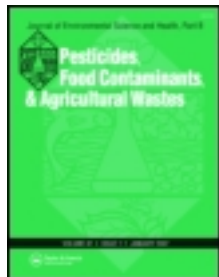


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### Photocatalytic oxidation of propoxur in aqueous titanium dioxide suspensions

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## PHOTOCATALYTIC OXIDATION OF PROPOXUR IN AQUEOUS TITANIUM DIOXIDE SUSPENSIONS

**Key Words:** Photocatalysis, titanium dioxide, UV light, propoxur, insecticide

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### ABSTRACT

The photocatalytic oxidation of propoxur, a nitrogen-containing pesticide, has been investigated using aqueous TiO<sub>2</sub> suspensions as catalyst in this study. The operating variables considered in the study were initial pH, temperature, [H<sub>2</sub>O<sub>2</sub>] and TiO<sub>2</sub> loading. Results showed that 1 g/l of TiO<sub>2</sub> was the optimum dosage for oxidizing propoxur in this system. Hydrogen peroxide can increase the oxidation rate with increasing its initial concentration. There was no obvious difference in the rate of propoxur oxidation at the initial pH of 4, 6 and 9, and the final pHs of reaction solutions were around 5.5. However, propoxur degraded slower at initial pH 2, and the pH did not vary during the period of photocatalytic reaction. The photocatalytic oxidation of propoxur using TiO<sub>2</sub> suspensions as the photocatalyst was reaction-controlled as indicated by the activation energy.

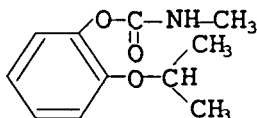
## INTRODUCTION

Surface waters and groundwaters have been found to contain substantial concentrations of pesticides (Lu et al, 1993; Gustafson, 1993; Domagalski et al., 1997). Several studies have been carried on the destruction of these pollutants (Benitez et al, 1994; Kiwi et al, 1994; Lu et al, 1994 and 1999). However, some of these pesticides are refractory to degradation by conventional biological processes because of their toxic characteristics. Therefore, advanced oxidation processes (AOPs) has become promising in the destruction of organic compounds in general and pesticides in particular.

Photocatalytic oxidation is an emerging technology using semiconductor as the catalyst to remove contaminants from polluted waters. A number of studies have shown that illumination of semiconductor powders in aqueous solutions containing organic compounds and oxygen induced effective decomposition of organic compounds (Al-Ekabi et al., 1988; Fu et al., 1995; Pelizzetti et al., 1990 & 1996; Lu et al., 1993; 1994; 1995; 1998).

Since the photo-oxidation reaction takes place at the surface of the photocatalyst, the adsorption characteristics of the solute become to be quite important. In previous studies, photocatalytic oxidation of pesticides was investigated with  $\text{TiO}_2$  coated on the inner surface of glass tube. The photocatalytic oxidation of pesticides followed the Langmuir-Hinshelwood-type behavior, indicating that surface reaction on the photocatalyst may play an important role in the oxidation reaction (Lu et al., 1993; 1995). Photocatalyst can be loaded on suitable adsorbents to concentrate the pollutants on the photocatalyst surface for the increase in photocatalytic efficiency. The use of granular activated carbon as a support for  $\text{TiO}_2$  was effective in the enhancement of the rate of propoxur removal (Lu et al., 1998). Matthews (1991) suggested that the use of  $\text{TiO}_2$  coated on sand permits economic scaling up of the process. Uchida et al. (1993) demonstrated the photomineralization of propyzamine, a herbicide, with  $\text{TiO}_2$  / activated carbon complexing agent in dilute aqueous solution. Kato et al. (1993) also used the porous alumina ceramic as the support to study the photocatalytic property of  $\text{TiO}_2$ .

Propoxur (2-isopropoxyphenyl N-methylcarbamate), commercially known as Baygon, was chosen as the test compound in this study; its structure is shown as below:



It is used for the control of household insects such as cockroaches, bedbugs, mosquitoes (Benitez et al, 1994). The use of granular activated carbon as a support for  $\text{TiO}_2$  was effective in the enhancement of the rate of propoxur removal. However, the oxidation efficiency for the titanium dioxide coated on support was much lower than that for the titanium dioxide suspensions, because mass transfer and photon utilization were limited in the coated system (Lu et al., 1999). Based on the energy efficiency, the  $\text{TiO}_2$  suspension system has its potential in the treatment of water and wastewater. Therefore, in this study, experimental results of the photocatalytic oxidation of propoxur in aqueous titanium dioxide suspensions are presented. The effects of varying experimental parameters such as initial pH, temperature,  $[\text{H}_2\text{O}_2]$  and  $\text{TiO}_2$  loading are also reported.

## MATERIAL AND METHODS

Propoxur was obtained from the Bayer Company with purity of 96.3%. The photocatalyst,  $\text{TiO}_2$ , used in this study was Degussa P25, 50  $\text{m}^2/\text{g}$  and 30 nm mean particle size obtained from the Degussa Company (Germany). The water used for experiments was purified by a Milli-Q/RO system (Millipore) and has a resistivity greater than 18  $\text{M}\Omega/\text{cm}$ . All other chemicals used were of reagent grade without further purification.

The reaction was conducted in a 1.2-liter double-jacked vessel (i.d. 11cm) with a quartz cover; the volume of reaction mixture was 1 liter. Quartz cover was required for the shorter wavelength of UV light. The UV radiators located above the reactor was a low pressure mercury UV lamp with a main wavelength of 254 nm (Sankyo, Japan).

Solutions containing  $4.78 \times 10^{-4}$  M (100 mg/l) of propoxur were used as the reaction mixtures. To investigate the effect of pH on the propoxur degradation, experiments at initial pH of 2.0, 4.0, 6.0 and 9.0, were conducted. For all experimental runs performed in this study, the solution pH was adjusted initially. The concentrations of hydrogen peroxide, ranging from  $0-4.9 \times 10^{-2}$  M, and 0.5, 1, 3 and 5 g/l of  $\text{TiO}_2$  were also selected to study their influence on the reaction rate. During experiments, the reactant solution was agitated continuously with a magnetic stirrer and oxygen (99.9 % purity) was bubbled into the solutions at a constant flow-rate of 50 ml/min to insure oxygen saturation. The samples were taken from the solution with certain time intervals, and then filtered by Gelman  $0.2 \mu\text{m}$  microfilters to be analyzed.

Propoxur was analyzed by an HPLC (Waters LC module 1) with a Nova-Pack  $\text{C}_{18}$  column and UV detector. The eluent was a mixture of water and acetonitrile in the volume ratio of 42/58. Detection was made at 280 nm. The retention time for propoxur under the experimental conditions was 2.2 min. Quantum yield (QY) was used to evaluate the photon efficiency for the photocatalytic reactor. QY can be defined as the ratio of the number of molecules reacting to that the photons supplied. Based on reaction with  $\text{TiO}_2$  - free actinometry solutions for the reactor, the flux rate was  $7.2 \times 10^{-4}$  M/min (Lu et al., 1999).

## RESULTS AND DISCUSSION

### Comparison of UV/ $\text{H}_2\text{O}_2$ , $\text{TiO}_2$ / $\text{H}_2\text{O}_2$ and $\text{TiO}_2$ /UV/ $\text{H}_2\text{O}_2$ processes

The results of the experiments conducted at initial pH 4 in the presence of UV,  $\text{H}_2\text{O}_2$ ,  $\text{TiO}_2$ ,  $\text{TiO}_2$ /UV, UV/ $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$ /UV/ $\text{H}_2\text{O}_2$  are presented in Figure 1. The propoxur concentration was plotted as a function of the reaction time. As shown in Figure 1, a very small decrease in the concentration of propoxur in the presence of  $\text{H}_2\text{O}_2$ ,  $\text{TiO}_2$  or UV light only was observed. However, propoxur was oxidized obviously when  $\text{TiO}_2$  and UV were combined.

The fit of the data indicated that the oxidation of propoxur followed a first-order kinetics rate law

$$-d[\text{Propoxur}]/dt = k [\text{Propoxur}] \quad (1)$$

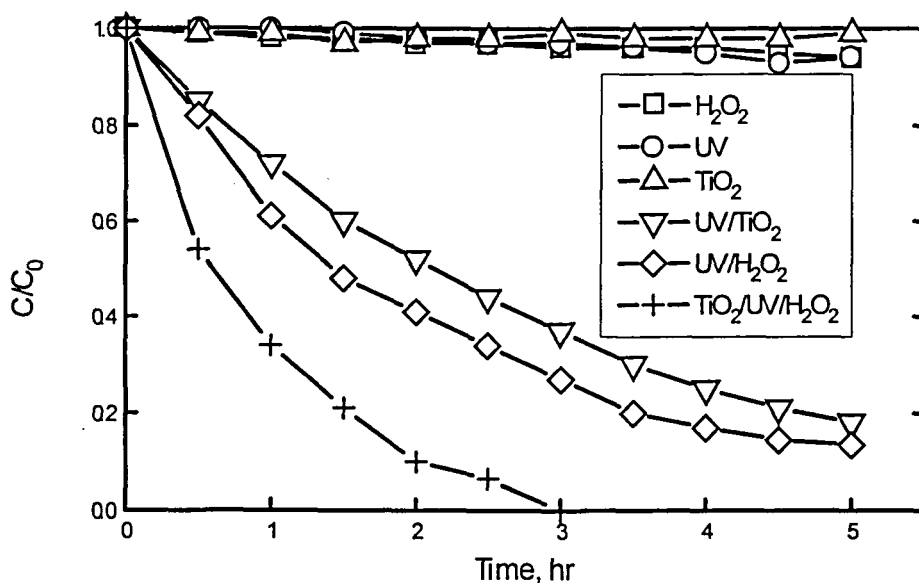


FIGURE 1

Comparison of propoxur oxidation by different advanced oxidation processes. Experimental conditions: [propoxur] =  $4.78 \times 10^{-4}$  M, pH=4.0, 1 g TiO<sub>2</sub>, Temperature 30°C, [H<sub>2</sub>O<sub>2</sub>] =  $4.9 \times 10^{-2}$  M.

and thus

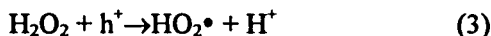
$$\ln\left(\frac{[\text{Propoxur}]}{[\text{Propoxur}]_0}\right) = -kt \quad (2)$$

where  $k$  is the observed first-order rate constant and  $[\text{Propoxur}]$  and  $[\text{Propoxur}]_0$  are the concentrations of propoxur in solution at any time  $t$  and time zero, respectively. The lines shown in Figure 1 were fitted to the data by linear regression, which produced correlation coefficients  $> 0.98$ . The first order pattern was observed for all of the experiments performed in this study. This is in agreement with the first-order rate kinetics reported earlier for other organic compounds (Al-Ekabi et al., 1988; Lu et al., 1993, 1994, 1995 & 1998). As reported earlier, hydrogen peroxide may increase or decrease the rate of photocatalytic oxidation (Harada et al., 1990; Auguliario et al., 1990; Lu et al., 1994). In this experiment,  $4.9 \times 10^{-2}$  M of H<sub>2</sub>O<sub>2</sub> was added to the solution to compare the oxidation efficiency among UV/H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub>.

processes. All the reactions followed a first-order kinetic behavior, and UV/H<sub>2</sub>O<sub>2</sub> has a slightly higher efficiency than UV/TiO<sub>2</sub>. Based on the kinetic analysis, the rate constants for UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> processes are 0.343 hr<sup>-1</sup>, 0.441 hr<sup>-1</sup> and 1.18 hr<sup>-1</sup>, respectively. In other word, the initial rates for UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> are 1.64×10<sup>-4</sup> M/hr<sup>-1</sup>, 2.11×10<sup>-4</sup> M/hr<sup>-1</sup> and 5.62×10<sup>-4</sup> M/hr<sup>-1</sup>, respectively. According to the comparison of the initial rates, it was found that UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> has a rate higher than the sum of the other two processes.

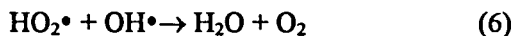
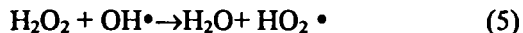
### Effect of H<sub>2</sub>O<sub>2</sub>

Hydroxyl radicals can be produced directly from H<sub>2</sub>O<sub>2</sub> and UV light. Hydrogen peroxide is also a better electron acceptor, therefore, the rate of photocatalytic oxidation can be enhanced due to better hole and electron utilization efficiency because recombination of electrons and holes can be reduced. These reactions are shown as below (Auguliaro et al.,1990).



Auguliaro et al. (1990) have reported that hydrogen peroxide can increase the oxidation rate of phenol. Harada et al. (1990) also found the increase in dichlorvos oxidation in the presence of hydrogen peroxide.

However, there were some contradictory results reported on the effect of hydrogen peroxide on photocatalytic reaction. Hydrogen peroxide could react with OH• leading to a competition with organic compounds for degradation. The reactions are shown in the following.



Mailard et al. (1992) reported the inhibition of benzamide oxidation in the presence of hydrogen peroxide. Peterson et al. (1991) observed that the photocatalytic reaction decrease in oxidation rate when hydrogen peroxide presented in the solution.

In a previous study, it was found that hydrogen peroxide inhibited the photocatalytic oxidation of dichlorvos. However, hydrogen peroxide can increase

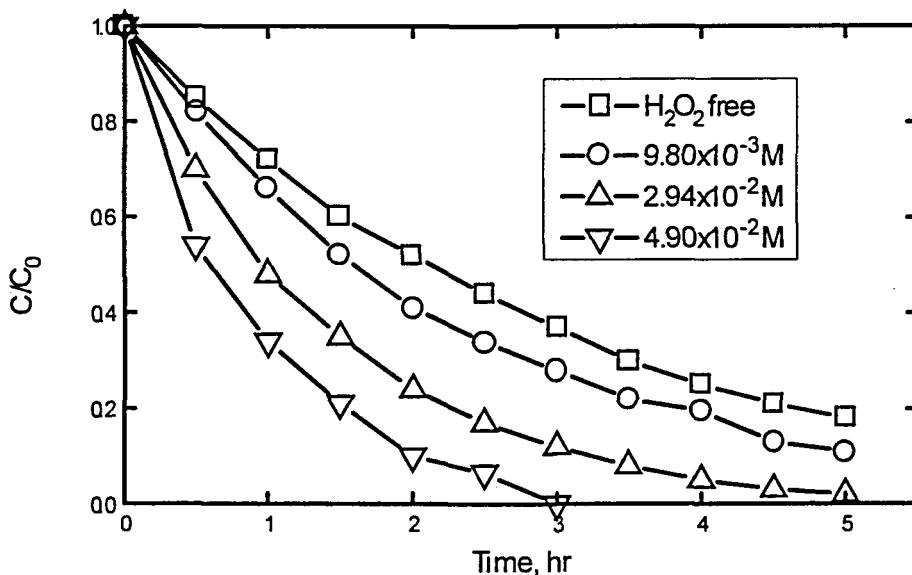


FIGURE 2

Effect of  $H_2O_2$  on the photocatalytic oxidation of propoxur. Experimental conditions: [propoxur] =  $4.78 \times 10^{-4} M$ , pH=4.0, 1 g  $TiO_2$ , Temperature  $30^\circ C$ . 1 g  $TiO_2$ .

the photocatalytic oxidation of propoxur under the present experimental conditions. As shown in Figure 2, the oxidation rate increased with increasing the concentration of hydrogen peroxide, ranging from 0- $4.9 \times 10^{-2} M$ . Therefore, the first-order rate constant in terms of the initial  $[H_2O_2]$  was obtained as shown below:

$$k = 0.98[H_2O_2]^{0.58} \quad (7)$$

#### Effect of $TiO_2$ Loading

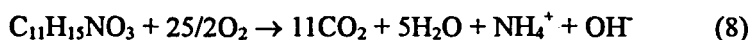
The optimum catalyst loading for this reactor geometry was determined in this study. Theoretically, the more  $TiO_2$  loading, the higher reaction rate if the photons entering the reactor can be almost absorbed by the photocatalyst as  $TiO_2$  dispersed completely in the reactor. However,  $TiO_2$  may not utilize all the photons entering the reactor to produce radicals for degrading propoxur because light scattering and reflection are greater at a over-high  $TiO_2$  concentration. In this study, 0.5, 1, 3 and



5 g/l of TiO<sub>2</sub> were selected to investigate the influence on the photocatalytic degradation. Figure 3 displays the variation of rate constant versus TiO<sub>2</sub> loading for experiments with an initial propoxur concentration of  $4.78 \times 10^{-4}$  M. This plot shows that 1 g/l of TiO<sub>2</sub> was the optimum dosage in this system. The rate of propoxur oxidation decreased when the TiO<sub>2</sub> concentration was higher or lower than 1 g/l. The kinetic constants are also listed in Table 1. Turchi (1989) reported the optimum TiO<sub>2</sub> loading occurring at 1 g/l. Tseng (1991) found the rate of chlorophenol oxidation reached a maximum value at 3 g/l using test tubes as the reactor. Consequently, the optimum catalyst concentration depends on the reaction conditions including reactor geometry and light source intensity.

#### Effect of pH

For the material used in this work, the zero zeta potential occurred at pH 6.4 (Lu et al., 1996). At more acidic pH, the semiconductor particle surface was positively charged, while at pH > 6.4, the surface was negatively charged. In order to understand the effect of pH on the propoxur degradation rate, experiments at initial pH of 2.0, 4.0, 6.0 and 9.0, were conducted. The photoinduced mineralization of propoxur occurred stoichiometrically using oxygen as an oxidizing agent; the total reaction is shown as below (Lu et al., 1994):



Result showed that there was no obvious difference in the degradation rate of propoxur at the initial pH of 4.0, 6.0 and 9.0, and the final pH of reaction solution was around 5.5 (see Figure 4 and Figure 5). The photocatalytic degradation of propoxur followed a pseudo-first-order kinetics in this study, and all kinetic constants are listed in Table 1. However, propoxur degraded slower at initial pH 2, and the pH did not vary obviously during photocatalytic reaction without controlling pH.

#### Effect of temperature

Reaction temperature had a significant effect on photocatalytic oxidation. The influence of temperature on the rates of chemical reaction is usually interpreted in terms of the Arrhenius equation. The oxidation rate as a function of temperature

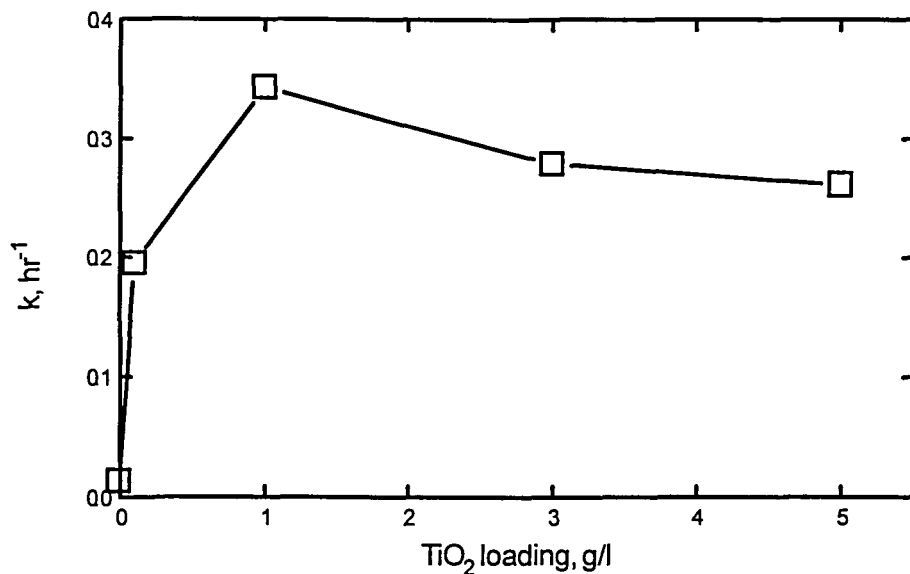


FIGURE 3

Effect of TiO<sub>2</sub> loading on the photocatalytic oxidation of propoxur. Experimental conditions: [propoxur] =  $4.78 \times 10^{-4}$  M, pH=4.0, Temperature 30°C.

TABLE 1  
Apparent Kinetics of Propoxur Oxidation

pH	[H <sub>2</sub> O <sub>2</sub> ] ( $\times 10^{-2}$ M)	Temp. (°C)	TiO <sub>2</sub> loading (g/l)	k (hr <sup>-1</sup> )	Initial rate ( $\times 10^{-5}$ M/hr)
2	-	30	1	0.136	6.50
4	-	30	1	0.343	16.4
6	-	30	1	0.358	17.1
9	-	30	1	0.370	17.7
4	-	10	1	0.101	4.83
4	-	20	1	0.225	10.8
4	-	40	1	0.586	28.0
4	-	30	0.1	0.195	9.32
4	-	30	3	0.279	13.3
4	-	30	5	0.261	12.5
4	0.98	30	1	0.451	21.6
4	2.94	30	1	0.738	35.3
4	4.90	30	1	1.18	56.4
4	4.90	30	-	0.441	21.1

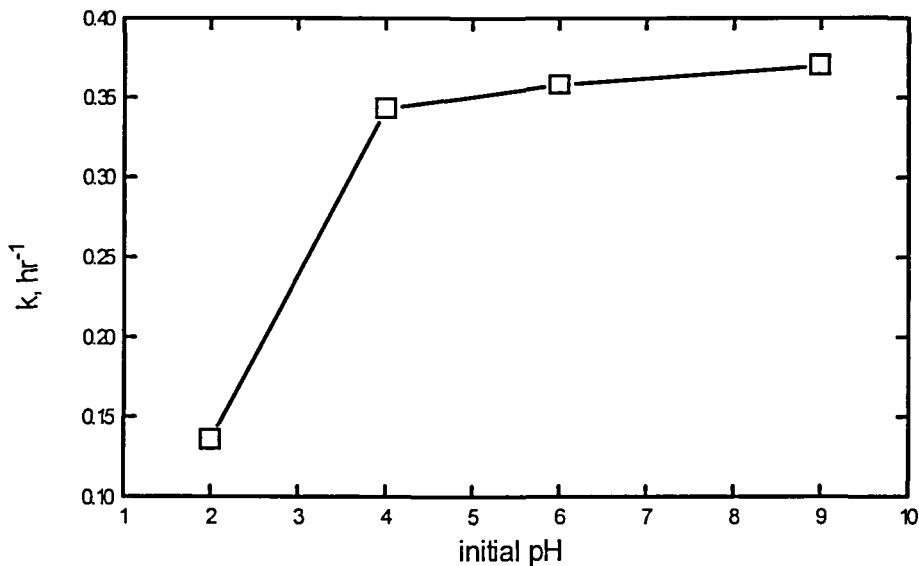


FIGURE 4

Effect of initial pH on the photocatalytic oxidation of propoxur. Experimental conditions:  $[\text{propoxur}] = 4.78 \times 10^{-4} \text{ M}$ , Temperature  $30^\circ\text{C}$ ,  $1 \text{ g TiO}_2$ .

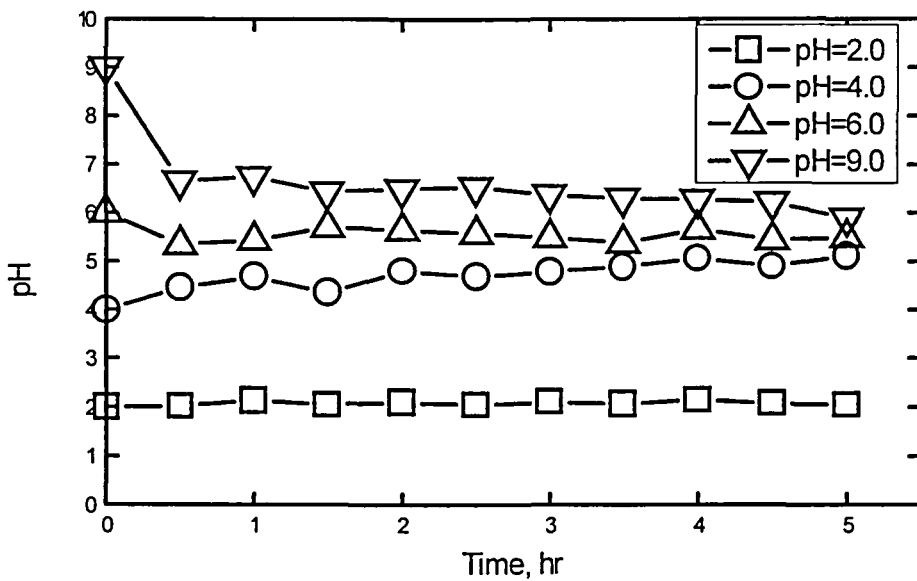


FIGURE 5

Changes of pH during the photocatalytic oxidation. Experimental conditions:  $\text{TiO}_2 = 1 \text{ g/l}$ ;  $\text{Temp.} = 30^\circ\text{C}$ ;  $[\text{propoxur}] = 4.78 \times 10^{-4} \text{ M}$

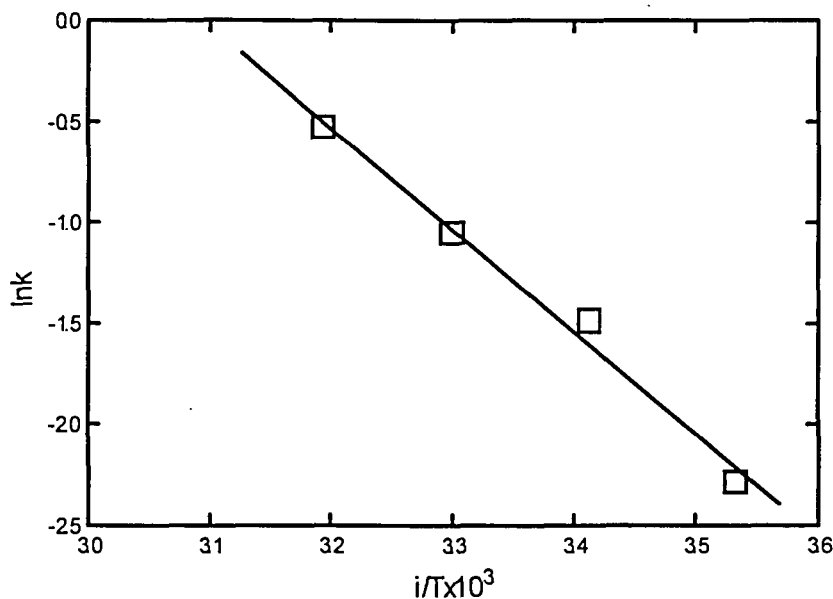


FIGURE 6

Effect of temperature on the photocatalytic oxidation of propoxur. Experimental conditions: [propoxur] =  $4.78 \times 10^{-4}$  M, pH=4.0, 1 g  $\text{TiO}_2$ , 1 g  $\text{TiO}_2$ .

was studied in a system containing  $4.78 \times 10^{-4}$  M of propoxur. The oxidation reactions over a range from 10 to 40 °C after 5 hours of photocatalytic reaction were compared. The degradation rate increased with increasing temperature and the rate constants are listed in Table 1. As shown in Figure 6, the activation energy can be obtained from the Arrhenius plot,  $\ln k$  versus  $T^{-1}$ , which was found to be 10.1 kcal/mol. The activation energy of a diffusion controlled reaction is typically 2-6 kcal/mol (Connors, 1990). In a previous study,  $\text{TiO}_2$  was coated on the surface of granular activated carbon to enhance the catalytic capability of  $\text{TiO}_2$ . It was found that the activation energy of propoxur oxidation was 3.66 kcal/mol, and therefore it was considered a diffusion-controlling reaction (Lu et al., 1999). However, the photocatalytic oxidation of propoxur using  $\text{TiO}_2$  suspensions as the photocatalyst was reaction-controlled.

## CONCLUSIONS

Photocatalytic oxidation of propoxur was effective and followed a first-order expression. Hydrogen peroxide can increase the rate of photocatalytic oxidation of propoxur with increasing the initial  $[H_2O_2]$ . There was no obvious difference in the degradation rate of propoxur at the initial pH of 4.0, 6.0 and 9.0, and the final pH of reaction solution was around 5.5. According to the study on the effect of  $TiO_2$  loading on the photocatalytic reaction, it can be concluded that  $TiO_2$  may not utilize all the photons entering the reactor to produce radicals for degrading propoxur because light scattering and reflection was greater at a over-high  $TiO_2$  concentration. The photocatalytic oxidation of propoxur using  $TiO_2$  as the photocatalyst was reaction-controlled.

The use of supports for  $TiO_2$  was effective in the enhancement of the rate of propoxur removal. However, the oxidation efficiency for the titanium dioxide coated on support was much lower than that for the titanium dioxide suspensions, because mass transfer and photon utilization were limited in the coated system. Photocatalytic process has the potential for using solar radiation to destroy organic chemicals. However,  $TiO_2$  can utilize only a small portion of the solar spectrum, therefore, reactor system with higher efficiency of photon utilization is necessary. Hence,  $TiO_2$  suspension system still can be applied in the treatment of water and wastewater.

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