



# PRETREATMENT OF PESTICIDE WASTEWATER BY PHOTOCATALYTIC OXIDATION

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## ABSTRACT

The toxic chemicals, 2,4-D (a herbicide) and propoxur (an insecticide), were used as the model compounds in these experiments. Total organic carbon analyzer was used to assess the efficiency of photocatalytic mineralization. Microtox bioassay was employed in evaluating the toxicity of solutions treated by photocatalysis. Ultraviolet absorption spectra were also used for showing the different characteristics of the compounds undergoing photocatalytic oxidation. Results show that propoxur is less degradable than 2,4-D, and the photomineralization of these pesticides follows a behavior of first-order reaction. Products of 2,4-D and propoxur are more toxic than the parent compound after partial photodegradation. This shows that complete mineralization is necessary for total detoxification of these pesticides. In other words, toxicity is an important criteria in assessing the pretreatment process. © 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Photocatalytic oxidation; titanium dioxide; 2,4-D; propoxur; microtox bioassay

## INTRODUCTION

Several technologies have been reported for toxic materials treatment but many of them are generally difficult to apply due to inefficiency, or too expensive. Photocatalytic oxidation is considered a promising technology for the elimination of toxic organic pollutants. Investigation of the photocatalytic oxidation of pesticides in aqueous media irradiated by near-UV light has been a rapidly growing field of research (Pelizzetti *et al.*, 1990; Lu *et al.*, 1995). Barení *et al.* (1987) have found the photocatalytic degradation of 2,4,5-trichlorophenoxyacetic acid and 2,4,5-trichlorophenol to CO<sub>2</sub> and HCl occurs with half-lives of 30-90 minutes. Organophosphorus insecticides in aqueous solution were also reported to be degraded efficiently by this method (Matthews, 1990).

For toxic chemical treatment, the formation of harmless mineral products is obviously important because incomplete oxidation could result in more toxic intermediates than the parents (Matthews, 1990). Therefore, the critical point in evaluating the possibility of photocatalysis to be a pretreatment process is the toxicity assessment of photodegradation products. Manilal *et al.* (1992) have investigated the toxicity of photodegradation products of methyl vinyl ketone, pentachlorophenol and 2,4-dichlorophenol by using respiration rate measurements in activated sludge as a measure of the toxicity. However, this method is not

as sensitive as Microtox test. The Microtox test is a simple and rapid technique for indicating toxicity by making use of the luminescent bacterium *Photobacterium phosphoreum*. This test involves the measurement of the quantity of light emitted by the bacteria before and after exposure to an aqueous sample. This test can be used in evaluating the toxicity of wastewater (Arbuckle *et al.*, 1992). Svenson *et al.* (1989) were also successful in studying the photochemical conversion of chlorinated phenolic substances in aquatic media by Microtox tests.

In the study, 2,4-D (a herbicide), and propoxur (an insecticide) were used as the model compounds in these experiments. Results from experiments on photocatalytic oxidation of pesticides over  $\text{TiO}_2$  supported on glass are presented. Total organic carbon analysis was used as a measure of mineralization of pesticides to assess the efficiency of photocatalytic mineralization. Toxicity assessment of the original pesticides and their photocatalytic degradation products were tested with Microtox tests. The UV spectra of photocatalytically treated and untreated samples were taken for showing their characteristics.

## MATERIAL AND METHODS

Titanium dioxide was provided by Degussa (Frankfurt, Germany). According to the information of manufacture, the specific surface area of  $\text{TiO}_2$  is  $50 \pm 15 \text{ m}^2/\text{g}$  and is mostly in the anatase form. The water employed in all preparations has a resistivity of  $\rho > 18 \text{ M}\Omega/\text{cm}$ . Propoxur (99.2% purity) and 2,4-D (99% purity) were obtained from Bayer A. G. (Leverkusen, Germany) and Aldrich Chem. Co. (Milwaukee, Wisconsin, USA), respectively. The reagents for Microtox test were supplied by Microbic Corporation (Carlsbad, California, USA). All other chemicals are laboratory reagent grade and purchased from Merck A. G. (Darmstadt, Germany). As shown in Figure 1, the photoreactor was a Pyrex glass tube (0.6 cm i.d. and 6.6 m long) wound 48 times to form a coil which supported 175 mg of  $\text{TiO}_2$  on the inner surface of the tube. A 20-W black light blue fluorescent tube (Iwaski Electric Co., Japan) fitted down the center of the spiral and was mounted in a standard 20-W fluorescent tube domestic lamp holder. Solutions were circulated through the spiral phototube via reservoir and peristaltic pump in a loop. The reservoir was surrounded by a thermostatically controlled water bath.

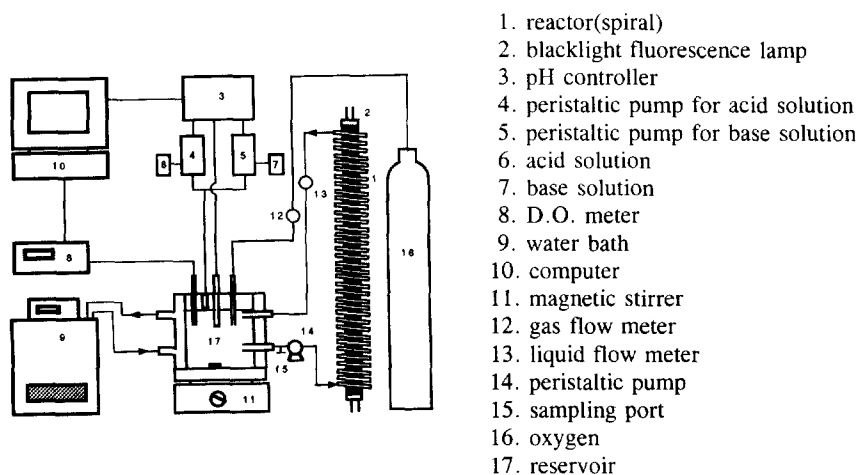


Figure 1. Photocatalytic reactor used in this study.

A 1000-ml sample, which was diluted from the stock solution, was prepared for each experiment. Prior to irradiation, the sample was bubbled by pure oxygen, and adjusted to the preselected pH. Solution was then circulated through the reactor for 15 min before turning on the UV light. After each run, the catalyst was regenerated by washing the spiral with 0.1 M  $\text{NaHCO}_3$ , 0.1M  $\text{HClO}_4$ , and pure water.

The Microtox method is based on bioluminescent activity of *Photobacterium phosphoreum*. Tests were performed on a Microtox model 500 (Microbics Corp., Carlsbad, California). The standard Microtox procedure was detailed in the Microbic Operating Manual (Microbics, 1991). The measurements of light output were carried out after 15 minutes. The addition of toxic chemicals were indicated by a decrease in the light output. The toxicity was recorded as the percent decrease in light output, which was calculated using the formula:

where  $I_s$  is the light level of the blank, and  $I_e$  is the light level of toxicant exposure.

Total organic carbon (TOC) determination was carried out by a total organic carbon analyzer (ASTRO 2001 system 2, League City, Texas, USA). The UV adsorption spectra of samples were taken using a Hitachi U-3210 spectrophotometer (Tokyo, Japan).

## RESULTS AND DISCUSSION

Figure 2 shows that both toxic compounds studied were mineralized in a first-order expression in terms of TOC oxidation. The rate constants and half-lives obtained are given in Table 1.

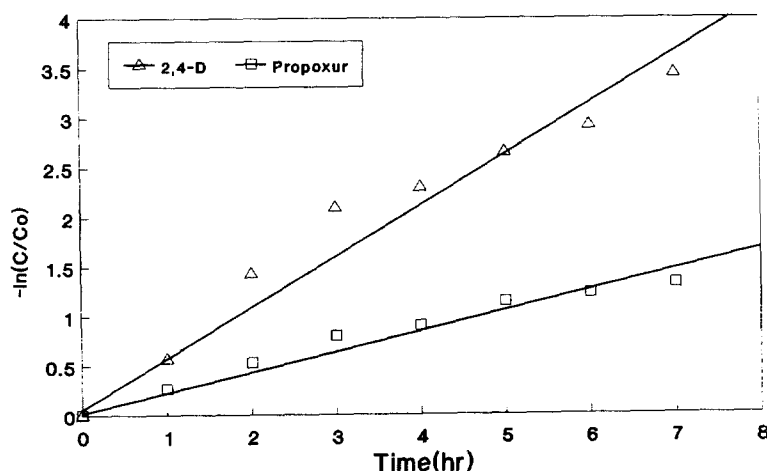


Figure 2. Apparent first kinetics for 2,4-D and propoxur in photocatalytic mineralization experimental conditions: temperature, 30°C; flow rate, 500 ml/min; initial concentration, 50 mg/l; initial pH(pH<sub>0</sub>), 4; O<sub>2</sub> purge, 50 ml/min.

Table 1. First order rate constants and half-lives

Compound	$k_{app}(10^{-2} \text{ hr}^{-1})$	$t_{1/2}$ (hr)
2,4-D	$51.1 \pm 6.6$	$1.36 \pm 0.17$
Propoxur	$20.0 \pm 2.2$	$3.47 \pm 0.37$

After seven-hour photocatalytic oxidation, the mineralization efficiencies of 2,4-D and propoxur are 96.8% and 73.4%, respectively. As it is not kept constant during the reaction period, solution pH will vary as the photocatalytic reaction takes place. For photocatalytic oxidation of 2,4-D, the solution pH will decrease. Propoxur, a kind of carbamate, is different from 2,4-D. The solution pH will increase in the reaction period for the formation of ammonium ion. The final pH of 2,4-D and propoxur solution after photocatalytic

treatment are 3.52 and 5.23, respectively. According to our findings, however, it made no obvious difference in inhibiting *Photobacterium phosphoreum* activity between pH 3.5~8 in blank study.

The general trend observed in the experiments was that the TOC extent decreased with time of illumination. However, the tendency of toxicity variation was not identical to that of mineralization. The toxicity (inhibition, %) suddenly increased as soon as the photocatalytic oxidation started. This indicates that toxic products were formed as the toxic parent compound was photocatalyzed. With the photocatalytic reaction occurring, inhibition gradually decreased since toxic products went on being oxidized. Eventually, after seven-hour treatment, toxicity of treated solution is lower than that of the parent. For 2,4-D, the solution toxicity increased quickly in the first-hour reaction. Afterwards, the solution toxicity diminished with illumination time (Figure 3A). Figure 3B shows the toxicity of unit TOC for 2,4-D oxidized.

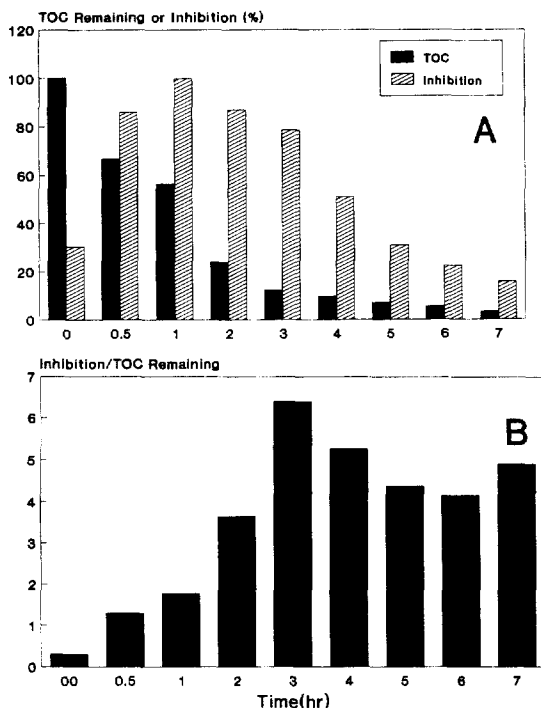


Figure 3. Microtox test and total organic carbon analysis of 2,4-D versus illumination time.

A series of UV spectra of 2,4-D solution were recorded in the 190-350 nm range with time of illumination to monitor the disappearance of the contaminants. Typical spectra, obtained with a 2,4-D solution, are shown in Figure 4. There was a marked drop in the ultraviolet absorption as photocatalytic degradation occurred. The appearance of new bands in the range of 300-350 nm is shown at 0.5 hour of illumination. After three hours, the presence of these bands depleted, suggesting the formation and the subsequent destruction of unknown intermediate compounds. In mineralization of propoxur, a similar trend was observed to that of 2,4-D in the first-hour reaction (Figure 5A). However, at the time of one to four hours, a substantial reduction in toxicity was not significant. The toxicity of samples of propoxur was fairly constant during this period. Finally, the solution toxicity decreased to a level lower than the parent. Figure 5B shows the toxicity of unit TOC for propoxur oxidized. A series of ultraviolet spectra were also recorded in order to monitor the appearance of intermediate species and their subsequent disappearance (Figure 6). These spectra indicate that during the first 2-3 hours of reaction, the intensities of the absorption band exhibits sudden variation, after which their intensities tend to decrease gradually. Similarly, there are new bands presenting in the range of 300-350 nm at 0.5 hour of illumination then disappear after three hours.

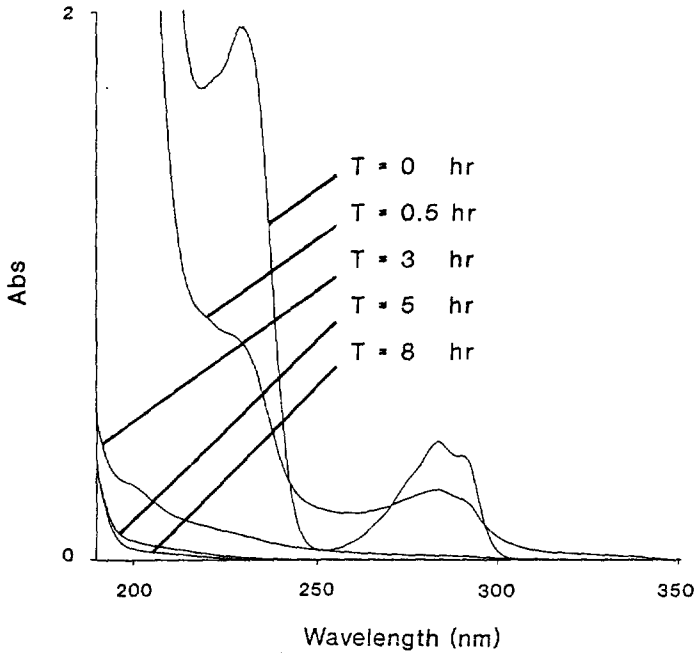


Figure 4. Ultraviolet absorption spectra of 2,4-D on photocatalytic treatment.

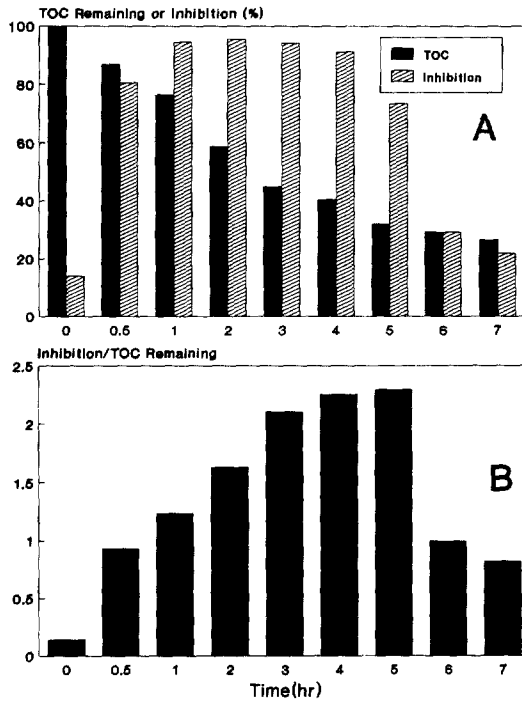


Figure 5. Microtox test and total organic carbon analysis of propoxur versus illumination time.

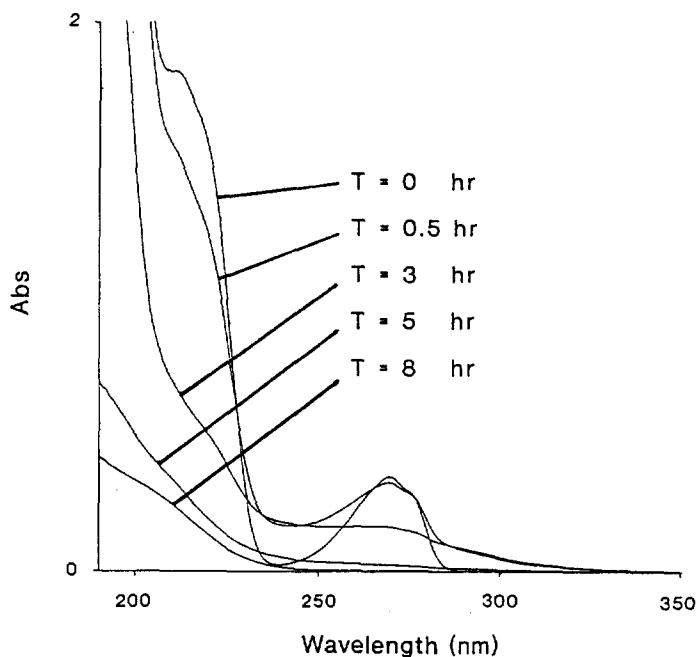


Figure 6. Ultraviolet absorption spectra of propoxur on photocatalytic treatment.

## CONCLUSIONS

In these experiments, photomineralization of 2,4-D and propoxur is a first-order reaction. It can be found that incomplete oxidation results in more toxic intermediates than the parent. The information indicates that pretreatment of wastewater containing 2,4-D and propoxur by photocatalytic oxidation is possible ahead of the conventional biological process after the toxicity of the wastewater has reduced.

## ACKNOWLEDGEMENT

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