Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst

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Abstract

This study examines how Fenton's reagent (Fe^{2+} and H_2O_2) decomposed dichlorvos insecticide. Results showed that dichlorvos decomposed in a two-stage reaction. The first stage is a Fe^{2+}/H_2O_2 reaction in which dichlorvos swiftly decomposed. In the second stage, dichlorvos decomposed somewhat less rapidly, and it is a Fe^{3+}/H_2O_2 reaction. The detection of ferrous ions also supports the theory of the two-stage reaction for the dichlorvos oxidation with Fenton's reagent. The dissolved oxygen of the solution decreased rapidly in the first stage reaction, but it slowly increased in the second stage with a zero-order kinetics. The Fenton system decomposed dichlorvos most rapidly when the initial pH in the solution is 3–4. In addition, increasing the concentration of hydrogen peroxide or ferrous ions can enhance the decomposition of dichlorvos. Consequently, the relationship of rate constant (k_{obs}), [H_2O_2] and [Fe^{2+}] at initial pH 3 is determined as $k_{obs} = 2.67 \times 10^4 [H_2O_2]^{0.7} [Fe^{2+}]^{1.2}$. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fenton's reagent; Dichlorvos; Insecticide; Ferrous ion; Hydrogen peroxide

1. Introduction

Surface waters and groundwaters have been found to contain substantial concentrations of pesticides [1]. Many studies have been carried out on the destruction of these

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pollutants. Conventional purification methods for polluted water containing pesticides include carbon adsorption, ozonation, microbial action, hydrolysis, and photooxidation, but many of them are inefficient [2–4].

Hydrogen peroxide was first used to reduce odor in wastewater treatment plants, and from then on, hydrogen peroxide entered the realm of wastewater treatment. Hydrogen peroxide is a non-contaminating oxidant because its products are non-toxic substances, and can conform to strict environmental regulations [5]. Besides, some contaminants may be oxidized into biologically degradable matter using hydrogen peroxide, and oxygen produced from hydrogen peroxide is also supplied to enhance the biodegradability. However, hydrogen peroxide can be toxic to microorganisms if its concentration is too high. Pardieck et al. [6] found that when the concentrations of hydrogen peroxide is higher than 5.0×10^{-2} M, it becomes a toxicant to microorganisms.

The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants [7–10].

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \tag{1}$$

Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics [11]:

$$\cdot OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{2}$$

$$\cdot OH + Organics \rightarrow products \tag{3}$$

Hydroxyl radicals can react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, which are shown as below [11]:

$$\cdot OH + H_2O_2 \rightarrow H_2O + \cdot HO_2 \tag{4}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{5}$$

Ferrous ions and radicals are produced during the reactions. The reactions are as shown in Eqs. (6)–(9) [11]:

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \tag{6}$$

$$FeOOH^{2+} \rightarrow \cdot HO_2 + Fe^{2+} \tag{7}$$

$$\cdot HO_2 + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \tag{8}$$

$$\cdot HO_2 + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \tag{9}$$

The reaction rate in Eq. (6) is much slower than that in Eq. (1). It is derived that ferrous ions are consumed quickly, but reproduced slowly [12]. Consequently, the oxidation rate of organic compounds is fast when large amount of ferrous ions are present because large amount of hydroxyl radicals are produced. However, the Fenton reaction may slow down due to the slow ferrous ion production.

Dichlorvos ($C_4H_7Cl_2O_4P$, 2-dichlorovinyl dimethylphosphate, DDVP) was commercially manufactured in 1961 and used as an insecticide. Its solubility in water, vapor pressure at 20°C and boiling point are 10 g l^{-1}, 1.2×10^{-2} mm Hg and 74°C at 13 Pa, respectively [13]. In previous studies, the photocatalytic degradation of dichlorvos on glass supported titanium dioxide was investigated. Results indicated that photocatalysis could be an effective process for the degradation of dichlorvos [14]. The mineralization of dichlorvos and the reduction of toxicity were investigated via the photocatalytic reaction [15]. This study used Fenton's reagent to oxidize dichlorvos with an attempt to explore the behavior of dichlorvos oxidation and how factors such as pH, $[H_2O_2]$ and $[Fe^{2+}]$ may influence the dichlorvos decomposition.

2. Material and methods

Dichlorvos was obtained from Bayer (purity, 96.33%). Ferrous sulfate and hydrogen peroxide (purity, 30%) were manufactured by Merck. The standard dichlorvos solution was purchased from RDH (purity > 99%), and the rest of the used reagents were at least reagent grade. Aqueous solutions used for oxidation reactions were prepared with Millipore Milli-Q water.

A dichlorvos solution was prepared by stirring an excess amount of dichlorvos in pure water at room temperature. Reaction mixtures were obtained by mixing a stock solution with pure water, followed by taking an appropriate amount of dichlorvos solution, adding ferrous ion and the background ions, diluting with pure water to 100 ml, and adjusting the initial pH ranging from 2.5 to 5.0. After the pH adjustment, the solution was poured into a 250-ml flask, and then placed in a thermal oscillator tank at 30°C. The reactions were initiated after adding hydrogen peroxide with a range of 1.0×10^{-3}–1.0×10^{-2} M. As the literature reported [12], Fenton reaction cannot happen at pH > 10. Therefore, Fenton reaction was stopped instantly by adding NaOH to the reaction mixtures before analysis. Concerning the measurement of ferrous ions, separate experiments were conducted in tubes. Ferrous ions were tested by the TPTZ method using a Hitachi spectrophotometer [16]. Beer–Lambert law is obeyed to approximately 7.1×10^{-6} M of Fe^{2+} by this method. Ferrozine was added to the testing solutions to form the complexes with ferrous ions and therefore the Fenton reaction was stopped. In this experiment, we chose 5, 10, 15, 30 and 45 s as the time point for analysis. Although the time point is not very precise for the analysis of ferrous ion in such a short time, the changes of $[Fe^{2+}]$ during the reaction time can still be confirmed.

Dichlorvos was extracted by hexane from the reaction mixture and analyzed by an HP 5980II gas chromatography with an electron capture detector and a Supelco PTE-5 column (0.53 mm in inside diameter, 15 m long). Hydrogen peroxide was analyzed by an iodometric titration with $Na_2S_2O_3$ solution [17]. In the dissolved oxygen measurement, the experiment was conducted with a 1.2-l well-sealed reactor to monitor the change of dissolved oxygen during the oxidation of dichlorvos. A DO meter (MTW Microprocessor Oximeter OXI 196) was used to monitor the concentration of dissolved oxygen.

3. Results and discussion

3.1. Two stages of dichlorvos decomposition

In our previous study, dichlorvos hardly decomposed at all in the duration of 90 min if only hydrogen peroxide or ferrous ions were added [18]. Therefore, it can be confirmed that the disappearance of dichlorvos was due to the Fenton reaction. Results from the experiment showed that the decomposition rate of dichlorvos gradually slowed down after approximately 30 s. As shown in Fig. 1, obviously, it is a two-stage reaction; the decomposition rate of dichlorvos before 30 s was far more rapid than that after 30 s. The main reason for the two-stage reaction is that ferrous ions reacted very quickly with hydrogen peroxide to produce large amount of hydroxyl radicals (see Eq. (1)). The produced hydroxyl radicals can react rapidly with organic matter, thus in the first stage, dichlorvos decomposed quickly; this is referred to as the Fe^{2+}/H_2O_2 stage. The ferric ions produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals ($\cdot HO_2$) and ferrous ions, and the reactions are shown in Eqs. (6) and (7).

Hydroxyl radicals and hydroperoxyl radicals formed in the reactions are able to continue to decompose dichlorvos. The reaction rate constant (M^{-1} s^{-1}) of ferrous ions reacting with hydrogen peroxide to produce hydroxyl radicals is 53 and the reaction rate constant of ferric ions reacting with hydrogen peroxide to form ferrous ions is 0.02 [19]. Therefore, it can be derived that the former reaction is far more swifter than the latter, resulting in a higher rate of hydroxyl radical formation in the first stage reaction than that in the second stage reaction. The rate of dichlorvos oxidation in the second stage was slower than that in the first stage, and the second stage will be referred to here as the Fe^{3+}/H_2O_2 stage. As the literatures reported [12,19,20], Fe^{3+} has a lower catalytic activity than Fe^{2+} and may complex with target organic substrates or their degradation
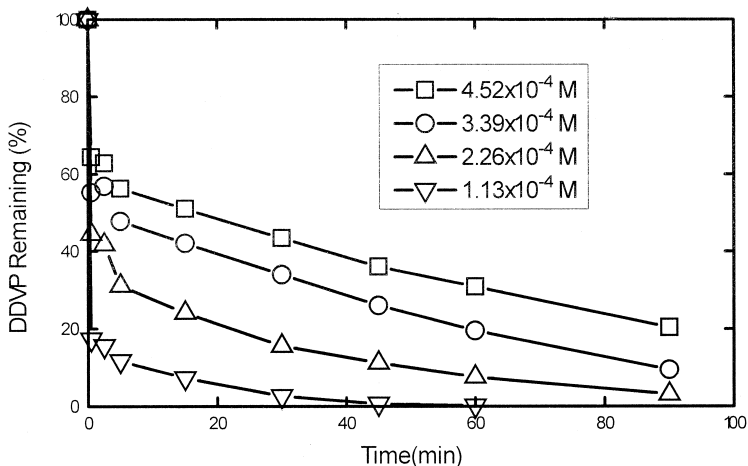

Fig. 1. Changes in the concentration of dichlorvos at different initial [DDVP]. Experimental conditions: $[Fe^{2+}] = 2.5 \times 10^{-4}$ M; $[H_2O_2] = 5 \times 10^{-3}$ M; $[NaClO_4] = 0.2$ M; pH = 3.

intermediates that can produce weaker oxidants than hydroxyl radicals. Hence, UV light was used to generate Fe^{2+} from Fe^{3+} in order to increase the concentration of hydroxyl radical, which promoted the oxidation efficiency. In the present study, the two-stage reaction may have resulted from the lower generation of Fe^{2+} from Fe^{3+} (see Eqs. (6)–(9)), and the complexation of Fe^{3+} and degradation intermediates.

The detection of ferrous ions also supports the theory of the two-stage reaction for the dichlorvos oxidation with Fenton's reagent. Under the condition that different amounts of ferrous ions were added, most of the ferrous ions were transformed to ferric ions, which were undetectable after 30 s, as shown in Fig. 2. In order to discuss the first and second stage reactions separately, the reaction which occurred in the first stage is discussed by the initial rate, and the other is discussed by the first-order rate constant in the following sections.

3.2. The variation of [H₂O₂] and dissolved oxygen during the Fenton reaction

It can be seen from Fig. 3 that very little of the hydrogen peroxide concentration was reduced; only 5×10^{-4} M is utilized after 90 min. There are three mechanisms that might consume hydrogen peroxide: (1) ferrous ions reacting with hydrogen peroxide (Eq. (1)), (2) ferric ions reacting with hydrogen peroxide (Eq. (6)), and (3) hydrogen peroxide reacts with organic chemicals or radicals. In the Fe^{2+}/H_2O_2 stage, only 1.0×10^{-4} M of hydrogen peroxide was consumed. The consumption ratio of hydrogen peroxide and ferrous ions is 0.44:1, lower than the anticipated 1:1. The reason for this result is probably due to regeneration of hydrogen peroxide through Eq. (5), and the consumption of hydrogen peroxide was lessened. Another reason could be that hydroxyl radicals reacted with ferrous ions (see Eq. (2)) and produce oxygen molecules. The total amount of hydrogen peroxide consumed in the second stage is 4×10^{-4} M.
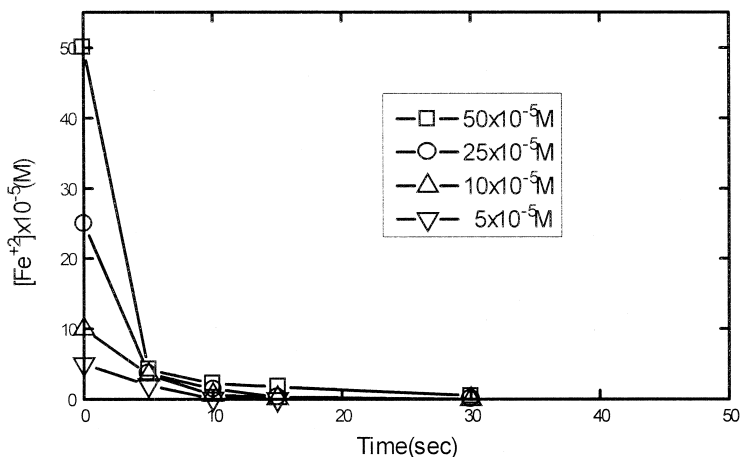

Fig. 2. Changes in the concentration of [Fe^{2+}]. Experimental conditions: [DDVP] = 2.26×10^{-4} M; [H_2O_2] = 5×10^{-3} M; [$NaClO_4$] = 0.2 M; pH = 3.
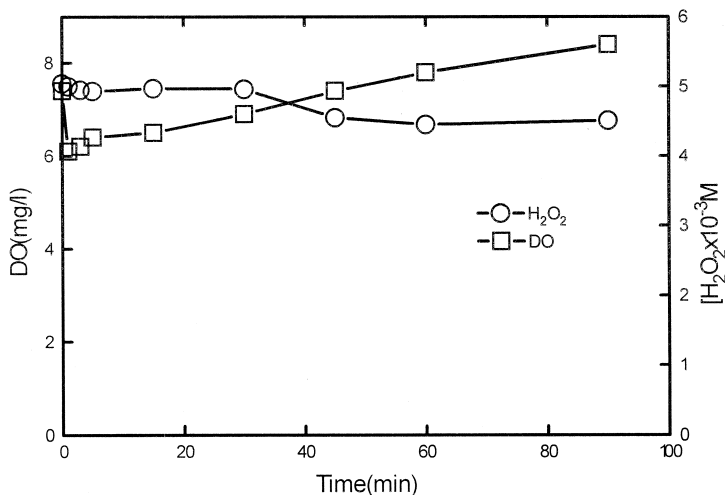
Fig. 3. Changes in the concentration of oxygen and hydrogen peroxide during the Fenton reaction. Experimental conditions: $[DDVP] = 2.26 \times 10^{-4}$ M; $[Fe^{2+}] = 2.5 \times 10^{-4}$ M; $[H_2O_2] = 5 \times 10^{-3}$ M; $[NaClO_4] = 0.2$ M; pH = 3.

The initial dissolved oxygen was 7.4 mg l^{-1}, and then it rapidly dropped to 6.1 mg l^{-1} at 30 s of reaction. The dissolved oxygen continually increased after 30 s; it was 6.9 mg l^{-1} after 30 min, and 8.4 mg l^{-1} after 90 min. As observed from the change in dissolved oxygen, oxygen molecules have participated in the oxidation reaction. In the Fe^{2+}/H_2O_2 reaction stage, the dissolved oxygen dropped from 7.4 mg l^{-1} to 6.1 mg l^{-1}. The consumption of dissolved oxygen is large because most of dichlorvos was decomposed. Sun and Pignatello [19] have shown that O_2 can enhance Fenton reaction due to its reaction with intermediate organoradicals.

In the Fe^{3+}/H_2O_2 stage, the dissolved oxygen concentration rose from 6.1 mg l^{-1} to 8.4 mg l^{-1}, although dichlorvos was still being decomposed at this stage. Because the ferric ions produced in the Fe^{2+}/H_2O_2 stage will catalyze hydrogen peroxide to produce oxygen (see Eqs. (6)–(9)), dissolved oxygen was consumed slowly and produced rapidly, resulting in the continuous increase of dissolved oxygen in the Fe^{3+}/H_2O_2 stage. Basu and Wei [21,22] reported the profiles of dissolved oxygen with time of Fenton reaction. The dissolved oxygen level dropped immediately at the start of the Fenton reaction, then increased with time of reaction. Walling [11] also reported that the production of oxygen is a zero-order kinetics in the reaction of ferric ions catalyzing hydrogen peroxide. The zero-order reaction constant can also be obtained in the reaction of the Fe^{3+}/H_2O_2 stage. The equation and rate constant are shown as,

$$d[O_2]/dt = 0.026 \tag{10}$$

3.3. Effect of initial pH

In the reaction of dichlorvos decomposition by ferrous ions catalyzing hydrogen peroxide, the pH dropped with time of reaction. However, only the effect of initial pH

Table 1
DDVP oxidation rates and rate constants at different initial pHs

$pH_{initial}$	pH_{final}	Initial rate $(\times 10^{-4} \text{ M min}^{-1})$	k $(\times 10^{-2} \text{ min}^{-1})$
2.5	2.4	2.32	1.74
3.0	2.8	2.51	2.90
3.5	3.1	2.40	4.09
4.0	3.1	2.47	4.15
5.0	3.1	2.40	2.08

Experimental conditions: $[DDVP] = 2.26 \times 10^{-4}$ M; $[Fe^{2+}] = 2.5 \times 10^{-4}$ M; $[H_2O_2] = 5 \times 10^{-3}$ M; $[NaClO_4] = 0.2$ M.

on dichlorvos decomposition will be discussed here. The initial and final pHs of solutions are listed in Table 1. Fig. 4 shows the relationship between residual dichlorvos and time under the initial condition of $[Fe^{2+}] = 2.5 \times 10^{-4}$ M and $[H_2O_2] = 5 \times 10^{-3}$ M. It can be observed from Fig. 4 that 90% of dichlorvos elimination can be reached after 90 min. However, in the Fe^{2+}/H_2O_2 stage, the difference in dichlorvos oxidation rates among different initial pH is not obvious; all the dichlorvos remaining fell between 44.5%–48.6%. It can be derived that initial pH does not have an obvious influence on the Fe^{2+}/H_2O_2 reaction. Pignatello [12] also showed that pH does not influence the Fe^{2+}/H_2O_2 reaction greatly.

In the Fe^{3+}/H_2O_2 stage, the dichlorvos oxidation obeys a first-order kinetics and the rate constants are listed in Table 1. It indicates that the initial pH inducing the best Fe^{3+}/H_2O_2 reaction is between 3–4. Basu and Wei [22] found the optimum pH of 2,4,6-trichlorophenol using Fenton's reagent is between 2.0–3.5. According to the findings of Sedlak and Andren [23,24], the most ideal pH for chlorodiphenyl and
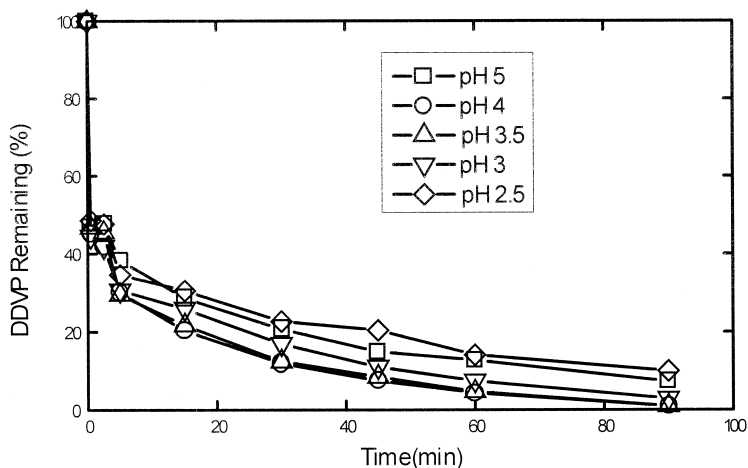

Fig. 4. Effect of initial pH on the oxidation of dichlorvos. Experimental conditions: $[DDVP] = 2.26 \times 10^{-4}$ M; $[Fe^{2+}] = 2.5 \times 10^{-4}$ M; $[H_2O_2] = 5 \times 10^{-3}$ M; $[NaClO_4] = 0.2$ M.

chlorobenzene is between 2–4. Pignatello's research [12] on 2,4-D decomposition also had similar results. At higher pH, the degradation of organic chemicals decreased because ferric ions will form $Fe(OH)_3$. It can be calculated that when the pH is greater than 3, $Fe(OH)_3$ will appear [25]. $Fe(OH)_3$ has low activity and will not react with hydrogen peroxide [12]. Therefore, the ferric ions in the solution that can react with hydrogen peroxide were reduced. In the mechanism in which ferric ions react with hydrogen peroxide, Eq. (6) is the rate-limiting step. When the pH is too low and the concentration of hydrogen ions is too high, the high concentration of hydrogen ions will cause the formation of $FeOOH^{2+}$ to slow down, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well. The above reactions may retard the dichlorvos decomposition.

3.4. Effect of hydrogen peroxide

Hydrogen peroxide plays the role of an oxidizing agent in the Fenton reaction. It was discovered that if only ferrous ions were added in the solution instead of adding hydrogen peroxide as well, dichlorvos did not decomposed [18]. This shows that ferrous ions alone cannot decompose dichlorvos. As Table 2 shows, the rate of dichlorvos removal increases with the increase in initial concentration of hydrogen peroxide. The elimination ratio can reach approximately 99.9% after 90 min when $[H_2O_2]$ is 1.0×10^{-2} M.

In the Fe^{2+}/H_2O_2 stage, when $[H_2O_2] = 1.0 \times 10^{-2}$ M–1.0×10^{-5} M, the remaining dichlorvos was approximately 50% within 30 s. The concentration transformation of hydrogen peroxide has no significant effects on the elimination rate of dichlorvos. The reason is may be that the concentration of hydrogen peroxide is much higher than that of ferrous ions ($[H_2O_2]/[Fe^{2+}] \geq 20$), and it will not become the limiting factor of reaction rate in this reaction stage. When $[H_2O_2] = 2.5 \times 10^{-3}$ M and 1.0×10^{-3} M, the remaining dichlorvos were 50.9% and 57.1%, respectively. Therefore, the elimination rate of dichlorvos rose with the increase in hydrogen peroxide concentration after 30 s.

In the Fe^{3+}/H_2O_2 stage, the dichlorvos oxidation follows a first-order kinetics, and the rate constants are listed in Table 2. The reaction rates increase with the increase of the hydrogen peroxide concentration. Pignatello [12] reported that an increase in hydrogen peroxide concentration could increase the rate of 2,4-D mineralization. As

Table 2
DDVP remaining and rate constants at different initial $[H_2O_2]$

$[H_2O_2]$ ($\times 10^{-3}$ M)	Initial rate ($\times 10^{-4}$ M min^{-1})	k_h ($\times 10^{-2}$ min^{-1})
10	2.50	4.90
5.0	2.50	2.45
2.5	2.22	1.71
1.0	1.94	1.23

Experimental conditions: $[DDVP] = 2.26 \times 10^{-4}$ M; $[Fe^{2+}] = 2.5 \times 10^{-4}$ M; initial pH = 3; $[NaClO_4] = 0.2$ M.

pointed out by Rahhal and Richter [26], the higher the concentration of hydrogen peroxide, the faster it decomposed. Moon et al. [27] discovered that when $[FeCl_3] = 2.15 \times 10^{-4}$ M and $[H_2O_2] < 5 \times 10^{-2}$ M, the reaction rate increased with increasing hydrogen peroxide concentration. But when $[H_2O_2] > 5 \times 10^{-2}$ M, the reaction rate decreased with the increase of hydrogen peroxide concentration. The reason is may be either the reaction of $\cdot OH$ and H_2O_2, or the combination of two $\cdot OHs$ to form H_2O_2 (Eqs. (4) and (5)). These two reactions reduced the probability of dichlorvos attacked by hydroxyl radicals, and caused the oxidation rate of dichlorvos to drop. Khan and Watts [28] also reported the catalytic oxidation of perchloroethylene (PCE) using goethite as catalyst with initial concentrations of 0.15, 2, 5, 10, 20 and 30 mM hydrogen peroxide. They found that the reaction rate was the highest using the initial $[H_2O_2]$ of 10 mM during the 25-h reaction time and increased the ratios of H_2O_2/PCE with the increase in initial $[H_2O_2]$; higher $[H_2O_2]$ may favor scavenging hydroxyl radicals to form hydroper-oxyl radicals as shown in Eq. (4). However, Li et al. [20] reported the increasing 2,4,6-trinitrotoluene oxidation with increasing hydrogen peroxide concentration. In this study, the oxidation of dichlorvos did not inhibited by increasing the concentration of hydrogen peroxide. Our result is the same as that of Refs. [12,20,26]. The reason could be that the amount of hydrogen peroxide added in this experiment has not yet reached the degree of inhibition.

3.5. Effect of ferrous ions

Because hydrogen peroxide with an oxidation potential of 1.77 V has a less oxidizing power [29], dichlorvos cannot be effectively oxidized by only adding hydrogen peroxide in the solution. Ferrous ions are the main species that can catalyze hydrogen peroxide to produce hydroxyl radicals with strong oxidizing ability [18]. Because the added amount of ferrous ions directly influenced the production of hydroxyl radicals, it has a large influence on the decomposition rate of dichlorvos. When 5.0×10^{-3} M of H_2O_2 was used for the reaction, it was observed how the concentration of dichlorvos changes periodically, if different amounts of ferrous ions were added. As Table 3 shows, the elimination rates of dichlorvos are proportional to the added amounts of ferrous ions.

In the Fe^{2+}/H_2O_2 stage, there was a large change in the dichlorvos oxidation rate. When $[Fe^{2+}] = 5 \times 10^{-4}$ M, the remaining dichlorvos in the solution was 13.2%, and when $[Fe^{2+}] = 5 \times 10^{-5}$ M, 84.2% of dichlorvos still remained. It can be observed that

Table 3
Initial rate of DDVP oxidation and rate constants at different initial $[Fe^{2+}]$

$[Fe^{2+}]$ ($\times 10^{-4}$ M)	Initial rate ($\times 10^{-5}$ M min^{-1})	k_f ($\times 10^{-2}$ min^{-1})
5.0	39.2	9.01
2.5	25.1	2.97
1.0	13.8	1.02
0.5	7.14	0.56

Experimental conditions: $[DDVP] = 2.26 \times 10^{-4}$ M; initial pH = 3; $[H_2O_2] = 5 \times 10^{-3}$ M; $[NaClO_4] = 0.2$ M.

the dichlorvos decomposition is clearly influenced by the amount of ferrous ions added in the solution. When the added amount of ferrous ions increased, the elimination rate of dichlorvos increased as well. In the Fe^{3+}/H_2O_2 stage, the same tendency as the Fe^{2+}/H_2O_2 stage could be found, and the rate constants are listed in Table 3.

3.6. Determination of bi-factor rate constant

The oxidation of dichlorvos in the Fe^{3+}/H_2O_2 stage obeys a first-order behavior. It was found that the value of rate constant, k_h, increases with the increase in initial $[H_2O_2]$. Therefore, the pseudo-first-order rate constant in terms of the initial $[H_2O_2]$ is obtained as:

$$k_h = 1.11[H_2O_2]^{0.7} \tag{11}$$

The efficiencies of dichlorvos oxidation for the first stage and the pseudo-first-order rate constants (k_f) in terms of the initial $[Fe^{2+}]$ for the second stage are listed in Table 3. It can be seen that the initial concentration of ferrous ion is a function of dichlorvos oxidation. In this case, the relationship of k_f and $[Fe^{2+}]$ is can be expressed by Eq. (12):

$$k_f = 724[Fe^{2+}]^{1.2} \tag{12}$$

Combining Eqs. (11) and (12), Eq. (13) is obtained:

$$k_{obs} = k[H_2O_2]^{0.7}[Fe^{2+}]^{1.2} \tag{13}$$

where k is the bi-factor constant.

By substituting the initial concentration of $[H_2O_2] = 5.0 \times 10^{-3}$ M and $[Fe^{2+}] = 2.5 \times 10^{-4}$ M, and comparing with Eqs. (11) and (12), the bi-factor constant, 2.67×10^4 min^{-1} M^{-2}, for the second stage reaction is given. Consequently, the relationship of k_{obs}, $[H_2O_2]$ and $[Fe^{2+}]$ can be written as:

$$k_{obs} = 2.67 \times 10^4[H_2O_2]^{0.7}[Fe^{2+}]^{1.2} \tag{14}$$

4. Conclusions

This study employed the Fenton's reagent to oxidize dichlorvos insecticide. Results show that the efficiencies are fairly satisfactory. At acidic and saturated dissolved oxygen conditions, only 90 min were needed to push the elimination ratio up to 98%. The dichlorvos decomposition in this system underwent a two-stage reaction. The first stage was the reaction before 30 s in which the decomposition rate of dichlorvos was high, and it is a Fe^{2+}/H_2O_2 reaction. The second stage is the reaction that took place after 30 s. The decomposition rate of dichlorvos in the stage was slower, and it is a Fe^{3+}/H_2O_2 reaction. This can be also proved from the detection of ferrous ions.

In this system, because the concentration of hydrogen peroxide was much higher than that of ferrous ions ($[H_2O_2]/[Fe^{2+}] \geq 20$), only slight amount of hydrogen peroxide was reduced. The dissolved oxygen dropped rapidly, then slowly rose in the later

reaction. Moreover, because ferric ions can catalyze hydrogen peroxide to produce oxygen, the amount of dissolved oxygen increased gradually; its increasing rate follows a zero-order kinetics. The most ideal pH for the Fenton reaction to decompose dichlorvos in solution is between 3–4. As the added amount of hydrogen peroxide or ferrous ions increased, the decomposition rate of dichlorvos also increased.

References

[1] J.W. Eichelberger, J.J. Lichtenberg, Persistence of pesticides in river water, Environ. Sci. Technol. 5 (1971) 541–544.

[2] E. Gal, P. Aires, E. Chamarro, S. Esplugas, Photochemical degradation of parathion in aqueous solution, Water Res. 26 (1992) 911–915.

[3] E. Pelizzetti, V. Maurino, C. Minero, V. Carlin, E. Pramauro, O. Zerbinati, M.L. Tosato, Photocatalytic degradation of atrazine and *s*-triazine herbicides, Environ. Sci. Technol. 24 (1990) 1559–1565.

[4] A.P. Dillon, Pesticide disposal and detoxification, Noyes Data, NJ, 1981, pp. 223–326.

[5] K. Elizardo, Fighting pollution with hydrogen peroxide, Pollution Engineering (September 1991) 106–109.

[6] D.L. Pardieck, E.J. Bouner, A.T. Stone, Hydrogen peroxide use to increase oxidant capacity for in situ bioremediation of contaminated soils and aquifers: a review, J. Contam. Hydrol. 9 (1992) 221–242.

[7] W. Spacek, R. Bauer, G. Heisler, Heterogeneous and homogeneous wastewater treatment-comparison between photodegradation with TiO_2 and the photo-Fenton reaction, Chemosphere 30 (1995) 477–484.

[8] E. Lipczynska-Kochany, G. Sprah, S. Harms, Influence of some groundwater and surface waters constitutes on the degradation of 4-chlorophenol by the Fenton reaction, Chemosphere 30 (1995) 9–20.

[9] R.J. Watts, S.E. Dilly, Evaluation of iron catalysts for Fenton-like remediation of diesel-contaminated soil, J. Hazard. Mater. 51 (1996) 209–224.

[10] C.T. Chen, A.N. Tafuri, M. Rahman, M.B. Forest, Chemical oxidation treatment of petroleum contaminated soil using Fenton's reagent, J. Environ. Sci. Health A 33 (1998) 987–1008.

[11] C. Walling, Fenton reagent: V. Hydroxylation and side-chain cleavage of aromatics, Acc. Chem. Res. 8 (1975) 125–131.

[12] J.J. Pignatello, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[13] A. Waterson, Pesticide Users' Health and Safety Handbook, Van Nostrand-Reinhold, New York, 1988, pp. 188–189.

[14] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, Factors affecting the photocatalytic degradation of dichlorvos over titanium dioxide supported on glass, J. Photochem. Photobiol. A: Chem. 76 (1993) 103–110.

[15] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, Photocatalytic mineralization of toxic chemicals with illuminated TiO_2, Chem. Eng. Commun. 139 (1995) 1–13.

[16] M.C. Lu, J.N. Chen, C.P. Chang, Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton reagent, Chemosphere 35 (1997) 2285–2293.

[17] I.M. Kolthof, E.B. Sandell, E.J. Meehan, S. Buckstein, Quantitative Chemical Analysis, 4th edn., Macmillan, New York, 1969, pp. 1862–1867.

[18] P.F. Collins, H. Diehl, G.F. Smith, 2,4,6-Tripyridyl-*s*-triazine as a reagent for iron, Anal. Chem. 31 (1959) 1862–1867.

[19] Y. Sun, J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$, Environ. Sci. Technol. 27 (1993) 304–310.

[20] Z.M. Li, S.D. Comfort, P.J. Shea, Destruction of 2,4,6-trinitrotoluene by Fenton oxidation, J. Environ. Qual. 26 (1997) 480–487.

[21] S. Basu, I.W. Wei, Advanced chemical oxidation of 2,4,6-trichlorophenol in aqueous phase by Fenton's reagent: Part I. Effects of the amounts of oxidant and catalyst on the treatment reaction, Chem. Eng. Commun. 164 (1988) 111–137.

[22] S. Basu, I.W. Wei, Advanced chemical oxidation of 2,4,6-trichlorophenol in aqueous phase by Fenton's reagent: Part I. Effects of various parameters on the treatment reaction, Chem. Eng. Commun. 164 (1988) 139–151.

[23] D.L. Sedlak, A.W. Andren, Aqueous-phase oxidation of polychlorinated biphenyl radicals, Environ. Sci. Technol. 25 (1991) 777–782.

[24] D.L. Sedlak, A.W. Andren, Oxidation of chlorobenzene with Fenton's reagent, Environ. Sci. Technol. 25 (1991) 1419–1427.

[25] V.L. Snoeyink, D. Jenkins, Water Chemistry, Wiley, 1982, pp. 262–269.

[26] S. Rahhal, H.W. Richter, Reduction of hydrogen peroxide by the ferrous iron chelate of diethylenetri-amine-N,N,N',N,N'-pentaacetate, J. Am. Chem. Soc. 110 (1988) 3126–3133.

[27] D.-K. Moon, T. Maruyama, K. Osakada, T. Yamamoto, Chemical oxidation of polyaniline by radical generating reagent, Chemistry Letter (1991) 1633–1636.

[28] M.D.A. Khan, R.J. Watts, Mineral-catalyzed peroxidation of tetrachloroethylene, Water Air Soil Pollut. 88 (1996) 247–260.

[29] H.W. Prengle, C.E. Mauk, New technology: ozone/UV chemical oxidation wastewater process for metal complexes, organic species and disinfection, AIChE Symp. Ser. 74 (1978) 228–232.