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Application of Nanosized Zero-valent Iron-Activated Persulfate for Treating Groundwater Contaminated with Phenol

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ABSTRACT

Persulfate (PS) activated with nanosized zero-valent iron (NZVI) was tested as a reagent to remove phenol from groundwater. Batch degradation experiments indicated that NZVI/PS molar ratios between 1 : 2 and 1 : 5 were appropriate for complete removal of phenol, and that the time required for complete removal varied with different PS and NZVI dosages. Chloride ions up to 100 mM enhanced the phenol oxidation rate, and nitrate of any concentration up to 100 mM did not significantly affect the oxidation rate. NZVI showed greater performance than ferrous iron did as an activator for PS. A by-product was formed along with phenol degradation but subsequently was completely degraded, which showed the potential to attain mineralization with the NZVI/PS system. Tests with radical quenchers indicated that sulfate radicals were a predominant radical. The results of this study suggest that NZVI is a promising activator of PS for treating contaminated groundwater.

Key words : Phenol, Nanosized zero-valent iron, Persulfate, Groundwater anions, Sulfate radical

1. Introduction

Subsurface water and soil contamination are becoming serious environmental issues that affect not only environment quality itself but also the health of humans and other living organisms that live near these polluted areas. Toxic chemicals from the land's surface or underground storage tanks can leak through the soil and find their way into groundwater (Masciopinto, 2006; Ren et al., 2017). When numerous adverse health effects were observed, substantial environmental remediation actions were then carried out to remediate polluted sites where numerous recalcitrant contaminants were present (Gomes et al., 2012; Li et al., 2014b). Although the search for more effective techniques never ceases, in situ chemical oxidation (ISCO) is considered as "a relatively mature technology" for treating contaminated source zones and plumes (Siegrist et al., 2011).

Persulfate (PS; $S_2O_8^{2-}$) is the newest oxidant being used in ISCO for soil and groundwater remediation. The reasons for the widespread use of PS lie in its stability at ambient conditions, its high solubility, and its ability to form benign products. More importantly, it can be activated to form sulfate radicals, which are nonselective and much stronger oxidants with $E_h = 2.6$ V (Eberson, 1982), and hydroxyl radicals, depending on the activating conditions. This indicates that PS can treat a wide range of contaminants. PS can be activated to produce reactive radicals by various activators/ mechanisms, such as heat, electron transfer (metal ions), and UV light (Tsitonaki, 2010; Siegrist et al., 2011).
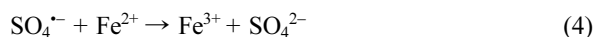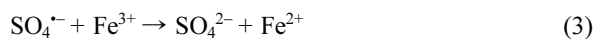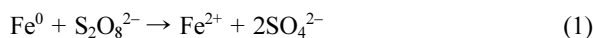
Nanosized zero-valent iron (NZVI) was investigated in this study as a source of Fe^{2+} and Fe^{3+} ions. The NZVI-activated PS mechanism is based on the activation reactions below (Equations (1) and (2)) (Oh et al., 2009). Fe^{3+} can be reduced back to Fe^{2+} (Equation (3)), thus maintaining the effectiveness of the system (Budaev et al., 2015). One limited characteristic that PS activated by iron species has is that when ferrous ions are produced in excess, sulfate radicals are likely quenched and the efficiency of the system therefore is compromised (Equation (4)). However, when NZVI is utilized as an activator, the increase in NZVI dosage sometimes enhances the degradation efficiency of pollutants. In this case, the mechanism driving the system is

presumably not only oxidation, but also reduction (Al-Shamsi and Thomson, 2013).

$$Fe^0 + S_2O_8{}^{2-} \rightarrow Fe^{2+} + 2SO_4{}^{2-} \qquad (1)$$

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

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

$$SO_4{}^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4{}^{2-} \qquad (4)$$

The aims of this study were to examine the performance of an NZVI/PS system in treating a phenol-contaminated groundwater and the effect of operating parameters on the phenol removal efficiency. Initially, various NZVI/PS molar ratios were evaluated. The chloride concentration of the target aquifer was reported to be as high as 337.8 mM and the nitrate concentration up to 6.5 mM. Hence, it was essential to study the effect of chloride and nitrate at wide ranges of concentrations. To elucidate effective radicals in the NZVI/PS system, different radical quenchers were adopted for degradation tests.

2. Materials and methods

2.1. Materials

All reagents were used as received, without any further purification. The NZVI used was NANOFER 25 (20% slurry in water, Nanoiron, Czech Republic) with average particle size of 1818.6 ± 104.9 Å and a specific surface area of 33.1 ± 1.0 m^2/g. Sodium persulfate (>98%) was used as the persulfate source instead of potassium persulfate or ammonium persulfate because of its higher solubility and rather benign nature. Sodium salts (NaNO$_3$ (99%), NaCl (99%)) served as the anion suppliers. The sources of ferrous and ferric ions were FeSO$_4$ (>99%) and Fe$_2$(SO$_4$)$_3$ (60%-80%), respectively. Other chemicals used were ethanol (99.9%), tert-butyl alcohol (TBA; 99%), hexane (95%), and phenol (>99.5%).
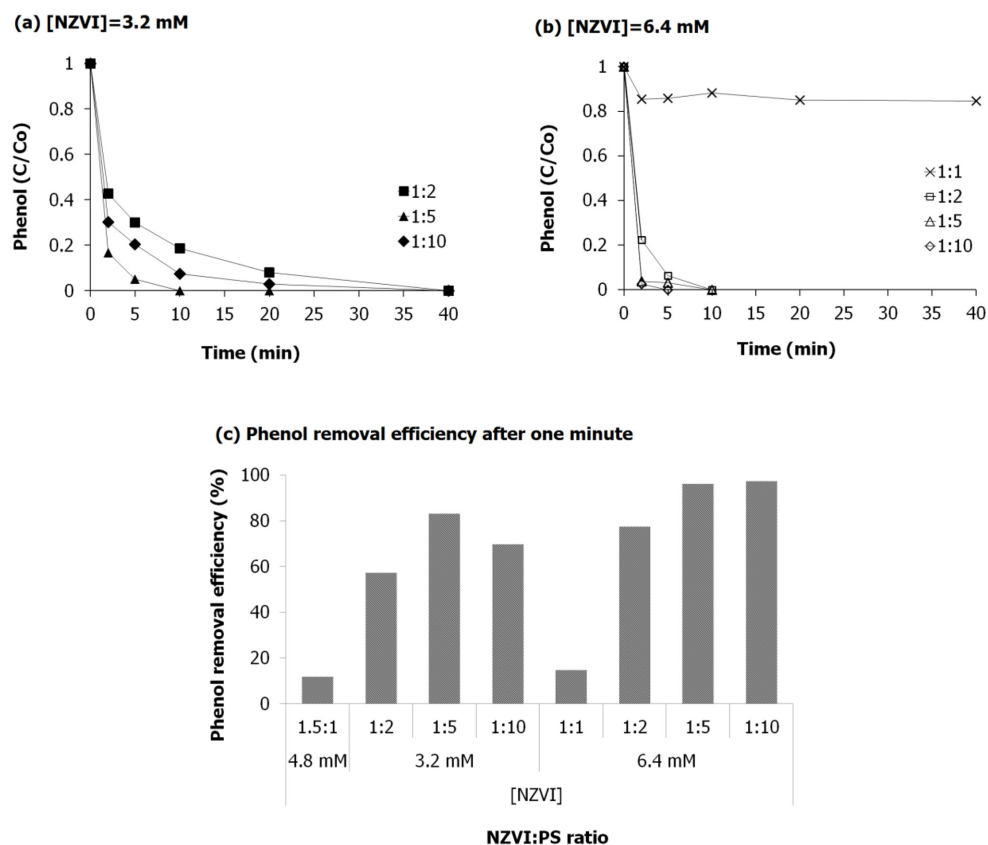
2.2. Phenol degradation tests

Batch experiments were conducted using 40 mL transparent borosilicate glass vials capped with poly (tetrafluoroethylene) septa. Phenol solutions were prepared by adding the desired amount of phenol to deionized water (resistivity of 18.2 MΩ cm^{-1}). Reactions were initiated by adding aliquots of a sodium persulfate solution and activator (NZVI, Fe^{2+}, or Fe^{3+}) solutions to the prepared phenol solutions. Then, the vials were placed on a rotary shaker operated at 30 rpm. Experiments were conducted at room temperature (20.5 ± 4ºC) and the initial pH was not adjusted. The pH of the solutions remained near 2.5 throughout the reactions.

To determine the effective NZVI/PS ratio, a sequence of experiments was performed with different NZVI/PS ratios and dosages. For the experiments with anions, the anions were added initially with the phenol to the solutions. NO$_3^-$ and Cl$^-$ were examined at increasing concentrations from 0 mM to 100 mM. To study the mechanism of the NZVI-activated PS system further, Fe^{2+} and Fe^{3+} were also tested as PS activators at the same concentration as NZVI on a molar basis, i.e., [Fe^{2+}] = [Fe^{3+}] = [NZVI] = 6.4 mM. TBA and ethanol were used to identify effective radicals in the NZVI/PS systems. Anipsitakis and Dionysiou (2004) state that the reaction rate of TBA with hydroxyl radicals is approximately 1000 times higher than that of TBA with sulfate radicals. Thus, TBA is considered a hydroxyl radical quencher. On the other hand, ethanol can react with hydroxyl radicals 50 times faster than with sulfate radicals. This makes ethanol a quencher for both hydroxyl and sulfate radicals. The alcohol/phenol (ethanol/phenol and TBA/phenol) ratio was increased from 0 to 40, and phenol removal efficiency was recorded after 30 minutes of reaction.

2.3. Analysis

Phenol concentrations were determined using gas chromatographs equipped with an electron capture detector and a flame ionization detector (GC-ECD and GC-FID, respectively) via a microextraction method. A high performance liquid chromatograph (HPLC) with a UV detector was used to detect phenol by-products. X-ray diffractometry (XRD) was conducted using a Shimazu XRD 6000 at Kα wavelength radiation (λ = 1.5406) and a step size of 0.017º with a count time of 194.945 s per step. The scan range of 2θ varied from 5º to 80º, and the results were matched with the help of PDF2 search software and the JCPDS (Joint Committee on Powder Diffraction Standards) database.

Fig. 1. Phenol degradation with different NZVI/PS ratios ([phenol] = 0.32 mM) (a) Phenol degradation with NZVI concentration = 3.2 mM (b) Phenol degradation with NZVI concentration = 6.4 mM (c) Removal efficiency of phenol after one minute.

3. Results and discussion

3.1. Effect of NZVI/PS ratio

Fig. 1(a) shows the kinetics of phenol degradation when the NZVI concentration was 3.2 mM and the concentration of PS increased from 6.4 mM to 32 mM. Three selected NZVI:PS ratios worked successfully in removing phenol within 40 minutes. Fig. 1(b) shows the degradation kinetics when the NZVI concentration was 6.4 mM and the concentration of PS increased from 6.4 mM to 64 mM. At the ratio of 1 : 1, 15% of the phenol was removed and the reaction then was quenched, probably because of the excessive ferrous ions formed in the solution. Fig. 1(b) indicates that the increase in both NZVI and PS dosages with NZVI/PS ratios similar to the 3.2 mM NZVI experiments shortened reaction times for complete removal from 40 minutes to 10 minutes. This reactivity is considered competitive when it is compared with the kinetics observed by Diao el al.

(2016). They obtained a phenol removal efficiency of 70% after 30 minutes of reaction with a bentonite-supported NZVI and PS system when the PS : phenol ratio (10 : 1.1) was substantially lower than that of the present work.

Neither pseudo-first-order nor second-order rate law was able to describe the phenol degradation kinetics. This is probably because of the involvement of several reaction mechanisms, described in Equations (1) to (4). Phenol was degraded rapidly within the first one minute for both the 3.2 mM and 6.4 mM experiments. Hence, phenol removal efficiency after one minute was used to compare the reaction rates of different systems in this study.

Fig. 1(c) shows that the increase in NZVI/PS ratio from 1 : 2 to 1 : 5 enhanced phenol removal noticeably, i.e., by 25% at [NZVI] = 3.2 mM and by 20% at [NZVI] = 6.4 mM, but when the NZVI/PS ratio continued to increase from 1:5 to 1 : 10, the efficiency was either lessened by 10% when [NZVI] = 3.2 mM or did not differ much from that of the
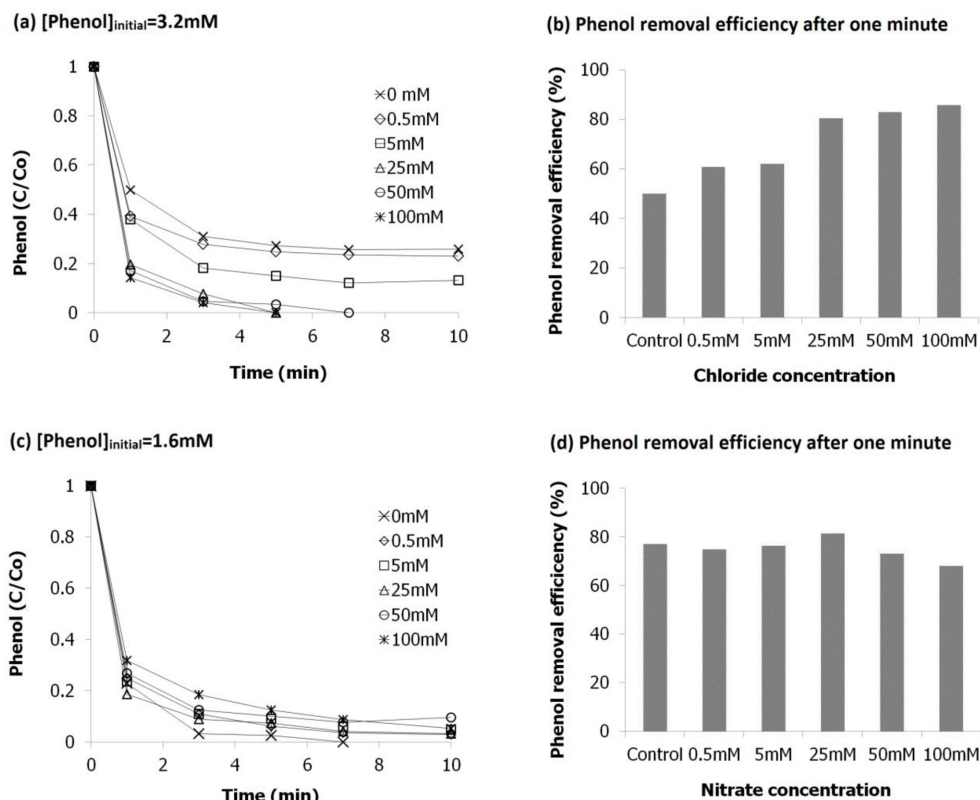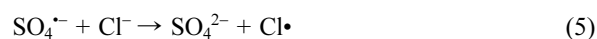
1 : 5 ratio experiment when [NZVI] = 6.4 mM. An additional experiment with a NZVI/PS ratio of 1 : 1.5 yielded a very low degradation efficiency of 10%. This again indicates that an excessive dosage of NZVI quenches radicals. The effect of doubling the PS concentration at different NZVI/PS ratios can also be seen in Fig. 1(c). One-minute removal efficiency increased by 20%, 13%, and 30% for the NZVI/PS ratios of 1 : 2, 1 : 5, and 1 : 10, respectively.

These results reveal that an optimum NZVI/PS ratio lies between 1 : 2 to 1 : 5 and that this ratio range can be utilized for groundwater treatment. The NZVI/PS ratio of 1 : 2 with [NZVI] = 3.2 mM was exploited to investigate the effect of other parameters (except when examining the effect of chloride) in this study.

3.2. Effect of chloride and nitrate ions

As shown in Fig. 2(a) and (b), the presence of chloride enhanced phenol removal steadily with increasing chloride concentration. The increase in the concentration of chloride

from 0.5 mM to 100 mM increased the phenol removal efficiency after one minute from 50% to 86% (Fig. 2(b)). This can be attributable to the role of chloride as an iron corrosion enhancing agent (Ma, 2012). Fang et al. (2012) explained this enhancement by claiming that the presence of chloride ions increased the total reactive radical concentration by forming other radicals such as described in Equations (5) to (10) below (Pennington and Haim, 1968; Buxton et al., 1999; Magazinovic et al., 2004; Huang et al., 2005).

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl\bullet \tag{5}$$

$$OH^\bullet + Cl^- \rightarrow ClOH^{\bullet-} \tag{6}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \tag{7}$$

$$Cl^\bullet + OH^- \rightarrow ClOH^{\bullet-} \tag{8}$$

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2 \tag{9}$$

$$ClOH^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + OH^- \tag{10}$$

Fig. 2. (a) Phenol degradation in the presence of chloride at different concentrations. [Phenol] = 3.2 mM, [PS] = 64 mM, [NZVI] = 32 mM. (b) Phenol degradation efficiency after one minute. (c) Phenol degradation in the presence of nitrate at different concentrations. [Phenol] = 1.6 mM, [PS] = 64 mM, [NZVI] = 32 mM. (d) Phenol degradation efficiency after one minute.

Fig. 2(c) and (d) show that nitrate presence from 0.5 mM to 100 mM generally did not cause substantial effects on phenol removal. However, a closer look at Fig. 2(a) reveals that phenol could not be completely degraded within 10 minutes when nitrate was present, whereas the system could completely remove 1.6 mM phenol within 7 minutes in the absence of nitrate ions. This indicates that the presence of nitrate ions, in general, slightly inhibited phenol degradation. This inhibition can be explained by the formation of $NO_3^{\bullet}$ (Exner et al., 1992) (Equation (11), $E_h = 2.5$ V), which has oxidation potential equal to or less than that of sulfate radicals ($E_h = \sim2.5$ V to 3.1 V; Neta et al., 1977). In addition, Ahn et al. (2016) state that nitrate reacted with NZVI and produced NH_4^{+} as the final product. This suggests that nitrate introduced into the system competed with the PS in reacting with NZVI and moderately inhibited phenol degradation.

$$SO_4^{\bullet-} + NO_3^{-} \rightarrow NO_3^{\bullet} + SO_4^{2-} \qquad (11)$$
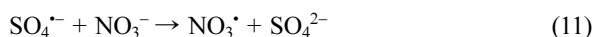
It is encouraging to observe that chloride can enhance, whereas nitrate does not significantly affect, phenol degradation. This implies that PS/NZVI can be applied to treat groundwater with very high concentrations of major anions, such as chloride and nitrate.

3.3. Reaction mechanisms and by-products

3.3.1. Effect of different iron sources as activators

Fig. 3 shows the effectiveness of different iron species as activators. NZVI showed the greatest activating proficiency by completely removing phenol within 5 minutes although the soluble irons were initially expected to perform better as activators. The NZVI/PS system was six times more efficient in completely removing phenol than ferrous iron was. This is consistent with previous studies (Peluffo et al., 2016; Pardo et al., 2015; Li et al., 2015) that reported the improvement of NZVI-activated PS systems over Fe^{2+}-activated PS systems. Pardo et al. (2016) claim that NZVI slowly releases soluble iron to prevent the formation of radical scavengers and thus improves the performance. Fig. 3 also shows that an Fe^{3+}-activated PS system can remove a significant amount of phenol. This implies that Fe^{3+} and Fe^{2+} can be recycled, which can maintain the effectiveness of the system for extended periods. Thus, NZVI is a prom-

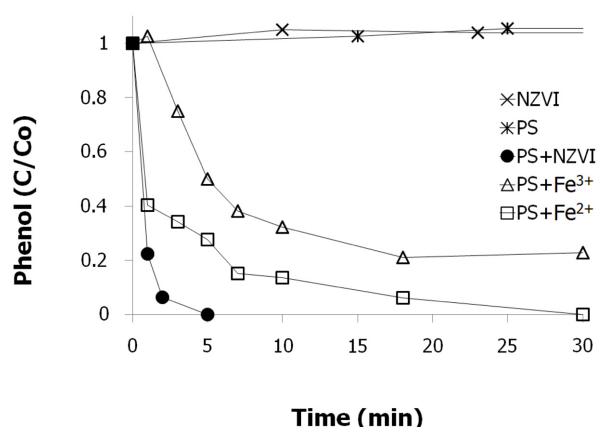**Fig. 3.** Phenol degradation in the presence of different iron activators. [Phenol] = 0.32 mM, [PS] = 12.8 mM, [NZVI] = [Fe^{2+}] = [Fe^{3+}] = 6.4 mM.
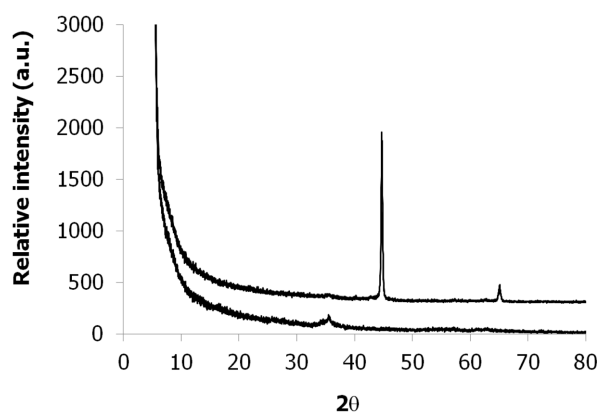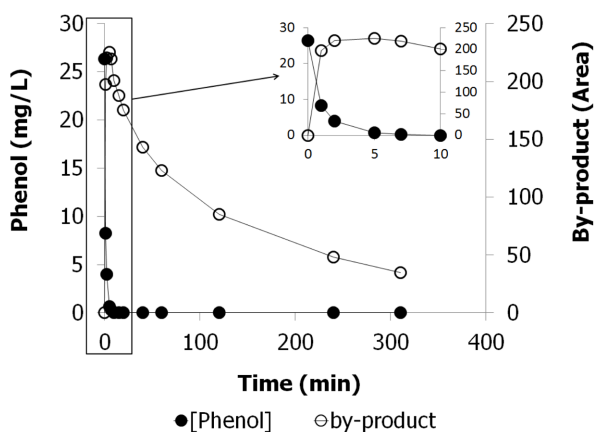
Fig. 4. XRD patterns of NZVI particles before and after 1 hour of reaction with phenol. [Phenol] = 0.32 mM, [PS] = 12.8 mM, [NZVI] = 6.4 mM.

ising activator for field application because it not only has the highest activating efficiency but also can steadily produce ferrous and ferric ions to increase the treatment longevity.

3.3.2. XRD

XRD testing was conducted to examine the changes on the surface of NZVI particles and to clarify iron speciation. The XRD pattern presented in Fig. 4 shows the major components in NZVI particles before and after reaction with PS to eliminate phenol. A strong peak at 2θ of 44.7° before the reaction confirmed that Fe^0 was the major iron species of NZVI particles. In the XRD pattern after the reaction, this large peak completely disappeared, implying that Fe^0 had been completely consumed to form soluble iron forms,
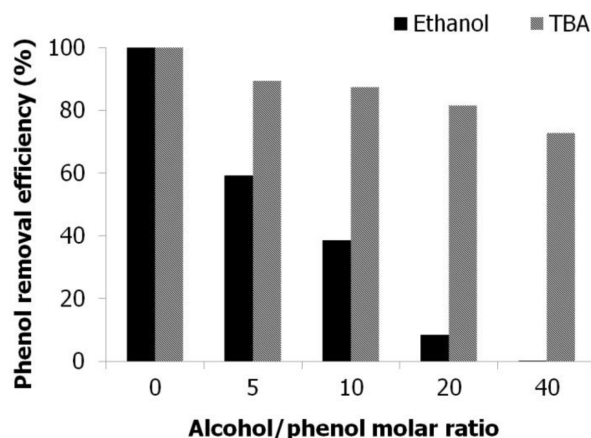
Fig. 5. Formation and disappearance of a phenol by-product. [Phenol] = 0.32 mM, [PS] = 12.8 mM, [NZVI] = 6.4 mM.

Fig. 6. Phenol degradation efficiency after 20 minutes of reaction in the presence of radical quenchers. [Phenol] = 1.6 mM.

other types of iron minerals, or both. This agrees well with a study conducted by Li et al. (2015). The small peak in the XRD pattern after the reaction at 2θ of 35.5° was suspected to be due to hematite, goethite, magnetite, and schwertmannite (Li et al., 2014a). Li et al., 2014a claimed that schwertmannite was able to activate PS with relatively slow kinetics. Therefore, the formation of iron corrosion products, such as schwertmannite, together with soluble iron species in an NZVI/PS system can help increase the treatment longevity.

3.3.3. Phenol by-product

Fig. 5 shows that a by-product formed rapidly during the phenol degradation. The inset of Fig. 5 reveals that as the concentration of phenol rapidly decreased during the first one minute, the formation of the by-product correspondingly increased. Our HPLC results suggest that the by-product was likely either benzoquinone or hydroquinone (data not shown). Previous papers also state that the major by-products of phenol degradation are hydroquinone, benzoquinone, and catechol (Boukari et al., 2011; Olmez-Hanci and Arslan-Alaton, 2013). When phenol was completely removed from the system after five minutes, the concentration of by-product gradually decreased. This suggests that by-products formed can be degraded completely and mineralization may occur in the current NZVI/PS system. However, further work on TOC concentration should be conducted to confirm the mineralization.

3.3.4. Reactive radicals

Fig. 6 depicts the effect of different radical quenchers on phenol removal efficiency. Phenol removal efficiency decreased significantly as the alcohol : phenol ratio increased from 0 to 40. Phenol degradation was almost completely quenched at the alcohol : phenol ratio of 40. Phenol removal efficiency also decreased as the TBA : phenol ratio increased. Nevertheless, the effect was far less than that of ethanol. At the TBA : phenol ratio of 40, the phenol removal efficiency only dropped from 100% to 78%. This indicates that in the system where TBA, a hydroxyl radical quencher, was added, sulfate radicals were responsible for phenol degradation, whereas in the system where ethanol was added, both hydroxyl and sulfate radicals were quenched. These results indicate that the major reactive radical in the system was the sulfate radical.

4. Conclusion

The NZVI/PS system has demonstrated its efficiency to remove phenol that may be present in a groundwater environment rapidly. Appropriate PS and NZVI loads were crucial when designing a treatment scheme. It was found that the amount of NZVI should necessarily be less than that of PS on a molar basis in order to avoid the radical quenching caused by excess ferrous ions. The optimum NZVI/PS ratio for the highest removal rate was between 1 : 2 to 1 : 5, and an NZVI/PS ratio in this range was considered appropriate for groundwater treatment. NZVI, as an activator for PS,

proved to be superior to other soluble iron species. The soluble iron species Fe^{2+} and Fe^{3+} formed from NZVI were able to activate PS and were expected to yield a long-term treatment system through recycling processes. Chloride up to a concentration of 100 mM enhanced phenol degradation noticeably, whereas nitrate up to a concentration of 100 mM did not significantly impact the system. The system therefore could be applied to treat groundwater in which concentrations of anions are high. A series of radical quenching tests confirmed that sulfate radicals were predominant in the system. Analysis on the by-products suggested that mineralization of by-products may be attainable. This study shows that NZVI is a promising activator of PS that is suited to groundwater treatment and can potentially provide long-term treatment.

Acknowledgement

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