to rearrange under UV-light (Elad et al., 1965) and anilide herbicides might be expected to behave similarly (Crosby and Ming-Yu, 1969). However, virtually nothing has been reported on the photodecomposition of this group of herbicides.

The goal of this work was to study the photolysis of I under visible and UV-light at different reaction conditions, to isolate and identify the photoreaction products, and to check for their phytotoxic properties.

Experimental Section

Materials

Propachlor (I) (provided by Agan Ltd., Israel) was crystallized from 2-propanol-water m.p. 71-72°C (lit.mp 67-76°C, Martin, 1972).

N-Isopropyl oxyndol (2H indol-2-one, 1,3-dihydro, 1-isopropyl, II) was synthesized by cyclization of I with anhydrous AlCl_3 (Stolle, 1930). This reaction gave, beside II, the dealkylated oxyndol, IIa, m.p. 125-6°C (lit. m.p. 127°C, Harris, 1965).

m-Hydroxy 2-chloro-N-isopropyl acetanilide (V) - The methyl ether derivative was synthesized from m-anisidine by a method described by Walker et al. (1970). The cleavage of the methyl ether with BBr_3 (Benton and Dillon, 1942) afforded V.

The sensitizers riboflavin (RF) (BDH, H21632 Q) and methylene blue (MB) (BDH, H21632 Q) were used as freshly prepared water (deionized) solutions (200 mg L^{-1} for RF and 100 mg L^{-1} for MB) or dissolved directly into the herbicide solutions before irradiation.

The solutions tested by bioassay were different concentrations of I ($0.5, 1, 5, 10 \text{ mg L}^{-1}$), and an irradiated solution (initial concentration 40 mg L^{-1} ; RF: I, 0.3 mole/mole, pH 4). The irradiated reaction mixture still contained 0.7 mg L^{-1} I after 10 h of irradiation; its pH was adjusted to 6.5 before use. This solution was checked as such (A) and after dilution 1:4 (B).

The test plants used were oat (Avena sativa), sorghum (Sorghum bicolor), and tomatoes (Solanum lycopersicum).

Methods

The gas chromatograph used was a Tracor No.506 instrument equipped with a Tracor No.702 NP-detector and a glass column (1.2 m x 2mm ID) filled with

3% OV-17 on Gas Chrom Q 80-100 mesh. The gas carrier was dry N₂ (15 ml/min). The chromatograms were carried out isothermally at an oven temperature of 190°C. Compound V was silylated (Va) with BSTFA [bis(trimethylsilyl) tri-fluoroacetamide] before GC analysis.

Chemical ionization (CI) mass spectra (70 eV) were performed on a DuPont No.490 B, low-resolution mass spectrometer, equipped with a dual EI/CI ion source (source temperature: 190°C; sample temperature: 200°C). High-resolution mass spectra were recorded on a MS-Varian MAT No. 731. The IR spectra were run on a Perkin Elmer No. 257 instrument in KBr pellets. The H-NMR spectra were carried out on a Varian FT-80A spectrometer (80 MHz) using CDCl₃ (unless otherwise stated), and all spectra are reported in δ from Me₄Si (internal standard). A Varian UV-vis spectrophotometer Techtron No. 635 was used for spectrophotometric measurements. The light intensity in the 400-700 nm range was measured by a quantum sensor (Lambda Instrument Corp., Nebraska) connected to a digital-integrator (Type TS 100A). The melting points were determined by using a Fisher Digital melting point analyzer No. 355, and were not corrected.

The photoreactions with UV light were carried out in an open dish equipped with a magnetic stirrer. The UV source (254 nm) consisted of four lamps (57413P/40, TUV 30W, Philips, Holland) mounted above the dish.

The photoreactions with visible light were carried out in graduated Pyrex cylinders, with direct outdoors solar irradiation (from May to September, 1982; altitude 100m, latitude 32°N, longitude 34°50'E), or in a laboratory photoreactor equipped with a 400-W visible light lamp (Osram-Power Star-HQI, Germany) mounted vertically and cooled by an air blower. The cylinders containing the solutions were arranged in a circle around the lamp and about 3 cm distant from it.

Column chromatography was performed on silica gel (230-400 mesh, Merck art. 9385) using a rapid chromatographic technique (Still et al., 1978). Columns were eluted with ethyl acetate (EA): Methylene chloride photoproducts from the (MC) 98:2 for separation of the/mixture irradiated with UV-light (unless stated otherwise) and with MC:EA 10:1 for the mixture irradiated with visible light. Thin layer chromatography (tlc) was performed on aluminum sheets precoated with silica gel (60 F 254, Merck art. 5549), and were developed in MC:EA, 9:1. The spots were revealed by UV-light or by iodine vapors.

Photodecomposition Procedure

a. Using UV-light

Ethanollic solutions of I (1.0g, 150 mL) were exposed to UV-light, while stirring. The photodecomposition progress was followed by tlc. After irradiation, the solvent was removed and the dry residue was submitted to column chromatography.

b. Using visible light

Aqueous solutions of I (0.5 g, 1L) and RF (125 mg) adjusted to pH 4 (0.01 N HCl) were exposed to visible light in the photoreactor ($\sim 2400 \mu\text{Em}^{-2}\text{s}^{-1}$). During the irradiation, air (water-washed) was flushed through an 0.1 mL pipette at the bottom of the solutions. The temperature of the solutions reached about 40°C.

The irradiations were followed by continuous sampling of the irradiated solutions and the injection of their ethyl acetate extracts to GC. The extracts were prepared by shaking the sample (1 mL) with ammonium sulfate (0.5g) and EA (5 mL) in a stoppered test tube for about 30 seconds. The upper layer was further diluted with the same solvent to a final concentration of only a few mg L^{-1} . This diluate was injected into the GC-column (2 μL).

After irradiation the solution was lyophilized and the dry residue obtained was submitted to column chromatography.

Bioassay Procedure

Seedlings (2-day-old oat germinated on filter paper and 7- and 11-day-old sorghum and tomatoes, respectively, germinated in vermiculite) were transferred to glass tubes (10 mL) with the root immersed in the test solutions. The experiment was carried out in a growth chamber, at constant temperature (25°C) and normal light conditions (16 h light, 8 h dark), and was run in ten repetitions. The parameters used to evaluate the response of the plants were visual assessments of injury symptoms, root and shoot elongation, and the dry weight. The results are mean values eventually expressed as percent of the control (seedlings grown under the same conditions, in distilled water).

Results and Discussion

a. Photolysis of I with UV-light

Irradiation of ethanolic solution of I with UV-light (5h) resulted in about 80% decomposition (based on recovered I) and gave a complex mixture of photoproducts, the composition of which was dependent on the irradiation time. Longer irradiation times caused further decomposition of I and its photoproducts. Careful column chromatography of the irradiated mixture separated unreacted I ($R_f = 0.55$) and three degradation products: II ($R_f = 0.40$), III ($R_f = 0.21$) and IV ($R_f = 0.28$) in low yields (scheme 1).

Compounds II and III were fully characterized while the final structure of compound IV is still under consideration.

2H Indol-2-one 1,3-dihydro, 1-isopropyl (II)

Chromatographically pure II was obtained in about 5% yield by column chromatography (MC) of a mixture of I and II. This mixture was separated from the reaction mixture residue by rapid column chromatography. White needles of II, m.p. 52-3°C, were obtained by crystallization from n-hexane. Its mass spectrum showed a molecular ion with m/e 175 corresponding to $C_{11}H_{13}NO$, indicating elimination of an HCl molecule from I (Table 1). The H-NMR spectrum indicated the presence of an isopropyl group (1.47, d, 6H, and 4.67, septet, 1H) a methylene group (3.49, s, 2H) and four aromatic protons (7.20, m); IR spectrum showed the carboxyl band at 1715 cm^{-1} .

Based on the above spectral data two possible structures could be suggested for II: the first one - formed through cyclization of I via elimination of an HCl molecule, and the second one - formed through rearrangement of the acyl group from the nitrogen atom, to the aromatic ring prior to the cyclization. The possibility of such rearrangement prior to cyclization has been considered since N-aryl amides of carboxylic acids are known to cleave and rearrange themselves under the influence of UV-light (the photo Fries rearrangement, Elad et al., 1965). The final assignment of the structure of II was done by comparing it with an authentic sample of N-isopropyl oxyndol (Stolle, 1930). The identity of the compounds ruled out the possibility of rearrangement prior to cyclization.

2H Indol-2-one 1,3-dihydro, 1-isopropyl, 3-hydroxy (III)

Crystallization of crude III, obtained by column chromatography of the irradiated mixture residue, in about 5% yield, gave crystals of III, m.p. 88-90°C (n-hexane). The mass spectrum showed a molecular ion with m/e 191 corresponding to $C_{11}H_{13}NO_2$, indicating the elimination of an HCl molecule and the addition of one oxygen atom (Table 1). The H-NMR spect-

rum showed the presence of: two prochiral CH_3 groups of the isopropyl group (1.07 and 1.08, d,d, $j=8$ cps, 6H); one hydroxyl group (3.45, d, $j=15$ cps, 1H); one CHOH group (4.68, d, $j=15$ cps, 1H); one $\text{CH}(\text{CH}_3)_2$ proton (4.88 septet, 1H); and four aromatic protons (7.42, m, 4H). Addition of D_2O led to the disappearance of the doublet at 3.45 and conversion of the doublet at 4.68 to a singlet.

Treatment of III with acetic anhydride and pyridine gave the corresponding acetate, IIIa, the H-NMR spectrum of which showed the disappearance of the hydroxyl proton, the appearance of an acetyl group (2.07, s, 3H), and a large shift of the proton α to the acetyl group (6.45, s, 1H).

The degradation product, IV

This compound was isolated during column chromatography ($R_f = 0.28$) of the irradiated mixture residue and crystallized from n-hexane to give white needles, m.p. 118-120°C. The mass spectrum of IV indicated the loss of chlorine and gave a molecular ion at m/e 207 corresponding to $\text{C}_{11}\text{H}_{13}\text{NO}_3$ (Table 1). The H-NMR spectrum showed signals which might be attributed to: an isopropyl group (1.38, $j = 8$ cps, 6H and 3.5, septet, 1H), a methylene group (4.34, s, 2H), and a para-substituted aromatic ring (6.49, m, AA'xx', 4H).

b. Photolysis of I with visible light

Aqueous solutions of I were found to be photostable upon exposure to visible light. However, addition of RF to these solutions was very efficient in sensitizing the photodecomposition reaction; the dye, MB, did not have a significant sensitizing effect.

The decomposition rate of I was found to depend on the initial pH of the reaction mixture and on the molecular ratio RF to I. The most suitable working conditions used were pH 3 to 4 (the fastest decomposition) and a ratio of RF to I of ~ 0.1 .

Irradiation of the aqueous solution of I ($2.8 \times 10^{-3} \text{M}$) in the presence of RF ($3.5 \times 10^{-4} \text{M}$) at pH 4 for 9h resulted in 60% decomposition of I. Tlc analysis of the irradiated solution showed, in addition to the spot corresponding to I, a weak spot corresponding to V ($R_f=0.20$), visualized in iodine. Further irradiation of this solution (12h) resulted in the complete decomposition of both I and V. Column chromatography of the dry residue after lyophilization of the solution separated unreacted I and its m-hydroxylated derivative V (3% yield) (scheme I).

m-Hydroxy 2-chloro-N-isopropyl acetanilide (V)

The crude V, obtained from column chromatography, was crystallized from ethyl acetate, m.p. $217-8^\circ\text{C}$. The MS gave a molecular ion at m/e 227 which indicated addition of an oxygen atom to I (Table 1). The H-NMR (DMSO) spectrum showed the presence of an isopropyl group (1.00, d, $j=10$ cps, 6H and 4.70, septet, 1H), a methylene group (3.82, s, 2H), and four aromatic protons. Three aromatic protons overlap near 6.75, while the fourth proton, meta to the substituents, resonates at a lower field (7.25) as a di ortho triplet. The IR spectrum indicated the presence of an OH group (3230 cm^{-1}) and a meta disubstituted benzene ring ($720, 780 \text{ cm}^{-1}$). Compound V was found to be identical to m-hydroxy 2-chloro-N-isopropyl acetanilide prepared by chemical methods (Walker *et al.*, 1970; Benton and Dillon, 1942).

Irradiation of aqueous solution of V (180 mgL^{-1} V, 20 mgL^{-1} RF, pH 4) for 15 min resulted in its almost complete decomposition ($\sim 95\%$) but no degradation products could be detected.

The above data suggested that the primary step in the sensitized photodecomposition of I is the hydroxylation of the aromatic ring to the corresponding phenol derivative (V), which eventually disappeared from the reaction mixture either by further photodegradation or by photopoly-

merization processes. Since these processes are very fast, only small quantities of V could be detected.

c. The phytotoxicity test

Since the practical goal of the photodegradation studies of herbicides is the detoxification of polluted water in order to enable its re-utilization in crop irrigation, the characterization of the phytotoxicity of irradiated herbicide solutions is necessary.

In a recent study Klendgen (1980) showed that I applied to the roots of young barley seedlings decreased the accumulation of fresh and dry matter and reduced root and shoot elongation. Based on this and previous information, a study was made of the effect of solutions and irradiated reaction mixtures of I on the early seedling growth of susceptible plants. Visual estimation of plant development showed that differences in the root system between seedlings grown in a solution of I and the control, appeared as early as after 4 days. Therefore, the assessments were made at this early stage, which also avoids the interference of eventual injury caused by the lack of nutrient elements and root aeration in the solution tested.

Dose-response curves considering all the parameters measured showed that the order of sensitivity of the test plants to I was oat > sorghum > tomatoes. Oat, which was the most sensitive (even at 0.5 mg L^{-1}) and had an almost quantitative response to I, was selected to be used for the toxicity test of irradiated solutions. Fig. 2 shows the effect of irradiated reaction mixtures of I (A and B) on root and shoot length and root weight as compared with the same effects of a solution of 10 mg L^{-1} of I (S) and distilled water (R). The non-lethal effect of S may be attributed to the very young age of the oat seedlings.

The irradiated mixture A, which initially contained 40 mg L⁻¹ of I, had a slight growth-inhibiting effect. It decreased root elongation by 21%, as compared with a 49% decrease caused by 10 mg L⁻¹ I. The decrease in shoot elongation was 9%, and the decrease in root weight was only 2%, whereas the effect of the non-irradiated solution was 47% and 35%, respectively. The diluted (1:4) irradiated mixture, B, did not affect the development of the young oat seedlings; the values obtained for all the parameters measured were similar to the control.

The above results showed that the photodegradation products present in the tested solutions had no growth-inhibiting effects. The decrease in root elongation caused by A was proportional to the residual concentration of I in the photoreaction mixture.

Conclusions

The photodecomposition of I was achieved by either UV or visible light. The UV light irradiation led to oxyndol derivatives (II, III) which were formed by cyclization of I.

The irradiation of the sensitized solutions with visible light led to hydroxylation of the aromatic ring to a phenol derivative (V).

The low yields of the degradation compounds might be explained by their lability under the photoreaction conditions, which obviate their accumulation and cause their rapid disappearance when the parent compound is depleted.

The bioassay demonstrated that the sensitized photodecomposed mixture lost its phytotoxicity, indicating the possibility of using this method for the detoxification of I residues in water.

Acknowledgments

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List of Figures and Tables

Fig. 1: The main photodegradation products of propachlor (I).

Fig. 2: The effect of photodegradation mixtures on oat seedlings.

R - distilled water; S - 10 mg L^{-1} I, A - 40 mg L^{-1} I
irradiated; B - the same as A, diluted 1:4.

Table 1: High-Resolution MS, Significant peaks, and Major Fragmentation of Photodecomposition Products of I.

* Another M^+ peak was present, corresponding to the ^{37}Cl isomer.

Table I High-resolution MSⁱ, significant peaks, and major fragmentation of photodecomposition products of I^{*}

Product	Mass found	% abundance	Composition	
II	175.0995	49.52	C ₁₁ H ₁₃ NO	M ⁺
	160.0796	34.09	C ₁₀ H ₁₀ NO	M ⁺ - CH ₃
	133.0539	44.73	C ₈ H ₇ NO	M ⁺ - C ₃ H ₆
	132.0809	100.00	C ₉ H ₁₀ N	M ⁺ - C ₂ H ₃ O
III	191.0899	30.94	C ₁₁ H ₁₃ NO ₂	M ⁺
	163.0960	24.13	C ₁₀ H ₁₃ NO	M ⁺ - CO
	162.0929	78.84	C ₁₀ H ₁₂ NO	M ⁺ - CHO
	120.0434	100.00	C ₇ H ₆ NO	M ⁺ - C ₄ H ₇ O
IV	207.0865	89.89	C ₁₁ H ₁₃ NO ₃	M ⁺
	192.0683	20.45	C ₁₀ H ₁₀ NO ₃	M ⁺ - CH ₃
	165.0403	84.52	C ₈ H ₇ NO ₃	M ⁺ - C ₃ H ₆
	134.0585	96.94	C ₈ H ₈ NO	M ⁺ - C ₃ H ₅ O ₂
V	227.0662	57.36	C ₁₁ H ₁₄ NO ₂ Cl [*]	M ⁺
	212.0409	21.06	C ₁₀ H ₁₁ NO ₂ Cl [*]	M ⁺ - CH ₃
	192.1005	54.67	C ₁₁ H ₁₄ NO ₂	M ⁺ - Cl
	185.0194	30.88	C ₈ H ₈ NO ₂ Cl [*]	M ⁺ - C ₃ H ₆
	136.0586	100.00	C ₈ H ₈ O ₂	M ⁺ - C ₃ H ₆ NC1

* Another M⁺ peak, corresponding to the ³⁷Cl isomer was present.

Fig. 1: The main photodegradation products of propachlor (I).

Fig. 2: The effect of photodegradation mixtures on oat seedlings

R - distilled water; S - 10 mg L⁻¹ I, A - 40 mg L⁻¹ I irradiated; B - the same as A, diluted 1:4.

SUNLIGHT PHOTOSENSITIZED DEGRADATION OF HERBICIDES IN WATER

The dye-sensitized photolysis of aerated aqueous solutions of uracil and s-triazine herbicides exposed to sunlight was investigated under different reaction conditions.

The composition and the relative concentration of the photodecomposition products present in the irradiated solutions depend upon the experimental conditions (sensitizer's nature and concentration, pH of solution and the time of irradiation). Dye-sensitizers, mainly methylene blue and riboflavin, were used at concentrations of 1 to 10 mg/l and at pH of 3 to 9.

The uracil herbicides, bromacil (5-bromo-3-sec-butyl-6-methyluracil) and terbacil (3-tert-butyl-5-chloro-6-methyluracil) were decomposed after 2 h of exposure to sunlight to a main product, 3-sec-butyl-5-acetyl-5-hydroxyhydantoin (83%) and 3-tert-butyl-5-acetyl-5-hydroxyhydantoin (49%), respectively. Other minor photodegradation products were bromacil dimer and a mono-N-dealkylated terbacil dimer. The s-triazine herbicides, ametryne (2-ethylamino-4-isopropylamino-6-methyl-mercapto-s-triazine), atraton (2-ethylamino-4-isopropylamino-6-methoxy-s-triazine), and atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) were degraded after 2 h of irradiation primarily to 6-N-de-ethylated-s-triazines (a) and the oxidized products 6-N-acetamido-s-triazines (b). The yields of these products were 55-70% for a and 3-7% for b. Further irradiation of the reaction mixtures led to the decomposition of a and b with the formation of 4,6-diamino-s-triazine derivatives, which eventually photolyzed to unidentified compounds.

The exposure of the above herbicides aqueous solutions to sunlight for 6-8 h, under optimal reaction conditions, led to the complete disappearance of the herbicides and their degradation products. The bioassay tests of these solutions showed that they lost their phytotoxic properties, indicating the possibility of using this method for the detoxification of herbicides polluted water.

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The development and design
of dye-sensitized photooxidation waste stabilization ponds
for the treatment of industrial waste.

Interim dissertation report

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INTRODUCTION

Currently, industries and municipalities spend substantial capital in controlling waste discharges. The Chemical Manufacturers Association claimed that United States chemical industries spent 900 million dollars in expenditures to comply with U.S. Environmental Protection Agency regulations in 1979, approximately 10 percent of the industry's total plant and equipment outlays (Siegrist 1981). Furthermore, this capital spending is expected to increase to an average of 11.1 percent of total spending for the years 1981 through 1983.

Waste stabilization ponds are an inexpensive process for treating wastes where land costs are nominal (Eckenfelder 1966). Waste stabilization ponds may be facultative, aerobic, or aerated. Detention time of these ponds may vary from a few days to two weeks, depending upon the removal desired (Metcalf and Eddy 1979).

Waste stabilization ponds utilize biochemical processes to decompose wastes. Biochemical methods have proved to be an effective method for waste treatment since microorganisms are efficient at assimilating organic matter in wastes. Organic chemicals, such as those from chemical industry wastes, pose a threat to biochemical treatment processes due to their toxicity and resultant inhibition of microbial growth, or their resistance to microbial degradation (Nemerow 1978).

Ludzack and Ettinger (1960) reviewed the resistance of numerous classes of organic chemicals to aerobic biochemical degradation.

Ethers showed substantial resistance to biological treatment. Ketones were found to be more resistant than alcohols, aldehydes, or acids, but less resistant than ethers. Other species which were found to be resistant or inhibitory to microbial oxidation include alkyl benzenes, diols, 2,4,5-trichlorophenol, and morpholines with a nitrogen-containing heterocyclic ring. Numerous other classes of organics pose problems in biochemical industrial waste treatment. These include polychlorinated biphenyls, phenolic wastes, halogenated aromatics, and refractory pesticides (Nemerow 1978).

Tabak et al. (1981) investigated the degradability and/or the rate of biological acclimation of 96 organic priority pollutants using a static-culture flask-screening procedure. The priority pollutants studied included phenols, phthalate esters, naphthalenes, monocyclic and polycyclic aromatics, polychlorinated biphenyls, halogenated ethers, nitrogenous organics, halogenated aliphatics, and organochlorine insecticides. Phenols were generally degraded effectively with rapid adaptation by the microbial cultures. Pentachlorophenol was significantly degraded, but with gradual adaptation. The only phenol studied that was not significantly degraded was 4,6-dinitro-o-cresol. All phthalate esters and naphthalenes studied showed significant degradation with rapid adaptation with the exception of two phthalate esters, which showed gradual adaptation. The simple monocyclic aromatic compounds studied (benzene, toluene, ethylbenzene) were significantly degraded. A number of dichlorobenzenes and 2,4-dinitrotoluene and 2,6-dinitrotoluene showed significant degradation with gradual adaptation, followed by toxicity in subsequent subcultures. Generally, halogenated ethers,

larger polycyclic aromatic hydrocarbons, and polychlorinated biphenyls and organochlorine pesticides were resistant to microbial degradation.

Traditionally, acclimated cultures of microorganisms have been used for the treatment of toxic and refractory wastes. Such a procedure can be costly and requires thorough operational guidance (Eckenfelder 1966). Moreover, this system is sensitive to the accumulation of environmental factors such as temperature, dissolved oxygen, and synergistic toxicity of chemicals, which may result in failure of the plant or lagoon. Acclimated microbial cultures are also not exempt from dose-response phenomenon: i.e., there is some dose of the toxic substance high enough that, when entering the system, will cause toxicity to the population of microorganisms (Loomis 1974).

Some physico-chemical means of toxic industrial waste treatment have become increasingly common in recent years. These include the use of activated carbon, ozone, and incineration. Such methods have high operation and maintenance costs and are, therefore, used on a more limited basis (Siegrist 1981). Photodegradation of toxic organic wastes, however, is a novel approach, in that sunlight needed to drive the decomposition is available without cost.

Photodegradation of organic compounds may occur by two processes: direct photodegradation and sensitized photooxidation. In the direct photoreaction process, each particle of light, or quanta, excites one substrate molecule. Excited molecules may lose this energy by dissociation, dehalogenation, isomerization, or other deactivation routes (Plimmer 1971). Many organic pollutants absorb light primarily in the ultraviolet (UV) region. There is, however, less energy reaching the earth's

surface in the UV region than in the visible region, rendering direct photodegradation an inefficient environmental process (Thorington 1980).

In the sensitized photooxidation process, sensitizing molecules absorb light in the visible region, where there is a wealth of energy reaching the earth's surface. The electronically excited sensitizing molecule, or triplet sensitizer, then returns to ground state by transferring its excess energy to molecular oxygen, resulting in the formation of singlet oxygen.

Singlet oxygen is a highly reactive species of oxygen with a life-time of 3 μ sec (Kearns 1971). It readily attacks organic substrates, yielding oxidized photoproducts. Kasha and Khan (1970) stated that singlet molecular oxygen, even though it is a short-lived species, is proving to be an almost ubiquitous intermediate in systems that were once considered to be the exclusive domain of normal molecular oxygen.

Spikes and Straight (1967) concluded that many classes of organic compounds are susceptible to sensitized photooxidation. Those mentioned included alcohols, nitrogen heterocycles, organic acids, benzenoids, and aromatic heterocyclic compounds. Sargent and Sanks (1974) postulated that many of the compounds present in industrial wastes, such as phenols, cresols, trinitrotoluene, and unsaturated nitriles should be susceptible to sensitized photooxidation.

Nearly all environmental photodegradation research has been performed on pesticides, resulting in a wealth of knowledge on their photodegradation products. Bromacil is a widely used nonselective herbicide. It is both toxic and refractory. The bromacil acute oral LD₅₀ for rats is 5200 mg/kg. The 72-hour LC₅₀ for rainbow trout is

28 mg/l (Sherman and Kaplan 1975). The biological half-life of bromacil is five to six months (Sherman and Kaplan 1975). Bromacil is, therefore, a fitting model for a toxic, recalcitrant waste that is incompatible with state-of-the-art biological treatment.

Waste treatment and detoxification of pesticide wastes is a propitious concern. 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 was 664 million pounds in 1978, below the average of 677 million pounds (Fowler 1978). Pesticide manufacture and use is less pronounced 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 United States' levels of pesticides (Cremlyn 1978). Pesticide waste streams contain formulation precursors as well as the parent compound. The parent compound is, generally, more recalcitrant than the precursors (Van Valkenburg 1973). Therefore, if the parent compound is effectively degraded or detoxified by a waste treatment process, the precursors will also be degraded or detoxified. In a waste stream for the synthesis of bromacil, the precursors used in formulation would, therefore, not present a major problem if bromacil itself is degraded.

The use of solar energy for domestic and industrial purposes has, of late, increased in popularity. However, this no-cost source of energy has rarely been applied to waste treatment. The purpose of this research is to provide rational engineering design criteria for the development and construction of sensitized photooxidation lagoons 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) Oxygen requirements for sensitized photooxidation reactions.
- 4) The effect of temperature on photooxidation rates.
- 5) Construction and operation and maintenance costs of sensitized photooxidation lagoons.

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

Based on the lagoon construction and operation and maintenance costs, sensitized photooxidation waste stabilization ponds may prove to be an inexpensive and low-maintenance alternative to traditional waste treatment systems. These lagoons may provide a cost-effective means by which chemical industries may find greater incentive to treat toxic and refractory wastes.

METHODOLOGY

Effect of pH on Sensitized
Photooxidation Rate

Experiments involving sensitized photooxidation rate as a function of pH were conducted at the Utah Water Research Laboratory (UWRL). Experiments 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 (passed through a 1 N NaOH solution to remove contamination) at a flow rate of 0.25 l/min (0.5 SCFH), which maintained dissolved oxygen at saturation during the experiments. Temperature was maintained at $25^{\circ}\text{C} \pm 3^{\circ}\text{C}$. Constant light was provided by Duro-Test Vitalite™ lamps, which are 97 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 a Optronic spectroradiometer.

The effect of pH on sensitized photooxidation was investigated with pH held constant during the course of the experiments. Buffered laboratory reagent grade water from a Millipore 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 12 at 1 unit pH intervals using the sensitizers methylene blue (2 mg/l) and riboflavin (10 mg/l). Bromacil and terbacil solutions were 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 appropriately adjusted with 5 N NaOH or 20 percent HCl, and placed under the previously described temperature, aeration, and light conditions. The experiment was started by adding the sensitizer to the solutions, and samples were collected for determination of dye concentration and substrate concentration at 15 minute intervals over 90 minutes. 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.

Dye 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 the parent compound was monitored after a 1:1 ethyl acetate extraction followed by analysis by gas chromatography using a Hewlett-Packard 5880A gas chromatograph. 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 included injector port temperature 250°C; oven temperature initial value 170°, program rate 20°C; detector temperature 250°C; 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° (isothermal), injector port temperature 250°C, detector port temperature 220°C; nitrogen carrier flow rate 30 ml/min.

Reaction Rate as a Function of Depth

In a lagoon containing a small amount of sensitizer, the quantity of light decreases and the quality of light changes with depth. The mechanistic approach involved in this study used a constant light source of 107 W/m^2 impinging on reaction chambers, temperature of $25^\circ\text{C} \pm 5^\circ\text{C}$, and aeration of 0.5 l/min (1.0 SCFH). Eight reaction chambers were used to simulate depths of a sensitized photooxidation lagoon. These chambers consisted of a $150 \text{ mm} \times 15 \text{ mm}$ 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 $15 \text{ cm} \times 5.5 \text{ cm}$ deep amber glass dish covered with black electrical tape. The plastic sleeve attached to the petri dish contained two ports: One for a glass air diffuser into the reaction vessel, and the other a port for sampling the reaction vessel. 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 succeeding deeper cross-sections of a lagoon. For instance, for a 1 mg/l lagoon concentration of methylene blue to simulate a depth of 60 cm , a 60 mg/l solution 1 cm deep in the petri dish would be necessary. This 1 cm deep solution, however, 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 during experiments was negligible since NaN_3 , a singlet oxygen quencher, was added to the petri dishes at a final concentration of 25 mg/l. Simulated lagoon sensitizer concentrations, 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 terbacyl as the substrate in deionized water buffered with 1000 mg/l Na_2HPO_4 adjusted to pH 3 with 20 percent H_2SO_4 . These conditions were used in order to obtain the highest reaction rates possible under the relatively low indoor light regime. Experiments using eight simulated depths were initiated by the addition of sensitizer to the reaction vessel and lasted 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 terbacyl 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.

Dissolved Oxygen Requirements of Sensitized Photooxidation

Studies to determine sensitized photooxidation rate as a function of dissolved oxygen were performed under Duro Test Vitalite™ lamps

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

Lagoon Sensitizer Concentration							
0.1 mg/l		0.25 mg/l		1.0 mg/l		2.0 mg/l	
Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration
Methylene Blue							
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
1.0 mg/l		2.5 mg/l		5.0 mg/l		10.0 mg/l	
Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration	Simu- lated Depth	Petri Dish Concen- tration
Riboflavin							
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

with radiation impinging upon the reactions of 107 W/m^2 . Temperature was maintained at $25^\circ\text{C} \pm 5^\circ\text{C}$.

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 terbacyl as substrate in deionized water buffered with 1000 mg/l Na_2HPO_4 adjusted to pH 3 with 20 percent H_2SO_4 . pH values were chosen to obtain high reaction rates under the relatively low light regime.

Two hundred mls of bromacil-methylene blue or terbacyl-riboflavin solutions were aerated with a total gas flow of 0.5 l/min (1.0 SCFH), regardless of dissolved oxygen residual maintained. This was accomplished by mixing compressed air with compressed molecular nitrogen in the correct proportions to maintain the dissolved oxygen residual at the chosen level. These tests were performed at 0, 0.2, 0.7, 1.0, 2.5, 4.0, and 7.0 mg/l dissolved oxygen residual.

Experiments were conducted for 2 hours with samples collected at 30 minute intervals. These samples were collected for analysis of residual bromacil or terbacyl, sensitizer concentration, and chemical oxygen demand. Residual bromacil and terbacyl were measured by gas chromatography after 1:1 ethyl acetate extraction using the same chromatographic conditions used previously in this study. Methylene

blue and riboflavin concentrations were measured by optical density at 660 and 445 nm, respectively, on a Bausch and Lomb Spectronic 70.

Chemical oxygen demand was measured by 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 1981).

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 10°C to 35°C. Light was supplied by Duro Test Vitalite™ with radiation impinging upon reaction solutions of 107 W/m². Aeration was maintained at 0.5 l/min (1.0 SCFH).

The experiments were run 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 at 11°, 16°, 21°, 26°, 31°, and 35°C. Sufficient time was allowed for the solutions to reach the temperature chosen. Experiments, performed in triplicate, were conducted for 2 hours and were initiated by adding the sensitizer to aerated solutions of bromacil or terbacil. Samples were collected at 30 minute 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

Data obtained for experiments investigating the effects of pH on sensitized photooxidation rate were plotted as $\ln C_t/C_o$ as a function of time. The result was a straight line with R^2 generally greater than 0.95. These reactions, therefore, fit the criterion for first order or psuedo-first order reaction kinetics (Atkins 1977). Acher and Saltzman (1980) found sensitized photooxidation of bromacil to follow first order kinetics. The results of this study show that sensitized photooxidation of terbacil and fluometuron also follows first order kinetics.

The results of riboflavin (10 mg/l), methylene blue (2 mg/l), and riboflavin-methylene blue (10 mg/l-2 mg/l) sensitized photooxidation of bromacil and terbacil are shown in Figures 1 and 2, respectively. The riboflavin (10 mg/l) and methylene blue (2 mg/l) sensitized photooxidation of fluometuron is shown in Figure 3.

The results of sensitized photooxidation which are most consistent are related to sensitization by methylene blue, which, regardless of substrate, is most efficient above pH 7. Methylene blue has been shown in numerous studies to be a generator of singlet oxygen (Nilsson et al 1972; Halmann and Levy 1979). The generation of singlet oxygen by methylene blue is governed by the quantum yield of triplet formation of methylene blue, which is related to the ionic nature of the dye. Methylene blue is an organic cation, existing in the ionic form at acidic and neutral pH, and in the neutral form at basic pH. The quantum yield of methylene blue triplet formation correlates strongly with the percentage of molecules existing in the neutral state. Bonneau et al.

Figure 1. 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 under radiation of 47 W/m².

Figure 2. 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 terbacyl as a function of pH under radiation of 47 W/m².

Figure 3. First order rate constants for riboflavin (10 mg/l) and methylene blue (2 mg/l) sensitized photooxidation of 30 mg/l fluometuron as a function of pH under radiation of 47 W/m².

(1975) reported that the variation of singlet oxygen production with pH in methylene blue sensitization is related to the lifetimes of the triplet dye and the energy difference between the donor, triplet dye, and acceptor, singlet oxygen.

Figure 3 indicates that fluometuron was relatively resistant to methylene blue-sensitized photooxidation. This may be attributed to resistance of fluometuron to singlet oxygen attack. Nilsson et al. (1972) mentioned two possible pathways of sensitized photooxidation: 1) attack of singlet oxygen on the substrate, 2) reaction between the triplet sensitizer and the substrate with subsequent reaction with oxygen. In methylene blue-sensitized photooxidation of fluometuron, the rate of decomposition was not nearly as large as that of bromacil and terbacil, which presumably occurred by the singlet oxygen mechanism. It was also not affected by pH. Therefore, the latter pathway may be more important in fluometuron photooxidation, since, this pathway has been suggested to be independent of pH.

Riboflavin-sensitized photooxidation of bromacil, terbacil, and fluometuron follows a less consistent pattern. Riboflavin-sensitized photooxidation of bromacil was most effective at high pH, but was more efficient at low pH with terbacil and fluometuron as substrates. Acher and Saltzman (1980) found a similar trend in the riboflavin-sensitized photooxidation of bromacil. They found sensitized photooxidation rates to be greater at pH 9.2 than 6.8. Acher (1981) observed a trend similar to that found in this study with the riboflavin-sensitized photooxidation of terbacil. He found the low pH riboflavin-sensitized to be more efficient than that in basic solution.

It is unlikely that riboflavin and methylene blue are acting by identical mechanisms, since riboflavin and methylene blue reaction rates as a function of pH show no similarities with the three substrates. Since the mechanism of methylene blue sensitized photooxidation has been described primarily as singlet oxygen generation (Nilsson et al. 1972), other mechanisms may be taking place with riboflavin-sensitized photooxidation. Riboflavin has been shown to generate singlet oxygen in the sensitized photooxidations of histidine (Tomita et al. 1969) and adenosine and guanosine (Penzer and Radda 1968). Riboflavin has also been shown to oxidize by radical and hydrogen extraction mechanisms. Flash photolysis studies have shown that flavins can abstract a hydrogen atom or electron from substrates such as amino acids, phenols, and alcohols (Lasser and Teielson 1975; Heelis et al. 1978). Therefore, in the riboflavin-sensitized photooxidation of bromacil, terbacil, and fluometuron, there may be a variety of mechanisms taking place, which may depend upon the substrate and pH of the solution.

The combined effects of methylene blue and riboflavin sensitization of 30 mg/l bromacil and terbacil solutions were investigated. The results of these experiments are shown on Figures 1 and 2. Compared to the results obtained using methylene blue and riboflavin separately, the reaction rates using both dyes were additive in the neutral pH ranges, with an antagonistic effect upon sensitized photooxidation rate at pH extremes. There appears to be some advantage of using two dyes to attain higher photooxidation rates at neutral pH, but the benefits would have to be warranted by an economic analysis.

Methylene blue concentration, measured at 15 minute intervals over 90 min, was found to oscillate. Such reversible decomposition

has been described by Matsumura (1972). The degradation of methylene blue in these experiments did not follow any typical kinetic expressions, so a weighted average was used to calculate percent dye degradation. The concentration of methylene blue was averaged using time of the experiment as a weighting factor. This weighted average of methylene blue concentration during the experiment was then divided by the initial concentration of the dye times 100 to give percent methylene blue degradation:

$$\text{Weighted Average of Methylene Blue Concentration During Experiment} = \frac{C_{15} \cdot 15 + C_{30} \cdot 30 + C_{45} \cdot 45 + C_{60} \cdot 60 + C_{75} \cdot 75 + C_{90} \cdot 90}{15 + 30 + 45 + 60 + 75 + 90} \quad (1)$$

$$\text{Percent Methylene Blue Degradation} = \frac{\text{Weighted Methylene Blue Concentration}}{\text{Methylene Blue Concentration at } t=0} \times 100 \quad (2)$$

Figures 4, 5, and 6 show percent methylene blue degradation as a function of pH for the substrates bromacil, terbacil, and fluometuron, respectively. Methylene blue was least stable at high pH for all substrates investigated, with the sharpest increase in methylene blue bleaching between pH 8 and 9. The degradation of the dye is probably related to the production of singlet oxygen, which, when generated at basic pH, attacks the dye which originally generated it.

Riboflavin concentration determined at 15 minute intervals over the 90 minute experiments followed first-order kinetics, as demonstrated by a linear relationship of $\ln(C_t/C_0)$ as a function of time. First-order rate constants of riboflavin degradation

Figure 5. Effect of pH on first order rate constants of methylene blue-sensitized photooxidation of terbacil and percent methylene blue degraded in the 90 minute experiment. Initial terbacil concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

Figure 4. Effect of pH on first order rate constants of methylene blue-sensitized photooxidation of bromacil and percent methylene blue degraded in the 90 minute experiment. Initial bromacil concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

Figure 6. Effect of pH on first order rate constants of methylene blue-sensitized photooxidation of fluometuron and percent methylene blue degraded in the 90 minute experiment. Initial fluometuron concentration was 30 mg/l; initial methylene blue concentration was 2 mg/l.

as a function of pH are presented in Figures 7, 8, and 9 along with the rate constants of bromacil, terbacil, and fluometuron, respectively. The degradation of riboflavin as a function of pH is consistent with all three substrates. Riboflavin decomposition is minimal at low and neutral pH, but increases rapidly above pH 7. This degradation of the riboflavin appears to be substrate-independent, since it is consistent with all three substrates investigated. It may be due to singlet oxygen attack on riboflavin or a radical mechanism between riboflavin molecules.

Bench scale studies undertaken to assess the effect of pH on sensitized photooxidation rate of an uncharacterized waste should also monitor dye degradation. The degradation rates of riboflavin and methylene blue used with the three substrates studied in this investigation showed very consistent degradation patterns--a sharp increase in methylene blue degradation rate above pH 8 and a sharp increase in riboflavin degradation rate above pH 7. However, the degradation rate of the dye as a function of pH should be determined for the specific substrate studied.

The rate of dye decomposition to waste decomposition is extremely important in terms of lagoon hydraulics. Most lagoons which are not aerated follow plug flow hydraulics. Aerated lagoon hydraulics also closely follow plug flow. In the plug flow regime of a lagoon the dye will bleach as it progresses through the lagoon. One solution to dye bleaching would be to have numerous dye feeds along the plug flow regime of the lagoon. Otherwise, the dye concentration added at the headworks of the lagoon must be such that, when the plug of water reaches the outlet of the lagoon the following conditions are met: 1) The sensitized photooxidation rate is still significant; 2) the concentration of dye

Figure 7. 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.

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Figure 8. 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 9. Effect of pH on first order rate constants of riboflavin-sensitized photooxidation of fluometuron and riboflavin bleaching. Initial terbacyl concentration was 30 mg/l; initial riboflavin concentration was 10 mg/l.

is below toxic levels for discharge for agricultural reuse. The toxicity of methylene blue is particularly critical, since low levels are phytotoxic and toxic to bacteria (Acher and Juven 1977; Acher and Rosenthal 1977). Ultimately, a minimum of dye bleaching is desired to minimize dye addition to maintain the lowest dye cost possible.

A good example of sensitized photooxidation conditions that allow for efficient degradation of waste with minimal degradation of dye is the riboflavin-sensitized photooxidation of fluometuron at pH 7. From Figure 9, the k for fluometuron degradation is 0.055 min^{-1} and the k for riboflavin-degradation is 0.013 min^{-1} . This type of waste would make for an efficient dye sensitized lagoon since:

- 1) No pH adjustment would be required, assuming the waste enters the lagoon near natural pH;
- 2) relatively fast photooxidation of fluometuron is available;
- 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 are for methylene blue-sensitized photooxidation of terbacil at pH 7, as shown in Figure 5. In this case the k for terbacil degradation was 0.008 min^{-1} , whereas 12 percent of the methylene blue was degraded in 90 minutes. A lagoon designed to treat terbacil with these conditions would be of poor design, since the methylene blue would degrade much faster than the waste in the plug flow regime, leaving some of the waste untreated when the wastewater is discharged.

In a completely mixed regime such as an oxidation ditch, 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. A lagoon that would follow complete mix hydraulics

would need an ion exchange recovery system for the dye, with subsequent recycle of the dye to the headworks of the lagoon.

It must be emphasized that no waste treatment system follows complete plug flow or total complete mix regimes. Usually the systems are somewhere in between, but closer to one regime or the other. The only means, therefore, of checking the feasibility of a scheme where dye degradation is planned for maximum efficiency and minimum toxicity is by pilot lagoon studies. Only by the operation of a pilot scale lagoon with variation of parameters can the design parameters developed in this study be actualized.

Photooxidation rate as a function of depth

First order rate constants, k , were calculated for the disappearance of parent herbicide at depths in petri dish-reaction chambers. These rate constants as a function of simulated depth are presented in Figures 10 and 11 for a range of concentrations for methylene blue and riboflavin, respectively. With increasing depth the quantity of total radiation decreases, leading to decreased reaction rate with depth. In a simulated lagoon with high dye concentration, a high reaction rate is maintained at the surface, with a sharp decline in reaction rate owing to decreased light present to drive the photochemical reactions. With a small amount of dye present in solution (e.g. 0.1 mg/l methylene blue), the surface photooxidation rate is low, but the rate does not decrease significantly with depth, due to the small amount of dye absorbing light.

As the light penetrates through successive layers of a lagoon, not only will the total quantity of light decrease, but the quantity of light will decrease in different proportions as a function of

Figure 10. 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 11. 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.

700 nm). When riboflavin is used as sensitizer, Beer-Lambert Law calculations must be monitored to 350 nm, since riboflavin absorbs light down to 350 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 1965). The extinction coefficient of the sensitizer is a measure of the amount of light absorbed by a known concentration of these molecules in solution. Therefore, the model must include the extinction coefficient of the dye which is undergoing the photochemical reaction.

The model must also include a term that quantifies the efficiency of the photochemical reaction taking place. This quantity is the quantum yield, ϕ_{trip} , which is defined as the number of molecules excited to the triplet state per mole of photons absorbed. The model is most easily developed for predicting the specific rate of dye triplet excitation, with extrapolation to a model for herbicide degradation after this initial model development. Relating all the terms described leads to the following model of sensitizer triplet formation:

$$\text{Rate of Sensitizer Triplet Formation} = \int_{350 \text{ nm}}^{800 \text{ nm}} I_{z,\lambda} \cdot \epsilon_{\lambda} \cdot \phi_{trip} d\lambda \quad . \quad . \quad . \quad . \quad (4)$$

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

Mole triplet sensitizer formed/min/mole sensitizer =

$$\left(\frac{I_{z,\lambda}}{\text{dm}^2 \cdot \text{min}} \right) \cdot \left(\frac{\epsilon_{\lambda}}{\text{moles photons} \cdot \text{dm} \cdot \frac{\text{moles sensitizer}}{\text{dm}^3}} \right) \cdot$$

$$\phi_{\text{trip}} = \left(\frac{\text{moles triplet sensitizer formed}}{\text{moles photons absorbed}} \right) \quad (5)$$

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

$$k \propto \text{Specific rate of triplet sensitizer formation} \quad . . . (6)$$

or

$$k = \text{Constant} \times \text{specific rate of triplet sensitizer formation} \quad (7)$$

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

$$\phi_{\text{rxn}} = \phi_{\text{trip}} \cdot \text{Constant} \quad (8)$$

This constant then cancels on both sides of the model, and the pseudo first order rate constant of sensitized photooxidation of a specific substrate may be related to the more generalized model:

$$k = \int_{350 \text{ nm}}^{800 \text{ nm}} I_{z,\lambda} \cdot \epsilon_{\lambda} \cdot \phi_{\text{rxn}} d\lambda \quad (9)$$

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

- I) Convert spectroradiometer data for light impinging on the reaction chamber from W/m^2 to $E/dm^2 \cdot min$.
- II) Integrate the 1 nm bands provided by the spectroradiometer in 5 nm bands using Simpson's Integration.
- III) Determine the extinction coefficient for the sensitizer over the visible range at 5 nm intervals from ϵ_{max} and spectrum of sensitizer.
- IV) Numerically integrate

$$k = \int_{350 \text{ nm}}^{800 \text{ nm}} \phi_{rxn} \cdot \epsilon_{\lambda} \cdot I_{\lambda} d\lambda$$

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 set conditions (e.g. pH, aeration, etc.). The quantum yield of reaction calculated can then be used to calculate k at successive depths. Spikes and Straight (1968) 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 at 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

$$k = \int_{350 \text{ nm}}^{800 \text{ nm}} \phi_{rxn} \cdot \epsilon_{\lambda} \cdot I_{z,\lambda} d\lambda$$

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

Rate constants calculated using the model related to rate constants determined in the laboratory are shown in Figures 12 a, b, c, and d and 13 a, b, d, and d, respectively, for methylene blue and riboflavin-sensitized photooxidation as a function of depth. The model showed excellent correlation with laboratory data, and may therefore be used for the design of sensitized photooxidation lagoons.

The model can be used for any quantity and quality of light impinging on a lagoon. It can also be used for a waste of any spectral quality. The quantity and quality of light impinging upon the lagoon would be supplied by spectroradiometer data collected for the least efficient scenario, i.e. a cloudy day near December 21. The lagoon would also be designed using a sample of waste that would enter the lagoon. Such a sample with sensitizer addition would be placed in a UV-visible spectrophotometer and compared with known solutions of sensitizers to estimate ϵ_{λ} of the waste. These ϵ_{λ} values could then be used in the Beer-Lambert law calculations to determine $I_{z,\lambda}$, which is used in the model to predict k with depth.

Effect of Residual Dissolved Oxygen on Sensitized Photooxidation Rate

Sensitized photooxidation rate constants as a function of residual dissolved oxygen are shown in Figures 14a and 14b using methylene blue as the sensitizer for 30 mg/l and 250 mg/l bromacil solutions, respectively. These figures show that a relatively low dissolved oxygen residual is required to maintain sensitized photooxidation rates at saturation levels. For 30 mg/l bromacil, 1 mg/l dissolved oxygen is necessary for maximum photooxidation rate, whereas for 250 mg/l bromacil approximately 2 mg/l dissolved oxygen is required for maintenance of

Figure 12. Comparison of mean of three replicates of laboratory data and data generated by depth model (Equation 9) for methylene blue-sensitized photooxidation of bromacil first order rate constants as a function of depth for 0.1 mg/l methylene blue (Figure 12a), 0.5 mg/l methylene blue (Figure 12b), 2.0 mg/l methylene blue (Figure 12c), and 4.0 mg/l methylene blue (Figure 12d).

Figure 12. Continued.

Figure 13. Comparison of mean of three replicates of laboratory data and data generated by depth model (Equation 9) for riboflavin-sensitized photooxidation of terbacyl first order rate constants as a function of depth for 1.0 mg/l riboflavin (Figure 13a); 2.5 mg/l riboflavin (Figure 13b); 5.0 mg/l riboflavin (Figure 13c); and 10.0 mg/l riboflavin (Figure 13d).

Figure 13. Continued.

(a)

(b)

Figure 14. First order rate constants for methylene blue-sensitized photooxidation of 30 mg/l bromacil (Figure 14a) and 250 mg/l bromacil (Figure 14b) as a function of dissolved oxygen residual. Initial methylene blue concentration was 2 mg/l.

maximum photooxidation rate. The higher dissolved oxygen residual requirement for the 250 mg/l bromacil may be due to the higher stoichiometric oxygen requirement for the higher levels of bromacil oxidized. The maximum rate of photooxidation was lower with the 250 mg/l bromacil samples than with the 30 mg/l bromacil samples. This may be due to a low ratio of sensitizer molecules to substrate molecules. Higher concentrations of sensitizers may be required for high-strength wastes.

Figures 15a and 15b represent riboflavin-sensitized photooxidation rate constants for 30 mg/l terbacil and 250 mg/l terbacil, respectively. These figures are tentative, and more data are currently being collected for photooxidation rate constants in the 2 to 8 mg/l range. With the preliminary data it appears that dissolved oxygen requirements for riboflavin-sensitized photooxidation are much greater than for methylene blue sensitized photooxidation. This may be due to the variety of mechanisms taking place in riboflavin-sensitized photooxidation. Besides singlet oxygen generation, riboflavin sensitized photooxidation involves hydrogen extraction, radical generation, etc., involving the photoreduced riboflavin molecule. The high dissolved oxygen requirements for riboflavin sensitized photooxidation may be due to the necessity of bringing the photoreduced riboflavin molecule back to ground state. As with methylene blue-sensitized photooxidation, riboflavin-sensitized photooxidation rates are lower with 250 mg/l substrate.

Figures 16 and 17 represent photooxidation rates of 30 mg/l and 250 mg/l substrate for methylene blue-sensitized photooxidation of bromacil and riboflavin-sensitized photooxidation of terbacil, respectively. Temperature appears to have very little effect on sensitized photooxidation rate. Spikes and Straight (1968) noted similar

(a)

(b)

Figure 15. First order rate constants for riboflavin-sensitized photo-oxidation of 30 mg/l terbamil (Figure 15a) and 250 mg/l terbamil (Figure 15b) as a function of dissolved oxygen residual. Initial riboflavin concentration was 10 mg/l.

Figure 16. First order rate constants for methylene blue-sensitized photooxidation of 30 mg/l bromacil (Figure 16a) and 250 mg/l bromacil (Figure 16b) as a function of temperature. Initial methylene blue concentration was 2 mg/l. Vertical bars represent standard deviation for three replicates.

(a)

(b)

Figure 17. First order rate constants for methylene blue-sensitized photooxidation of 30 mg/l bromacil (Figure 17a) and 250 mg/l bromacil (Figure 17b) as a function of temperature. Methylene blue concentration was 2 mg/l. Vertical bars represent standard deviation for three replicates.

results. They stated that the temperature effects of sensitized photooxidation is generally small, with temperature differences in experimental activation energies of approximately 3-5 kcal/mole. The small temperature effect makes sensitized photooxidation a promising process for cold weather regions.

DESIGN OF SENSITIZED PHOTOOXIDATION LAGOON

The sizing of a sensitized photooxidation lagoon is regulated primarily by the quantity of light impinging on the lagoon, since light energy is the principal driving force in the photochemical reactions. In the sizing of the lagoons, the first order rate constant, k , is generated as a function of lagoon depth using Equation 9. From the rate vs depth curve, numerous depths are chosen for the design. For each depth picked for design, a composite k is calculated by averaging k 's from successive control volumes of 2 cm in depth. With a composite k calculated for a lagoon of specific depth, the k is used in the plug flow design equation (Metcalf and Eddy 1979):

$$\ln \frac{C}{C_0} = -k \left(\frac{\text{Vol}}{Q} \right) \quad (10)$$

Since the influent concentration of contaminant, C_0 , the desired contaminant removal, C , flow rate, Q , and k are known, the volume of lagoon may be solved. The area required for the lagoon may be determined by dividing the volume by the depth. The reason for choosing numerous depths on the k vs depth curve is to design for minimum lagoon area, thereby minimizing land costs.

For further clarification, a step-by-step outline of the design of a sensitized photooxidation lagoon follows.

1. Using bench scale equipment (e.g. beakers), measure the photooxidation rate of the waste to be treated using numerous sensitizer concentrations. For the design to be performed for the treatment of a 30 mg/l bromacil waste, five methylene blue concentrations were evaluated on bench scale: 0.1, 0.25, 0.5, 1.0, and 2.0 mg/l

methylene blue. If the waste is at a pH not compatible with sensitized photooxidation, a number of pH values may be evaluated. The cost of pH adjustment of the waste would then need to be considered in the design. For instance if a waste to be sensitized with methylene blue is at pH 6, the bench scale experiments may be performed at pH 6, 7, 8, and 9, each at 5 methylene blue concentrations, i.e. a matrix of 4 pH values x 5 dye concentrations. The lagoons would then be designed for the least-cost option of the 20 points on the matrix.

2. The bench-scale rate constant is used to initialize the depth model, Equation 9. Using Equation 9, a k vs depth curve is generated for each condition in the bench scale matrix. For the design to be conducted below, one pH value was used and five dye concentrations. Therefore, five k vs depth curves will be generated.
3. Numerous depths on the k vs depth curve are chosen for volume and area determination of the lagoons. An optimum depth is chosen where minimum area is achieved, ensuring low land purchase.
4. 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 lagoons.

The waste from bromacil synthesis has been described by A. J. Acher (personal communication), who obtained a sample in Israel. Attempts to obtain pesticide waste samples in the United States were unsuccessful, since the waste characteristics are considered proprietary. Acher described a bromacil waste as having high total dissolved solids, pH 9, 30 mg/l bromacil, and red in color. A synthetic waste shown in

Table 2 was made and compared to methylene blue for spectral quality, and then entered into the depth model.

Design criteria, including effluent bromacil concentration, hydraulic loading, and solar radiation are shown in Table 3. Depth vs rate curves, generated by the depth model (Equation 9) are shown in Figures 18a and b and Figures 19a, b, and c for the synthetic waste described in Table 2 for 0.1 mg/l, 0.25 mg/l, 0.5 mg/l, 1.0 mg/l and 2.0 mg/l methylene blue, respectively. Total quantity of light used in the model was 1000 W/m². The design of a 0.1 mgd pilot lagoon follows.

Table 2. Chemicals in synthetic industrial waste used to design for pilot lagoon.

Constituent	Concentration
Bromacil	30 mg/l
Sodium chloride (TDS)	10,000 mg/l
Rose bengal (red color)	10 mg/l

Table 3. Design criteria 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 for 12 hour period:	1000 W/m ² (minimum) as measured by pyronometer
Maximum duration of successive cloudy days:	3 days

(a)

(b)

Figure 18. First order rate constants as a function of depth for synthetic bromacil waste. Radiation used for design was 1000 W/m². Methylene blue concentrations were 0.1 mg/l (Figure 18a) and 0.25 mg/l (Figure 18b).

(a)

(b)

(c)

Figure 19. First order rate constants as a function of depth for synthetic bromacil waste. Radiation used for design was 1000 W/m². Methylene blue concentrations were 0.5 mg/l (Figure 19a), 1.0 mg/l (Figure 19b) and 2.0 mg/l (Figure 19c).

I. Flow equalization basin: A holding pond for waste that is generated at night or on cloudy days. Since it is assumed that there is a three day maximum of successive cloudy days with steady wastewater flow rate of 0.1 mgd, the flow equalization basin volume = $3 \times 0.1 \text{ mgd} = 0.3 \text{ million gal} = 1,136 \text{ m}^3$. Design for 5 m depth; area = 227.1 m^2 . Dimensions: 5 m deep $\times$ 15.1 m $\times$ 15.1 m. Flow equalization basin can also be used for solids settling.

II. Physical roughing filter. Pesticide wastes are generally low in suspended solids (usually less than 100 mg/l). However, suspended solids, such as clays and colloids, can absorb sensitizing dyes, resulting in decreased dye activity (Acher and Saltzman 1980). A physical roughing filter is necessary, therefore, to remove these particles which may inactivate the sensitizers. The absence of particulates will also enhance light penetration. Intermittent or rapid, high permeability sand filters would be most efficient design.

III. Photooxidation lagoon design: An example of lagoon sizing will be provided for illustrative purposes. Once the example is given, only final design criteria will be given for other situations. The example involves lagoon sizing for 0.1 mg/l methylene blue at 20 cm in depth.

1. From Figure 18a, determine composite k:

Using weighted control volumes,

$$\frac{1(0.0390) + 2(0.0332) + 2(0.0293) + 2(0.0263) + 2(0.0238) + 2(0.0217) + 2(0.0197) + 4(0.0172) + 3(0.0155)}{20}$$

. (11)

$$\bar{k} = 0.0231 \text{ min}^{-1}$$

2. Using design criteria and plug flow design equation, solve for volume of lagoon.

$$\frac{C}{C_o} = e^{-k (V/Q)}$$

where

$$C_o = 30 \text{ mg/l bromacil}$$

$$C = 0.1 \text{ mg/l bromacil}$$

$$k = 0.0231 \text{ min}^{-1}$$

$$Q = 0.526 \text{ m}^3/\text{min} \text{ (0.263 m}^3/\text{min for 24 hr, but lagoon operates for 12 hr)}$$

$$\text{Volume} = 129.9 \text{ m}^3$$

$$\text{Area} = (129.9 \text{ m}^3 / 0.2 \text{ m}) = 649.4 \text{ m}^2$$

The design outlined above was performed on approximately 20 depths for each of the five dye concentrations selected. The areas calculated as a function of depth selected are shown in Figures 20 and 21 for 0.1 mg/l and 0.25 mg/l methylene blue, and 0.5 mg/l, 1.0 mg/l, and 2.0 mg/l methylene blue, respectively. The five curves generated indicate that large area requirements are required for very shallow depths, followed by a large decrease in area per unit depth, and finally an asymptotic section of the curve. The asymptotic section of the curve is related to the decreasing reaction rate with depth balanced by the increase in volume. Therefore, with increasing depth the composite first order rate constant decreases, but the detention time of the lagoon, V/Q , increases, resulting in a near-constant change in area with depth.

Optimum depth selection for the lagoons was chosen at the minimum depth on the asymptotic section of the depth-area curve. The reasons

Figure 20. Effect of depth on lagoon area requirements for 99.7 percent bromacil removal of synthetic industrial waste.

Figure 21. Effect of depth on lagoon area requirements for 99.7 percent bromacil removal of synthetic industrial waste.

for this point for design are: 1) Land requirements are at a practical minimum; 2) The shallow depth should make mixing and diffusion important enough so that aeration is not necessary; 3) With a deep lagoon (e.g. 2-3 m deep), mechanical mixing would be required to bring the contaminants from the aphotic to the photic zone; this may not be required with a shallow lagoon; 4) A lagoon with a high composite first order reaction rate and low detention time will possibly guard against algal and bacterial growth, negating any dye adsorption and light attenuation problems associated with such suspended solids. The consequent lagoon design is a shallow lagoon with very short detention time rather than a deep lagoon with long detention time.

The ultimate criterion for most efficient lagoon design is minimum cost. Cost estimates for lagoon design based on 0.1 mg/l, 0.25 mg/l, 0.5 mg/l, 1.0 mg/l, and 2.0 mg/l methylene blue concentrations are shown in Table 4. Aeration costs are assumed to be zero due to the shallow depth of the lagoon. This assumption, however, must be validated by a pilot scale study. Land costs are based on a figure of \$6000 per acre. The 0.1 mg/l was found to have the least land requirement of the five concentrations of methylene blue. This resulted from a high composite first order rate constant over depth. Acher and Saltzman (1980) found the optimum methylene blue concentration for sensitized photooxidation of bromacil to be 5 mg/l. But this value is for a surface reaction. In a lagoon design, successive control volumes of depth must be taken into account, as was performed with the depth model (Equation 9) to determine the optimum engineering design criteria of minimum land requirement and lowest dye cost. In this study the much lower dye concentration of 0.1 mg/l as compared to 5 mg/l found by Acher and Saltzman (1980) was found

Table 4. Minimum practical depth associated with asymptotic section of area as a function of depth curve, and corresponding area calculated from plug flow design equation.

Methylene Blue Concentration	Area	Depth
0.1	486 m ²	36 cm
0.25	624 m ²	32 cm
0.5	618 m ²	20 cm
1.0	653 m ²	13 cm
2.0	698 m ²	11 cm

to be optimum for engineering design. The reason for such a low concentration of methylene blue providing optimum design is related to the low light attenuation associated with the low concentration of dye--a 5 mg/l methylene blue concentration in a lagoon would have a high photooxidation rate at the surface, but the rate would be extinguished to nil in a few cm by the high light attenuation. A low concentration of methylene blue, however, will maintain the moderate reaction rate of the surface with depth, since very little light is attenuated with depth. In summary, regarding land requirements and land costs, 0.1 mg/l methylene blue provides optimum conditions.

Dye costs represent an ongoing cost for operation of a sensitized photooxidation lagoon. Therefore, a minimum dye concentration in the lagoon is optimum. Based on a cost of \$6.00 per pound of methylene blue, dye costs are presented in Table 5. Since methylene blue is bleached under light, a dye feed would be necessary periodically along the regime of the plug flow reactor. The assumption is made that four dye feeds may be needed for 0.1 mg/l, 0.25 mg/l, and 0.5 mg/l methylene blue, and two feeds for 1.0 mg/l and 2.0 mg/l methylene blue. The

Table 5. Land aeration and dye costs for five methylene blue concentrations, based on rational design.

Methylene Blue Concentration (mg/l)	Aeration Cost per 1000 gal	Dye Cost per 1000 gal	Land Cost
0.1	0	\$0.02 ^a	\$ 721
0.25	0	\$0.05 ^a	\$ 925
0.5	0	\$0.10 ^a	\$ 916
1.0	0	\$0.10 ^b	\$ 968
2.0	0	\$0.20 ^b	\$1030

^aBased on four dye feeds along plug flow regime, each calibrated to add original concentration of methylene blue.

^bBased on two dye feeds along plug flow regime, each calibrated to add original concentration of methylene blue due to bleaching of dye.

reason for the necessity of four feeds with the low concentration of methylene blue is due to low initial concentration of dye: A 50 percent decrease from 0.1 mg/l methylene blue may result in an ineffective dye concentration. Even with four dye feeds, dye costs for the maintenance of 0.1 mg/l methylene blue are low--\$0.02 per 1000 gallons, which is negligible. In summary, based on land costs and dye costs, 0.1 mg/l methylene blue results in optimum and most economic lagoon design. This lagoon design, however, must be verified by pilot scale studies.

Sensitized photooxidation has been proposed as an efficient means of disinfection prior to land application. A pilot sensitized disinfection pond was designed based on the criteria in Table 6.

Results of rate constant as a function of depth, generated by Equation 9, are shown in Figure 22. The results of the depth vs k values, when entered into the plug flow design equation (Equation 10), are shown in Figure 23, where area is plotted as a function of depth.

Figure 22. First order rate constants for 3-log kill of coliform bacteria as a function of depth for Hyrum Wastewater Treatment Plant effluent. Incident radiation was 1000 W/m^2 ; methylene blue concentration was 0.5 mg/l .

dye feeds
blue, and two feeds for

Figure 23. Lagoon area requirements as a function of depth for 3-log disinfection of Hyrum Wastewater Treatment Plant effluent.

Table 6. Design criteria for a sensitized disinfection lagoon.

Coliform removal:	3 log
Surface removal rate (assumed):	.15 min ⁻¹
Methylene blue concentration:	0.5 mg/l
Radiation:	12 hrs at 1000 W/m ²
Wastewater sample:	Hyrum Wastewater Treatment Plant Effluent

As with the industrial waste design, the optimum design is deemed the minimum depth along the asymptotic section of the depth-area curve. Thus, optimum design criteria for a disinfection lagoon is 25 cm deep with an area requirement of 432 m². Total dye costs are \$0.025 per 1000 gal, and land costs are \$641, based on a cost of \$6000 per acre. As with industrial waste treatment, sensitized photooxidation for disinfection looks promising, but must be verified by pilot studies.

SUMMARY AND CONCLUSIONS

A rational engineering approach was involved in the development of design criteria for dye-sensitized photooxidation lagoons. Effects of pH, dissolved oxygen, and temperature were investigated using bench-scale studies under Duro-Test™ Vitalite lamps. A model was developed to predict photooxidation rate as a function of depth dependent upon spectral quantity and quality, waste spectral quality, and sensitizer concentration. A design of a sensitized photooxidation lagoon for the treatment of a bromacil industrial waste was performed. A sensitized photooxidation pond for disinfection of municipal effluent prior to agricultural reuse was also designed. From this study the following conclusions may be drawn:

1. Methylene blue-sensitized photooxidation is most efficient at high pH, but effective rates of photooxidation can be maintained at neutral pH. The rate of bleaching of methylene blue is highest above pH 8.
2. The optimum pH of riboflavin-sensitized photooxidation is dependent upon the substrate. The optimum pH, therefore, will depend on the nature of the substrate. The rate of riboflavin bleaching is highest above pH 7.
3. A model based on light intensity, extinction coefficient, and quantum yield integrated over wavelengths across the visible spectrum provided excellent correlation with laboratory data. This 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 dye concentration.

4. A dissolved oxygen residual of 1-2 mg/l is required for methylene blue-sensitized photooxidation. Higher dissolved oxygen residuals are required for riboflavin-sensitized photooxidation. With a shallow-depth design, diffusion and mixing may be sufficient to maintain sufficient dissolved oxygen residuals.

5. Temperature from 10° to 35° seems to have little effect on sensitized photooxidation rates.

6. The design of a pilot sensitized photooxidation lagoon to remove 99.7 percent of bromacil in an industrial waste showed promising economic and engineering design. To treat a 0.1 mgd (0.263 m³/min) bromacil waste, a 0.1 mg/l methylene blue concentration, 36 cm depth, and 486 m² surface area is required. An economic analysis showed dye costs at \$0.02 per 1000 gal of waste treated and a \$721 land cost for the lagoon.

7. A sensitized photooxidation pond was designed to disinfect 0.1 mgd municipal effluent prior to application for agricultural reuse. To achieve a 3-log kill of coliform bacteria, a pond 25 cm deep with an area of 432 m² would be required, with a land cost of \$641. Dye costs to maintain 0.5 mg/l methylene blue are \$0.025 per 1000 gal disinfected.

8. Photooxidation lagoons for waste treatment and disinfection look promising from an engineering and economic standpoint. However, pilot scale facilities must be developed to investigate the practical design of the lagoons.

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