

# Photodegradation of parathion in aqueous titanium dioxide and zero valent iron solutions in the presence of hydrogen peroxide

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## Abstract

The photocatalytic degradation of parathion using UV radiation in combination with hydrogen peroxide and titanium dioxide or iron compounds was studied. Apparent first-order rate constants ( $k_{\text{obs}}$ ) and initial rate constants were used to describe the degradation behavior of parathion under different conditions. The addition of  $\text{TiO}_2$  or iron compounds in combination with hydrogen peroxide was effective in the detoxification of parathion. The  $k_{\text{obs}}$  and initial rate constants increased with the increase of  $\text{TiO}_2$  loading from  $0.1 \text{ g l}^{-1}$  to  $1 \text{ g l}^{-1}$ . However, the degradation rates of parathion decreased when the  $\text{TiO}_2$  dose was increased to  $2 \text{ g l}^{-1}$ . No significant difference between buffered and unbuffered solutions was observed. The addition of oxyanion oxidant can enhance the degradation rate of parathion in the order of  $\text{ClO}_2^- > \text{IO}_3^- > \text{BrO}_3^- > \text{ClO}_3^-$ . The existence of oxygen increased the initial rate of parathion in a  $\text{TiO}_2$ -amended system, but has little effect on  $k_{\text{obs}}$ . Also, the addition of iron compounds is a promising technique for the photodegradation of parathion. The rate constants for parathion ranged from  $0.029$  to  $0.033 \text{ min}^{-1}$  in the iron-amended system, which corresponds to 3-fold increase relative to UV/ $\text{H}_2\text{O}_2$  system. Diethylphosphoric acid, *p*-nitrophenol, diethylmonothiophosphoric acid, *O,O*-ethyl *p*-nitrophenyl monothiophosphoric acid and oxalate were identified as intermediates and shown to be oxidized further. Moreover, oxalate and 4-nitrophenol were found to be the major intermediates in the degradation of parathion. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Photodegradation; Parathion; Hydrogen peroxide; Titanium dioxide; Metal iron

## 1. Introduction

Parathion (diethyl-4-nitrophenyl phosphorothionate) has been the most widely used broad-spectrum insecticide in Taiwan. The annual use has been estimated to be approximately  $5 \times 10^5 \text{ kg}$  in Taiwan. Its widespread use has caused environmental concern due to the frequent detection of parathion and other pesticides in surface water and groundwater at concentrations frequently exceeding the maximum contamination level of  $0.1 \text{ mg l}^{-1}$ . Parathion is acutely toxic to mammals. It acts by inhibiting the enzyme acetylcholinesterase (AChE) in the nerve tissue. With respect to its suspected carcinogenicity and ubiquitous contamination, a more thorough understanding the impact of such chemicals is an important task.

Photocatalytic oxidation of organic compounds by titanium dioxide or iron compounds has attracted attention for treating contaminated wastewater [1–5]. The utilization of an aqueous suspension of  $\text{TiO}_2$  illuminated by near-UV light to photodegrade organic compounds has been well estab-

lished [6–8]. The photoexcitation of a semiconductor promotes valence band electrons into the conduction band leaving free electron holes. However, the recombination of electrons and holes hampers the photocatalytic reaction process. Recently, research has demonstrated that the addition of hydrogen peroxide can enhance the oxidation of organic compounds [9]. Hydrogen peroxide can react with electrons to decrease the recombination rates of electrons and holes and is more effective than  $\text{TiO}_2$  in enhancing the photodegradation of toxic pollutants. The degradation rates have shown to be controlled by  $\text{TiO}_2$  loading, oxygen concentration, oxyanion oxidant and light intensity [10–12]. However, the effect of  $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$  on the photodegradation of parathion receives less attention.

A Fenton or photo-assisted Fenton process is another potential technique for the degradation of hazardous wastes, like PCBs, chlorinated herbicide and chlorophenols [13–16]. Typically, high-valent irons, such as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were used in combination with hydrogen peroxide to generate OH radicals that can attack organic compounds. Recently, the photoreduction of chlorinated hydrocarbons and nitroaromatic compounds in the presence of metal iron ( $\text{Fe}^0$ ) has

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been reported [16,17]. Matheson and Tratnyek [17] showed that iron metal will react with dissolved oxygen to generate ferrous iron and further oxidation of ferrous ion by dissolved oxygen leads to the formation of ferric hydroxide. This means that the addition of iron metal in combination with hydrogen peroxide may be a novel technique for rapidly degrading parathion.

The objective of this study is to elucidate the effects of titanium dioxide and iron compounds on the photodegradation of parathion. Apparent first-order rate constant and initial rate constant were used to describe the degradation behavior of parathion under different conditions. The influence of oxyanion on the degradation of parathion in the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system was also demonstrated. Additionally, a possible degradation pathway in UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system was proposed.

## 2. Experimental details

### 2.1. Chemicals and reagents

Parathion (C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>PS<sub>3</sub>, 99.2%) was purchased from Merck (Germany). Titanium dioxide (TiO<sub>2</sub>) was Degussa P-25. Acetonitrile (99.97%, HPLC/Spectro grade) was obtained from Tedia (USA). Hydrogen peroxide (35%) was obtained from Showa Chemical (Tokyo, Japan). Zero-valent iron (>99.5%) was obtained from Santoku (Japan). Deionized distilled water (Millipore, Bedford, MA, USA) was used throughout the experiment unless otherwise mentioned. All other reagents were analytical grade and were used without further treatment.

### 2.2. Photodegradation procedure

The experiments were carried out in a 1.2-l hollow cylindrical photoreactor equipped with a water jacket. The inner wall of the water jacket is made of quartz and the outer wall is made of Pyrex. A 100 W medium pressure mercury lamp (ACE glass, NJ, USA) was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the lamp. At a distance of 0.5 m, the radiant exitance of 100 W yielded 230 μW cm<sup>-2</sup> in the wavelength of 253–578 nm. From these values, the radiant exitance close to the surface of the lamp was calculated as 575 mW cm<sup>-2</sup> using the equation  $\ln(E_{e,r}) = 2 \ln(r) + \ln(E_{e,o})$  [18].

Batch experiments were conducted at 25 ± 1°C. A standard experiment involved the addition of 10 mg of parathion (dissolved in acetonitrile) to 1-l deionized distilled water. After TiO<sub>2</sub> or iron compounds (metal iron and ferrous ion) 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 or nitrogen for 30 min at a rate of 50 ml min<sup>-1</sup> and equilibrated in the dark for 10 min prior to illumination to maintain the oxygenated (DO > 15 mg l<sup>-1</sup>) or deoxygenated (DO < 1 mg l<sup>-1</sup>) con-

dition. An appropriate volume of the stock solution of H<sub>2</sub>O<sub>2</sub> (10,000 mg l<sup>-1</sup>) was added into the mixture to create a concentration of 20 mg l<sup>-1</sup>. Immediately after the addition of the hydrogen peroxide, the light was turned on. Aliquots (10 ml) were withdrawn from the solution at various time intervals for analysis after removal of TiO<sub>2</sub> or Fe<sup>0</sup> by centrifugation at 14,000 rev min<sup>-1</sup> for 10 min. All of the experiments were buffered with phosphate buffer solutions consisting of 10 mM Na<sub>2</sub>HPO<sub>4</sub> and 10 mM NaH<sub>2</sub>PO<sub>4</sub> to yield a pH value of 7.0 ± 0.1.

Two control experiments were conducted under the same experimental conditions in thermostatic baths at the temperatures indicated. The first set of experiment involved the presence of a catalyst and stirring in the dark to determine the reaction in darkness. The second experiment involved the irradiation of the dispersion without the addition of a catalyst to account for any direct photolysis. Results showed no obvious degradation of the parathion after 24 h in darkness. Degradation of 52% of the original parathion was accomplished within 240 min under direct photolysis. The photocatalytic process follows apparent first-order rate reaction. Rate constant (*k*<sub>obs</sub>), calculating for the disappearance of parathion from linear regression analysis of ln(C/Co) verse time, was 0.003 min<sup>-1</sup> for direct photolysis system.

### 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 × 0.46 mm × 5.0 μm) was employed for determining the parathion and the metabolites. The mobile phase was a mixture of 60:40 acetonitrile:water. The elute was delivered at a rate of 1.0 ml min<sup>-1</sup> and the wavelength for detection was 254 nm. Sulfate, nitrate and phosphate were determined by ion chromatography (Biotronik IC 1000) on a Biotronik BT II AN column and conductivity detector. The elute was 2 ml min<sup>-1</sup> of 1.7 mM NaHCO<sub>3</sub>/1.8 mM Na<sub>2</sub>CO<sub>3</sub>. Reaction intermediates were identified by HPLC/MS (Joel, SX-102A, Japan).

Oxygen concentration was measured during irradiation using an oxygen-sensitive membrane electrode, which is capable of detecting accurately oxygen levels up to 0.5 mg l<sup>-1</sup>. The concentrations of hydrogen peroxide and ferrous iron were determined by iodometrical and ferrozine methods, respectively. Ferric ion was first reduced to ferrous ion using ascorbic acid as the reducing agent and then analyzed with the ferrozine method. The crystal structure of the TiO<sub>2</sub> particles determined by an X-ray powder diffractometer (MAC, MXP10) showed that anatase is the primarily form, with greater than 99.9% purity. The average particle diameter and specific BET surface area of TiO<sub>2</sub>, determined by laser particle analyzer (Photal, LPA-300) and Micromeritics ASAR 2000 apparatus, were 5.6 μm and 7.25 ± 0.14 m<sup>2</sup> g<sup>-1</sup>, respectively.

### 3. Results and discussion

#### 3.1. Influence of oxyanion on the degradation of parathion in UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system

The study of the effect of anions on the photodegradation of parathion is important in two aspects. First, anions, such as phosphate and bicarbonate are often presented in natural water and wastewater systems as buffer solutions and second, oxyanion are produced during chlorination processes. In this study, 10 mM Na<sub>2</sub>HPO<sub>4</sub> and 10 mM NaH<sub>2</sub>PO<sub>4</sub> was used to control the pH value of the solution. To understand the effect of phosphate ions on photodegradation of parathion in the presence of titanium dioxide, experiments with and without the addition of buffer solution were performed. As depicted in Fig. 1, no significant difference between buffered and unbuffered solutions was observed. The initial rate constants of parathion in buffered and unbuffered systems were almost the same and only a 10% decrease in apparent first-order rate constant ( $k_{\text{obs}}$ ) of buffered solution relative to unbuffered solution was demonstrated. Pelizzetti and Minero [19] depicted that the presence of inorganic anions in the solution during the degradation can rapidly sorb onto TiO<sub>2</sub> and compete the adsorption sites with oxygen. This can promote the recombination process of electron hole pairs and hamper the formation of hydrogen peroxide, subsequently reducing the photodegradation efficiency of parathion.

To further elucidate the effect of anions on the photodegradation of parathion, an experiment involving the addition of 30 mM oxyanions oxidants was performed. Fig. 2 illustrates the effect of oxyanions on the photodegradation of parathion in the buffered UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system. The addition of oxyanions increased the degradation rate of parathion in the order of ClO<sub>2</sub><sup>-</sup> > IO<sub>3</sub><sup>-</sup> > BrO<sub>3</sub><sup>-</sup> > ClO<sub>3</sub><sup>-</sup>. The apparent first-order rate constants were 0.14 min<sup>-1</sup> for ClO<sub>2</sub><sup>-</sup>, 0.051 min<sup>-1</sup> for IO<sub>3</sub><sup>-</sup>, 0.046 min<sup>-1</sup> for BrO<sub>3</sub><sup>-</sup> and 0.027 min<sup>-1</sup> for ClO<sub>3</sub><sup>-</sup>. This corresponds to a 2- to 7-fold increase in  $k_{\text{obs}}$  relative to the non-ion system, implying that the oxy-

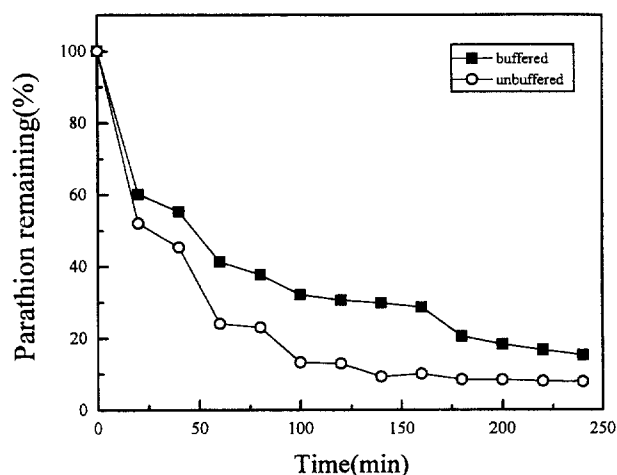


Fig. 1. The photodegradation of parathion with and without the amendment of phosphate buffer solution in the presence of titanium dioxide.

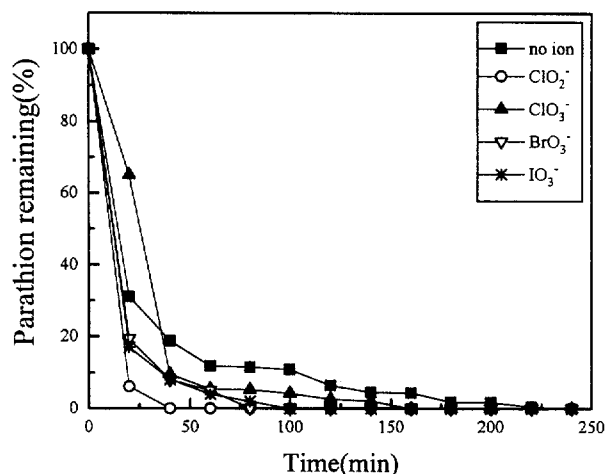


Fig. 2. The effect of oxyanions on the photodegradation of parathion in the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system.

anions oxidants could scavenge conduction-band electrons and reduce charge-carrier recombination.

#### 3.2. Effect of TiO<sub>2</sub> on the photodegradation of parathion

Fig. 3 illustrates the apparent first-order rate constants and initial rate constants of parathion with the amendment of different doses of TiO<sub>2</sub>. The  $k_{\text{obs}}$  increased from  $0.92 \times 10^{-2} \text{ min}^{-1}$  to  $4.4 \times 10^{-2} \text{ min}^{-1}$  when the TiO<sub>2</sub> loading increased from 0.1 g l<sup>-1</sup> to 1 g l<sup>-1</sup>. Further increasing the TiO<sub>2</sub> dose to 2 g l<sup>-1</sup>, however, the  $k_{\text{obs}}$  decreased to  $3.8 \times 10^{-2} \text{ min}^{-1}$ . A similar distribution pattern in the initial rate was observed. The initial rate increased from 31.5  $\mu\text{M min}^{-1}$  at 0.1 g l<sup>-1</sup> TiO<sub>2</sub> to 151.4  $\mu\text{M min}^{-1}$  at 1 g l<sup>-1</sup> TiO<sub>2</sub> and then decreased to 99.8  $\mu\text{M min}^{-1}$  when TiO<sub>2</sub> increased to 2 g l<sup>-1</sup>. These results suggest that the 1 g l<sup>-1</sup> was the optimal dose for TiO<sub>2</sub> to degrade parathion.

Several researches have demonstrated that the photo-composition rates of pollutants are influenced by the active site and the photo absorption of the catalyst used. Al-Sayyed et al. [20] depicted that the decomposition rate of 4-chlorophenol increased linearly with the amount of TiO<sub>2</sub> added. Tseng and Huang [21] reported that the oxidation rate of chlorophenols increased with the concentration of TiO<sub>2</sub>. The rate of degradation reached a maximum level of 3 g l<sup>-1</sup> and then decreased to a constant value upon further increasing the TiO<sub>2</sub> amount. Recently, Ku et al. [22] reported that the rate constant of 2-chlorophenol increased with an increasing TiO<sub>2</sub> dosage, subsequently approaching a limiting value of 2 g l<sup>-1</sup> under acidic environments. Whereas the rate constant decreased with the increasing TiO<sub>2</sub> amount for loading above 0.1 g l<sup>-1</sup> under alkali condition. In this study, the optimal dosage of TiO<sub>2</sub> was shown to be 1.0 g l<sup>-1</sup> under neutral condition. Adequate TiO<sub>2</sub> loading increased the electron/hole pairs to promote the degradation of parathion. However, the decrease of initial rate constants at higher dosage of TiO<sub>2</sub> may be attributed to the decrease of light penetration by the photocatalyst suspensions.

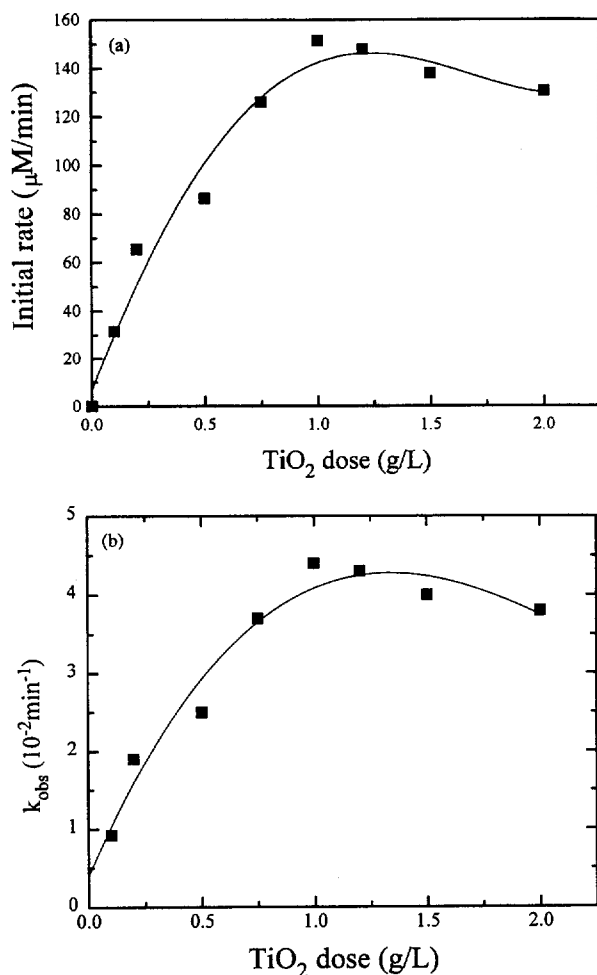


Fig. 3. The apparent first-order rate constants and initial rate constants of parathion with the amendment of different doses of TiO<sub>2</sub>.

The degradation of parathion with and without the presence of oxygen under UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system was illustrated in Fig. 4. No significant difference between oxygenated and deoxygenated systems was observed. Removal of 99.9% of the parathion was observed within 240 min in all systems. However, the presence of oxygen can increase the initial degradation rate of parathion. As shown in Table 1, the pseudo-first order rate constants of parathion in oxygenated and deoxygenated systems were 0.017 min<sup>-1</sup> and 0.012 min<sup>-1</sup>. Whereas a 3-fold difference in the initial rate constants between these two systems was observed, showing that the effect of oxygen on the initial rate constant is more important than that on the pseudo-first-order rate constant.

Titanium dioxide is widely recognized as the most suitable semiconductor to mediate the photocatalytic processes. It can absorb light to generate electron/hole pairs. The holes are either trapped by surface hydroxyl groups to yield an hydroxyl radical or combined with electrons to hamper the photocatalytic process [10–12]. In an oxygenated solution, oxygen may adsorb on the surface of titanium dioxide to prevent the recombination process. Therefore, the degrada-

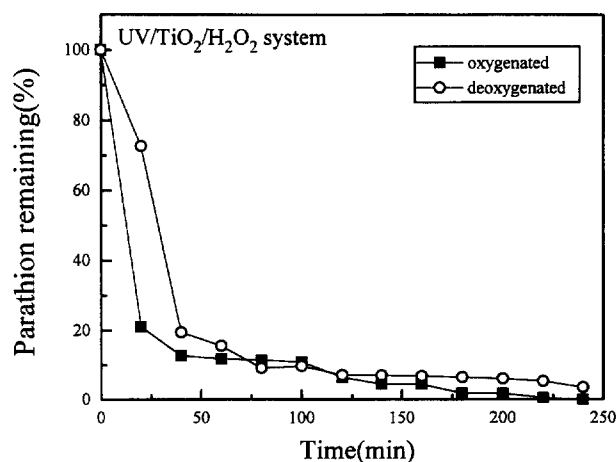
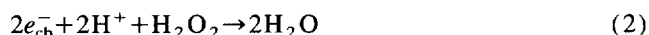


Fig. 4. The degradation of parathion with and without the presence of oxygen in the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system.

tion rate in the oxygenated system is much higher than the deoxygenated system. However, the addition of hydrogen peroxide in a deoxygenated system can compensate for the decrease of the degradation rate of parathion by reacting with positive holes and electrons to decrease the recombination rate of holes and electrons in the following reactions:



Besides the reaction with electron/hole, hydrogen peroxide can absorb UV light to generate a hydroxyl radical, subsequently enhancing the oxidation efficiencies of organic pollutants. Fig. 5 illustrates the concentration profiles of hydrogen peroxide in oxygen-amended and nitrogen-amended systems. The concentration of hydrogen peroxide in oxygenated and deoxygenated systems decreased with a similar pattern. However, the initial decrease of hydrogen peroxide in oxygenated system was more rapid than that in a deoxygenated system. This implies that the function of hydrogen peroxide in an oxygenated system was primarily to increase the generation rate of the hydroxyl radical in the initial (Eq. (3)). Whereas H<sub>2</sub>O<sub>2</sub> was mainly acting as the hole/electron scavenger in deoxygenated system.

Table 1  
The apparent first-order ( $k_{obs}$ ) and initial rate constants of parathion in the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and UV/Fe/H<sub>2</sub>O<sub>2</sub> systems

System	$k_{obs}$ (min <sup>-1</sup> )		Initial rate (μM min <sup>-1</sup> )	
	Oxygenated	Deoxygenated	Oxygenated	Deoxygenated
UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	0.017	0.012	1.352	0.467
UV/Fe <sup>0</sup> /H <sub>2</sub> O <sub>2</sub>	0.011	0.010	0.911	0.925
UV/Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	0.012	0.011	0.884	0.926

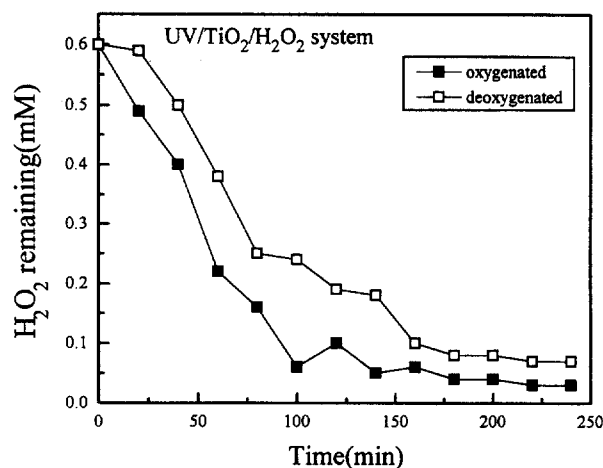
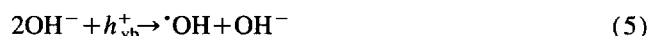


Fig. 5. The concentration profiles of hydrogen peroxide in oxygenated and deoxygenated systems.



### 3.3. Effect of iron compounds on the photodegradation of parathion

To evaluate the effects of iron compounds on the photodegradation of parathion,  $1 \text{ g l}^{-1}$  zero-valent iron or  $50 \mu\text{M}$  ferrous ion was added into the system. Fig. 6 illustrates the photodegradation of parathion in the iron compound systems. Nearly complete degradation of parathion was observed within 240 min. The rate constants for parathion was  $0.033 \text{ min}^{-1}$  in UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  system and was  $0.029 \text{ min}^{-1}$  in UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system. A nearly 3-fold increase in  $k_{\text{obs}}$  relative to UV/ $\text{H}_2\text{O}_2$  system was obtained, depicting that the addition of iron compounds can significantly enhance the photooxidation efficiency of parathion.

Fig. 7 demonstrates the concentration profiles of iron compounds and hydrogen peroxide in the UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  and UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  systems. In the UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system, the ferrous iron decreased rapidly with the production of ferric iron and reached a maximum concentration of  $49.8 \mu\text{M}$  at 60 min. Unlike the UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system, the ferrous and ferric ions in the UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  system increased simultaneously with the decrease of hydrogen peroxide. The concentration of ferrous ion reached a maximum value of  $21.6 \mu\text{M}$  at 160 min and then converted to ferric iron rapidly. Matheson and Tratnyek [17] showed that metal iron can be coupled with the reduction of oxygen to produce a spontaneous corrosion reaction in water and further oxidation of  $\text{Fe}^{2+}$  by dissolved oxygen leads to the formation of ferric iron. In this study, the oxygen concentration decreased from  $15 \text{ mg l}^{-1}$  initially to  $4.8 \text{ mg l}^{-1}$  at 240 min, suggesting that the decrease of ferrous ion was mainly due to oxidation with oxygen.

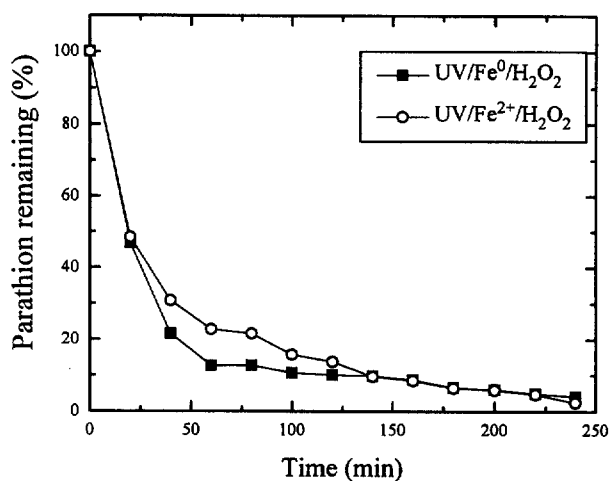


Fig. 6. The photodegradation of parathion in the UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  and UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  systems.

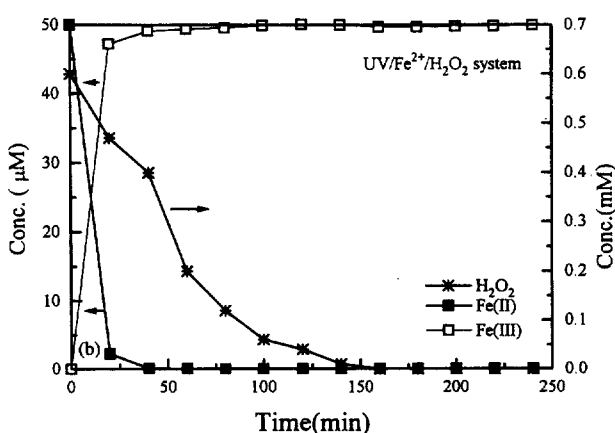
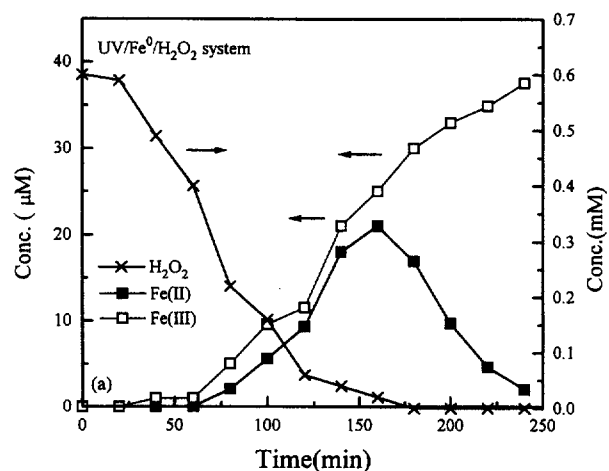
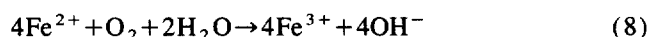
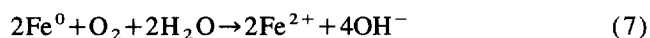
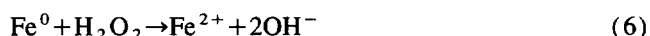


Fig. 7. The concentration profiles of iron compounds and hydrogen peroxide in the UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  and UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  systems.



Research has demonstrated that ferric ion in the photo-Fenton system can be photolyzed to form ferrous ion and

hydroxyl radical [15]. In this study, ferrous ion was nearly completely converted to ferric ion within 20 min. and a low conversion ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  was observed. This implies that the illumination of UV light did not exert much influence on the conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . This may be due to the excess hydrogen peroxide in the system. Pignatello [13] also depicted that the  $\text{Fe}^{2+}$  can be reoxidized to  $\text{Fe}^{3+}$  in the presence of hydrogen peroxide, which is consistent with our results. The pH value may be another reason hampering the conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Several researches have shown that acidic environments were conducive to the conversion of ferric ion. Therefore, the neutral environment in this study might hamper the conversion process. Moreover, similar patterns between the depletion of hydrogen peroxide and the degradation of parathion were observed, implying that  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  is the predominant system for the oxidation of parathion.

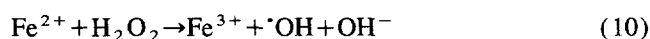
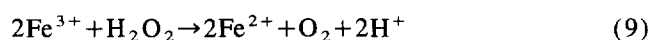


Fig. 8 illustrates the effect of oxygen on the photodegradation of parathion in a Fenton system. No significant difference of  $k_{\text{obs}}$  nor initial rate constants between oxygenated and deoxygenated systems was observed (Table 1), depicting that oxygen has little effect on the photodegradation of parathion in an UV-illuminated solution in combination with hydrogen peroxide and iron compounds.

Research has reported that the coupled semiconductors can effectively apply to enhance photoreaction processes [23,24]. Serpone et al. [24] depicted that the coupling of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  leads to enhance the rate of disappearance of chlorophenols. Since iron compound is relatively inexpensive and nontoxic, it implies that it could be useful for the treatment of contaminated wastewaters by coupling with iron compounds and titanium dioxide to increase the production of hydroxyl radical by applying interpartical electron transfer pathway.

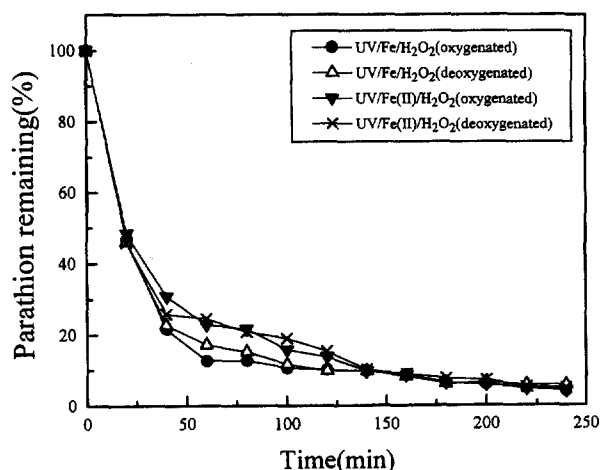


Fig. 8. The effect of oxygen on the photodegradation of parathion in the UV/ $\text{Fe}^0/\text{H}_2\text{O}_2$  and UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  systems.

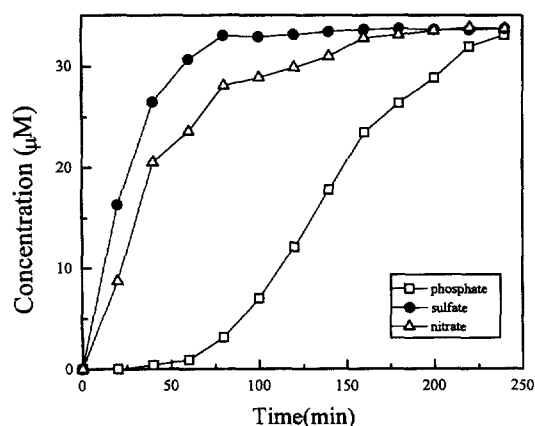


Fig. 9. The formation profiles of inorganic ions by the photodegradation of  $10 \text{ mg l}^{-1}$  parathion in the UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$  system.

### 3.4. Photodegradation pathways of parathion in UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ system

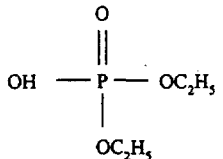
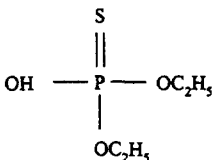
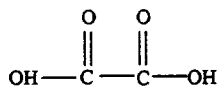
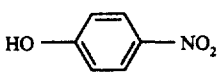
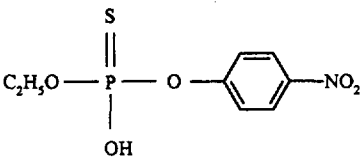
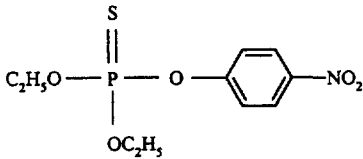
Fig. 9 depicts the formation profile of inorganic ions by the photodegradation of  $10 \text{ mg l}^{-1}$  parathion in the UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$  system. Sulfate appeared nearly simultaneous with the loss of parathion, while nitrate lagged slightly. Phosphate evolved quantitatively after 230 min. The equilibrium concentration of these inorganic ions reached  $0.034 \text{ mM}$ , showing the complete oxidation of the parathion.

A set of compounds having structures related to parathion was identified by HPLC-MS as possible degradation intermediates. As shown in Table 2, the organic intermediates formed include diethylphosphoric acid(IA), diethylmonothiophosphoric acid(IB), oxalate(II), *p*-nitrophenol (IV) and *O,O*-ethyl *p*-nitrophenyl monothiophosphoric acid. However, compounds III and V and VI could not be identified in the HPLC-MS profile. Pignatello and Sun [15] depicted that oxalic acid, *p*-nitrophenol, dimethyl phosphoric acid and *O,O*-dimethyl-4-nitrophenyl phosphoric acid were the major intermediates when methyl parathion was decomposed in a photoassisted Fenton reaction. On the basis of the results, a degradation scheme can be proposed which accounts for simultaneous attack of radical species on different points of the starting molecules. From the abundant data, oxalate and 4-nitrophenol were the major intermediates in the degradation of parathion in the UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$  system.

## 4. Conclusions

The results obtained in this study showed that the addition of  $\text{TiO}_2$  or iron compounds in combination with hydrogen peroxide was effective in the detoxification of parathion. In the  $\text{TiO}_2$ -amended system, the apparent first-order and initial rate constants increased with the increase of  $\text{TiO}_2$  loading from  $0.1 \text{ g l}^{-1}$  to  $1 \text{ g l}^{-1}$ . However, degradation rates of parathion decreased when the  $\text{TiO}_2$  dose was increased to  $2 \text{ g l}^{-1}$ . In an iron compound-amended system,  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$

Table 2  
Mass spectra of the photodegradation products of parathion in the UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system

Item	Proposed structure	m/z (intensity)
IA		170(100), 154(10.1), 138(1.6), 76(4.7), 73(3.6), 49(2.3)
IB		170(100), 154(10.1), 138(1.6), 76(4.7), 73(3.6), 49(2.3)
II		154(63.6), 136(76), 123(100), 106(70.8), 89(59.7), 77(95.9), 65(11.4)
IV		140(100), 123(44), 107(13.3), 89(15.5), 77(16.4), 65(11.4)
VII		262(100), 233(8.3), 155(9.7), 126(1.9), 96(1.6)
VIII		292(100), 275(22.8), 23.6(40.4), 218(7.9), 125(10.6), 97(17.4)

was demonstrated to be the predominant system for the oxidation of parathion.

No significant difference between phosphate buffered- and unbuffered-solutions was observed. The addition of oxyanion oxidant serves as the electron scavenger and can enhance the degradation rate of parathion in the order of  $\text{ClO}_2^- > \text{IO}_3^- > \text{BrO}_3^- > \text{ClO}_3^-$ . Oxygen had little effect on  $k_{\text{obs}}$  due to the existence of hydrogen peroxide. The HPLC/MS analysis showed that diethylphosphoric acid, diethylmonothiophosphoric acid, oxalate, *p*-nitrophenol and *O,O*-ethyl *p*-nitrophenyl monothiophosphoric acid were identified as intermediates and shown to be oxidized further. Moreover, oxalate and 4-nitrophenol were found to be the major intermediates in the degradation of parathion.

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### References

- [1] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
- [2] T. Gerfin, M. Gratzel, L. Walder, Prog. Inorg. Chem. 44 (1997) 345.
- [3] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis—Fundamentals and Applications, Wiley-Interscience, New York, 1989.
- [4] P.C. Calza, C. Minero, E. Pelizzetti, Environ. Sci. Technol. 31 (1997) 2198.

- [5] J. Arantegui, J. Prado, E. Chamorro, S. Esplugas, J. Photochem. Photobiol. A: Chem. 88 (1995) 65.
- [6] M.S. Dieckmann, K.A. Gray, Water Res. 20 (1996) 1169.
- [7] A. Haarstrick, O.M. Kut, E. Heinzle, Environ. Sci. Technol. 30 (1996) 817.
- [8] Y. Sun, J.J. Pignatello, Environ. Sci. Technol. 30 (1995) 2065.
- [9] R.A. Doong, W.H. Chang, J. Photochem. Photobiol. A: Chem. 107 (1997) 239.
- [10] Z. Hua, Z. Manping, Z. Zongfeng, G.K.-C. Low, Water Res. 29 (1995) 2681.
- [11] J. Kiwi, Environ. Toxicol. Chem. 13 (1994) 1569.
- [12] M. Bekbolet, I. Balcioglu, Proc. 18th IAWQ Biennial International Conference and Exhibition, 23–28 June 1996, 56.
- [13] J.J. Pignatello, Environ. Sci. Technol. 26 (1992) 994.
- [14] J.J. Pignatello, G. Chapa, Environ. Toxicol. Chem. 13 (1994) 423.
- [15] J.J. Pignatello, Y. Sun, Water Res. 29 (1995) 1837.
- [16] M.M. Scherer, J.C. Westall, M. Ziomek-Moroz, P.G. Tratnyek, Environ. Sci. Technol. 31 (1997) 2385.
- [17] L.J. Matheson, P.G. Tratnyek, Environ. Sci. Technol. 28 (1994) 2045.
- [18] J.P. Percherancier, R. Chapelon, B. Pouyet, J. Photochem. Photobiol. A: Chem. 87 (1995) 261.
- [19] E. Pelizzetti, C. Minero, Electrochim. Acta 38 (1993) 47.
- [20] G. Al-Sayyed, J.C. D'Oliveira, P. Pichat, J. Photochem. Photobiol. A: Chem. 58 (1991) 99.
- [21] J.M. Tseng, C.P. Huang, Water Sci. Technol. 23 (1991) 377.
- [22] Y. Ku, R.M. Leu, K.C. Lee, Water Res. 30 (1996) 2569.
- [23] N. Serpone, E. Borgarello, M. Gratzel, J. Chem. Soc. Chem. Commun. (1984) 342.
- [24] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, J. Photochem. Photobiol. A: Chem. 85 (1995) 247.