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Application of ascorbic acid to enhance trichloroethene degradation by Fe(III)-activated calcium peroxide

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Abstract

The enhancement effect of an environmentally friendly reducing agent, ascorbic acid (AA), on trichloroethene (TCE) degradation by Fe(III)-activated calcium peroxide (CP) was evaluated. The addition of AA accelerated the transformation of Fe(III) to Fe(II), and the complexation of Fe(III)/Fe(II) with AA and its products alleviated the precipitation of dissolved iron. These impacts enhanced the generation of reactive oxygen species (ROSs). Investigation of ROSs using chemical probe tests, electron paramagnetic resonance (EPR) tests, and radical scavenger tests strongly confirm large production of hydroxyl radicals (HO•) that is responsible for TCE degradation. The generation of Cl⁻ from the degraded TCE was complete in the enhanced CP/Fe(III)/AA system. The investigation of solution matrix effects showed that the TCE degradation rate decreases with the increase in solution pH, while Cl⁻, SO₄²⁻ and NO₃⁻ anions have minor impact. Conversely, HCO₃⁻ significantly inhibited TCE degradation due to pH elevation and HO• scavenging. The results of experiments performed using actual groundwater indicated that an increase in reagent doses are required for effective TCE removal. In summary, the potential effectiveness of the CP/Fe(III)/AA oxidation system for remediation of TCE contaminated groundwater has been demonstrated. Additional research is needed to develop the system for practical implementation.

Keywords

Calcium peroxide; Ascorbic acid; Fe(III) reduction; Trichloroethene; Groundwater remediation; ISCO

1. Introduction

Groundwater and soil contamination by chlorinated solvents is ubiquitous, and continues to pose significant threats to the environment and human health. The development of remediation technologies for chlorinated-solvent contaminated sites has attracted

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tremendous attention worldwide. Trichloroethene (TCE), a typical chlorinated solvent extensively applied in chemical and manufacturing industries, is a primary hazardous organic contaminant in groundwater and soil [1]. Several remediation technologies, such as in-situ chemical oxidation, in situ chemical reduction, and bioremediation, have been reported for TCE degradation [2–4].

Calcium peroxide (CaO_2 , CP) is a stable and environmentally friendly inorganic compound. It is widely used as oxygen fertilizer in agriculture and animal husbandry, and as an antiseptic, disinfectant and bleaching agent in industries [5]. CP possesses the property of continuous and long-term oxygen release, e.g., oxygen can be slowly released when CP is in contact with water. Thus, CP is considered an oxygen release compound and is extensively applied to enhance bioremediation and phytoremediation of organic pollutants in contaminated groundwater [6,7]. Moreover, the application of CP as an H_2O_2 supplier has also been frequently reported in the last several years [8]. Compared to the traditional liquid H_2O_2 , the H_2O_2 liberated from CP is auto-regulated by the dissolution of CP in solution via Eq. (1), and a maximum amount of 0.47 g H_2O_2 can be liberated from 1.0 g of CP.

It has been reported that CP follows two paths for the generation of O_2 and H_2O_2 that occur in parallel with a competitive relationship [9]. The H_2O_2 release process followed a pseudo-zero-order kinetic pattern while O_2 followed a pseudo-first order kinetic rate law. Increasing the pH of the solution decreases the H_2O_2 yield but increases the O_2 yield. Northup and Cassidy found that with the increase of pH from 6 to 12 the H_2O_2 yield decreased significantly, and that no H_2O_2 yield was observed at pH 12 and CP was transformed solely to O_2 [8]. CP is one of the most versatile and safest solid forms of H_2O_2 that avoids the loss of H_2O_2 due to disproportionation reaction, which is favorable for cost-effective transportation and storage. It has been documented that H_2O_2 produced in the dissolution of CP can degrade contaminants through direct oxidation or indirect oxidation by forming hydroxyl radical ($\text{HO}\bullet$) and other oxidative/reductive species after activation [10].

Several studies have reported the application of CP for remediation of various contaminants in groundwater and soil. Chou et al. investigated the application of CP in soil remediation and demonstrated that CP addition in soil improved arsenic immobilization through the reaction of As(III) with H_2O_2 [11]. Qian et al. reported the application of conventional and nanoscale CP for the removal of 2,4-dichlorophenol in contaminated groundwater [12]. Goi et al. used CP in the treatment of electrical insulating oil contaminated soil and complete removal of contaminant was achieved [10]. Efficient degradation of TCE and benzene by CP activated with Fe(II) have also been reported [13,14].

Oxidation by H_2O_2 alone is not efficient for removal of certain refractory contaminants, such as endocrine disrupting chemicals, pharmaceuticals and personal care products. The reason for this is the relatively low oxidation potential of H_2O_2 (1.80 V) compared with other commonly used oxidants such as O_3 (2.07 V), persulfate (2.01 V), sulfate radical anion

(2.60 V), and HO• (2.80 V at pH = 3 and 1.90 V at pH = 7) [15,16]. Transition metals, ozone, and ultraviolet radiation can activate H₂O₂ to generate HO• which is a stronger oxidant able to oxidize various contaminants non-selectively at high rates [15]. Fe(II), a transition metal ion, is the most common activator for H₂O₂ due to its relatively low toxicity and cost, and general effectiveness [17]. The use of Fe(II) for H₂O₂ activation is known as the Fenton reaction. Various species are produced in the Fenton reaction including HO• in acidic conditions, Fe(IV) at near neutral pH, and organic free radicals in the presence of organic substrates [18, 19]. HO• is generated in the reaction as shown in Eq. (2) that possesses strong oxidizing properties capable of oxidizing a wide variety of organic and inorganic substrates. In the presence of excess H₂O₂, Fe(IV) is formed in the reaction of Fe^{III}(-O₂H)_{aq} complex with Fe(II) [20]. Fe(III) can also activate H₂O₂ through spontaneous superoxide/perhydroxyl-driven reactions as shown in Eqs. (3–6), while Fe(II) regenerates from Fe(III) through the above free radical propagation reactions [21]. However, Fe(III) activation has some drawbacks such as low Fe(II)/Fe(III) recycling and Fe(III) precipitation at near neutral pH conditions [22].

Recently, many efforts have been employed to overcome the above-mentioned shortcomings. Reducing agents, such as hydroxylamine (HA) and ascorbic acid (AA), were introduced to the iron activation of H₂O₂ to accelerate Fe(II)/Fe(III) recycling. Chen et al. tested the effect of HA amendment to Fenton oxidation of benzoic acid and found an increase in HO• generation rate and extension of feasible pH range [23]. However, HA and some of its products (i.e., N₂O and NO₂⁻) might be toxic [24]. Bolobajev et al. reported the improvement of HO• generation for alachlor degradation by Fenton-like reaction with the addition of AA [25]. The effects of AA, HA, p-hydroquinone, oxalic, gallic, and humic acids on a heterogeneous Fenton-like system with an iron-loaded natural zeolite as catalyst were compared in Fukuchi's study. It was found that Fe(III) on the surface of the catalyst was

successfully reduced to Fe(II) by AA [26]. H₂ was also used as a reductant with the catalysis of Pd to reduce Fe(III) to Fe(II) in accelerated catalytic Fenton reaction [27].

AA is an environmentally benign organic compound with antioxidant properties ubiquitously occurring in nature. As an essential nutrient, AA plays an important physiological role in biological systems. It has various agricultural, pharmaceutical, and food industry applications [28]. However, to date there has been minimal investigation to evaluate the effect of AA on chlorinated pollutant removal by CP oxidation. Therefore, the impact of AA on enhancing Fe(III)-activated CP oxidation of TCE was evaluated in this study. The main objective of this study was to assess the enhancement of AA on the generation of reactive oxygen species (ROSs) for the CP/Fe(III) system and the application of this technology on TCE degradation in contaminated groundwater. The dominant species responsible for TCE degradation were identified with radical scavenger tests. The complete mineralization of TCE was elucidated through the measurement of the released Cl⁻, and the mechanism of TCE degradation was proposed accordingly.

2. Materials and methods

2.1. Materials

TCE was selected as the model contaminant. Calcium peroxide (75% CP, < 150 µm particle size) and trichloroethene (TCE, 99.0%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Carbon tetrachloride (CT, 99.5%), n-hexane (C₆H₁₄, 97%), ascorbic acid (AA, 99.7%), ferrous sulfate heptahydrate (FeSO₄·7H₂O, 99.5%) and ferric sulfate (Fe₂(SO₄)₃, 99.0%) were acquired from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). 1,10-phenanthroline monohydrate (C₁₂H₈N₂·H₂O, 98%), isopropanol (IPA, 99.5%), trichloromethane (CF, 99.0%) and nitrobenzene (NB, 99.0%) were purchased from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Sigma Co. Ltd. (Shanghai, China). All chemicals were used without further purification.

Solutions in all experiments were prepared with ultrapure water obtained from a Milli-Q water system (Classic DI, ELGA, Marlow, UK.). The actual groundwater used in the tests was obtained from a well screened approximately 10 m below the ground surface in Jinshan, Shanghai, China. Water quality characteristics are provided in Table S1 (Supplementary Materials).

2.2. Experimental procedures

A series of batch experiments was conducted with a glass cylinder reactor (250 mL) with two mouths on top for dosing and sampling separately. A magnetic stirrer was used to maintain the uniformity of solution in the reactor and a thermostat-controlled circulating water bath was used to maintain the temperature at 20 ± 0.5°C. NB and CT were used as probes to characterize the generation of ROSs. Electron paramagnetic resonance (EPR) detection was conducted to confirm the primary radical species using DMPO to trap the radicals in solution. At the desired time intervals, samples (1.0 mL) were collected and thoroughly mixed with 1.0 mL DMPO solution (88.4 mM) for 1 min, then the mixed

samples were analyzed by EPR. Free radical scavengers (IPA and CF) were used to evaluate the contribution of oxidative or reductive species to TCE degradation by adding individual scavenger to TCE solution before the reaction started.

TCE degradation was initiated by dosing CP to the aqueous solution in the reactor after the previous addition of other chemicals such as Fe(II) or Fe(III). AA was added simultaneously with CP to reduce Fe(III) to Fe(II). Sampling was conducted at designated time intervals and samples were analyzed immediately. The pH value of aqueous solution containing Fe(II) or Fe(III) without addition of CP and AA was recorded as initial pH, and the initial and final pH values in each experiment were reported (Table 1). Initial solution pH was not adjusted except in the tests to investigate the influence of pH on TCE degradation, wherein it was adjusted with 0.1 M NaOH or 0.1 M H₂SO₄. Groundwater tests were conducted by replacing ultrapure water with actual groundwater. Control tests were carried out in parallel without addition of CP. All experiments were performed in duplicate and the mean values reported.

2.3. Analytical methods

TCE, CT and NB in aqueous solution samples were quantified using a gas chromatograph (GC) equipped with electron capture detector (ECD) and flame ionization detector (FID) after extraction with n-hexane. The specific conditions for the analyses are reported in our previous study [13]. Ferrous ions and H₂O₂ in aqueous solution were quantified spectrophotometrically with 1,10-phenanthroline method and titanium sulfate method, respectively [29,30]. Total soluble iron was measured using inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 725 ES, Santa Clara, USA). The changes of AA and dehydroascorbic acid (DHAA) concentrations were monitored with high performance liquid chromatography (Shimadzu LC-20A, Kyoto, Japan) [31]. Chloride anions and organic acids released along with TCE degradation were analyzed by ion chromatography (Dionex ICS-I000, Sunnyvale, CA, USA). The free radicals were detected by EPR (EMX-8/2.7C, Bruker, Germany) using DMPO as a spin trap with the instrumental settings of followings: 100 G of field sweep, 9.866 GHz of microwave frequency, 2.016 mW of microwave power, 1 G of modulation amplitude, and 3.17×10^4 of receiver gain. The volatile organic intermediates formed in TCE degradation were identified with purge and trap - GC/MS (Agilent 7890/5975, USA) instrument. The solution pH was measured by a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

3. Results and discussion

3.1 Enhancement of the generation of ROSs in Fe(III) activated CP system by ascorbic acid

Both oxidative and reductive species were generated in the Fe(II)/Fe(III) activated CP system. HO• is a strong oxidant known as the primary free radical in Fenton reaction under acidic conditions, while a weaker oxidant Fe(IV) is reported as a Fenton intermediate at near-neutral pH condition, and O₂•⁻ is presented as a reductant [18,32]. In our previous studies, the generation of HO• and O₂•⁻ in CP/Fe(II), CP/Fe(III) and CP/Fe(III)/citric acid systems have been confirmed with the use of chemical probe compounds, i.e. NB and CT [13,33]. The chemical probes NB and CT were also used in this study to determine the

presence and reactivity of ROSs generated in the Fe(II)/Fe(III) activated CP system and evaluate the enhancement by AA.

As shown in Fig. 1a, NB removal with AA addition was comparable to the result of the control test, suggesting that AA couldn't reduce NB individually. Approximately 40% NB was removed in 5 min but no further removal was observed in the later 85 min in the CP/Fe(II) system. The stagnation of NB degradation after 5 min suggests that the generation of HO• ended quickly due to the formation of ferric hydroxide precipitates. Compared to the CP/Fe(II) system, the removal of NB in the CP/Fe(III) system was much slower, and 15% NB removal was reached in 90 min. One possible cause of this behavior might be the rapid formation of Fe(III) oxyhydroxide precipitates, such that only a small amount of soluble iron was available for the generation of HO• due to the low solubility of Fe(III) at the measured pH range as shown in Table 1 (less than 1×10^{-3} M at pH = 3 and 1×10^{-6} M at pH = 4). Moreover, the reaction rate of soluble Fe(III) with H₂O₂ (Eq. (3)) is four orders of magnitude lower than that of Fe(II) with H₂O₂ (Eq. (2)) [22]. The ferric precipitates are more inactive than free Fe(III) due to the additional reaction required to release soluble iron on the surface of the precipitates, which results in slower HO• generation [34].

NB removal was significantly improved to 43% in 5 min and 59% in 90 min with the addition of AA into the CP/Fe(III) system. The degradation of NB in this case can be divided into a fast stage in the initial 5 min followed by a slow stage in the following 85 min. These results indicate that more HO• was produced with the addition of AA and the continuous formation of HO• lasted for a longer period, which resulted in continued NB degradation. Similar magnitudes of CT degradation (approximately 12–15% in 90 min, higher than the removal of 5% in control test due to volatilization) were also observed in the Fe(II)/Fe(III) activated CP systems (Fig. 1b), suggesting the similar intensity of O₂•⁻ in these three systems.

To further confirm the formation of HO•, EPR tests were conducted to detect the presence of HO•, and the EPR spectrums are shown in Fig. S1. The DMPO-OH adduct was observed with high intensity in the EPR spectrum of CP/Fe(II) and CP/Fe(III)/AA systems, with the spectrum peak representing the intensity of HO•. The EPR spectrum, which has a specific quartet spectrum with peak height ratios of 1:2:2:1, indicates the formation of HO• in the CP/Fe(II) and CP/Fe(III)/AA systems. Conversely it was not observed in the CP/Fe(III) system. The peaks of other species including O₂•⁻ were not observed during the EPR analyses, which could be attributed to the low intensity of these species and the complicated solution composition in these systems.

Based on the above results, both oxidative (HO•) and reductive (O₂•⁻) species were present in the Fe(II)/Fe(III) activated CP systems. The addition of AA showed no increase in the generation of O₂•⁻ but did increase HO• generation owing to the reduction property of AA on Fe(III) (Eq. (7)) [35].

AA has two ionizable hydroxyl groups and generally acts as a mild acid in aqueous solution and exists partly as ascorbate anion through dissociation of a proton ($pK_{a1} = 4.25$) [36]. Ascorbate anion is oxidized with loss of one electron to form radical cation and then with loss of a second electron to form dehydroascorbic acid (DHAA) [36]. As 2.0 mole of Fe(III) is reduced by 1.0 mole of AA in the pH range between 2.6 and 6.0 [37], this process leads to the regeneration of sufficient Fe(II), therefore resulting in a large amount of $HO\bullet$ generation according to Eq. (2). This result is in agreement with the findings of Bolobajev et al. in their investigation of AA enhanced Fenton reaction [25]. Additionally, the complexation of Fe(III)/Fe(II) by AA and AA degradation products would also prevent the precipitation of dissolved iron, which was beneficial to $HO\bullet$ generation [38]. Meanwhile, excess AA would also act as an $HO\bullet$ scavenger and its scavenging effect was verified in the following section [26].

3.2 TCE degradation performance in CP/Fe(III)/AA system

The TCE removal efficiencies in various aqueous systems were evaluated and the results are shown in Fig. 2. TCE degradation was negligible in the CP/AA system without addition of activator, illustrating that H_2O_2 and AA do not react with TCE although they have oxidative and/or reductive capacity. TCE removal reached 5%, 56% and 75%, respectively, in 5 min in the CP/Fe(III), CP/Fe(II) and CP/Fe(III)/AA systems. However, TCE degradation was ended quickly in the CP/Fe(II) system, which is in accordance with the pattern observed in the degradation of $HO\bullet$ probe in Section 3.1, and two-fold larger Fe(II) dosage was required to achieve the complete TCE removal [13]. In contrast, the addition of AA to the CP/Fe(III) system improved TCE removal significantly, with 98% TCE removal achieved in 90 min. Moreover, the CP/Fe(III) system had the advantage of long-term TCE degradation performance compared to CP/Fe(II) system. The slow TCE degradation performance in CP/Fe(III) system has been observed in our previous study which indicated that more than 180 min was required for complete TCE removal even at higher dosages of CP and Fe(III) [33]. Therefore, the introduction of reducing agent AA reduced both the reaction time and chemical load required, which is favorable to the application of CP/Fe(III) technology for contaminant degradation. However, more efforts are needed in improving dosing methods when applying this technology under complicated conditions in the field, and this will be focused on in our next work.

The variation of Fe(II) and total soluble iron in these three systems were monitored and the results are displayed in Fig. 3. It was observed that Fe(II) concentration in the CP/Fe(II) system dropped to a very low level after TCE degradation started. Whereas, Fe(II) generation was accelerated in the presence of AA in the CP/Fe(III)/AA system and Fe(II) concentration remained higher than that in CP/Fe(II) system in the initial 1 min. The reduction of Fe(III) by AA is responsible for the rapid TCE degradation in the initial stage.

The changes of AA and DHAA were also determined and the results agreed with the previous study in which AA concentration decreased dramatically at the beginning of contaminant degradation (Fig. 4). It was believed that AA transformed to DHAA and also partly oxidized to other products such as oxalic acid and L-threonic acid [39]. AA and its products can be oxidized by $HO\bullet$ due to its scavenging property and also by other organic

species such as $\text{CH}_3\text{O}_2^\bullet$ which reacts with AA at a rate constant of $1.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ [40]. Gorman and Clydesdale reported that both oxidation-reduction reactions and complexation of Fe(III)/Fe(II) occurred simultaneously in the presence of AA [38]. Since AA was oxidized and undetectable after 1 min reaction, it was deduced that the complexation of Fe(III)/Fe(II) with AA and its products contributed to the degradation of TCE in the remaining reaction period. For example, iron ions complexed with ascorbate and its products by removing proton from the hydroxyl groups [41]. As shown in Fig. 3b, without addition of AA, Fe(III) converted to precipitates quickly and total soluble iron decreased to a very low level. With the addition of AA, a portion of dosed Fe(III) was converted to insoluble precipitates after 10 min while total soluble iron remained at approximately 0.2 mM due to the decrease of solution pH and the complexation of Fe(III) with AA and its products.

In order to investigate the specific effect of acidification by AA on TCE degradation, an experiment was conducted in which the solution pH in CP/Fe(III) system was adjusted to the same value over time as in the CP/Fe(III)/AA system during the entire reaction period. The results shown in Fig. S2 indicate that pH adjustment to the same values in CP/Fe(III)/AA system during the entire reaction did not significantly improve the degradation of TCE in the CP/Fe(III) system. Only a slight increase was observed for TCE degradation, from 12% without pH adjustment to 17% with pH adjustment in 90 min. Even though the decrease of pH could increase available soluble iron in solution, the acidification by AA can be only a minor effect responsible for the enhancement of TCE degradation. Thus, the enhancement by AA addition can be ascribed primarily to the reduction of Fe(III) to Fe(II) in the initial stage and the complexation of Fe(III)/Fe(II) with AA and its products in the following stages.

The liberation and consumption of H_2O_2 in the various systems were further investigated and the results are shown in Fig. 5. The theoretical maximum concentration of 0.6 mM H_2O_2 will be released from 0.6 mM CP according to the chemical stoichiometry. In the Fe-free system, CP dissolution in water released 0.46 mM H_2O_2 , and increased the solution pH to 11.15 in 90 min. This dissolution was much higher than the result of a previous study by Nouthup and Cassidy, which might be due to the differences in CP purity grade and the particle size of powders [9]. The addition of AA did not increase H_2O_2 yield, and rather H_2O_2 concentration decreased to 0.41 mM in 90 min. It is proposed that part of the released H_2O_2 was consumed in the reaction with AA. Compared with the Fe-free system, the addition of Fe(III) increased H_2O_2 yield in the initial 10 min but not in the case of Fe(II) addition due to the rapid H_2O_2 consumption in the CP/Fe(II) system. The final residual H_2O_2 concentrations were 0.41 mM, 0.26 mM, and 0.06 mM in the CP/Fe(III), CP/Fe(II) and CP/Fe(III)/AA systems respectively, indicating that the consumption of H_2O_2 was positively associated with TCE removal as expected.

It has been confirmed with chemical probe compounds in Section 3.1 that both oxidative ($\text{HO}^\bullet$) and reductive ($\text{O}_2^{\bullet-}$) species are generated simultaneously in the CP/Fe(III)/AA system. Their relative contributions to TCE degradation in the CP/Fe(III)/AA system was delineated with IPA and CF individual scavenger tests. As shown in Fig. 6a, the presence of IPA significantly inhibited the degradation of TCE, with only 17%, 10%, and 8% of TCE removed with the addition of 3.0, 10, and 30 mM IPA, respectively. Due to the high rate

constant of IPA reaction with HO• and its sufficiently high concentration, HO• produced in the system was quenched effectively. The potential HO• consumers in the CP/Fe(III)/AA system include TCE, AA, H₂O₂, Fe(III), Fe(II), and the external scavengers IPA and CF. Their second-order rate constants for reaction with HO• are 4×10⁹ M⁻¹s⁻¹ (k₁ for TCE), 1.0×10¹⁰ M⁻¹s⁻¹ (k₂ for AA), 1.9×10⁹ M⁻¹s⁻¹ (k₃ for IPA), 7×10⁶ M⁻¹s⁻¹ (k₄ for CF), 3.3×10⁷ M⁻¹s⁻¹ (k₅ for H₂O₂), 3.1×10⁵ M⁻¹s⁻¹ (k₆ for Fe(III)) and 3.2×10⁸ M⁻¹s⁻¹ (k₇ for Fe(II)), respectively [26,42,43]. In the absence of scavengers, the consuming rate of HO• by TCE and other substances can be expressed as follow:

$$-d[\text{HO}\bullet]/dt = k_1[\text{TCE}][\text{HO}\bullet] + k_2[\text{AA}][\text{HO}\bullet] + k_5[\text{H}_2\text{O}_2][\text{HO}\bullet] + k_6[\text{Fe(III)}][\text{HO}\bullet] + k_7[\text{Fe(II)}][\text{HO}\bullet];$$

(8)

while in the presence of IPA, the rate of HO• consumption is as follow:

$$-d[\text{HO}\bullet]/dt = k_1[\text{TCE}][\text{HO}\bullet] + k_2[\text{AA}][\text{HO}\bullet] + k_3[\text{IPA}][\text{HO}\bullet] + k_5[\text{H}_2\text{O}_2][\text{HO}\bullet] + k_6[\text{Fe(III)}][\text{HO}\bullet] + k_7[\text{Fe(II)}][\text{HO}\bullet].$$

(9)

The scavenging effect of H₂O₂, Fe(III) and Fe(II) can be neglected in the calculations due to their relatively low rate constants and concentrations. Therefore, the scavenging effect of IPA on HO• can be considered as $k_3[\text{IPA}][\text{HO}\bullet]/(k_1[\text{TCE}][\text{HO}\bullet] + k_2[\text{AA}][\text{HO}\bullet] + k_3[\text{IPA}][\text{HO}\bullet])$. Because AA in the system initially reacted with Fe(III) to produce Fe(II) before HO• formation, the calculated scavenging efficiencies varied in a range with the variation of AA concentration. According to the rate constants and the concentrations of IPA and TCE, the scavenging efficiencies of IPA on TCE degradation were calculated as 61.3%–90.5%, 84.1%–96.9% and 94.1%–99.0% at 3.0, 10 and 30 mM IPA concentration respectively. The actual experimental results of IPA scavenging efficiencies were 87.0%, 95.4% and 97.4%, which fall within the calculated ranges. The decrease in TCE removal indicated that HO• was the dominant species responsible for TCE degradation, but the contribution of other species cannot be neglected as well. Because IPA reacts with Fe(IV) at a very slow rate (3.2×10³ M⁻¹s⁻¹) compared to HO• (1.9×10⁹ M⁻¹s⁻¹) [44], the results of the IPA scavenging tests strongly support the predominant role of HO• rather than Fe(IV) in TCE degradation. Meanwhile, minor inhibition was found in TCE degradation in the presence of CF, though it was much smaller than that of IPA. The degradation of 94%, 85% and 71% TCE was observed in the presence of 3.0, 10 and 30 mM CF, respectively (Fig. 6b). CF has a smaller effect on TCE removal but its reactivity with HO• (7×10⁶ M⁻¹s⁻¹) cannot be ignored. The inhibitive effect of CF on TCE degradation may also be due to the quenching reaction with HO•. Similarly, the rate of HO• consumption when the scavenger was CF is as follow:

$$-d[\text{HO}\bullet]/dt = k_1[\text{TCE}][\text{HO}\bullet] + k_2[\text{AA}][\text{HO}\bullet] + k_4[\text{CF}][\text{HO}\bullet] + k_5[\text{H}_2\text{O}_2][\text{HO}\bullet] + k_6[\text{Fe(III)}][\text{HO}\bullet] + k_7[\text{Fe(II)}][\text{HO}\bullet].$$

(10)

The scavenging effect of CF on HO• can be considered as $k_4[\text{CF}][\text{HO}\bullet]/(k_1[\text{TCE}][\text{HO}\bullet] + k_2[\text{AA}][\text{HO}\bullet] + k_4[\text{CF}][\text{HO}\bullet])$. With the addition of 3.0, 10 and 30 mM CF, the calculated scavenging effects of CF on HO• were 0.6%–3.4%, 1.9%–10.4% and 5.5%–26.0%. The actual scavenging effects of CF on TCE degradation were 4.1%, 14.0%, and 28.8% at the concentration of 3.0, 10 and 30 mM respectively. The gap between calculated results and experimental results indicates that there must be the quenching effect on both HO• and O₂•[−] due to the higher reactivity of CF with O₂•[−] ($3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), which resulted in the inhibition of TCE degradation.

As the reactions occurring in the system are very complicated, the above calculations are just rough estimations, however these data could reflect the different roles of ROSs to some extent. Although O₂•[−] reacted slowly with TCE, a small degree of O₂•[−] generation was confirmed and it was reported to participate in the transformation of Fe(III) to Fe(II) in Fenton chemistry [43]. Huang et al. also documented the vital role of O₂•[−] in the recycle of soluble iron [45]. The inhibitive effect of CF reduced to 27% in the CP/Fe(III)/AA system compared to 39% in the CP/Fe(II) system with the same addition of 30 mM CF in our previous study [13]. It was deduced that the addition of AA occupied the domain position in Fe(II)/Fe(III) recycling in the CP/Fe(III)/AA system. On the other hand, AA might replace O₂•[−] as reducing agent in providing Fe(II) for Fenton reaction in the system [46]. In conclusion, TCE degradation in the CP/Fe(III)/AA system was mainly due to the oxidative pathway by HO•, but part of HO• generation resulted from the reductive action of O₂•[−] on Fe(III).

As discussed above, TCE degradation in the CP/Fe(III)/AA system was mainly due to HO• oxidation. Based on previous studies, the unsaturated carbon-carbon double bond in the molecular structure of TCE is electron-rich and more reactive to HO• compared to other single bonds. Therefore, the degradation of TCE was proposed to be initiated with the addition of HO• to the double bond to produce unstable radical intermediates like geminal chlorohydrin carbon-centered radical (ClCH(OH)-CCl₂•). The unstable radical intermediate transformed rapidly to OHC-CCl₂• by elimination of HCl [47]. OHC-CCl₂• was further oxidized to various intermediates, and the chloride in these intermediates could be further abstracted forming dichloroacetic acid, and glyoxylic, oxalic, and formic acids through various pathways, and finally decomposing to CO₂ and H₂O [48].

Chloride formation was monitored in parallel with TCE degradation to confirm the Cl[−] release extent, and the results are displayed in Fig. 7. Theoretically, the complete dechlorination of 0.15 mM TCE would release 0.45 mM Cl[−]. The gap between the detected Cl[−] and the theoretical Cl[−] suggests that there were chlorinated byproducts formed during the 120 min reaction period. No volatile chlorinated byproducts were detected by GC/MS,

while formic acid, oxalic acid, and dichloroacetic acid (the chlorinated byproduct) were detected by ion chromatography (Fig. S3). At 120 minutes of reaction, the measured Cl^- release was closely aligned to the theoretical Cl^- release, which strongly indicates that TCE degradation in the CP/Fe(III)/AA was complete. This is in agreement with the results observed in the CP/Fe(II) system in our previous study [13].

3.3 Effect of chemical dosage and initial TCE concentration on TCE degradation performance

As shown in Fig. 8a, TCE degradation highly depended on the dosage of CP. TCE degradation of 65%, 88%, 98%, and 25% were achieved after 90 min at the CP dosages of 0.15 mM, 0.3 mM, 0.6 mM, and 1.2 mM, respectively. Appropriate increase of CP dosage could lead to the improvement in TCE degradation as more $\text{HO}\bullet$ were generated as shown in Eqs. (1–3). However, excess CP dosage could negatively affect TCE degradation as well, due to the generation of $\text{Ca}(\text{OH})_2$ and elevation of solution pH. The final solution pH increased from 3.6 to 7.5 when excessive CP was added from 0.6 mM to 1.2 mM. High pH conditions were not favorable to CP reaction to produce H_2O_2 but beneficial to the inefficient parallel reaction to release O_2 [49]. The dissolution rate decreased with increasing solution pH. Less H_2O_2 was released and decomposed easily at higher pH since H_2O_2 is more unstable in high pH condition. The pH-induced conversion of $\text{HO}\bullet$ to Fe(IV) may also have an effect on TCE degradation [18]. Moreover, high solution pH would result in the transformation of soluble iron to inactive precipitates [50]. Since ferric precipitates were more inactive than free Fe(III) due to the additional reaction of iron dissolution in aqueous media, it was deduced that the minor TCE removal was contributed to the addition of AA at the beginning of the reaction. It was reported that the catalytic capability of ferric precipitates in Fenton based process would be accelerated by acid reaction media and chelating agents [32]. In addition to this, excessive CP produced high concentration of H_2O_2 , which also acted as $\text{HO}\bullet$ quencher (Eq. (6)). Therefore, CP dosage is a critical factor for the supply of ROSs and controlling the solution pH in the CP/Fe(III)/AA system.

The effect of Fe(III) concentration was also investigated because of its role as the source of Fe(II). As shown in Fig. 8b, TCE degradation was improved with the increase of Fe(III) concentration from 0.15 mM to 1.2 mM. Final TCE removal in 90 min reached 6.0%, 23%, 62%, and 98% respectively at Fe(III) concentrations of 0.15, 0.3, 0.45, and 0.6 mM. Table 1 shows that with the increase of Fe(III) dosage, both the initial and final solution pH decreased significantly. With the addition of 1.2 mM Fe(III), the initial and final pH reached 3.16 and 3.15. Therefore, it was speculated that it was the increase of soluble iron concentration that contributed to the higher TCE removal rate rather than the increase in the surface area of the precipitates because the lower pH benefited to the dissolution of Fe(III). The dosage of 0.6 mM Fe(III) was sufficient for $\text{HO}\bullet$ generation to achieve complete TCE degradation.

On the other hand, as shown in Fig. 8c, the addition of 0.15 and 0.3 mM AA promoted TCE degradation from 12% (without AA) to 90% and 98%, which could be the result of Fe(III) reduction by AA as mentioned in Sections 3.1 and 3.2. However, AA can also act as an $\text{HO}\bullet$ scavenger. Ascorbate anions react with $\text{HO}\bullet$ at a rate constant of $1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ which is

higher than that of TCE with HO• [26]. Therefore, further increase of AA dosage would decrease TCE removal, for instance, the final TCE removal decreased to 89% and 67% in the presence of 0.6 and 1.20 mM AA. In conclusion, the optimal dosing ratio of CP/Fe(III)/AA/TCE in this study was 4/4/2/1 when the absolute concentrations were 0.60 mM (CP), 0.60 mM (Fe(III)), 0.30 mM (AA), respectively.

TCE concentration at contaminated sites varies over a wide range from tens of ppb to hundreds of ppm depending on local conditions [51,52]. Degradation of TCE at various initial concentrations ranging from 0.01 mM to 0.6 mM were performed to investigate the effect of this parameter (Fig. 9). No significant impact was found on the degradation of low concentrations of TCE from 0.01 to 0.15 mM, and the final TCE degradation was over 98% at various concentrations. The sufficient HO• generated in the system maintained the complete TCE degradation and excess HO• was exhausted in the reaction with other scavengers such as H₂O₂ and AA [53]. HO• generated from this system was not sufficient to degrade TCE completely when the initial TCE concentration was higher than 0.15 mM, and TCE removal decreased to 91% and 63% respectively at initial TCE concentrations of 0.3 and 0.6 mM, suggesting that more chemical dosing was needed for remediation of highly contaminated groundwater, as would be expected.

3.4 Influences of groundwater characteristics and the potential application of CP/Fe(III)/AA to actual groundwater

To evaluate the applicability of CP/Fe(III)/AA for actual groundwater remediation, the influences of groundwater characteristics such as solution pH and anions were initially tested using ultrapure water. The effect of initial solution pH was investigated by adjusting the initial solution pH to 3, 4, 5, 6 and 7. As shown in Fig. 10, the pH had significant influence on TCE degradation. TCE removal efficiency decreased from 99% to 18% with increase in initial solution pH from 3 to 7. With the increase of solution pH, Fe(III) existed as iron hydroxides which resulted in less HO• production. Even though TCE degradation could occur on the surface of ferric precipitates, the ferric precipitates were less active than free Fe(III) due to the lower intrinsic activity [34]. Hence we presumed that the minor TCE removal at pH 7 was the result of AA addition at the beginning which enhanced the dissolution of ferric precipitates. Moreover, Ca(OH)₂ produced in the reaction of CP with water would increase solution pH as well. The results shows that the final pH was higher than the initial pH in all experiments. Even though AA can act as a chelating agent, the iron-ascorbate complex was reported to be unstable at pH over 6 due to the low stability constant [38]. Deng investigated the effect of pH on the reductive dissolution rate of Fe(III) hydroxide by ascorbate and found the optimal pH was under 6 [54].

The influences of anions were also investigated with the individual addition of four common anions, i.e., Cl⁻, HCO₃⁻, SO₄²⁻ and NO₃⁻. The results in Fig. 11 show that 10 mM Cl⁻, SO₄²⁻ and NO₃⁻ had minor impact on TCE degradation while HCO₃⁻ inhibited TCE degradation significantly. TCE removal decreased from 98% to 21% in the presence of 10 mM HCO₃⁻ in 120 min. Cl⁻, SO₄²⁻ and NO₃⁻ had minor influence on the initial solution pH while HCO₃⁻ elevated the initial solution pH from 3.2 to 6.8 (Table. 1). This elevation of pH by HCO₃⁻ inhibited TCE degradation strongly. In addition, HCO₃⁻ has been reported to act

as an HO• scavenger. However, the reaction rate constant of HCO_3^- with HO• ($8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$) is much smaller than that of TCE with HO• ($4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [55]. It was reported that $\text{CO}_3^{\cdot-}$ was formed instead of HO• in Fenton like oxidation reactions in the presence of HCO_3^- , and the oxidation potential of $\text{CO}_3^{\cdot-}$ ($E^0 = 1.5 \text{ V}$) was considerably lower than that of HO• [56]. Therefore, the elevation of pH and the transformation of HO• to weaker oxidizing species are suspected to be the primary factors for the inhibition of TCE degradation.

Further tests were conducted by replacing ultrapure water with actual groundwater obtained from a site in Jinshan, Shanghai, China. Table S1 provides the characteristics of the groundwater. As shown in Fig. 12, TCE degradation in groundwater was much lower than that in ultrapure water. Only 5% and 18% TCE removals were achieved at the CP/Fe(III)/AA/TCE molar ratio of 4/4/2/1 and 10/10/5/1 in 120 min. Addition of the reagents had minimal impact on solution pH due to the buffering capacity of actual groundwater. Most Fe(III) became ferric precipitates and minimal soluble iron was detected (Table S2). The presence of HCO_3^- at the level of 188.3 mg/L in groundwater could be the reason for the inefficient TCE degradation. Moreover, total organic carbon analysis indicated the presence of natural organic matter in groundwater. It was reported that natural organic matter could react with HO• at higher constants and reduce the degradation of target contaminants [57]. Therefore, increased dosages of reagents were tested further, and encouragingly, with the increase of Fe(III) and AA dosages TCE degradation increased to 73% and 96% at the CP/Fe(III)/AA/TCE molar ratio of 10/20/5/1 and 10/20/10/1, respectively. These results suggest that CP/Fe(III)/AA technique may be applicable in remediation of TCE contaminated groundwater.

4. Conclusion

In this study, the enhanced HO• generation in the CP/Fe(III) system caused by AA addition was investigated for its impact on TCE degradation. The generation of HO• and $\text{O}_2^{\cdot-}$ in the CP/Fe(III)/AA system were confirmed with chemical probes. TCE degradation was significantly improved with the addition of AA, and HO• was proved to be the dominant species responsible for TCE degradation. These results were mainly due to the promotion of efficient utilization of Fe(III) and H_2O_2 with the addition of AA in the system. In addition, the effect of initial solution pH was evaluated, indicating the decrease in TCE degradation with the increase in solution pH. The tests in the presence of common anions showed that Cl^- , SO_4^{2-} and NO_3^- had minor impact on TCE degradation while HCO_3^- possessed significant inhibition due to the elevation of solution pH. The testing of CP/Fe(III)/AA for actual groundwater demonstrated the potential effectiveness of this technique for remediation of TCE contaminated groundwater, though more attempts are needed for actual site implementation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Degradation of probe compounds in various systems, (a) NB, (b) CT. $[CP]_0 = 0.6$ mM, $[Fe(II)]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[NB]_0 = 0.15$ mM, $[CT]_0 = 0.01$ mM.

Fig. 2. TCE degradation performance in various systems. $[CP]_0 = 0.6$ mM, $[Fe(II)]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM.

Fig. 3. Variation of (a) Fe(II) and (b) total soluble iron concentrations in various systems. $[CP]_0 = 0.6$ mM, $[Fe(II)]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM.

Fig. 4. Changes of AA and DHAA concentrations versus reaction time in CP/Fe(III)/AA/TCE system. $[CP]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM.

Fig. 5.
 H_2O_2 liberation and decomposition in various systems. $[\text{CP}]_0 = 0.6$ mM, $[\text{Fe(II)}]_0 = 0.6$ mM, $[\text{Fe(III)}]_0 = 0.6$ mM, $[\text{AA}]_0 = 0.3$ mM, $[\text{TCE}]_0 = 0.15$ mM.

Fig. 6. TCE degradation in the presence of radical scavengers in CP/Fe(III)/AA/TCE system, (a) IPA, (b) CF. $[CP]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM.

Fig. 7. Cl⁻ liberation from TCE degradation in CP/Fe(III)/AA/TCE system. [CP]₀ = 0.6 mM, [Fe(III)]₀ = 0.6 mM, [AA]₀ = 0.3 mM, [TCE]₀ = 0.15 mM.

Fig. 8. Influence of chemical dosages on TCE degradation in CP/Fe(III)/AA/TCE system: (a) CP, $[TCE]_0 = 0.15 \text{ mM}$, $[Fe(III)]_0 = 0.6 \text{ mM}$, $[AA]_0 = 0.3 \text{ mM}$; (b) Fe(III), $[TCE]_0 = 0.15 \text{ mM}$, $[CP]_0 = 0.6 \text{ mM}$, $[AA]_0 = 0.3 \text{ mM}$; (c) AA, $[TCE]_0 = 0.15 \text{ mM}$, $[CP]_0 = 0.6 \text{ mM}$, $[Fe(III)]_0 = 0.6 \text{ mM}$.

Fig. 9.

Influence of initial TCE concentration on TCE degradation performance in CP/Fe(III)/AA/TCE system. $[CP]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM.

Fig. 10.

Influence of initial solution pH on TCE degradation in CP/Fe(III)/AA/TCE system. $[CP]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM, Time = 120 min.

Fig. 11. Influence of anions on TCE degradation in CP/Fe(III)/AA/TCE system. $[CP]_0 = 0.6$ mM, $[Fe(III)]_0 = 0.6$ mM, $[AA]_0 = 0.3$ mM, $[TCE]_0 = 0.15$ mM, $[Cl^-] = [HCO_3^-] = [NO_3^-] = [SO_4^{2-}] = 10$ mM.

Fig. 12.
Degradation of TCE in actual groundwater test. $[TCE]_0 = 0.15$ mM, Time = 120 min.

Table 1

Initial and final pH values in all experiments

Corresponding figure	No.	Operational conditions	Initial pH	Final pH
Fig. 1a	A1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [NB] ₀ = 0.15 mM	3.25	5.71
	A2	[CP] ₀ = 0.6 mM, [Fe(II)] ₀ = 0.6 mM, [NB] ₀ = 0.15 mM	5.32	9.46
	A3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [NB] ₀ = 0.15 mM	3.28	3.96
Fig. 1b	B1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [CT] ₀ = 0.01 mM	3.31	5.83
	B2	[CP] ₀ = 0.6 mM, [Fe(II)] ₀ = 0.6 mM, [CT] ₀ = 0.01 mM	5.35	9.88
	B3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [CT] ₀ = 0.01 mM	3.30	4.14
Fig. 2	C1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [TCE] ₀ = 0.15 mM	3.33	5.69
	C2	[CP] ₀ = 0.6 mM, [Fe(II)] ₀ = 0.6 mM, [TCE] ₀ = 0.15 mM	5.31	9.65
	C3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.22	3.63
Fig. 6a	D1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [IPA] = 3.0 mM	3.38	3.33
	D2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [IPA] = 10 mM	3.38	3.41
	D3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [IPA] = 30 mM	3.36	4.20
Fig. 6b	E1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [CF] = 3.0 mM	3.42	3.47
	E2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [CF] = 10 mM	3.40	3.37
	E3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [CF] = 30 mM	3.31	3.35
Fig. 8a	F1	[CP] ₀ = 0.15 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.35	3.28
	F2	[CP] ₀ = 0.3 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.31	3.39
	F3	[CP] ₀ = 1.2 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.40	7.46
Fig. 8b	G1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.15 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.72	8.03
	G2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.3 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.53	6.85
	G3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.45 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.41	4.32
Fig. 8c	H1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 1.2 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM	3.16	3.15
	H2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.15 mM, [TCE] ₀ = 0.15 mM	3.34	3.60
	H3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.6 mM, [TCE] ₀ = 0.15 mM	3.32	3.57
Fig. 9	I1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 1.2 mM, [TCE] ₀ = 0.15 mM	3.32	4.70
	I1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.01 mM	3.23	3.71

Corresponding figure	No.	Operational conditions	Initial pH	Final pH
Fig. 10	I2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.05 mM	3.21	3.74
	I3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.30 mM	3.26	3.66
	I4	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.60 mM	3.24	3.69
	J1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, initial pH=3	3.00	3.55
	J2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, initial pH=4	4.00	4.67
Fig. 11	J3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, initial pH=5	5.00	6.14
	J4	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, initial pH=6	6.00	7.8
	J5	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, initial pH=7	7.00	10.61
	K1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [Cl ⁻] = 10 mM	3.30	3.56
	K2	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [HCO ₃ ⁻] = 10 mM	6.82	6.68
Fig. 12	K3	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [NO ₃ ⁻] = 10 mM	3.24	3.46
	K4	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM, [SO ₄ ²⁻] = 10 mM	3.45	3.67
	L1	[CP] ₀ = 0.6 mM, [Fe(III)] ₀ = 0.6 mM, [AA] ₀ = 0.3 mM, [TCE] ₀ = 0.15 mM in groundwater	6.70	7.02
	L2	[CP] ₀ = 1.5 mM, [Fe(III)] ₀ = 1.5 mM, [AA] ₀ = 0.75 mM, [TCE] ₀ = 0.15 mM in groundwater	6.45	6.94
	L3	[CP] ₀ = 1.5 mM, [Fe(III)] ₀ = 3 mM, [AA] ₀ = 0.75 mM, [TCE] ₀ = 0.15 mM in groundwater	6.25	5.87
	L4	[CP] ₀ = 1.5 mM, [Fe(III)] ₀ = 3 mM, [AA] ₀ = 1.5 mM, [TCE] ₀ = 0.15 mM in groundwater	6.25	5.94