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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 $S_2O_8^{2-}$/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.

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].

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

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

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

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

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	pH	Nitrate ($mg\,L^{-1}$)	Fe_t ($mg\,L^{-1}$)	Fe^{2+} ($mg\,L^{-1}$)	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 Fe_2O_3, FeO, CaO, SiO_2, SO_3, Al_2O_3, TiO_2, CaO, MgO, SiO_2, P_2O_5, and MgO due to their mass percentage. There is 5–20% of FeO and 1–8% of Fe_2O_3 present in the BOF slag [21,22]. Furthermore, FeO can be dissociated to produce Fe^{2+} in aqueous solution, and the released Fe^{2+} has the potential to react with persulfate to produce $SO_4^{-\bullet}$ 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 mass-transfer 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 (≧99.5% purity) (Fisher Scientific, USA) and sodium persulfate ($Na_2S_2O_8$, 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, Fe^{2+}, total iron (Fe_t), and Fe^{3+}). 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 Fe^{2+} 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 HNO_3/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 $S_2O_8^{2-}$/Tween 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 × 0.32 mm DB-624 capillary column with a 0.25 μm 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