Benzene oxidation by Fe(III)-activated percarbonate: matrix-constituent effects and degradation pathways

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Abstract: Complete degradation of benzene by the Fe(III)-activated sodium percarbonate (SPC) system is demonstrated. Removal of benzene at 1.0 mM was seen within 160 minutes, depending on the molar ratios of SPC to Fe(III). A mechanism of benzene degradation was elaborated by free-radical probe-compound tests, free-radical scavengers tests, electron paramagnetic resonance (EPR) analysis, and determination of Fe(II) and H₂O₂ concentrations. The degradation products were also identified using gas chromatography-mass spectrometry method. The hydroxyl radical (HO•) was the leading species in charge of benzene degradation. The formation of HO• was strongly dependent on the generation of the organic compound radical (R•) and superoxide anion radical (O₂•⁻). Benzene degradation products included hydroxylated derivatives of benzene (phenol, hydroquinone, benzoquinone, and catechol) and aliphatic acids (oxalic and fumaric acids). The proposed degradation pathways are consistent with radical formation and identified products. The investigation of selected matrix constituents showed that the Cl⁻ and HCO₃⁻ had inhibitory effects on benzene degradation. Natural organic matter (NOM) had accelerating influence in degrading benzene. The developed system was tested with groundwater samples and it was found that the Fe(III)-activated SPC has a great potential in effective remediation of benzene-contaminated groundwater while more further studies should be done for its practical application in the future because of the complex subsurface environment.

Keywords: percarbonate; Fe(III); benzene; organic compound radical (R•); reactive oxygen species; groundwater remediation;

1. Introduction

In situ chemical oxidation (ISCO), an effective technique for remediating contaminated sites, has been applied for the last three decades in removing numerous chlorinated organic compounds and petroleum hydrocarbons [1-5]. Hydrogen peroxide is a strong oxidant catalyzed in water to generate wide variety of free radicals. Both oxidants and reductants generated in catalyzed hydrogen peroxide (CHP) can be used in water treatment processes. Hydroxyl radicals ($\text{HO}^\bullet$), formed from the Fenton process (Eqs. 1-3) [6,7], are highly reactive with a large number of organic contaminants (10^7 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$).

The application of $\text{HO}^\bullet$ radicals has been used widely in ISCO [8-10]. However, traditional Fenton process has significant drawbacks for practical applications, which include requirement of acidic pH condition and the rapid consumption of iron [11]. Therefore, modifications of the conventional Fenton reaction have been carried out [12-14], for example, Fe(III) driving a Fenton-like reaction [15], the mediation of chelating agents (CA) [16-18], and the application of novel heterogeneous activator [19,20].

One of the modified Fenton's reactions is the application of Fe(III) in place of Fe(II) to activate H_2O_2 . Under the circumstance of Fe(III), Fe(II)-hydroperoxy

complexes preferentially generate via the unprompted reaction between Fe(III) and H₂O₂ (Eq. 4). These complexes decompose to Fe(II) and produce superoxide anion radicals (O₂^{•-}) and perhydroxyl radicals (HO₂[•]), which can reduce Fe(III) to Fe(II) (Eqs. 5-7). [21-24]

According to Eqs. 4-7, the concentration of Fe(II) may be controlled by the slow decomposition of H₂O₂ in the Fe(III)-activated H₂O₂ system. A gradual generation of HO[•] through slow generation of Fe(II) in the system is advantageous over the conventional Fenton reaction, which has usually rapid scavenging of HO[•] by H₂O₂ (Eqs. 2-3). Hence, in practical implementations, the application of the Fe(III)-activated H₂O₂ system may be preferred over the Fe(II)-activated H₂O₂ system because HO[•] would mostly react with an intended target contaminant [25].

In recent years, attention has been on the application of sodium percarbonate (2Na₂CO₃•3H₂O₂, SPC), a solid carrier of H₂O₂ that releases H₂O₂ when mixed with water (2Na₂CO₃•3H₂O₂ → 2Na₂CO₃ + 3H₂O₂). Moreover, in comparison to the liquid H₂O₂, SPC has advantages, which include a wider pH range suitability, better handle and transport safety. Additionally, SPC has an alkaline property, which prevents the undesired groundwater acidification [26].

The Fe(II)/SPC system has been shown to be effective for degradation of

benzene and trichloroethylene [27,28]. The results showed that this system requires high chemical dosages to achieve complete benzene degradation in the Fe(II)/SPC system. Researchers have applied chelating agents to maintain iron solubility and enhance oxidative performance for the Fe(II)/SPC system [29]. Unfortunately, the chelating agents can also compete for HO[•] and thus lower the oxidative performance of the system. Furthermore, the oxidation products of the competing reaction (i.e. reaction between chelating agent and HO[•]) may have adverse effects to the groundwater environment [6,29].

In the present study, we have developed Fe(III)-activated SPC process, which is an innovative and environmental friendly system. The aims of the current paper are: (i) demonstrate the oxidation efficiency of this system by selecting benzene as the target contaminant, (ii) explore the role of free-radicals to elucidate the mechanism involved in the Fe(III)-activated process, (iii) propose degradation pathways for benzene by analyzing intermediates using gas chromatography-mass spectrometry (GC/MS) technique, (iv) elaborate the influence of pH, ions (SO₄²⁻, NO₃⁻, Cl⁻ and HCO₃⁻), and natural organic matter (NOM) on the efficiency of the system to degrade benzene, and (v) investigate the removal performance of benzene in groundwater sample to seek potential practical application of the developed system.

2. Materials and methods

2.1. Materials

Sodium percarbonate (2Na₂CO₃•3H₂O₂, SPC, 98%) was purchased from Acros

Organics (Shanghai, China). Benzene (C_6H_6 , 99.7%), methanol (CH_3OH , 99.8%), isopropyl alcohol ($(CH_3)_2CHOH$, IPA, 99.5%), carbon tetrachloride (CCl_4 , CT, 99.5%), chloroform ($CHCl_3$, CF, 99.0%), nitrobenzene ($C_6H_5NO_2$, NB, 99.0%), ferric sulfate ($Fe_2(SO_4)_3$, >99.0%), sodium bicarbonate ($NaHCO_3$, 99.5%), sodium sulphate (Na_2SO_4 , 99.0%), sodium chloride ($NaCl$, 99.5%), sodium nitrate ($NaNO_3$, 99.0%) were purchased from Aladdin (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was obtained from Sigma (Shanghai, China). Humic acid (HA, > 90%, was used as a representative of dissolved organic matter (DOM) in this study as fulvic acid is one of the main fractions of DOM in nature with high solubility), 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$, 98%), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, HH, 99.0%) and potassium biphthalate ($C_8H_5KO_4$, 99.0%) were purchased from Shanghai Jingchun Reagent Ltd. Co. (Shanghai, China). H_2SO_4 (0.1 M) or $NaOH$ (0.1 M) was selected for solution pH adjustment. All of the reagents were applied as received. Ultrapure water from a Milli-Q water process (Classic DI, ELGA, 102Marlow, U.K.) was used to prepare the aqueous solutions, with the exception of the experiments conducted with actual groundwater. The groundwater for this manuscript is same as the real groundwater used in our previous work [29].

2.2. Experimental procedures

Desired dosage of benzene stock-solution prepared by mixing benzene with Milli-Q water or real groundwater uniformly was added to a 250 mL cylindrical glass

reactor with two openings at the top: one for dosing and the other for sampling.. The desired initial concentration of benzene was 1.0 mM. A temperature bath (DC, Ningbo, China) was used to provide a temperature-controlled condition (20°C). Pre-determined dosages of $\text{Fe}_2(\text{SO}_4)_3$ and SPC were added sequentially to the reactor containing benzene solution. A magnetic stirring was selected to ensure the homogeneous mixing of all chemicals in the aqueous solution. The addition of other reagents and the adjustment of the initial solution pH were fulfilled before adding $\text{Fe}_2(\text{SO}_4)_3$ and SPC. The experimental procedures of sample analysis and EPR detection are same as our reported study [29].

2.3. Analytical methods

The benzene concentration was detected by a headspace-gas chromatograph [29]. The reaction products were analyzed by GC/MS (Agilent 6890/5973N) in Fudan University and free-radicals were identified by EPR. More details of GC/MS and EPR were showed in Supplementary Material. The pH was measured with a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland). The concentrations of ferrous ion (Fe(II)) and total soluble iron ions were measured by using the 1,10-phenanthroline method [30]. H_2O_2 concentration in aqueous solution was quantified using titanium sulfate [31].

3. Results and discussion

3.1 Benzene degradation effectiveness

Benzene degradation for the Fe(III)-activated SPC system with ultrapure water is presented in Fig. 1. Less than 7.0 % loss of benzene in control tests without ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$ (2.0 mM) or SPC (4.0 mM) indicates that benzene volatilization during the test period could be neglected. However, benzene removal could increase to 100% when dosages of SPC and Fe(III) dosages increase (Fig. 1). This demonstrates the effectiveness of Fe(III)-activated SPC system in degrading benzene.

It is noted that the time required to achieve 100% benzene removal was shortened with an increase of Fe(III) dosage (Fig. 1a). In addition, we could observe that benzene degradation displayed a two-stage reaction, i.e. approximately 30% benzene was degraded in the first stage where the reaction rate was slow, followed by a more rapid rate of degradation in the second stage. Benzene degradation in the first stage could be interpreted by the pseudo-first-order kinetic model (i.e. plots of $\ln([C]/[C]_0)$ versus time were linear, Table 1). The apparent reaction rate constants ($k_{b,\text{Fe(III)}} \cdot t = \ln([C]/[C]_0)$) in the first stage, calculated under various Fe(III) dosages with fixed SPC dosage, are listed in Table 1. The $k_{b,\text{Fe(III)}}$ values increased from $1.36 \times 10^{-3} \text{ min}^{-1}$ to $1.41 \times 10^{-2} \text{ min}^{-1}$ with the increase of Fe(III) dosages from 4.0 mM to 16 mM (test No. 1-5). It appears that the higher Fe(III) dosage promoted Fe(II)-hydroperoxy complexes generation, which subsequently generated more $\text{HO}^\bullet$, leading to faster benzene degradation.

The degradation of benzene was also observed when the SPC dosages increased from 1.0 mM to 5.0 mM (Fig. 1b). The apparent first-order rate constants ($k_{b,\text{SPC}} \cdot t = \ln([C]/[C]_0)$) in the first stage at constant Fe(III) dosage increased from 2.14×10^{-3} to

$6.0 \times 10^{-3} \text{ min}^{-1}$ when SPC dosages was increased from 1.0 mM to 5.0 mM (Table 1, test No. 3 and 6-8). Further increase in SPC dosage led to an reduced rate of benzene degradation. This may be due to consumption of $\text{HO}^\bullet$ radicals by excessive SPC (see Eq. 2) (Table 1, test No. 9).

3.2 Mechanism of benzene degradation in Fe(III)-activated SPC system

3.2.1 Generation of reactive oxygen species

According to Eqs. 1-7, both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ may be generated in the Fe(III)-activated SPC system, thus a series of tests with probe compounds was conducted to characterize the generation of reactive oxygen species in which initial dosages of SPC and Fe(III) were kept at 4.0 and 8.0 mM, respectively. Nitrobenzene (NB) was employed to investigate the generation of $\text{HO}^\bullet$ because it can react with $\text{HO}^\bullet$ at a high rate constant of $3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [6]. Meanwhile, CT was applied as a reductant probe because it can be readily degraded by reductant ($k = 1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) but is not reactive with $\text{HO}^\bullet$ ($k_{\text{HO}^\bullet} < 2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) [10,32]. Compared to the control tests in which minor loss of NB and CT was observed, 81.37% NB and 26.27% CT were degraded in the Fe(III)-activated SPC system, indicating that both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ were present (shown in Fig. S1). The presence of $\text{HO}^\bullet$ was also verified by EPR tests (shown in Fig. S2). However, $\text{O}_2^{\bullet-}$ was not detected perhaps due to its weak intensity in the system.

3.2.2 The role of reactive oxygen species in benzene-Fe(III)-SPC system

In this set of experiments, a series of investigations were conducted by employing radical-scavenging tests and EPR analysis to elaborate the role of reactive oxygen species and further to illustrate the mechanism of benzene degradation (Figs. 2-5). IPA and CF were employed as the scavenging compound of $\text{HO}^\bullet$ and reductant, respectively, because of their reactivity with reactive oxygen species (IPA: $k_{\text{HO}^\bullet} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_e = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and CF: $k_{\text{HO}^\bullet} = 7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_e = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [33].

Fig. 2a shows that benzene degradation decreased with increasing concentration of IPA, and almost no benzene degradation was observed when the IPA concentration increased to 100 mM. These results suggested that the $\text{HO}^\bullet$ was the leading reactive oxygen species responsible to benzene removal in the Fe(III)-activated SPC system. Benzene degradation was significantly inhibited when CF concentrations increased from 1.0 mM to 100 mM (Fig. 2b). This indicated that reductants might also be involved in the degradation of benzene. The $\text{O}_2^{\bullet -}$ possibly played a role in the generation of $\text{HO}^\bullet$ and benzene degradation through Eqs. 1-7.

Along with the benzene degradation caused by $\text{HO}^\bullet$, the corresponding generated organic compound radicals ($\text{R}^\bullet$) and/or products such as $\text{ROH}^\bullet$, ROH and $\text{HO}_2^\bullet$ are also generated (Eqs. 8-9) [10,34]. Fe(II) could be generated by the reduction of Fe(III) by $\text{R}^\bullet$ (Eq. 10); further enhancing the generation of $\text{HO}^\bullet$. Therefore, we hypothesize that there was generation of $\text{R}^\bullet$ (discussed in section 3.2.3), which could rapidly convert Fe(III) to Fe(II), leading to more activation of H_2O_2 and faster benzene degradation in the second stage. The above hypothesis is confirmed indirectly by the increase of Fe(II) concentration and by the rapid decrease of H_2O_2 concentration at

the beginning of the second stage (Fig. 3). This is also consistent with the reduced intensity of HO[•] observed with the increase of CF concentration (Fig. 4). In total, the results indicated that HO[•] was primarily responsible for benzene degradation. It should be pointed out that the formation of HO[•] depend strongly on the generation and intensity of R[•] and O₂^{•-} radicals.

or $\rightarrow$ ring-opened products

3.2.3 Degradation pathway

The GC-MS analysis identified phenol, hydroquinone, resorcinol, catechol, fumaric acid or maleic acid, benzoquinone, oxalic acid, [1,1-biphenyl]-2,5-diol and 4-phenoxy-phenol in the degradation of benzene in the Fe(III)-activated SPC process (mass spectra are shown in Fig. S3). Based on the above detected compounds, two routes for benzene degradation are proposed: (1) the generated HO[•] yielded a cyclohexadienyl radical in which oxygen was added and subsequently eliminated the HO₂[•] radical with the production of phenol. Phenol may be further transformed into hydroquinone, resorcinol, catechol, benzoquinone, and 1,2-dihydroxybenzene by reacting with reacting oxygen species. These aromatic compounds were ultimately oxidized by ring opening reaction to yield aliphatic compounds such as oxalic acid, formic acid or maleic acid, then finally mineralized into CO₂ and H₂O [35]. In

addition, phenol can also react with hydroquinone and eliminate H₂O to produce [1,1-biphenyl]-2,5-diol and 4-phenoxy-phenol, which can be further oxidized by HO[•], and (2) HO[•] attacked the benzene ring and opened the benzene ring directly, leading to the 1,3-diene adipaldehyde generation, which can be also sequentially oxidized to generate aliphatic compounds, followed by mineralization to CO₂ and H₂O.

Based on the aboved analyses, the possible benzene degradation pathways are presented in Fig. 5. The detection of benzoquinone and phenol suggested that hydroxycyclohexadienyl radical and benzoquinone radical, the intermediate radicals in forming benzoquinone and phenol, may be involved in the reduction of Fe(III) to Fe(II). Moreover, hydroquinone can also accelerate the generation of Fe(II). The pathway of Fe(III) reduction by hydroquinone (HQ) is shown in Eqs. 11,12 [36]. It is hypothesized that these intermediates compounds initially formed from benzene degradation led to rapid benzene degradation in the second stage reaction, which in agreement with the discussion in section 3.2.2.

3.3 Influence of solution characteristics

The results of several studies have indicated the effect of solution characteristics

on the oxidation/reduction systems, which include solution pH, inorganic anions (Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-), and NOM. Such impacts should be considered for field-scale ISCO applications [37-39]. A series of experiments at a fixed SPC/Fe(III)/benzene molar ratio of 4:8:1 was conducted to investigate the influence of solution characteristics on the degradation of benzene. The influences of SO_4^{2-} , NO_3^- and initial solution pH were negligible when their concentrations were 1.0~100 mM. The details of these findings are reported in Supplementary Material (Fig. S4- Fig. S6).

3.3.1 Effect of Cl^- and HCO_3^- ions

Fig. 6(a) shows the impact of Cl^- varying from 1.0 mM to 100 mM on benzene degradation. Complete benzene degradation was observed when the concentrations of Cl^- were 1.0 and 10 mM. The time to reach 100% benzene removal was delayed. With the increase in concentration of Cl^- to 100 mM, the removal of benzene decreased to 33.1%. This indicates that high concentration of Cl^- had a significant inhibitor effect on benzene degradation. The causes of the inhibition may be that (1) strong complexes of Cl^- with ferrous and ferric ions formed on the iron surface through Eqs. 13-15 may lessen the activate ability of iron [40-42] and (2) less reactive radicals (e.g., $\text{Cl}^\bullet$, $\text{ClOH}^\bullet$ and $\text{Cl}_2^\bullet$) might be formed via a few reaction of propagation (Eqs. 16-22) [41-44]. Therefore, if Cl^- concentration reached a sufficiently high level, the reducing activity of activator (Fe(II)/Fe(III)) and the decreasing concentration of reactive $\text{HO}^\bullet$ radicals would result in the significant inhibition of benzene degradation. Because the Cl^- concentration in typical groundwater is low, it is unlikely that such extensive

inhibition would occur [45].

As shown in HO[•], benzene degradation was suppressed markedly when the concentration of HCO₃⁻ was > 10 mM, suggesting that HCO₃⁻ had a scavenging effect on benzene degradation, consistent with the results of prior research [27,38] The adverse effect of bicarbonate might be due to the decreased activator concentration resulting from the formation of solid precipitates or aqueous complexes through the reaction between metals and bicarbonate, which further lead to the reducing generation of HO[•]. An additional consumption of HO[•] by bicarbonate in the aqueous phase via reactions (23) and (24) would also suppress benzene degradation. However, benzene could still be completely degraded with a SPC/Fe(III)/benzene molar ratio of 8/16/1 at the HCO₃⁻ concentration of 10 mM (Fig. S7). This indicates that Fe(III)-activated SPC system could minimize the adverse influence of bicarbonate

through the increase of the SPC/Fe(III)/benzene molar ratio to some extent.

3.3.2 Effect of NOM

In our previous work, NOM was observed to adversely affect benzene degradation in SPC/Fe²⁺ and SPC/chelated-Fe(II) systems [27,29]. In order to investigate the effect of NOM on benzene removal in the Fe(III)-activated SPC system, various HA dosages were added into the system with the concentrations of SPC, Fe(III), benzene set at 4.0, 8.0 and 1.0 mM, respectively. As shown in Fig. 6(c), a low concentration of HA had only slight influence on benzene degradation. Conversely, enhanced degradation was observed with the increased concentration of HA from 40 to 400 mg L⁻¹. This effect is opposite from the effect of HA on benzene degradation in SPC/Fe²⁺ and SPC/chelated-Fe(II) systems. We hypothesize that this enhanced effect may be caused by the following three reasons: (1) HA can serve as a chelating agent, keeping iron in solution and more available for use in activation, (2) some intermediates of HA may react with HO[•] and contribute to Fe(II)/Fe(III) recycling and promote Fe(II) generation (see discussion in section 3.2.2), and (3) reactivity of H₂O₂ with chelated-Fe(II) is higher than with Fe(II) aqua complexes. Therefore, the ubiquitous NOM in groundwater may have a favorable effect on benzene degradation when applying the Fe(III)-activated SPC process in practical applications even though unfavorable effect of NOM on benzene degradation was

observed in some cases [27].

3.3.3 Removal of benzene in groundwater

Fig. 7 shows the removal of benzene in real groundwater when the SPC/Fe(III)/benzene molar ratios were set at 2:4:1, 4:8:1, 6:12:1 and 8:16:1, respectively, at the initial benzene concentration of 1.0 mM. It was observed that benzene removal decreased to 21% in the groundwater compared to the complete benzene degradation in ultrapure water at SPC/Fe(III)/benzene molar ratio of 4:8:1. This may be caused by the impact of selected constituents present in the groundwater such as Cl^- and HCO_3^- (77.9 and 121.6 mg/L), which could act as scavengers (see discussion in section 3.3.1). However, complete benzene degradation could still be achieved when SPC/Fe(III)/benzene molar ratio was increased to 6:12:1, encouragingly suggesting that the Fe(III)-activated SPC system can be applied successfully in real groundwater while more further studies should be conducted for its practical application because of the complex subsurface environments.

4. Conclusions

Degradation of benzene (1.0 mM) was complete within 180 min in the system when the SPC/Fe(III)/benzene molar ratio was 4:6:1. Free-radical probe-compound tests and free-radical scavengers tests demonstrated that $\text{HO}^\bullet$ was the leading species responsible for benzene degradation. Organic compound radical ($\text{R}^\bullet$) and superoxide anion radical ($\text{O}_2^{\bullet-}$) also played important parts in benzene degradation. The identified

degradation products of benzene described the degradation pathways of benzene by the Fe(III)-activated SPC system. The major organic compound radical ($R^\bullet$), produced in the Fe(II)-SPC-benzene promoted the benzene degradation by accelerating the generation of Fe(II). The solution pH and ions, SO_4^{2-} and NO_3^- showed negligible effect on the degradation. Concentration increase of Cl^- and HCO_3^- anions had a slightly adverse influence at low concentration (1.0 mM), an obvious inhibition at high concentration (10~100 mM) was seen. NOM had a significant accelerating effect on the oxidation of benzene. Finally, benzene degradation in real groundwater tests indicated that Fe(III)-activated SPC process was potentially applicable to benzene-contaminated groundwater remediation. Results clearly demonstrated that the Fe(III)-activated SPC oxidation is a highly promising technique for remediating organics contaminated groundwater.

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Table 1. Rate constants of benzene degradation in the first stage reaction under various conditions

Test No.	SPC dosage (mM)	Fe(III) dosage (mM)	rate constant $k \times 10^2$ (min ⁻¹)	correlation coefficient R^2
1	4	4	0.14 ± 0.02	0.9289
2	4	6	0.27 ± 0.02	0.9733
3	4	8	0.40 ± 0.04	0.9865
4	4	12	0.55 ± 0.04	0.9649
5	4	16	1.42 ± 0.02	0.9187
6	1	8	0.21 ± 0.02	0.9577
7	3	8	0.37 ± 0.02	0.9807
8	5	8	0.60 ± 0.02	0.9930
9	8	8	0.28 ± 0.01	0.9903

Figure Captions

Fig. 1 Benzene degradation at various SPC/Fe(III)/benzene molar ratios for the Fe(III)-activated SPC system employing ultrapure water matrix ($[\text{Benzene}]_0 = 1.0$ mM): (a) various Fe(III) dosages at a fixed SPC/benzene molar ratio of 4:1 ($[\text{SPC}]_0 = 4.0$ mM), (b) various SPC dosages at a fixed Fe(III)/benzene molar ratio of 8:1 ($[\text{Fe(III)}]_0 = 8.0$ mM).

Fig. 2 The effect of scavengers on benzene degradation under various scavenger concentrations for the Fe(III)-activated SPC system ($[\text{Benzene}]_0 = 1.0$ mM, $[\text{SPC}]_0 = 4$ mM, $[\text{Fe(III)}]_0 = 8$ mM): (a) IPA, (b) CF.

Fig. 3 The changes of (a) Fe(II) concentration and, (b) H_2O_2 concentration under various CF concentrations for the Fe(III)-activated SPC system ($[\text{Benzene}]_0 = 1.0$ mM, $[\text{SPC}]_0 = 4.0$ mM, $[\text{Fe(III)}]_0 = 8.0$ mM).

Fig. 4 The intensity of $\text{HO}\cdot$ at various CF concentrations for the Fe(III)-activated SPC system ($[\text{Benzene}]_0 = 1.0$ mM, $[\text{SPC}]_0 = 4.0$ mM, $[\text{Fe(III)}]_0 = 8.0$ mM).

Fig. 5 Proposed benzene degradation pathways for the Fe(III)-activated SPC system.

Fig. 6 Effect of solution matrix on benzene degradation for the Fe(III)-activated SPC system ($[\text{Benzene}]_0 = 1.0$ mM, $[\text{SPC}]_0 = 4.0$ mM, $[\text{Fe(III)}]_0 = 8.0$ mM): (a) Cl^- , (b) HCO_3^- , (c) NOM.

Fig. 7 Benzene degradation at various SPC/Fe(III)/benzene molar ratios for the Fe(III)-activated SPC system in actual groundwater ($[\text{Benzene}]_0 = 1.0$ mM).

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.