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Enhanced effect of HAH on citric-acid chelated Fe(II)-catalyzed percarbonate for trichloroethene degradation

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Abstract

This work demonstrates the impact of hydroxylamine hydrochloride (HAH) addition on enhancing the degradation of trichloroethene (TCE) by the citric acid (CA)-chelated Fe(II)-catalyzed percarbonate (SPC) system. The results of a series of batch-reactor experiments show that TCE removal with HAH addition was increased from approximately 57% to 79% for a CA concentration of 0.1 mM and from 89 to 99.6% for a 0.5 mM concentration. Free-radical probe tests elucidated the existence of hydroxyl radical (HO[•]) and superoxide anion radical (O₂^{•-}) in both CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems. However, higher removal rates of radical probe compounds was observed in the HAH/CA/Fe(II)/SPC system, indicating that HAH addition enhanced the generation of both free radicals. In addition, increased contribution of O₂^{•-} in the HAH/CA/Fe(II)/SPC system compared to the CA/Fe(II)/SPC system was verified by free-radical scavengers tests. Complete TCE dechlorination was indicated based on the total mass balance of released Cl⁻ species. Lower concentrations of formic acid were produced in the later stages of the reaction for the HAH/CA/Fe(II)/SPC system, suggesting that HAH addition favors complete TCE mineralization. Studies of the impact of selected groundwater matrix constituents indicates that TCE removal in the HAH/CA/Fe(II)/SPC system is pH-dependent, with higher removal rates under acidic conditions. Although HCO₃⁻ was observed to have an adverse impact on TCE removal for the HAH/CA/Fe(II)/SPC system, the addition of HAH reduced its inhibitory effect compared to the CA/Fe(II)/SPC system. Finally, TCE removal in real groundwater was greater with the addition of HAH to the CA/Fe(II)/SPC system. The study results indicate that HAH amendment has potential to enhance effective remediation of TCE-contaminated groundwater.

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Keywords

Sodium percarbonate; Hydroxylamine hydrochloride; Citric acid; ISCO; Trichloroethene; Groundwater remediation

1. Introduction

Trichloroethene (TCE), one common chlorinated organic compound, has been reported as one of the main pollutants in groundwater because of its wide prior usage and previously employed disposal practices. Contamination of groundwater by TCE has attracted much attention due to the concern of toxicity and carcinogenicity, thus its maximum contaminant level in drinking water is set at 5 µg/L by EPA [1]. Natural-attenuation based remediation of TCE is generally a quite slow process, and therefore numerous remediation techniques have been examined for the cleanup of TCE [2-5]. In situ chemical oxidation (ISCO) using strong oxidants has drawn much attention for being one promising remedial alternative [5-9]. Several strong oxidants, such as ozone [10], Fenton's reagent [11], permanganate [12], calcium peroxide [13] as well as persulfate [14,15], have been used for ISCO applications.

Recently, a solid-phase oxidant, percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, SPC), has been examined as a substitute for the liquid-phase hydrogen peroxide (H_2O_2) [16-18]. As a granulated solid carrier of H_2O_2 , SPC is easier to transport and able to release H_2O_2 after mixing with H_2O ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2$). This makes it possible to initiate the well-known Fenton-like reaction when catalyzed by iron. In addition, SPC has a wider pH range of applicability compared to standard hydrogen peroxide [19]. Fu et al. demonstrated the effective degradation of benzene by Fe(II)-catalyzed SPC [16], and their results indicated that Fe(II)-catalyzed SPC could be applied in weakly alkaline conditions for benzene degradation. In addition, effective degradation was observed for actual groundwater systems. Miao et al. introduced various organic chelating agents to the Fe(II)-catalyzed SPC process to help maintain availability of ferrous iron in solution, and thereby improve overall degradation rates [20]. Prior work has shown higher reactivity of SPC with chelated-Fe(II) than with Fe(II) aqua complexes, thus improving SPC utilization [21]. However, it is noteworthy that ferrous ions would transfer to ferric ions rapidly when SPC was added to the chelated-Fe(II) catalyzed SPC system. For example, Zang et al. reported that Fe(II) concentration dropped to 1.25 from 25.5 mg/L quickly after SPC addition, and Fe(III) was the main form of soluble iron in a citric acid-chelated Fe(II)-catalyzed SPC (CA/Fe(II)/SPC) process [22]. Therefore, seeking a suitable reducing agent for Fe(II) regeneration by reducing Fe(III) in the chelated Fe(II)-catalyzed SPC process is of considerable interest to further improve iron availability and promote contaminant degradation.

Recently, hydroxylamine hydrochloride (HAH) has been investigated as a reducing agent to expedite the regeneration of Fe(II) because of its higher reduction ability and lower reactivity with $\text{HO}^\bullet$ [23]. Zou [24] et al. reported that the presence of HAH in a Fe(II)-catalyzed peroxymonosulfate process could promote Fe(III)/Fe(II) cycling and reactive oxidant generation, and thus accelerate benzoic acid degradation. Miao et al. [25] demonstrated that HAH possessed the best effect on enhancing degradation of

tetrachloroethene in which various reducing agents were investigated for the Fe(II)/Fe(III)-catalyzed SPC system. Chen et al. [26] also reported that addition of HAH in Fenton's reagent could result in more stable Fe(II) regeneration and faster HO• generation than that in the conventional Fenton system. Based on the above discussion, it is hypothesized that the addition of HAH to the CA/Fe(II)/SPC system will enhance Fe(II) regeneration by reducing Fe(III) accumulation. It can also improve the oxidation ability of the CA/Fe(II)/SPC system by enhancing the utilization of SPC and Fe(II), and thereby improve pollutant degradation efficiency. Therefore, in this study we developed an innovative HAH/CA/Fe(II)/SPC system and (i) investigated the oxidation efficiency of TCE in this system, (ii) delineated the role of free-radicals on TCE degradation by using radical scavengers tests, (iii) evaluated the mineralization of TCE by measuring Cl⁻ release, and (iv) explored the effect of solution matrix constituents on TCE degradation efficiency.

2 Materials and methods

2.1 Materials

Trichloroethene (> 99.0%), citric acid monohydrate (C₆H₈O₇•H₂O, CA, >99.0%), hydroxylamine hydrochloride (NH₂OH•HCl > 98.5%), sodium bicarbonate (NaHCO₃, 99.5%), sodium chloride (NaCl, 99.5%), and 1,4-benzoquinone (BQ, > 97%) were purchased from Aladdin (Shanghai, China). Sodium percarbonate (Na₂CO₃•1.5H₂O₂, SPC, 98%) was obtained from Acros Organics (Shanghai, China). Ferrous sulfate heptahydrate (FeSO₄•7H₂O, 99.0%), tert-butyl alcohol (> 99%), sodium phosphate dibasic dodecahydrate (Na₂HPO₄•12H₂O, 99.0%), sodium dihydrogen phosphate dihydrate (NaH₂PO₄•2H₂O, 99.0%) and humic acid (HA, fulvic acid > 90%), were purchased from Shanghai Jingchun Reagent Ltd. Co. (Shanghai, China). The HA was used as the model natural organic material in the present study because it is one of the major fractions of natural dissolved organic matter. All of the reagents were applied without further treatment. Ultrapure water from a Milli-Q water process (Classic DI, ELGA, 102Marlow, U.K.) and actual groundwater from a well screened approximately 10 m deep (Minhang, Shanghai, China) were employed to prepare aqueous solutions.

2.2 Experimental design

TCE stock solution was obtained by mixing the pure non-aqueous phase liquid TCE with Milli-Q water under stirring for 1 h, and then diluted into a 250 mL cylindrical glass reactor with desired initial concentration (0.15 mM). A magnetic stirrer in the reactor was applied to keep chemicals mixing uniformly, and a temperature bath (DC, Ningbo, China) was employed to control the temperature at 20°C. Predetermined dosages of CA, Fe(II), HAH and other required chemicals were added to the reactor in succession and reactions were initiated by the addition of SPC. Control tests without any reagent addition were conducted to determine TCE volatilization loss. 1.0 mL aqueous samples were placed into sample vials containing 1.0 mL hexane for extraction using a vortex stirrer at the desired time intervals. After 3 min extraction and 5 min static separation, the upper organic phase was transferred to a GC vial.

2.3 Free-radicals probe tests

The generation of HO• was confirmed by the degradation of nitrobenzene (NB), an oxidant probe compound, which can react with HO• at high rate constant of $3.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [23]. The generation of superoxide anion radical ($\text{O}_2^{\bullet-}$) was ascertained by carbon tetrachloride (CT) degradation, a reductant probe compound, which is extremely reactive with reductant ($k = 1.6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) but less reactive with HO• ($k_{\text{HO}^\bullet} < 2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) [23]. The procedure used for the free radical probe tests is the same as TCE experimental design.

2.4 Scavenger tests

Tert-butyl alcohol (TBA) was selected as a scavenger of HO• because it can react with HO• at a high constant rate of $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ but at low constant rate of $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ with reductants. 1,4-benzoquinone (BQ) was applied as a reductant scavenger due to its high reactivity with reductants ($3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$), but minimal reactivity with HO• ($7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) [23,27]. In addition, a contribution degree (ConD) test was conducted to compare the relative contribution of HO• and $\text{O}_2^{\bullet-}$ to TCE degradation in the CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems. As shown in Eq. 1, R_s and R_0 represent TCE final degradation rate with and without addition of scavenger, respectively. Meanwhile, it is noted that ConD can only approximate the contributions of both free-radicals in TCE degradation owing to the interconnectedness of the reactive oxygen species generation.

$$\text{ConD} = (R_0 - R_s) / R_0 \times 100\% \quad (1)$$

2.5 Analytical methods

One microliter (1- μL) extracted TCE or CT samples were analyzed immediately by a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with an electron capture detector (ECD), an autosampler (Agilent 7693), and a DB-VRX column (60 m length, 250 μm i.d., and 1.4 μm thickness). The split ratio was 20:1. The injector and detector temperatures were 240 and 260°C, respectively, and the temperature of oven was held at 75°C constantly. TCE recovery was in the range of 87-95%. Analysis procedure of extracted CT samples is in accordance with TCE analysis procedure except the constant oven temperature of 100°C. Extracted NB samples were analyzed using flame ionization detector (FID) equipped with a HP-5 column (30 m length, 250 μm i.d., and 0.25 μm thickness), keeping temperatures of injector, detector and oven at 250°C, 300°C, and 175°C, respectively. 1- μL extracted NB samples were injected into GC at a split ratio of 5:1. Ion chromatography (Dionex ICS-I000, Sunnyvale, CA) was applied to detect the concentration of chloride anion (Cl^-) and formic acid (HCOOH). The measured concentration of chloride anion with HAH addition before adding SPC in HAH/CA/Fe(II)/SPC system was acted as a background level. Fe(II) and total soluble iron were determined with 1,10-phenanthroline method [28]. pH values were measured by a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

3. Results and discussion

3.1 The enhanced effect of HAH on the generation of free-radicals

Based on our previous research, both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ were identified as predominant free-radicals responsible for TCE degradation in the CA/Fe(II)/SPC system [22]. In order to explore the effect of HAH on the generation of free-radicals, several tests with probe compounds (NB and CT) were conducted and the results are shown in Fig 1. The initial concentrations of HAH, CA, Fe(II), SPC, NB and CT were set at 1.5, 0.5, 0.45, 0.75, 0.15 and 0.15 mM, respectively. Results of control tests with only NB or CT showed that their volatilization loss could be neglected during the entire test period.

The results demonstrate that NB removal in both CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems within 2 min was nearly the same, indicating that HAH addition had little effect on $\text{HO}^\bullet$ generation in the first 2 min (Fig. 1a). This could be explained by the similar initial concentrations of Fe(II) in both systems, which is the major factor affecting $\text{HO}^\bullet$ generation. In addition, it is also noted that most NB was degraded within the initial 30 min and minor NB degradation was observed during the later 60 min. This illustrates the rapid production and consumption of $\text{HO}^\bullet$ in the two systems. Finally, complete removal of NB increased to 84% with the addition of HAH, compared to 70% without HAH addition. This interesting result suggests that HAH enhances the generation of $\text{HO}^\bullet$ during the reaction. This effect is deduced to result from the accelerated regeneration of Fe(II) because HAH, as a strong reducing agent, can promote Fe(III)/Fe(II) cycling. While Fe(III) was the primary form of soluble iron after the initial 2 min reaction in the CA/Fe(II)/SPC process. In addition, the slower regeneration of Fe(II) from Fe(III) reduction through chain reactions with H_2O_2 and $\text{HO}_2^\bullet$ involved via Eqs. (2)-(4) could also limit the generation of $\text{HO}^\bullet$ for the CA/Fe(II)/SPC system.

As depicted in Fig. 1b, greater CT removal (%) in the HAH/CA/Fe(II)/SPC system than in the CA/Fe(II)/SPC system was observed, indicating that addition of HAH can also promote $\text{O}_2^{\bullet-}$ generation. The enhanced formation of $\text{O}_2^{\bullet-}$ with the presence of NH_2OH is likely to result from the following two steps: 1) $\text{H}_2\text{NO}^\bullet$ radical generated from NH_2OH via one-electron oxidation when NH_2OH reduces Fe(III) to Fe(II) (as shown in Eq. 5), 2) $\text{HNO}^\bullet$ radical produced via deprotonation of $\text{H}_2\text{NO}^\bullet$ radical ($pK_a = 12.6 \pm 0.3$), which could react with O_2 to generate $\text{O}_2^{\bullet-}$ via one electron-transfer at a rate constant of $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (as shown in Eqs. 6-7) [29]. Therefore, the addition of HAH to the CA/Fe(II)/SPC system could

enhance both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ generation, which are the dominate reactive oxygen species for contaminant degradation.

3.2 Oxidation performance of TCE in HAH/CA/Fe(II)/SPC system

3.2.1 Enhanced effect of HAH on TCE removal—The enhanced effect of HAH on TCE degradation is shown in Fig 2 and Fig S1. The initial Fe(II)/SPC/TCE molar ratio and TCE concentrations were set at 3/5/1 and 0.15 mM, respectively. Less than 6% loss of TCE within 120 min was observed in the control test, indicating that volatilization loss of TCE during the entire experimental period is minimal (Fig S1). As shown in Fig 2, the removal of TCE increased from 89 to 99.6% with the increase of HAH concentration from 0 to 2.25 mM when CA concentration was 0.5 mM. This indicates that the addition of HAH to the CA/Fe(II)/SPC system can enhance TCE degradation. This is due to the enhanced generation of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ when HAH was added to the CA/Fe(II)/SPC system, as discussed in section 3.1. The similar effect of HAH on TCE degradation was observed when CA concentration was set at 0.1 mM. However, for both cases, further increased HAH concentration of 3.0 mM resulted in a decrease of TCE removal.

Higher Fe(II) concentrations were observed in the HAH/CA/Fe(II)/SPC system compared to the CA/Fe(II)/SPC system (as shown in Table S2). This confirms that the addition of HAH can enhance the regeneration of Fe(II), which is critical for Fenton-like processes. This enhanced availability of Fe(II) is likely partly responsible for the enhanced TCE degradation performance of the HAH/CA/Fe(II)/SPC system. The degradation pattern of TCE in the HAH/CA/Fe(II)/SPC system is in accordance with a pseudo first order reaction kinetics model, as shown in Eqs. 8 and 9. $C_{t,TCE}$ and $C_{0,TCE}$ are TCE concentrations (mM) at reaction time t (min) and time zero, respectively. The fitting lines on the basis of Eqs. 8 and 9 at different HAH concentrations with fixed CA concentration (2.0 mM) are shown in Fig. S2, and its slope (k_{TCE}) represents the rate constant of the pseudo first order reaction kinetics model and its linear correlation coefficient (R^2) are summarized in Table S1.

$$-dC_{t,TCE}/dt = k_{TCE} \cdot C_{t,TCE} \quad (8)$$

$$-\ln(C_{t,TCE}/C_{0,TCE}) = k_{TCE} \cdot t \quad (9)$$

The rate constants increased to 0.069 min^{-1} from 0.026 min^{-1} when HAH concentration increased to 2.25 mM compared to the control test. This demonstrates that the addition of HAH to the CA/Fe(II)/SPC system did quantitatively enhance the degradation efficiency of TCE. While further increasing addition of HAH (3.0 mM) led to a decreased rate constant (0.059 min^{-1}) because of the quenching of $\text{HO}^\bullet$ by the excess HAH.

3.2.2 The role of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ in TCE degradation—Scavenger tests were conducted to explore the contribution of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ to TCE removal in the HAH/CA/Fe(II)/SPC system and the results are shown in Fig 3. Fe(II)/SPC/TCE molar ratio was fixed at 3/5/1, while initial concentrations of TCE, CA, and HAH were 0.15, 0.5 and 1.5 mM, respectively. As shown in Fig 3a, 99.3% TCE removal was observed in 60 min for the system without addition of TBA. Conversely, in the presence of 10 and 20 mM TBA, TCE removal decreased significantly to 38.1% and 20.6%, respectively. In addition, the generated $\text{HO}^\bullet$ radical was effectively scavenged by TBA due to the higher TBA concentration than TCE. This inhibited TCE degradation suggests that $\text{HO}^\bullet$ was the predominant radical responsible for TCE removal in the HAH/CA/Fe(II)/SPC system. However, higher TBA concentration (30 mM) did not lead to further inhibition, and 20% of TCE was still removed, indicating that a non- $\text{HO}^\bullet$ oxidation mechanism exists.

As shown in Fig 3b, TCE removal decreased from 99.3% to 77.5% and 75.7% respectively with the BQ concentrations of 10 and 20 mM. This inhibition of TCE removal (~23%) with BQ addition suggests the significant contribution of $\text{O}_2^{\bullet-}$ to TCE removal in the HAH/CA/Fe(II)/SPC system. In addition, the relative contribution of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ to TCE removal in the HAH/CA/Fe(II)/SPC system were determined to be approximately 79% and 24%, compared to 90% and 12% in the CA/Fe(II)/SPC system (data not shown). This indicates that the addition of HAH increases the contribution of $\text{O}_2^{\bullet-}$ to TCE removal.

3.2.3 The dechlorination of TCE—According to previous research, the change of Cl^- concentration can be applied to evaluate the extent of destruction of chlorinated hydrocarbons [14,30]. Theoretically, complete dechlorination of 1 mol TCE would release 3 mol of Cl^- . In this study, the concentrations of Cl^- along with TCE degradation in the CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems were measured and the results are shown in Fig 4. It is obvious that the measured Cl^- concentrations in the CA/Fe(II)/SPC system were consistent with the theoretical Cl^- concentrations (Fig. 4a). Conversely, as depicted in Fig. 4b, the measured Cl^- concentration was lower than the theoretical Cl^- concentration for the first 60 min in the HAH/CA/Fe(II)/SPC system. This observation suggests the existence of some chlorinated intermediates. However, after 60 min the measured Cl^- concentration was equal to the theoretical Cl^- concentration. This indicates that the possible chlorinated intermediates were further degraded leading to a complete dechlorination of TCE in the HAH/CA/Fe(II)/SPC system. Unfortunately, no chlorinated intermediate products were detected by GC/MS (data not shown).

Formic acid was detected in both CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems. The concentration of formic acid in the CA/Fe(II)/SPC system continuously increased along with the reaction and its final concentration was 3.3 mg/L. The concentration of formic acid in the HAH/CA/Fe(II)/SPC system slightly increased within 60 min and its concentration

reached 6.6 mg/L. However, a significant decrease of formic acid concentration was observed after 60 min and its final concentration was 1.4 mg/L, which was lower than that in the CA/Fe(II)/SPC system. The additional degradation of formic acid illustrated that $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ remained in the system after 60 min. The above results suggest that the addition of HAH to the CA/Fe(II)/SPC system is in favor of complete mineralization of TCE.

3.3 Influence of solution matrix

Several studies have documented the effect of solution matrix conditions on iron catalyzed oxidation reactions, such as the significant scavenging effect of high concentration of Cl^- and HCO_3^- on TCE degradation in the CA/Fe(II)/SPC system [22]. Therefore, the effects of ionic composition (SO_4^{2-} , HCO_3^- , Cl^- and NO_3^-), solution pH, and humic acid on TCE removal were investigated. Molar ratio of Fe(II)/SPC/TCE was fixed at 3/5/1, and initial concentrations of TCE, CA, and HAH were 0.15, 0.5 and 1.5 mM, respectively. NO_3^- , Cl^- , SO_4^{2-} and HA at the tested ranges had negligible effects on TCE removal (see Fig. S3).

The effect of pH was investigated using initial solution pH of 6.0, 7.0 and 8.0 buffered by phosphate (0.1 M), as well as an unadjusted pH solution (pH 5.21), and two solutions at extreme pH 3.0 and 11.0 (adjusted with H_2SO_4 (0.1 M) and NaOH (0.1 M), respectively). As shown in Fig. 5, TCE removal decreased with the initial solution pH increasing from 3 to 11, and only 32.5% and 26.6% TCE removal were obtained at pH 8 and 11, respectively. However, >99% TCE removal was achieved when the initial solution pH were 3 and 5.2, for which the final solution pH was near 2.5 for both cases. These results indicate that TCE removal in the HAH/CA/Fe(II)/SPC system was pH-dependent and favored under acidic conditions. This is in accordance with general behavior for Fenton reaction processes [31].

The adverse effect of HCO_3^- on advanced oxidation processes has been reported in several previous research works [32-34]. TCE removal was significantly suppressed in the CA/Fe(II)/SPC system at high concentration of HCO_3^- (> 10 mM, as shown in Fig. S4). The result of HCO_3^- effect on TCE removal in the HAH/CA/Fe(II)/SPC system is shown in Fig. 6. TCE removal decreased to 91.8%, 79.6% and 47.3% when concentrations of HCO_3^- were 1.0, 10 and 100 mM, respectively. This indicated HCO_3^- at high concentrations also has a significant adverse effect on TCE removal in the HAH/CA/Fe(II)/SPC system.

It should be noted that the initial solution pH increased to 6.5, 7.6 and 8.2 when HCO_3^- concentration were 1.0, 10 and 100 mM, respectively. And the final solution pH values when HCO_3^- was added were much higher than that without HCO_3^- addition. The increasing solution pH, to some extent, could lead to the decrease of TCE removal. Meanwhile, HCO_3^- could react with Fe(II)/Fe(III) through a series of reactions to generate aqueous complexes/solid precipitates, and thereby decrease the catalyst concentration which would further reduce $\text{HO}^\bullet$ generation [34]. In addition, bicarbonate, believed to be a $\text{HO}^\bullet$ scavenger, could result in excess $\text{HO}^\bullet$ consumption. All these factors led to the adverse effect of HCO_3^- on TCE removal in the HAH/CA/Fe(II)/SPC system.

However, as shown by comparing Fig. 6 and Fig. S4, much higher TCE removal was observed in the HAH/CA/Fe(II)/SPC system compared to the CA/Fe(II)/SPC system. The inhibition ratio (I_{TCE}) was calculated to compare the effect of HCO_3^- on CA/Fe(II)/SPC and

HAH/CA/Fe(II)/SPC systems. As shown in Eq. 10, $R_{e,TCE}$ and $R_{c,TCE}$ represent TCE final removal with and without HCO_3^- addition, respectively. With HAH addition to CA/Fe(II)/SPC system, I_{TCE} decreased to 7.6, 19.9 and 52.4 from 8.5, 38.8 and 72.7 when HCO_3^- concentration were 1.0, 10 and 100 mM, respectively (Fig. S5). This indicated that HAH addition could, to a certain extent, overcome the adverse effect of HCO_3^- on TCE removal.

$$I_{TCE} = (R_{c,TCE} - R_{e,TCE}) / R_{c,TCE} \times 100\% \quad (10)$$

Due to the complex effect of solution matrix on TCE removal, experiments with actual groundwater were performed to study TCE degradation performance. TCE removal in actual groundwater (Fig. 7) decreased to 63.5% from 99.7% in ultrapure water (see Fig. S6) at Fe(II)/SPC/TCE molar ratio of 5/5/1 when CA concentration was 0.5 mM. This could be ascribed to the consumption of oxidant and catalyst caused by the complex constituents of groundwater (see Table S3). However, TCE removal increased to 85.3% when 1.5 mM HAH was added. This demonstrates that the HAH/CA/Fe(II)/SPC system was more effective for the remediation of TCE-contaminated groundwater.

4. Conclusions

In this research, the enhanced effect of HAH on the CA/Fe(II)/SPC system for TCE degradation was investigated. It is hypothesized that HAH addition accelerated Fe(II) regeneration from Fe(III), thereby enhancing TCE removal. Free-radical probe tests and scavengers tests showed that $HO^\bullet$ and $O_2^{\bullet-}$ were the dominant species responsible for TCE removal that the contribution of $O_2^{\bullet-}$ to TCE removal increased with HAH addition. The concentrations of Cl^- species along with TCE removal indicated the complete dechlorination of TCE. Lower concentration of formic acid detected in the HAH/CA/Fe(II)/SPC system indicated that HAH addition was more beneficial to complete mineralization of TCE. Investigation of matrix constituents showed TCE removal was significantly affected by solution pH and HCO_3^- . HAH addition could partly overcome the adverse effect of HCO_3^- . Finally, better TCE removal performance in actual groundwater was obtained by addition of HAH. In conclusion, the HAH/CA/Fe(II)/SPC system shows great potential for effective treatment of TCE-contaminated groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. U.S. Environmental Protection Agency (EPA). National Primary Drinking Water Regulations. EPA 816-F-09-004; 2009.
2. National Research Council. Alternatives for managing the nation's complex contaminated groundwater sites. National Academies Press; Washington, D.C.: 2013.
3. Stroo HF, Leeson A, Marqusee JA, et al. Chlorinated ethene source remediation: Lessons learned. *Environ Sci Technol*. 2012; 46:6438–6447. [PubMed: 22558915]
4. U.S. Environmental Protection Agency (EPA). The DNAPL Remediation Challenge: Is There a Case for Source Depletion?. EPA 600-R-03-143; 2003.
5. Interstate Technology and Regulatory Council (ITRC). DNAPL Source Reduction: Facing the Challenge, ITRC/DNAPLs-2. 2002
6. Siegrist, RL., Crimi, ML., Brown, RA. In situ chemical oxidation: Technology description and status. Springer; New York: 2011.
7. Tsitonaki A, Petri B, Crimi ML, et al. In situ chemical oxidation of contaminated soil and groundwater using persulfate: a review, *Crit. Rev Environ Sci Technol*. 2010; 40:55–91.
8. Krembs FJ, Siegrist RL, Crimi ML, et al. ISCO for groundwater remediation: analysis of field applications and performance. *Ground Water Monit R*. 2010; 30:42–53.
9. Interstate Technology and Regulatory Council (ITRC). Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. Second Edition. ITRC/ISCO-2; 2005.
10. Choi H, Lim HN, Kim J, et al. Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation. *J Contam Hydrol*. 2002; 57:81–98. [PubMed: 12143994]
11. Rosas JM, Vicente F, Saguillo EG, et al. Remediation of soil polluted with herbicides by Fenton-like reaction: kinetic model of diuron degradation. *Appl Catal B: Environ*. 2014; 144:252–260.
12. Liang SH, Chen KF, Wu CS, et al. Development of KMnO_4 -releasing composites for in situ chemical oxidation of TCE-contaminated groundwater. *Water Res*. 2014; 54:149–158. [PubMed: 24568784]
13. Zhang X, Gu X, Lu S, et al. Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion. *J Hazard Mater*. 2015; 284:253–260. [PubMed: 25463240]
14. Gu X, Lu S, Fu X, et al. Carbon dioxide radical anion-based $\text{UV}/\text{S}_2\text{O}_8^{2-}/\text{HCOOH}$ reductive process for carbon tetrachloride degradation in aqueous solution. *Sep Purif Technol*. 2017; 172:211–216.
15. Liu H, Bruton TA, Doyle FM, et al. In situ chemical oxidation of contaminated groundwater by persulfate: decomposition by Fe(III)- and Mn(IV)-containing oxides and aquifer materials. *Environ Sci Technol*. 2014; 17:10330–10336.
16. Fu X, Gu X, Lu S, et al. Benzene depletion by Fe^{2+} -catalyzed sodium percarbonate in aqueous solution. *Chem Eng J*. 2015; 267:25–33.
17. Sindelar HR, Brown MT, Boyer TH. Evaluating $\text{UV}/\text{H}_2\text{O}_2$, $\text{UV}/\text{percarbonate}$, and $\text{UV}/\text{perborate}$ for natural organic matter reduction from alternative water sources. *Chemosphere*. 2014; 105:112–118. [PubMed: 24405969]
18. Viisimaa M, Goi A. Use of hydrogen peroxide and percarbonate to treat chlorinated aromatic hydrocarbon-contaminated soil. *J Environ Eng Lands*. 2014; 22:30–39.
19. Fu X, Gu X, Lu S, et al. Benzene oxidation by Fe (III)-activated percarbonate: matrix-constituent effects and degradation pathways. *Chem Eng J*. 2017; 309:22–29. [PubMed: 28959136]
20. Miao Z, Gu X, Lu S, et al. Mechanism of PCE oxidation by percarbonate in chelated Fe(II)-based catalyzed system. *Chem Eng J*. 2015; 275:53–62.
21. ElShafei GMS, Yehia FZ, Dimitry OIH, et al. Degradation of nitrobenzene at near neutral pH using Fe^{2+} -glutamate complex as a homogeneous Fenton catalyst. *Appl Catal B: Environ*. 2010; 99:242–247.
22. Zang X, Gu X, Lu S, et al. Enhanced degradation of trichloroethene by sodium percarbonate activated with Fe (II) in the presence of citric acid. *Water Sci Tech-W Sup*.

23. Buxton GV, Greenstock CL, Helman WP, et al. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solution. *J Phys Chem Ref Data*. 1988; 17:513–886.
24. Zou J, Ma J, Chen L, et al. Rapid acceleration of ferrous iron/peroxymonosulfate oxidation of organic pollutants by promoting Fe(III)/Fe(II) cycle with hydroxylamine. *Environ Sci Technol*. 2013; 47:11685–11691. [PubMed: 24033112]
25. Miao Z, Gu X, Lu S, et al. Enhancement effects of reducing agents on the degradation of tetrachloroethene in the Fe(II)/Fe(III) catalyzed percarbonate system. *J Hazard Mater*. 2015; 300:530–537. [PubMed: 26257094]
26. Chen L, Ma J, Li X, et al. Strong Enhancement on Fenton Oxidation by Addition of Hydroxylamine to Accelerate the Ferric and Ferrous Iron Cycles. *Environ Sci Technol*. 2011; 45:3925–3930. [PubMed: 21469678]
27. Haag WR, Yao CCD. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ Sci Technol*. 1992; 26:1005–1013.
28. Tamura H, Goto K, Yotsuyanagi T, Nagayama M. Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III). *Talanta*. 1974; 21:314–318. [PubMed: 18961462]
29. Lind J, Merényi G. Kinetic and Thermodynamic Properties of the Aminoxyl ($\text{NH}_2\text{O}^\bullet$). *Radical J Phys Chem A*. 2006; 110:192–197.
30. Liang C, Wang ZS, Bruell CJ. Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere*. 2007; 66:106–113. [PubMed: 16814844]
31. Pignatello JJ, Oliveros E, MacKay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit Rev Environ Sci Technol*. 2006; 36:1–84.
32. Liang CJ, Wang ZS, Mohanty N. Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20°C. *Sci Total Environ*. 2006; 370:271–277. [PubMed: 17014891]
33. Khan NE, Adewuyi YG. Absorption and oxidation of nitric oxide (NO) by aqueous solutions of sodium persulfate in a bubble column reactor. *Ind Eng Chem Res*. 2010; 49:8749–8760.
34. Valentine RL, Wang HA. Iron oxide surface catalyzed oxidation of quinoline by hydrogen peroxide. *J Environ Eng*. 1998; 124:31–38.

Fig. 1.

Radical probe tests in CA/Fe(II)/SPC and HAH/CA/Fe(II)/SPC systems ($[\text{Fe(II)}]_0 = 0.45$ mM, $[\text{SPC}]_0 = 0.75$ mM, $[\text{CA}]_0 = 0.5$ mM, $[\text{HAH}]_0 = 1.5$ mM): (a) NB ($[\text{NB}]_0 = 2.0$ mM), (b) CT ($[\text{CT}]_0 = 0.05$ mM).

Fig. 2.

Effect of HAH dosage on TCE removal in HAH/CA/Fe(II)/SPC system with different CA concentration ($[\text{Fe(II)}]_0 = 0.45 \text{ mM}$, $[\text{SPC}]_0 = 0.75 \text{ mM}$, $[\text{TCE}]_0 = 0.15 \text{ mM}$).

Fig. 3. Scavengers tests for the HAH/CA/Fe(II)/SPC system ($[Fe(II)]_0 = 0.45$ mM, $[SPC]_0 = 0.75$ mM, $[CA]_0 = 0.5$ mM, $[HAH]_0 = 1.5$ mM): (a) TBA, (b) BQ.

Fig. 4.

Cl^- and formic acid concentrations along with TCE removal at a Fe(II)/SPC/TCE molar ratio of 3/5/1 in (a) the CA/Fe(II)/SPC system, (b) the HAH/CA/Fe(II)/SPC system ($[\text{CA}]_0 = 0.5$ mM, $[\text{HAH}]_0 = 1.5$ mM, $[\text{TCE}]_0 = 0.15$ mM).

Fig. 5.

Effect of initial solution pH on TCE removal and the final solution pH in the HAH/CA/Fe(II)/SPC system at a Fe(II)/SPC/TCE molar ratio of 3/5/1 ($[CA]_0 = 0.5$ mM, $[HAH]_0 = 1.5$ mM, $[TCE]_0 = 0.15$ mM).

Fig. 6.

Effect of HCO_3^- concentration on TCE removal and solution pH in the HAH/CA/Fe(II)/SPC system at a Fe(II)/SPC/TCE molar ratio of 3/5/1 ($[\text{CA}]_0 = 0.5$ mM, $[\text{HAH}]_0 = 1.5$ mM, $[\text{TCE}]_0 = 0.15$ mM).

Fig. 7.

TCE removal performance in actual groundwater at a Fe(II)/SPC/TCE molar ratio of 5/5/1 ($[CA]_0 = 0.5$ mM, $[HAH]_0 = 1.5$ mM, $[TCE]_0 = 0.15$ mM)