

Enhanced degradation of trichloroethene by sodium percarbonate activated with Fe(II) in the presence of citric acid

Xueke Zang, Xiaogang Gu, Shuguang Lu, Zhouwei Miao, Xiang Zhang, Xiaori Fu, George Y. Fu, Zhaofu Qiu and Qian Sui

ABSTRACT

Trichloroethene (TCE) degradation by Fe(II)-activated sodium percarbonate (SPC) in the presence of citric acid (CA) in aqueous solution was investigated. The results indicated that the presence of CA enhanced TCE degradation significantly by promoting HO• generation. The presence of Cl⁻, HCO₃⁻ and the initial solution pH appeared to be not negligible on the effect of TCE oxidation, while humic acid had no influence on TCE degradation. The generation of HO• and O₂^{-•} in the SPC/Fe(II)/CA system was confirmed with chemical probes, and the radical scavenging tests showed that TCE degradation was due to direct oxidation by HO•. Acidic pH condition was favorable for TCE degradation. In summary, this study provided detailed information for the application of the CA-enhanced Fe(II)-activated SPC technique for TCE-contaminated groundwater remediation.

Key words | citric acid, ferrous ion, groundwater remediation, sodium percarbonate, trichloroethene

Xueke Zang
Shanghai Institute of Geological Engineering
Exploration,
Shanghai 200072,
China

Xueke Zang
Xiaogang Gu
Shuguang Lu (corresponding author)
Zhouwei Miao
Xiang Zhang
Xiaori Fu
Zhaofu Qiu
Qian Sui

State Environmental Protection Key Laboratory of
Environmental Risk Assessment and Control on
Chemical Process,
East China University of Science and Technology,
Shanghai 200237,
China
E-mail: lvshuguang@ecust.edu.cn

George Y. Fu
Department of Construction Management & Civil
Engineering Technology,
Georgia Southern University,
Statesboro, GA 30460-8047,
USA

INTRODUCTION

Trichloroethene (TCE), a typical chlorinated solvent which was widely used in metal degreasing, dry cleaning, etc., is a ubiquitous contaminant. Due to its harmful characteristics such as cytotoxicity, carcinogenicity and persistence in groundwater environments, TCE has been identified as one of the priority existing chemicals under the toxic substances control act by the United States Environmental Protection Agency (USEPA 2014).

During the last few decades, various techniques have been developed for chlorinated solvent contaminated groundwater remediation, such as permeable reactive barriers, soil vapor extraction, air sparging and *in situ* chemical oxidation (ISCO). ISCO accomplished by injecting chemical oxidants (including ozone, potassium permanganate, persulfate, and Fenton's reagent) directly into contaminated groundwater to

degrade contaminants is an increasingly popular technology (Krembs *et al.* 2010). Among the above-mentioned chemical oxidants, Fenton's reagent has attracted much attention because of its strong capacity for oxidizing organic contaminants via the hydroxyl radical (HO•) (2.76 V) generated from the decomposition of H₂O₂. Though HO• has a higher redox potential than ozone (2.07 V), permanganate (1.68 V), and persulfate (2.01 V) (Gu *et al.* 2011), other radicals may also play roles in the process, such as the superoxide radical (O₂^{-•}) and perhydroxyl radical (HO₂[•]), which promote chain free-radical reactions in the presence of Fe(II) or Fe(III).

However, Fenton's reagent has some stubborn drawbacks, e.g. the rapid accumulation of Fe(III), easy precipitation of Fe(OH)₃, and the narrow applicable pH ranges (2–4), therefore limiting its widespread application

(Ahn *et al.* 2013). It is reported that the addition of chelating agents can effectively stabilize and minimize the loss of soluble iron (Luca *et al.* 2014). For example, chelating agents such as citric acid (CA) (Jho *et al.* 2010), ethylenediaminetetraacetic (EDTA) (Chang *et al.* 2013) and (S,S)-ethylenediamine-N,N-disuccinic acid (EDDS) (Ahmad *et al.* 2012), have been documented as efficient agents in modified Fenton processes in the degradation of contaminants.

Sodium percarbonate (SPC) ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$) is a cheap, stable and environmentally friendly oxidant (Kabalka *et al.* 1989). In recent years, SPC has been used as an alternative oxidant in ISCO practice (de la Calle *et al.* 2012). SPC naturally decomposes generating a theoretical available active oxygen as shown in Equation (1) (Wu & Zhou 2000):



According to the equation, SPC may have the same functional benefits as liquid H_2O_2 . Besides, in comparison to Fenton's reagent, SPC can effectively oxidize organic compounds over a wide pH range. In the meantime, the products of SPC during the reaction are CO_2 and H_2O , which are non-toxic and friendly to the environment (Zang *et al.* 2014). In addition, SPC might have the same shortcomings as Fenton's reagent when applied to actual site-remediation. As CA has been documented as an efficient chelating agent in the modified Fenton process to surmount the shortcomings of the traditional Fenton process, the CA-chelated Fe(II)-based catalyzed SPC oxidation process may show extensive practical prospects for the remediation of contaminated groundwater.

To the best of our knowledge, the ability of CA in enhancing the Fe(II)-catalyzed oxidative capacity of SPC for TCE degradation has not been investigated. Therefore, the main purpose in this study is to figure out the effect of CA on TCE degradation. We will specifically focus on: (1) investigating the effect of CA dosage on TCE degradation performance in the SPC/Fe(II)/CA system; (2) assessing the effects of inorganic anions (Cl^- , HCO_3^- ions) and natural organic matter (NOM) on TCE degradation performance; and (3) identifying the reactive oxygen radicals generated in the SPC/Fe(II)/CA system through probe tests and their contribution to TCE degradation through scavenger tests.

MATERIALS AND METHODS

Materials

Trichloroethene (TCE, >99.0%), SPC ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, >98%), hydroxylamine hydrochloride (>98.5%) and 1,4-benzoquinone (>97%) were obtained from Aladdin (Shanghai, China). Ferrous sulfate heptahydrate (>99%), sodium bicarbonate (>99.5%), EDTA acid (>99%), CA (>99%), humic acid (HA, fulvic acid >90%), nitrobenzene (>97%), carbon tetrachloride (>97%) and tert-butyl alcohol (>99%) were purchased from Shanghai Jingchun Reagent Ltd Co. (Shanghai, China). (S,S)-ethylenediamine-N,N-disuccinic acid (EDDS, 35% in water) was obtained from Sigma-Aldrich (Shanghai, China). All of these reagents were used as received without further purification. Ultrapure water from a Milli-Q water process (Classic DI, ELGA) was used for the preparation of aqueous solutions.

Experimental procedures

TCE stock solution was prepared by allowing the pure non-aqueous-phase liquid TCE to equilibrate with Milli-Q water overnight under gentle stirring in darkness. The TCE stock solution was then diluted to the desired concentration (initial TCE concentration = 0.15 mM). Batch tests were conducted in a 250 mL cylindrical glass reactor to evaluate the effectiveness of activated SPC oxidation for the remediation of TCE-contaminated groundwater. A magnetic stirrer was used to ensure uniform mixing of contaminants in the aqueous solution. At the start of a run, the reactor was completely filled by the TCE-containing solution to remove head space and avoid loss of TCE from volatilization. The initial solution pH in all experiments was unadjusted and the temperature was controlled at 20 °C. Control tests without Fe(II) and SPC were also conducted in parallel to examine the behavior of the contaminants in an aqueous system. Aqueous samples were taken at the desired time intervals and analyzed immediately, and the tests were conducted at least in duplicate and the mean values were reported.

Analytical methods

Aqueous samples (1.0 mL) were analyzed following extraction with hexane (1.0 mL) for 3 min using a vortex stirrer,

and allowed to separate for 5 min. Then the organic phase (TCE in hexane) was transferred to a 2 mL GC vial. TCE, nitrobenzene and carbon tetrachloride in hexane were analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA), and specific conditions can be found in our previous research (Zhang *et al.* 2015). The recovery of TCE through the above procedure was in the range of 87%–95%. The chloride anion was analyzed by ion chromatography (Dionex ICS-1000, Sunnyvale, CA). The concentrations of ferrous ion (Fe(II)) and total iron ions (Fe(II) and Fe(III)) were measured by using the 1,10-phenanthroline method (Tamura *et al.* 1974). Specifically, for ferrous ion measurement, a 1.0 mL sample was mixed with 5.0 mL potassium biphthalate (0.2 M) and 10 mL 1,10-phenanthroline monohydrate (0.3%) in a 25 mL colorimetric tube. After complete mixing the absorbance at 512 nm was measured. The total iron ions were measured with the same procedure, but with the addition of 1.0 mL hydroxylamine hydrochloride (10%) in the samples. The solution pH was measured with a pH meter (Mettler-Toledo DELTA 320).

RESULTS AND DISCUSSION

The performance of TCE degradation in chelated Fe(II)-catalyzed SPC system

In order to enhance TCE degradation performance in the Fe(II)/SPC system, three chelating agents, EDTA, CA and EDDS, were introduced into the Fe(II)/SPC system individually. The experiments were conducted at the initial SPC/Fe(II)/TCE molar ratio of 5/3/1 (TCE = 0.15 mM, SPC = 0.75 mM, FeSO₄·7H₂O = 0.45 mM) and each with chelating agent concentration of 1.0 mM. The results showed that the addition of CA increased TCE degradation significantly (Figure 1). For example, TCE degradation within the initial 90 min increased from 33% in the SPC/Fe(II) system without chelating agent to approximately 98% in the CA addition system. This suggested that the addition of favorable chelating agents indeed enhanced the catalytic ability in the SPC/Fe(II) system for TCE degradation. Enhanced TCE degradation performance in the CA chelated Fe(II) system was due to the increase of soluble Fe(II) concentration in aqueous solution (Table 1), as well

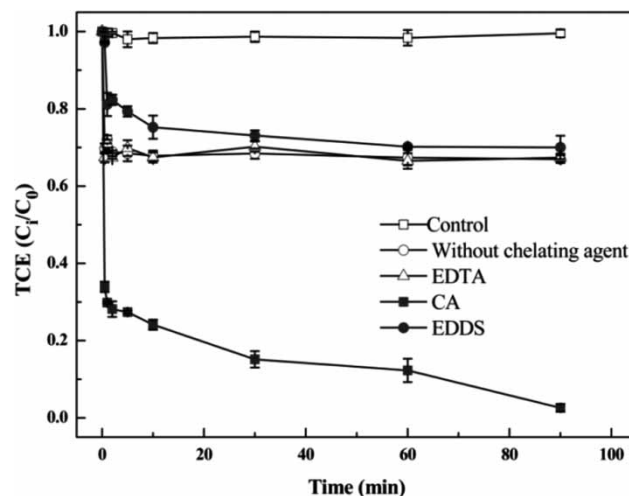


Figure 1 | Effect of different chelating agents on TCE degradation performance (initial TCE concentration = 0.15 mM, SPC = 0.75 mM, FeSO₄·7H₂O = 0.45 mM, SPC/Fe(II)/TCE = 5/3/1).

Table 1 | Soluble Fe(II) concentration in solution at different reaction times in CA chelated and without CA systems (mg/L)

Time (min)	Without CA	CA
0	25.6	25.8
0.5	1.5	5.5
1	0.9	1.3
2	0.45	1.0
5	0.4	1.9

as the reduction of solution pH (pH < 3.5), which is acknowledged as the optimal pH range in the traditional Fenton reaction, thus providing a continuous generation of Fe(II) and HO• through chain reactions.

It should be noted that the addition of EDTA and EDDS showed no positive effect on TCE degradation (Figure 1). The reasons for this result could be due to: (1) the different chelating ability of different chelators, leading to the different activated capacity of chelated Fe(II), and finally affecting free-radical production and TCE degradation. Specifically EDTA and EDDS have strong chelating ability with Fe(II), hence limited available Fe(II) involved in HO• generation chain reactions; (2) the high reaction rate of EDTA with HO• ($k_{\text{EDTA}/\text{HO}\cdot} = 4.0 \times 10^8 \text{ L M}^{-1} \text{ s}^{-1}$ at pH 4.0) (Pignatello 1992). In addition, the solution pH decreased below 4.0 in the SPC/Fe(II)/EDTA system (Table 2) because EDDS was a weak acid compared with CA and EDTA. As a

Table 2 | TCE degradation and solution pH changes with different chelating agents

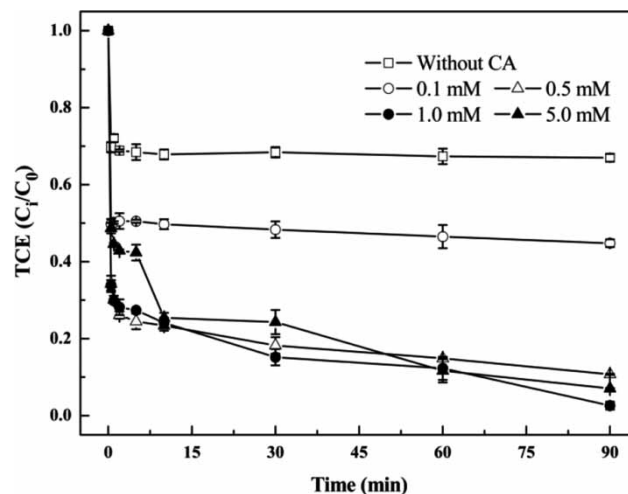
Experiment conditions	pH of solution Initial/Final (90 min)	TCE degradation (%)	
		2 min	90 min (Final)
Without chelating agent	7.42/3.33	31	33
EDTA	7.62/3.65	33	33
CA	7.13/3.17	73	98
EDDS	7.02/7.13	18	30

biodegradable chelating agent, EDDS could also react with HO• (Vandevivere et al. 2001). So EDTA and EDDS could not elevate TCE degradation by scavenging the HO• radical.

Although the traditional Fenton reagent has a strong capacity for oxidizing organic contaminants, when applying Fenton's reagent, the pH had to be adjusted to 2–4, and the hydrogen peroxide (H₂O₂) was unstable and had a short life-time after injection into the subsurface (Duesterberg & Waite 2006). However, based on the following experiment, the SPC/Fe(II)/CA system did not need adjustment of the solution pH and the concentration of inorganic carbon from SPC was too low to inhibit TCE degradation. Because of the positive effect of CA on TCE degradation, the CA chelating system was investigated in detail in the following experiments.

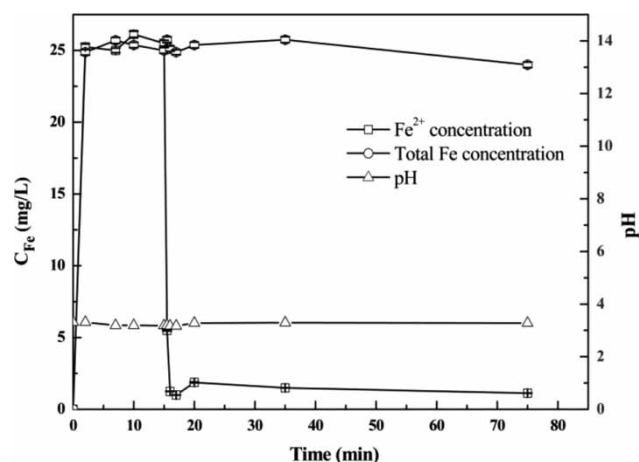
The role of CA in TCE degradation performance in SPC/Fe(II)/CA system

The effect of CA dosages of 0.1, 0.5, 1.0 and 5.0 mM on TCE degradation performance was investigated. As shown in Figure 2, TCE degradation increased from 33% to 55%, 89% and 98% in 90 min at the CA dosages of 0, 0.1, 0.5 and 1.0 mM, respectively. When increasing the CA to 5.0 mM, TCE degradation slightly decreased to 92%. These results may be due to the high reaction rate between CA and HO• ($k_{CA/HO\cdot} = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 6.6) (Xue et al. 2009), which may lead to the radical scavenging effect when they are used at high concentration. Therefore, in the following experiments the initial TCE and CA concentrations were set at 0.15 mM and 0.5 mM, respectively, at the SPC/Fe(II)/TCE molar ratio of 5/3/1. Interestingly, TCE was degraded rapidly in the first stage due to the rapid depletion of free Fe(II) and intensive generation of

**Figure 2** | Effect of CA dosage on TCE degradation performance (initial TCE concentration = 0.15 mM, SPC = 0.75 mM, FeSO₄·7H₂O = 0.45 mM, SPC/Fe(II)/TCE = 5/3/1).

HO•. However, after the significant reduction of SPC and TCE within the initial 5 min, TCE decrease slowed down in the system because Fe(II) was transferred to Fe(III), and free radicals were completely consumed.

In order to better understand the role of CA in the SPC/Fe(II)/CA/TCE system, the variations of Fe(II), Fe(III) and the change of solution pH were measured during the reaction. If FeSO₄·7H₂O completely dissolved, the concentration of total iron in the solution should be 25.6 mg/L theoretically. As shown in Figure 3, the initial 15 min was the chelating period of Fe(II) with CA, then SPC

**Figure 3** | The variations of concentrations of Fe²⁺ and total Fe and change of solution pH during TCE degradation (CA = 0.5 mM, initial TCE concentration = 0.15 mM, SPC = 0.75 mM, FeSO₄·7H₂O = 0.45 mM, SPC/Fe(II)/TCE = 5/3/1).

was added in 15 min and the reaction began. During the chelating process, the main form of iron (99.9%) in this system was Fe(II) as shown in Figure 3. The measured iron concentration in solution was around 25 mg/L, showing an excellent comparison agreeable with the theoretical yield. And there was no precipitation along with the reaction compared to previous experimental results in which iron precipitation appeared. This phenomenon suggested that the addition of CA could effectively inhibit the precipitation. It is worth noting that in the initial 15 min, Fe(II) concentration did not show obvious change, indicating that CA had a strong chelating ability. When adding SPC at 15 min, the concentration of Fe(II) decreased from 25.5 mg/L to 1.25 mg/L suddenly, it was noted that Fe(II) transferred to Fe(III) quickly, and an equilibrium was reached eventually. From the addition of CA, the solution pH remained around 3.2 as the reaction processing. CA and the acid pH may have promoted the generation of HO•, which would benefit the SPC/Fe(II) system.

Influence of solution matrix on TCE degradation in SPC/Fe(II)/CA system

Given the ubiquitous existence of Cl^- , HCO_3^- , and HA in groundwater, the influences of these constituents at different concentrations on TCE degradation in the SPC/Fe(II)/CA system were investigated separately. As shown in Figure 4(a), with the increase of Cl^- concentration from 0 to 1.0 M, TCE degradation efficiency decreased from 70% to 25% within 1 min, and from 98% to 39% in 90 min (Table 3). It can be seen that the effect of chloride ions on the oxidation of TCE was not obvious at low concentration (10 mM). However, apparent inhibition occurred at the concentrations of 100 mM, 500 mM and 1.0 M. It is reported that Cl^- could react with HO•, and a series of propagation reactions may proceed to form Cl^\bullet (Equation (3)) (Liao et al. 2001), which could lead to an enhanced degradation efficiency (Yuan et al. 2011). It has to be noted that the pH of all the solutions was around 3.0~4.0 during reactions. This inhibition can be ascribed, under acidic pH conditions, to the competitive interaction of chloride with HO•, resulting in much less reactive HOCl• (Equation (2)) and thus decreasing the

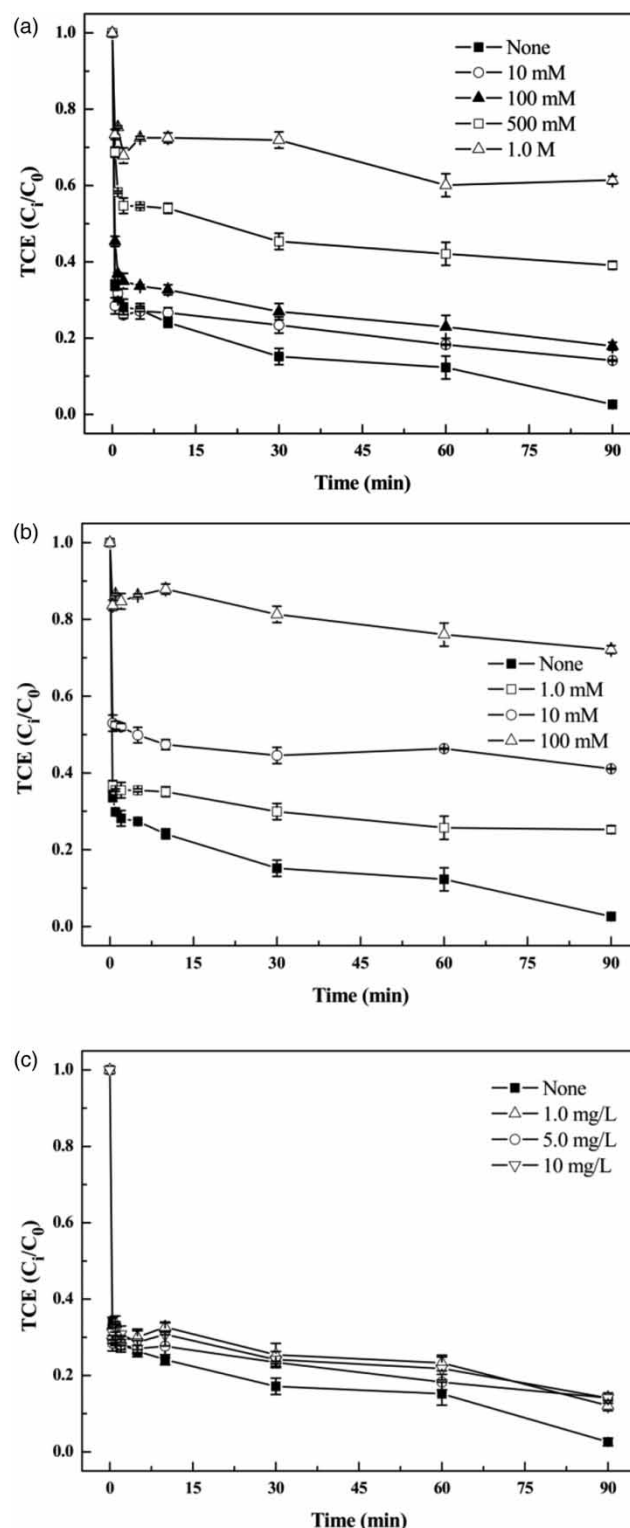


Figure 4 | Effects of anions and HA on TCE degradation performance: (a) Cl^- , (b) HCO_3^- , (c) HA (CA = 0.5 mM, initial TCE concentration = 0.15 mM, SPC/Fe(II)/TCE = 5/3/1).

Table 3 | Effects of Cl^- , HCO_3^- and HA on TCE degradation performance

Experiment conditions	TCE degradation (%)		pH of solution Initial/Final
	1 min	90 min	
None (pH unadjusted)	70 (1 min)	98 (90 min)	3.98/3.17
$\text{Cl}^- = 10 \text{ mM}$	68 (1 min)	86 (90 min)	3.72/3.19
$\text{Cl}^- = 100 \text{ mM}$	63 (1 min)	82 (90 min)	3.88/3.17
$\text{Cl}^- = 500 \text{ mM}$	42 (1 min)	61 (90 min)	3.84/3.27
$\text{Cl}^- = 1.0 \text{ M}$	25 (1 min)	39 (90 min)	3.79/3.08
$\text{HCO}_3^- = 1.0 \text{ mM}$	65 (1 min)	75 (90 min)	5.73/4.04
$\text{HCO}_3^- = 10 \text{ mM}$	48 (1 min)	59 (90 min)	6.98/6.67
$\text{HCO}_3^- = 100 \text{ mM}$	14 (1 min)	28 (90 min)	8.22/7.89
pH = 3.0	68 (1 min)	93 (90 min)	3.01/2.85
pH = 6.0	61 (1 min)	74 (90 min)	6.03/4.08
pH = 7.0	43 (1 min)	56 (90 min)	7.02/6.19
pH = 8.0	20 (1 min)	25 (90 min)	8.01/7.17
pH = 11.0	10 (1 min)	19 (90 min)	11.05/8.81
HA = 1.0 mg/L	68 (1 min)	28 (90 min)	3.73/3.09
HA = 5.0 mg/L	66 (1 min)	88 (90 min)	3.76/3.02
HA = 10 mg/L	67 (1 min)	86 (90 min)	3.87/3.13

effectiveness of TCE degradation (Abdelraheem et al. 2015).

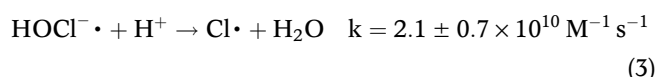
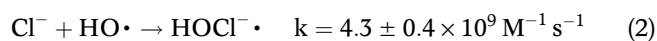
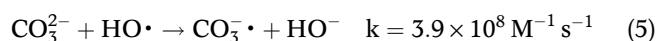
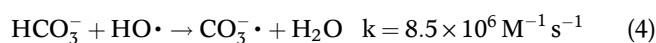


Figure 4(b) shows the influence of HCO_3^- on TCE degradation. The increase of HCO_3^- concentrations from 0 to 1.0, 10, and 100 mM led to decreases in TCE degradation from 70% to 65%, 48%, and 14% within 1 min, and from 98% to 75%, 59% and 28% in 90 min, respectively. The presence of HCO_3^- elevated solution pH from 3.1 to 4.0, 6.6, and 7.8 respectively in the presence of 1.0, 10 and 100 mM HCO_3^- . In addition, TCE degradation performance in the SPC/Fe(II)/CA system under various pH values is shown in Table 3. The solutions varying from pH 6.0 to pH 8.0 were phosphate (0.1 M) buffered, except at pH 3.0 and 11.0, which were adjusted with 0.1 M sulfuric acid and sodium hydroxide. The results indicated that TCE degradation in the SPC/Fe(II)/CA system was pH-dependent. High pH

inhibited the generation of $\text{HO}\cdot$ and promoted the precipitation of iron, both of which are adverse to TCE degradation. However, it should be noted that the best result was obtained in the pH-unadjusted test, possibly because the reaction in the unadjusted process was accompanied with the drop of solution pH, and the adjusted solution prevented the decrease in solution pH, and hence limited TCE degradation. Moreover, HCO_3^- could also perform as a scavenger of $\text{HO}\cdot$, as shown in Equations (4) and (5) (Liao et al. 2001). HCO_3^- converted to CO_3^{2-} , which had a higher reactivity with $\text{HO}\cdot$ in high pH, and therefore the scavenging effect was enhanced.



HA was used as a model to investigate the influence of NOM on TCE degradation. As shown in Figure 4(c), the increase of HA concentrations from 0 to 1.0, 5.0 and 10 mg/L led to the decrease in TCE degradation from 70% to 68%, 66%, and 67% in 1 min, and from 98% to 86%, 88% and 86% in 90 min, respectively. It suggested that HA concentrations of 1.0, 5.0 and 10 mg/L had minimal impact on TCE degradation. Wang & Lemley (2004) studied the effect of HA on alachlor degradation by an anodic Fenton process, and the results indicated that the competition of HA with alachlor for $\text{HO}\cdot$ slowed down the rate of alachlor degradation significantly. Thus the negative effect of high HA concentration should not be neglected in the application of the SPC/Fe(II)/CA system to actual groundwater remediation. In one word, Cl^- , HCO_3^- , and HA could all quench the radical species in the SPC/Fe(II)/CA system, and prohibit TCE degradation. Antoniou & Andersen (2015) also found that the presence of Cl^- , HCO_3^- , and HA at concentrations relevant to a well-water sample showed the negative effect in a UVC/ H_2O_2 system.

Free radicals generated in SPC/Fe(II)/CA system

Identification of radicals with chemical probes

As the traditional Fenton process could generate lots of reactive oxygen species ($\text{HO}\cdot$, $\text{O}_2\cdot^-$ and so on) (Watts et al. 2005),

and SPC has the similar function with a Fenton reagent, it is expected that these reactive oxygen species may also exist similarly in the SPC/Fe(II)/CA system. Based on our previous research, nitrobenzene and carbon tetrachloride were using as a chemical probe for assessing HO• and O₂^{-•}, respectively (Miao *et al.* 2015), and the initial concentrations of both nitrobenzene and carbon tetrachloride were kept at 0.15 mM.

As shown in Figure 5, a control test with only initial nitrobenzene and carbon tetrachloride concentration of 0.15 mM in aqueous solution in 90 min showed less than 3% loss of nitrobenzene and carbon tetrachloride, suggesting that

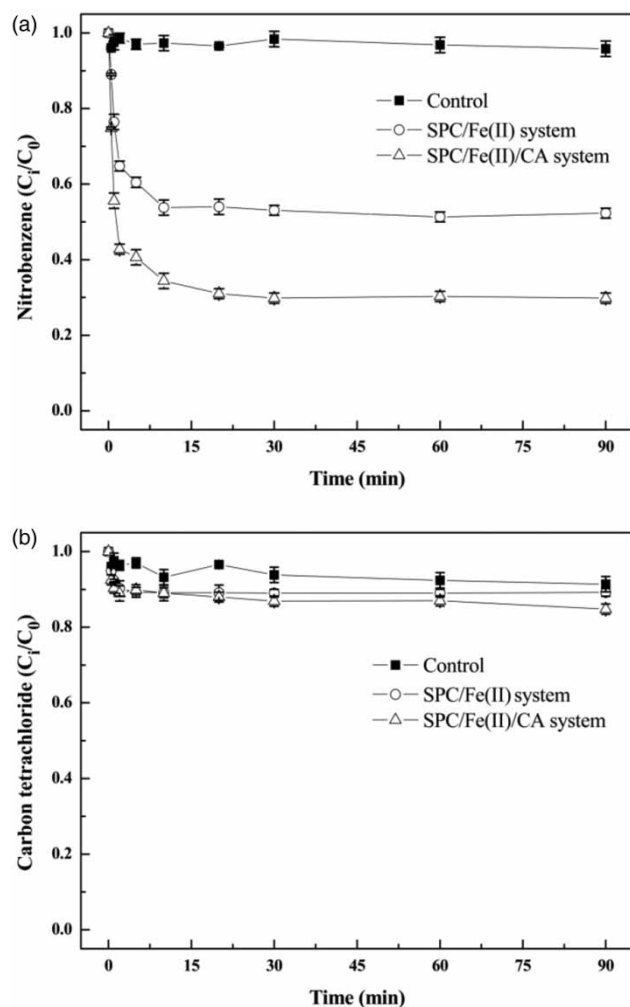


Figure 5 | Degradation of probe compounds in SPC/Fe(II) and SPC/Fe(II)/CA systems: (a) nitrobenzene; (b) carbon tetrachloride (CA = 0.5 mM, initial TCE concentration = 0.15 mM, SPC = 0.75 mM, FeSO₄·7H₂O = 0.45 mM, SPC/Fe(II)/TCE = 5/3/1).

volatilization of nitrobenzene and carbon tetrachloride during the test period could be ignored. Figure 5(a) shows that approximately 58.2% and 70.1% declines in nitrobenzene concentration were observed in the SPC/Fe(II) and SPC/Fe(II)/CA systems, respectively, demonstrating the generation of HO• in both systems. However only 5.3% and 6.5% removals of carbon tetrachloride were observed within 90 min in the SPC/Fe(II) and SPC/Fe(II)/CA systems, respectively, suggesting that reductants (O₂^{-•} or other solvated electrons) were present with a similar intensity in the SPC/Fe(II) and SPC/Fe(II)/CA systems and CA did not promote the generation of reductants. Similar results were obtained in modified Fenton systems when more than 0.1 M of H₂O₂ was introduced, in which O₂^{-•} was confirmed to be the species responsible for CT transformation (Smith *et al.* 2004). This is ascribed to the addition of CA in our study not changing the solvation sphere in the SPC/Fe(II)/CA system, which has been proven to be the main reason why O₂^{-•} plays a role of reduction in modified Fenton systems (Smith *et al.* 2004).

Free-radical scavenging tests

Based on the results of the probe tests, free-radical scavenging tests were conducted to elucidate the role of HO• and O₂^{-•} in TCE degradation. Experiments were conducted independently with the addition of different free-radical scavengers. Tert-butyl alcohol was an effective scavenger for HO• due to the rate constant between tert-butyl alcohol and HO• ($k = 5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Sun *et al.* 2013). And 1,4-benzoquinone could scavenge O₂^{-•} effectively ($k = 9.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) through rapid transference of electrons and generation of benzoquinone radicals (Haag & Yao 1992).

The control tests were also conducted in parallel without the scavenger. As shown in Figure 6(a), a significant reduction in TCE degradation was observed in the SPC/Fe(II)/CA system amended with the addition of tert-butyl alcohol. In the absence of tert-butyl alcohol, TCE degradation was 90.1% in 90 min. With the addition of 10 and 20 mM tert-butyl alcohol, TCE degradation decreased greatly to 15.9% and 5.7%, respectively. As the concentration of tert-butyl alcohol was much higher than that of TCE, HO• generated in the system was scavenged by tert-butyl alcohol effectively. The decline in TCE degradation

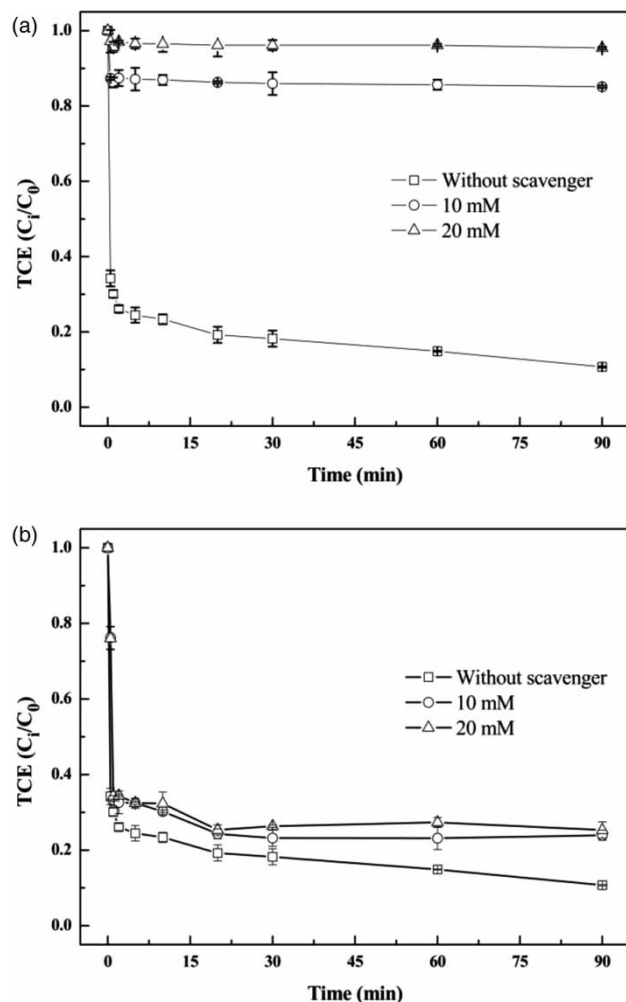


Figure 6 | Effect of radical scavengers on TCE degradation in the SPC/Fe(II)/CA system: (a) tert-butyl alcohol; (b) 1,4-benzoquinone (CA = 0.5 mM, initial TCE concentration = 0.15 mM, SPC/Fe(II)/TCE = 5/3/1).

elucidated that TCE degradation was caused predominantly by the strong oxidation activity of $\text{HO}\cdot$, and $\text{HO}\cdot$ was identified as the dominant radical responsible for TCE degradation in the SPC/Fe(II)/CA system.

TCE degradation in the SPC/Fe(II)/CA system in the presence of 1,4-benzoquinone is shown in Figure 6(b). As can be seen, the degradation of TCE decreased from 90.1% to 76.9% and 74.7% respectively with the addition of 10 and 20 mM 1,4-benzoquinone. The scavenging effect of 1,4-benzoquinone demonstrated the presence of $\text{O}_2\cdot^-$ in the SPC/Fe(II)/CA system and its contribution to the degradation of TCE. Thus it can be concluded that $\text{HO}\cdot$ was mainly responsible for TCE degradation in the SPC/Fe(II)/CA

system. In the traditional Fenton process, the main principle in Fenton's reaction owes to the Fe(II)-catalyzed decomposition of H_2O_2 in producing $\text{HO}\cdot$ (Walling 1975).

CONCLUSIONS

This study investigated TCE degradation performance using chelated Fe(II)-activated SPC in the presence of CA in aqueous solution. The experimental results showed that the presence of CA promoted H_2O_2 generation in solution, resulting in significant improvement in TCE degradation. The presence of Cl^- and HCO_3^- has an inhibitive effect on TCE oxidation, and HA has a negative effect on TCE degradation only at relatively high concentration. The initial solution pH appeared to be not negligible for TCE degradation. The generation of $\text{HO}\cdot$ and $\text{O}_2\cdot^-$ in the SPC/Fe(II)/CA system was confirmed with chemical probes. Meanwhile, free-radical scavenging tests verified that $\text{HO}\cdot$ was the dominant radical that contributed to TCE degradation and $\text{O}_2\cdot^-$ promoted TCE degradation by participating in $\text{HO}\cdot$ generation. In summary, the findings in this study strongly support the prospect of using CA to enhance Fe(II)-activated SPC *in situ* for remediation of TCE-contaminated groundwater.

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REFERENCES

- Abdelraheem, W. H. M., He, X., Duan, X. & Dionysiou, D. D. 2015 Degradation and mineralization of organic UV absorber compound 2-phenylbenzimidazole-5-sulfonic acid (PBSA) using UV-254 nm/ H_2O_2 . *Journal of Hazardous Materials* **282**, 233–240.
- Ahmad, M., Teel, A. L., Furman, O. S., Reed, J. I. & Watts, R. J. 2012 Oxidative and reductive pathways in iron-ethylenediaminetetraacetic acid-activated persulfate

- systems. *Journal of Environmental Engineering* **138** (4), 411–412.
- Ahn, S., Peterson, T. D., Righter, J., Miles, D. M. & Tratnyek, P. T. 2013 Disinfection of ballast water with iron activated persulfate. *Environmental Science and Technology* **47** (20), 11717–11725.
- Antoniou, M. G. & Andersen, H. R. 2015 Comparison of UVC/ $S_2O_8^{2-}$ with UVC/ H_2O_2 in terms of efficiency and cost for the removal of micropollutants from groundwater. *Chemosphere* **119**, 81–88.
- Chang, Y. Y., Roh, H. & Yang, J. K. 2013 Improving the clean-up efficiency of field soil contaminated with diesel oil by the application of stabilizers. *Environmental Technology* **34** (11), 1481–1487.
- de la Calle, R. G., Gimeno, O. & Rivas, J. 2012 Percarbonate as a hydrogen peroxide carrier in soil remediation processes. *Environmental Engineering Science* **29** (10), 951–955.
- Duesterberg, C. K. & Waite, T. D. 2006 Process optimization of Fenton oxidation using kinetic modeling. *Environmental Science and Technology* **40**, 4189–4195.
- Gu, X., Lu, S., Li, L., Qiu, Z., Sui, Q., Lin, K. & Luo, Q. 2011 Oxidation of 1,1,1-trichloroethane stimulated by thermally activated persulfate. *Industrial and Engineering Chemistry Research* **50** (19), 11029–11036.
- Haag, W. R. & Yao, C. C. D. 1992 Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science and Technology* **26** (5), 1005–1013.
- Jho, E. H., Singhal, N. & Turner, S. 2010 Fenton degradation of tetrachloroethene and hexachloroethane in Fe(II) catalyzed systems. *Journal of Hazardous Materials* **184** (1–3), 234–240.
- Kabalka, G. W., Wadgaonkar, P. P. & Shoup, T. M. 1989 Sodium percarbonate: a convenient reagent for efficiently oxidizing organoboranes. *Tetrahedron Letters* **30** (38), 5103–5104.
- Krembs, F. J., Siegrist, R. L., Crimi, M. L., Furrer, R. F. & Petri, B. G. 2010 ISCO For groundwater remediation: analysis of field applications and performance. *Groundwater Monitoring and Remediation* **30** (4), 42–53.
- Liao, C. H., Kang, S. F. & Wu, F. A. 2001 Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H_2O_2 /UV process. *Chemosphere* **44** (5), 1193–1200.
- Luca, D. A., Dantas, R. F. & Esplugas, S. 2014 Assessment of iron chelates efficiency for photo-Fenton at neutral pH. *Water Research* **61**, 232–242.
- Miao, Z., Gu, X., Lu, S., Zang, X., Wu, X., Xu, M., Ndong, L. B. B., Qiu, Z., Sui, Q. & Fu, G. Y. 2015 Perchloroethylene (PCE) oxidation by percarbonate in Fe^{2+} -catalyzed aqueous solution: PCE performance and its removal mechanism. *Chemosphere* **119**, 1120–1125.
- Pignatello, J. J. 1992 Dark and photoassisted Fe(III)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **26** (5), 944–951.
- Smith, B. A., Teel, A. L. & Watts, R. J. 2004 Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. *Environmental Science and Technology* **38** (20), 5465–5469.
- Sun, S. P., Zeng, X. & Lemley, A. T. 2013 Kinetics and mechanism of carbamazepine degradation by a modified Fenton-like reaction with ferric-nitritotriacetate complexes. *Journal of Hazardous Materials* **252–253**, 155–165.
- Tamura, H., Goto, K., Yotsuyanagi, T. & Nagayama, M. 1974 Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III). *Talanta* **21** (4), 314–318.
- US Environmental Protection Agency 2014 TSCA Work Plan Chemicals: Methods Document. http://www.epa.gov/sites/production/files/2015-01/documents/tscs_work_plan_chemicals_2014_update-final.pdf (accessed 21 August 2015).
- Vandevivere, P. C., Saveyn, H., Verstraete, W., Feijtel, T. C. J. & Schowanek, D. R. 2001 Biodegradation of metal-[S,S]-EDDS complexes. *Environmental Science and Technology* **35** (9), 1765–1770.
- Walling, C. 1975 Fenton's reagent revisited. *Accounts of Chemical Research* **8** (4), 125–131.
- Wang, Q. & Lemley, A. T. 2004 Kinetic effect of humic acid on alachlor degradation by anodic Fenton treatment. *Journal of Environmental Quality* **33** (6), 2343–2352.
- Watts, R. J., Howsawkung, J. & Teel, A. L. 2005 Destruction of a carbon tetrachloride dense nonaqueous phase liquid by modified Fenton's reagent. *Journal of Environmental Engineering* **131** (7), 1114–1119.
- Wu, Y. & Zhou, R. 2000 Application and development of sodium percarbonate. *Guangxi Journal of Light Industry* **2**, 8–10.
- Xue, X., Hanna, K., Despas, C., Wu, F. & Deng, N. 2009 Effect of chelating agent on the oxidation rate of PCP in the magnetite/ H_2O_2 system at neutral pH. *Journal of Molecular Catalysis A: Chemical* **311** (1–2), 29–35.
- Yuan, R., Ramjaun, S. N., Wang, Z. & Liu, J. 2011 Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: implications for formation of chlorinated aromatic compounds. *Journal of Hazardous Materials* **196** (1), 173–179.
- Zang, X., Gu, X., Lu, S., Qiu, Z., Sui, Q., Lin, K. & Du, X. 2014 Trichloroethylene oxidation performance in sodium percarbonate (SPC)/ Fe^{2+} system. *Environmental Technology* **35** (5–8), 791–798.
- Zhang, X., Gu, X., Lu, S., Miao, Z., Xu, M., Fu, X., Qiu, Z. & Sui, Q. 2015 Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion. *Journal of Hazardous Materials* **284**, 253–260.

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