Int. J. Environ. Sci. Technol. (2014) 11:483–492
DOI 10.1007/s13762-013-0212-5

ORIGINAL PAPER

A study of the applicability of various activated persulfate processes for the treatment of 2,4-dichlorophenoxyacetic acid

C. Liang · Y.-Y. Guo · Y.-R. Pan

Received: 17 April 2012 / Revised: 27 December 2012 / Accepted: 13 February 2013 / Published online: 16 March 2013

Abstract This paper reports an investigation of different persulfate (PS) activations, including PS at 20 °C (PS), thermally activated PS at 70 °C (T-PS), ferrous-ion activated PS at 20 °C [Fe(II)-PS)], hydrogen peroxide activated PS at 20 °C, and sodium hydroxide activated PS at 20 °C, for degradation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous phase. Several findings were made in this study including the followings: the 2,4-D degradation rates in T-PS and Fe(II)-PS systems were higher than other systems. However, complete degradation of 2,4-D and associated derivatives can be reached in all oxidation systems, with various reaction times. When considering the results of PS consumption during the 48 h reaction time to reach complete 2,4-D degradation, the T-PS system consumed all of the PS while only 10 % of the PS was consumed in the Fe(II)-PS system. The evaluation of optimum PS and ferrous ion doses indicated that under a fixed initial PS concentration, increasing Fe^{2+} concentration generally increased the amount of initial rapid degradation of 2,4-D and dissolved organic carbon. However, the effectiveness of the Fe(II)-PS system may be inhibited by the presence of excess iron. When a fixed level of Fe^{2+} was employed, various PS concentrations resulted in approximately equal 2,4-D degradation. The Fe(II)-PS system was found to be sensitive to the initial Fe^{2+} concentration, and the presence of soil revealed minor influence on the 2,4-D degradation by the Fe(II)-PS system. These findings indicate that the iron-activated PS process may be an effective method for remediating 2,4-D contamination.

Keywords Sodium persulfate · Hydrogen peroxide · Base-activated persulfate · Iron-activated persulfate · Groundwater · Herbicide

Introduction

2,4-dichlorophenoxyacetic acid (2,4-D) is a member of the phenoxy family of herbicides widely used to control broadleaf weeds for agriculture. The characteristics of low aqueous solubility (900 mg L^{-1} at 25 °C) (Elbahri and Taverdet 2005), non-volatility, and poor biodegradability makes 2,4-D the most commonly detected herbicide in both surface water and groundwater when rainfall or irrigation occurs soon after application (Alberta-Government 2012). Table 1 presents some chemical and physical properties of 2,4-D. Taiwan Environmental Protection Administration's drinking water regulation for 2,4-D (2012) is the same as the World Health Organization's with a maximum concentration level of 0.07 mg L^{-1}. Seeking effective environmental remediation processes for 2,4-D contamination is an issue faced by environmental scientists. In situ chemical oxidation (ISCO) offers a promising treatment option and has been successfully applied for remediation of contaminated soil and groundwater. Among many ISCO oxidants, persulfate (PS) ($S_2O_8{}^{2-}$, $E^0 = 2.01$ V) is a stable reagent in the subsurface environment. Upon activation, cleavage of the O–O bond in the $S_2O_8{}^{2-}$ structure results in the production of sulfate radical directly ($SO_4^{-\cdot}$, $E^0 = 2.6$ V) and/or hydroxyl radical indirectly ($HO^{\cdot}$, $E^0 = 2.7$ V) (Liang and Su 2009), which significantly improves destruction of organic contaminants. Different approaches for PS

Electronic supplementary material The online version of this article (doi:10.1007/s13762-013-0212-5) contains supplementary material, which is available to authorized users.

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activation have been researched. ISCO PS activation may be initiated by heat, iron, alkaline conditions, and hydrogen peroxide, as detailed in the following Eqs. (1) to (8), respectively.

Heat activation (Liang et al. 2003; Huang et al. 2005):

$$S_2O_8^{2-} + \mathrm{Heat} \rightarrow 2SO_4^{\cdot -} \quad k = 5.7 \times 10^{-5} s^{-1} (70\,°C) \tag{1}$$

Iron activation (George et al. 1997; Liang et al. 2004a):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot -} + SO_4^{2-}$$
$$k = 2.0 \times 10^{1}\ M^{-1}s^{-1} \tag{2}$$

Alkaline activation (Furman et al. 2010; Liang and Guo 2012):

$$S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} HO_2^- + 2SO_4^{2-} + 3H^+ \tag{3}$$

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + H^+ + O_2^{\cdot -} \tag{4}$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + HO^{\cdot} \quad k = 6.5 \times 10^{7} M^{-1} s^{-1} \tag{5}$$

Hydrogen peroxide activation (Waldemer et al. 2007; Song et al. 2008; Liang and Guo 2012):

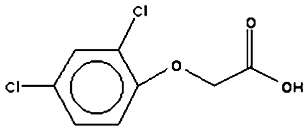
$$H_2O_2 \rightarrow H_2O + 0.5O_2 \qquad \Delta H^0 = -98.2\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad pk_a = 11.62 \tag{7}$$

$$H_2O_2 + S_2O_8^{2-} \rightarrow 2H^+ + 2SO_4^{2-} + O_2 \tag{8}$$

Heat and iron PS activations have been more comprehensively documented in literature than others. Heat activation is very aggressive and capable of destroying a wide range of organic contaminants (Huang et al. 2005; Ghauch and Tuqan 2012; Liang et al. 2003; Deng and Ezyske 2011).

Table 1 Physical and chemical properties of 2,4-D

Properties	Values
Structure	
Molecular formula	$C_8H_6Cl_2O_3$
Molecular weight (g/mole)	221.04
Odor	Odorless
Appearance	White to brown crystalline solid
Melting point (°C)	138
Boiling point (°C)	160
Solubility in water (mg/L, 25 °C)	677
Density (g/cm^3, 20 °C)	1.416
log Kow, 20 °C	2.81
Vapor pressure (mmHg, 25 °C)	8.25×10^{-5}
Henry's constant (atm-m^3/mole, 25 °C)	1.02×10^{-8}
pk$_a$	2.64

Source: Taiwan Environmental Protection Administration (EPA), Soil and Groundwater Remediation Fund Management Board (2012)

In iron PS activation, it is common to apply dissolved ferrous ion as an activator and in some ways, this process is similar to Fenton's reaction. Adjusting the acidic pH condition may not be necessary to ensure that iron is present in divalent form for PS activation (Liang et al. 2004a). Moreover, excess Fe^{2+} concentration would pose stronger scavenging of sulfate radicals and result in less organics degradation. The available ferrous ion activator concentration has been demonstrated to significantly influence organics degradation efficiency (Liang et al. 2004a, b). Hence, it is necessary to optimize the iron dose (e.g., sequential addition or ferrous ion buffering) to achieve effective activation.

The alkaline PS activation is promoted by the alkaline hydrolysis of PS anion (Eq. 3), and the generated hydroperoxyl ion (HO_2^-) then reacts with PS anion to form $SO_4^{\cdot -}$ and the superoxide radical ($O_2^{\cdot -}$) (Furman et al. 2010). Furthermore, $SO_4^{\cdot -}$ would undergo radical interconversion to form $HO^{\cdot}$ under alkaline conditions (Eq. 5) (Liang and Su 2009).

In hydrogen peroxide PS activation, hydrogen peroxide decomposes exothermically upon contact with aquifer water and aqueous species (Eq. 6) and, therefore, indirectly induces heat PS activation. Also, when pH is increased to above the pK$_a$ of hydrogen peroxide, the deprotonated species, HO_2^- (Eq. 7), may interact with $S_2O_8^{2-}$ in accordance with (Eq. 4) (Goi and Trapido 2010; Goi et al. 2012). However, hydrogen peroxide would directly react with PS and result in simultaneous decompositions of both peroxide and PS (Eq. 8).

In this study, the feasibility of degradation of 2,4-D under different PS activations, denoted as PS (PS at 20 °C), T-PS (thermally activated PS at 70 °C), Fe(II)-PS (iron-activated PS at 20 °C), H_2O_2-PS (hydrogen peroxide activated PS at 20 °C), and NaOH-PS (sodium hydroxide activated PS at 20 °C), was initially investigated. The decomposition of PS, the destruction of dissolved organic carbon (DOC), and the formation of 2,4-D degradation byproducts during the reaction were monitored to determine a suitable PS activation process for degrading 2,4-D in the aqueous system. Furthermore, the optimal doses of oxidant and activator were studied in aqueous system and subsequently applied in soil slurry systems.

Materials and methods

Materials

The chemicals used were purchased from the following sources: 2,4-dichlorophenoxyacetic acid ($C_8H_6Cl_2O_3$, 98 %), Alfa Aesar; activators: hydrogen peroxide (H_2O_2, 30 %), Riedel-deHaën, sodium hydroxide (NaOH, 99 %) and ferrous sulfate7-Hydrate ($FeSO_4{\cdot}7H_2O$, 98 %), UNION Taiwan; analysis of sodium persulfate: sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$, ≥99.5 %), sodium bicarbonate ($NaHCO_3$, ≥99.7 %), and starch [$(C_6H_{10}O_5)n$, 99.8 %], Riedel-deHaën, sodium persulfate (SPS) ($Na_2S_2O_8$, ≥99 %), Merck, acetic acid (CH_3COOH, ≥80 %), J. T. Baker, potassium iodide (KI, ≥99.5 %), UNION Taiwan, sulfuric acid (H_2SO_4, 95–97 %), Fluka, potassium dichromate ($K_2Cr_2O_7$, ≥99 %), Sigma-Aldrich; analysis of hydrogen peroxide: cerium sulfate [$Ce(SO_4)_2$, 97 %], arsenic trioxide (As_2O_3, 99.95 %), osmium tetroxide (OsO_4) and 1,10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$, 99 %), Alfa Aesar; analysis of 2,4-D: 2-Propanol (C_3H_8O, 99 %), J. T. Baker, acetonitrile (CH_3CN, 99.99 %), Echo, *p*-Bromophenol (BrC_6H_4OH, 99 %) and potassium hydroxide (KOH, 99.99 %), Aldrich; DOC analysis: phosphoric acid (H_3PO_4, 86.5 %), J. T. Baker, potassium hydrogen phthalate ($C_8H_5KO_4$, 99.99 %), Acros; analysis of iron: Ferrover and Ferrous iron reagent, HACH.

2,4-D contaminated solutions were prepared in water purified using a Millipore reverse osmosis (RO) purification system. Soils (sieved between sieve#30–#200, particle diameters ranged from 0.074–0.59 mm) used for slurry system were obtained from farm land approximately 2 m below the ground surface in southern Taiwan, and the properties of the soils were reported in Liang et al. (2008b). Some characteristics are: soil pH 5.6, total organic carbon 0.53 %, water content of 0.73 %, cation exchange capacity of 7.5 meq/100 g, iron concentration of 32,190 ± 106 mg/kg, Mn concentration of 190 ± 6 mg/kg, and copper concentration of 11 ± 6 mg/kg.

Experimental procedure

All aqueous experiments were carried out with 250 mL glass reaction bottles with PTFE-lined caps in a temperature controlled chamber at 20 °C or at 70 °C for heat activation. The 2,4-D contaminated solution of 100 mg/L (0.452 mM) was prepared. Note that through a literature survey, the 2,4-D concentration range of 22–230 mg/L was commonly found in surface and ground water at 2,4-D contaminated sites (Sun and Pignatello 1993; Brillas et al. 2000; Jackman et al. 2001; Kwan and Chu 2003; Bandala et al. 2007). A fixed SPS concentration of 100 mM and different activator concentrations of 300 mM H_2O_2, 50 mM NaOH, and 10 mM Fe^{2+} were used to evaluate the performance of PS in degrading 2,4-D in aqueous phase (Liang et al. 2008a; Liang and Su 2009). Note that selections of the concentration levels were also in accordance with the concentration range recommended by the SPS manufacturer (FMC-Corporation 2012) (note, see Table SI2 for FMC recommended reagent dosage in the PS system, Supporting Information). At each sampling interval, 10 mL of solution was withdrawn and filtered through a 0.2 μm PTFE filter for analysis of 2,4-D, DOC, SPS, H_2O_2, ferrous, and total dissolved iron concentrations and pH. Note that the solution withdrawn was immediately analyzed for 2,4-D and other parameters at each sampling interval, so as to quench further oxidation reaction. In the further evaluation of iron activation processes, experiments were designed into two categories including examination of the influence of Fe^{2+} concentration ranging from 0.5 to 20 mM under a fixed SPS concentration of 100 mM, and of SPS concentrations ranging from 2.5 to 100 mM to determine optimized oxidant and activator doses. All experiments were run in triplicate and averaged data were reported. Control experiments in the absence of either oxidant or activator were also conducted in parallel.

In soil slurry experiments, 10 g of soils were added into a series of 40 mL bottles prior to filling with 10 mL of 2,4-D contaminated solution (100 mg/L). The resulting soil slurries were shaken on a reciprocal shaker (IKA HS 260 control) at 110 rpm at 20 °C for 24 h before supplementing 0.5 ml of PS and/or ferrous ion stock solutions into every bottle to reach designated concentration levels. At each sampling time, three bottles were sacrificed and 10 mL methanol was added into each bottle to extract the total mass of 2,4-D from the soil slurries (AOAC 1990). Extractions were done by 2 min shaking on a vortex shaker at 1400 rpm and then centrifuged at 800 rpm for 15 min. The supernatant was collected and filtered for analysis. Control tests were also conducted in parallel.

Analytical methods

2,4-D concentration in the supernatant was analyzed using a high performance liquid chromatography (HPLC, Agilent Model 1100) equipped with a UV–visible detector and an Agilent Eclipse XDB-C18 column. Two HPLC methods were used, i.e., method #1 (mobile phase acetonitrile/0.3 M NaOH (25:75, v/v) at a rate of 1.2 mL/min and controlled temperature of 40 °C, and *p*-bromophenol used as the internal standard at a UV wavelength of 280 nm) was used for PS, T-PS, H_2O_2-PS, and NaOH-PS systems; method #2 (mobile phase acetonitrile/0.15 % acetic acid (50:50, v/v) at a rate of 1.5 mL/min and controlled temperature of 20 °C at a UV wavelength of 283 nm) was used for the Fe(II)-PS system (AOAC 1990). It should be noted that to prevent iron precipitates being injected into the TOC analyzer, the solution were filtered through a 0.45 μm PTFE filter and hence, the term of DOC was used instead of TOC. DOC analysis was performed using a TOC analyzer (O.I. Analytical Aurora 1030 W). Ferrous ion and total dissolved iron were colorimetrically measured using a spectrophotometer at 510 nm (Hach DR/2400) (APHA 1998). Total oxidant concentration ($H_2O_2 + S_2O_8{}^{2-}$) in H_2O_2-PS system or PS concentrations in PS, T-PS, H_2O_2-PS, and Fe(II)-PS systems were determined by iodometric titration with sodium thiosulfate (Liang et al. 2003). Furthermore, H_2O_2 in the H_2O_2-PS system was analyzed using cerium (IV) sulfide titrimeric method (Vogel 1978), and PS concentration was then determined by subtracting H_2O_2 concentration from the total oxidant concentration. The pH was measured using a pH/Ion meter (Thermo Orion 720A+).

Results and discussion

Evaluation of various persulfate activation processes

The results of the effectiveness of various PS activations are presented in Fig. 1. The rapid disappearance of 2,4-D occurred within 48 h in the T-PS and Fe(II)-PS systems, but extended reaction times were required in other systems (PS, H_2O_2-PS, and NaOH-PS) to achieve higher 2,4-D degradations. However, complete degradation of 2,4-D can nearly be attained, dependent on the reaction time, for all PS activations evaluated (see Fig. 1f). Due to complicated radical based reaction mechanisms in these PS activation systems, general and comparable kinetics may not be obtained for comparison and would require further evaluation for individual oxidation systems. However, via examining the results of 2,4-D variation with time, it can still be preliminarily concluded that the 2,4-D degradation with different PS activations are in an order of T-PS > Fe(II)-PS > NaOH-PS > H_2O_2-PS > PS.

In the HPLC chromatograms, in addition to the parent compound 2,4-D peak, other peaks were present (see Figs. SI1–SI5, Supporting Information). In all oxidation systems except for Fe(II)-PS, three additional peaks appeared in the HPLC chromatograms and were denoted as byproducts 1, 2, and 3 [at retention times (RT) of 3.175, 5.458, and 10.602 min, respectively]. Two byproducts were detected in the Fe(II)-PS system (denoted as byproducts 4 and 5 at RT of 5.317 and 5.726, respectively). Through literature survey pertaining to chemical oxidation of 2,4-D, it was found that 2,4-dichlorophenol (2,4-DCP) is the most commonly detected byproduct (review summary is provided in Table SI1, Supporting Information). Therefore, 2,4-DCP was analyzed using both HPLC method #1 and #2 (see Figs. SI6 and SI7, respectively, Supporting Information) and confirmed that byproduct 4 which appeared in the Fe(II)-PS system is 2,4-DCP. Even though not all byproducts were identified at this time, byproducts formed in T-PS and Fe(II)-PS systems can also be effectively destroyed. In addition, the results of DOC analysis indicates the extent of mineralization of 2,4-D by different PS activations. Again, both T-PS and Fe(II)-PS systems resulted in superior DOC removals (i.e., 97.6 and 100 %, respectively, at the end of 48 h). It should be noted that DOC in H_2O_2-PS system was not measured (not presented in Fig. 1f) because of the interference of hydrogen peroxide during DOC analysis which employed the thermally activated PS wet chemical oxidation (see Table SI3, Supporting Information). When comparing the results of PS decomposition, the T-PS used up all PS while only 9 % of PS was consumed in the Fe(II)-PS system at 48 h. Note that the variations of PS or peroxide and DOC as a function time are detailed in Fig. SI8 (Supporting Information). When comparing the consumption of PS and hydrogen peroxide at each sampling time, $\Delta S_2O_8{}^{2-}/\Delta H_2O_2$ molar ratio ranged from 0.6–1.0 which is comparable to the stoichiometric ratio of Eq. (8). pH variations in all oxidations decreased from the initial pH of 5.6 (RO water) to acidic conditions at the end of the reactions (i.e., pH 2.7, 1.3, 2.2, and 1.9 for PS, T-PS, Fe(II)-PS, and H_2O_2-PS systems, respectively) with exception that in the NaOH-PS system, initial pH of 13.1 slightly decreased to 12.6. Based on these observed results, the Fe(II)-PS system exhibits complete destruction of 2,4-D and its associated degradation byproducts and less consumption of PS. Table 2 shows the cost analysis based upon laboratory batch tests (see Fig. 1f). The estimated treatment cost per unit mass of 2,4-D removed are in the range of US $0.62–0.90 per gram of 2,4-D for various PS activation systems, while the cost for DOC removed are in the range of US $1.43–8.00 per gram of DOC. There is a slight difference for the cost to destroy 2,4-D among different systems. However, it can be seen that the cost to destroy DOC is generally higher than to destroy 2,4-D. The T-PS and Fe(II)-PS systems exhibit the relatively lower treatment cost. It should be noted that the estimated costs have been made based upon the cost of chemicals and a cost for energy needed to heat water to 70 °C in the T-PS was not included. Therefore, the Fe(II)-PS system appears to have a lower unit treatment cost and better 2,4-D and DOC removal efficiencies.

Furthermore, in the case of Fe(II)-PS system, the total iron and ferrous ion concentrations were also measured during the course of reaction. Interestingly, the rapid disappearance of Fe^{2+} ($\sim$91 % reduction) within 1 h of the start of experiment can be an indicator of immediate PS activation according to Eq. (2) (Fig. SI9, Supporting Information) which would explain the significant degradation of 2,4-D in the early stage of the reaction. Supposedly, without the presence of Fe^{2+}, the iron PS activation would be stalled and no further sulfate radical would be generated (Liang et al. 2004a; Liang et al. 2008a). However, it was observed that the 2,4-D

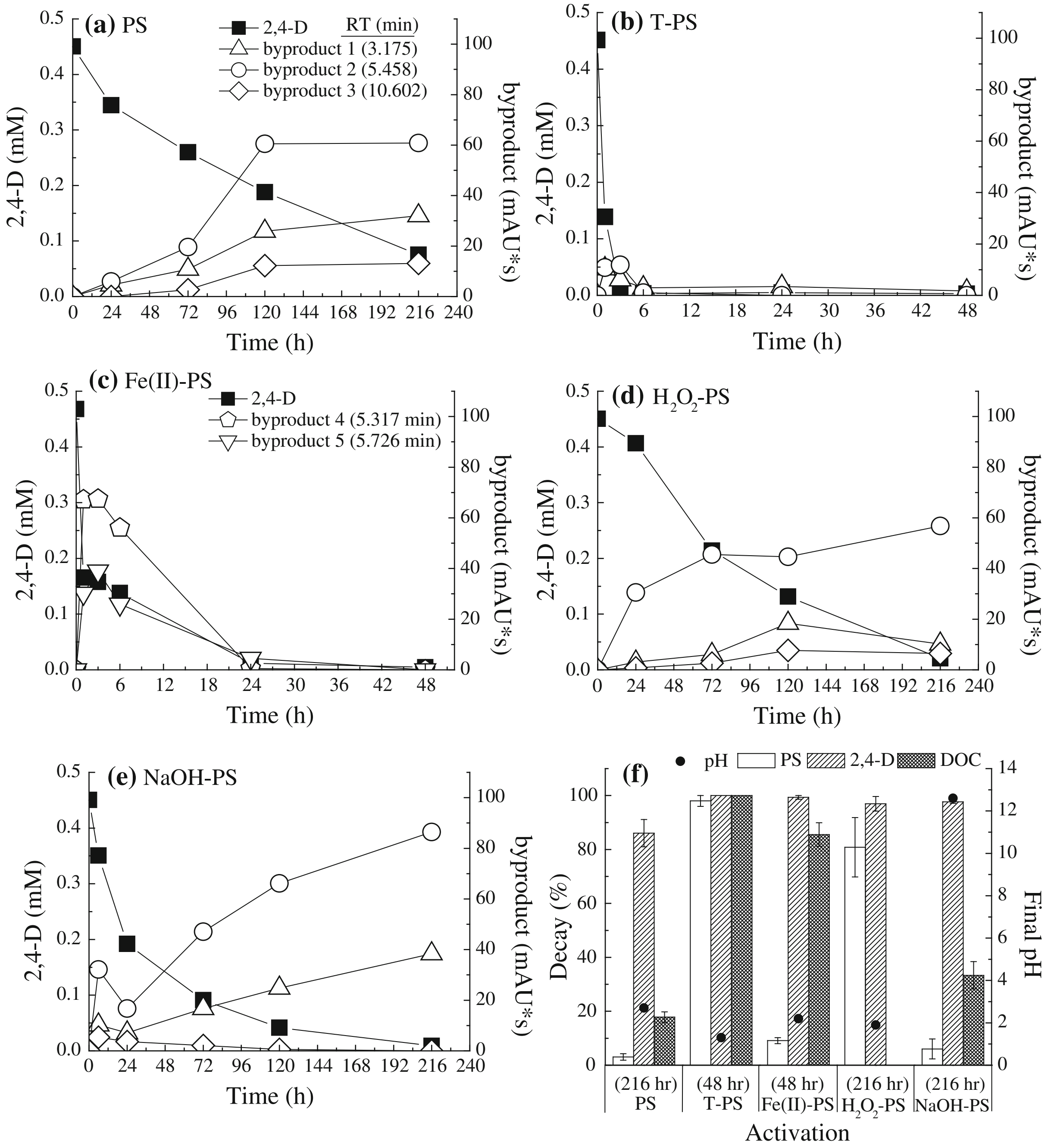


Fig. 1 Effect of various persulfate activations: **a** PS, **b** T-PS, **c** Fe(II)-PS, **d** H_2O_2-PS, and **e** NaOH-PS on 2,4-D degradation and byproducts formation; **f** summary of removals of 2,4-D, DOC, and PS. Note: Quantities of byproducts are measured using HPLC/UV detector responses, i.e., *mAU*s* mili absorbance unit*second. Experimental conditions: Temp. = 20 °C (except for T-PS system Temp. = 70 °C) and fixed [PS] = 100 mM; [H_2O_2] = 300 mM; [NaOH] = 50 mM; [Fe] = 10 mM

concentration still continuously decreased at a low Fe^{2+} concentration level, whereas total iron concentration was the same as the ferrous ion concentration initially added. This phenomena of the condition, where total iron was dissolved and a low concentration of Fe^{2+} was present with iron activated PS, is similar to those studies using complexing agents such as citric acid (Liang et al. 2004b; Liang et al. 2008a; Crimi and Taylor 2007) and cyclodextrin (Liang et al. 2008a; Liang et al. 2007) in maintaining available Fe^{2+} in solution to activate PS. Therefore, it could be speculated that dissolved total iron (i.e., ferric ions) may be reduced to ferrous ions during the course of reaction by 2,4-D degradation byproducts in accordance with the proposed Eqs. (9) and (10) for successive PS activation in the Fe(II)-PS system. These observations trigger an interesting subject for further evaluation. It

Table 2 Cost analysis for the laboratory batch tests

Activation system	Reagent	Price US$/kg	Conc. (mM)	US$/test	2,4-D mg (%)	DOC removal	Treatment cost*	
							US$/g 2,4-D	US$/g DOC
PS	$Na_2S_2O_8$	2.6	100	0.015	20.8 (83.3)	1.9 (17.8)	0.74	8.00
T-PS	$Na_2S_2O_8$	2.6	100	0.015	24.8 (99.4)	10.8 (99.5)	0.62	1.43
Fe(II)-PS	$Na_2S_2O_8$	2.6	100	0.016	24.7 (99.0)	9.3 (85.6)	0.64	1.71
	$FeSO_4 \cdot 7H_2O$	0.6	10					
H_2O_2-PS	$Na_2S_2O_8$	2.6	100	0.021	23.8 (95.4)	n.d.	0.90	n.d.
	H_2O_2 (30 %)	0.7	300					
NaOH-PS	$Na_2S_2O_8$	2.6	100	0.016	24.5 (98)	3.6 (33.3)	0.65	4.40
	NaOH	0.9	50					

Prices for reagents were provided by the local vendor. The cost was calculated based on the chemical used in a solution volume of 250 mL in each test. Percentages of 2,4-D and DOC removals were obtained at the end of reactions in different oxidation systems based on the results of Fig. 1f, i.e., PS (216 h); T-PS (48 h); Fe(II)-PS (48 h); H_2O_2-PS (216 h); and NaOH-PS (216 h). A cost for energy needed to heat water to 70 °C was not included

n.d. not determined

* cost per gram of 2,4-D or DOC removed

should be noted that a control test in the presence of 10 mM Fe(III) and 0.452 mM 2,4-D showed no disappearance of 2,4-D within 48 h (data not shown) and therefore, indicated that electron transfer between Fe^{3+}/Fe^{2+} may not be able to induce degradation of 2,4-D.

$$SO_4^{-\cdot} + HQH \rightarrow HQ^{\cdot} + HSO_4^{-} \quad (9)$$

$$HQ^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + Q + H^{+} \quad (10)$$

where Q represents organics.

Optimization of SPS and Fe^{2+} doses

Influence of initial Fe^{2+} concentration

Because of the superior performance of the Fe(II)-PS system (as discussed in previous section), favorable operating conditions (i.e., PS and Fe^{2+} doses) for the Fe(II)-PS system in treating 2,4-D were further investigated. It should be mentioned that the phenomena of 2,4-D degradation that occurred in the Fe(II)-PS system can be separately considered: initial rapid degradation and subsequent slow degradation. Under a fixed SPS concentration of 100 mM, it can be seen in Fig. 2a and b that increasing Fe^{2+} concentrations from 0.5 to 10 mM generally exhibited increases in the extent of initial degradation of 2,4-D and DOC. However, little difference was observed when Fe^{2+} concentration was increased from 10 to 20 mM. Coincidently, when using 20 mM Fe^{2+}, significant generation of byproducts was observed compared to the use of 5 and 10 mM of Fe^{2+} which exhibited a relatively slower byproduct formation rate and complete degradation of byproducts within 24 h (see Fig. SI10, Supporting Information). Nevertheless, 2,4-D can be completely degraded within 48 h under all Fe^{2+} concentration levels except for the condition of 0.5 mM Fe^{2+} and 100 mM SPS in which initial Fe^{2+} concentration was relatively low compared to others. These results indicate that excess Fe^{2+} (20 mM) negatively affects 2,4-D and its byproduct degradations and also reduces the DOC removal. Figure 2c illustrates that PS was decomposed proportionally to the concentration of iron used. However, additional PS decomposition may not necessarily contribute to 2,4-D degradations. An explanation for this could be that the sulfate radicals produced through iron activation are capable of degrading 2,4-D, but the competition for sulfate radicals by excess iron and other intermediate byproducts was too great to allow efficient degradation of 2,4-D (Liang et al. 2004a). To briefly summarize, the Fe^{2+} concentrations of 5 and 10 mM would be suitable concentration levels and were selected for further evaluation.

Influence of initial SPS concentration

Further experiments were conducted to discover the influence of SPS for achieving effective 2,4-D degradation. It can be seen in Fig. 3 that when the same level of Fe^{2+} concentration was used under different SPS concentrations, similar initial 2,4-D or DOC degradations were attained (See Figs. 3a, b). For example, comparing Fe^{2+}/SPS of from 10/100 to 10/10, both experimental conditions initially achieved the same ~65 % of 2,4-D degradation. It was proven that free Fe^{2+} governed the initial phase of 2,4-D degradation. Moreover, lowering PS concentration under a fixed level of Fe^{2+} concentration is generally reflected in the 2,4-D degradation rate that occurs after the initial rapid 2,4-D degradation. However, for those experiments using a Fe^{2+}/SPS molar ratio of 2:1, i.e., the stoichiometric molar

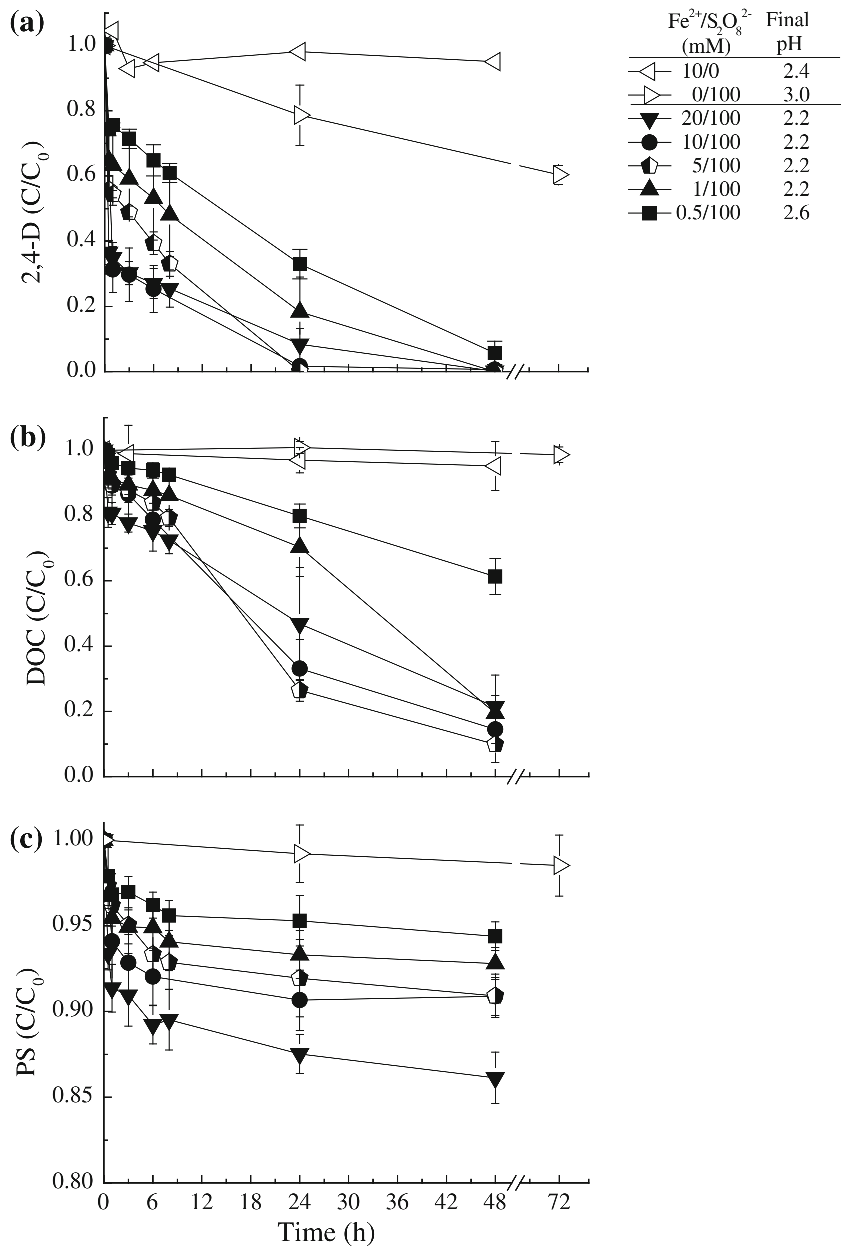


Fig. 2 Dependence of initial ferrous ion concentrations on **a** degradation of 2,4-D; **b** destruction of DOC, and **c** decomposition of persulfate by iron activated persulfate. Experimental conditions: Temp. = 20 °C; [PS] = 100 mM; [Fe^{2+}] = 0.5–20 mM

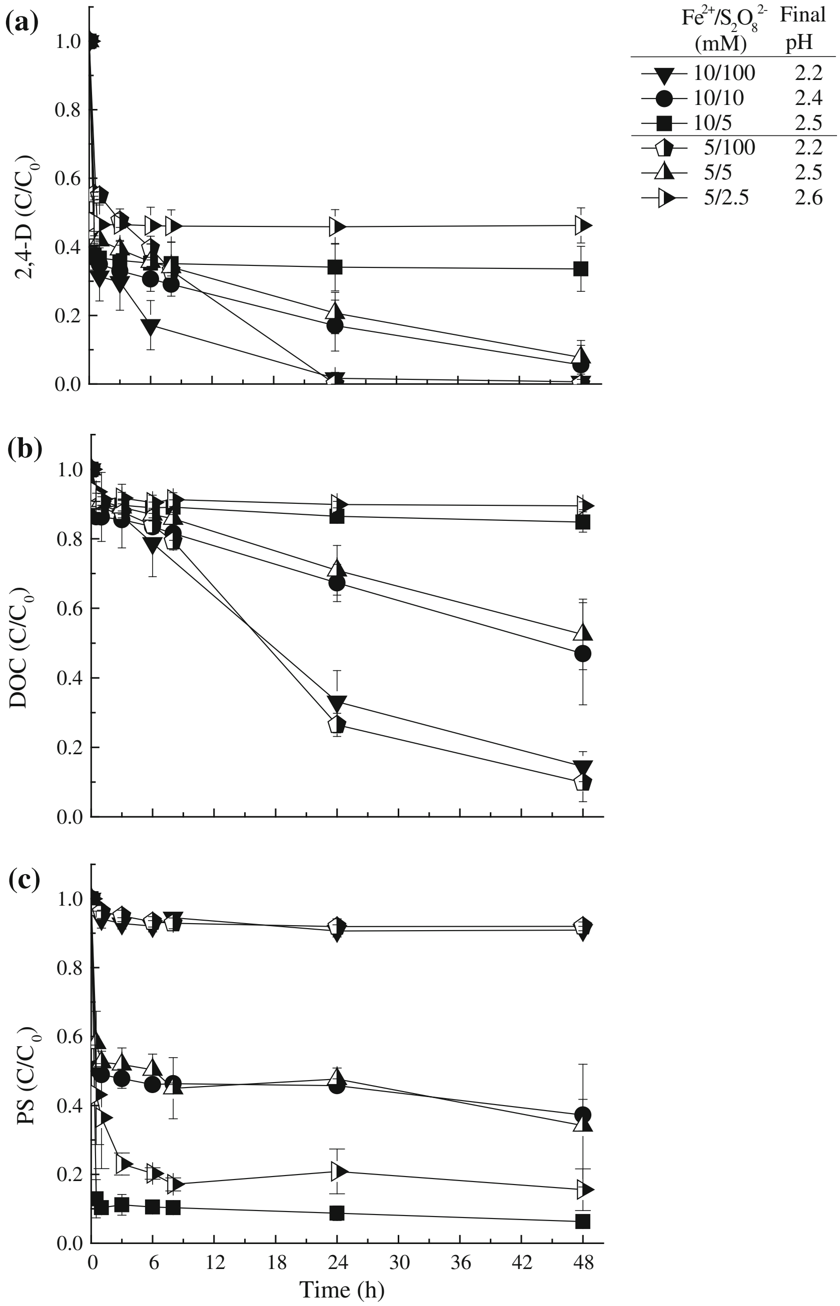
ratio between Fe^{2+} and SPS (Eq. 11), insufficient PS concentration resulted in the stalling of 2,4-D degradation beyond the initial rapid 2,4-D degradation (note: comparing the results between Figs. 3a, c).

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \tag{11}$$

Influence of soils

As shown in Fig. 4, experiments employing iron-activated PS with 5 mM Fe^{2+} and 100 mM SPS for 2,4-D degradation in a soil slurry system was evaluated to verify the potential Fe(II)-PS application in the presence of soil. It appeared that the degradation rate of 2,4-D and all associated byproducts was slightly lower than observations in an aqueous system. 2,4-D is an acidic herbicide with $pK_a \sim 3$ and its solubility is weak at pH lower than pK_a (e.g., 311 mg L^{-1} at pH = 1 at 25 °C) (Elbahri and Taverdet 2005). The final pH measured in the soil slurry system was around 4.2 (for Fe^{2+}/SPS of 5 mM/100 mM experiment) which was higher than the pH obtained in the previous aqueous system experiment (e.g., pH ~ 2). Therefore, it can be confirmed that the preponderant species of 2,4-D in the aqueous phase of the soil slurry system is the anionic form. Thereby, 2,4-D degradation occurred predominantly in the aqueous phase where Fe(II)-PS oxidation occurred. The results demonstrated that the Fe(II)-PS system is a suitable process for treating 2,4-D in the presence of soil.

Fig. 3 Dependence of initial persulfate concentrations on **a** degradation of 2,4-D; **b** destruction of DOC, and **c** decomposition of persulfate by iron activated persulfate. Experimental conditions: Temp. = 20 °C; [PS] = 2.5–100 mM; [Fe^{2+}] = 5–10 mM



Conclusion

The 2,4-D degradation and DOC removal in different PS activation systems were investigated. The results showed that all activated PS processes are very beneficial to the 2,4-D degradation. Data obtained from the aqueous experiments revealed that thermally activated PS resulted in the fastest degradations of both 2,4-D and byproducts, followed by the iron-activated PS system. Both oxidation systems achieved complete 2,4-D degradation and 85–100 % of DOC removal within 48 h. As for other oxidation systems, extended reaction times are required to achieve higher efficiency of 2,4-D degradation (e.g., 216 h). Comparing heat activation to iron activation, less PS consumption occurred in the iron-activated PS system and hence, the Fe(II)-PS system was selected for further evaluation. Therefore, the efficiency of 2,4-D degradation was compared by varying the initial concentrations of SPS and Fe^{2+}. It was demonstrated that the optimum concentration of Fe^{2+} required for this process was found to be between 5 and 10 mM, and the SPS concentration should be at least greater than the Fe^{2+}/SPS stoichiometric ratio of 2. The presence of soil seems unlikely to affect the 2,4-D degradation by iron-activated PS process. In this study, we

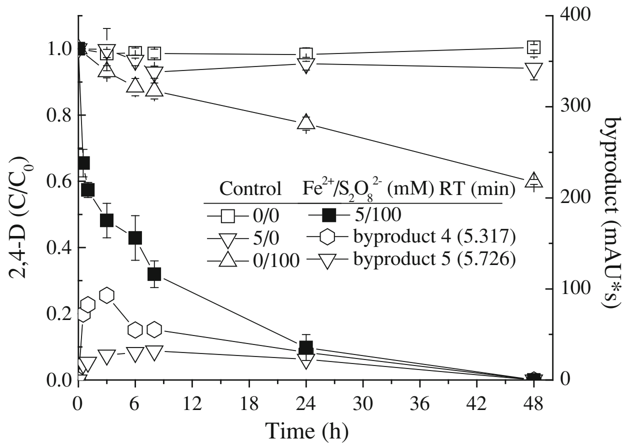


Fig. 4 The soil slurry system. Degradation of 2,4-D and byproducts by iron activated persulfate. Note: Quantities of byproducts are presented with HPLC/UV detector responses, i.e., *mAU*s* mili absorbance unit * second. Experimental conditions: Temp. = 20 °C; [PS] = 100 mM; [Fe^{2+}] = 5 mM

have proven the feasibility of the PS activation process for remediating 2,4-D contamination, and specifically examined the optimum doses of SPS and Fe^{2+} for the Fe(II)-PS system. It should be noted that the operational cost needs to be considered for activated PS application at sites of varying sizes and complexity. Further investigation of the mechanisms involved in various PS activation processes is needed.

Acknowledgments This study was funded by the National Science Council (NSC) of Taiwan under project number of NSC99-2622-E-005-005-CC2.

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