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Treatment of tetrachloroethylene-contaminated groundwater by surfactant-enhanced persulfate/BOF slag oxidation—A laboratory feasibility study

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ABSTRACT

The main objective of this study was to evaluate the feasibility of remediating tetrachloroethylene (PCE)contaminated groundwater (with initial PCE concentration of approximately 20 mg L^{-1}) via persulfate oxidation activated by basic oxygen furnace slag ($S_2O_8^{2-}$ /BOF slag) with the addition of biodegradable surfactant (Tween 80). Results indicate that only 15% of PCE can be removed in experiment with the addition of $S_2O_8^{2-}$ only ($S_2O_8^{2-}/PCE = 30/1$). PCE removal can be increased to 31% while both $S_2O_8^{2-}$ and BOF slag (10 g L^{-1}) were added. This indicates that BOF slag was able to activate the persulfate oxidation mechanism, and cause the decrease in PCE concentration via oxidation process. Results also reveal that PCE degradation rates increased to 92% with the presence of Tween 80 ($S_2O_8^{2-}$ /Tween 80/PCE = 30/2/1). In the presence of 10 g L^{-1} BOF slag, the reaction rate constant (k_{obs}) values were found to be 3.1×10^{-3} , 8.7×10^{-3} , 1.6×10^{-2} , and 5.8×10^{-2} h⁻¹, as the S₂O₈²⁻/Tween 80/PCE molar ratios were 30/0/1, 30/0.5/1, 30/1/1, and 30/2/1, respectively. The reaction rate constant increased as the Tween 80 concentration increased. The significantly increased k_{obs} could be caused by the enhanced solubilization of PCE by Tween 80. The increase in initial surfactant concentration would cause the increase in the solubilization of PCE, and thus, enhance the oxidation rate. This was confirmed by the total amount of chloride ions produced after the reaction. Results from this study indicate that BOF slag-activated persulfate oxidation enhanced by surfactant addition is a potential method to efficiently and effectively remediate chlorinated solvents contaminated groundwater.

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1. Introduction

Contamination by dense non-aqueous phase liquids (DNAPLs) [e.g., tetrachloroethylene (PCE)] in groundwater has become an issue of great concern in many industrialized counties [1,2]. Dissolution of DNAPL into the water phase can cause long-term contamination due to a low aqueous solubility characteristic (e.g., PCE has a relatively low aqueous solubility of 150 mg L^{-1}) [1,3,4]. Thus, groundwater remediation becomes a real challenge when DNAPLs are present in the subsurface [5,6].

Among various remediation technologies [7–9], there has been considerable interest in the use of persulfate for the in situ chemical oxidation (ISCO) to treat or destruct chlorinated solvents (e.g., PCE). Persulfate is relatively stable at ambient temperature of 25 °C. It possesses the advantages similar to that of hydrogen peroxide and permanganate. Persulfate itself is a strong oxidant; however, it

usually requires higher activation energy than other ISCO oxidants such as permanganate. It has been postulated that persulfate anion $(S_2O_8^{2-})$ can be activated by transition metal ions such as ferrous ion (Fe^{2+}) to produce a powerful oxidant known as the sulfate free radical $(SO_4^{-\bullet})$ [Eqs. (1)–(3)] with a redox potential of 2.4 V, which can potentially destroy chlorinated solvents [10–12].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\bullet}$$
 (1)

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$$
 (2)

From reactions (1) and (2), overall reaction is obtained as reaction (3):

$$2Fe^{2+} + S_2O_8^{2-} \to 2Fe^{3+} + 2SO_4^{2-}$$
(3)

Persulfate activated by Fe^{2+} has been applied for the treatment of many groundwater contaminants including chlorinated organics and petroleum hydrocarbons [13–16]. In addition, persulfate reacts less with natural organic matters (NOM) so that this oxidant seems to be more appropriate for the remediation of contaminated aquifers containing high NOM. For this reason, costs of site remediation using persulfate oxidation may be lower in comparison with

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Table 1 Characteristics of tested groundwater.

Parameters	рН	Nitrate (mg L ⁻¹)	$\operatorname{Fe}_{t}(\operatorname{mg} L^{-1})$	$Fe^{2+}(mgL^{-1})$	Sulfate (mg L ⁻¹)	Sulfide (mg L ⁻¹)	Methane (mg L ⁻¹)	Ammonia nitrogen (mg L ⁻¹)	Phosphate $(mg L^{-1})$
Value	5.3	7.1	1.9	1.2	35	3	0.04	6	1.22

other oxidants [17,18]. These benefits make persulfate a promising alternative for groundwater remediation.

In recent years, the management of basic oxygen furnace slag (BOF slag) has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints [19,20]. BOF slag is heterogeneous oxide materials which are compounded by some main oxides such as Fe₂O₃. FeO, CaO, SiO₂, SO₃, Al₂O₃, TiO₂, CaO, MgO, SiO₂, P₂O₅, and MgO due to their mass percentage. There is 5–20% of FeO and 1–8% of Fe₂O₃ present in the BOF slag [21,22]. Furthermore, FeO can be dissociated to produce Fe²⁺ in aqueous solution, and the released Fe²⁺ has the potential to react with persulfate to produce SO₄^{-•} for subsequent chlorinated solvents oxidation.

Persulfate oxidation that is used to treat chlorinated solvents is usually most effective when contaminants are present in the dissolved phase [23,24]. Therefore, effective oxidation of chlorinated solvents in DNAPLs phases are highly dependent on the masstransfer mechanism between aqueous and DNAPL phases. Kim and Chrysikopoulos [25] and Chrysikopoulos et al. [26] have shown that the mass transfer coefficient at the NAPL–water interface in water saturated porous media is very sensitive to the effective diffusion coefficient, interstitial velocity, transverse hydrodynamic dispersion coefficient and NAPL dimension. Accelerated oxidation of a contaminant in the aqueous phase could lead to an increase in the concentration gradient for the contaminant (e.g., DNAPL dissolving into the aqueous phase). Hence, treatment of the contaminants where DNAPLs are present would be limited by low solubilities of target contaminants [11,27].

In the subsurface, where the presence of DNAPLs could provide a continuous source for groundwater contamination, the use of surfactants to increase the contaminant solubility and enhance the performance of the pump-and-treat method has been successfully demonstrated in the laboratory and in the field [28-32]. If the introduction of suitable chemicals (e.g., surfactant) to increase the aqueous contaminant concentration can be combined with ISCO, the increased solubility may result in an increased effective contact between the oxidant and the contaminant within the aqueous phase and thereby accelerate the oxidation reaction [8,24,33-35]. The main objective of this study was to evaluate the feasibility of remediating PCE-contaminated groundwater via persulfate oxidation activated by BOF slag) with the addition of biodegradable surfactant (Tween 80). It was expected that the addition of surfactant would increase PCE solubility and make it more available for persulfate oxidation. In addition, the kinetic equations were also derived based upon the observed experimental results.

2. Materials and methods

2.1. Materials

All chemicals used were reagent grade: PCE (\geq 99.5% purity) (Fisher Scientific, USA) and sodium persulfate (Na₂S₂O₈, min. 99.0%) from Merck (Merck KGaA Chemicals, German). The BOF slag was obtained from China Steel Corp., Taiwan and it was sieved with a No. 100 mesh sieve to remove large slag. BOF slag was washed with distilled water, dried at 200 °C in an oven, and cooled down in a desiccator before use. BOF slag was analyzed to determine the iron components (e.g., amorphous iron, extractable iron, Fe²⁺, total iron (Fe_t), and Fe³⁺). X-ray powder diffraction (XRD) was

also applied to analyze the characteristics of BOF slag. Amorphous iron concentration was quantified by ammonium oxalate extraction [36]. Extractable iron was determined using hydroxylamine chloride solution as an extract following the procedures described by Hesse [37]. The Fe²⁺ and Fe_t contents were calorimetrically determined using a HACH DR 2400 spectrophotometer, in accordance with HACH methods 8146 and 8008, respectively [38].

Biodegradable surfactant (Tween 80) was purchased from J.T. Baker, Inc. (USA) [39]. The molecular weight (g/mole) and hydrophile–lipophile balance (HLB) [calculated as HLB = wt.% EO (ethylene oxide)/5] were 166 and 13.4 for Tween 80, respectively. The critical micelle concentration (CMC) value for Tween 80 was 0.012 mM [40]. The tested groundwater was sampled from a background and uncontaminated area of a chlorinated solvents-contaminated site in southern Taiwan. The analytical procedures for groundwater analyses were described in Standard Methods [38]. Table 1 shows the characteristics of tested groundwater.

2.2. Experimental conditions and procedure

All batch experiments were performed in triplicates in a continuous stir batch reactor system (CSBR) (close system), composed of a 250-mL brown bottle with a chloride electrode inserted into the reaction solution. The initial PCE concentration was approximately 20 mg L^{-1} (after equilibration). Initial oxidation experiments were designed to determine the influence of BOF slag. Furthermore, the operating parameters included concentrations of sodium persulfate, and concentrations of Tween 80. Control tests in the absence of BOF slag, persulfate, and surfactant solution were also conducted in parallel under every experimental condition. The pH of the CSBR system was controlled by the addition of 0.1N HNO₃/NaOH at the beginning of the experiment.

Each CSBR system contained 200-mL of collected groundwater, 2 g of BOF slag (10 g L^{-1}), and various molar ratios of $S_2O_8^{2-}/T$ ween 80/PCE (e.g., 0/0/1, 5/0/1, 10/0/1, 30/0/1, 50/0/1, 30/0.5/1, 30/1/1, and 30/2/1) in the bottle sealed with a thick butyl rubber septum. In the batch experiments, different concentrations of $S_2O_8^{2-}$ (e.g., 144, 287, 861, and 1435 mg L^{-1}) were added to tested groundwater in the presence of surfactant (Tween 80). The resulting solution was mixed for a few minutes and a predetermined amount of sodium persulfate based on measured initial PCE concentration, with adjustment for volume change, was subsequently added and mixed briefly. The experiment was conducted at room temperature, and water samples were collected at different time points (e.g., 0, 10, 20, 40, 60, and 120 h) for the analysis of PCE, persulfate, chloride ion (Cl⁻), and Tween 80 during the reaction. The first-order decay constant (k_{obs} , h^{-1}) of PCE was calculated to evaluate the effect of BOF slag and surfactant addition on the persulfate reaction rate [23].

Concentrations of PCE were analyzed in accordance with EPA Method 601, using a Tekmer Purge-and Trap Model LSC 2000 with a Varian Model 3800 Gas Chromatograph. A 50 m \times 0.32 mm DB-624 capillary column with a 0.25 μ m film (J&W Sci.) was used for sample separation. Sodium persulfate concentration was determined by the iodometric method. Chloride concentrations were measured by chloride electrode (HORIBA 6560 10C, Japan). The breakage of Cl–carbon bonds and the release of chloride ion by persulfate oxidation is an index of toxic degradation of PCE. Analysis of Tween 80 extract was performed using a 6850 N gas chromatography

equipped with a flame ionization detector and a HP-1 capillary column (0.53 mm \times 30 m).

2.3. Statistical analysis

All experiments were performed and analyzed at each time point. All of the oxidation experiments were performed in triplicate. A Student's *t*-test was used to evaluate differences between the experimental and the control groups, and a level of 0.05 was used as the lower bound to determine the significance of the variation. The results are presented as the mean \pm standard deviation.

3. Results and discussion

3.1. Persulfate oxidation by with/without BOF slag

Results from the BOF slag analyses indicate that the measured extractable iron (e.g., Fe²⁺, Fe³⁺) and amorphous iron in BOF slag were approximately 48.2 and 16.5 g kg⁻¹, respectively, which could be used to continuously supply iron catalyst to activate the persulfate oxidation process. PCE oxidation by persulfate with/without the addition of BOF slag was conducted to determine the effectiveness of BOF slag (initial pH 5.3 ± 0.2) on persulfate activation. Fig. 1 presents the effect of BOF slag addition on the efficiency of PCE (with initial PCE concentration of approximately 20 mg L^{-1}) removal with the molar ratio of 30/1 of $S_2O_8^{2-}/PCE$. In the experiment without BOF slag, the PCE concentrations dropped from 20 to 17 mg L^{-1} (15% of PCE removal) after 120 h of reaction. On the other hand, the results show that approximately 31% of PCE was removed in experiments with BOF slag dosages of 10 g L^{-1} after 120 h of oxidation reaction. Chemical activation of persulfate with BOF slag addition is a potential approach over a single persulfate addition (without BOF slag addition). Results of this study reveal that BOF slag contained a significant amount of Fe²⁺, which could be used to continuously supply iron catalyst to activate the persulfate oxidation process for the oxidation of PCE. Similar researches [20-22] have pointed out that large amounts of Fe₂O₃ and FeO are present in the BOF slag, and thus, can be used repeatedly for iron supplement. This study has also demonstrated that the addition of BOF slag is a feasible method to enhance the treatment efficiency of PCE-contaminated groundwater.



Fig. 1. Effect of BOF slag addition on the efficiency of PCE removal with the molar ratios of 30/1 of $S_2O_8^{2-}$ /PCE; conditions: [PCE]₀ ≈ 20 mg L⁻¹, [Tween 80]₀ = 0 mg L⁻¹, initial pH 5.3 \pm 0.2.



Fig. 2. Influence of persulfate concentrations on PCE degradation in groundwater over 120 h reaction; Conditions: $[PCE]_0 \approx 20 \text{ mg } L^{-1}$, $[Tween 80]_0 = 0 \text{ mg } L^{-1}$, BOF slag dosages = 10 g L⁻¹, initial pH 5.3 ± 0.2.

3.2. PCE removal with varying $S_2O_8^{2-}$ /PCE ratios

Fig. 2(a) and (b) present the efficiencies of PCE (with initial PCE concentration of approximately 20 mg L⁻¹) removal versus reaction time with different molar ratios of $S_2O_8^{2-}/PCE$ (e.g., 0/1, 5/1, 10/1, 30/1, and 50/1) without surfactant addition (BOF slag = 10 g L^{-1} and pH 5.3 \pm 0.2). Results indicate that approximately 4%, 10%, 17%, 31%, and 32% of PCE removal were observed for the molar ratios of S₂O₈²⁻/PCE 0/1, 5/1, 10/1, 30/1, and 50/1, respectively after 120 h of reaction [Fig. 2(a)]. Moreover, the increase in k_{obs} values of PCE was observed when the persulfate concentration increased. In the presence of 10 g L^{-1} of BOF slag, the k_{obs} values were found to be 3×10^{-4} , 9×10^{-4} , 1.5×10^{-3} , 3.1×10^{-3} , and $3.3 \times 10^{-3} \text{ h}^{-1}$, and half-life values were 2310, 770, 462, 224, and 210 h, as the S₂O₈²⁻/PCE molar ratios were 0/1, 5/1, 10/1, 30/1, and 50/1, respectively [Fig. 2(b) and Table 2]. As shown in Fig. 2(b), the overall kinetic data indicate that the degradation rate of PCE can be characterized by a first-order reaction kinetic model (with a correlation coefficient, $R^2 = 0.9486$) (data presented in Table 2). Results indicate that the PCE oxidation can be enhanced under conditions of higher persulfate concentration. Results from this study are in agreement with those from other studies [23,24,41]. Although a molar ratio of 30/1 shows less removal efficiency than $S_2O_8^{2-}/PCE 50/1$, it was selected in the following batch study of persulfate oxidation experiments because it is more cost effective.

Trials	S ₂ O ₈ ²⁻ /Tween 80/PCE (molar ratio)	$Na_2S_2O_8 (mgL^{-1})$	Reaction time (h)	PCE removal efficiency ^a (%)	Avg. k_{obs} (×10 ⁻³ h ⁻¹)	Avg. $t_{1/2}$ (h)	Avg. Cl [–] conc. (mg L ^{–1})	Avg. Cl− mass balance
1	0/0/1	0	120	4 ± 1	0.3	2310	0.3	0.44
	5/0/1	144	120	10 ± 1	0.9	770	0.8	0.47
	10/0/1	287	120	17 ± 1	1.5	462	2.0	0.69
	30/0/1	861	120	31 ± 1	3.1	224	4.2	0.80
	50/0/1	1435	120	32 ± 1	3.3	210	4.6	0.87
2	30/0.5/1	861	120	40 ± 1	8.7	80	6.2	0.92
	30/1/1	861	120	53 ± 2	16	44	8.7	0.96
	30/2/1	861	120	92 ± 2	58	12	15.0	0.95

 Table 2

 Results of PCE oxidation by persulfate/Tween 80/PCE.

 Cl^{-} mass balance = $[Cl^{-}]_t/[Cl^{-}$ (theoretical value)]_t.

^a Average \pm standard deviation of three replicates.

3.3. PCE removal with varying S₂O₈/Tween 80 ratios

Results of persulfate and surfactant (Tween 80) addition on PCE (with initial PCE concentration of approximately 20 mg L^{-1}) degradation are shown in Fig. 3. The degradation rates, reaction rate constants, and half-life values of PCE that employed various molar ratios of $S_2O_8^{2-}$ /Tween/PCE are shown in Table 2. Fig. 4 presents the influence of Tween 80 concentrations on averaged PCE and persulfate remaining over 120 h of reaction. Fig. 3 depicts that the efficiencies of PCE degradation with surfactant (Tween 80) additions were 31%, 40%, 53%, and 92% when the molar ratios of



Fig. 3. Influence of Tween 80 concentrations on (a) PCE degradation and (b) persulfate decomposition in groundwater over 120 h reaction; conditions: $[PCE]_0 \approx 20 \text{ mg L}^{-1}$, BOF slag dosages = 10 g L^{-1} , initial pH 5.3 ± 0.2.

 $S_2O_8^{2-}$ /Tween 80 were 30/0, 30/0.5, 30/1, and 30/2, respectively. The results indicate that the effect of surfactant addition on the enhancement of PCE degradation was significant. Compared with the results shown in Fig. 1, results from Fig. 3 imply that PCE oxidation could be significantly enhanced with the addition of reasonable amount of surfactant (Tween 80). Results show that approximately 31% of PCE removal was observed in experiment without the addition of surfactant (Tween 80) (only with $S_2O_8^{2-}$ and BOF slag addition). However, up to 92% of PCE removal was observed with the presence of $315 \, \text{mgL}^{-1}$ of Tween 80 ($S_2O_8^{2-}$ /Tween 80/PCE = 30/2/1) and $10 \, \text{gL}^{-1}$ BOF slag.

The overall reaction between PCE and persulfate can be written as a first-order reaction if the PCE dissolution rate is faster than its degradation rate. In the presence of 10 g L^{-1} BOF slag, the k_{obs} values of PCE were found to be 3.1×10^{-3} , 8.7×10^{-3} , 1.6×10^{-2} and $5.8 \times 10^{-2} \text{ h}^{-1}$, and half-life values were 224, 80, 44 and 12 h, as the $\text{S}_2\text{O}_8^{2-}$ /Tween 80 molar ratios were 30/0, 30/0.5, 30/1, and 30/2, respectively (see Table 2). The reaction rate constant increased as the Tween 80 concentration increased. The significantly increased k_{obs} might be induced by the enhanced solubilization of PCE by Tween 80.

In the case of a $S_2O_8^{2-}$ /Tween 80/PCE molar ratio of 30/2/1, PCE degradation and persulfate decomposition were 92% and 90%, respectively, after 120 h of reaction (Fig. 4). Results indicate that the addition of Tween 80 would cause the decrease in persulfate concentrations and increase in oxidation efficiencies of PCE after reaction. Fig. 5 presents the remaining of Tween 80 and persulfate consumption during the oxidation processes (molar ratios for $S_2O_8^{2-}$ /Tween 80 = 30/2, Tween 80 = 315 mg L⁻¹) without PCE addition. Results from Fig. 5 show that Tween 80 concentrations dropped from 315 to 267 mg L⁻¹ (15% of Tween 80 removal), and persulfate consumption also dropped from 861 to 753 mg L⁻¹ (12% of persulfate consumption) after 120 h of reaction with the presence



Fig. 4. Influence of Tween 80 concentrations on averaged PCE and persulfate remaining over 120 h reaction; conditions: [PCE] ≈ 20 mg L⁻¹, BOF slag dosages = 10 g L⁻¹, initial pH 5.3 \pm 0.2.



Fig. 5. Remaining of Tween 80 and persulfate consumption during the oxidation processes; conditions: $S_2O_8^{2-}$ /Tween 80 molar ratios = 30/2, [Tween 80]₀ = 315 mg L⁻¹, [PCE]₀ = 0 mg L⁻¹, BOF slag dosages = 10 g L⁻¹, initial pH 5.3 ± 0.2.

of 315 mg L⁻¹ of Tween 80 ($S_2O_8^{2-}/T$ ween 80 = 30/2) and 10 g L⁻¹ of BOF slag without PCE addition. Results indicate that the addition of high concentration of Tween 80 (315 mg L⁻¹) might also hinder persulfate from contacting with PCE, and thus, caused the decrease in oxidation efficiency of PCE (Fig. 4).

3.4. Degradation of PCE oxidation byproducts chloride ion

Fig. 6 presents the influence of Tween 80 concentrations on the amounts of chloride ion generated in groundwater over 120 h of reaction (with initial PCE concentration of approximately 20 mg L⁻¹). The oxidative dechlorination of PCE was demonstrated with the increse of chloride production when surfactant (Tween 80) was added. Without surfactant addition $(S_2O_8^{2-}/Tween$ 80/PCE = 30/0/1), PCE concentration dropped from 20 to 14 mg L^{-1} while the chloride concentation increased from 0 to 4.2 mg L^{-1} . The amount of chloride generated increased as the initial surfactant concentration increases, reflecting a higher amount of PCE solubilized in the presence of a higher surfactant concentration (see Fig. 6). The production of chloride ion, and decreased PCE concentration in the batch experiment confirmed the occurrence of PCE oxidation. Results indicate that PCE concentrations dropped from 20 to 1.5 mg L⁻¹, and chloride concentations increased from 0 to 15.0 mg L^{-1} after 120 h of reaction with the presence of 315 mg L^{-1} of Tween 80 ($S_2O_8^{2-}/T$ ween 80/PCE = 30/2/1) and 10 g L⁻¹ of BOF slag.

Because the molecular weight of PCE consists of 84% of chloride and the initial PCE concentration in this experiment was 20 mg L^{-1} , approximately 17.1 mg of chloride per liter during PCE oxidation would be detected in the reactor at the end of the experiments if PCE was completely oxidized to CO₂ and H₂O. Results show that 15.0 and 1.5 mg L⁻¹ of chloride and PCE concentrations were detected in the reactor. This indicates that approximately 15.8 mg L⁻¹ of chloride ion should be detected theoretically. In the control experiments, 0.3 mg L⁻¹ of chloride ion concentration was detected at the end of the experiment (data not shown). Thus, the calculated variation between the theoretical chloride concentrations, observed chloride concentration, observed chloride mass balance, and observed chloride concentration in control experiment was 0.3 mg L^{-1} (see Table 2). This indicates that the depletion of PCE corresponded with the oxidation reactions and release of chloride ions very well in this study. Experimental results demonstrate that surfactant (Tween 80) enhanced the mass transfer of PCE from NAPL to the dissolved phase, and made it more amenable for destruction in the dissolved phase by chemical oxidation process. Results from this study also



Fig. 6. Influence of Tween 80 concentrations on chloride generated in groundwater over 120 h reaction (a) Cl⁻ concentration (b) avg. Cl⁻ mass balance; Conditions: $[PCE]_0 \approx 20 \text{ mg L}^{-1}$, BOF slag dosages = 10 g L^{-1} , Initial pH 5.3 ± 0.2.

reveal that the combination of persulfate with a proper type of surfactant can improve the efficiency of contaminant oxidation in situ. This indicates that combining surfactant-enhanced persulfate oxidation is a promising technology to remediate PCE-contaminated groundwater in a synchronized "flush-while-treat" step.

4. Conclusions

The application of biodegradable surfactant to enhance $S_2O_8^{2-}/BOF$ slag oxidation of PCE was investigated in this study. Results indicate that the addition of BOF slag can activate persulfate oxidation, and cause approximately 31% of PCE removal in the batch experiment without the addition of surfactant (only with $S_2O_8^{2-}$ and BOF slag addition). Results also reveal that up to 92% of PCE can be oxidized if Tween 80 was present in the batch system. The amounts of PCE degraded by persulfate oxidation processes were significantly enhanced, particularly when the molar ratio of $S_2O_8^{2-}/T$ ween 80/PCE was 30/2/1. The dissolved PCE concentration could be greatly increased due to PCE solubilization by surfactant micelles. Furthermore, the concentration of chloride ion generated increased as the initial surfactant concentration increased. This indicates that a higher amount of PCE solubilized in the presence of a higher surfactant concentration. Results demonstrate that the biodegradable surfactant (Tween 80) enhanced the mass transfer of PCE from NAPL phase to the dissolved phase, and made them more amenable for destruction in the dissolved phase by chemical oxidation. This study show that it is feasible to combine surfactant-enhanced persulfate oxidation to remediate PCE-contaminated groundwater in a synchronized "flush-while-treat" remedial approach. The knowledge and comprehension obtained in this study will be helpful in designing a practical system for the in situ treatment of DNAPL-contaminated groundwater.

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References

- C.M. Kao, Y.L. Chen, S.C. Chen, T.Y. Yeh, W.S. Wu, Enhanced PCE dechlorination by biobarrier systems under different redox conditions, Water Res. 37 (2003) 4885–4894.
- [2] A. Volpe, G.D. Moro, S. Rossetti, V. Tandoi, A. Lopez, Remediation of PCEcontaminated groundwater from an industrial site in southern Italy: a laboratory-scale study, Process Biochem. 42 (2007) 1498–1505.
- [3] C.M. Kao, S.C. Chen, J.K. Liu, Development of a biobarrier for the remediation of PCE-contaminated aquifer, Chemosphere 43 (2001) 1071–1078.
- [4] F. Aulenta, A. Bianchi, M. Majone, M.P. Papini, M. Potalivo, V. Tandoi, Assessment of natural or enhanced in situ bioremediation at a chlorinated solventcontaminated aquifer in Italy: a microcosm study, Environ. Int. 31 (2005) 185–190.
- [5] T.T. Tsai, C.M. Kao, A. Hong, S.H. Liang, H.Y. Chien, Remediation of TCEcontaminated aquifer by an in situ three-stage treatment train system, Colloids Surf. A: Physicochem. Eng. Aspects 322 (2008) 130–137.
- [6] T.T. Tsai, C.M. Kao, T.Y. Yeh, M.S. Lee, Chemical oxidation of chlorinated solvents in contaminated groundwater: a review, Pract. Periodical Hazard. Toxic Radioactive Waste Manage. 12 (2) (2008) 116–126.
- [7] L.K. MacKinnon, N.R. Thomson, Laboratory-scale in situ chemical oxidation of a perchloroethylene pool using permanganate, J. Contam. Hydrol. 56 (1/2) (2002) 49–74.
- [8] Z. Li, Surfactant-enhanced oxidation of trichloroethylene by permanganate-proof of concept, Chemosphere 54 (2004) 419-423.
- [9] C.K.J. Yeh, C.Y. Hsu, C.H. Chiu, K.L. Huang, Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes, J. Hazard. Mater. 151 (2008) 562–569.
- [10] I.M. Kolthoff, A.I. Medalia, H.P. Raaen, The reaction between ferrous iron and peroxides. IV. Reaction with potassium persulfate, J. Am. Chem. Soc. 73 (1951) 1733–1739.
- [11] ITRC (Interstate Technology Regulatory Council), Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Interstate Technology and Regulatory Council, Washington, DC, 2005.
- [12] S.G. Huling, B.E. Pivetz, In-situ Chemical Oxidation. USEPA/600/R-06/072, 28 358 July, 2006.
- [13] K.C. Huang, R.A. Couttenye, G.E. Hoag, Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE), Chemosphere 49 (2002) 413–420.
- [14] G.P. Anipsitakis, D.D. Dionysiou, Transition metal/UV-based advanced oxidation technologies for water decontamination, Appl. Catal. B: Environ. 54 (2004) 155–163.
- [15] C. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ remediation of TCE I-activated by ferrous ion with and without a persulfatethiosulfate redox couple, Chemosphere 55 (2004) 1213–1223.
- [16] C. Liang, I.L. Lee, I.Y. Hsu, C.P. Liang, Y.L. Lin, Persulfate oxidation of trichloroethylene with and without iron activation in porous media, Chemosphere 70 (2008) 426–435.

- [17] R.A. Brown, D. Robinson, G. Skladany, Response to Naturally Occurring Organic Material: Permanganate versus Persulfate. ConSoil 2003, Ghent, Belgium, 2003.
- [18] P.A. Block, R.A. Brown, D. Robinson, Novel activation technologies for sodium persulfate in situ chemical oxidation, in: Proceedings of the 4th International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterrey, CA, 2004.
- [19] C.S. Chiou, F.S. Chang, C.Y. Chang, C.T. Chang, Y.L. Li, Degradation of 2naphthalenesulfonate in aqueous solution by hydrogen peroxide in the presence of basic oxygen furnace slag, J. Chin. Inst. Chem. Eng. 35 (2004) (2004) 285–292.
- [20] C.S. Chiou, Application of steel waste with UV/H_2O_2 to mineralize 2-naphthalenesulfonate in aqueous solution, Sep. Purif. Technol. 55 (2007) 110–116.
- [21] Y.S. Li, The use of waste basic oxygen furnace slag and hydrogen peroxide to degrade 4-chlorophenol, Waste Manage. 19 (1999) 495–502.
- [22] C.S. Chiou, C.F. Chang, C.T. Chang, J.L. Shie, Y.H. Chen, Mineralization of reactive black 5 in aqueous solution by basic oxygen furnace slag in the presence of hydrogen peroxide, Chemosphere 62 (2006) 788–795.
- [23] C. Liang, Z.S. Wang, C.J. Bruell, Influence of pH on persulfate oxidation of TCE at ambient temperatures, Chemosphere 66 (2007) 106–113.
- [24] C. Liang, C.F. Huang, N. Mohanty, C.J. Lu, R.M. Kurakalva, Hydroxypropyl-âcyclodextrin-mediated iron-activated persulfate oxidation of trichloroethylene and tetrachloroethylene, Ind. Eng. Chem. Res. 46 (2007) 6466–6479.
- [25] T.-J. Kim, C.V. Chrysikopoulos, Mass transfer correlations for nonaqueous phase liquid pool dissolution in saturated porous media, Water Resour. Res. 35 (2) (1999) 449–459.
- [26] C.V. Chrysikopoulos, P.-Y. Hsuan, M.M. Fyrillas, K.Y. Lee, Mass transfer coefficient and concentration boundary layer thickness for a dissolving NAPL pool in porous media, J. Hazard. Mater. B97 (2003) 245–255.
- [27] S.H. Conrad, R.J. Glass, W.J. Peplinski, Bench-scale visualization of DNAPLs remediation processes in analog heterogeneous aquifers: surfactant floods and in situ oxidation using permanganate, J. Contam. Hydrol. 58 (2002) 13–49.
- [28] V. Dwarakanath, K. Kostarelos, G.A. Pope, D. Shotts, W.H. Wade, Anionic surfactant remediation of soil columns contaminated by nonaqueous phase liquids, J. Contam. Hydrol. 38 (1999) 465–488.
- [29] G.A. Loraine, Effects of alcohols, anionic and nonionic surfactants on the reduction of PCE and TCE by zero-valent iron, Water Res. 35 (6) (2001) 1453–1460.
- [30] Z. Li, C. Willms, J. Alley, P. Zhang, R.S. Bowman, A shift in pathway of ironmediated perchloroethylene reduction in the presence of sorbed surfactant-A column study, Water Res. 40 (2006) 3811–3819.
- [31] K.S. Kim, T.S. Kwon, J.S. Yang, J.W. Yang, Simultaneous removal of chlorinated contaminants by pervaporation for the reuse of a surfactant, Desalination 205 (2007) 87–96.
- [32] A.J. Kaye, J. Cho, N.B. Basu, X. Chen, M.D. Annable, J.W. Jawitz, Laboratory investigation of flux reduction from dense non-aqueous phase liquid (DNAPL) partial source zone remediation by enhanced dissolution, J. Contam. Hydrol. 102 (2008) 17–28.
- [33] X. Zhai, I. Hua, P.S.C. Rao, L.S. Lee, Cosolvent-enhanced chemical oxidation of perchloroethylene by potassium KMnO₄, J. Contam. Hydrol. 82 (2006) 61–74.
- [34] Z. Li, H. Hanlie, Combination of surfactant solubilization with permanganate oxidation for DNAPL remediation, Water Res. 42 (2008) 605–614.
- [35] T.T. Tsai, C.M. Kao, T.Y. Yeh, S.H. Liang, H.Y. Chien, Application of surfactant enhanced permanganate oxidation and bidegradation of trichloroethylene in groundwater, J. Hazard. Mater. 161 (2009) 111–119.
- [36] J.A. Mckeague, J.H. Day, Dithionite and oxalate extractable Fe and Al as acids in different various classes of soils, Can. J. Soil. Sci. 46 (1966) 13–22.
- [37] P.R. Hesse, Textbook of Soil Chemical Analysis, Chemical Publishing Company, New York, 1971, 332.
- [38] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA-AWWA-WEF, Washington, DC, 2001.
- [39] A. Franzetti, P.Di. Gennaro, G. Bestetti, M. Lasagni, D. Pitea, E. Collina, Selection of surfactants for enhancing diesel hydrocarbons-contaminated media bioremediation, J. Hazard. Mater. 152 (3) (2007) 1309–1316.
- [40] I.S. Kim, J.S. Park, K.W. Kim, Enhanced biodegradation of polycyclic aromatic hydrocarbons using nonionic surfactants in soil slurry, Appl. Geochem. 16 (2001) 1419–1428.
- [41] C. Liang, I.L. Lee, In situ iron activated persulfate oxidative fluid sparging treatment of TCE contamination-A proof of concept study, J. Contam. Hydrol. 100 (2008) 91–100.