Enhance degradation of insecticide chlorpyrifos by iron salts and potassium persulfate during zerovalent iron treatment in aqueous solution

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Abstract Degradation of the insecticide O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (chlorpyrifos) in aqueous solution was investigated using iron salts and potassium persulfate during ZVI treatment through a series of batch experiments. The degradation rate of chlorpyrifos increased with increases in the concentrations of iron salts and potassium persulfate in the aqueous system. Ferric chloride was found to be the most effective iron salt for the ZVI-mediated degradation of chlorpyrifos in aqueous solution. Further, the iron salts tested could be arranged in the following order in terms of their effectiveness: $FeCl_3 > Fe_2(SO_4)_3 > Fe(NO_3)_3$. The persulfate-ZVI system could significantly degrade chlorpyrifos present in the aqueous medium. This revealed that chlorpyrifos degradation by treatment with Fe^0 was promoted on adding ferric chloride and potassium persulfate. The kinetics of the degradation of chlorpyrifos by persulfate-amended Fe^0 was higher than that for iron-salt-amended Fe^0. This suggests that using a sequential Fe^0 reduction-ferric chloride or Fe^0 reduction-persulfate process may be an effective strategy to enhance the removal of chlorpyrifos in contaminated water.

Keywords Aqueous solution · Chlorpyrifos · Degradation · Iron salts · Potassium persulfate · Zerovalent iron

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Introduction

O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (chlorpyrifos) is a broad-spectrum organophosphorus insecticide used widely for controlling various foliage- and soil-borne pests on a variety of crops. Many researchers [1-4] found chlorpyrifos as a common surface-water contaminant even five years after use, based on surface-water monitoring data for agricultural regions. Because of its widespread use in agriculture, this compound could be considered as an important environmental organic contaminant in the water ecosystem.

Zerovalent iron (Fe^0, ZVI) has drawn great interest as an inexpensive, effective, and eco-friendly material because of its easy accessibility and its ability to degrade various organic pollutants in contaminated water effectively while generating very little waste. ZVI is also an attractive material because its smaller particle size means that it has an increased surface area per unit mass as well as a higher reactivity than the larger iron particles [5]. The high reductive capacity of ZVI has been known for a long time. However, the recent development of efficient methods for the preparation of nanoscale ZVI (nZVI) particles has resulted in the widespread use of this powerful reductant. nZVI performs well in the decontamination of various organic pollutants [6-8].

When a reducible organic contaminant reacts with ZVI, either the formation of new reactive sites or the continuous generation of electrons is necessary to keep the degradation rate constant. This may be achieved by adding corrosion promoters to the contaminated water sample [9,10]. Previous studies have shown that major anions can affect the reactivity of Fe^0 with respect to groundwater contaminants [11]. The presence of electrolytes in high concentrations can slow the passivation process by allowing the reaction products to diffuse away from the Fe^0 surface and precipitate in the bulk solution [7]. The passivation of the metal surface occurs when the reactive sites become saturated with a metal oxide or other species, which lowers the exchange current density and significantly reduces the reaction rate. Under these conditions, the transfer of electrons from ZVI becomes the

limiting step in the reaction. To overcome the limitations related to passivation and nonreactivity in aqueous media, abiotic catalysts are used for the effective degradation of organic contaminants. In order to increase the degradation kinetics and overcome the passivation-related issues, halide ions have used to promote the degradation of HMX and increase the sustainability of ZVI in the corresponding reaction [10]. During zerovalent iron treatment, the herbicide metolachlor destruction kinetics were greatly enhanced when Fe(II) or Fe(III) salts were added [12]. Considering this fact, various iron salts were selected for this study. Devlin and Allin [11] observed that the reactivity of granular iron during the reduction of 4-chloronitrobenzene was increased by adding a sulfate and a chloride; this was either due to an increase in the surface activity of ZVI or in its sorption capacity. Nitrate have been reported to inhibit the reduction of hydrophobic organic contaminants (HOCs) by ZVI while being reduced to a nitrite and ammonia [7,13]. The anion effect depends on the experimental conditions, including the composition of the precipitations [14] and the anion concentrations [15]. In recent years, persulfates ($S_2O_8^{2}$) have drawn increasing attention as potential alternatives for the chemical oxidation of organic pollutants [16-18]. Zhang et al. [19] observed that the oxidation of aniline by a persulfate occurred due to the rapid formation of sulfate free radicals from the persulfate-Fe^{2+} reaction. In the persulfate-ZVI system, the decomposition of the persulfate results in the rapid generation of sulfate radicals because of the release of Fe^{2+} ions from ZVI. Thus, persulfates can be used for the effective degradation of p-chloroaniline [18]. Persulfates have numerous advantages as oxidizing agents because they are nonselectively reactive, relatively stable at room temperature, exhibit reactivity with respect to a large number of environmental contaminants, and are highly stable in aqueous systems [16]. Given these facts, the aim of this study was to elucidate the efficacy of various iron salts and potassium persulfate with respect to the degradation of chlorpyrifos during treatment with ZVI in an aqueous solution.

Materials and Methods

Chemicals
Chlorpyrifos (>99.7% purity) was purchased from Dow Agrosciences (Indianapolis, IN, USA). The ZVI (Fe^0) used in the study was Peerless iron (Peerless Metal Powders, Detroit, MI), a commercial ZVI product. The annealed iron sample, which was heat-treated in a hydrogen-nitrogen atmosphere, exhibited a smooth surface, while the unannealed sample showed a rough, pitted surface under during scanning electron microscopy analysis. The surface coating of the annealed iron particles was a thin layer of magnetite (Fe_3O_4), whereas that on the unannealed iron particles was mostly maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) [12]. The iron salts used, which were $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$, and $Fe_2(SO_4)_3 \cdot xH_2O$, were purchased from Sigma-Aldrich Chemical Co. (St.

Louis, MO, USA), while potassium persulfate ($K_2S_2O_8$) was obtained from Yakuri Pure Chemicals Co. Ltd. (Osaka, Japan). Acetone, ethyl acetate, and deionized water were acquired from Burdick & Jackson Inc. (Muskegon, MI, USA). All the chemicals were used as received.

Batch experiments
Batch experiments were performed in a shaking incubator at 25 $^{\circ}$C and 200 rpm. A stock solution of chlorpyrifos was prepared in acetone (10%) and diluted accordingly to obtain a standard solution of the desired concentration. Then, the standard solution was added to deionized water containing acetone to prepare a solution with an initial concentration of 5 mg/L prior to each batch experiment. For the ZVI treatments, the pesticide solution was transferred into 250 mL Erlenmeyer flasks and the desired amounts of ZVI powder were added. In order to investigate the effects of the iron salts on the degradation of chlorpyrifos, the salts were mixed thoroughly with the chlorpyrifos solution containing ZVI to achieve salt concentrations of 0.1, 0.5, and 1.0% (w/v). In the case of the persulfate-ZVI treatment, the reaction mixture was obtained by taking an appropriate amount of the chlorpyrifos (5 mg/L) solution. Next, a predetermined amount of ZVI powder was added to it. This was followed by the addition of potassium persulfate (0.05, 0.1, and 0.2% (w/v)). The reactions were carried out in 250 mL Erlenmeyer flasks, which functioned as complete mixed-batch reactor systems. Aliquots of the samples were removed at intervals of 0, 1, 3, 6, 12, and 24 h during each batch experiment. Exactly 4 mL was withdrawn at the predetermined time, and 2 mL of the supernatant was used for chlorpyrifos extraction by ethyl acetate. Next, 2 mL of ethyl acetate was evaporated to dryness in a rotatory evaporator. The residue in the flask was resolved in acetone and used to confirm the presence of chlorpyrifos using a gas chromatography system with an electron capture detector. Each treatment was replicated three times. For each experiment, controls that did not contain Fe^0, the ferric salts, or potassium persulfate were run in parallel under identical conditions.

Analytical methods
The concentration of chlorpyrifos in the aqueous phase was measured with a GC system (GC-2010, Shimadzu, Kyoto, Japan) equipped with DB-5 capillary column (30 m×0.25 mm i.d) and an ECD detector. The column temperature was kept at 150 $^{\circ}$C (2 min) and then ramped to 280 $^{\circ}$C (10 min) at the rate of 10 $^{\circ}$C/min. The temperatures of the injection port and detector were set at 260 and 280 $^{\circ}$C, respectively. The flow rate of the carrier gas (N_2) was fixed at 1 mL/min; the split-less mode was used. The injection volume was 1 μL. Under these conditions, the recoveries of chlorpyrifos in the aqueous solution by the analytical method were 93-98% and the coefficients of variation were acceptable at <10%.

Degradation kinetics parameters
The kinetics of the degradation of chlorpyrifos in the aqueous

phase can be described using a pseudo-first-order model, as shown in Eq. (1).

$$C_t = C_0\, e^{kt} \tag{1}$$

where k is the first-order rate constant (h^{-1}), C_0 is the initial concentration of chlorpyrifos (mg/L), and C_t is the concentration of chlorpyrifos at time t (mg/L).

Results and Discussion

Degradation of chlorpyrifos by ZVI

During the chlorpyrifos degradation experiments, ZVI was added to the aqueous system as one of the components in an amount of 1.0% (w/v), in order to compare the degradation efficiencies of annealed ZVI (aZVI) and unannealed ZVI (uZVI). The decrease in the chlorpyrifos concentration after 24 was only 15.8% from the initial concentration in the case of aZVI. On the other rate, the degradation rate of chlorpyrifos using uZVI was much higher (Fig. 1). When used alone, unannealed Fe^0 resulted in the effective degradation of chlorpyrifos, while annealed Fe^0 did not. This difference might be attributed to the lower specific surface area of annealed Fe^0 (0.134 versus 2.55 m^2/g for unannealed Fe^0) and its resistance to corrosion in aqueous solutions [20]. A similar trend was reported by Min et al. [21], who stated that unannealed ZVI is more effective for degrading tolclofos-methyl in aqueous solutions than are other zero-valent metals. In order to achieve a better understanding of the ZVI-mediated degradation of chlorpyrifos, in this study, uZVI was considered an abiotic catalyst on the basis of its degradation efficiency.

The degradation rate of chlorpyrifos in the aqueous solution was investigated by adding 0.1, 0.5, and 1.0% (w/v) uZVI. The degradation rates of chlorpyrifos after 24 h were found to 10.8, 23.2, and 43.6%, respectively (Fig. 2). For an initial chlorpyrifos
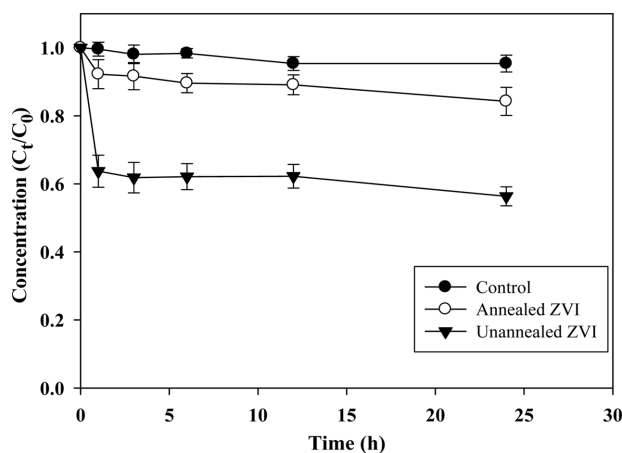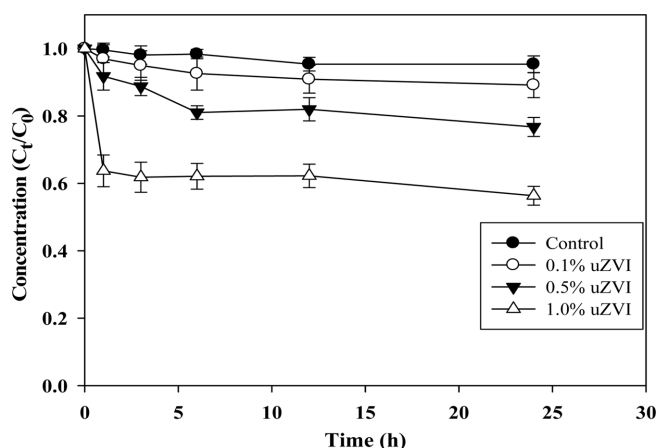
Fig. 2 Degradation of chlorpyrifos as affected by the concentration of unannealed ZVI in aqueous solution. Error bars indicate standard deviation of mean (n =3)

concentration of 5 mg/L, 43.6% of the pesticide was degraded within 24 h when 1.0% (w/v) uZVI was added. The highest degradation rate of chlorpyrifos was achieved for a reaction time of 24 h, irrespective of the amount of uZVI used (Fig. 2). This degradation of chlorpyrifos in the ZVI system was owing to the reduction or adsorption of chlorpyrifos on the ZVI surface. These results were in agreement with the findings of Kim et al. [22], and Min et al. [21], who studied the degradation of chlorpyrifos, and tolclofos-methyl using ZVI in different concentrations.

Degradation of chlorpyrifos by iron salts

The effects of various iron salts on the degradation of chlorpyrifos in aqueous solutions were assessed; the iron salts tested were $FeCl_3$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$. The iron salts were added after initiating the treatment to determine whether the reactivity of Fe could be restored after passivation. The salt concentrations were adjusted to be 0.1, 0.5, and 1.0% (w/v) in the chlorpyrifos solution treated with 1.0% (w/v) uZVI. In the aqueous system, 59.8, 66.8, and 71.2% of the chlorpyrifos was eliminated within 24 h after treatment with 0.1, 0.5, and 1.0% (w/v) $FeCl_3$, respectively (Fig. 3). The highest chlorpyrifos degradation rate (71.2%) was obtained for a reaction time of 24 h, irrespective of the amount of $FeCl_3$ added (Table 1). When ZVI was used alone, only 43.7% of the chlorpyrifos was degraded within 24 h. Further, during the ferric-chloride-amended Fe^0 treatment, the reaction-rate constant (k) for the degradation of chlorpyrifos was from 0.020 to 0.030 h^{-1}, whereas it was 0.012 h^{-1} during the treatment with ZVI alone (Table 1). When the aqueous solution of chlorpyrifos was treated with unannealed Fe^0, the degradation kinetics was enhanced in the presence of Cl^- ions resulting from the addition of $FeCl_3$. This result indicated that the presence of Cl^- ions along with Fe^0 resulted in a highly reactive Fe surface being maintained, resulting in the rate of chlorpyrifos removal remaining high, in contrast to the case when ZVI alone was used. This might be attributed to the

Fig. 1 Degradation of chlorpyrifos by treatment with annealed and unannealed ZVI (1.0% w/v) in aqueous solution. Error bars indicate standard deviation of mean (n =3)
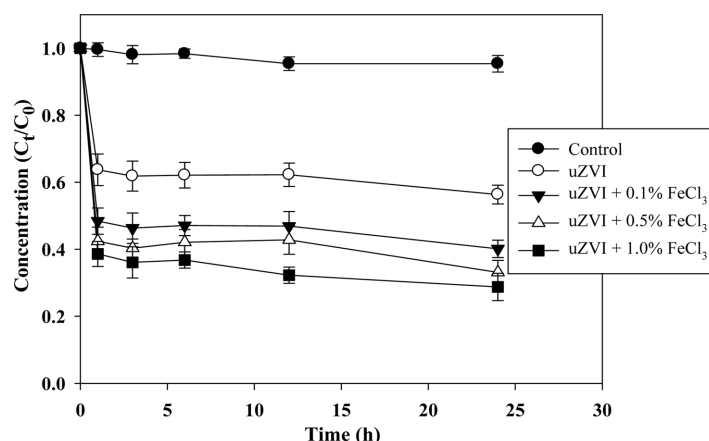
Fig. 3 Effect of ferric chloride on chlorpyrifos degradation by unannealed ZVI (1.0%) in aqueous solution. Error bars indicate standard deviation of mean (n =3)

fact that the addition of $FeCl_3$ resulted in the removal of the passivating oxide layer on Fe^0, as well as in the formation of additional corrosion pits. The sorption of Fe(II) on the ZVI surface might also be attributable to the pitting- and corrosion-inducing nature of Cl^- ions. In fact, Cl^- ions are known to be pitting and crevice corrosion promoters [9], and their presence in the aqueous solution could have accelerated electron generation from the metallic species and created new reactive sites on the surface of Fe^0 [23]. In the presence of the chloride ions, the iron reacted with the Cl^- ions instead of reacting only with OH^- ions, resulting in an increase in the solubility of the Fe ions [24]. The formation of hydrochloric acid during the reaction with the oxidized Fe^0 or the reaction of the acid with Fe^{2+} produced $FeCl_2$ and H^+ (Eqs. (3)-(5)). The further hydrolysis of $FeCl_2$ resulted in $Fe(OH)_2$ and HCl (Eq. (6)). The net production of HCl and H^+ ions resulted in a decrease in the solution pH, further facilitating anodic dissolution. This caused the formation of counter-balancing OH ions.

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH \qquad (2)$$
$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl \qquad (3)$$
$$Fe^0 + 2HCl \rightarrow FeCl_2 + 2H^+ \qquad (4)$$
$$Fe^{2+} + 2HCl \rightarrow FeCl_2 + 2H^+ \qquad (5)$$
$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \qquad (6)$$

A similar phenomenon was observed by Su et al. [23], who reported that the degradation kinetics of hexachlorobenzene by nZVI were enhanced in the presence of Cl^- ions, given the corrosion-promoting nature of the ions. Further, chloride ions can efficiently remove the passive film formed on granular iron and accelerate the rate of degradation of nitrobenzene [25]. Devlin and Allin [11] reported that the presence of chloride ions increased the surface reactivity, which, in turn, increased the extent of 4-chlorobenzene removal. Kim et al. [10] reported that the addition of chloride salts along with Fe^0 (1.0% w/v) greatly enhanced the degradation rates of TNT, RDX, and HMX in aqueous solutions.

During the treatment of aqueous solutions of chlorpyrifos with Fe^0, 55.5, 58.0, and 64.5% of chlorpyrifos was removed within 24

Table 1 Kinetics parameters for the degradation of chlorpyrifos in aqueous solution during ZVI treatment using various salts

Salts	Concentration (%)	Rate constant, k (h^{-1})	Degradation efficiency[a] (%)
Control (without salt)	0.00	0.012	43.7
Ferric nitrate	0.10	0.012	44.6
	0.50	0.013	46.2
	1.00	0.014	47.6
Ferric sulfate	0.10	0.019	55.5
	0.50	0.020	58.0
	1.00	0.023	64.5
Ferric chloride	0.10	0.020	59.8
	0.50	0.024	66.8
	1.00	0.030	71.2
Potassium persulfate	0.05	0.037	74.8
	0.10	0.050	82.2
	0.20	0.166	100.0

[a]Degradation efficiency was determined at 24 h

h after the addition of 0.1, 0.5, and 1.0% (w/v) $FeCl_3$, respectively (Fig. 4). When a sulfate salt was added in the amount of 1.0% (w/v), the increase in the chlorpyrifos degradation rate was the highest. That is to say, the presence of ferric sulfate enhanced the rate of chlorpyrifos degradation by Fe^0 particles compared to that in the absence of the salt. Aqueous solutions of chlorpyrifos were treated with ZVI in the presence and absence of iron salt to determine the degradation kinetics. The results showed that reaction-rate constant (k) was from 0.019 to 0.023 h^{-1} when the $Fe_2(SO_4)_3$ concentration was increased from 0.1 to 1.0% (w/v) in the reaction solution (Table 1). Thus, the degradation kinetics were improved when $Fe_2(SO_4)_3$ was added to the reaction solution. The kinetics of the degradation of chlorpyrifos by ZVI were faster when 1.0% (w/v) $Fe_2(SO_4)_3$ was used than when no salt was used (Table 1). This finding might be attributed to the removal of iron oxides and hydroxides from the surfaces of the
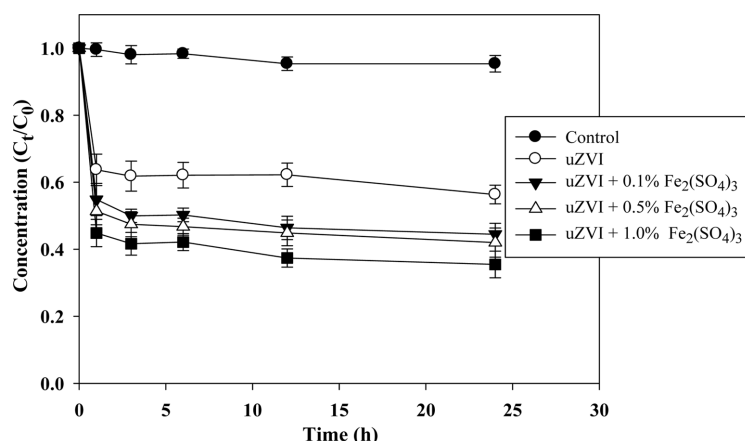
Fig. 4 Effect of ferric sulfate on chlorpyrifos degradation by unannealed ZVI (1.0%) in aqueous solution. Error bars indicate standard deviation of mean (n =3)

iron particles, resulting in the passivating film becoming unstable and nonuniform. This, in turn, increased the number of reactive sites on the surfaces of the iron particles. These observations were in agreement with previously reported studies on the degradation of organic contaminants [26]. Earlier studies have shown that SO_4^{2-} ions have an enhancing effect on the degradation of carbon tetrachloride [26] and trichloroethylene [7] by granular iron. The presence of a sulfate in the reaction solution is also associated with the formation of green rust, which increases the contaminant removal rate during metolachlor dechlorination [12]. Devlin and Allin [11] observed that the reactivity of granular iron during the reduction of 4-chloronitrobenzene was increased by a sulfate, either owing to an increase in the ZVI surface activity or in its sorption capacity. Similar trend of experimental finding was reported by Reddy et al. [27], who stated that the degradation rate of chlorpyrifos was greatly enhanced by augmenting $Al_2(SO_4)_3$ with ZVI.

During the ferric nitrate-amended Fe^0 treatment of chlorpyrifos, 44.6, 46.2, and 47.6% of the chlorpyrifos was removed within 24 h after treatment with 0.1, 0.5, and 1.0% (w/v) ferric nitrate, respectively (Fig. 5). When the degradation results of chlorpyrifos in the absence and presence of an iron salt were compared, it was found that ferric nitrate did not have a significant effect during the treatment with uZVI. The effects of the various concentrations of $Fe(NO_3)_3$ on the degradation kinetic of chlorpyrifos when treated with ZVI are listed in Table 1. As the ferric nitrate concentration was increased from 0.1 to 1.0% (w/v), the reaction-rate constant was from 0.012 to 0.014 h^{-1}. On the other hand, the reaction-rate constant (k) was 0.012 h^{-1} during treatment with ZVI alone. This result showed that the increase in the reaction-rate constant was not significant when ferric nitrate was used along with uZVI. This may be attributable to the reduction of the nitrate by ZVI, resulting in the formation of ferric nitrite and ammonia on the ZVI surface, where they acted as inhibitors of electron generation. The nitrate ion is a ZVI-reducible anion and may react with ZVI as shown in Eqs. (7)-(8).
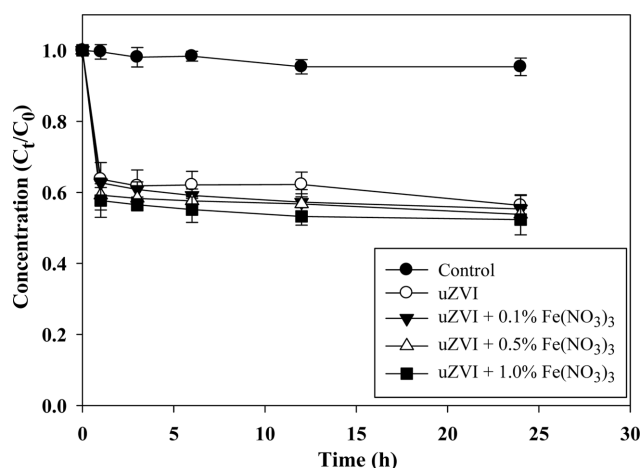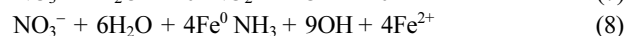

Fig. 5 Effect of ferric nitrate on chlorpyrifos degradation by unannealed ZVI (1.0%) in aqueous solution. Error bars indicate standard deviation of mean (n =3)

$$NO_3^- + H_2O + Fe^0\ NO_2^- + 2OH + Fe^{2+} \qquad (7)$$
$$NO_3^- + 6H_2O + 4Fe^0\ NH_3 + 9OH + 4Fe^{2+} \qquad (8)$$

Similar findings have been reported by Sohn et al. [28], who found that the nitrate ion accepts electrons from iron to form the nitrite ion and ammonia. Further, ferric nitrate has been reported to inhibit the reduction of HOCs with ZVI while being reduced to ferric nitrite and ammonia [7,13]. It was also reported by El-Nagger [29] that the products of the nitrate reduction reaction are adsorbed by the metal surface and thus protect the active reaction sites on the surface for the reaction, resulting in a decrease in the reduction rate. In Fe^0-water systems, nitrate reduction by Fe^0 was accompanied by substantial Fe^0 oxidation by water [30]. The experimental results shown in Fig. 6 indicated that degradation rate of chlorpyrifos was enhanced with an increase in the concentrations of the iron salts in the aqueous system. Ferric chloride was found to be most effective iron salt for promoting the degradation of chlorpyrifos in aqueous solution using ZVI. The
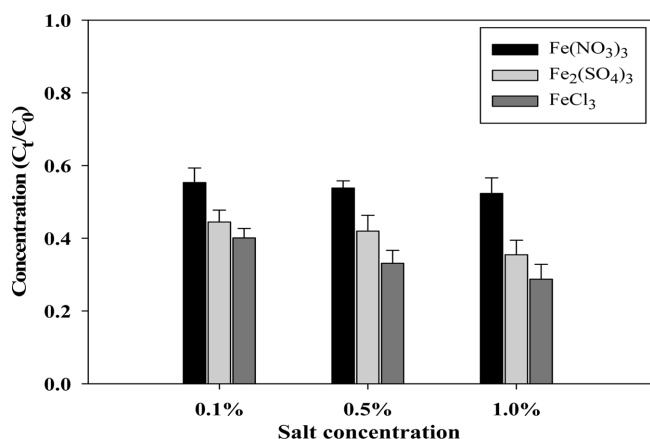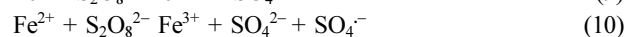
Fig. 6 Degradation of chlorpyrifos as affected by various iron salts during treatment with unannealed ZVI (1.0%) in aqueous solution (concentration =5 mg/L; reaction time =24 h). Error bars indicate standard deviation of mean (n =3)

iron salts could be arranged in the following order in terms of their effectiveness: $FeCl_3 > Fe_2(SO_4)_3 > Fe(NO_3)_3$.

Degradation of chlorpyrifos by potassium persulfate

Chlorpyrifos was also degraded by uZVI in aqueous solutions by adding potassium persulfate in amounts of 0.05, 0.1 and 0.2% (w/v); the reaction times tested were 0, 1, 3, 6, 12, and 24 h. For the persulfate-ZVI system, the degradation efficiencies were 74.8 and 82.2% for 0.05 and 0.1% (w/v) of potassium persulfate, respectively, for a reaction time of 24 h (Table 1). As shown in Fig. 7, 94.32% of the chlorpyrifos was degraded within 12 h by using 0.2% (w/v) potassium persulfate in the aqueous solution containing uZVI. Further, the addition of 0.2% (w/v) potassium persulfate resulted in the complete degradation of chlorpyrifos within 24 h; in contrast, only 12.6 and 43.7% of the chlorpyrifos was removed after treatment for 24 h with potassium persulfate and ZVI alone, respectively (Fig. 7). The rate of chlorpyrifos degradation increased

with the increase in the concentration of potassium persulfate. Thus, the addition of potassium persulfate to the ZVI solution resulted in a greater degree of chlorpyrifos degradation. Calculations related to the degradation kinetics of chlorpyrifos (Table 1) showed that the reaction-rate constant (k) changed from 0.037 to 0.166 h^{-1}; this confirmed that the active sites of the persulfate-ZVI system had a positive effect on the kinetics. Further, this result showed that the combination of ZVI and potassium persulfate was more effective in degrading chlorpyrifos in aqueous solutions than was the ZVI system. This suggested that, in the case of the persulfate-ZVI system, chlorpyrifos degradation occurred through persulfate-related oxidation rather than through reduction by ZVI. The activation of potassium persulfate by Fe^0 is attributable to the release of Fe^{2+} ions from ZVI in the persulfate-Fe^0 system. During the oxidation of Fe^0 by potassium persulfate, Fe^{2+} ions were supplied continuously to the persulfate system, such that the persulfate ions were transformed into sulfate radicals effectively. In this study, Fe^0 was found to be a good source of Fe^{2+} ions for the transformation of the persulfate ions into sulfate radicals. The stoichiometric reactions between the persulfate and Fe^0 can be expressed as shown in Eqs. (9)-(11) [31].

$$Fe^0 + S_2O_8^{2-} \; Fe^{2+} + 2SO_4^{2} \tag{9}$$
$$Fe^{2+} + S_2O_8^{2-} \; Fe^{3+} + SO_4^{2-} + SO_4^{·-} \tag{10}$$
$$SO_4^{·-} + Fe^{2+} \; Fe^{3+} + SO_4^{2-} \tag{11}$$

These results were in agreement with those obtained during the degradation of 2, 4-dinitrotoluene by persulfate activated with ZVI [17]. Further, Liang et al. [32] reported that the addition of Fe^{2+} ions to a persulfate-water system significantly enhances the oxidative degradation of organic contaminants when the Fe^{2+} ions are supplied continuously in small increments. Hussain et al. [18] also reported that the extent of the degradation of p-chloroaniline increased when persulfate was activated by ZVI, as this generated a strong oxidizing species (sulfate radicals) in the aqueous solution.

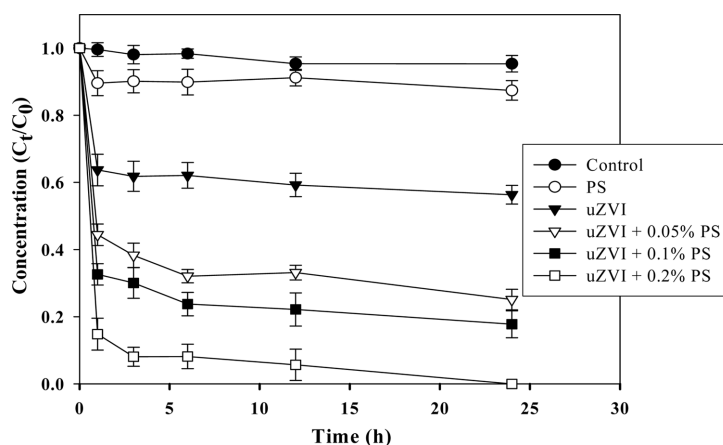The present study showed clearly that the degradation of

Fig. 7 Effect of potassium persulfate on chlorpyrifos degradation by unannealed ZVI (1.0%) in aqueous solution. Error bars indicate standard deviation of mean (n =3)

chlorpyrifos through treatment with Fe^0 was enhanced by adding ferric chloride or potassium persulfate to the aqueous solution. The increase in the degradation rate of chlorpyrifos depended not only on the type of cations added but also on their counter anions. In Fe^0-persulfate system, chlorpyrifos was degraded primarily through oxidation by Fe^0-activated persulfate rather than reduction by Fe^0. Increased Fe^0 loading resulted in enhanced chlorpyrifos degradation, presumably due to increasing activation of persulfate by Fe^0 and Fe^{2+}. As a persulfate-activating agent, Fe^0 was more effective and longer-lasting than Fe^{2+} and potentially more suitable for environmental applications. Therefore, the degradation rate of chlorpyrifos using persulfate-amended Fe^0 was faster than those for the degradation using iron-salt-amended Fe^0. This suggested that employing a sequential Fe^0 reduction-ferric chloride or Fe^0 reduction-persulfate process would be an effective strategy for accelerating the degradation of chlorpyrifos in contaminated waters. However, further studies are needed to elucidate the reaction mechanism and degradation pathway of chlorpyrifos by ZVI in the presence of potassium persulfate and ferric chloride.

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