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Remediating phenol-contaminated groundwater and aquifer using persulfate oxidation

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ABSTRACT

A chemical spill in Chachoengsao province, Thailand resulted in a phenol-contaminated aquifer. Our objective was to remediate the phenol-contaminated groundwater and aquifer using oxidation with persulfate (PS). Groundwater and aquifer collected near a source zone were characterized and used in the experiments. The experimental design was set up under the criteria of specific sites and contaminants. To optimize efficacy, various experimental variables were tested: initial persulfate (PS) and phenol concentrations, pH, transition metals as persulfate activators, and the concentration ratios of PS to Fe^{2+}. The phenol degradation rates enhanced when the pH was increased from 3 to 7 but then continually decreased as the pH was increased from 7 to 9. Five transition metal (Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}) were tested as PS activators. By using equivalent molar concentrations, we found the rate of phenol degradation was highest when PS was activated by Fe^{2+}. By using a 500:5 PS to Fe^{2+} ratio, phenol removal efficiency increased almost three-fold over a 500:1 PS to Fe^{2+} ratio (k_{obs} = 0.35 h^{-1} vs. k_{obs} = 0.12 h^{-1}). Using a statistical-based response surface methodology, we found that the optimum conditions for treating phenol-contaminated groundwater were 522.40 mg PS L^{-1} with 4.85 mg Fe^{2+} L^{-1} at pH 6.99. The use of activated persulfate to remove phenol during miscible displacement was also investigated. Column leaching experiments were performed where persulfate was injected into an aquifer column containing 1% zerovalent iron (w/w) as an activator. The results showed that after displacing three pore volumes, phenol concentrations decreased 82%. Using activated persulfate also increased the percentage of phenol oxidized during transport by 20%. These results confirmed the use of activated persulfate for the removal of phenol from contaminated groundwater and aquifer.

Keywords: Aquifer; Groundwater remediation; Persulfate; Phenol; Response surface methodology

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1. Introduction

Phenol is a common reagent used in the manufacturing of plywood, automotive parts, and appliances. Other commercial products using phenol include paper, pulp mill processes, and plastics [1]. Prevalent phenol use in industrial processes has caused environmental concerns by creating soil and groundwater contamination [2]. Based on the moderately low sorption partition coefficient (1.21–1.96 L kg^{-1}) of phenol, phenol is expected to leach to groundwater and some may partition with aquifer [3]. Often, inadvertent leakage or illegal dumping have been causes of groundwater contamination and this was the case in Chachoengsao province, Thailand where unusually high concentrations of phenol (29.14 mg L^{-1}) were found in the groundwater at Nong Nae, Phanom Sarakham that exceeded the Thailand standard value (≤1.0 mg L^{-1}) [4] and environmental concern level of World Health Organization (0.02 μg L^{-1}) [5]. The US Environmental Protection Agency (EPA) set a maximum contaminant level (MCL) of 4 mg L^{-1} for human health in the consumption of water and organism [6]. To prevent this source zone from spreading, efficient treatment was needed.

Several techniques have been applied for the remediation of surface water, soil, and groundwater contaminated with phenol and its derivatives, such as adsorption, biological treatment, and chemical oxidation [7–9]. Adsorption is effective at removing phenol but it has the disadvantage of a high regeneration cost [7]. Moreover, while bioremediation can produce less chemical toxicity from all the processes, this technique needs to enhance the biodegradation capacity to improve the efficiency to 70%–80% for treating phenol [8]. Compared with adsorption, chemical oxidation has a great capacity to pretreat or rapidly treat groundwater and soil contaminated with phenol [9]. Among the many remediation techniques, chemical oxidation has been proposed as a good candidate for removing phenol from groundwater and soil [10]. Chemical oxidation has been applied using conventional oxidants for *in situ* chemical oxidation (ISCO) such as permanganate (MnO_4^-; 1.7 V), hydrogen peroxide (H_2O_2; 1.8 V), ozone (O_3; 2.1 V), and persulfate ($S_2O_8^{2-}$; 2.1 V) [11]. Persulfate is consistently outstanding compared to other oxidants because it has a relatively higher redox potential of 2.8 V with sulfate radicals forming and it does not generate a secondary contaminant. Moreover, persulfate remains in a stable form in the subsurface after activation, with most of the organic pollutants being degraded by the reactive oxygen species that are produced by persulfate [12]. Based on its relative stability, persulfate can be delivered relatively long-distances in the subsurface to contaminated zones [13].

Persulfate oxidation is a novel technique for the remediation of soil and groundwater contaminated with organic pollutants [14]. Some researchers have suggested that persulfate oxidation technology showed high efficiency at degrading various types of organic pollutants [15], such as antibiotics (sulfamethazine; SMZ) [16], polycyclic aromatic hydrocarbons (PAHs) [17], parabens [18], and phenolic compounds [19]. To enhance the efficiency of PS oxidation, there are several methods to activate PS such as heat, UV, metal ion, and alkaline conditions [20]. However, activating persulfate has been problematic to date for the field because the activation of the basic condition often stalls at a site when the pH is below 10.5, and activation with other minerals or iron(II) is often ineffective [15]. Kambhu et al. [21] and Chokejaroenrat et al. [22] developed a slow-release Fe^0 that was effective in activating persulfate. By controlling the release of Fe^{2+} into solution, Kambhu et al. [21] avoided having too much Fe^{2+} available for persulfate activation, which can quench the persulfate radical.

In this study, we determined the efficacy of persulfate oxidation to degrade phenol in contaminated groundwater and aquifer. Groundwater and aquifer collected near a source zone in Chachoengsao province, Thailand were characterized and used in the experiments. All experimental designs were based on the real-world treatment application, which was, therefore, area- and contaminant-dependent. This was accomplished by quantifying the effects in batch experiments of the initial persulfate concentration, the PS/Fe^{2+} ratio, initial phenol concentration, pH, and type of activator on phenol degradation. A response surface methodology (RSM) and a statistical-based experimental design were also used to determine the optimum experimental parameters for phenol oxidation. Furthermore, to further scale our work toward field treatment, we determined phenol adsorption and transport properties using materials from the field site and quantified phenol removal by persulfate oxidation during miscible displacement.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments were of analytical grade. Phenol (C_6H_5OH) was purchased from Fisher Scientific (Loughborough, UK). Sodium persulfate ($Na_2S_2O_8$) and sulfuric acid (H_2SO_4, 98%) were purchased from Qrec (Auckland, New Zealand), sodium hydroxide (NaOH, 99.0%) from CARLO ERBA REAGENT company (Milan, Italy), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) from J.T. Baker (New Jersey, USA). Potassium iodide (KI, 99.5%), starch (ACS grade), sodium bicarbonate ($NaHCO_3$), and additional chemicals needed for phenol analysis such as potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), and potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$) were purchased from Ajax (Auckland, New Zealand), ammonium hydroxide (NH_4OH) (95%) (Phillipsburg, USA), and 4-amino antipyrine was purchased from LOBA Chemie (Mumbai, India).

2.2. Groundwater and aquifer characterization

The groundwater and aquifer were collected from six new monitoring wells in Chachoengsao province, Thailand at approximately 10 m below the soil surface. Initial groundwater characteristics were measured on-site using a multi-meter. The samples of the aquifer were dried and screened through a sieve before hand-milling. Organic matter (OM) was analyzed using standard methods [23]. The aquifer texture was analyzed using a hydrometer following the standard method [24]. Cation exchange capacity (CEC) was determined using the method of Rhoades [25]. Atomic absorption spectrometry (AAS) was used to quantify heavy metal concentrations in the collected groundwater and aquifer. Samples were analyzed with a flame atomic absorption spectrometer (Agilent 200 Series AA, USA) with a hollow cathode lamp (multi-element type) and photomultiplier tube detector. The quantify of heavy metal concentrations was conducted according to the procedure in the standard method [26].

2.3. Experimental setup

Site groundwater was spiked with phenol and the treatment was continuously agitated for 12 h on a reciprocal shaker. All treatments were run in triplicate. The residual in the phenol solution was determined using a diode array UV-visible spectrophotometer (Libra S6, Biochrom; Cambridge, United Kingdom) at 500 nm and preselected times. For each treatment, the removal efficiency at 12 h was calculated using Eq. (1):

$$\%\ \text{Phenol removal efficiency} = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{1}$$

where C_0 is the initial phenol concentration in the groundwater or soil and C_t is the concentration of phenol after treatment (t = 12 h).

2.4. Kinetics degradation of phenol by persulfate

Batch experiments were conducted in Erlenmeyer flasks each with 100 mL of contaminated groundwater. Treatments consisted of phenol-contaminated groundwater treated with persulfate or the control (no persulfate). All experimental units were conducted on a reciprocal shaker at room temperature for 12 h in triplicate. Temporal changes in residual phenol concentrations were determined, and pseudo-first-order kinetic rates (k) of phenol oxidation by persulfate were calculated using Eq. (2):

$$C = C_0 e^{-kt} \tag{2}$$

where C_0 is the initial phenol concentration and C is the concentration of phenol at time (t).

2.5. Effect of treatment parameters on phenol degradation rates

The persulfate dosage, initial phenol concentration, type of activator and dosage, and pH were systematically varied to quantify the treatment effects on the phenol degradation rates. To quantify the concentration effects, phenol concentrations of 2, 4, 6, 8, and 10 mg L^{-1} were treated with 500 mg L^{-1} of persulfate. To quantify the effects of PS dosage, phenol-contaminated groundwater samples (10 mg L^{-1}) were treated with sodium persulfate at 300, 500, and 700 mg L^{-1}. To determine the effects of transition metals as persulfate activators, phenol-contaminated groundwater samples were treated with sodium persulfate (500 mg L^{-1}) that was paired with either $FeSO_4$, $CuSO_4$, $ZnSO_4$, $PbSO_4$, or $CdSO_4$ at a ratio of 500:5. Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} were found in the groundwater from the contaminated site. To study the effect of the activator dosage, 100 mL samples of phenol-contaminated groundwater (10 mg L^{-1}) were treated with sodium persulfate and $FeSO_4$ at ratios of 500:1, 500:3, and 500:5. To study the effect of the pH, the initial pH values of phenol-contaminated groundwater samples (10 mg L^{-1}) were adjusted to 3, 5, 7, and 9 using either 0.1 N of HNO_3 or 0.1 N of NaOH and treated with sodium persulfate (500 mg L^{-1}) and $FeSO_4$ (5 mg L^{-1}). All the experimental variables were tested for the phenol destruction rate.

2.6. Phenol and intermediate compound analysis

The phenol analysis procedure followed the direct photometric method [27]. Specifically, each sample was diluted to 100 mL and mixed with 2.5 mL of 0.5 N NH_4OH solution and then the pH was adjusted immediately to pH 7.9 ± 0.1 using a phosphate buffer. Then, we added 1.0 mL of 4-amino antipyrine solution and after mixing the solution well, we added 1.0 mL of $K_3Fe(CN)_6$ solution and mixed again. After 15 min, the mixture was transferred to a UV spectrophotometer cell and the absorbance was read against a blank at 500 nm. A preliminary for degradation analysis was performed to identify intermediate compounds occurred in this study. Phenol (20 mg L^{-1}) were treated by 500 mg L^{-1} persulfate activated by 5 mg L^{-1} Fe^{2+}. At 30 min, a 10 mL sample was collected and extracted with 1 mL dichloromethane for three times [28]. The extracted solutions were analyzed by GC-MS (Shimadzu QP 2020) equipped with a HP-5 silica capillary column. The temperature program was as follows: initial temperature of 40°C held for 10 min, then increased at a rate of 10°C min^{-1} to 300°C, and held for 10 min. The injector temperature was 200°C. The transfer line temperature was 250°C. The mass detector was operated in the standard electron ionization (EI) mode of 70 eV in the 50–400 amu scan range [29].

2.7. Persulfate analysis

The iodometric titration method developed by Liang et al. [30] was used to measure the persulfate concentration. In brief, the following steps were used: (1) samples were diluted to approximately 30 mL; (2) 2 g of $NaHCO_3$ were added to prevent oxygen oxidation with iodide from KI; (3) 4 g of KI were added and mixed and the solution was allowed to stand for 15 min; (4) 2–3 drops of starch indicator were added; (5) the solution was acidified using 1 mL of CH_3COOH; and (6) the mixture was titrated with 0.025 N of standard $Na_2S_2O_3$ to the end-point. The concentration of sodium persulfate was calculated using Eq. (3):

$$Na_2S_2O_8\left(\text{mg/L}\right) = \frac{\left(A \pm B\right)}{2} N\ \text{MW of}\ Na_2S_2O_8 + \frac{1}{\text{mL sample}}\text{DF} \tag{3}$$

where A is the titration for the sample (mL); B is the titration for the blank (mL); N is the normality of $Na_2S_2O_3$; MW of $Na_2S_2O_8$ is the molecular weight in mg mol^{-1} (238.13×10^3 mg mol^{-1}); and DF is the dilution factor.

2.8. Investigation of optimum conditions using RSM

The statistical design of experiments was analyzed using the Design Expert Software (version 7.0). In this study, RSM and central composite design (CCD) were used to optimize the three most important variables: persulfate (PS) and activator dosage, and pH. Initial experiments provided an initial test to determine a better range of PS and activator dosage and pH before deciding on the future experimental conditions. The treatment variable ranges chosen were: PS dosage 300–700 mg L^{-1}, activator dosage 3–7 mg L^{-1} for Fe^{2+}, and pH range from 3 to 9. The CCD method was used to investigate combinations of these three factors. The number of experiments required was determined using Eq. (4):

$$N = k^2 + 2k + C_p \tag{4}$$

where k is the factor number and C_p is the replicate number of the central point. These factors were calculated with five levels (–α, –1, 0, +1, +α), where $\alpha = 2^{k/4}$ [31]. This experimental design was studied using five-level values: (+1.68), +1, 0, –1, and (–1.68). Analysis of variance was used for the investigation of the data to determine interactions among the process variables and responses. The coefficient of determination (R^2) was used to indicate the performance of the polynomial model, and statistical significance was analyzed using Fisher's F-test. Moreover, the model terms were calculated using a P-value with 95% confidence levels. The respective contour plots and 3-dimensional plots were achieved for the three parameters. In addition, the optimum value was analyzed using an overlay plot of these parameters [32].

2.9. Total oxidant demand

The total oxidant demand (TOD) was used to consider the amount of oxidant consumed during the persulfate-based *in situ* chemical oxidation process. The quantification of the amount of sodium persulfate consumed by reactions in the aquifer matrix was shown by the TOD values. TOD results can be used to estimate the amount of sodium persulfate required to remediate a contaminated aquifer. The TOD for each sample was conducted in a batch experiment containing site aquifer, aquifer with Ottawa sand and DI water or site groundwater that was kept to <15°C, which was representative of the typical groundwater temperature. The combined aquifer and aquifer with sand (50 g) in tubes had initial concentration of the PS solution of 100; 250; 500; 1,000; and 5,000 mg L^{-1}. The residual PS was measured at 120 h using the iodometric method and then PS demand was calculated using Eq. (5) [33]:

$$\text{TOD}\left(\text{g}\left(\text{PS}\right)/\text{kg}\left(\text{aquifer}\right)\right) = \frac{\left(C_{\text{PS,initial}} - C_{\text{PS,time}}\right) \times \text{Volume liquid}}{\text{Mass soil}} \tag{5}$$

where $C_{\text{ps,initial}}$ is initial persulfate concentration, and $C_{\text{ps,time}}$ is persulfate concentration at the given time.

2.10. Batch adsorption isotherm

Phenol adsorption to aquifer was measured using batch adsorption isotherm experiments. Stock solutions of phenol (10 mg L^{-1}) were prepared in distilled water. The experiments were carried out in centrifuge tubes containing 40 mL of phenol solutions of different concentrations (2, 4, 6, 8, and 10 mg L^{-1}) and 5 g of aquifer. The adsorption experiment was conducted at neutral pH. Aquifer-phenol mixtures were shaken at 120 rpm for 24 h on an orbital shaker. Phenol concentrations after shaking were measured using the direct photometric method [27]. Calculated phenol adsorbed versus equilibrium solutions were then plotted and the results were fitted to Langmuir and Freundlich equation.

2.11. Column experiments

Miscible displacement experiments were performed using acrylic columns (7.5 cm diameter by 26.5 cm length). Each column was carefully packed with 1,065 g of aquifer that consisted of a 70:30 ratio (w/w) of sand and aquifer from the field site. Aquifer columns were equilibrated with 10 mg L^{-1} phenol in a 3 mM $CaCl_2$ matrix to maintain a constant ionic strength. The solution was delivered to the top of the columns at 4.7 mL min^{-1}, which produced a solution flux of 0.1064 cm min^{-1}. An additional Fe^0 1% (w/w) was added to a second column to quantify its effect as an activator of persulfate. After the columns were equilibrated with 10 mg L^{-1} phenol, the columns were flushed with 500 mg L^{-1} L of PS at the same flow rate (4.7 mL min^{-1}). Once persulfate was added to the eluent, temporal effluent samples from the bottom of the column were taken every hour and analyzed for phenol and persulfate.

3. Results and discussion

3.1. Groundwater and aquifer characteristics

Groundwater and aquifer collected in monitoring wells at Chachoengsao province were analyzed (Tables 1 and 2). The analytical results indicated that basic groundwater parameters, pH, EC, total hardness, total dissolved solids were in the range of WHO (World Health Organization) natural groundwater characteristics [34] and Thailand groundwater standard [35]. The aquifer at this site had a high percentage of sand (52%), and the texture was sandy clay loam with low organic matter (0.16%). Sand texture can assist the delivery of persulfate to oxidize contaminants then, led to enhance the removal efficiency [36]. Element analysis indicated that high iron content was found in groundwater (Fe^{2+}, 2.29 ± 2.55 mg L^{-1}) and aquifer (total Fe, 6.48%). It may be useful to enhance the phenol removal efficiency using persulfate with these iron that exists in groundwater and aquifer from this site as the activators. Generally, iron occurs naturally in the aquifer, but levels in groundwater can be changed by dissolution from geological parent materials and leaching of metals from soil and aquifer through natural processes, especially pH changes [37]. The Department of Groundwater Resources, Thailand revealed that the geological parent materials of this area were semi-metamorphic rocks and metamorphic rocks, including laterite. The major chemical composition of laterite contains a high concentration of iron in the form of Fe_2O_3 (40.80%), SiO_2 (37.44%), and Al_2O_3 (13.90%) [38]. To identify sources of iron in groundwater through the leaching process from top soil, soil samples (0.5 m depth) in the study site were collected, and total

Table 1
Comparison of groundwater quality with standards and groundwater samples from the field site

Parameters	Natural groundwater [34]	Thailand standard value [35]	Groundwater Sample value
pH	6.5–8.0	7.0–8.5	6.77 ± 0.44
EC, µS cm^{-1}	<500	<500	417.44 ± 0.41
Total hardness, mg L^{-1}	<500	<300	148.67 ± 0.43
Total dissolved solids, mg L^{-1}	<5,000	<600	0.63 ± 0.33
Fe, mg L^{-1}	<0.5	<0.5	2.29 ± 2.55
Cu, mg L^{-1}	0.05	<0.5	0.63 ± 0.69
Zn, mg L^{-1}	5.0	<5.0	11.2 ± 5.46
Pb, mg L^{-1}	–	0.00	2.85 ± 2.09
Cd, mg L^{-1}	–	0.00	0.32 ± 0.15

Table 2
Aquifer materials characteristics and metal concentrations from the field site

Parameters	Value
pH	7.7
Sand (%)	52.0
Silt (%)	26.0
Clay (%)	22.0
Texture	Sandy clay loam
Organic matter (%)	0.16
Cation exchange capacity, cmol$_c$ kg^{-1}	6.29
Fe, mg kg^{-1}	64,895.5 ± 1.32
Cu, mg kg^{-1}	8.44 ± 5.31
Zn, mg kg^{-1}	27.80 ± 0.73
Pb, mg kg^{-1}	47.91 ± 3.96
Ni, mg kg^{-1}	23.55 ± 2.73
Cd, mg kg^{-1}	1.57 ± 0.01

iron was analyzed. The high concentrations of iron in soil (64,895.5 ± 1.32 mg kg^{-1}) were correlated with total iron in an aquifer and in parent materials. The evidence of both parent materials and soil results in high concentrations of iron in groundwater. Besides iron, other bivalent metal ions, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} were also found in groundwater with above the groundwater standards. These metal ions can play an important role in activating persulfate [39].

3.2. Treatment effects of phenol degradation

The results from a variety of batch experiments showed differences among treatments, cation activators, initial phenol concentration, PS dosage, pH, and ratio between PS and activator. As we mentioned earlier, some metals (Fe^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}) were found in both the groundwater and aquifer in contaminated areas of Chachoengsao province. We assumed that these contaminated cations were able to activate PS reaction during *in situ* remediations. In this study, five transitions of metal-contaminated groundwater were tested as PS activators. The ratios between persulfate and the metal ions were chosen to cover the amounts of metal ions added (500 mg L^{-1} PS:5 mg L^{-1} activator). We found that the rate of phenol degradation was highest when PS was activated by Fe^{2+} (Fig. 1). This indicated that PS was able to be activated by available metals, especially Fe^{2+} contaminated in groundwater. Some studies reported that metal ions performed as activators in converting to sulfate radicals from persulfate [39,40]. Anipsitakis and Dionysiou [39] reported that Ag^{+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Ce^{3+}, and Ru^{3+} were metal catalysts for the activation of persulfate and peroxymonosulfate to produce sulfate and hydroxyl radicals. The recent study confirmed that cobalt, iron, manganese, copper, and mixing metals had potential to activate persulfate [41]. Their results found that the redox behavior of a particular transition metal in the solution could not be concluded based on the size and charge of metals. In this case, metal hydrolysis presented in solution affected the overall thermodynamics process [40]. In addition, Zhang et al. [40] found that Fe^{2+} was more efficient than Cu^{2+} in the activation of persulfate to generate sulfate radicals ($SO_4^{-\bullet}$) because of the stronger reduction power in the degradation process. Our study indicated that Fe^{2+} was the best activator for phenol removal by persulfate. Yang et al. [42] and Li et al. [43] also reported that Fe^{2+} played an important role in generating sulfate radicals, then phenol removal efficiency was enhanced. A previous study also showed that the effect of iron species (Fe^{0}, Fe^{2+}, and Fe^{3+}) on the capability in activating persulfate oxidation. At the equivalent mole of activator, the highest sulfate radicals were produced by activating Fe^{2+} while Fe^{0} might serve as a slow-releasing source of dissolved Fe^{2+}. However, persulfate activated by Fe^{2+} might be limited by the scavenging due to excessive iron. Moreover, excessive iron might cause the formation of iron oxides in the treatment [44]. Our finding indicated that we could treat phenol-contaminated groundwater by persulfate activated by natural iron found in this contaminated area without adding chemical activators.

Using different initial phenol and persulfate concentrations also altered the destruction rates. Phenol removal rates decreased from 0.224 to 0.1036 h^{-1} as the initial phenol concentration increased from 2 to 10 mg L^{-1} (Fig. 2a). Increasing the persulfate concentration from 300 to 500 mg L^{-1} increased the phenol destruction rates (0.1155–0.1738 h^{-1}), but no further incremental increase was observed when the

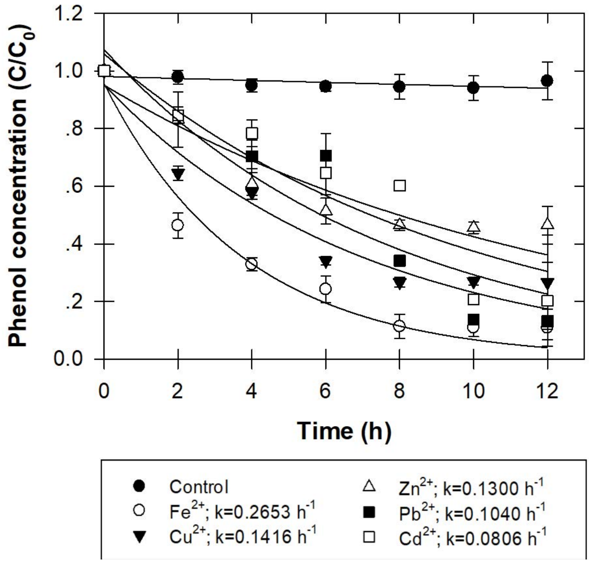

Fig. 1. Phenol (10 mg L^{-1}) degradation by 500 mg L^{-1} persulfate activated by 5 mg L^{-1} of various metal ions. The optimal activator was Fe^{2+}.

persulfate concentration increased to 700 mg L^{-1} (Fig. 2b). When the phenol concentration was increased, the amount of sulfate radicals produced from the fixed persulfate concentrations did not increase proportionally. The excess sulfate radicals in the solution can also act as a scavenger of sulfate radicals and hydroxyl radicals. This result was similar to a previous study of Satapanajaru et al. [45] studying the effect of the persulfate dose on the decolorization of reactive black 5 by persulfate.

Further increases in the persulfate concentration resulted in decreasing phenol degradation as although more $SO_4^{-\bullet}$ ions were produced at higher persulfate dosages, the excessive persulfate would deplete $SO_4^{-\bullet}$ [46] according to Eq. (6):

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-\bullet} \tag{6}$$

We observed enhanced phenol degradation rates when the pH was increased from 3 to 7 but then the rate continually decreased as the pH was increased from 7 to 9 (Fig. 2c). Similarly, using Fe^{2+}-activated persulfate, Zhang et al. [47] found aniline degradation increased with pH from 5 to 7 but sulfate radicals did not result in any further increases at pH 8.5. One possible explanation for the decreased rate of transformation at pH 9 was the known reaction of $SO_4^{-\bullet}$ with OH^- to SO_4^{2-} and $HO^{\bullet-}$ form [48]. Angkaew et al. [49] suggested that the degradation rate of 17β-estradiol by UV-activated persulfate was delayed due to the decrease of both radicals ($HO^\bullet$ and $SO_4^{\bullet-}$). The $SO_4^{-\bullet}$ formed may have reacted with H_2O or OH^- to generate $^\bullet OH$ under basic pH condition following Eqs. (7) and (8), respectively [47]:

All pH values:

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \tag{7}$$

Alkaline pH:

$$SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \tag{8}$$

At alkaline pH levels, the hydroxyl radicals showed a lower standard reduction potential than sulfate radicals [39]. In addition, at pH 7 to 9, the concentration of Fe^{2+} could decrease due to the formation of iron oxides which hinder the further reaction of Fe^{2+} with persulfate [45]. In this study, it was also shown that the reaction rate in a neutral condition was faster than that in under acid conditions. A similar result was also found in the recent work of Zhao et al. [50] which revealed that the removal efficiencies of phenol by persulfate oxidation were high at acidic (92.72% at pH 4.26) and neutral (95.88%, pH 6.45). It was that the sulfate radical exhibited a high standard redox potential (2.5–3.1 V) under acidic and neutral condition [51]. However, many research indicated phenol removal efficiency was higher under acidic conditions [52]. A related result was also found in Chokejaroenrat et al. [53], which confirmed that at pH 5, the degradation rate of sulfadimethoxine antibiotics was the fastest.

Furthermore, Ahmad et al. [54] found that phenol (pKa of 10.0) was an activator of persulfate at pH 12 with the deprotonation process to produce the phenoxide form. Nevertheless, we decided to limit the highest pH of our synthesized groundwater to 9 because the pH of groundwater in the real world could not be higher than that. This reason showed that the activation was not because of phenoxide for our study.

The effect of the ratio between PS and the activator was investigated. The higher the ratio between PS and the activator, the higher the phenol removal rate, as shown in Fig. 2d. Increasing the Fe^{2+} concentration initially enhanced $SO_4^{-\bullet}$ generation (Eq. (9)), but further increasing the Fe^{2+} concentration resulted in a consumption reactions between $SO_4^{-\bullet}$ and Fe_2^+ (Eq. (10)) which resulted in $SO_4^{-\bullet}$ formation [46].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\bullet} + \left(SO_4^{-\bullet} \text{ or } SO_4^{2-}\right) \tag{9}$$

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{10}$$

Zhang et al. [47] also observed breakdown when the molar ratio of persulfate to Fe^{2+} was increased. The Fe^{2+} acted as a scavenger of sulfate radicals and consumed $SO_4^{-\bullet}$.

Previous studies reported the possible intermediate compounds during the persulfate oxidation of phenol. Hydroquinone, benzoquinone, and catechol were found in the first state of oxidation [29,55,56]. Then, the phenolic compounds (2-phenoxy-phenol, 4-phenoxyphenol, 2,2-dihydroxybiphenyl, 3,3-dihydroxybiphenyl, and 4,4-dihydroxybiphenyl) [29] and organic acids (oxalic acid, glyoxylic acid, propionic acid, acetic acid, and formic acid) [56] were discovered in next state. Finally, these organic acids were degraded to carbon dioxide and water [50]. Our preliminary study revealed that the possible intermediate compounds were catechol, hydroquinone, and 4-phenoxy-phenol as shown in Fig. 3. Zhao et al. [50] revealed that intermediates such as hydroquinone and benzoquinone occurred during

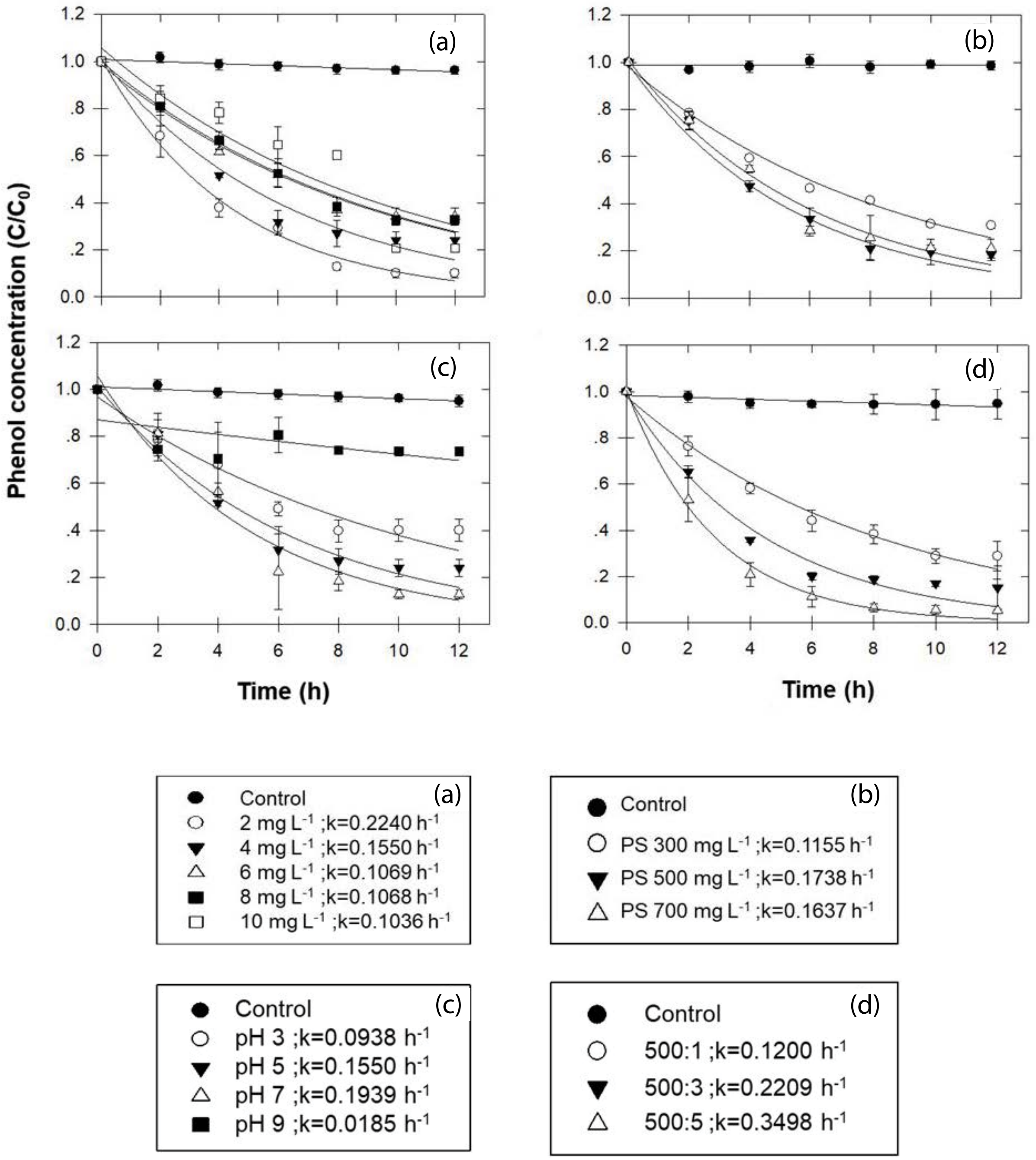

Fig. 2. Phenol degradation using persulfate activated by Fe^{2+}: (a) initial phenol concentration: the optimal condition was 2 mg L^{-1} phenol treated by 500 mg L^{-1} PS and 5 mg L^{-1} Fe^{2+}, (b) initial persulfate dosage: the optimal condition was 10 mg L^{-1} phenol treated by 500 mg L^{-1} PS and 5 mg L^{-1} Fe^{2+}, (c) pH: the optimal condition was 10 mg L^{-1} phenol treated by 500 mg L^{-1} PS and 5 mg L^{-1} Fe^{2+} at pH 7, and (d) ratio of PS:Fe^{2+}, the optimal condition was 10 mg L^{-1} phenol treated by 500 mg L^{-1} PS and 5 mg L^{-1} Fe^{2+}, 500 PS:5 activator.

persulfate oxidation of phenol were further degraded and finally mineralized to water and carbon dioxide.

3.3. Response surface methodology

RSM and CCD were used to optimize the most extensive of the three variables: persulfate dosage (PS; X_1), activator dosage (X_2), and pH (X_3). The treatment variable ranges chosen were: PS dosage, 300–700 mg L^{-1}; activator dosage, 3–7 mg L^{-1} for Fe^{2+}; and pH range, from 3 to 9. The CCD method was used to determine the combinations with these factors. This experimental design followed Eq. (4) and all factors were performed with five levels. Also, the experimental design for RSM was showed in Table 3. The analysis of variance was used to investigate the interactions of both the responses and the process variables, as

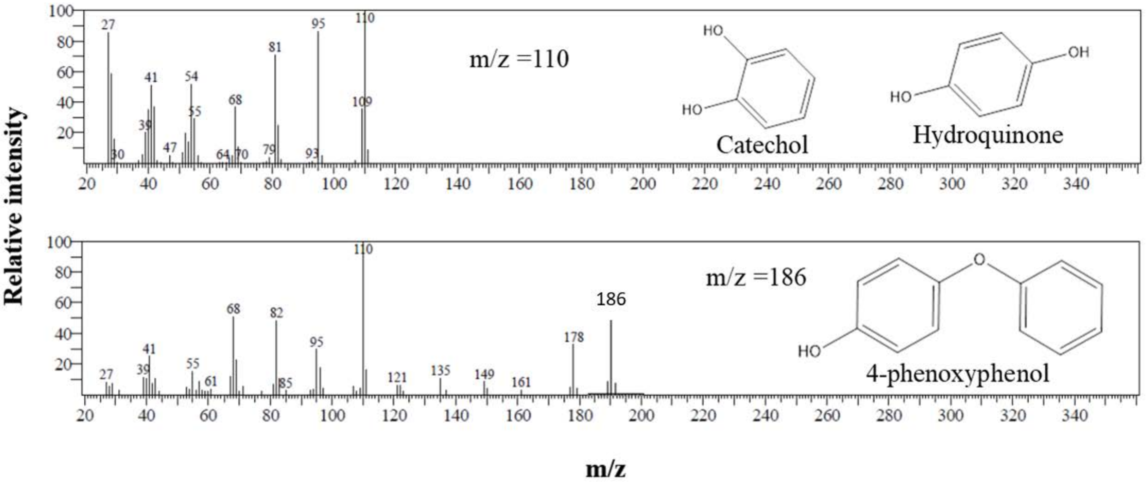

Fig. 3. Possible intermediate compounds of 10 mg L^{-1} phenol treated by 500 mg L^{-1} PS and 5 mg L^{-1} Fe^{2+} at 30 min treatment.

shown in Table 4. The polynomial model had a coefficient of determination (R^2), F-, and P-value of 0.9218, 9.17, and 0.0040, respectively. Eq. (11) shows the relationship between the response (phenol removal efficiency, Y) and the three significant factors for the model ($P < 0.05$). In the present investigation, X_2, X_1X_2, X_2X_3, and X_2^2 were significant factors (Table 4).

$$Y = -132.00 + 60.125X_2 - 0.02687X_1X_2 + 2.6875X_2X_3 - 6.25X_2^2 \tag{11}$$

The phenol degradation efficiency was developed using Eq. (11) in three-dimensional response surface plots, as shown in Fig. 4. The effects of the persulfate dosage and Fe^{2+} dosage, the persulfate dosage and pH, and the Fe^{2+} dosage and pH are shown in Figs. 4a–c, respectively. To investigate the interactive effects of the independent variables (PS dosage, concentration of activator, and pH) on responses, one variable was kept constant while the other two variables were varied. In this study, the response plots and contour plots indicated that the optimum conditions for maximum values of the responses were attributed to the persulfate dosage, the Fe^{2+} dosage, and the pH, respectively. The experimental design data with actual values for all treatments and the removal efficiency results from the experimental and model predictions are shown in Table 3. The good compatibility between the predicted and experimental results verified the validity of the model and showed the existence of the optimal point [32]. Calculating the predicted value from the model and the values from the experiment showed a positive relationship with $R^2 = 0.9053$. These results indicated that the phenol removal efficiencies for all response parameters obtained from the experiments and the model predictions were in close compatibility.

Finally, based on the RSM of our results, we found that the optimum conditions for treating 10 mg L^{-1} phenol-contaminated groundwater were 522.40 mg L^{-1} PS with 4.85 mg L^{-1} Fe^{2+} at pH 6.99 (Fig. 3). Previous studies also indicated that the persulfate dosage, the activator dosage, and the pH were the major factors for remediating organic chemicals by PS, for example, reactive dyes [45], and toluene [46]. A limitation of using these optimized values to treat contaminated groundwater should be realized. There are other factors that affect the degradation efficiency using persulfate, for example, temperature, humic acid exists in groundwater, and ions in persulfate system (Cl^-, HCO_3^-, K^+, and Na^+) [15]. Therefore, other factors should be considered when PS was applied in the contaminated site.

Table 3
Experimental design for RSM and phenol removal efficiency (%) by persulfate oxidation with Fe^{2+} as activator

Trial	Actual value			Removal efficiency (%)	
	X_1	X_2	X_3	Experimental	Predicted
1	300.00	5.00	5.00	82.78	80.22
2	700.00	7.00	7.00	56.93	51.14
3	700.00	3.00	7.00	76.22	73.90
4	500.00	5.00	7.00	93.06	89.04
5	700.00	5.00	9.00	89.09	87.96
6	500.00	3.00	9.00	34.12	37.02
7	500.00	7.00	5.00	67.23	65.34
8	300.00	3.00	7.00	54.45	56.30
9	300.00	7.00	7.00	77.01	70.09
10	500.00	3.00	5.00	66.43	63.05
11	500.00	7.00	9.00	78.45	70.87
12	500.00	5.00	7.00	93.56	90.45
13	300.00	5.00	9.00	85.67	82.56
14	500.00	5.00	7.00	93.08	90.45
15	500.00	5.00	7.00	93.78	90.32
16	700.00	5.00	5.00	80.08	76.01
17	500.00	5.00	7.00	93.22	90.97
18	300.00	5.00	5.00	82.95	80.19
19	700.00	7.00	7.00	56.62	55.67
20	700.00	3.00	7.00	76.45	72.18

Table 4
Analysis of variance of RSM model for phenol removal by persulfate oxidation

Source	Sum of Squares	df	Mean square	F-value	P-value Prob. > F
Model	4,207.25	9	467.4722	9.172545	0.0040
X_1	1.125	1	1.125	0.022074	0.8861
X_2	288	1	288	5.651016	0.0491*
X_3	10.125	1	10.125	0.198669	0.6693
X_1X_2	462.25	1	462.25	9.070077	0.0196*
X_1X_3	9	1	9	0.176594	0.6869
X_2X_3	462.25	1	462.25	9.070077	0.0196*
X_1^2	21.31579	1	21.31579	0.41825	0.5384
X_2^2	2,631.579	1	2,631.579	51.63575	0.0002*
X_3^2	191.8421	1	191.8421	3.764246	0.0435
Residual	356.75	7	50.96429		
Lack of fit	356.75	3	118.9167		
Pure error	0	4	0		
Cor. total	4,564	16			

R^2 = 0.9218, adjusted R^2 = 0.8213, predicted R^2 = 0.2507, and adequate precision = 9.063.

3.4. Total oxidant demand

In the real application of PS treatment, the amount of oxidant consumed by both organic and inorganic components of aquifer is necessary to study. We measured the sodium persulfate concentrations after 120 h to calculate the TOD values to show the amount of persulfate consumed by the organic matter containing in aquifer. We conducted the experiments to quantify the total oxidant demand for the aquifer and groundwater collected from the contaminated field site. For comparison, soil oxidant demand was measured on six different combinations of aquifer and groundwater. For the control, we measured the TOD on the sand and deionized (DI) water for five different persulfate concentrations. The control had the lowest TOD, with all TOD values less than 0.1 g kg^{-1} (Fig. 5). When aquifer or groundwater were used, the TOD values were 6–10-fold higher than the control, with the highest TOD observed when aquifer and groundwater were combined and tested. To be able to leach solute through a column in a reasonable time, aquifer collected from the field site were mixed with sand using 50:50 and 30:70 ratios. These combinations also had similarly high TOD levels. Our results showed that the TOD was approximately 0.2–1.0 g kg^{-1} in the range of the persulfate concentration of 100–5,000 mg L^{-1} (Fig. 5).

The TOD values based on the subsurface condition and occurrence parameters. TOD of aquifer originated from limestone or clean sand with low metals content, and low natural organic matter was generally low (<0.1–0.5 g kg^{-1}). Aquifer with oxic conditions, mildly reducing condition or moderately reducing condition with elevated dissolved oxygen, ferrous iron, or sulfate was able to elevate TOD values (0.1–5 g kg^{-1}) [57]. Persulfate preferentially oxidizes the OM first, and then the contaminant oxidation process commences because some components of OM, such as humic acid compete with the pollutants during the oxidation reaction, affecting the removal efficiency [58]. Humic acid could consume sulfate radicals because some functional groups of the humic acid molecule could react with sulfate radicals and could be regarded as the sink of radicals [32,58]. Beside OM, pH of aquifer also affected on TOD. At moderate acidic condition (pH 5.7–5.9), TOD of aquifer with lower OM content (0.52% OM) was lower than TOD of aquifer with high amount of OM (2.41% OM). On the other hand, very strong alkaline conditions (pH 10), TOD values of aquifer with either low or high OM content were increased significantly [59].

3.5. Phenol adsorption and transport with persulfate and activated persulfate

Phenol adsorption was measured on the aquifer-sand combination (30:70) used in the miscible displacement experiments. The purpose of this measurement was to quantify adsorption and verify that the lack of phenol leaching from the aquifer column experiments was due to oxidation by the persulfate and not adsorption. The results of Langmuir and Freundlich isotherm models are shown in Table 5. The higher R^2 value indicated that the Freundlich model fitted the isotherm data of phenol better than the Langmuir model. The phenol isotherm result had a nonlinear model (n < 1.0). Our result based on a sandy clay loam aquifer (Table 2) showed that phenol adsorption was low with a low soil distribution coefficient (K_d) value (fitted linear K_d = 1.25 L kg^{-1}) (Fig. 6). In this study, the K_d value can be substituted by the K_{oc} value (K_{oc} = 1,349.98 L kg^{-1}). The K_{oc} depends on the OM content of aquifer. The higher OM content, the greater K_{oc} value. OM is one of the aquifer properties, which usually plays a dominant role in sorption [60]. Our experiment also identified a low OM content, which was a cause of the phenol adsorption capacity in this study being low. Our result was similar to the previous study of Ololade et al. [61] on sorption capacity for phenol and its derivatives. It was reported that the OM content could positively influence the adsorption potential of phenol. In addition, the aliphatic carbon, humic acid,

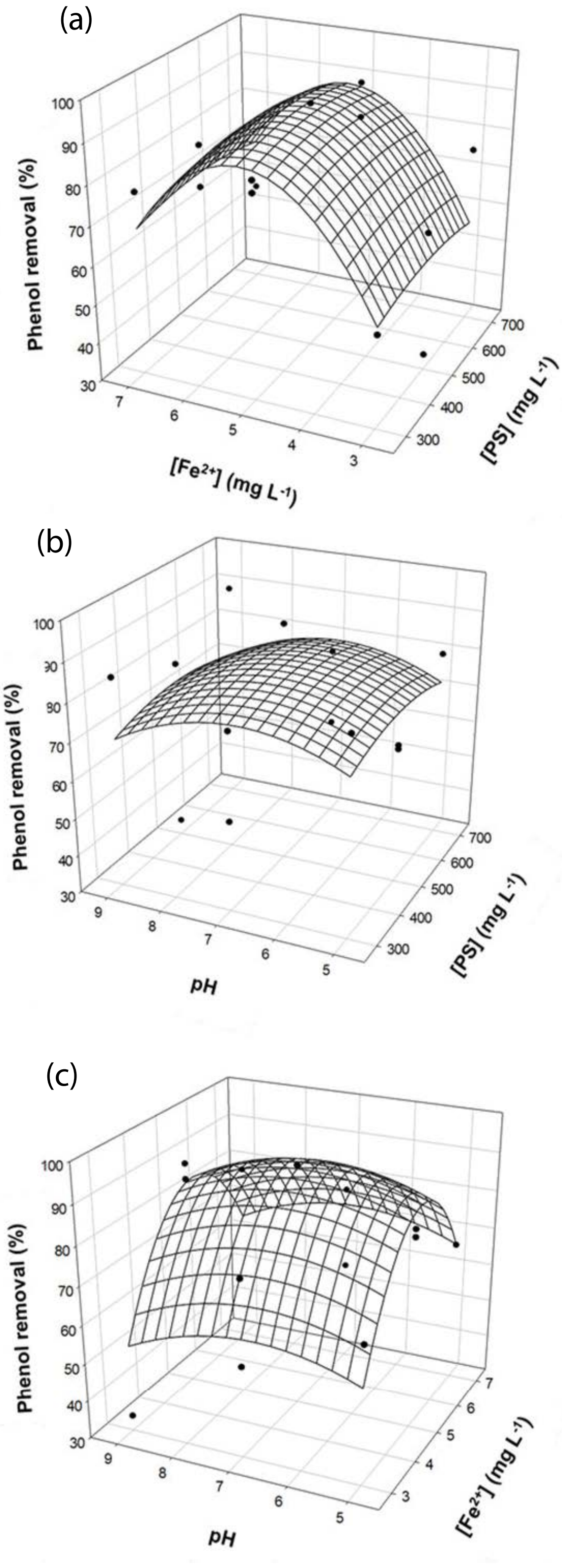

Fig. 4. Response surface plots of treating10 mg L^{-1} phenol in groundwater: (a) PS and Fe^{2+}, the optimal condition was 525 mg L^{-1} PS and 4.97 mg L^{-1} Fe^{2+}, (b) PS and pH, the optimal condition was 518 mg L^{-1} PS at pH 6.7, and (c) Fe^{2+} and pH, the optimal condition was 4.97 mg L^{-1} Fe^{2+} at pH 6.5.

Table 5
Parameters for Langmuir and Freundlich isotherm models of phenol adsorption on aquifer

Langmuir isotherm			Freundlich isotherm		
A (q_m)	B (K_L)	R^2	K_F	n	R^2
22.98	0.16	0.96	3.84	0.59	0.99

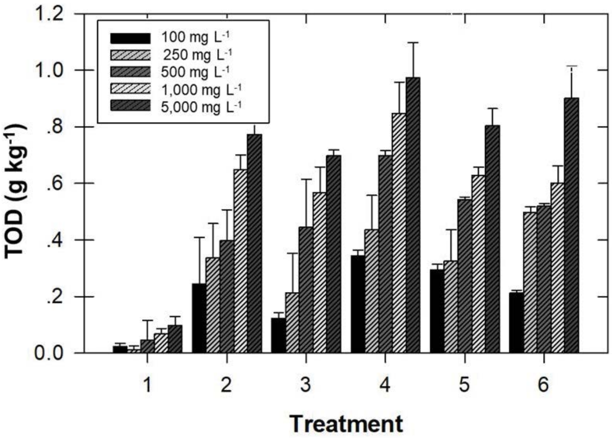

Fig. 5. Total oxygen demand (TOD) of aquifer material applying different PS concentration (100–5,000 mg L^{-1}) and treatment conditions (treatment 1: sand + DI, treatment 2: aquifer + DI, treatment 3: sand + groundwater, treatment 4: aquifer + groundwater, treatment 5: aquifer mixed with: sand (50:50) + groundwater, and treatment 6). Aquifer mixed with sand (30:70) + groundwater.

and fulvic acid of OM had shown a positive correlation to the sorption of phenolic compounds [62]. Furthermore, a previous study showed that a pseudo-second-order model presented phenol adsorption as a chemical sorption process [63]. Their result proved that phenolic compounds were absorbed in aquifer via 2 forms: (1) a sorbed form consisting of ionic, hydrogen, and hydrophobic bonds due to the ability of the –OH group of phenolic compounds to act as proton acceptors in aquifer particles; and (2) a polymerized form, consisting of humic substances bound with OM [64].

Miscible displacement experiments have shown that soil columns equilibrated with 10 mg L^{-1} phenol could be treated with persulfate. The use of activated persulfate to remove phenol during miscible displacement was also investigated. Column leaching experiments were performed where persulfate was injected into an aquifer column containing a zero-valent iron (1%, w/w) as an activator. The results showed that after displacing three pore volumes, the phenol concentration decreased 82% (Fig. 7). Yang et al. [42] showed that the breakthrough of phenol was observed after approximately 2.86 pore volumes of phenol solution pumped into the column containing rich-iron soil. These results confirmed the use of activated persulfate for removing phenol from contaminated groundwater. By using the concentrations of phenol in the effluent and the cumulative volume of effluent recovered, we recaptured approximately 64% of the phenol initially present. Given

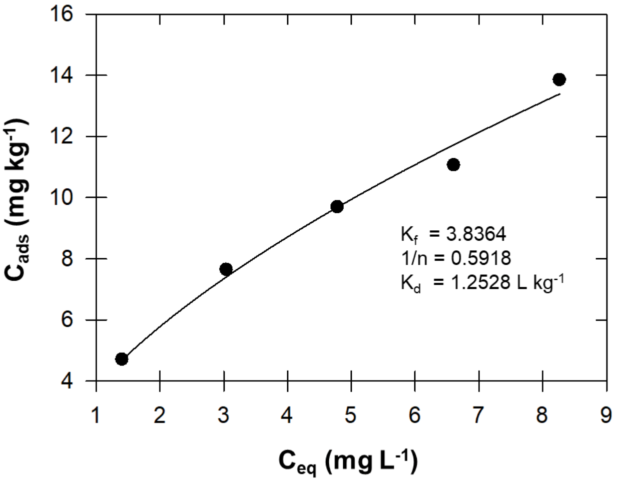

Fig. 6. Adsorption isotherm of phenol at pH 7 on aquifer at equilibrium time (24 h).

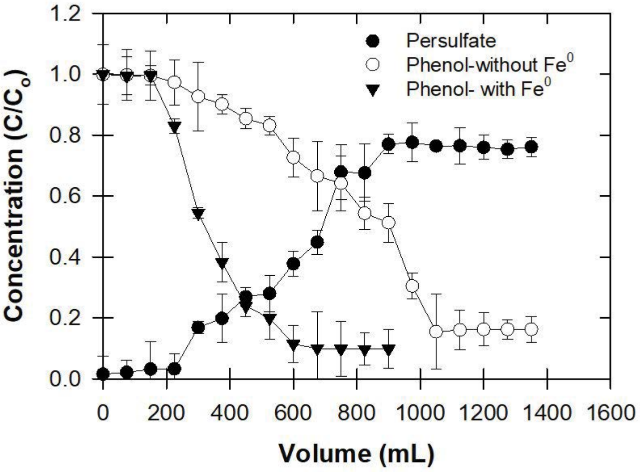

Fig. 7. Breakthrough curves of phenol (10 mg L^{-1}) at pH 7 and persulfate (500 mg L^{-1}) through the aquifer column with Fe^0 (1%, w/w) and without Fe^0 added. Bars on symbols represent standard deviations; where absent, bars fall within symbols.

the adsorption isotherm confirmed that the sorption of phenol was minimal (Fig. 5), most of the unrecovered phenol could be attributed to oxidation (~36%). By including a zero-valent iron in the sand mixture (1% w/w), much less phenol mass was recovered in the effluent (~44%), corresponding to ~56% oxidation of phenol during transport when the activated persulfate was used. This corresponded to a 20% increase in the percentage of phenol oxidized during transport when Fe^0 activation was used.

Experiments were conducted to investigate persulfate transport in the presence of phenol in the aquifer column. In the phenol treatment experiments, the results indicated that the persulfate solution would push dissolved phenol from the column (solution displacing phenomena). Therefore, the effluent phenol concentration gradually increased to a maximum when about an amount of three pore volume was replaced with the flushing solution in the column. The presence of Fe^0 within the column caused a quick drop in effluent phenol concentration and more phenol degradation was observed (Fig. 6). The pHs in the effluent during experiments ranged from 4.0 to 4.4. At strong acidic condition, the dissolution of zerovalent iron increased yields of Fe^{2+} in the system. The higher amount of activator (Fe^{2+}) enhanced phenol removal efficiency. This is supported by our results in batch experiment (Fig. 1e). On the other hand, the columns without Fe^0 addition were able to eliminate phenol even though it took longer. Although the high concentration of iron content was found in aquifer (Table 2), iron occurred as iron oxide/oxyhydroxide forms. These forms of iron was an insoluble form that was difficult to dissolve [65] and was not strong enough to activate PS in column.

4. Conclusions

An inadvertent chemical spill in Chachoengsao province, Thailand resulted in a phenol-contaminated aquifer. This prompted an investigation into developing suitable technology to remove the phenol. Our research found that activated persulfate has the potential to treat the phenol-contaminated aquifer. The results from treatment variable testing and our statistical analysis indicated the optimum conditions for treating phenol-contaminated groundwater included using 522.40 mg PS L^{-1} with 4.85 mg Fe^{2+} L^{-1} as an activator at pH 6.99. Our miscible displacement experiments confirmed that activated PS could be used to treat phenol-contaminated groundwater and aquifer during transport. We recommend the experiment conducting in three dimensions tank for the further study before applying in real situation.

Acknowledgments

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