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## Enhancement effects of chelating agents on the degradation of tetrachloroethene in Fe(III) catalyzed percarbonate system

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### Abstract

The performance of Fe(III)-based catalyzed sodium percarbonate (SPC) for stimulating the oxidation of tetrachloroethene (PCE) for groundwater remediation applications was investigated. The chelating agents citric acid monohydrate (CIT), oxalic acid (OA), and Glutamic acid (Glu) significantly enhanced the degradation of PCE. Conversely, ethylenediaminetetraacetic acid (EDTA) had a negative impact on PCE degradation, which may due to its strong Fe chelation and HO<sup>•</sup> scavenging abilities. However, excessive SPC or chelating agent will retard PCE degradation. In addition, investigations using free radical probe compounds and radical scavengers revealed that PCE was primarily degraded by HO<sup>•</sup> radical oxidation in both the chelated and non-chelated systems, while O<sub>2</sub><sup>•-</sup> also participated in the non-chelated system and the OA and Glu modified systems. According to the electron paramagnetic resonance (EPR) studies, the presence of HO<sup>•</sup> in the Fe(III)/SPC system was maintained much longer than that in the Fe(II)/SPC system. The results indicated that the addition of CIT, OA or Glu indeed enhanced the generation of HO<sup>•</sup> in the first 10 min and promoted degradation efficiency by increasing the amount of Fe(III) and maintaining the concentration of HO<sup>•</sup> radicals in solution. In conclusion, chelated Fe(III)-based catalyzed SPC oxidation is a promising method for the remediation of PCE-contaminated groundwater.

### Keywords

Tetrachloroethene (PCE); Sodium percarbonate (SPC); Chelating agents (CAs); Hydroxyl radical (HO<sup>•</sup>); Groundwater remediation

### 1. Introduction

Tetrachloroethene (PCE), one of the most widely used chlorinated solvents in dry cleaning, degreasing and electronics manufacturing, is one of the most common soil and groundwater contaminants due to unregulated usage and disposal in the past. The cytotoxicity and

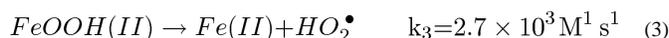
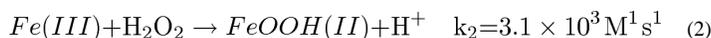
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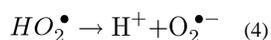
carcinogenicity of PCE in combination with its persistence in the subsurface environment imparts significant threats to public health and water resources. The United States Environmental Protection Agency (EPA) has classified PCE as a probable human carcinogen (Class B2). The maximum contaminant level of PCE has been set and regulated at  $5 \mu\text{g L}^{-1}$  under the Safe Drinking Water Act [1].

In past decades, various remediation technologies have been developed, involving individual units or combined physical, chemical and biological processes, such as air sparging [2], thermal treatment [3], enhanced-solubilization flushing [4], in situ bioremediation, and permeable reactive barriers (PRB) [5]. While each technology has met with success for certain applications, each of them has specific limitations. In situ chemical oxidation (ISCO) technologies are promising alternatives to accomplish high treatment efficiency with relatively low cost and over a relatively short time. ISCO involves the use of strong oxidants such as ozone [6], permanganate [7], Fenton's reagent [8], and activated persulfate [9, 10]. Of these, Fenton reagent and some modified Fenton systems have attracted significant attention due to their low environmental impacts, high reactivity and potential for the destruction of most organic contaminants. Generally, the traditional Fenton reaction employs aqueous Fe(II) to catalyze hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), leading to the production of hydroxyl radicals ( $\text{HO}^\bullet$ ) as shown in Eq. (1) [11].



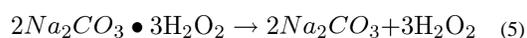
The  $\text{HO}^\bullet$  generated in the Fenton system is a strong and nonspecific oxidant with reactive rate constants commonly in the order of  $10^7$ - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [12]. Due to the high redox potential of  $\text{HO}^\bullet$  (2.76 V), it is capable of degrading a wide variety of organic compounds in groundwater. Since the reaction is catalyzed by Fe(II) ion in solution, maintaining acidic pH (pH = 2-4) [11] is of great importance for achieving optimum degradation rates. However, this may be difficult for field applications due to the buffering capacity of the natural environments. Furthermore, under less acidic or neutral conditions, the iron catalyst will precipitate as ferric hydroxide ( $\text{Fe(OH)}_3$ ) instead of generating the  $\text{HO}^\bullet$ , leading to the early termination of the Fenton reaction. To surmount this limitation and enhance contaminant removal efficiency under natural conditions, researchers have developed novel modifications of the classic Fenton process. One of the common modifications involves the use of Fe(III), instead of Fe(II) to catalyze the reactions with the generation of reactive oxygen species [13]. In the Fe(III)/ $\text{H}_2\text{O}_2$  system, the spontaneous reaction between  $\text{H}_2\text{O}_2$  and Fe(III) primarily forms Fe(III)-hydroperoxy complexes (Eq. 2) [14]. The Fe(III)-hydroperoxy complexes further decompose to Fe(II) (Eq. 3) [15] and then perhydroxyl radicals ( $\text{HO}_2^\bullet$ ) and superoxide anion radicals ( $\text{O}_2^{\bullet-}$ ) are generated (Eq. 4) [16].





According to Eqs. (1) and (2), in the Fe(III)/H<sub>2</sub>O<sub>2</sub> system, the H<sub>2</sub>O<sub>2</sub> decomposition is well controlled because the production of Fe(II) is slow, which reacts rapidly with H<sub>2</sub>O<sub>2</sub>. However, the low solubility of Fe(III) at neutral pH requires chelating agents to enhance the presence of Fe(III) in the aqueous phase. Soluble Fe(III) combined with metal chelating agents can minimize non-specific losses of soluble Fe catalyst. For example, ferric iron chelated with CIT, OA, or EDTA retains a catalytic ability to increase rates of hydroxyl radical generation at natural pH regimes (pH = 5-7) by avoiding the precipitation of iron [17].

Researchers are also engaged in finding alternative oxidants with similar oxidation capacity to hydrogen peroxide [18-20]. Sodium percarbonate (2Na<sub>2</sub>CO<sub>3</sub>•3H<sub>2</sub>O<sub>2</sub>, SPC) salt has been considered as a potential replacement for H<sub>2</sub>O<sub>2</sub> because it is much safer to handle and does not introduce any additional potentially harmful by-products into the water matrix [21-23]. SPC possesses similar function as liquid H<sub>2</sub>O<sub>2</sub>, as free H<sub>2</sub>O<sub>2</sub> is released into solution when percarbonate is mixed with water (Eq. 5) [21].



SPC has many advantages for use as an oxidant: (1) it is applicable in a wide pH range [24]; (2) it does not introduce any chemicals into the water matrix that would be considered toxic besides H<sub>2</sub>O<sub>2</sub>; (3) the end products of oxidation are usually carbon dioxide, water, and sodium carbonate, which occur naturally in groundwater, making it compatible with subsequent bioremediation; and (4) percarbonate acts as a base, raising the pH when introduced into water. This may lead to a buffering effect when SPC is used as an advanced oxidant in the system because the oxidation of contaminants always lowers the pH of the water matrix. Therefore Fe(III) catalyzed SPC oxidation has significant potential in the remediation of groundwater contaminated by chlorinated solvents.

So far, many studies focusing on the remediation of PCE-contaminated groundwater and soil have been documented [25-26]. However, most of these studies were conducted by applying Fenton-like processes. To the best of our knowledge, few studies to date have investigated Fe(III) catalyzed SPC oxidation of chlorinated-solvent compounds [22]. And the issue of Fe(III) stability in catalyzed SPC system has not been addressed. The objective of this study was to investigate the oxidative degradation of PCE by Fe(III)-catalyzed SPC. The effect of several chelating agents (CA), such as citric acid monohydrate (CIT), oxalic acid (OA), ethylenediaminetetraacetic acid (EDTA), and glutamic acid (Glu) on the reaction was examined. Reaction mechanisms were investigated by using free radical probe compounds and free radical scavengers to elucidate the dominant free radicals present. Electron paramagnetic resonance (EPR) was used to identify the main reactive oxygen species in PCE degradation.

## 2. Materials and methods

### 2.1. Materials

The following reagents were purchased from Aladdin (Shanghai, China) and used without further purification: tetrachloroethene (PCE,  $C_2Cl_4$ , >99.0%), carbon tetrachloride (CT,  $CCl_4$ , >99.5%), isopropyl alcohol ( $(CH_3)CHOH$ , >99.5%), nitrobenzene (NB,  $C_6H_5NO_2$ , >99.0%), chloroform ( $CHCl_3$ , >99.0%), ferric sulfate ( $Fe_2(SO_4)_3$ , >99.0%), hexane ( $C_6H_{14}$ , >97%), citric acid monohydrate (CIT,  $C_6H_8O_7 \cdot H_2O$ , >99.0%), oxalic acid (OA,  $C_2H_2O_4 \cdot 2H_2O$ , >99.0%), ethylenediaminetetraacetic acid (EDTA,  $C_{10}H_{16}N_2O_8$ , >99.0%), glutamic acid (Glu,  $C_5H_9NO_4$ , 99.0%). SPC ( $Na_2CO_3 \cdot 1.5H_2O$ , >98%) was purchased from Acros Organics (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Sigma (Shanghai, China). Ultrapure water from a Milli-Q water process (Classic DI, ELGA, Marlow, U.K.) was used for the preparation of aqueous solutions.

### 2.2. Experimental procedures

PCE stock solution was prepared by allowing the neat liquid PCE to equilibrate with Milli-Q water overnight under gentle stirring in the dark. The PCE stock solution was then diluted to the desired concentration (initial PCE concentration = 0.12 mM). Batch tests were conducted with a 250 mL cylindrical glass reactor. A magnetic stirrer was used to ensure uniform mixing of contaminants in the aqueous solution. The pre-determined amount of  $Fe_2(SO_4)_3$  and chelating agent was added to the PCE solution and thoroughly mixed, after which the pre-determined amount of SPC was added to start the reaction immediately. The initial solution pH in all experiments was unadjusted and the temperature was controlled at 20 °C. Control tests without Fe(III) and SPC were also conducted in parallel to examine the behavior of the contaminants in aqueous systems. Aqueous samples were collected at the desired time intervals (at 1, 3, 5, 10, 20, 30, 45, 60 min) and analyzed immediately, and the tests were conducted in duplicate and the mean values were reported.

The free radical scavengers, isopropyl alcohol and chloroform, were added before SPC. In the probe test, NB and CT stock solutions were prepared by dissolving pure NB and CT into Milli-Q water and stirring in the dark overnight. And then the stock solution was diluted to the desired concentration.

EPR analysis was conducted to confirm the main free radicals present in the reaction. This method entails using a radical trapping compound (DMPO) to trap the free radicals in solution to allow their measurement. Samples (1.0 mL) were collected at the desired time intervals and thoroughly mixed with 1.0 mL DMPO solution (8.84 mM) for 1 min. The mixed liquid was then transferred to a capillary tube with a microinjector for analysis by EPR.

### 2.3. 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. Aliquots of the extractant were transferred to a 2-mL GC vial. The concentrations of PCE and CT in hexane were analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with an electron

capture detector (ECD), an auto-sampler (Agilent 7693), and an DB-VRX column (60-m length, 250- $\mu\text{m}$  i.d., 1.4- $\mu\text{m}$  thickness). The temperatures of the injector and detector were 240 and 260 °C, respectively, and the oven temperature was kept constant at 120 °C. The amount of sample injected was 1.0  $\mu\text{L}$  with a split ratio of 40:1. The recovery of PCE through the above procedure was in the range of 87-95%. The concentration of NB was analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA) equipped with a flame ionization detector (FID), an auto-sampler (Agilent 7693), and an HP-5 column (30-m length, 320- $\mu\text{m}$  i.d., 0.25- $\mu\text{m}$  thickness). The temperatures of the injector and detector were 200 and 250 °C, respectively, and the oven temperature was constant at 170 °C. The amount of sample injected was 1.0  $\mu\text{L}$  with a split ratio of 1:1. The chloride anion was analyzed by ion chromatography (Dionex ICS-I000, Sunnyvale, CA). The free radicals were identified by EPR (EMX-8/2.7C, Bruker, Germany) using DMPO as a spin trap. All spectra were obtained under the following conditions: field sweep, 100 G; microwave frequency, 9.866 GHz; microwave power, 2.016 mW; modulation amplitude, 1 G; conversion time, 40.96 ms; time constant, 163.84 ms; receiver gain,  $3.17 \times 10^4$ ; and number of scans, 1. The solution pH was measured with a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

### 3. Results and discussion

#### 3.1. PCE degradation in the Fe(III)/SPC system

Fig. 1 presents the results of PCE degradation in the Fe(III)-catalyzed SPC system, where “ $C_i$ ” means the concentration of PCE at time “ $i$ ”. The results from the control tests in the absence of SPC showed less than 5% loss of PCE during the experimental period under all test conditions (see blank). The experiments were conducted at a fixed initial Fe(III)/SPC molar ratio of 1/1 based on our previous work. Fig. 1 shows that PCE could be effectively degraded for appropriate dosages of Fe(III) and SPC. For example, PCE was almost completely degraded after 60 min with 10 mM Fe(III) and SPC addition. Because the reaction rate of Eqs. (2-4) is much slower than that of Eq. (1), the PCE degradation rate in the Fe(III)/SPC system is much slower than in the Fe(II)/SPC system [24]. This requires the use of higher molar concentrations of catalyst (Fe) and SPC for the Fe(III)/SPC system.

To investigate the effects of Fe(III) and SPC concentrations on PCE (0.12 mM) degradation, a series of experiments were conducted using 1.0, 5.0, and 10.0 mM of Fe(III) and/or SPC (Fig. 2). The results showed that the degradation of PCE was enhanced when more Fe(III) was added. However, increasing the SPC concentration had a negative effect on the degradation of PCE. For example, when the concentration of Fe(III) was fixed at 5 mM, the final degradation decreased from 95.6% to 64.9% as the SPC concentration increased from 5 to 10 mM. This phenomenon is similar to the Fenton-like reaction. In Fenton-like reactions, it is generally accepted that when increasing Fe(II)/Fe(III) or  $\text{H}_2\text{O}_2$  concentration, the degradation rate of organic compounds also increases but only to a certain level, and further addition of Fe(II)/Fe(III) or  $\text{H}_2\text{O}_2$  becomes inefficient or possibly less effective [27]. This phenomenon is due primarily to the fact that excessive ferrous ion will generate large amounts of  $\text{HO}^\bullet$ , but  $\text{HO}^\bullet$  may also be scavenged by  $\text{HO}^\bullet$  itself (Eq. (6)). It has also been reported that a quenching reaction consuming  $\text{HO}^\bullet$  can occur in the Fenton system with high Fe(II) and/or  $\text{H}_2\text{O}_2$  concentration (Eqs. (7-8)). Khan and Watts [28] found that higher  $\text{H}_2\text{O}_2$

concentrations may favor scavenging hydroxyl radicals to form hydroperoxyl radicals in the goethite catalytic oxidation of PCE with initial concentrations of 0.15, 2.0, 5.0, 10, 20 and 30 mM H<sub>2</sub>O<sub>2</sub>.



Based on the above discussion, the fraction of HO<sup>•</sup> that reacts with PCE ( $f_{HO^{\bullet},PCE}$ ) can be expressed by Eq. (9) when considering the self reaction of HO<sup>•</sup> (Eq. (6)) compared with that proposed by Lee and Sedlak, which did not consider the self reaction of HO<sup>•</sup> [29]:

$$f_{HO^{\bullet},PCE} = \frac{k_{HO^{\bullet},PCE}[PCE]}{k_{HO^{\bullet},PCE}[PCE] + k_{HO^{\bullet},H_2O_2}[H_2O_2] + k_{HO^{\bullet},Fe(II)}[Fe(II)] + k_{HO^{\bullet},HO^{\bullet}}[HO^{\bullet}]} \quad (9)$$

According to Eq. (9), we can expect that an increase in H<sub>2</sub>O<sub>2</sub> concentration will lead to a decrease in  $f_{HO^{\bullet},PCE}$ , and consequently a decrease in the PCE degradation rate, which is consistent with the results shown in Fig. 2.

In addition, it should be noted that the degradation of PCE in the Fe(III)/SPC system is sustained for a longer time compared to the Fe(II)/SPC system, which may be an important advantage of the Fe(III)/SPC system. According to our previous study [24], the degradation of PCE in the Fe(II) system ended after approximately 5 min even though PCE was still present. However, a continuous degradation of PCE was observed in this study, which might be due to the persistent generation of the reactive oxygen species.

### 3.2. PCE degradation performance in chelated Fe(III)-based catalyzed system

The impact of four chelating agents, CIT, OA, EDTA, and Glu, was investigated for enhancing PCE degradation of the Fe(III)/SPC system. The experiments were conducted at both fixed initial Fe(III) and SPC concentration of 5 mM and with three levels of chelating agent concentrations (i.e. 1.0, 2.0 and 5.0 mM as illustrated in Fig. 3). The addition of CIT, OA, and Glu all increased the degradation of PCE, with the order of OA < Glu < CIT. For example, PCE degradation within the initial 20 min increased from approximately 74.6% in the Fe(III)/SPC system without CA to approximately 99.9%, 86.9% and 99.0% in 2.0 mM CIT, OA and Glu, respectively. This indicates that the addition of favorable chelating agents indeed enhanced the catalytic ability of the Fe(III)/SPC system for the degradation of PCE. The reason that chelating-agent addition enhances PCE degradation performance is associated with the increase in the stability of complexed Fe(III) in aqueous solution. The introduction of chelating agents to some extent prevented iron from precipitating and increased the concentration of soluble Fe(III) in solution, thus causing a continuous generation of Fe(II) and HO<sup>•</sup>. In addition, it also contributed to the decrease of solution pH (initial pH < 4, shown in Table 1), which is acknowledged as the optimal pH range of a

conventional Fenton reaction. In contrast to the other three chelating agents, the addition of EDTA caused a reduction in PCE degradation (Fig. 3c). This phenomenon may be due to multiple factors: First, since EDTA chelates strongly with Fe(III) ( $\log K_{\text{Fe(III)}} = 25.0$  [30]), EDTA may retard the Fe-catalyzed oxidation. This is consistent with the fact that the Fe-chelating ability ( $\log K_{\text{Fe(III)}}$ ) of EDTA is significantly greater than that of the other three CAs: Glu = 12.0 [31], CIT = 11.85 [32] and OA = 9.4 [32]. Second, the high reaction rate between EDTA and  $\text{HO}^\bullet$  ( $k_{\text{EDTA}/\text{HO}^\bullet} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at pH 4.0) [33] may lead to an ineffective loss of  $\text{HO}^\bullet$ . Third, EDTA can be partly oxidized by  $\text{H}_2\text{O}_2$  and  $\text{HO}^\bullet$ , which would reduce the concentration available for chelation [15].

According to Fig. 3a, the degradation efficiency of PCE increased and achieved almost complete degradation (>99.0%) after a 10-min reaction when the concentration of CIT was 1.0 mM. However, when the concentration of CIT was 5.0 mM, the degradation of PCE in 10 min decreased to approximately 60.2%, which was only slightly better than that achieved without CIT (56.0%, control curve). These results may be due to the effect of excessive chelating agents, which may inhibit the decomposition of organic compounds by scavenging the  $\text{HO}^\bullet$  rapidly ( $k_{\text{CIT}/\text{HO}^\bullet} = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at pH 6.6) [33]. Even though there was no inhibitive effect observed in OA and Glu modified Fe(III)/SPC systems, we speculate that it may happen at higher OA and Glu concentration because of their relatively high reaction rate with  $\text{HO}^\bullet$ . The reaction rate of the hydroxyl radical with OA is  $k_{\text{OA}/\text{HO}^\bullet} = 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [33] and the free glutamate would also react with  $\text{HO}^\bullet$  at a high reaction rate constant of  $k = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [34]. Experiments with 20 mM of OA or Glu addition were carried out to confirm the effect of excessive OA or Glu on PCE degradation. The results indicated that PCE degradation were indeed hindered by excessive OA or Glu (Fig. 3b and d) with a remarkable decrease of the PCE degradation rate (Table 3).

By assuming that  $\text{HO}^\bullet$  concentration is constant during the reaction, the kinetics of PCE degradation in the aqueous phase can be described by the pseudo-first-order reaction kinetics [33]:

$$-\frac{d[\text{PCE}]}{dt} = k[\text{PCE}] \quad (10)$$

It can be deduced to

$$\ln \frac{C_t}{C_0} = -kt \quad (11)$$

where  $C_t$  and  $C_0$  are the concentrations of PCE ( $\text{mg L}^{-1}$ ) at time  $t$  and time zero, respectively, and  $k$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ).

PCE degradation was well described by the pseudo-first-order kinetic model. The rate constants and linear correlation coefficients are summarized in Table 2 and Table 3.

### 3.3. Identification of free radicals using free radical probe tests

It is widely accepted that there are various reactive oxygen species generated in conventional or modified Fenton systems. For example,  $\text{HO}^\bullet$  has been recognized as the

most active free radical in the conventional Fenton system. However, in the modified Fenton system, the generation of other reactive oxygen species, such as  $O_2^{\bullet-}$ ,  $HO_2^{\bullet}$  and hydroperoxide anion ( $HO_2^-$ ), have also been observed in high  $H_2O_2$  concentration conditions [4, 35].  $O_2^{\bullet-}$  is a weak reductant that reacts with CT at a rate constant of  $3800 M^{-1} s^{-1}$  in dimethyl sulfoxide and it is documented that  $O_2^{\bullet-}$  can reduce CT in Fenton-like systems [36]. Our previous study has demonstrated the presence of  $O_2^{\bullet-}$  in CIT and OA modified Fe(II)/SPC systems [37]. Therefore, it is quite possible that the oxidation and reduction reactions contributing to the degradation of contaminants may simultaneously occur in the Fe(III)/SPC or CAs modified Fe(III)/SPC systems. Therefore, experiments were conducted to identify the yields of  $HO^{\bullet}$  and  $O_2^{\bullet-}$  using the chemical probe method.

The probe compounds were selected according to their reactivity with each of the reactive oxygen species potentially present in the chelated Fe(III)-catalyzed SPC system. Nitrobenzene (NB) was selected to characterize the presence of  $HO^{\bullet}$  because it reacts rapidly with  $HO^{\bullet}$  ( $k_{HO^{\bullet}}=3.9 \times 10^9 M^{-1} s^{-1}$ ) [38]. CT was selected as a probe for  $O_2^{\bullet-}$  because it possesses high reactivity with reductants ( $k_e = 1.6 \times 10^{10} M^{-1} s^{-1}$ ) [36, 38], but has negligible reactivity with  $HO^{\bullet}$  ( $k_{OH^{\bullet}} < 2 \times 10^6 M^{-1} s^{-1}$ ) [38]. The initial concentrations of NB and CT were kept at 2.0 and 0.05 mM, respectively, and the initial concentrations of SPC and Fe(III) were both maintained at 5 mM. The generation of  $HO^{\bullet}$  in SPC systems with 5.0 mM of CAs added, quantified through NB degradation, is shown in Fig. 4a, where " $C_i$ " means the concentration of NB at time " $i$ ". The results indicate that  $HO^{\bullet}$  was present in the Fe(III)/SPC system, regardless of the presence of chelating agent, which led to an apparent degradation of NB. The degradation of NB was significantly greater in the CIT, OA, and Glu modified systems according to the increased NB degradation rates, i.e., approximately 26.7%, 66.1%, 53.3% and 39.5% degraded in 60 min in the Fe(III)/SPC (no-CA), and CIT, OA and Glu modified systems, respectively, further indicating that the intensity of  $HO^{\bullet}$  in the presence of CIT or OA was much higher than that in the non-chelated system. In contrast, a lower degradation rate was observed (14.9% degraded in 60 min) in the EDTA added system, which was consistent to the PCE degradation performance. It should be noted that the NB degradation was delayed after the reactions started in all systems except the CIT one, which was because of the slow Fe(III) reduction reaction and slow production rates of  $HO^{\bullet}$  in Fe(III)/SPC systems. However, this phenomenon was not observed in PCE degradation, probably because PCE is more liable to be oxidized by  $HO^{\bullet}$  than NB or other non-  $HO^{\bullet}$  degradation mechanisms are present in the system.

The generation of  $O_2^{\bullet-}$  in 5.0 mM of CAs modified Fe(III)/SPC systems was quantified by CT degradation, as shown in Fig. 4b, where " $C_i$ " means the concentration of CT at time " $i$ ". A slight CT degradation was also observed in the tested systems, suggesting that  $O_2^{\bullet-}$  was present in these systems.

Based on the results discussed above, it is deduced that both  $HO^{\bullet}$  and  $O_2^{\bullet-}$  were present in the Fe(III)/SPC and CAs modified systems. Similar results were obtained in modified Fenton systems when more than 0.1 M of  $H_2O_2$  was introduced [35], in which  $O_2^{\bullet-}$  was confirmed to be the species responsible for CT transformation, but have not been reported for the catalyzed SPC systems. These observations are, to some extent, in agreement with the EPR results, which are discussed in Section 3.5.

### 3.4. Elucidation of the role of free radicals using free radical scavengers

Theoretically, PCE can be degraded by both  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$  [39], but the degradation rate by  $\text{HO}^\bullet$  ( $k_{\text{HO}^\bullet} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is significantly faster than that by  $\text{O}_2^{\bullet-}$  ( $k = 15.0 \pm 4.5 \text{ M}^{-1} \text{ s}^{-1}$  in dimethyl formamide). To elucidate the role of  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$  in the Fe(III)/SPC and CAs modified Fe(III)/SPC systems, experiments were conducted independently with the addition of different free radical scavengers. Isopropanol was used to scavenge  $\text{HO}^\bullet$  because it reacts rapidly with oxidants ( $k_{\text{HO}^\bullet} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and slowly with reductants ( $k_e = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) [36]. Chloroform was used as the  $\text{O}_2^{\bullet-}$  scavenger because chloroform possesses relatively weak reactivity with  $\text{HO}^\bullet$  ( $k_{\text{HO}^\bullet} = 7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) and high reactivity with reductants ( $k_e = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) [24]. Isopropanol and chloroform were added to the solution at 50 and 2.0 mM respectively. Control tests without a scavenger were also conducted. The results are shown in Fig. 5. PCE degradation in the initial 10 min were 56.0%, 99.9%, 75.2%, 34.3% and 85.2% in the no-CA and CIT, OA, EDTA and Glu modified systems, respectively. In contrast, PCE degradation was significantly inhibited in the presence of isopropanol, decreased to 10.6%, 5.7%, 7.1%, 8.8% and 5.4% in the initial 10 min for the no-CA, CIT, OA, EDTA, and Glu modified systems, respectively. These results indicate that  $\text{HO}^\bullet$  was dominant in these systems, but other non- $\text{HO}^\bullet$  mechanisms which cause PCE degradation were also active.

PCE degradation in the presence of excess chloroform is also shown in Fig. 5. In the CIT modified system, PCE was almost completely degraded in 10 min even with the addition of chloroform. These and the prior results confirm that  $\text{O}_2^{\bullet-}$  is not involved in PCE degradation in the CIT system and that degradation was primarily caused by  $\text{HO}^\bullet$  oxidation. In contrast, in the presence of 2.0 mM chloroform, PCE degradation in the no-CA, OA, and Glu modified systems was slightly inhibited, with PCE degradation in 10 min decreased to 32.4%, 42.6%, and 75.2%, respectively. These results indicate that  $\text{O}_2^{\bullet-}$  participated in the degradation of PCE in those systems.

### 3.5. Detection of free radicals by EPR analysis

To confirm the presence of  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$ , we conducted EPR tests using DMPO as hydroxyl radical adduct. A DMPO hydroxyl radical adduct was observed with high intensity in the EPR spectra in all systems except the EDTA modified one (Fig. 6). This phenomenon is consistent with the observed PCE (Fig. 3c) and NB (Fig. 4a) degradation behavior in EDTA modified Fe(III)/SPC, where their degradation rates were the slowest among the investigated systems. This may be caused by production of  $\text{HO}^\bullet$  being too slow and  $\text{HO}^\bullet$  itself reacting with other species in the system too quickly, therefore, the intensity of  $\text{HO}^\bullet$  adduct (DMPO-OH) is too weak. The EPR spectrum (quartet lines with a peak height ratio of 1:2:2:1) were consistent with those reported for  $\text{HO}^\bullet$  in other studies [24]. However, the intensity of  $\text{HO}^\bullet$  in the Fe(III)-based system was much lower than that in the Fe(II)-based system because of the slow reaction rate of Eqs. (2-4) as discussed above. These results, together with the data shown in Figs. 4 and 5, indicate that  $\text{HO}^\bullet$  was the predominant oxidant in all the Fe(III)/SPC systems. It should be noted that the generation of  $\text{HO}^\bullet$  in the Fe(III)-based system can last much longer than that in the Fe(II)-based system (as shown in Fig. 7) [37]. The intensity of  $\text{HO}^\bullet$  was greater in the CIT, OA, and Glu modified systems than that in no-CA system. These results were, to some extent, consistent to the PCE

degradation performance as shown in Fig. 3. Unfortunately, the production of  $O_2^{\bullet-}$  was not confirmed during the EPR analyses, which could be attributed to the complicated solution composition and relatively weak intensity of  $O_2^{\bullet-}$  in these systems.

## 4. Conclusions

This study investigated PCE degradation performance using chelated Fe(III)-based catalyzed SPC oxidation. The experimental results demonstrated that PCE removal was significantly affected by the concentrations of Fe(III) and SPC, and PCE could be almost completely removed in 60 min with a concentration of 5.0 mM of Fe(III) and SPC. The addition of CIT, OA and Glu improved the PCE degradation remarkably by increasing the concentration of Fe(III) in solution and reducing the solution pH, which led to a continuous generation of  $HO^{\bullet}$ . The free radical probe tests and scavenging studies suggested that PCE was degraded primarily by  $HO^{\bullet}$  oxidation in all investigated systems, as confirmed by EPR detection. In addition,  $O_2^{\bullet-}$  radical reduction also participated in the degradation of PCE in the Fe(III)/SPC system and OA or Glu modified systems, but not in the CIT or EDTA modified systems. The generation of  $HO^{\bullet}$  in CIT or OA modified systems could last much longer than that in the Fe(II)/SPC system. In conclusion, chelated Fe(III)-based catalyzed SPC oxidation for PCE contaminated groundwater remediation shows great practical prospects with the advantages of persistent generation of  $HO^{\bullet}$  radicals, no requirement for pH adjustment, and general effectiveness.

## Acknowledgments

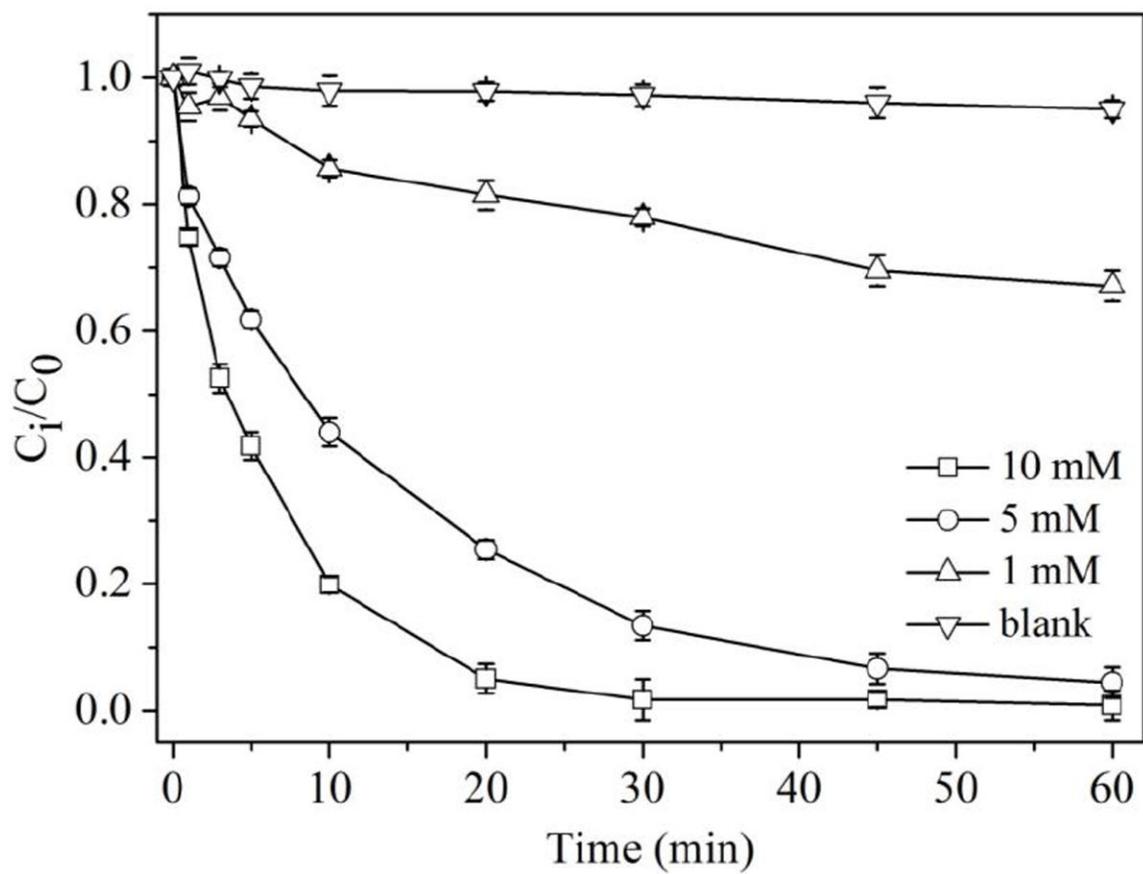
This study was financially supported by the grant from the National Natural Science Foundation of China (No. 41373094 and No.51208199), and the Fundamental Research Funds for the Central Universities. The contributions of Dr. Mark Brusseau were supported by the NIEHS Superfund Research Program (P42 ES ES04940).

## Literature Cited

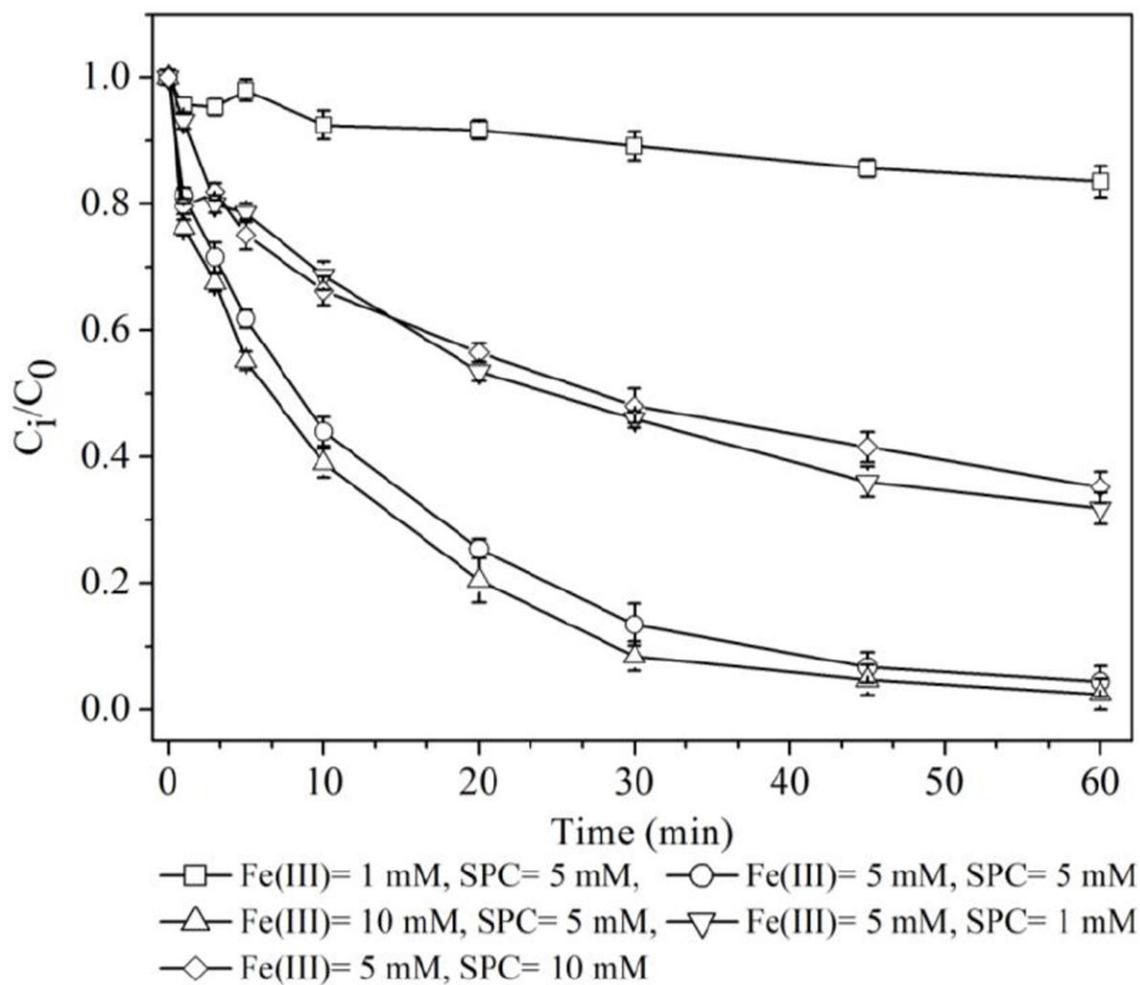
1. EPA. National Primary Drinking Water Regulations, EPA 816-F-09-004. 2009. available at: <http://www.epa.gov/safewater/consumer/pdf/mcl.pdf> (consulted 02.06.13)
2. Adams JA, Reddy KR, Tekola L. Remediation of chlorinated solvent plumes using in-situ air sparging-A 2-D laboratory study. *Int J Environ Res Public Health*. 2011; 8:2226–2239. [PubMed: 21776228]
3. Johnson, R.; Tratnyek, P.; Sleep, B.; Krol, M. Final report: In situ thermal remediation of DNAPL source zones, SERDP Project ER-1458. Department of Defense Strategic Environmental Research and Development Program (SERDP); 2011.
4. Watts RJ, Howsawkung J, Teel AL. Destruction of a carbon tetrachloride dense nonaqueous phase liquid by modified Fenton's reagent. *J Environ Eng*. 2005; 131:1114–1119.
5. Vogan JL, Focht RM, Clark DK, Graham SL. Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. *J Hazard Mater*. 1999; 68:97–108. [PubMed: 10518666]
6. Clancy PB. Treatment of chlorinated ethenes in groundwater with ozone and hydrogen peroxide. *Environ Prog*. 1996; 15:187–193.
7. Tsai TT, Kao CM, Yeh TY, Liang SH, Chien HY. Application of surfactant enhanced permanganate oxidation and bidegradation of trichloroethylene in groundwater. *J Hazard Mater*. 2009; 161:111–119. [PubMed: 18436375]
8. Che H, Bae S, Lee W. Degradation of trichloroethylene by Fenton reaction in pyrite suspension. *J Hazard Mater*. 2011; 185:1355–1361. [PubMed: 21071138]

9. Gu X, Lu S, Li L, Qiu Z, Sui Q, Lin K, Luo Q. Oxidation of 1,1,1-Trichloroethane Stimulated by Thermally Activated Persulfate. *Ind Eng Chem Res.* 2011; 50:11029–11036.
10. Gu X, Lu S, Qiu Z, Sui Q, Miao Z, Lin K, Liu Y, Luo Q. Comparison of photodegradation performance of 1,1,1-trichloroethane in aqueous solution with the addition of H<sub>2</sub>O<sub>2</sub> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidants. *Ind Eng Chem Res.* 2012; 51:7196–7204.
11. Yap CL, Gan S, Ng HK. Fenton based remediation of polycyclic aromatic hydrocarbons-contaminated soils. *Chemosphere.* 2011; 83:1414–1430. [PubMed: 21316731]
12. Siedlecka EM, Wieckowska A, Stepnowski P. Influence of inorganic ions on MTBE degradation by Fenton's reagent. *J Hazard Mater.* 2007; 147:497–502. [PubMed: 17383092]
13. Khan E, Wirojanagud W, Sermsai N. Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds. *J Hazard Mater.* 2009; 161:1024–1034. [PubMed: 18502575]
14. Jho, EunHea; Singhal, N.; Turner, S. Tetrachloroethylene and hexachloroethane degradation in Fe(III) and Fe(III)-citrate catalyzed Fenton systems. *J Chem Technol Biot.* 2012; 87:1179–1186.
15. Chen F, Li Y, Guo L, Zhang J. Strategies comparison of eliminating the passivation of non-aromatic intermediates in degradation of Orange II by Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>. *J Hazard Mater.* 2009; 169:711–718. [PubMed: 19414214]
16. Venny S, Gan HK, Ng. Inorganic chelated modified-Fenton treatment of polycyclic aromatic hydrocarbon (PAH)-contaminated soils. *Chem Eng J.* 2012; 180:1–8.
17. Pereira, JoãoHOS.; Queirós, DB.; Reis, AC.; Nunes, OC.; Borges, MT.; Boaventura, Rui AR.; Vilar, Vítor JP. Process enhancement at near neutral pH of a homogeneous photo-Fenton reaction using ferric-carboxylate complexes: Application to oxytetracycline degradation. *Chem Eng J.* 2014; 253:217–228.
18. Northup A, Cassidy D. Calcium peroxide (CaO<sub>2</sub>) for use in modified Fenton chemistry. *J Hazard Mater.* 2008; 152:1164–1170. [PubMed: 17804164]
19. Goi A, Viisimaa M, Trapido M, Munter R. Polychlorinated biphenyls-containing electrical insulating oil contaminated soil treatment with calcium and magnesium peroxides. *Chemosphere.* 2011; 82:1196–1201. [PubMed: 21146854]
20. Qian Y, Zhou X, Zhang Y, Zhang W, Chen J. Performance and properties of nanoscale calcium peroxide for toluene removal. *Chemosphere.* 2013; 91:717–723. [PubMed: 23466092]
21. Rivas FJ, Gimeno O, Borralho T, Carbajo M. UV-C radiation based methods for aqueous metoprolol elimination. *J Hazard Mater.* 2010; 179:357–362. [PubMed: 20347220]
22. de la Calle RG, Gimeno O, Rivas J. Percarbonate as a hydrogen peroxide carrier in soil remediation processes. *Environ Eng Sci.* 2012; 29:951–956.
23. Sindelar HR, Brown MT, Boyer TH. Evaluating UV/H<sub>2</sub>O<sub>2</sub>, UV/percarbonate, and UV/perborate for natural organic matter reduction from alternative water sources. *Chemosphere.* 2014; 105:112–118. [PubMed: 24405969]
24. Miao Z, Gu X, Lu S, Zang X, Wu X, Xu M, Bi Ndong LB, Qiu Z, Sui Q, Fu GY. Perchloroethylene (PCE) oxidation by percarbonate in Fe<sup>2+</sup>-catalyzed aqueous solution: PCE performance and its removal mechanism. *Chemosphere.* 2015; 119:1120–1125. [PubMed: 25460751]
25. Kang N, Hua I, Suresh P, Rao C. Enhanced Fentons destruction of non-aqueous phase perchloroethylene in soil systems. *Chemosphere.* 2006; 63:1685–1698. [PubMed: 16324735]
26. Wang X, Brusseau ML. Effect of pyrophosphate on the dechlorination of tetrachloroethene by the Fenton reaction. *Environ Toxicol Chem.* 1998; 17:1689–1694.
27. Wu Y, Zhou S, Qin F, Zheng K, Ye X. Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid. *J Hazard Mater.* 2010; 179:533–539. [PubMed: 20359821]
28. Khan AJ Md, Watts RJ. Mineral-catalyzed peroxidation of tetrachloroethylene. *Water Air Soil Poll.* 1996; 88:247–260.
29. Lee C, Sedlak DL. A novel homogeneous Fenton-like system with Fe(III)-phosphotungstate for oxidation of organic compounds at neutral pH values. *J Mol Catal A-Chem.* 2009; 311:1–6. [PubMed: 22267951]
30. Sillanpää MET, Kurniawan TA, Lo W. Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP). *Chemosphere.* 2011; 83:1443–1460. [PubMed: 21349569]

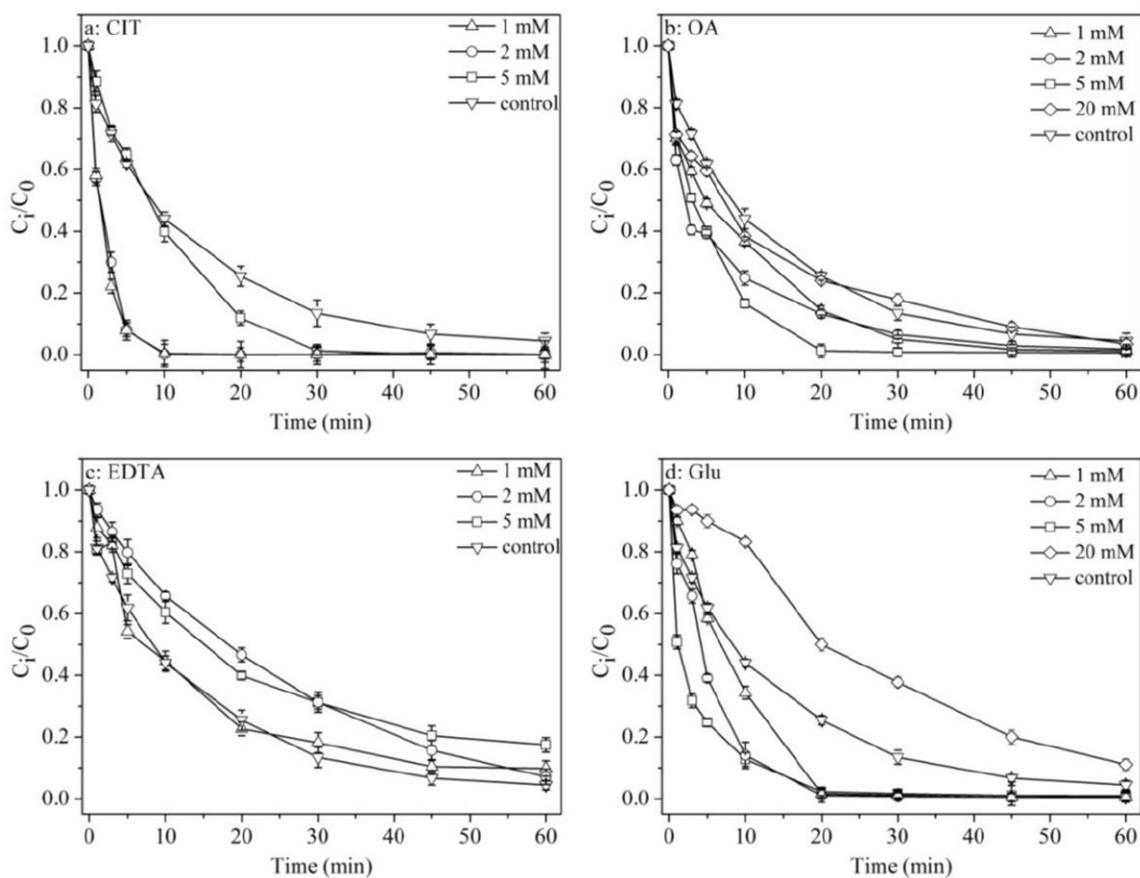
31. Djurdjevi P, Jeli R. Solution equilibria in L-glutamic acid and L-serine + iron(III) systems. *Transit Metal Chem.* 1997; 22:284–293.
32. Xu J, Xin L, Huang T, Chang K. Enhanced bioremediation of oil contaminated soil by graded modified Fenton oxidation. *J Environ Sci.* 2011; 23:1873–1879.
33. Xue X, Hanna K, Despas C, Wu F, Deng N. Effect of chelating agent on the oxidation rate of PCP in the magnetite/H<sub>2</sub>O<sub>2</sub> system at neutral pH. *J Mol Catal A-Chem.* 2009; 311:29–35.
34. ElShafei GMS, Yehia FZ, Dimitry OIH, Badawi AM, Eshaq Gh. Degradation of nitrobenzene at near neutral pH using Fe<sup>2+</sup>-glutamate complex as a homogeneous Fenton catalyst. *Appl Catal B-Environ.* 2010; 99:242–247.
35. Smith BA, Teel AL, Watts RJ. Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. *Environ Sci Technol.* 2004; 38:5465–5469. [PubMed: 15543752]
36. Teel AL, Watts RJ. Degradation of carbon tetrachloride by modified Fenton's reagent. *J Hazard Mater.* 2002; B94:179–189. [PubMed: 12169420]
37. Miao Z, Gu X, Lu S, Dionysiou DD, Al-Abed SR, Zang X, Wu X, Qiu Z, Sui Q, Danish M. Mechanism of PCE oxidation by percarbonate in a chelated Fe(II)-based catalyzed system. *Chem Eng J.* 2015; 275:53–62.
38. Watts, RJ. Final report: enhanced reactant-contaminant contact through the use of persulfate in situ chemical oxidation (ISCO), SERDP Project ER-1489. Department of Defense Strategic Environmental Research and Development Program (SERDP); 2011.
39. Watts RJ, Sarasa J, Loge FJ, Teel AL. Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions. *J Environ Eng.* 2005; 131:158–164.



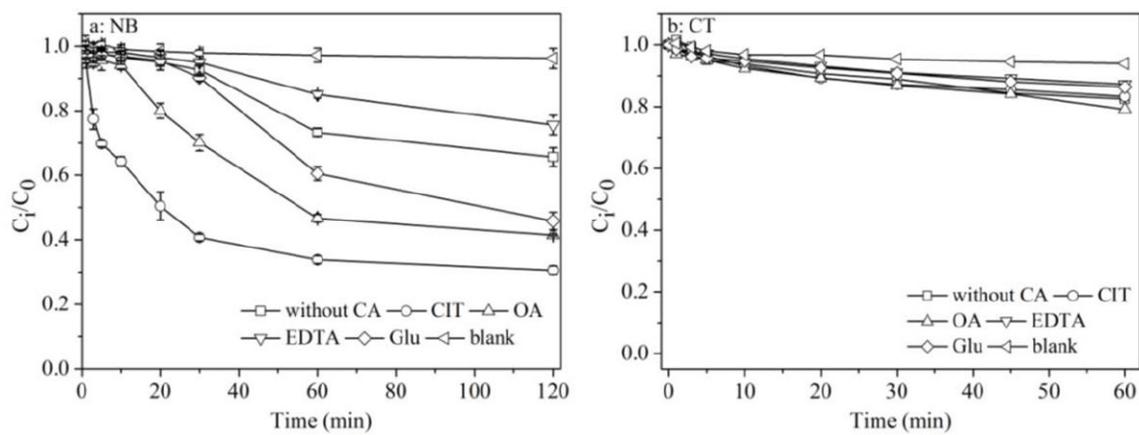
**Fig. 1.** PCE degradation for different Fe(III) and SPC concentrations at a fixed Fe(III)/SPC molar ratio of 1/1, [PCE] = 0.12 mM, [Fe(III)] = [SPC] = 0, 1, 5 and 10 mM



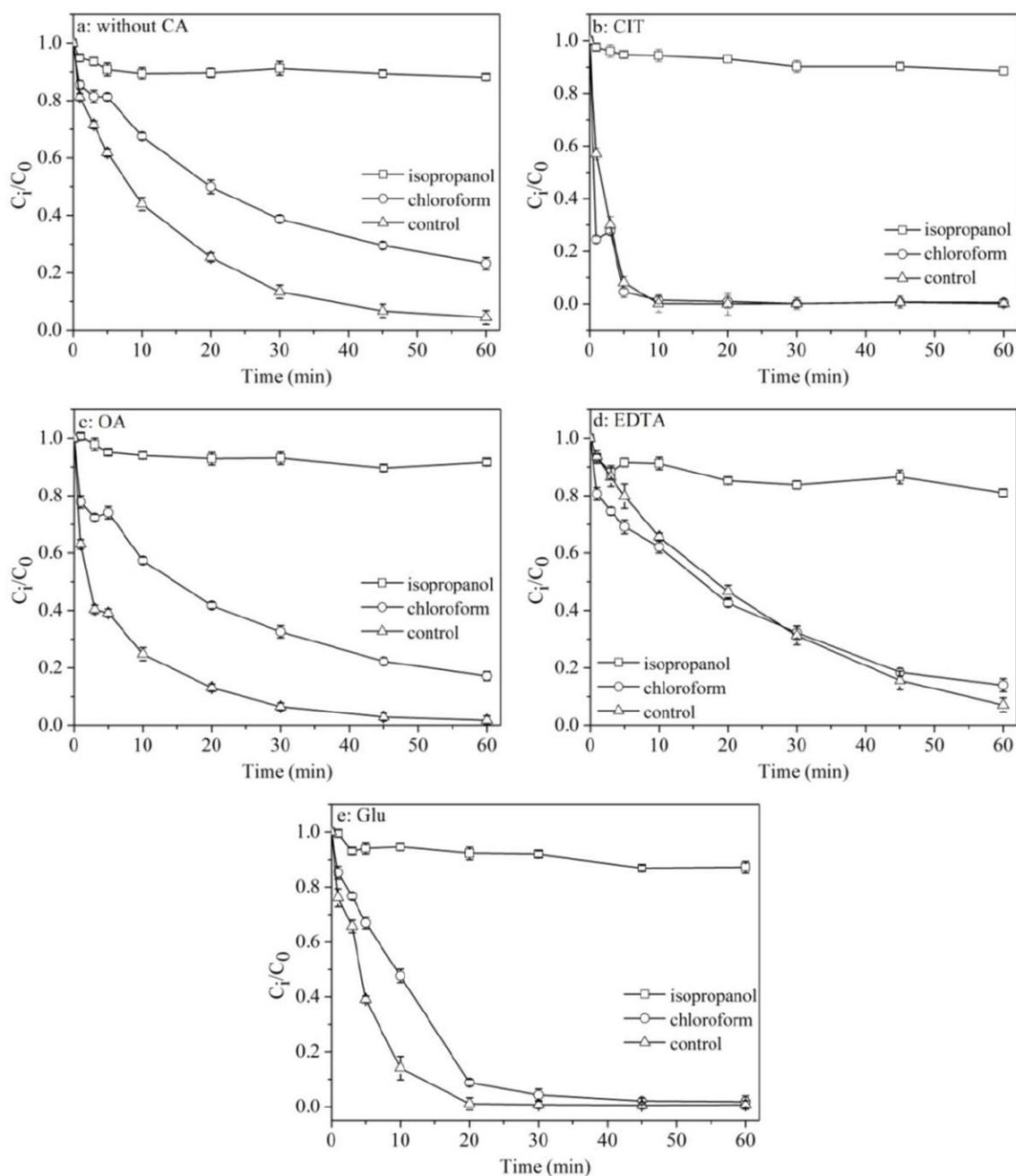
**Fig. 2.** Effect of various Fe(III) and SPC concentrations on PCE degradation in Fe(III)/SPC system, [PCE] = 0.12 mM, [Fe(III)] = 1, 5 and 10 mM, [SPC] = 1, 5 and 10 mM



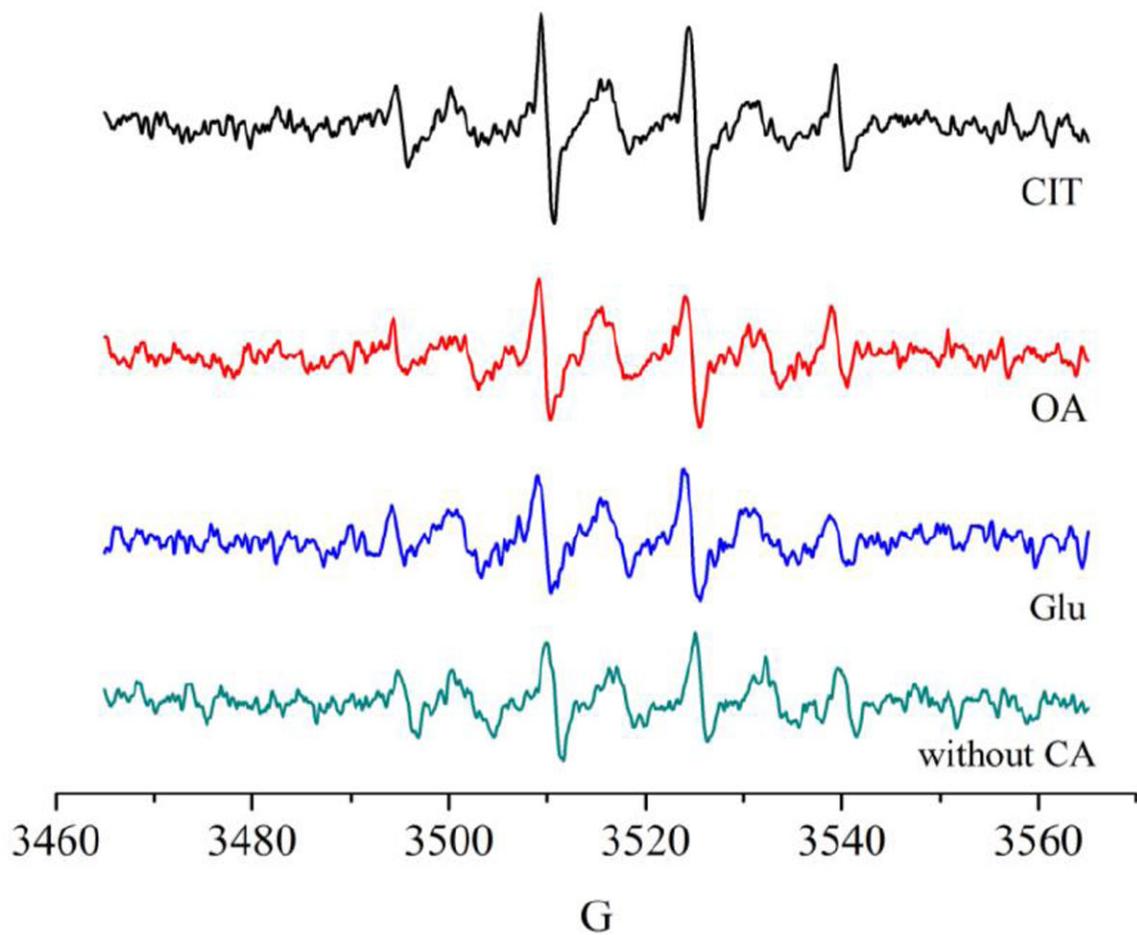
**Fig. 3.** Effect of chelating agent concentrations on PCE degradation in Fe(III)/SPC systems chelated by: (a) CIT, (b) OA, (c) EDTA, (d) Glu, [PCE] = 0.12 mM, [CA] = 0, 1, 2, 5 and 20 mM, [Fe(III)] = [SPC] = 5 mM



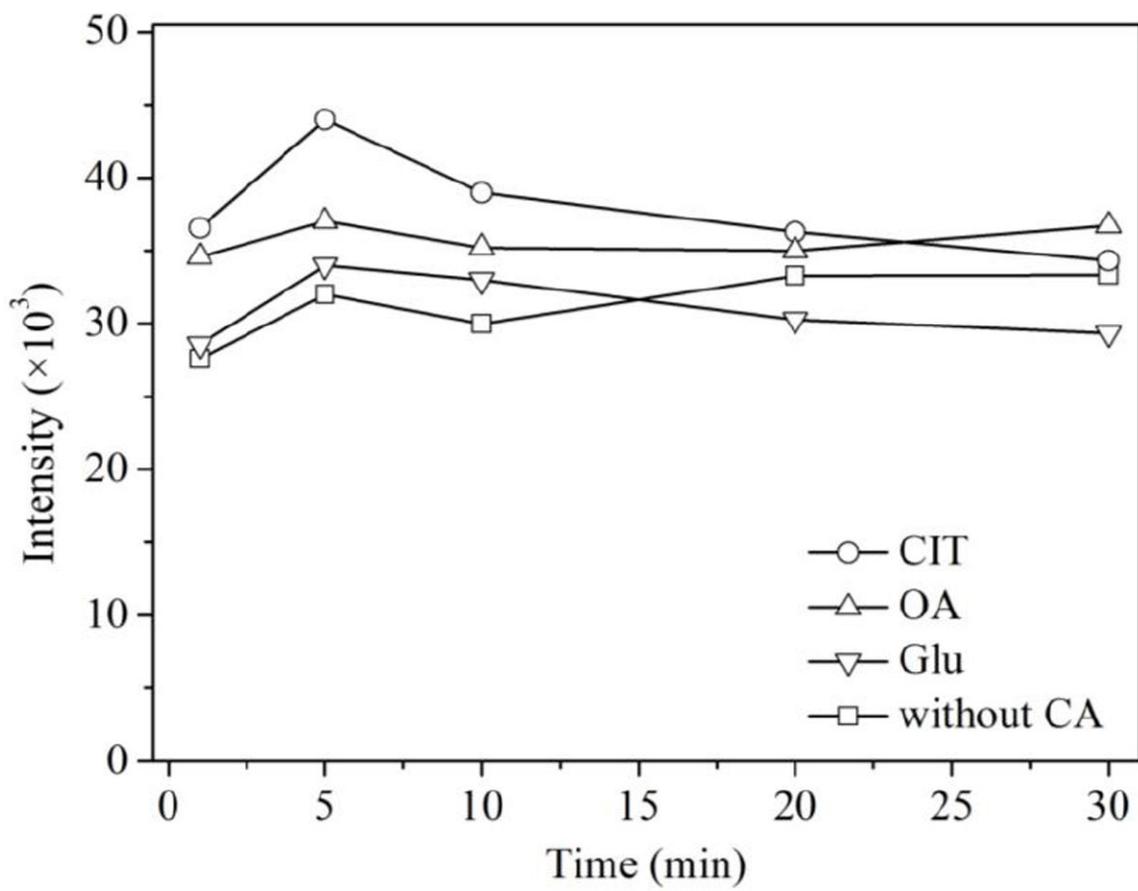
**Fig. 4.** Free radical probe test: a) NB, b) CT, [NB] = 2 mM, [CT] = 0.05 mM, [Fe(III)] = [SPC] = 5 mM



**Fig. 5.** Effect of isopropanol and chloroform on PCE degradation performance: Fe(III) = 5.0 mM, SPC = 5.0 mM, Isopropanol = 50 mM, Chloroform = 2.0 mM, (a) without CA (b) CIT = 2.0 mM, (c) OA = 2.0 mM, (d) EDTA = 2.0 mM, (e) Glu = 2.0 mM



**Fig. 6.**  
EPR spectra at the reaction time of 1 min in different systems



**Fig. 7.**  
HO• intensity versus reaction time in different systems: Fe(III) = 5.0 mM, SPC = 5.0 mM,  
CIT = 2.0 mM, OA = 2.0 mM, Glu = 2.0 mM

**Table 1**

The initial and final pH values under different CAs concentrations in the chelated Fe(III)/SPC systems

CA concentration	CIT initial/final pH	OA initial/final pH	EDTA initial/final pH	Glu initial/final pH
1 mM	2.33/2.68	2.54/2.61	2.53/2.60	2.52/2.68
2 mM	2.13/2.56	2.30/2.53	2.37/2.33	2.31/2.66
5 mM	2.05/2.16	2.13/2.34	2.22/2.24	2.28/2.46

Fe(III) and SPC = 5 mM

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**Table 2**

PCE degradation rate constants under different Fe(III) and SPC concentrations in the Fe(III)/SPC system

No.	Fe(III) (mM)	SPC (mM)	k (min <sup>-1</sup> )	R <sup>2</sup>
1	1	1	0.0082	0.9244
2	5	5	0.0635	0.9926
3	10	10	0.1332	0.9935
4	1	5	0.0027	0.9218
5	10	5	0.0618	0.9805
6	5	1	0.0188	0.9532
7	5	10	0.0157	0.9386

k: pseudo-first-order rate constant, min<sup>-1</sup>; R<sup>2</sup>: correlation coefficient

**Table 3**

PCE degradation rate constants under different CAs concentrations in the chelated Fe(III)/SPC systems

	CIT	OA	EDTA	Glu
CA concentration	k (min <sup>-1</sup> )/R <sup>2</sup>			
1 mM	0.5488/0.9978	0.0899/0.9943	0.0500/0.9518	0.2031/0.9404
2 mM	0.6502/0.9711	0.0733/0.9839	0.0425/0.9953	0.2261/0.9920
5 mM	0.1050/0.9930	0.2117/0.9876	0.0341/0.9815	0.1717/0.9706
20 mM	-	0.0511/0.9843	-	0.0368/0.9928

Fe(III) and SPC = 5 mM, k: pseudo-first-order rate constant, min<sup>-1</sup>; R<sup>2</sup>: correlation coefficient