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UV/ferrate(VI) oxidation of profenofos: efficiency and mechanism

Yiqun Chen, Ya Xiong, Zongping Wang*, Yong Chen, Guomeng Chen, Zizheng Liu

School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China, Tel. +86 27 87792406; emails: chenyiqun1991@163.com (Y. Chen), xy7948@163.com (Y. Xiong), zongpingw@hust.edu.cn (Z. Wang), ychen@hust.edu.cn (Y. Chen), 297150899@qq.com (G. Chen), 437355572@qq.com (Z. Liu)

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ABSTRACT

The elimination of organophosphorus pesticide profenofos was investigated in the UV/ferrate(VI) solution. The oxidation of profenofos was pH dependent and increased in the order of pH $6.0 < 7.0 < 8.0 < 10.0 < 9.0$. The degradation of profenofos increased with increasing ferrate(VI) dosage and decreased profenofos concentration. The UV254 was first found to exhibit a synergistic effect on the oxidation of profenofos by ferrate(VI). Up to 19.1% enhancement was observed with the introduction of ultraviolet light to the ferrate solution. The removal rate of profenofos increased via two-step addition of ferrate(VI) to the reaction solutions. By ESI-MS and MS/MS analysis, the main degradation product of profenofos in UV/ferrate(VI) solution was identified. The oxidation of profenofos proceeded via de-ethylation and de-propylation, leading to O-4-bromo-2-chlorophenyl O,S-dihydrogen phosphorothioate. The subsequent cleavage of C–O bond gave rise to the release of orthophosphate and possible generation of 4-bromo-2-chlorophenol. The results suggest that UV/ferrate(VI) is a good alternative for the treatment of organophosphorus pesticides in aqueous solution.

Keywords: Profenofos; UV/ferrate(VI); Synergistic effect; Products

1. Introduction

A wide variety of organophosphorus pesticides are introduced into the water system from agricultural run-off, chemical spills, and industrial effluent every year. They contribute up to one-third of world pesticide consumption and have been extensively detected in natural surface waters [1]. Organophosphorus pesticides are popular candidates to replace the more persistent organochlorine compounds, which are suspected to be bioaccumulated by the food chain [2]. As a wide-spectrum insecticide, profenofos is widely used in agriculture to control pests in cotton, fruit trees, and vegetables [3]. There is much evidence on the acute toxicity of profenofos to aquatic organisms [4,5]. Therefore, it is crucial for the elimination of profenofos in wastewaters.

UV, UV/H_2O_2, and Fenton reactions have been employed for the degradation of profenofos [6,7]. As an emerging water treatment chemical, ferrate (Fe(VI)) has received extensive attention recently [8,9]. Fe(VI) is a powerful oxidizing agent in water treatment, which has the oxidation–reduction potential of 2.20 V at acidic pH condition and 0.7 V at basic pH condition [10]. During the oxidation process of organic pollutants and micro-organisms in water, Fe(VI) ions is

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*Corresponding author.

reduced to Fe(III) ions or ferric hydroxide, which generates a coagulant and obtain photocatalysis property in the process simultaneously [11,12]. Due to its dual functions as an oxidant and a subsequent coagulant/precipitant as ferric hydroxide [13,14], Fe(VI) is regarded as an environmentally friendly oxidant in water and wastewater treatment [13–19].

UV systems including UV/O_3, UV/H_2O_2, and UV/Fe(III) have been proven to be effective for the elimination of organophosphorus pesticides [7,20–22]. In these advanced oxidation processes, UV exhibits great synergistic effect on the degradation of pollutants. The effect of UV on the TiO_2/Fe(VI) oxidation of dimethyl phthalate has been reported [23]. Until recently, there are few studies involving the synergistic effect of UV and Fe(VI) [24]. Although we have previously discussed the municipal landfill leachate treatment by UV/Fe(VI) [24], it still lacks systematic investigation on the oxidation ability of ferrate in the presence of ultraviolet light.

This work aims to investigate the oxidation ability of UV/Fe(VI) system. Profenofos was selected as the model pollutant. The effect of solution pH, Fe(VI) dosage, the concentration of profenofos, and the synergistic interaction of UV was examined. Moreover, we studied the effect of addition methods of Fe(VI) on the degradation of profenofos. The degradation products of profenofos were identified by LC-ESI-MS/MS.

2. Materials and methods

2.1. Materials

Profenofos (CAS: 41198-08-7, 99%) was purchased from Sigma and used as received. Stock solution of profenofos was prepared from the solid in deionized water All other chemicals used were of at least analytical reagent grade.

Sodium ferrate solution (Na_2FeO_4) used in the experiments was prepared through electrolysis onsite [25,26]. The anode and cathode were made of gray cast iron and nickel sheet, respectively. Saturated aqueous NaOH solution was used as electrolyte and separated by cationic semi-permeable membrane. Concentrations of Fe(VI) in the prepared solution were determined spectroscopically at a wavelength of 510 nm using an UV–vis spectrophotometer (Hitachi U3100, Japan). A molar absorption coefficient, $\varepsilon_{510\,\mathrm{nm}}=1{,}150\,\mathrm{M^{-1}\,cm^{-1}}$, was used to determine Fe(VI) concentration [27]. Fe (VI) stock solutions were prepared by addition of Na_2FeO_4 solution to 1 mM $Na_2B_4O_7{\cdot}10H_2O$ buffer solution at pH 9.0. In the oxidizing reaction, the pH values were also controlled by $Na_2B_4O_7{\cdot}10H_2O$ buffer solution.

2.2. Photochemical reactor

The experiments were carried out in a Pyrex photoreactor. The effective volume of the reactor was 600 mL (length 410 mm, O.D. 69 mm). Irradiation experiments were performed under a low-pressure UV lamp with light intensity 48.4 μW cm^{-2} (254 nm, 15 W, Yuelu Xinhui Electric Company, Changsha, P.R. China). An immersion well made of high purity quartz was placed inside the glass reactor and fitted with a standard joint at the top. The UV lamp was fixed inside the immersion well. Water was passed through the thin annular zone of the immersion well to prevent overheating of the reaction solutions (Fig. 1). In order to achieve a stabilized radiation emission, the lamp was always switched on for 30 min before being fitted into the reactor. Air was bubbled in the reaction system to homogenize the solutions throughout the experiments.

2.3. Degradation analysis

The removal efficiency of profenofos was quantified by the production of orthophosphate (PO_4-P). Orthophosphate (PO_4-P) and total phosphorus ($PO_{4\mathrm{tot}}$) were measured with a standard method spectrophotometrically at 880 nm, based on the formation of a blue molybdenum complex and after digestion using potassium peroxodisulfate ($K_2S_2O_8$), respectively [28]. The detection limit is 0.01 mg L^{-1} for PO_4-P. Each result was an average of triplicates. The standard errors of measurement were within 5%. The samples were

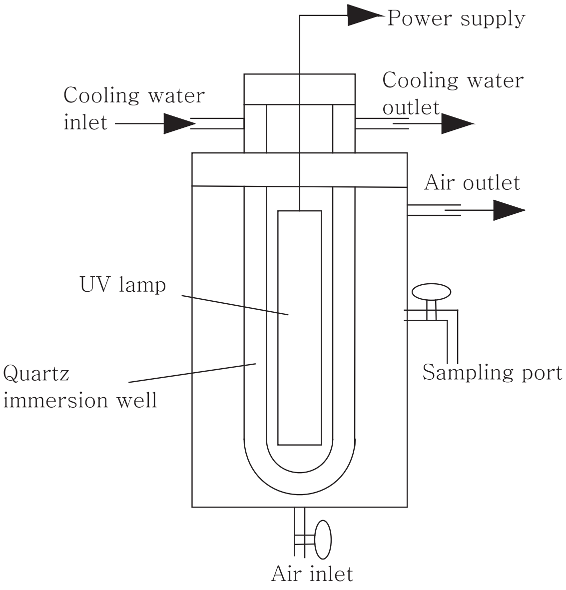

Fig. 1. The diagram of the oxidizing degradation reactor.

analyzed immediately after sampling to prevent further oxidation. The release of orthophosphates in the solution was calculated according to Eq. (1).

$$PO_4 - P(\%) = ([PO_4\text{-}P]_t\text{-}[PO_4\text{-}P]_0)/[PO_4]_{tot} \times 100 \qquad (1)$$

where PO_4-P (%) is the efficiency of orthophosphates release, $[PO_4\text{-}P]_t$ is the orthophosphate content at t irradiation time ($mg\,L^{-1}$), $[PO_4\text{-}P]_0$ is the orthophosphate content without irradiation, and $[PO_4]_{tot}$ is the total phosphorus content at t irradiation time ($mg\,L^{-1}$). The concentration of Fe(VI) was determined by measuring its maximum absorbance at 505 nm with UV–visible spectrophotometer [29].

2.4. Products identification

The degradation products of profenofos were analyzed using an Agilent Technologies 1100 series LC/MSD Trap XCT (Palo Alto, CA, USA) with electrospray ionization in positive ion mode. The MS or MS^2 conditions were set as follows: HV capillary 3,500 V; drying gas (N_2) temperature 325℃; drying gas (N_2) flow of 5 $L\,min^{-1}$; nebulizer pressure at 40 psi; trap drive 33.1; skimmer 40.0 V; octopole RF amplitude 152.8 V; capillary exit 113.5; max. accumulation time 200 ms; and ion charge control 200,000.

3. Results and discussion

3.1. Effect of Fe(VI) dosage, initial pH, and profenofos concentration

Initial Fe(VI) dosage is a significant factor for the degradation of profenofos. A series of photochemical experiments were designed to elucidate the effect of Fe(VI) dosage on profenofos elimination. As shown in Fig. 2(a), the removal rate of organophosphorus was enhanced with the increase of initial Fe(VI) dosage amount at pH 9.0. When 500 μM Fe(VI) was added into the solution, the 99.3% removal efficiency was achieved. However, overuse of Fe(VI) can give rise to increase of process cost and a great amount of iron sludge. Accordingly, the 250 μM ferrate dosage was used in the following experiments for considering cost and the 62.4% removal efficiency of profenofos.

It has been reported that Fe(VI) can be rapidly reduced to Fe(V) in the UV/TiO_2 solution, while the reduction process is not pronounced under only UV irradiation [30]. It is well known that the reduction or decomposition of Fe(VI) led to the formation $Fe(OH)_3$ (Eqs. (2) and (3)) [31,32].

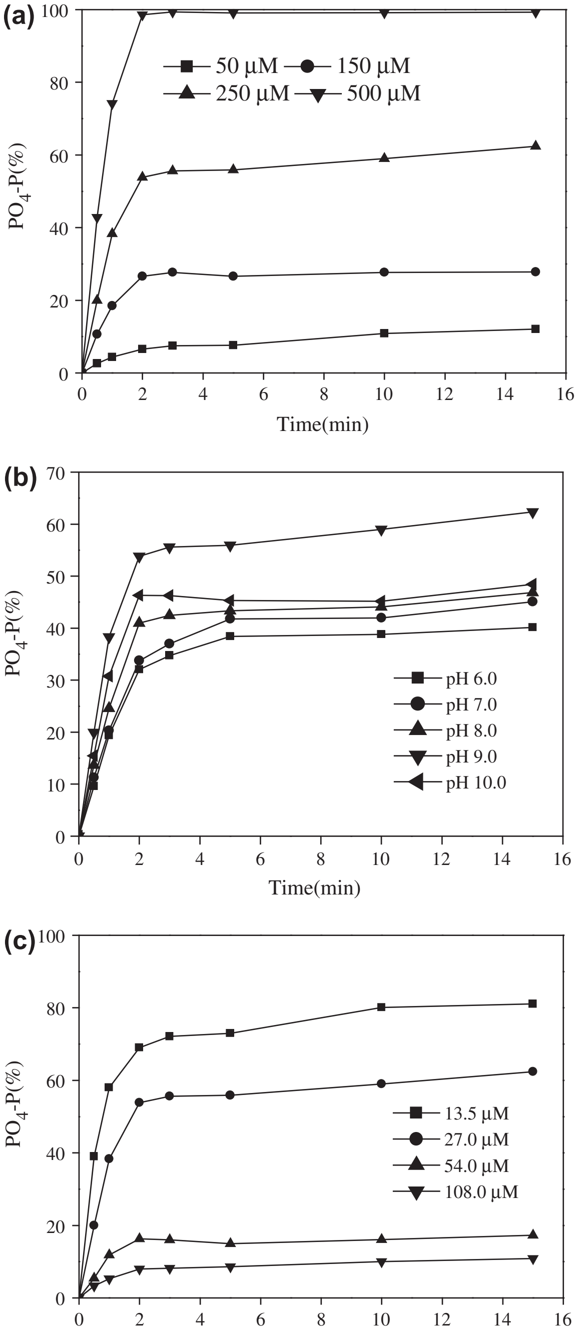

Fig. 2. (a) Degradation of profenofos (27 μM) under UV irradiation at pH 9.0 with different Fe(VI) dosage; (b) degradation of profenofos (27 μM) by UV/Fe(VI) (250 μM) at different pHs; (c) degradation of profenofos by UV/Fe(VI) (250 μM) at different initial concentrations with pH 9.0.

$$4HFeO_4^- + 6H_2O \rightarrow 4Fe(OH)_3 + 3O_2 + 4OH^- \qquad (2)$$

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 3/2O_2 + 4OH^- \qquad (3)$$

The resultant inorganic phosphorus in solution may be further removed by flocculation and sedimentation of $Fe(OH)_3$. Thus, profenofos and orthophosphate can be removed simultaneously in the UV/Fe(VI) system.

Fig. 2(b) illustrates the effect of pH on the degradation of profenofos by UV/Fe(VI) within the pH range from 6.0 to 10.0. The removal efficiency of profenofos increased in the order of pH $7.0 < 6.0 < 10.0 < 8.0 < 9.0$ after amounts of repetitive experiments due to the approach effect of different pH values. The pH dependence is usually related to the speciation of both Fe(VI) and substrates. There is no dissociation for profenofos, so the pH-dependent oxidation was predominantly associated with the speciation of Fe(VI). The dissociation of protonated Fe(VI) can be expressed in Eqs. (4)–(6) [33].

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \quad pK_{a1} = 1.6 \tag{4}$$

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \quad pK_{a2} = 3.5 \tag{5}$$

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pK_{a3} = 7.3 \tag{6}$$

The fraction of the different Fe(VI) species as a function of pH is calculated according to the dissociation constants [31]. It indicates that the main species of Fe (VI) between pH 3.0 and 11.0 are H_2FeO_4 and $HFeO_4^-$. The fraction of $HFeO_4^-$ species increases in the range of pH 2.0–6.0 and $HFeO_4^-$ becomes the main species in acidic media. This is consistent with the faster rate for the spontaneous decomposition of Fe(VI) in acidic solution. In the pH range from 6.0 to 10.0, two main forms of Fe(VI), $HFeO_4^-$ and FeO_4^{2-}, are responsible for the oxidation of profenofos. Compared to $HFeO_4^-$, FeO_4^{2-} is less stable but has higher redox potential [34–36]. The fraction of FeO_4^{2-} species enhances with the increase of pH from 6.0 to 10.0, which is in good agreement with the removal efficiency of profenofos. According to [34], the lowest rate of decomposition rate of Fe(VI) occurs at pH 9.4–9.7 and the rates increase below and above this pH range. The experimental results suggest that the Fe(VI) is more stable in alkaline condition than in acidic solution, but has a lower oxidative ability. In this study, the contrary effect of the oxidation ability and stability within the pH range from 6.0 to 10.0 led to the optimal pH 9.0 for the UV/Fe(VI) oxidation of profenofos.

Fig. 2(c) shows the efficiency of orthophosphate release at different initial profenofos concentrations. The orthophosphates' release efficiency increased with decreasing initial concentrations at the range of 13.5–108 μM. When the initial concentration of profenofos was 13.5 μM, the ferrate dosage was 250 μM and the initial pH was 9.0; 81.1% of profenofos could be transformed into orthophosphate (PO_4-P) after a 15 min irradiation. As for the lower initial concentrations, it could be suggested that higher degradation will be obtained.

According to the above discussion, Fe(VI) is an environment-friendly chemical in the treatment process which has the strong oxidizing ability. Profenofos can be eliminated to yield orthophosphate by Fe(VI), and the inorganic phosphorus in the solution can be further removed by $Fe(OH)_3$. At the lower initial concentrations, the amount of Fe(VI) in the solution is high enough for the oxidation of profenofos, and the existence of $Fe(OH)_3$ has an excellent effect by flocculation and sedimentation process. The orthophosphates release efficiency decreased at the higher initial concentrations. This may be partly attributed to the accumulation of intermediates produced in the reactions, which competed with profenofos for Fe(VI). The concentration effects were similar to other types of oxidation processes [27,37].

3.2. Effect of UV irradiation

Fig. 3 shows the orthophosphate release with or without UV254 irradiation at pH 9.0. Accordingly, profenofos removal by UV/Fe(VI) was mainly attributed to the oxidation of Fe(VI). The degradation of profenofos was negligible under UV irradiation only, which could due to the low light absorption of profenofos at 254 nm. 43.3% of profenofos was removed by Fe(VI) oxidation without UV irradiation. In contrast, up to 62.4% of profenofos removal efficiency was

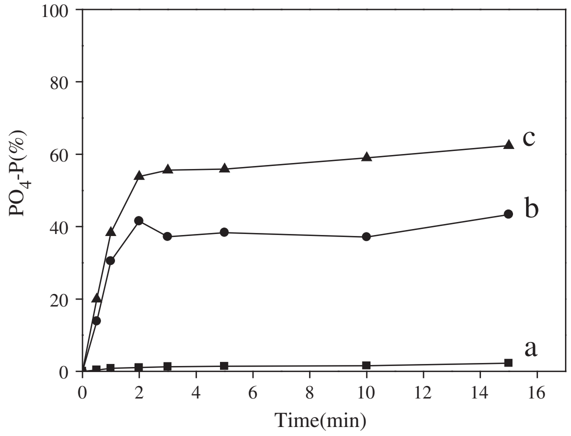

Fig. 3. Degradation of profenofos (27 μM) at pH 9.0 under different experimental conditions: (a) UV; (b) Fe(VI); (c) UV/Fe(VI). The concentration of Fe(VI) was 250 μM.

achieved in the UV/Fe(VI) system. The UV irradiation increased the oxidizing degradation of profenofos by 19.1%. Therefore, the UV254 has an important synergistic effect for the oxidation of profenofos by Fe(VI).

The noticeable enhancement effect was likely attributed to the easier Fe(VI) reduction under UV irradiation [38]. The Fe(VI) ions in the photoexcited state are closely related to the generation of Fe(V), which can be expressed in Eq. (7).

$$HFeO_4^- + e^- \leftrightarrow HFeO_4^{2-} \quad (7)$$

Fe(V) is 10^3–10^5 times reactive with pollutants than Fe(VI), resulting in the stronger oxidation ability of Fe(VI) solution with UV light irradiation. In addition, it is possible that the immediate products of profenofos absorb UV light and thus accelerate the degradation. The underlying synergistic effect needs further investigation. This experimental results indicated that ultraviolet light contributed to the oxidation of refractory organic contaminants by Fe(VI).

3.3. Effect of Fe(VI) addition methods

At constant concentration of profenofos, the dosage of Fe(VI) is the main influencing factor for the degradation of profenofos at pH 9.0. In order to further enhance the removal rate of profenofos, Fe(VI) was added into the solution by steps. The overuse of iron can give rise to increase of process cost and colourity of water [39]. Fe(VI) addition by steps may oxidize more organophosphorus pesticides to reduce the dosage of iron. Therefore, it is necessary to investigate the effect of Fe(VI) addition by steps on the oxidizing degradation.

In this study, two approaches were preliminarily chosen to investigate the removal rate of profenofos. (i) 250 μM Fe(VI) was added into the solution totally; (ii) 125 μM Fe(VI) was added into the solution at 0 and 5 min. As shown in Fig. 4, the removal efficiency of profenofos were 62.4 and 70.5% for one- and two-step addition of Fe(VI), respectively. It was obvious that there is a better effect on the oxidation of profenofos with two-step addition. As can be seen from Fig. 2((a)–(c)), the oxidation of profenofos by UV/Fe (VI) occurred rapidly and it was completed nearly within 3 min. Two-step addition provided more reaction time, facilitating the oxidation of substrate. For multi-step addition, the oxidation effect is expected to be further improved. Therefore, it is feasible for the UV/Fe(VI) oxidation treatment via multi- not one-step addition of dosage to obtain a better removal efficiency.

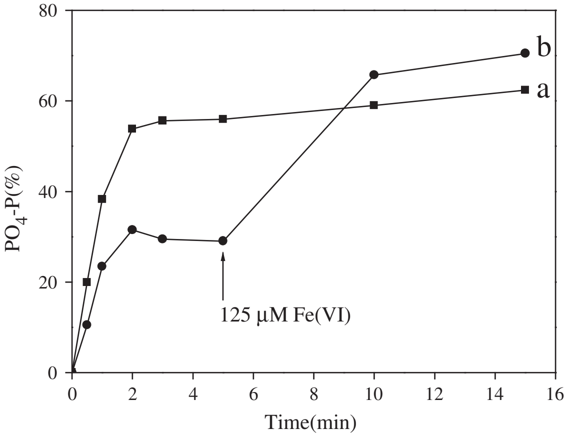

Fig. 4. Effect of Fe(VI) addition methods on degradation of profenofos (27 μM) by UV/Fe(VI) at pH 9.0: (a) one-step addition; (b) two-step addition. The total concentration of Fe(VI) was 250 μM.

3.4. Oxidation product and pathway

In order to gain a further insight into the degradation mechanism of profenofos in the UV/Fe(VI) system, the degradation products of profenofos were identified by LC-ESI-MS/MS. The MS and MS/MS data were used for the interpretation of main degradation products of profenofos. As shown in Fig. 5(a), one main product (*m/z* 304.9) was identified at 3.1 min in the total ion chromatogram. According to the ESI-MS and ESI-MS/MS spectra (Fig. 5(b) and (c)), the *m/z* 304.9 (O-4-bromo-2-chlorophenyl O,S-dihydrogen phosphorothioate) was the de-ethylation and de-propylation product of profenofos. The further oxidation of P–S to P–O was likely to proceed due to the formation of orthophosphate. In view of the production of orthophosphate in the whole experiment, the cleavage of P–O bond may occur to yield 4-bromo-2-chlorophenol during the oxidation of profenofos by UV/Fe(VI).

It has been documented that the de-ethylation product of profenofos upon polychromatic irradiation ($\lambda > 285$ nm) was identified in aqueous solution [6]. This indicates that the C–O bond at the oxypropyl group is subject to cleavage under irradiation. Due to the powerful oxidation ability of Fe(VI), de-propylation process also occurred in this experiments simultaneously, leading to O-4-bromo-2-chlorophenyl O,S-dihydrogen phosphorothioate. The proposed degradation pathway of profenofos in UV/Fe(VI) solutions is illustrated in Fig. 6.

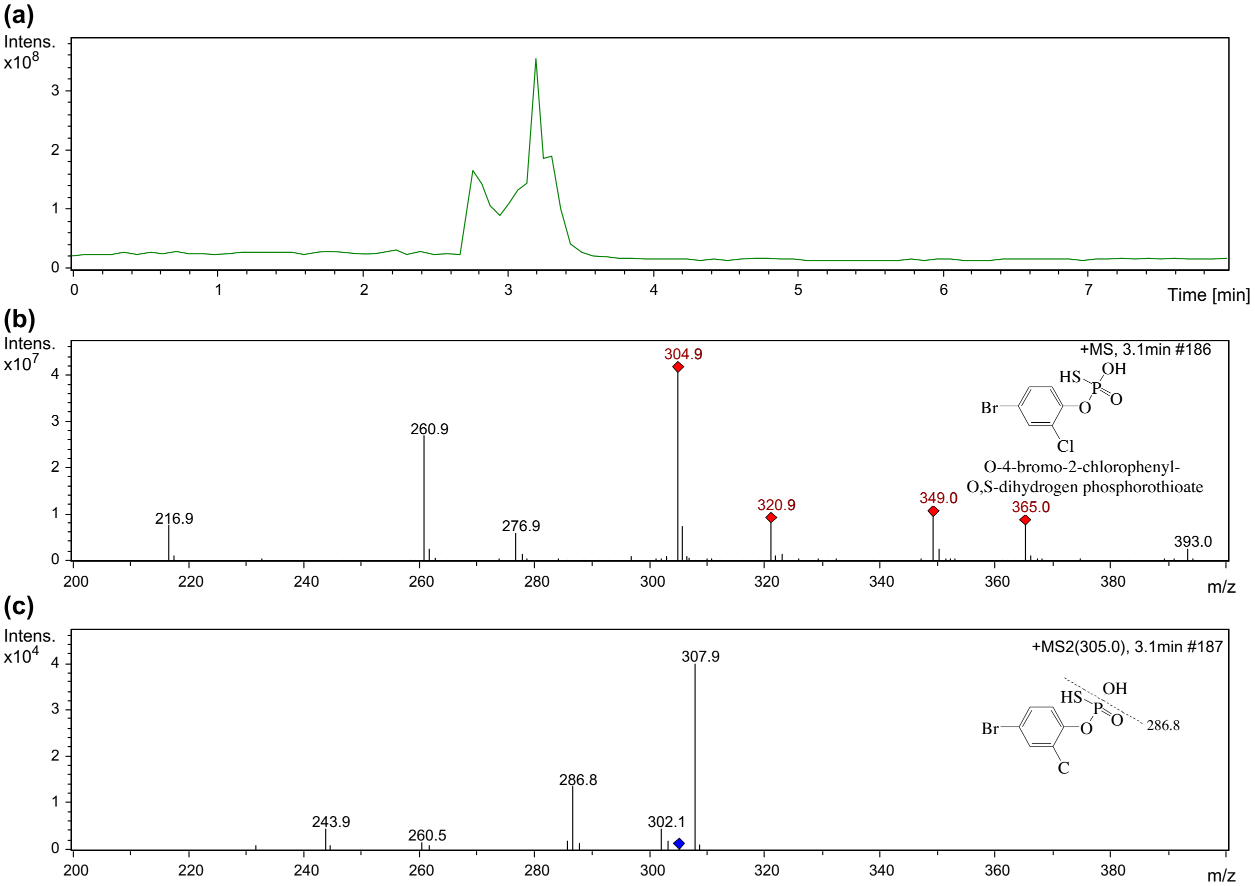

Fig. 5. The total ion chromatogram (a), full-scan (+)-ESI-MS (b), and (+)-ESI-MS/MS spectra (c) of main oxidation products of profenofos in UV/Fe(VI) solutions.

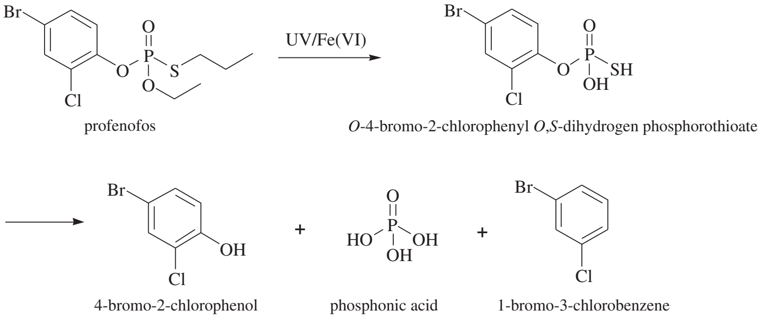

Fig. 6. The proposed degradation pathway of profenofos in UV/Fe(VI) solutions.

4. Conclusions

UV/Fe(VI) process is demonstrated to be an excellent alternative for the oxidation treatment of organophosphorus pesticides. The degradation efficiency of profenofos was strongly dependent on the Fe (VI) dosage and pH values. The photodegradation efficiency of profenofos followed the order of pH 6.0 < 7.0 < 8.0 < 10.0 < 9.0. At pH 9.0 and 250 μM Fe(VI) dosage, up to 81.1% of profenofos was transformed into orthophosphate (PO_4-P) after a 15 min irradiation. The UV254 was first found to exhibit a synergistic effect for the oxidation of profenofos by Fe(VI). The UV irradiation increased the oxidizing degradation of profenofos by 19.1%. The removal efficiency of profenofos was further enhanced by two-step addition of Fe(VI) to reaction solution. The attack of profenofos by Fe(VI) to led to the formation of O-4-bromo-2-chlorophenyl O,S-dihydrogen phosphorothioate, orthophosphate, and possible generation of 4-bromo-2-chlorophenol.

Acknowledgments

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References

[1] M. Tankiewicz, J. Fenik, M. Biziuk, Determination of organophosphorus and organonitrogen pesticides in water samples, TrAC, Trends Anal. Chem. 29 (2010) 1050–1063.
[2] S.B. Lartiges, P.P. Garrigues, Degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions, Environ. Sci. Technol. 29 (1995) 1246–1254.
[3] J. He, M. Fan, X. Liu, Environmental behavior of profenofos under paddy field conditions, Bull. Environ. Contam. Toxicol. 84 (2010) 771–774.
[4] A. Kumar, J.C. Chapman, Profenofos toxicity to the eastern rainbow fish, Environ. Toxicol. Chem. 17 (1998) 1799–1806.
[5] M. Ismail, R. Ali, T. Ali, U. Waheed, Q.M. Khan, Evaluation of the acute toxicity of profenofos and its effects on the behavioral pattern of fingerling common carp (*Cyprinus carpio* L., 1758), Bull. Environ. Contam. Toxicol. 82 (2009) 569–573.
[6] C. Zamy, P. Mazellier, B. Legube, Phototransformation of selected organophosphorus pesticides in dilute aqueous solutions, Water Res. 38 (2004) 2305–2314.
[7] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175.
[8] V.K. Sharma, G.W. Luther, F.J. Millero, Mechanisms of oxidation of organosulfur compounds by ferrate(VI), Chemosphere 82 (2011) 1083–1089.
[9] V.K. Sharma, Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism, Coord. Chem. Rev. 257 (2013) 495–510.
[10] Y. Lee, M. Cho, J.Y. Kim, J. Yoon, Chemistry of ferrate (Fe(VI)) in aqueous solution and its applications as a green chemical, J. Ind. Eng. Chem. 10 (2004) 161–171.
[11] V.K. Sharma, N.J.D. Graham, X.Z. Li, B.L. Yuan, F.J. Millero, Ferrate(VI) enhanced photocatalytic oxidation of pollutants in aqueous TiO_2 suspensions, Environ. Sci. Pollut. Res. 17 (2010) 453–461.
[12] J. Filip, R.A. Yngard, K. Siskova, Z. Marusak, V. Ettler, P. Sajdl, V.K. Sharma, R. Zboril, Mechanisms and efficiency of the simultaneous removal of metals and cyanides by using ferrate(VI): Crucial roles of nanocrystalline iron(III) oxyhydroxides and metal carbonates, Chem. Eur. J. 17 (2011) 10097–10105.
[13] J. Ma, W. Liu, Effectiveness of ferrate(VI) preoxidation in enhancing the coagulation of surface waters, Water Res. 36 (2002) 4959–4962.
[14] J. Ma, W. Liu, Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation, Water Res. 36 (2002) 871–878.
[15] V.K. Sharma, Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review, J. Environ. Sci. Health A 45 (2010) 645–667.
[16] J.Q. Jiang, S. Wang, A. Panagoulopoulos, The role of potassium ferrate(VI) in the inactivation of *Escherichia coli* and in the reduction of COD for water remediation, Desalination 210 (2007) 266–273.
[17] I. Ciabatti, F. Tognotti, L. Lombardi, Treatment and reuse of dyeing effluents by potassium ferrate, Desalination 250 (2010) 222–228.
[18] V.K. Sharma, M. Sohn, G.A.K. Anquandah, N. Nesnas, Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI), Chemosphere 87 (2012) 644–648.
[19] B. Yang, G.G. Ying, Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles, Water Res. 45 (2011) 2261–2269.
[20] J.L. Acero, F.J. Real, F. Javier Benitez, A. González, Oxidation of chlorfenvinphos in ultrapure and natural waters by ozonation and photochemical processes, Water Res. 42 (2008) 3198–3206.
[21] A. Manassero, C. Passalia, A.C. Negro, A.E. Cassano, C.S. Zalazar, Glyphosate degradation in water employing the H_2O_2/UVC process, Water Res. 44 (2010) 3875–3882.
[22] Y. Chen, F. Wu, Y. Lin, N.S. Deng, N. Bazhin, E. Glebov, Photodegradation of glyphosate in the ferrioxalate system, J. Hazard. Mater. 148 (2007) 360–365.
[23] B.L. Yuan, X.Z. Li, N. Graham, Reaction pathways of dimethyl phthalate degradation in TiO_2–UV–O_2 and TiO_2–UV–Fe(VI) systems, Chemosphere 72 (2008) 197–204.
[24] Z.P. Wang, L.Z. Huang, X.N. Feng, P.C. Xie, Z.Z. Liu, Removal of phosphorus in municipal landfill leachate by photochemical oxidation combined with ferrate pre-treatment, Desalin. Water Treat. 22 (2010) 111–116.
[25] X.W. Yu, S. Licht, Advances in electrochemical Fe(VI) synthesis and analysis, J. Appl. Electrochem. 38 (2008) 731–742.
[26] M. Alsheyab, J.Q. Jiang, C. Stanford, Electrochemical generation of ferrate (VI): Determination of optimum conditions, Desalination 254 (2010) 175–178.
[27] Z. Luo, M. Strouse, J.Q. Jiang, V.K. Sharma, Methodologies for the analytical determination of ferrate(VI): A review, J. Environ. Sci. Health A 46 (2011) 453–460.
[28] C. Lesueur, M. Pfeffer, M. Fuerhacker, Photodegradation of phosphonates in water, Chemosphere 59 (2005) 685–691.
[29] H.D. Jia, X.L. Yang, Y. Yang, Y.F. Gao, Direct spectrophotometric determination of ferrate(VI), Chin. J. Anal. Chem. 27 (1999) 617.

[30] V.K. Sharma, C.R. Burnett, W. Rivera, V.N. Joshi, Heterogeneous photocatalytic reduction of ferrate(VI) in UV-irradiated titania suspensions, Langmuir 17 (2001) 4598–4601.

[31] V.K. Sharma, C.R. Burnett, F.J. Millero, Dissociation constants of the monoprotic ferrate(VI) ion in NaCl media, Phys. Chem. Chem. Phys. 3 (2001) 2059–2062.

[32] V.K. Sharma, Oxidation of inorganic contaminants by ferrates (VI, V, and IV)–kinetics and mechanisms: A review, J. Environ. Manage. 92 (2011) 1051–1073.

[33] N. Noorhasan, B. Patel, V.K. Sharma, Ferrate(VI) oxidation of glycine and glycylglycine: Kinetics and products, Water Res. 44 (2010) 927–935.

[34] J.D. Carr, Kinetics and product identification of oxidation by ferrate(VI) of water and aqueous nitrogen containing solutes, ACS Symp. Ser. 985 (2008) 189–196.

[35] H.L. Wang, S.Q. Liu, X.Y. Zhang, Preparation and application of sustained release microcapsules of potassium ferrate(VI) for dinitro butyl phenol (DNBP) wastewater treatment, J. Hazard. Mater. 169 (2009) 448–453.

[36] G.A.K. Anquandah, V.K. Sharma, D.A. Knight, S.R. Batchu, P.R. Gardinali, Oxidation of trimethoprim by ferrate(VI): Kinetics, products, and antibacterial activity, Environ. Sci. Technol. 45 (2011) 10575–10581.

[37] X. Feng, Z. Wang, Y. Chen, T. Tao, F. Wu, Multivariate-parameter optimization for photodegradation of tetracycline by Fe(III)–citrate complexes at near neutral pH, J. Environ. Eng. 138 (2012) 873–879.

[38] K. Winkelmann, V.K. Sharma, Y. Lin, Reduction of ferrate(VI) and oxidation of cyanate in a Fe(VI)–TiO_2–UV–NCO^- system, Chemosphere 72 (2008) 1694–1699.

[39] Y. Chen, Z. Liu, Z. Wang, M. Xue, X. Zhu, T. Tao, Photodegradation of propranolol by Fe(III)–citrate complexes: Kinetics, mechanism and effect of environmental media, J. Hazard. Mater. 194 (2011) 202–208.