Photoassisted titanium dioxide mediated degradation of organophosphorus pesticides by hydrogen peroxide

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Abstract

The photooxidation of organophosphorus pesticides (OPP) such as methamidophos, phorate, malathion, diazion and EPN, was investigated in $UV-TiO_2$, $UV-H_2O_2$ and $UV-TiO_2-H_2O_2$ systems. Apparent first-order rate constants were used to describe the photodecomposition behaviors of OPP. Batch results demonstrate that the degradation efficiencies of OPP increased in the order of phorate > methamidophos > malathion ≈ diazion > EPN. The photooxidation of methamidophos and phorate is primarily attributed to direct photolysis. Whereas the presence of TiO_2 promotes the degradation efficiencies of diazion, malathion and EPN. Hydrogen peroxide was found to be an intermediate in $UV-TiO_2$ system during the photocatalytical reaction process. Longer irradiation decreased H_2O_2 concentration due to the high electron–hole recombination rate on the surface of TiO_2. Adding H_2O_2 is more effective on the photocatalytic oxidation of OPP than TiO_2. Threefold to tenfold of the quantum efficiency of the $UV-H_2O_2$ system was obtained for the $UV-TiO_2$ system. Moreover, the quantum efficiencies for degradation of OPP decreased when light intensity is increased from 100 to 450 W, although increasing light intensity can increase the apparent first-order rate constants of OPP. © 1997 Elsevier Science S.A.

Keywords: Photodegradation; Organophosphorus pesticides; Titanium dioxide; Hydrogen peroxide; Apparent first-order rate constants

1. Introduction

The contamination of soil, surface water and air with mixtures of pesticides has received considerable attention [1–3]. Organophosphorus pesticides have been used as an alternative to organochlorine compounds for pest control. Such chemicals are included in several priority lists of pollutants in Taiwan owing to their widespread use and high toxicity. Their persistence in natural water has led to the search for a highly effective method to mineralize the compounds into environmentally compatible products.

Photocatalytic oxidation is one of considerable technologies for eliminating OPP. Many investigators have utilized aqueous suspension of semiconductor illuminated by UV light to photodegrade organic compounds, such as chlorinated compounds, chlorophenols, nitrogen-containing pesticides and aromatic compounds [4–12]. Among the semiconductors used, titanium dioxide (TiO_2) is considered particularly efficient owing to the formation of electron–hole pairs under illumination with near-UV light. Nevertheless, the recombination of electrons and holes inhibit the photo-

catalytic reaction process. Recently, some investigations have examined the effect of H_2O_2 on the enhancement of oxidation of organic pollutants, such as chlorophenols and atrazine mediated by TiO_2 [13–15]. Adding H_2O_2 to react with electrons causes the recombination rate of electron and hole to decrease. However, the photodecomposition of OPP under different photo systems receives less attention. Also, roles of H_2O_2 and TiO_2 on the photodegradation of OPP still remain unclear.

This paper reports the results of the photooxidation of organophosphorus pesticides such as malathion, phorate, methamidophos, diazion, and EPN in the direct photolysis, $UV-H_2O_2$, $UV-TiO_2$ and $UV-H_2O_2-TiO_2$ systems. Apparent first-order rate constants were used to describe the degradation behaviors of OPP under different photo systems. Moreover, the effect of light intensity on the photocatalytic oxidation of OPP was also examined to clarify the relationship between the photo flux and decomposition rate of OPP.

2. Experimental details

2.1. Materials

Malathion (98.7%), phorate (95.3%), diazion (94.0%), methamidophos (96.7%) and EPN (99.2%) were purchased

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from Merck (Germany). Titanium dioxide (TiO$_2$) was Degussa P-25. Acetonitrile (99.97%, HPLC/Spectro grade) was obtained from Tedia (USA). Hydrogen peroxide was obtained from Showa Chemical (Tokyo, Japan). Doubly distilled water (Millipore, Bedford, MA) was used throughout the experiment unless otherwise mentioned. All other reagents were of analytical grade and used without further purification.

2.2. Photodegradation procedure

Experiments were performed in a 1.2-l hollow cylindrical photoreactor equipped with a water jacket. The inner wall of water jacket is made of quartz and the outer wall is made of Pyrex. A 100 W or 450 W medium pressure mercury lamp (ACE glass, NJ) was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the lamp. The Pyrex thimble together with the water circulation was used as an IR cut-off filter. In a distance of 0.5 m, the radiant exitance of 100 W and 450 W yielded 230 μW cm^{-2} and 3.6 mW cm^{-2}, respectively, in the wavelength of 253–578 nm (data from the lamp's manufacturer). According to those values, the radiant exitance close to the surface of the lamp was calculated as 575 mW cm^{-2} and 9 W cm^{-2}, respectively, using the relation $\ln E_{e,o} = 2\ln r + \ln E_{e,r}$ [16].

Batch experiments were conducted at 25 $\pm$ 0.2 °C. A standard experiment involved the addition of 10 mg of OPP (dissolved in acetonitrile) to 1-l doubly distilled water. After 1 g of TiO$_2$ was added into the suspension, the sample was sonicated for 20 min to obtain a good dispersion. The solution was magnetically stirred and purged with pure oxygen for 30 min at a rate of 50 ml min^{-1} and equilibrated in the dark for 10 min prior to illumination. An appropriate volume of the stock solution of H$_2$O$_2$ (10 000 mg l^{-1}) was added into the mixture to yield the concentration of 20 mg l^{-1}. Immediately after adding hydrogen peroxide, the light was turned on. Aliquots (10 ml) were withdrawn from the solution at various time intervals for analysis after removing TiO$_2$ by centrifugation at 14 000 rev min^{-1} for 10 min.

All the experiments were buffered with a phosphate buffer solution consisting of 10 mM Na$_2$HPO$_4$ and 10 mM NaH$_2$PO$_4$ to yield a pH value of 7.0 $\pm$ 0.1, which is close to the reported point zero charge (PZC) (pH 6.8 at 25 °C) [17]. Selecting a pH value close to PZC is a compromise to guarantee that

the neutral surface species –TiOH is predominant and similar amounts of acid and basic sites over the experimental period [18].

Two control experiments were performed under the same experimental conditions in thermostatic baths at the temperatures indicated. The first set of experiments involved the presence of catalyst which was stirred in the dark to account for dark reaction. The second experiment involved irradiating the dispersion without adding a catalyst to account for any direct photolysis.

2.3. Analytical methods

The samples were determined by high performance liquid chromatography (HPLC) equipped with a variable wavelength UV detector. A Supelcosil LC-18 column (15 cm $\times$ 0.46 mm $\times$ 5.0 μm) was employed for separation organophosphorus pesticides. The mobile phase was a mixture of 60:40 acetonitrile:water. The elute was delivered at a rate of 1.0 ml min^{-1} and the wavelength for detection was 254 nm. For these operating conditions, the retention times of methamidophos, malathion, diazion, phorate and EPN were 3.32, 4.69, 6.46, 7.64 and 9.10 min, respectively. The detection limits of OPP were 0.346 mg l^{-1} for methamidophos, 0.042 mg l^{-1} for malathion, 0.27 mg l^{-1} for diazion, 0.394 mg l^{-1} for phorate and 0.421 mg l^{-1} for EPN. The analytical error was controlled within 5%.

Oxygen concentration was measured during irradiation using an oxygen-sensitive membrane electron, which is capable of accurately detecting oxygen levels up to 0.5 mg l^{-1}. The concentration of hydrogen peroxide was determined by iodometrical method.

The crystal structure of TiO$_2$ particles determined by X-ray powder diffractometer (MAC, MXP10) revealed that anatase is the primary form, having a purity exceeding 99.9%. The average particle diameter and specific BET surface area of TiO$_2$, as determined by laser particle analyzer (Photal, LPA-300) and Micromertics ASAR 2000 apparatus, were 5.6 μm and 7.25 $\pm$ 0.14 m^2 g^{-1}, respectively.

3. Results and discussion

3.1. Dark reaction and direct photolysis

Table 1 displays the degradation of OPP in a dark reaction while amending TiO$_2$ and/or H$_2$O$_2$. No obvious degradation

Table 1
The degradation of OPP in the dark reaction under different experimental conditions

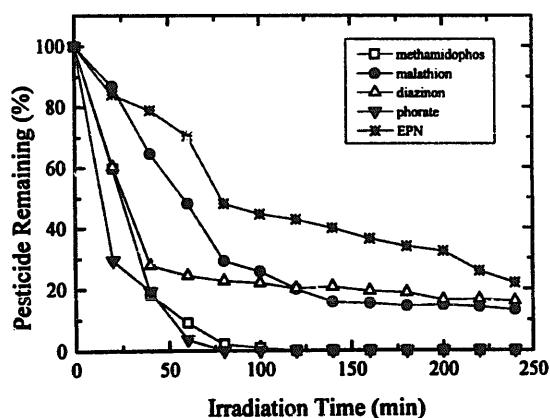| Reagent	Degradation ratio (%)				
	Methamidophos	Malathion	Diazinon	Phorate	EPN
No addition	1.3	1.4	1.6	1.9	1.7
H$_2$O$_2$ only	5.8	3.2	5.4	5.9	2.5
TiO$_2$ only	2.4	2.6	3.4	2.5	1.2
TiO$_2$–H$_2$O$_2$	7.2	2.9	5.2	3.8	1.9

Fig. 1. The photodecomposition of OPP in the direct photolysis with the illumination of 100 W medium mercury lamp. [OPP]$_{ini}$ = 10 mg l^{-1}; pH 7.0±0.1.

Fig. 2. The photodecomposition of OPP in the UV–TiO$_2$ system with the illumination of 100 W medium mercury lamp. [OPP]$_{ini}$ = 10 mg l^{-1}; [TiO$_2$] = 1 g l^{-1}; pH 7.0±0.1.

of OPP in dark reaction occurred within 4 h. This suggests that hydrolytic processes of OPP during the experimental course can be neglected. However, directly photolyzing 10 mg l^{-1} of OPP with the illumination of 100 W lamp significantly decreased OPP concentrations (Fig. 1). Removals of 76% to more than 99.9% of the original OPP were observed, depending on the nature of OPP. The photocatalytic degradation follows an apparent first-order reaction. The rate constants were 0.037 min^{-1} for phorate, 0.025 min^{-1} for methamidophos, 0.009 min^{-1} for malathion and 0.006 min^{-1} for diazion and EPN.

3.2. Photodegradation of OPP in UV–TiO$_2$ system

Fig. 2 illustrates the photodecomposition of OPP with the illumination of 100 W lamp in the presence of TiO$_2$. The degradation efficiency of OPP was slightly enhanced by adding TiO$_2$, compared with the results obtained from direct photolysis. The kinetic parameters shown in Table 2 demonstrate that the degradation efficiencies of OPP increased in the order phorate > methamidophos > malathion ≈ diazion > EPN. No difference of rate constants of methamidophos and phorate between direct photolysis and UV–TiO$_2$ system was observed, implying that the photodegradation of phorate and methamidophos was probably attributed to direct photolysis. Moreover, a nearly 2-fold increase in rate constants
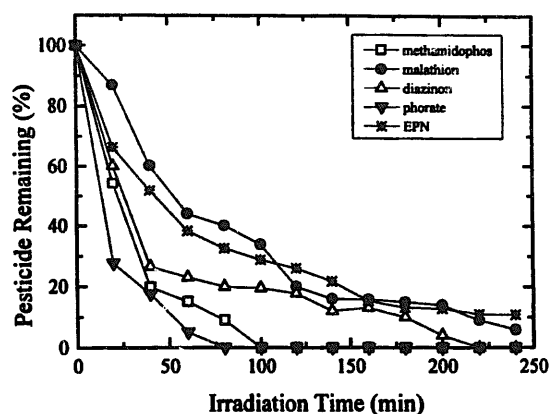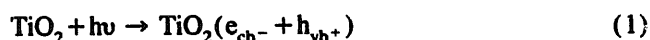
of malathion and EPN was demonstrated, suggesting that the decomposition was primarily owing to the indirect action of illuminating TiO$_2$.

Titanium dioxide, working as a catalyst with UV light to generate highly reactive oxidizing agents, is widely recognized as the most appropriate semiconductor for mediating the photocatalytic process, although ZnO, ZrO$_2$, SnO$_2$, WO$_3$ and Fe$_2$O$_3$ have also investigated [8,19,20]. When TiO$_2$ absorbs light, which encompasses an energy higher than the corresponding band gap (3.1 eV), electron–hole pairs are generated on the surface of TiO$_2$. The holes are then either trapped by surface hydroxyl group to yield hydroxyl radical that attack and destroy organic pesticides or recombined with electrons to inhibit the photocatalytic reaction process.

$$TiO_2 + h\upsilon \rightarrow TiO_2(e_{cb^-} + h_{vb^+}) \qquad (1)$$

$$h_{vb^+} + H_2O \rightarrow \cdot OH + H^+ \qquad (2)$$

$$e_{cb^-} + h_{vb^+} \rightarrow TiO_2 \qquad (3)$$

In an oxygenated solution, oxygen may adsorb on the surface of titanium dioxide to prevent the recombination process by trapping electrons resulting in the formation of superoxide radical and hydrogen peroxide.

Table 2
The kinetic parameters of photodecomposition of OPP in the UV–TiO$_2$ system with the illumination of 100 or 450 W lamp

Compounds	100 W lamp			450 W lamp		
	k_{obs} (min^{-1})	Initial rate (μM min^{-1})	Half life ($t_{1/2}$, min)	k_{obs} (min^{-1})	Initial rate (μM min^{-1})	Half life ($t_{1/2}$, min)
Methamidophos	0.024	1.42	28.9	0.115	2.98	6.1
Malathion	0.011	0.28	63.0	0.057	1.21	12.2
Diazinon	0.012	0.61	57.8	0.054	1.34	12.8
Phorate	0.039	1.39	17.8	0.099	1.59	7.0
EPN	0.012	0.52	57.8	0.053	1.12	13.1

$$O_2 + e_{cb^-} \rightarrow O_2^- \cdot \quad (4)$$

$$O_2^- \cdot + H^+ \rightarrow HO_2 \cdot \quad (5)$$

$$HO_2^- + HO_2 \cdot \rightarrow H_2O_2 + O_2 \quad (6)$$

$$O_2^- \cdot + HO_2 \cdot \rightarrow O_2 + HO_2^- \cdot \quad (7)$$

$$HO_2^- \cdot + H^+ \rightarrow H_2O_2 \quad (8)$$

Hydrogen peroxide was found in this study to function as an intermediate during the photooxidation of OPP on TiO_2. Fig. 3 illustrates the concentration profiles of oxygen and hydrogen peroxide in UV–TiO_2 system. The concentration of oxygen decreased with the accumulation of H_2O_2. The concentration of H_2O_2 reached a maximum of 55 μM after 60 min of illumination. Further irradiation yielded a lower peroxide concentration. This occurrence closely corresponds to other investigations [16,21]. The decrease of H_2O_2 at longer illumination time resulted from a faster reaction between the degradation products and H_2O_2 or the reaction of H_2O_2 with positive holes and electrons.

$$2h_{vb^+} + H_2O_2 \rightarrow \cdot O_2 + 2H^+ \quad (9)$$

$$2e_{cb^-} + 2H^+ + H_2O_2 \rightarrow 2H_2O \quad (10)$$
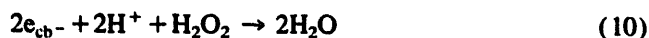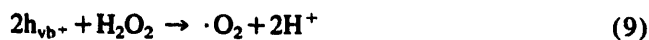
3.3. Effect of light intensity

Figs. 4 and 5 summarize the photodegradation of OPP in the direct photolysis and UV–TiO_2 systems, respectively, with the illumination of 450 W lamp. Nearly complete photodegradation of OPP was observed in 180 min. Rate constants shown in Table 2 depict that a higher light intensity can increase the degradation rate of OPP.

The quantum efficiency can be defined as an initial rate of degradation divided by the theoretical maximum rate of photon absorption [21,22].

$$\xi_{Xi} = \frac{(d[Xi]/dt)_0}{I_{inc}} \quad (16)$$

where ξ_{Xi} is the apparent quantum efficiency for OPP species (Xi), $d[Xi]/dt$ is the initial rate of degradation of OPP species, and I_{inc} is the incident photon flux. Notably, the apparent quantum efficiency represents lower limits of the actual quantum yield since estimations are based on the number of photos falling on the external reactor walls and some of the incident photos are lost by light scattering in the turbid TiO_2 suspension.

Table 3 lists the quantum efficiencies of direct photolysis and UV–TiO_2 systems with the illumination of 100 or 450 W. The apparent quantum efficiency for degradation of OPP decreased with an increasing light intensity. A 10- to 30-fold difference in quantum efficiency was demonstrated between these two systems. Terzian and Serpone [23] indicated that electron–hole pairs recombination is the predominate reaction at high light intensity. Whereas hole trapping competes effectively with electron–hole recombination at low light intensity. Higher apparent quantum efficiency obtained at
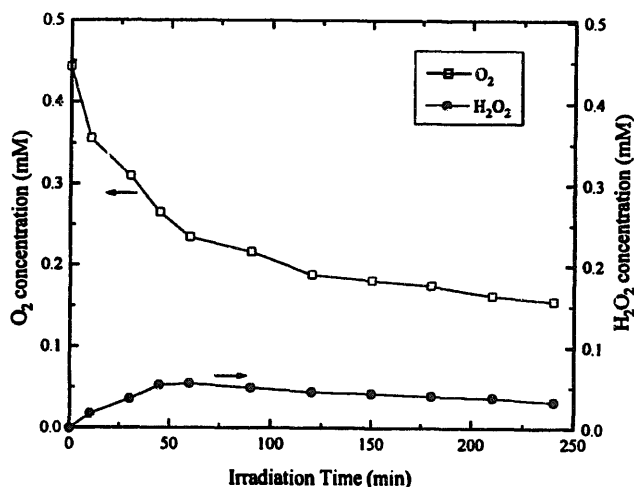

Fig. 3. The concentration profiles of oxygen and hydrogen peroxide in the UV–TiO_2 system. $[DO]_{ini} = 14.2$ mg l^{-1} (0.44 mM); $[TiO_2] = 1$ g l^{-1}; pH 7.0 ± 0.1.

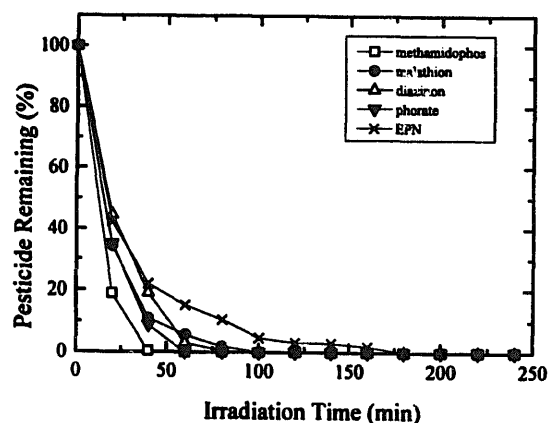Fig. 4. The photodecomposition of OPP in the direct photolysis with the illumination of 450 W medium mercury lamp. $[OPP]_{ini} = 10$ mg l^{-1}; pH 7.0 ± 0.1.
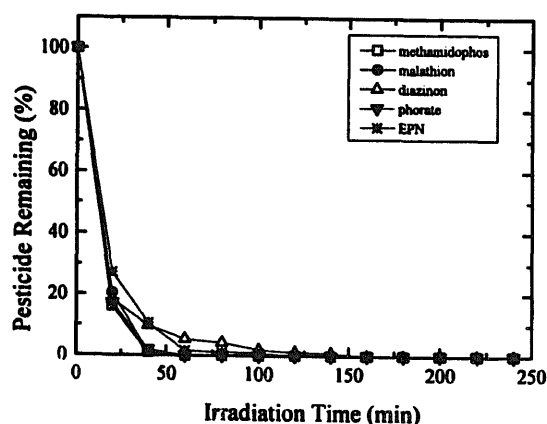

Fig. 5. The photodecomposition of OPP in the UV–TiO_2 system with the illumination of 450 W medium mercury lamp. $[OPP]_{ini} = 10$ mg l^{-1}; $[TiO_2] = 1$ g l^{-1}; pH 7.0 ± 0.1.

lower incident intensity is due to the decrease of charge-carrier recombination rate [23–25]. The effect of light intensity in this study follows such a trend, demonstrating that low flux intensity is more advantageous for detoxifying OPP.

Table 3

The quantum efficiencies of the direct photolysis and the UV–TiO_2 system with the illumination of 100 or 450 W lamp

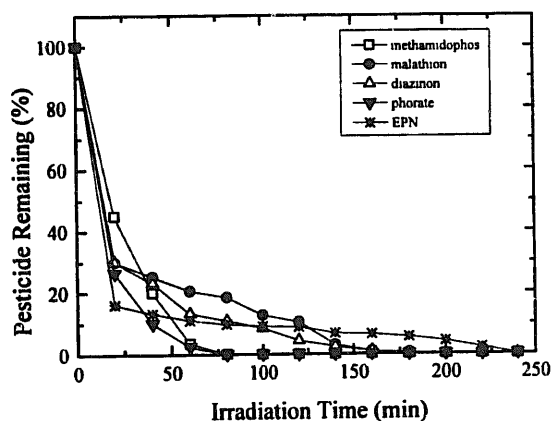| Compounds	Direct photolysis		UV–TiO_2 system	
	100 W	450 W	100 W	450 W
Methamidophos	0.358	0.022	0.351	0.021
Malathion	0.049	0.007	0.069	0.009
Diazinon	0.146	0.006	0.149	0.010
Phorate	0.335	0.009	0.343	0.011
EPN	0.060	0.006	0.128	0.008

Fig. 6. The photodecomposition of OPP in the UV–TiO_2–H_2O_2 system with the illumination of 100 W medium mercury lamp. $[OPP]_{ini} = 10$ mg l^{-1}; $[H_2O_2]_{ini} = 20$ mg l^{-1}; $[TiO_2] = 1$ g l^{-1}; pH 7.0 ± 0.1.

Fig. 7. The photodecomposition of OPP in the UV–H_2O_2 system with the illumination of 100 W medium mercury lamp. $[OPP]_{ini} = 10$ mg l^{-1}; $[H_2O_2]_{ini} = 20$ mg l^{-1}; pH 7.0 ± 0.1.

3.4. Photodegradation of OPP in UV–TiO_2–H_2O_2 system

Fig. 6 illustrates the photocatalytic degradation of OPP in the UV–TiO_2–H_2O_2 system. A significant enhancement on degradation efficiency of OPP was demonstrated when 20 mg l^{-1} of H_2O_2 were added into the system. The kinetic parameters in Table 2 demonstrate a 1.3- to 2.5-fold increase in k_{obs} compared to the results obtained in UV–TiO_2 systems.

Hydrogen peroxide is traditionally an effective oxidant only for certain compounds, such as phenol and cyanide. Combination ultraviolet and/or iron compounds (Fenton reaction), however, has been demonstrated to be an innovative technology for purifying water and wastewater. Researches have recently examined the effect of H_2O_2 on the enhancement of oxidation of organic pollutants, such as PCBs, humic substances and dyes mediated by TiO_2 [13–15]. An addition of small amounts of hydrogen peroxide can significantly increase the generation rate of hydroxyl radical, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO_2 by the following reactions.
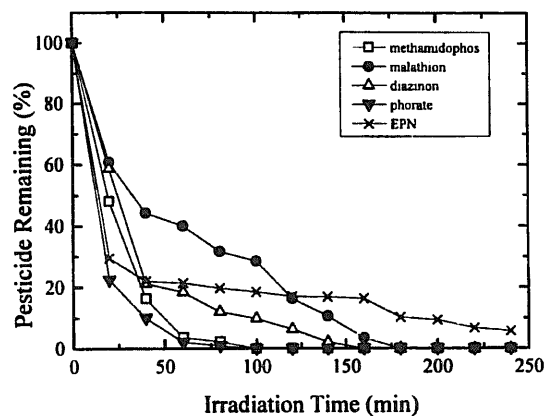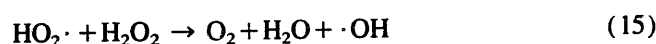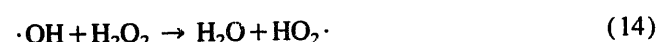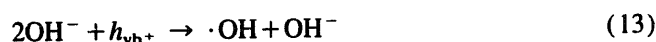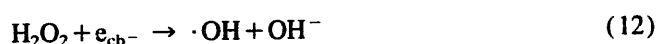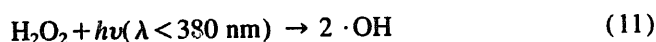
$$H_2O_2 + h\nu(\lambda < 380 \text{ nm}) \rightarrow 2 \cdot OH \qquad (11)$$

$$H_2O_2 + e_{cb}^- \rightarrow \cdot OH + OH^- \qquad (12)$$

$$2OH^- + h_{vb}^+ \rightarrow \cdot OH + OH^- \qquad (13)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2 \cdot \qquad (14)$$

$$HO_2 \cdot + H_2O_2 \rightarrow O_2 + H_2O + \cdot OH \qquad (15)$$

Although the presence of H_2O_2 on the TiO_2 has been observed, Matthews [26] demonstrated that hydroxyl radical generated from H_2O_2 can be negligible compared with that from holes (Eq. (2)). To further clarify the role of H_2O_2 on the photodegradation of OPP, experiments of photocatalytic degradation of OPP in UV–H_2O_2 system (without TiO_2) were conducted. Fig. 7 illustrates the degradation of OPP in the UV–H_2O_2 system. According to the Fig. 7, the addition of hydrogen peroxide can significantly enhance the degradation efficiencies of EPN. However, it has only a slight effect on the photodegradation of methamidophos and phorate. The rate constants in Table 4 demonstrate that the addition of H_2O_2 has more influence than TiO_2 on photocatalytic degradation of OPP. Also, threefold to tenfold of the quantum efficiency of the UV–H_2O_2 system was obtained for the UV–TiO_2 system. This occurrence may be due to the high recombination rate of hole and electron generated from TiO_2 surface. As already mentioned, oxygen can prevent the recombination of electron and hole and subsequently formation of H_2O_2. However, only about 15% of the O_2 was converted to H_2O_2 in UV–TiO_2 system (Fig. 2). This finding suggests that the recombination of electrons and holes are the major reaction for holes during photooxidation reaction process.

4. Conclusions

Results obtained herein demonstrate that photoassisted TiO_2 mediated degradation in combination with H_2O_2 is

Table 4
The kinetic parameters of photodecomposition of OPP in the $UV-H_2O_2$ and $UV-H_2O_2-TiO_2$ system with the illumination of 100 W lamp

Compounds	$UV-H_2O_2$ system			$UV-H_2O_2-TiO_2$ system		
	k_{obs} (min^{-1})	Initial rate (μM min^{-1})	Half life ($t_{1/2}$, min)	k_{obs} (min^{-1})	Initial rate (μM min^{-1})	Half life ($t_{1/2}$, min)
Methamidophos	0.051	1.84	13.6	0.054	1.95	12.8
Malathion	0.017	0.60	40.8	0.026	1.06	26.7
Diazinon	0.024	0.65	28.9	0.025	1.15	27.7
Phorate	0.054	1.49	12.8	0.055	1.41	12.6
EPN	0.008	1.09	86.6	0.011	1.29	63.0

highly effective in remediating OPP contaminated waters. The photodecomposition rate depends on the nature of OPP. Methamidophos and phorate are the easily degradable compounds due to the low bond energy of P–S and C–S bonds. Whereas the decomposition of diazion, malathion and EPN is primarily due to the indirect action of illuminating TiO_2.

Using UV radiation and H_2O_2 is a more effective method than $UV-TiO_2$ in degrading OPP due to the high electron–hole recombination rate on the surface of TiO_2. Also, our results indicate that H_2O_2 functions as an intermediate with the maximum concentration of 55 μM in $UV-TiO_2$ system. The combination of H_2O_2 and TiO_2 with the illumination of near UV light shows much promise in the photodegradation of OPP.

This study indicate that photocatalytic oxidation is a highly promising method for detoxifying OPP. However, the high electron–hole recombination rate will hinder any large scale applications. Investigations concerning the modification of the surface properties of TiO_2 are necessary to decrease the electron–hole recombination so that the quantum yield of the photocatalytic reaction can be ultimately increased.

Acknowledgements

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