

Solar photocatalytic mineralization of pesticides in polluted waters

L. Muszkat*, L. Bir, L. Feigelson

ARO, Volcani Center, Bet Dagan, Israel

Received 11 July 1994; accepted 6 September 1994

Abstract

Results are presented on the solar, titanium-dioxide-photocatalyzed degradation of pesticides in rinse waters of agricultural sprayers and in heavily polluted well water. The half-life time of solar photomineralization in the 100 ppb to 50 ppm concentration range was less than 1 h for most of the pesticides. Comparison of the reaction in open and polyethylene-film-covered vessels showed that efficient photodegradation also occurred in sealed systems. Samples of polluted waters prepared from liquid commercial pesticide formulations were also purified effectively by the titanium-dioxide-catalyzed solar photomineralization. The photodegradation of anionic detergents within the formulations was also observed. These results demonstrate the potential of solar photocatalytic oxidation in the removal of organic pollution in water and its practical value in the purification of highly polluted agricultural rinse waters.

Keywords: Photocatalytic degradation; Pesticides; Water treatment; Titanium dioxide; Solar energy organic micropollutants

1. Introduction

The removal of persistent organic chemicals from water is a pressing ecological problem. Persistent contaminants include pesticides, solvents, detergents and a variety of industrial chemicals which, due to the combination of chemical stability and resistance to biodegradation, together with sufficient water solubility, are capable of penetration deep into the soil and of reaching groundwater [1–3]. It should be noted that the microbial purification of water polluted by organic micropollutants at sub-parts per million levels is of extreme difficulty, as biodegradation, which is a major mechanism in wastewater treatment, is quite inefficient at low levels of the substrate [4]. The process of TiO₂-catalyzed photodegradation provides an adequate solution to this problem.

This process has been variously studied during the last decade [5–8]. In previously reported work [9] on this treatment, hydrogen peroxide (0.1 M) was used as additive. The efficacy of the method was illustrated in the treatment of well water polluted by a variety of pesticides and industrial organics. In the present study,

the potential of photocatalytic oxidation carried out in the absence of hydrogen peroxide has been examined in two particular cases: (a) purification of rinse water polluted with pesticide formulations from containers used by aircraft sprayers; (b) purification of groundwater pumped from a well polluted by a nearby pesticide industry.

Airplane spraying is the preferred technique of pest treatment in a wide range of crops. The pesticides (insecticides, fungicides and herbicides) are used as soluble liquids, emulsions or suspensions. The main groups of pesticides applied by spraying are organophosphorous compounds (malathion, glyphosate etc.), triazines (atrazine, prometryn, metribuzine), organochlorines (chlorotalonil, endosulfan) and, to a lesser extent, carbamates. Polluted waters resulting from the rinsing of spray containers contain significant levels of these pesticides, at concentrations in the range 10–100 ppm. Typical volumes of highly contaminated rinse waters per operator amount to about 10³ m³ per year. Suitable treatment is therefore required to prevent the pollution of surface waters, soil and groundwater on disposal of these contaminated waters, which pose a problem of widespread interest.

* Corresponding author.

2. Experimental details

The materials were obtained from the following sources and were used as received: titanium dioxide (P25, Degussa, Frankfurt am Main; surface area, 51–55 m² g⁻¹); malathion (Bayer) (99.3%) and atrazine (97.2%) (Dr. Ehrensotoffer, Augsburg); tetrapropyl benzene sulfonate (5% solution) (Merck, Darmstadt); methylene blue (Sigma, St. Louis, MO); atrazine and malathion formulations (Antranex and Malathion 50) were obtained from Machtshim Co. (Beer Sheva, Israel).

2.1. Sample preparation

Solutions were usually prepared from concentrated samples dissolved in acetone, with subsequent evaporation of the solvent, followed by dissolution in the required volume of water.

In several cases, solutions of detergent and pesticide formulations were prepared by direct mixing with water in the required proportions.

2.2. Illumination procedure

The samples were contained in Pyrex Erlenmeyer flasks or open glass crystallization dishes (volume, 3 l; internal diameter, 22.5 cm), fitted with magnetic stirrers and exposed to sunlight from 9 a.m. to 3 p.m. The visible light intensity in Bet Dagan (32 °N) is in the range 0.4–1.1 kW m⁻² at ground level. The temperature of the water samples was in the range 26–38 °C.

In long exposure runs, the samples were refrigerated overnight. Each series of photodegradation experiments was accompanied by dark reaction controls in the absence of TiO₂ (a) and with TiO₂ (b).

2.3. Analysis

All glassware was baked at 400 °C to eliminate interference trace organics.

2.4. Gas chromatographic (GC) and GC/MS analysis

Samples (50 or 100 ml) were centrifuged for 20 min at 8500 rev min⁻¹. After adding 10–20 g sodium chloride, samples were extracted with three portions of methylene chloride (10 ml). The combined extracts were dried on anhydrous sodium sulfate and, after filtration (and washing of drying agent with acetone), were concentrated in vacuum at room temperature. Two portions of 50 ml acetone were added followed by evaporation to 5 ml. Extracts were further concentrated in a Kuderna Danish test-tube. Final concentration was carried out with a gentle stream of pure nitrogen to a final volume of 0.5 or 1.0 ml.

GC measurements were performed on a Varian 6000 gas chromatograph equipped with a thermionic specific detector and a glass column (internal diameter, 3 mm; length, 2 m) packed with 2% OV-17. The injector temperature was 230 °C and the oven temperature was constant (195 °C for atrazine and metribuzine, 215 °C for malathion). Capillary gas chromatographic/mass spectrometric (GC/MS) analysis was carried out on a Finnigam 5100 system. A DB-5 column (length, 30 m; diameter, 0.25 mm) was used.

2.5. Analysis of anionic detergents

Following centrifugation, the methylene blue procedure recommended by Merck [10] was applied, using sodium tetrapropyl benzene sulfonate (TPBS) as standard. The concentrations of detergents are referred to tetrapropyl benzene sulfonate.

3. Results and discussion

The purpose of this study was to explore and select the best conditions for carrying out the solar, TiO₂-photocatalyzed mineralization of trace organics in polluted water. The first parameter considered was the irradiation time. In the present study, the irradiation times (half-life values of approximately 1 h for malathion, bromacil and triazine herbicides, Tables 1–6) are much shorter than the irradiation time used previously [7]. We examined the possibility of carrying out the photodegradation without the addition of hydrogen peroxide. Our results show that photodegradation is also effective in the absence of H₂O₂. While the role of hydrogen peroxide in the photodegradation of trace organics in the parts per billion to parts per million range is not entirely clear, we consider that it is indispensable for the decomposition of inhibitory constituents of polluted waters. We have encountered one such case when examining the photodegradation of polluted well water. Hydrogen peroxide in the presence of photo-oxidized TiO₂ is a known source of hydroxyl radicals [9].

The half-life value for malathion in an aerated solution, prepared by diluting the formulation to 70 ppm, is about 1 h (Table 1). This experiment was carried out in the presence of TiO₂ (100 mg l⁻¹) and in the absence of H₂O₂. The reaction follows first-order kinetics over several half-life times.

The data in Table 2 indicate that 100 mg l⁻¹ is the optimal concentration of photocatalyst, which gives rise to extensive degradation of malathion (from 50 ppm to 0.3 ppm) in 11 h of solar exposure.

The effect of a film of polyethylene (100 μm thick) on the solar photodegradation is shown in Tables 3 and 4. It should be noted that the reaction efficiency

Table 1
Solar, TiO₂-photocatalyzed decomposition of malathion (70 ppm) in dilute commercial formulation solution^{a,b}

Exposure (h)	Residual concentration (ppm)
1	34
2	26
3	15
4	10
5	5
6	3

^a Solar irradiation in open crystallizer; volume, 2 l; 100 mg l⁻¹ TiO₂.

^b Peak solar visible incident power, 0.97 kW m⁻².

Table 2
Solar, TiO₂-photocatalyzed decomposition of malathion solutions (50 ppm) as a function of the amount of catalyst used^a

TiO ₂ (mg l ⁻¹)	Exposure (h) ^b	Residual concentration (ppm)
1000	3	1.8
	6	<0.2
100	6	5.6
	11	0.3
50	3	8.5
	6	5.9
20	3	11

^a In the absence of H₂O₂ in open crystallizers (diameter, 22.5 cm); solution volume, 1 l; temperature, 25–30 °C.

^b Peak solar visible incident power, 0.90 kW m⁻².

Table 3
Effect of solar irradiation through polyethylene film on TiO₂-photocatalyzed decomposition of malathion (70 ppm)^{a,b,c}

Exposure (h)	Residual concentration (ppm)	
	Open ^d	Polyethylene cover
1	34	35
3	9	13
6	2.5	4.5
12	0.2	0.3
18	>0.2 ppb	0.8 ppb

^a Polyethylene film, 100 μm thick.

^b In the presence of 1.15 mg l⁻¹ detergent TPBS. Detergent is decomposed completely after 1 h of irradiation.

^c Irradiation in crystallizer (diameter, 22.5 cm); solution volume, 2 l; in the absence of H₂O₂.

^d Concentrations corrected for evaporation.

is satisfactory, which allows the process to be applied to closed systems. Obviously, such a use may be of interest for the treatment of water polluted by malodorous volatile and semivolatile micropollutants. A practical case of this type of situation is encountered in the decontamination of the spray tank rinse water from technical malathion formulations, which are highly

Table 4
Effect of solar irradiation through polyethylene film on TiO₂-photocatalyzed decomposition of atrazine (35 ppm)^a

Exposure (h)	Residual concentration (ppm)	
	Open	Polyethylene film
1	19	27
2	6.5	15

^a For details, see footnotes to Table 3.

Table 5
TiO₂-photocatalyzed decomposition

Exposure (h)	Residual concentration (ppb)			
	TiO ₂ 100 mg l ⁻¹		Blank (no TiO ₂)	
	Atrazine	Malathion	Atrazine	Malathion
0	90	104	90	104
4	17	0.34	81	83
12	0.1	0.2	73	84

Table 6
Solar, TiO₂-photocatalyzed decomposition of organic contaminants in water of well Nir Galim 1

Compound	Concentration (ppb) after exposure for			
	0 h	1 h	5 h	10 h
Dichloroaniline	45	13	12	4
Benzopyran (<i>m/z</i> 176)	10	4	3.5	3
Atrazine	23	9	6	5
Propazine	6	3	3	3
Alachlor	273	86	83	83
Prometryn	25	12	11	11
Bromacil	27	13	12	10
Cyanobenzoate (<i>m/z</i> 253)	24	12	10	8

objectionable, both environmentally and on account of the strong odor of the technical formulation. Also it will diminish the loss of water due to evaporation.

In Table 5, the photocatalytic degradation of atrazine and malathion is compared with the direct photodegradation (non-catalytic, direct excitation), emphasizing the decisive contribution of TiO₂ catalysis to the degradation process.

Table 6 presents the results of solar, TiO₂-photocatalyzed treatment of groundwater, pumped from a polluted well (Ref. [9], Nir Galim 1). The half-life value for representative micropollutants is of the order of 1 h.

The detergent TPBS (1.15 ppm), chosen to represent detergent dispersant and spreading agents in formulations, was shown to undergo complete degradation under the present conditions (see Table 3).

Acknowledgement

This research was supported by U.S. Agency for International Development, Grant no. CA13-025.

References

- [1] Z.Z. Cohen, C. Liden and M.N. Lorber, in W.Y. Garner (ed.), *Evaluation of Pesticides in Groundwater*, ACS Symp. Ser. 315, American Chemical Society, Washington, DC, 1986, pp. 170–196.
- [2] H.B. Pionke and D.E. Glotfelty, *Water Res.*, **23** (1989) 1031–1038.
- [3] L. Muszkat, D. Raucher, M. Magaritz and D. Ronen, in U. Zoller (ed.), *Groundwater Contamination and Control*, Marcel Dekker, 1994, pp. 257–271.
- [4] J. Moening, D. Bahnemann and K. Asmus, *Biol. Interact.*, **47** (1983) 15–27.
- [5] R.W. Matthews, in E. Pelizzetti and M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, 1991, pp. 427–449.
- [6] H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M.A. Fox and B. Draper, *Langmuir*, **5** (1989) 250–255.
- [7] N. Serpone, D. Lawless, R. Terzian and E. Pelizzetti, in E. Pelizzetti and M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, 1991, pp. 451–475.
- [8] H. Hidaka, S. Yamada, S. Suenaga and H. Kubota, *J. Photochem. Photobiol. A: Chem.*, **47** (1989) 103–112.
- [9] L. Muszkat, M. Halmann, D. Raucher and L. Bir, *J. Photochem. Photobiol. A: Chem.*, **65** (1992) 409–417.
- [10] (a) B.M. Milwidski, *Practical Detergent Analysis*, McNair-Dorland, New York, 1970, pp. 44–45, 149–150.
(b) E. Merck, *The Testing of Water*, Merck, Darmstadt, 10th edn., 1975.