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Remediation of phenol-contaminated groundwater using in situ Fenton and persulfate oxidation: performance and mechanism studies

Zong-Han Yang[a], Yih-Terng Sheu[b], Cheng-Di Dong[c], Chiu-Wen Chen[c], Shaohua Chen[d], Chih-Ming Kao[b,*]

[a]*Apollo Technology Co. Ltd., Kaohsiung, Taiwan*
[b]*Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, Tel. +886-935989780; Fax: 886-7-5254449; email: jkao@mail.nsysu.edu.tw (C.-M. Kao)*
[c]*Department of Marine Environmental Engineering, National University of Kaohsiung Science and Technology, Kaohsiung, Taiwan*
[d]*Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China*

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ABSTRACT

In this study, batch and column experiments were conducted to investigate the optimal operation conditions and kinetics for phenol-contaminated groundwater remediation by in situ chemical oxidation (ISCO) using hydrogen peroxide (H_2O_2) and sodium persulfate ($Na_2S_2O_8$) as oxidants. The major control factors included molar ratios of oxidant to phenol, phenol decay rate, soil oxidant demand (SOD), and catalyst additions. Results show that higher concentrations of H_2O_2 and persulfate oxidants caused higher phenol oxidation rates. Increased phenol removal rate was achieved with an increased oxidant to phenol molar ratio and extended reaction time. When [oxidant]/[phenol] was 300, the calculated pseudo-first-order decay rate constant (k') for phenol were 3.44×10^{-2} and 2.31×10^{-2} ($\min^{-1}$) when H_2O_2 and persulfate were used as oxidants with ferrous iron catalyst, respectively. Results from SOD tests reveal that persulfate was more stable and persistent than H_2O_2 in the presence of natural soil organic matters without ferrous iron catalyst. Thus, using persulfate as the oxidant for ISCO application would be a more practical approach when site soils contain high organic matters. Results from the column experiment show that up to 93% of phenol removal (initial concentration = 1 mg/L) could be obtained after flushing with 1.4 pore volumes of activated persulfate solution with a flow rate of 1.5 mL/min (persulfate = 315 mM and molar ratio of persulfate to ferrous iron = 10:1). An increased oxidant concentration also resulted in a decreased half-life of phenol. Thus, the oxidation rate would be affected by the initial oxidant concentrations. The findings would be useful in developing an ISCO system for a practical field application to cleanup phenol-contaminated groundwater.

Keywords: Fenton reaction; Groundwater contamination; In situ chemical oxidation (ISCO); Persulfate; Phenol

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1. Introduction

Phenol and its derivatives are commonly found organic chemicals in soils and groundwater at hazardous substance spill sites or hazardous waste dumping sites worldwide [1]. Phenol is likely to move down to groundwater zone from the spill locations due to its high solubility (83 g/L (46 times higher than benzene)) and short half-life (<5 d) in soils. Phenol may exist longer periods in groundwater as it consistently released from point sources [1]. Phenol and phenolic compounds (such as 2,4,5-trichlorophenol,

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* Corresponding author.

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pentachlorophenol and polychlorinated biphenyls) are very toxic and harmful for human health and ecosystems [2,3].

There are various novel ways could treat organic or non-organic compounds in water. Xiong et al. [4] used the Mg/Al layered double hydroxide-poly(m-phenylenediamine) (LDH-PmPD) composite to adsorb diclofenac sodium in medical wastewater [4]. Xiong et al. [5] used a novel magnesium silicate-hydrothermal carbon composite (MS-C) to remove the cadmium (Cd(II) and methylene blue (MB) from wastewater [5]. Wang et al. [6] studied the application of covalent organic frameworks [6]. Beside these treatment ways, researchers also studied extensive ways to treat phenol in water [7–10], but the completed methods for phenol-contaminated groundwater remediation are rare. Therefore, development of an effective remedial approach to treat groundwater contaminated by phenol is the purpose of this study.

In situ chemical oxidation (ISCO) is a commonly used technology to remediate soil and groundwater contaminated by organic compounds. When ISCO is applied, oxidants are injected into the subsurface to process chemical oxidation to destruct contaminants to non-toxic products. Compared to biological treatment technologies, ISCO can reach a more efficient contaminant removal rate. It can also minimize contaminant dispersion and lower the overall remediation cost [11–13]. Among the ISCO systems, Fenton reaction is a commonly used approach to oxidize organic compounds into less toxic products in groundwater [11,13–16]. During the Fenton reaction process, hydrogen peroxide (H_2O_2) can generate hydroxyl radical ($HO^{\bullet}$) or superoxide ($O_2^{\bullet}$) (E^0 = 1.8–2.8 V) with the supplement of ferrous iron (Fe^{2+}) catalysis into hydrogen peroxide solution [17,18]. Hydrogen peroxide can react with hydroxyl radical to produce $HO^{\bullet}$ or $HOO^{\bullet}$. In the presence of a ferrous iron, it can be oxidized by $HO^{\bullet}$ and produce Fe^{3+} (Eq. (1)). When an organic compound (RH) presents in Fenton reaction, it can be oxidized to $R^{\bullet}$ and H_2O (Eq. (2)). Following the reaction described in Eq. (3), $R^{\bullet}$ can reduce Fe^{3+} to Fe^{2+} when Fe^{3+} is excess in the reaction system [8,10,16,19].

Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HOO^{\bullet}$$

$$H_2O_2 + HOO^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + HO^{\bullet}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow OH^{-} + Fe^{3+} \qquad E^0 = 2.8\ \text{V} \tag{1}$$

Organic compound reacting with hydroxyl radical:

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{2}$$

Reaction with Fe^{3+}:

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + \text{product}$$

$$RO^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^{+} + \text{product} \tag{3}$$

Several studies have demonstrated that Fenton reaction could efficiently oxidize various organic contaminants in groundwater [20]. For example, Liang et al. [20] reported that up to 86% of methyl tertiary-butyl ether (MTBE) could be removed from MTBE-contaminated groundwater using Fenton reagent (hydrogen peroxide + ferrous iron) in a column study. Nazari et al. [16] used the electro-Fenton reaction to remove 96% of chlorobenzene in a batch reactor. Approximately 91% of diesel contaminant could be reduced by the Fenton oxidation mechanism in the laboratory batch experiment [21]. However, results of Fenton reaction are affected by pH, and oxidation efficiency decreases rapidly when pH is above 5. Thus, the pH value is a key factor in Fenton reaction [15,22].

Recently, application of persulfate (PS) oxidation for the remediation of organic contaminant polluted groundwater has been applied in many contaminated sites [23–25]. Peroxydisulfate ($S_2O_8^{2-}$), often referred to as persulfate, is a strong oxidant, which can be activated with ferrous iron for the production of sulfate radicals ($SO_4^{-\bullet}$) (E^0 = 2.6–3.1 V) (Eq. (4)) [26–29]. Its strong oxidation ability can degrade enormous organic compounds under ideal conditions following the reaction presented in Eq. (5) [25,30,31]. Researchers have suggested that sulfate radical is more stable than other oxidants (e.g., O_3, H_2O_2), and thus, it can exist in the subsurface environment for a longer period of time [12,32,33]. Therefore, it has more opportunities to contact with organic compounds to enhance the degradation efficiency [23,29,31,34]. In addition, persulfate has a lower affinity to natural organic matters (NOM), and thus, it can be applied to remediate contaminated sites with higher NOM [23,29,31,34].

Chemical activation using Fe^{2+}:

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

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \qquad E^0 = 2.6\text{–}3.1\ \text{V} \tag{4}$$

Organic compounds reacting with sulfate radical:

$$RH + SO_4^{-\bullet} \rightarrow R^{\bullet} + SO_4^{2-} \rightarrow CO_2 + H_2O \tag{5}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+}$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{6}$$

$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow SO_4^{2-}$$

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + SO_4^{2-} \tag{7}$$

In this study, hydrogen peroxide and persulfate were used to oxidize phenol to cleanup phenol-contaminated groundwater. The principal objectives of this study were to: (1) investigate the occurrence and effectiveness of self-decomposition of hydrogen peroxide and persulfate during the remediation process, (2) evaluate the soil oxygen demand (SOD) effects of hydrogen peroxide and persulfate, (3) determine the kinetics of phenol oxidation, and (4) determine the operational conditions for in situ practical application of hydrogen peroxide and persulfate oxidation via a column study.

2. Materials and methods

2.1. Materials

Pharma and analytical grade chemicals were used in this study. Phenol (90%, pharma grade, an ITW Company, Germany) was selected as the contaminant. H_2O_2 (30%, Ferak Laborat GMBH, Germany) and sodium persulfate ($Na_2S_2O_8$, min. 99%, Riedel-de Haën, Germany) were used as the oxidants. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$, min. 99.5%, Riedel-de Haën, Germany) was used as the activator to catalyze hydrogen peroxide and persulfate in this study.

2.2. Batch oxidation experiments

In the batch tests, 250 mL-serum bottles (batch reactors) were used to carry out the oxidation experiments. The reactors were covered and wrapped with aluminum foil and capped with lids to prevent the photolysis effects. Four groups of batch oxidation tests were conducted to determine the effects of different control factors on phenol oxidation efficiency.

Table 1 presents the control factors and components of four groups of tests. The objectives of the batch tests included the following: (1) depletion of H_2O_2 and $Na_2S_2O_8$ in water, (2) the SOD of H_2O_2 and $Na_2S_2O_8$ in soils, (3) the efficiency of phenol oxidation by H_2O_2 and $Na_2S_2O_8$, and (4) efficiency of phenol oxidation by H_2O_2 and $Na_2S_2O_8$ with ferrous iron catalyst. Triplicate samples of each group were samples and analyzed at each time point. Soils and solution used in this study were sterilized to prevent the occurrence of biological effect.

Group 1 of batch experiments was conducted with different concentrations of H_2O_2 or $Na_2S_2O_8$ (21, 105, and 315 mM). Water samples were analyzed for oxidant concentrations periodically during the 180 min operational period. Each reactor in Group 2 was contained different concentrations of H_2O_2 or $Na_2S_2O_8$ (21, 105, and 315 mM) and 30 g site soils. Water samples collected from the reactors were analyzed for oxidant concentrations periodically to evaluate the SOD values during the 180 min operational period. Table 2 presents the characteristics of soils collected from a background area of the saturated zone at a phenol-contaminated groundwater site. In Group 3, the reactors contained different concentrations of H_2O_2 or $Na_2S_2O_8$ (21, 105, and 315 mM), and 1 mg/L of phenol. In Group 4 reactors, except for the oxidants and phenol (same with Group 3), ferrous iron was also added to catalyze oxidants (the ratio of oxidant to ferrous was 10:1). Water samples collected from the reactors were analyzed for phenol concentrations to determine the effectiveness of oxidation mechanisms on phenol removal. The kinetics of phenol oxidation was also calculated.

Table 2
Characteristics of the studied groundwater and soils in laboratory experiments

Media	Parameter	Value
Soil	pH	8.90
	Oxidation reduction potential (mV)	55
	Electronic capacity (μS/cm)	106
	Total organic matter (%)	7.39
	Sand (%)	0.00
	Silt (%)	63.67
	Clay (%)	36.33
Groundwater	pH	7.76
	Oxidation reduction potential (mV)	94
	Electronic capacity (μS/cm)	502
	Total organic carbon (mg/L)	0.63
	Chloride (mg Cl^-/L)	124
	Sulfate (mg SO_4^{2-}/L)	54
	Manganese (Mn) (mg/L)	2.70
	Ferrous iron (mg Fe^{2+}/L)	0.01
	Total Iron (mg Fe/L)	18.2

2.3. Column study

The column study was operated to simulate the practical application of the oxidation system to cleanup site groundwater polluted by phenol. Fig. 1 presents the column system developed to assess the effectiveness of ISCO application on phenol-contaminated groundwater remediation.

Each glass column had a dimension of 25 cm in length and 5 cm in inside diameter. A peristaltic pump (Cole Parmer MasterFlex L/S®, USA) was used to pump phenol-contaminated groundwater to the column system. Each glass column was filled with clean aquifer soils and approximately 2.8 pore volumes (PVs) of influents (site groundwater with phenol addition (phenol concentration = 1.1 mg/L)) were pumped through the column system to equilibration of the column system (flow rate = 1.5 mL/min) (Stage 1).

Table 1
Objectives and operational conditions of batch phenol oxidation experiments

Group	Objective	Control factor	Components
1	Natural oxidant decay in a water system	[oxidant] = 21, 105 and 315 mM	100 mL of oxidant
2	Effect of SOD on H_2O_2 and $Na_2S_2O_8$ oxidation	[oxidant] = 21, 105 and 315 mM	100 mL of oxidant + 30 g of soil
3	Efficiency of phenol oxidation by H_2O_2 and $Na_2S_2O_8$	[oxidant] = 21, 105 and 315 mM	100 mL of deionized water + (H_2O_2 or persulfate) + 1 m/L of phenol
4	Efficiency of phenol oxidation by H_2O_2 and $Na_2S_2O_8$ with ferrous iron catalyst	[oxidant] = 21, 105 and 315 mM [oxidant]:[ferrous] = 10:1	100 mL of deionized water + (H_2O_2 or persulfate) + ferrous iron + 1 mg/L of phenol

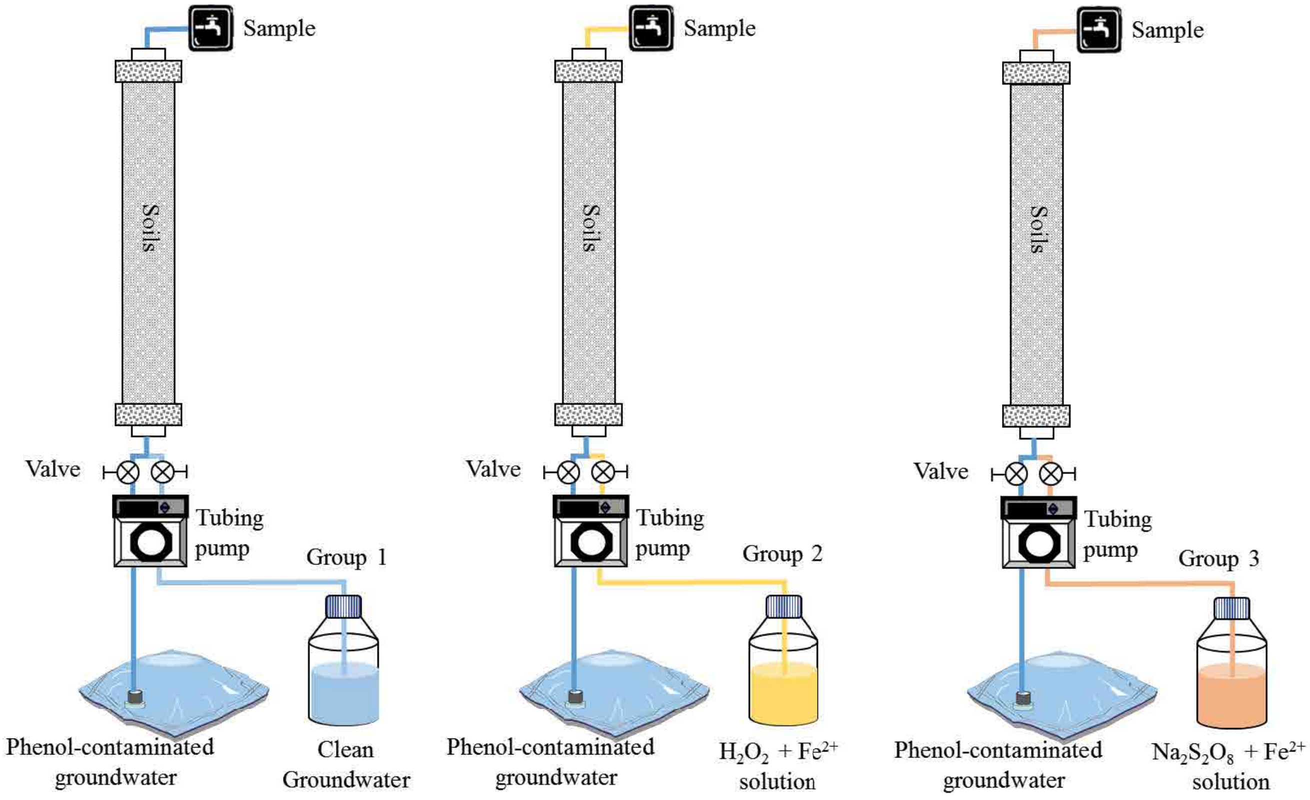

Fig. 1. Schematic diagram showing the layout of the column experiment.

After equilibration with phenol-contaminated groundwater, the column experiment was operated by pumping three different influent solutions (Groups 1 to 3) into the column system. Three influent solutions were used for Groups 1 to 3, respectively: (1) clean groundwater, (2) H_2O_2 + Fe^{2+} (H_2O_2 concentration = 315 mM, molar ratio of $[H_2O_2]/[Fe^{2+}]$ = 10:1), and (3) $Na_2S_2O_8$ + Fe^{2+} ($Na_2S_2O_8$ concentration = 315 mM, molar ratio of $[Na_2S_2O_8]/[Fe^{2+}]$ = 10:1). Table 2 shows the components and characteristics of the collected groundwater used for the column study. Effluents of each column system were collected and analyzed for phenol concentrations. Table 3 presents the operational conditions of the column study.

2.4. Analytical methods

The H_2O_2 concentrations were determined by iodometric titration with 0.1 N sodium thiosulfate [11]. Sodium persulfate concentration was determined by the colorimetric method [35]. In addition, the oxidation-reduction potential (ORP) (InLab 501) and pH (InLab 415) values were measured by a pH/ORP meter (Meter MP120). The phenol analysis was performed in accordance with National Institute of Environmental Analysis procedures W521.52A. The pH of the water samples was adjusted to pH 10 after distillation. The 4-aminoantipyrine and potassium ferricyanide were added into the solution to generate antipyrine. Chloroform was used to extract antipyrine, which was measured by an atomic absorption spectrophotometer (HACH, DR-4000U, Loveland, CO, USA) at 460 nm [36].

3. Results and discussion

3.1. Oxidant depletion experiments

In this study, H_2O_2 and $Na_2S_2O_8$ concentrations were monitored to assess their depletion in natural environment. The remaining H_2O_2 concentrations (C/C_0) in water phase with different initial concentrations are shown in Fig. 2a. Results show that a significant H_2O_2 depletion was not detected (H_2O_2 depletion <1%) in reactors with water only during the 180 min reaction period. Results reveal that H_2O_2 was relatively stable in systems without organic compounds. Fig. 2b presents the variations in $Na_2S_2O_8$ concentrations during the reaction period. Again, less than 1% of $Na_2S_2O_8$ depletion was observed in in systems with water only. This indicates that $Na_2S_2O_8$ was also stable when organic carbon was absent.

3.2. Effects of soil organic matters on oxidant consumption

Soil organic matter plays an important role in the practical application of ISCO for site remediation. Soil organic matters could consume a significant amount of oxidant during the oxidation process [13,37]. Because soil organic matters could reduce the availability of oxidants to target organic contaminants, the oxidation efficiency for phenol would be reduced. Fig. 3 shows the remaining H_2O_2 (Fig. 3a) and persulfate concentrations (Fig. 3b) in reactors with different concentrations of oxidants (21, 105 and 315 mM).

Results show that the remaining H_2O_2 concentrations (C/C_0) dropped to 1.3%, 5.2% and 18%, respectively, after

Table 3
Operational conditions of the column experiment

Parameters	Value
Pore volume (mL)	186.4
Soil density (g/cm^3)	1.796
Porosity	0.45
Packed height (cm)	23
Flow rate (mL/min)	1.5

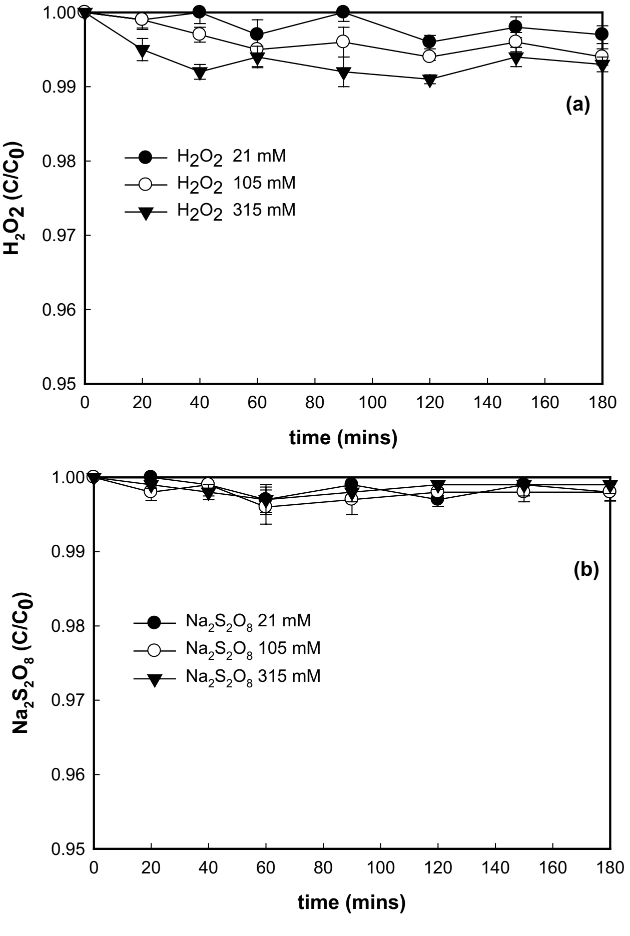

Fig. 2. Remained (a) H_2O_2 and (b) $Na_2S_2O_8$ concentrations.

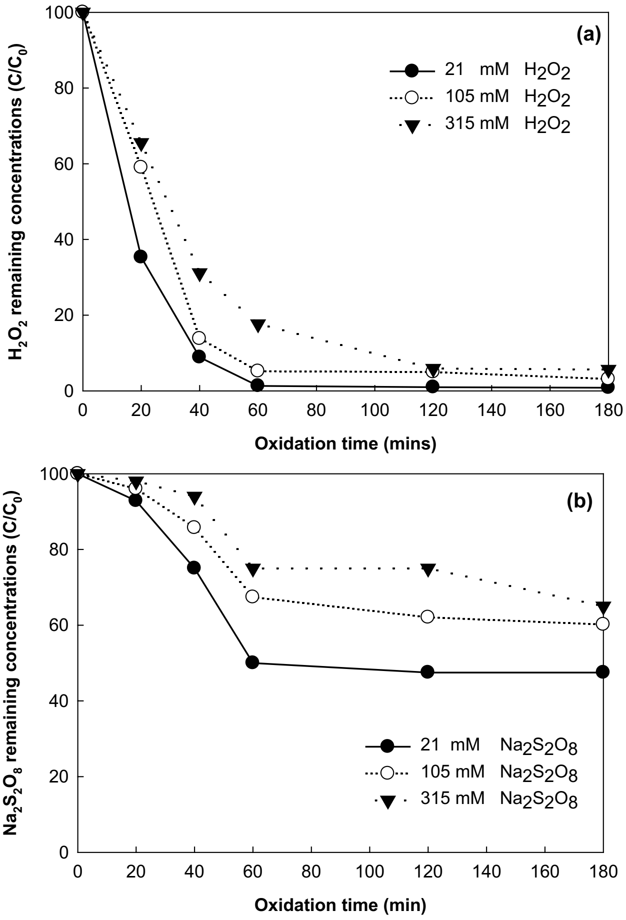

Fig. 3. Variations in remained (a) H_2O_2 and (b) $Na_2S_2O_8$ concentrations.

60 min of operation. The remaining persulfate concentrations (C/C_0) dropped to 51%, 67% and 75%, respectively, after 60 min of operation. These results indicate that persulfate was more stable than H_2O_2 in soil systems. Moreover, more residual oxidant doses were observed with increased oxidant concentrations. This result reveals that persulfate was more appropriate as an oxidant for ISCO remediation than H_2O_2 due to persulfate had a better stability and durability in the presence of soil organic matter.

The measured SOD values were 0.07, 0.33 and 0.86 mmol H_2O_2/g-soil after 60 min reaction when 21, 105 and 315 mM of oxidants were used for the tests, respectively. For persulfate, the SOD values were 0.03, 0.12 and 0.26 mmol $Na_2S_2O_8$/g-soil, respectively, under the same experimental conditions. Results indicate that the SOD value for H_2O_2 was approximately 2–3 times higher than persulfate. Thus, higher dosages of H_2O_2 are needed during the ISCO application. Results also demonstrate that the SOD values were 0.362, 0.361 and 0.142 mmol H_2O_2/g-soil for the first 20 min, second 20 min and third 20 min of reaction with H_2O_2 concentration of 315 mM, respectively. This implies that the NOM decreased during the oxidation process, which caused the decreased SOD values over time [38]. In contrast to the decreased SOD values observed during the SOD test using H_2O_2 as the oxidant, SOD values were 0.021, 0.042 and 0.200 mmol $Na_2S_2O_8$/g-soil for the first 20 min, second 20 min and third 20 min of reaction with $Na_2S_2O_8$ concentration of 315 mM. This is because that the affinity of persulfate with soil organic matter could be lower than H_2O_2 [17], and thus, the amount of $Na_2S_2O_8$ consumption was lower at the beginning of the experiment.

3.3. *Effects of [oxidant]/[phenol] ratio on phenol oxidation*

Fig. 4 presents the changes of phenol removal efficiency during the oxidation process (molar ratios of H_2O_2 to phenol: 0, 20, 100 and 300). The phenol removal efficiency was calculated using the ratio of removal mass to initial mass of phenol. Results show that when the highest H_2O_2 concentrations

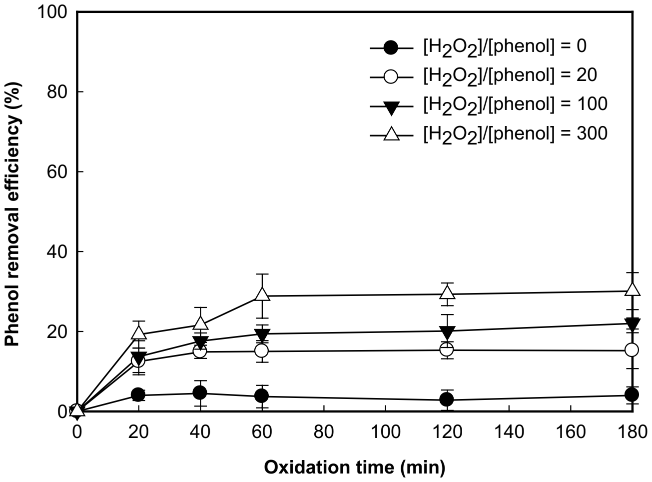

Fig. 4. Efficiencies of phenol oxidation with varied [H_2O_2]/[phenol] ratios.

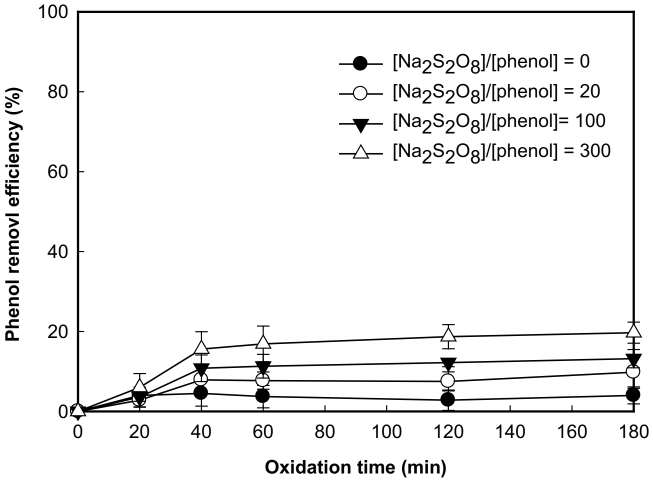

Fig. 5. Efficiencies of phenol oxidation with varied [$Na_2S_2O_8$]/[phenol] ratios.

(a molar ratio of 300) were used, the phenol removal efficiency was approximately 29% within 60 min of reaction. However, the phenol removal efficiency was dropped to 13% when the lowest H_2O_2 concentrations (a molar ratio of 20) were used. This reveals that the phenol oxidation can be enhanced using a higher H_2O_2 concentration. Because more hydroxyl radical could be produced with higher concentrations of H_2O_2, higher phenol oxidation efficiency could be obtained [13,21]. Results show that a decreased phenol oxidation rate was observed after 60 min of reaction. This could be due to the fact that the consumption of H_2O_2 caused the decreased hydroxyl radicals production, which resulted in the reduced phenol oxidation [39].

Fig. 5 shows the variations in phenol removal efficiency using $Na_2S_2O_8$ as the oxidant. Results show that a higher molar ratio of $Na_2S_2O_8$ to phenol caused higher phenol removal efficiency. Approximately 17% of phenol removal efficiency was obtained with a molar ratio of 300 within 60 min of operation. Results indicate that phenol removal efficiency increased with increased persulfate concentrations. When a relative lower molar ratio was used for phenol oxidation, a longer reaction period was needed. Moreover, more sulfate radicals could be produced when a higher persulfate concentration was applied during the oxidation process. Thus, the amount of oxidant used to oxidize phenol needs to be higher than the theoretical molar ratio of H_2O_2 or persulfate to phenol based on the stoichiometry equation to obtain a complete phenol removal (Eqs. (2) and (5)).

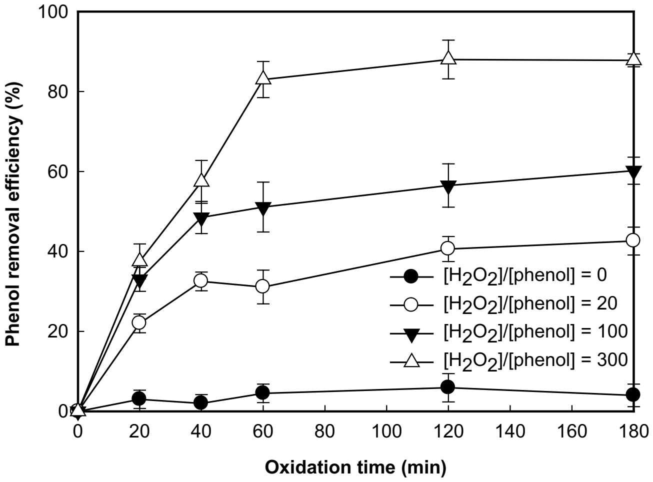

Fig. 6. Efficiencies of phenol oxidation with varied [H_2O_2]/[phenol] ratios using ferrous iron as catalyst.

3.4. Effects of [oxidant]/[phenol] ratio with ferrous iron on phenol oxidation

To evaluate the effect of ferrous iron catalyst addition on phenol oxidation, the given concentrations of ferrous iron was added in the simulated groundwater before oxidant addition. Fig. 6 shows the variations in phenol removal efficiency after oxidation with varied molar ratios of H_2O_2 with Fe^{2+} (as Fenton reaction) to phenol (0, 20, 100 and 300). Results show that the phenol removal efficiencies were 4.5%, 31%, 51% and 83% within 60 min of reaction when the molar ratios were 0, 20, 100, and 300, respectively. Results also show that the phenol removal efficiencies were slightly increased to 43%, 60% and 88% within 180 min of reaction with molar ratios of 20, 100, and 300, respectively. This indicates that the highest phenol removal efficiency was obtained with a H_2O_2 to phenol molar ratio of 300 after a 180 min reaction time. It suggests that higher H_2O_2 concentrations and longer reaction time were required to achieve a complete phenol remove. Results show that phenol removal efficiencies increased from 29% to 83% within 60 min of reaction when ferrous iron catalyst was added in the solution to active H_2O_2 (molar ratio of 300) for hydroxyl radicals production based on the stoichiometry equation (Eq. (1)). The increased phenol removal efficiency was due to the catalysis reaction, which resulted in the production of hydroxyl radicals [40,41]. This results is similar to other research which used calcined diatom with copper added as catalyst for peroxidation of phenol solution (1,000 mg/L) in a batch laboratory reactor, and its total organic carbon reduced 80% within 5 h test [42].

Fig. 7 shows the variations in phenol removal efficiency with different molar ratios of $Na_2S_2O_8$ oxidation with Fe^{2+} addition. Results show that the phenol removal efficiencies were 4.5%, 17%, 55% and 77% within 60 min of reaction with molar ratios of 0, 20, 100, and 300, respectively. Results also demonstrate that the phenol removal efficiencies were slightly increased to 24%, 62% and 78% within 180 min of reaction when the molar ratios were 20, 100 and 300, respectively. The trend of persulfate oxidation was similar to the one obtained from Fenton reaction. However, the phenol removal efficiency was relatively higher when Fenton reaction was applied as the oxidation process.

When Fe^{2+} is used to activate persulfate or H_2O_2, Fe^{2+} can be oxidized and transformed to ferric iron (Fe^{3+}), which reacts with water and form $Fe(OH)_3$ through hydrolysis. Persulfate activation by $Fe(OH)_3$ is not significant (Eq. (6)). Furthermore, during the persulfate activation process using as the catalyzer, the produced $SO_4^{-\bullet}$ can proceed either recombination mechanism with each other or inhibit excess persulfate oxidation (Eq. (7)) [23,43]. Therefore, the phenol removal efficiency was lower than that using Fenton reaction and the phenol oxidation rate might be reduced after 60 min.

Compared with the results from Fig. 5, the phenol removal efficiencies were increased from 17% to 78% within 60 min of reaction with molar ratio of 300 when ferrous iron catalyst was added in the solution to activate persulfate for sulfate radicals production based on the stoichiometry equation (Eq. (4)). During the catalysis reaction, more sulfate radicals could be produced, and thus, phenol removal efficiency could be enhanced. Results reveal that Fe^{2+} catalyzer played an important role in the phenol oxidation, which could result in approximately 50% of phenol removal. The enhancement of phenol oxidation was exerted by Fe^{2+} catalysis, which produced higher redox potential of radicals from H_2O_2 (E^0 = 2.8 V) and persulfate (E^0 = 3.1 V) than that without Fe^{2+} catalysis [17,43].

3.5. Kinetics of phenol oxidation

Oxidation kinetics using different oxidants following the pseudo-first-order kinetic model (Eq. (8)):

$$\ln\left(\frac{C}{C_0}\right) = -k't \tag{8}$$

where k' is the pseudo-first-order rate constant, and C_0 and C are phenol concentrations at the beginning of the oxidation and a specific reaction time (t), respectively. The rate constant can be calculated using the linear regression of $\ln(C/C_0)$ vs. oxidation time under the conditions of varied [oxidant]/[phenol] molar ratio with initial phenol concentrations of 1 mg/L. Fig. 8a presents the calculated oxidation rate constant based on Eq. (8). The calculated pseudo-first-order rate constants were 6.30×10^{-3}, 1.21×10^{-2} and 3.44×10^{-2} (min^{-1}) when the $[H_2O_2]/[phenol]$ molar ratio were 20, 100 and 300, respectively.

The k' value increased significantly with an increased molar ratio. This could be due to the increased reactive radicals ($HO^\bullet$) generated with higher molar ratios of $[H_2O_2]/[phenol]$, which could expedite the oxidation of phenol.

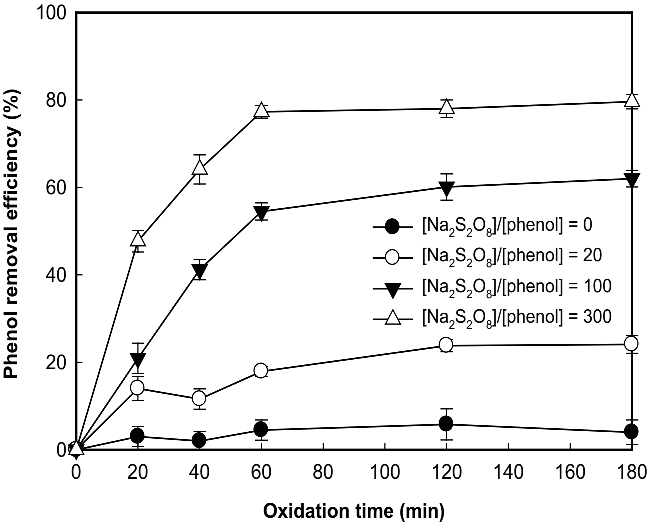

Fig. 7. Efficiencies of phenol oxidation with varied $[Na_2S_2O_8]/[phenol]$ ratios using ferrous iron as catalyst.

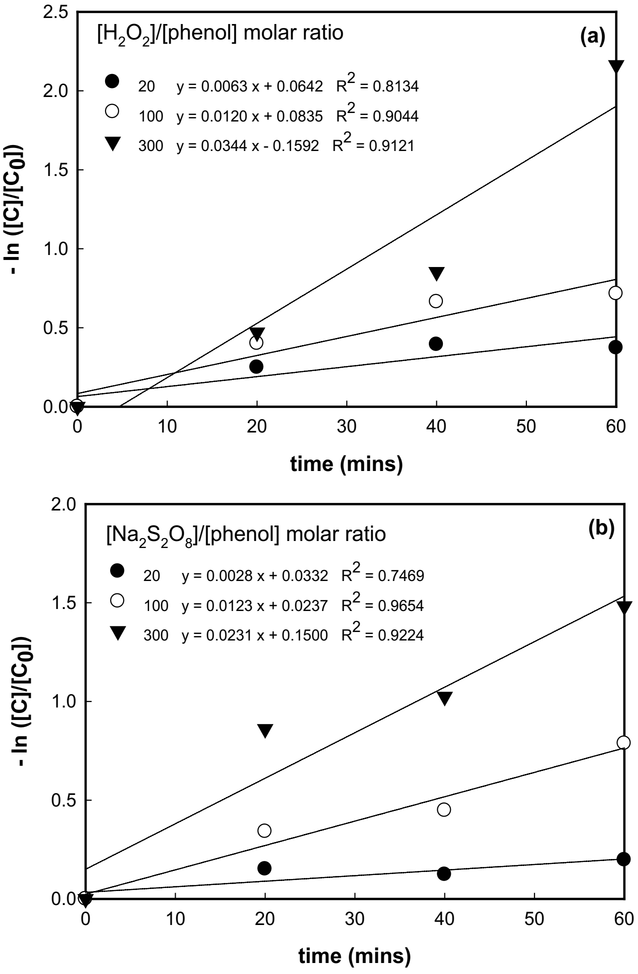

Fig. 8. Calculated pseudo-first-order oxidation rates under varied (a) $[H_2O_2]/[phenol]$ ratios and (b) $[Na_2S_2O_8]/[phenol]$ ratios.

Table 4 presents the calculated pseudo-first-order decay rates with varied [oxidant]/[phenol] ratios. The half-life values of phenol were 110, 57 and 20 min when the [H_2O_2]/[phenol] molar ratio were 20, 100 and 300, respectively. The half-life of phenol decreased with increased H_2O_2 concentrations. This indicates that more H_2O_2 dosages are required for a short-term remediation period.

Fig. 8b shows the calculated pseudo-first-order oxidation rate constant of varied molar ratio of [$Na_2S_2O_8$]/[phenol] with initial phenol concentrations of 1 mg/L. The calculated pseudo-first-order rate constants were 2.80×10^{-3}, 1.24×10^{-2} and 2.31×10^{-2} (min^{-1}) when the [$Na_2S_2O_8$]/[phenol] molar ratio were 20, 100 and 300, respectively. The half-life values of phenol were 248, 56 and 30 min when the [$Na_2S_2O_8$]/[phenol] molar ratio were 20, 100 and 300, respectively. Results show that a lower half-life value of phenol was observed with increased $Na_2S_2O_8$ concentrations. The results are similar to that obtained from H_2O_2 oxidation described in other studies [43].

3.6. Column study

The column study was conducted to assess the effectiveness of the phenol oxidation using three different flushing solution. Fig. 9 shows the variations in the measured phenol concentrations in effluents of the column system. In the column experiment, phenol-contaminated groundwater (phenol concentration = 1 mg/L) was pumped into the column before flushing solution was injected.

Results show that the breakthrough of phenol was observed after approximately 2.86 PVs of phenol solution were pumped into the column. In Group 1 experiment, phenol concentration dropped to 0.09 mg/L after another 10 PVs (total 12.86 PVs) of deionized water flushing. The results suggest that flushing with water could result in phenol removal via the dilution, dispersion, migration, and sorption, which caused the reduction of phenol concentration. However, due to the sorption mechanism between phenol and soil organic matters, a longer reaction time was needed for phenol removal.

Results from the Group 2 experiment show that phenol concentrations dropped to 0.08 mg/L after pumping of 2.53 PVs of H_2O_2 plus Fe^{2+} solution through the column (total 5.39 PVs). Results from the Group 3 experiment show that phenol concentrations dropped to 0.07 mg/L (93% removal) after another 1.4 PVs (total 4.26 PVs) of $Na_2S_2O_8$ plus Fe^{2+} solution were pumped through the columns. Approximately 10, 2.5 and 1.4 PVs of influent solution were pumped through the column to achieve 91%, 92% and 93% of phenol removal for Groups 1 to 3 experiments, respectively.

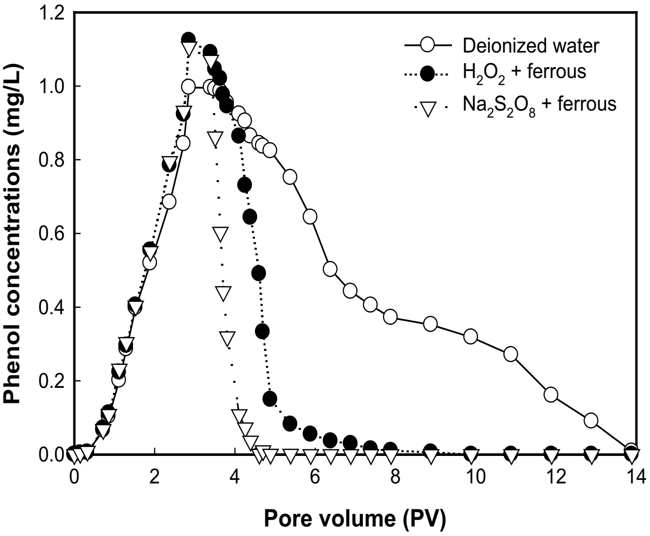

Fig. 9. Variations in phenol concentrations in column experiment using (a) H_2O_2 and (b) $Na_2S_2O_8$ as oxidants with ferrous iron addition.

Results indicate that both Fenton reaction and activated persulfate could effectively oxidize phenol and also oxidize soil organic matters, which resulted in the phenol dissolution and desorption from soil particles. However, results show that activated persulfate could oxidize phenol faster than Fenton reaction. This finding could be due to the following causes: (1) The observed SOD for persulfate was much less than that of H_2O_2. This indicates that more H_2O_2 consumption occurred due to the soil organic matters in the column [43]; (2) Activated persulfate could produce radicals with high redox potential (E^0 = 3.1 V), which is higher than that produced by Fenton reaction (E^0 = 2.8 V). Thus, activated persulfate can oxidize organic compounds more efficiently [27]; (3) Persulfate is more persistent than H_2O_2 in soil and groundwater environment, and thus, the oxidation of phenol would be more stable when persulfate is used as the oxidant [24]. The observed results herein are similar to the results from other literature reported by Zhong et al. [44] indicating that persulfate is superior to H_2O_2 for the degradation of organic compounds.

4. Conclusions

In this study, the effectiveness of phenol oxidation by ISCO using H_2O_2 and $Na_2S_2O_8$ as the oxidants were evaluated. Batch and column experiments were conducted to

Table 4
Calculated pseudo-first-order decay rates with varied [oxidant]/[phenol] ratios

	H_2O_2 with ferrous iron (Fenton reaction)			$Na_2S_2O_8$ with ferrous iron		
[oxidant]/[phenol] molar ratio	k' (min^{-1})	$t_{1/2}$ (min)	R^2	k' (min^{-1})	$t_{1/2}$ (min)	R^2
20	6.30×10^{-3}	110	0.8134	2.80×10^{-3}	248	0.7469
100	1.21×10^{-2}	57	0.9044	1.24×10^{-2}	56	0.9654
300	3.44×10^{-2}	20	0.9121	2.31×10^{-2}	30	0.9224

obtain the optimal operational conditions of the oxidation processes. Conclusions are as follows:

- H_2O_2 and $Na_2S_2O_8$ had lower decay rates when soils were not added in the system. However, a significant H_2O_2 (or $Na_2S_2O_8$) depletion was observed when soils were supplied in the system. The results indicate that the natural soil organic matters could react with oxidants (H_2O_2 and $Na_2S_2O_8$) and results in the consumption of oxidant concentrations. Thus, the available oxidant for phenol oxidation was reduced, and decreased phenol oxidation rate was observed. Compared to H_2O_2, $Na_2S_2O_8$ was more resistant to soil organic matters. Therefore, more $Na_2S_2O_8$ was available for phenol oxidation.
- Higher SOD value was obtained when higher oxidant concentrations were provided. From an engineering point of view, supplement of higher concentrations of H_2O_2 (or $Na_2S_2O_8$) is a necessity for a soil system with a high SOD value.
- H_2O_2 (or $Na_2S_2O_8$) to phenol molar ratio and time of oxidation were two control factors during the oxidation process. Increased phenol removal rate was achieved with an increased H_2O_2 (or $Na_2S_2O_8$) to phenol molar ratio. With a lower relatively lower molar ratio, a longer oxidation time was required to reach a higher phenol oxidation efficiency. The amount of H_2O_2 (or $Na_2S_2O_8$) used for phenol oxidation would be higher than the theoretical molar ratio to obtain a complete phenol removal.
- During the phenol oxidation, an increased H_2O_2 (or $Na_2S_2O_8$) concentration resulted in a decreased half-life of phenol. Thus, the oxidation rate would be affected by the initial oxidant concentrations.
- Results from the column study indicate that flushing with the activated persulfate solution could obtain an effective phenol removal efficiency due to the production of highly reactive and more stable sulfate radicals with the presence of soil organic matters. The findings would be helpful in designing a practical ISCO system for the remediation of phenol-contaminated groundwater.

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