Published in final edited form as:

J Hazard Mater. 2019 April 15; 368: 506–513. doi:10.1016/j.jhazmat.2019.01.057.

Enhanced redox degradation of chlorinated hydrocarbons by the Fe(II)-catalyzed calcium peroxide system in the presence of formic acid and citric acid

Wenchao Jiang^{a,b}, Ping Tang^a, Shuguang Lyu^{a,b,*}, Mark L. Brusseau^c, Yunfei Xue^a, Xiang Zhang^d, Zhaofu Qiu^a, Qian Sui^{a,b,*}

^aState Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China

^bShanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

^cSoil, Water and Environmental Science Department, School of Earth and Environmental Sciences, The University of Arizona, Tucson, AZ 85721, United States

^dShanghai Municipal Engineering Design Institute (Group) Co., Ltd, Shanghai 200092, China

Abstract

Two carboxylic acids (formic acid (FA) and citric acid (CIT)) enhanced the Fenton process using Fe(II)-activated calcium peroxide (CP) to develop a hydroxyl radical (HO•) and carbon dioxide radical (CO₂•⁻) coexistence process for the simultaneous redox-based degradation of three chlorinated hydrocarbons (CHs), namely carbon tetrachloride (CT), tetrachloroethene (PCE), and trichloroethene (TCE), was investigated. The experimental results showed that CT removal was increased while PCE and TCE degradation were decreased with the addition of FA to the Fe(II)/CP system. However, addition of CIT to the Fe(II)/CP/FA system enhanced the removal efficiency of all three contaminants. For example, 81.7%, 79.4%, and 96.1% of CT, PCE, and TCE, respectively, were removed simultaneously under the optimal molar ratio of 12/12/12/12/1 of CIT/CP/Fe(II)/FA/CHs. Investigations of the degradation mechanism confirmed the specific roles of HO• and the secondarily generated CO₂•⁻ radical, i.e., PCE and TCE were degraded oxidatively by HO• while CT was degraded via reductive dechlorination by CO₂•⁻. Carbonate reduced PCE and TCE degradation in actual groundwater as it consumed reactive oxygen species, whereas humic acid and neutral pH had minimal impact on contaminant removal. These results can help us better understand the synergistic effects of different carboxylic acids in the modified Fenton process for the redox-based degradation of refractory chlorinated hydrocarbons.

Keywords

Calcium peroxide; Formic acid; Citric acid; Selective redox degradation; Groundwater remediation; advanced oxidation process

*Corresponding author: Tel: +86 21 64250709, Fax: +86 21 64252737, lvshuguang@ecust.edu.cn (S. Lyu), suiqian@ecust.edu.cn (Q. Sui), JHM, Jan 2019.

1. Introduction

Chlorinated aliphatic hydrocarbon compounds are common groundwater and soil contaminants as they were widely used as degreasing agents, cleaning solvents, and refrigerants in chemical industries [1–3]. Specifically, carbon tetrachloride (CT), tetrachloroethene (PCE), and trichloroethene (TCE) are listed among the most frequently detected chlorinated organic compounds in contaminated groundwater. These compounds have been classified as Group 2B carcinogens and are a concern for public health [4,5]. Therefore, there is continuing great interest in the development of effective remediation methods.

In situ chemical oxidation (ISCO) has been a focus of attention for the past two decades, and has many advantages in effective remediation of contaminated groundwater. Current oxidants in widespread use for ISCO include hydrogen peroxide (H_2O_2), permanganate, persulfate, sodium percarbonate, and calcium peroxide (CP) [6]. H_2O_2 is one of the most employed ISCO oxidants for contaminant degradation in groundwater and soil. Various activation techniques lead to the conversion of H_2O_2 to reactive free radicals, and a large body of research literature has documented the role of hydroxyl radical ($\text{HO}\bullet$) and superoxide radical ($\text{O}_2^{\bullet-}$) generated in the conventional Fenton system for organic pollutant degradation (Eqs. 1–3, Table 1) [7,8]. Nevertheless, H_2O_2 possesses a short lifetime (hours) and decomposes to oxygen instead of $\text{HO}\bullet$ radicals at neutral pH, which limits its application for subsurface systems.

Recently, calcium peroxide has been demonstrated to be a promising H_2O_2 alternative in remediating contaminated soil and groundwater because of its ability to release significant quantities of H_2O_2 (Eq. 4) [9]. As a solid oxidant, CP is stable and can be delivered to greater distances in the subsurface compared to H_2O_2 . Laboratory studies have reported the modified Fenton (MF) system using CP as the oxidant in efficient degradation of highly chlorinated alkenes (i.e. PCE and TCE) and benzene [9–11]. Attempts to enhance TCE removal by the CP-based MF system involve employing novel alternative iron sources (such as chelated-Fe(II) and chelated-Fe(III)) and addition of reducing reagents [12–14]. Although these modification technologies have been applied, contaminants removal in the CP-based MF system still depends on the two generated reactive oxygen species (ROSs), namely $\text{HO}\bullet$ and $\text{O}_2^{\bullet-}$ radicals [12–14]. The $\text{HO}\bullet$ radical is a strong oxidant (redox potential = 2.76 V) which can achieve efficient removal of most organic compounds. For example, TCE and PCE are readily degraded by oxidants such as $\text{HO}\bullet$ and sulfate radical ($\text{SO}_4^{\bullet-}$) generated in advanced oxidation processes (AOPs). However, perchlorinated alkanes such as CT exhibit minimal reactivity with these oxidants because CT is highly oxidized and the carbon atom of CT is at the highest valence (+VI) [15]. Rather, CT is susceptible to chemical reductive dechlorination. Meanwhile, despite a redox potential of -2.4 V, $\text{O}_2^{\bullet-}$ radical is generally inefficient because of its short existence and high solvation in aqueous solution [6,16]. In summary, the CP-based modified Fenton system needs to be enhanced to improve its effectiveness for degradation of mixed CHs (for example, a mixture of CT, PCE, and TCE).

Formic acid (FA) and citric acid (CIT) are two short-chain carboxylic acids that are often generated as the main intermediates during the degradation of more complex organic

compounds by AOPs [17–19]. Some researchers used FA as a target pollutant when investigating the kinetics of several Fenton or photo-Fenton processes [20–22], while others examined its ability to scavenge most primary species to one-electron reductive carbon dioxide radical ($\text{CO}_2^{\bullet-}$, redox potential of -1.9 V) (Eqs. 5–10) [23,24]. A previous study has demonstrated the effectiveness of the CP-based MF system in the presence of FA for CT degradation [32]. It has been suggested that the addition of excess FA to AOPs can completely convert the oxidative system into a reductive one for the mineralization of contaminants that are refractory to oxidation [25–30]. CIT is another organic acid that can be biodegraded naturally. CIT has also been widely used as a chelating agent, as well as an acidifying agent in several Fenton processes to enhance the effectiveness of the Fenton process. CIT possesses the strong ability to chelate iron and prevent its precipitation [31].

Based on prior research, we hypothesize that the addition of moderate quantities of FA or CIT to the MF system can enhance the degradation of mixed CHs. To the best of our knowledge, there have been no prior studies investigating the selective redox degradation of mixed CHs including CT, PCE, and TCE by the Fe(II)-catalyzed CP system in the presence of FA and CIT. In addition, the role of CIT on the FA-involved MF system has never been reported. In this study, batch experiments have been conducted with the objective to evaluate the selective redox-based degradation efficiency of mixed CHs in both aqueous solution and actual groundwater. The influence of selected experimental parameters is investigated and the degradation mechanism of the chlorinated hydrocarbons are identified.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study are introduced in the Supplementary Material Text. S1.

2.2. Experimental procedures

CT, TCE, and PCE stock solutions were prepared with ultrapure water or actual groundwater under stirring in dark overnight. The solutions were diluted to the desired concentration ($[\text{CT}]_0 = 0.13$ mM, $[\text{TCE}]_0 = [\text{PCE}]_0 = 0.15$ mM). A 250 mL closed cylindrical glass reactor with two openings at the top was used to conduct the batch experiments with a water bath controlled at 20°C . The aqueous solutions were subjected to constant mixing by a magnetic stirrer at a speed of 600 rpm. Chemicals including ferrous sulfate, FA, and CIT were added to the contaminants-containing solution initially at the desired dosages and the addition of CP started the modified Fenton reaction (The molar ratio of chemicals/CHs was designed as chemicals/CT). The pH was unadjusted except for the experiment evaluating the effect of initial solution pH. Aqueous samples (1 mL) were collected from the reactor at predetermined times and added to sample vials containing 1 mL hexane for 3 min extraction under stirring and standing for 5 min separation.

Radical scavenger tests were conducted to identify the dominant reactive oxygen species for contaminant degradation. Chloroform (CF) was employed as a $\text{O}_2^{\bullet-}$ scavenger because of its remarkable reactivity with $\text{O}_2^{\bullet-}$ ($k = 3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$). Both IPA and TBA were selected as $\text{HO}^{\bullet}$ scavengers because of their high reactivity with $\text{HO}^{\bullet}$ at $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and 5.2×10^8

$\text{M}^{-1}\text{s}^{-1}$, respectively [33]. Methyl viologen (MV^{2+}) was used as the $\text{CO}_2^{\bullet-}$ scavenger ($k = 6.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [34]. The concentrations of ferrous iron ($[\text{Fe(II)}]$) and total iron ($[\text{Iron}]$) were determined using the 1,10-phenanthroline method [35], in which the concentration of ferric iron ($[\text{Fe(III)}]$) can be calculated as: $[\text{Fe(III)}] = [\text{Iron}] - [\text{Fe(II)}]$. Experiments were performed in duplicate and mean values were reported.

2.3. Analytical methods

Analytical methods are presented in the Supplementary Material Text. S2.

3. Results and discussion

3.1. Enhanced degradation of CT by the CP-based MF system in the presence of formic acid and citric acid

Fig. 1a presents the enhanced degradation of CT under various molar ratios of CP/Fe(II)/FA/CT along with the CT control group. CT recovery in the control group was 90.3%, indicating less than 10% CT loss by volatilization in the closed batch reactor. CT degradation increased from 21% to 30.1% and 88.9% as the molar ratio of CP/Fe(II)/FA/CT increased from 2/2/2/1 to 6/6/6/1 and 12/12/12/1, respectively. The rapid CT removal is hypothesized to be a result of a multi-step process. The modified Fenton reaction between H_2O_2 released from CP (the release of H_2O_2 by CP under similar conditions has been discussed in our previous work [32]) and Fe(II) produced $\text{HO}^{\bullet}$ radicals initially. The $\text{HO}^{\bullet}$ radicals were then scavenged by FA to generate $\text{CO}_2^{\bullet-}$ radicals. $\text{CO}_2^{\bullet-}$ is known to be a stable reductant with the ability to degrade CT by reductive dechlorination [32]. Fig. 1b shows the influence of FA dosage on CT removal. CT degradation in general is increased by the addition of FA, while excessive FA, i.e., molar ratio of 12/12/24/1 of CP/Fe(II)/FA/CT, reduced CT removal because of the self-coupling of $\text{CO}_2^{\bullet-}$ radicals (Eq. 11) [36].

It is observed in Fig. 1a that CT degradation was very rapid in the initial 5 min and then became slower. This two-stage behavior is due to Fe(III) precipitation caused by the rapid oxidation of Fe(II) by H_2O_2 , as well as the pH increase (from 3.1 to 5.2) which can reduce the Fenton reaction rate. In the Fe(II)-catalyzed CP process, larger consumption of Fe(II) occurred in the initial 5 min while less soluble Fe(III) was generated as shown in Fig. 2, indicating the decrease of soluble iron and the occurrence of iron precipitation. Thus, Fe(II) was maintained in a low concentration of 0.03 mM compared to its initial concentration of 0.78 mM. The presence of FA appeared to have no impact on Fe(II) and Fe(III) concentrations. This result is consistent with Baba et al. [37], who confirmed the ineffectiveness of FA in promoting Fe(III)/Fe(II) cycling in Fenton reactions.

A comparison of CT degradation with the addition of CIT and several other chelating agents (CA) under the molar ratio of 12/6/6/6/1 of CA/CP/Fe(II)/FA/CT is presented in Fig. S1 (Supplementary Material). CIT produced the greatest enhancement of CT removal from 30.9% to 75.6%, and OA only slightly increased CT removal to 33.5%. Meanwhile, ASC, CIT-3Na, and EDTA-2Na showed negative effects on CT removal. This may be caused at least in part by the role of final solution pH (shown in Fig. S1), however, other factors may also be pertinent.

To further investigate the influence of CIT on CT removal, various molar ratios of CIT/CP/Fe(II)/FA/CT were studied. As illustrated in Fig. 3, the CIT/CP/Fe(II)/FA process could negatively affect the CT degradation under the molar ratios of 3/12/12/12/1 and 6/12/12/12/1 of CIT/CP/Fe(II)/FA/CT. In addition, excessive dosage of CIT (24/12/12/12/1) only resulted in 88% CT removal, which is similar to the 12/12/12/1 CP/Fe(II)/FA/CT process. However, CT removal could be enhanced to 95.5% under the molar ratio of 12/12/12/12/1 of CIT/CP/Fe(II)/FA/CT, indicating there may be different roles of CIT on CT removal. On one hand, the presence of CIT scavenged HO• radicals ($k_{\text{CIT}/\text{HO}\cdot} = 3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). On the other hand, the presence of CIT can also reduce the redox potential of Fe(II)/Fe(III) because of the formation of Fe-CIT chelates. As shown in Fig. 2, with the presence of CIT, a large increase of soluble Fe(III) was observed owing to the formation of a Fe(III)-CIT complex. This could prevent iron precipitation [38]. In addition, the concentration of Fe(II) during the initial 5 min was lower than that without CIT. Fe-chelates can maintain solubility over a wide pH range, thereby maintaining higher concentrations of soluble Fe that can react with H₂O₂, leading to a faster decrease of Fe(II). Further discussion of the mechanism of CIT-induced CP/Fe(II)/FA system is presented in Section 3.3.

3.2. Redox degradation of CT vs. PCE and TCE by the CP-based MF system in the presence of formic acid and citric acid

Fig. 4a presents the degradation of CT, PCE, and TCE in the Fe(II)-catalyzed CP system. Considering CT loss due to volatilization, it is clear that the CP/Fe(II) system did not cause CT removal, and that the adsorption of CT by generated Ca(OH)₂ can be ignored. Meanwhile, 61 and 90.5% of PCE and TCE were degraded, respectively, because of the high oxidative ability of HO• radical generated in the CP-based MF system. With the addition of 1.56 mM FA (Fig. 4b), CT removal was enhanced to 66.5% but PCE and TCE degradation were reduced to 41.7% and 74.3%, respectively. These results indicate that the scavenging role of FA on HO• radicals was significant. Despite this scavenging, simultaneous degradation of CT, PCE, and TCE still occurred because the presence of FA enhanced the abundance of free radicals in the CP-based MF system. In addition, comparison of Fig. 4b to Fig. 1a shows that the presence of PCE and TCE also negatively affected CT degradation as they compete against FA for HO• radicals, therefore reducing the generation of CO₂•⁻ radicals for CT removal.

Fig. 4c shows that introducing CIT into the CP/Fe(II)/FA system greatly increased degradation of CT, PCE, and TCE to 81.7%, 79.4%, and 96.1%, respectively. CIT not only serves to maintain acidic solution pH, but also has a strong ability to chelate iron and maintain higher solution concentrations, thus enhancing both the activity of Fenton reaction and the production of HO• radicals. In contrast, the role of CIT as a HO• scavenger appeared to be insignificant because degradation of all three chlorinated hydrocarbons was enhanced. These results indicate that the CIT/CP/Fe(II)/FA process is a promising technology for simultaneous degradation of highly chlorinated alkenes such as PCE and TCE (via oxidation) and perchlorinated alkanes such as CT (via reduction).

Fig. 5a shows the effect of FA concentration on CHs degradation in the CIT/CP/Fe(II)/CHs system under the molar ratio of 12/12/12/1. As the concentration of FA increased from 0.52

mM to 3.12 mM (FA/contaminant from 4/1 to 24/1), CT removal increased significantly from 64.8% to 90.1%, while PCE and TCE removals decreased slightly. However, a significant inhibition effect occurred when FA was 3.12 mM (FA/contaminant = 24/1). These degradation behaviors of CT, PCE, and TCE indicate that only a moderate dosage of FA was suitable for redox degradation of CHs. Although the Fenton reaction was enhanced with the presence of initial 1.56 mM CIT in the system, excessive FA did have a significant effect on scavenging HO• radical and acted as a reductant turning the system into reductive conditions by generating CO₂•⁻ radical.

The effect of CIT concentration on CT, PCE, and TCE degradation under the initial molar ratio of 12/12/12/1 of FA/CP/Fe(II)/contaminant is presented in Fig. 5b. The removal of CT, PCE, and TCE increased by the addition of CIT ranging from molar ratio of 4/1 to 12/1 of CIT/contaminant. This outcome was the same as Zhang et al. [12] and Miao et al. [39], who investigated the enhanced degradation of TCE in the CP/Fe(II)/CIT system and PCE in the sodium percarbonate (SPC)/Fe(II)/CIT system, respectively. Compared with the absence of CIT (Fig. 4b), PCE and TCE degradation were enhanced while CT removal only slightly decreased from 65.5% to 59.2% with the addition of CIT under 4/1 of CIT/CHs. Moreover, excessive CIT (24/1 of CIT/CHs) can also adversely affect CT, PCE, and TCE removals.

Based on the above results, the roles of FA and CIT in the CIT/CP/Fe(II)/FA/CHs system were demonstrated as follows: (1) The presence of FA can improve CT degradation by generating CO₂•⁻ radicals, but its role as a HO• scavenger was significant and thus negatively affected PCE and TCE degradation; (2) The scavenging role of CIT was minimal and, in turn, the presence of CIT could overcome the drawback caused by FA because CIT could chelate iron and enhance the availability of soluble iron, therefore further promoting Fenton reaction and HO• radical generation.

3.3. Degradation mechanism of chlorinated hydrocarbons by CP-based MF system in the presence of FA and CIT

Fig. 6 reveals a comparison of EPR spectra of radicals under various testing conditions. With the absence of CIT (Fig. 6a), the main EPR spectra was assigned to the DMPO-CO₂•⁻ adduct [40]. This signal provided direct evidence of the formation of CO₂•⁻ radicals in the CP/Fe(II)/FA system. Fig. 6b–d reflects the changes of EPR signals with increased FA concentration from 1.56 to 15.6 mM and 156 mM with the initial presence of 1.56 mM CIT. A new signal known to be DMPO-HO• adduct with the character of a 1:2:2:1 quartet was observed upon addition of CIT, suggesting that CIT indeed enhanced HO• generation. The intensity of CO₂•⁻ radicals increased as more FA was added, whereas the intensity of HO• decreased minimally, even with 100-fold increase of initial FA added as the HO• scavenger. This outcome was not the same as those reported by Villamena et al. [41] and Liu et al. [42], in which HO• could be scavenged completely and transformed to CO₂•⁻ radicals with excessive FA (formate) in UV/H₂O₂ and UV/TiO₂ processes, respectively. So far few studies have succeeded in capturing the DMPO-CO₂•⁻ adduct in the Fe(II) activated Fenton system. Our results indicate that rather than the single CO₂•⁻ radical, the coexistence of HO• and CO₂•⁻ radicals was detected by EPR spectra in this study. Equations (5, 7, 12) in Table 1 also give the theoretical transformation between HO• and CO₂•⁻ radicals [43]. In addition, Fig.

S2 shows the difference in ORP profiles in the CP/Fe(II) and CIT/CP/Fe(II)/FA systems, indicating that the presence of FA and CIT strongly enhanced the CP/Fe(II) system and that the CIT/CP/Fe(II)/FA system remained in an oxidative circumstance. Based on the above discussion, it appears that the CIT/CP/Fe(II)/FA process does possess the ability for selective redox degradation of CHs.

To further distinguish the specific role of reactive oxygen species in the CIT/CP/Fe(II)/FA system, scavenging tests were conducted by employing CF, MV^{2+} , IPA, and TBA for the comparison of target contaminant degradation performance (Fig. 7). The addition of 65 mM CF reduced CT degradation by 11.5%, but only slightly affected PCE and TCE degradation, suggesting that $O_2^{\bullet-}$ radical was only involved in CT removal. In contrast, IPA and TBA inhibited PCE and TCE degradation as $HO^{\bullet}$ was scavenged. Hence, the degradation of PCE and TCE was initiated by $HO^{\bullet}$ radicals. In addition, the scavenging of $HO^{\bullet}$ decreased CT removal to 28% and 43.1% in TBA and IPA groups, respectively. These results confirmed that $CO_2^{\bullet-}$ radical was produced by the reaction between $HO^{\bullet}$ and FA. However, CT removal in the IPA group was higher than that in the TBA group because the reactivity of $O_2^{\bullet-}$ radical was strengthened with the presence of IPA, leading to the solvation effect in aqueous solution [14]. Moreover, MV^{2+} reduced CT removal from 81.8% to 19.9% as MV^{2+} competed with CT for $CO_2^{\bullet-}$ radicals. According to these outcomes, it is clear that the $HO^{\bullet}$ radical is responsible for TCE and PCE degradation and also involved in the generation of $CO_2^{\bullet-}$ radical. $CO_2^{\bullet-}$, and to a much lesser extent $O_2^{\bullet-}$, radicals caused CT degradation.

Further study was focused on the dechlorination efficiency of contaminants. Fig. 8 presents the detected chlorine ions released by CT, PCE, and TCE separately in the CIT/CP/Fe(II)/FA system. Meanwhile, chlorine ions released in simultaneous degradation of CT, PCE, and TCE was also monitored to compare the co-dechlorination efficiency at 20 min (inserted figure). Dechlorination magnitudes of 84.5%, 90.1%, and 99.2% for CT, PCE, and TCE, respectively, were all higher than the co-dechlorination efficiency of 71.8%, indicating some degree of cross-interference for the mixed system.

Dechlorination data reported in Table 2 reflect high degrees of mineralization of CT, PCE, and TCE, indicating that the chlorinated degradation intermediates can be rapidly degraded into end products CO_2 , H_2O , and Cl^- . No chlorinated compounds were detected by GC-MS in this study, suggesting that $CO_2^{\bullet-}$ and $HO^{\bullet}$ radicals degraded intermediates, supporting the observed high degrees of mineralization of the CHs. Based on the literature and our previous study [32, 44–45], a proposed pathway for CT, PCE, and TCE degradation is presented in Fig. S3.

3.4. Chlorinated hydrocarbons degradation by CIT/CP/Fe(II)/FA process in actual groundwater

The impact of groundwater as the solution matrix on CHs degradation was investigated. The groundwater was filtrated in order to avoid the adsorption of CT by suspended solids. Table S1 (in Supplementary Material) provides the primary parameters of the groundwater and Fig. 9a shows the average degradation performance of CHs. CT can be degraded up to 97.7% rapidly within 15 min, while PCE and TCE removal seemed to be inhibited, with removals of 24.8% and 40.4%, respectively, at the molar ratio of 12/1 of chemicals/

contaminant. The inhibition of PCE and TCE might be caused by the presence of natural organic matter (NOM, with TOC ranging from 10.7 ~ 20.3 mg/L) and inorganic carbonate ion (301 ~ 414 mg/L), as well as the effect of pH. Hence, the influence of HA (selected as the representative of NOM), carbonates (CO_3^{2-}), and initial solution pH on CHs degradation were investigated individually in ultrapure water.

Fig. S4 shows that 10 mg/L HA had minimum effect on CT removal and only slightly decreased PCE and TCE removals due to its scavenging of reactive radicals and the consumption of oxidants. It was also found that HA did not dissolve in the system because of the acidic solution caused by formic and citric acids. Hence, the effect of organic matter may be a function of the state of the NOM (soluble or sorbed) [46], and more complex than that of inorganic constituents in the Fenton system. Fig. S3 also illustrates that 600 mg/L carbonate negatively affected CT, PCE, and TCE degradation to 64.5%, 45.4% and 72.2%, respectively. Among common inorganic ions, carbonate is most likely to compete with contaminants for $\text{HO}\cdot$ radicals (Eq.13) [47] and deactivate the Fenton reaction by raising the solution pH and scavenging $\text{CO}_2\cdot^-$ radicals, as shown in Eq.14 [47].

Fig. S5 shows the effect of initial solution pH of 3, 6, and 9 on CHs removal in the CIT/CP/Fe(II)/FA system. The results indicate that the CIT/CP/Fe(II)/FA system may be not effective in basic condition, while remarkable contaminant removal was achieved under acidic and neutral pH conditions. Fig. 9b presents an improved average contaminant removal in groundwater as the molar ratio of CIT/CP/Fe(II)/FA/contaminant was increased to 24/24/24/24/1, indicating that the adverse effect caused by NOM or carbonates can be eliminated with increased dosage of the reagents. The above results indicate that the Fe(II)-catalyzed CP process with the presence of FA and CIT possesses resistant redox ability and is applicable for contaminated groundwater remediation.

4. Conclusions

The scope of the study was to establish a formic acid (FA) and citric acid (CIT) assisted modified Fenton process, i.e. FA/CIT/Fe(II)/calcium peroxide (CP), for the degradation of chlorinated hydrocarbons (CHs) including CT, PCE, and TCE. For single-solute studies of CT, preliminary results showed that the presence of FA enhanced CT degradation in the Fe(II)/CP process, and an equal molar ratio of 12/12/12/12/1 of CIT/FA/Fe(II)/CP/CT could increase CT removal up to 95.5%. For studies of a CT, PCE, and TCE mixture, FA inhibited PCE and TCE degradation, while the addition of CIT could overcome this drawback. Therefore, a redox circumstance that could simultaneously degrade CT, PCE, and TCE with removal efficiencies of 81.7%, 79.4% and 96.1%, respectively, could be achieved under the same experimental condition. Mechanism investigation through electron paramagnetic resonance detection and scavenging tests indicated that the FA and CIT amended Fe(II)/CP process simultaneously produced $\text{HO}\cdot$ (oxidant) and $\text{CO}_2\cdot^-$ (reductant) radicals, resulting in the oxidative degradation of PCE/TCE by $\text{HO}\cdot$ and the reductive dechlorination of CT by $\text{CO}_2\cdot^-$. Moreover, nearly complete dechlorination of CHs was achieved and no chlorinated intermediates were detected. PCE and TCE removals were inhibited in the presence of groundwater due to scavenging of reactive species by organic compounds and carbonates in groundwater. This effect was overcome by increasing the reagent dosage. The degradation of

CHs was more effective in acidic and neutral pH conditions. In conclusion, the results of this study provide useful information about the degradation of CHs by the Fe(II)/CP process with the presence of FA and CIT, and indicate that this process has promise for treating CH-contaminated groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This study was financially supported by a grant from the International Academic Cooperation and Exchange Program of Shanghai Science and Technology Committee (18230722700) and the contribution of Mark L. Brusseau were supported by the NIEHS Superfund Research Program of the United States (PS 42 ES04940). We thank the reviewers for their constructive comments.

References

- [1]. Choi K, Lee W, Reductive dechlorination of carbon tetrachloride in acidic soil manipulated with iron(II) and bisulfide ion, *J. Hazard. Mater.* 172 (2009) 623–630. [PubMed: 19660864]
- [2]. Jiao Y, Qiu C, Huang L, Wu K, Ma H, Chen S, Ma L, Wu D, Reductive dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion, *Appl. Catal. B* 91 (2009) 434–440.
- [3]. Moran MJ, Zogorski JS, Squillace PJ, Chlorinated solvents in groundwater of the United States, *Environ. Sci. Technol.* 41 (2007) 74–81. [PubMed: 17265929]
- [4]. Brusseau ML, Carroll KC, Truex MJ, Becker DJ, Characterization and remediation of chlorinated volatile organic contaminants in the vadose zone, *Vadose Zone J.* 12 (2013) 1–17.
- [5]. IARC, IARC Monographs on the evaluation of carcinogenic risks to humans: re-evaluation of some organic chemicals, hydrazine and hydrogen peroxide, IARC 1999.
- [6]. Huling SG, Pivetz BE, Engineering issue paper: In-situ chemical oxidation, U.S. Environmental Protection Agency (USEPA) office of research and development, national risk management research laboratory, Cincinnati, OH, USA, <http://www.epa.gov/tio/tsp/issue.htm#EF>. (searched 3, 2018)
- [7]. Devi P, Das U, Dalai AK, In-situ chemical oxidation: principle and applications of peroxide and persulfate treatments in wastewater systems, *Sci. Total Environ.* 571 (2016) 643–657. [PubMed: 27453139]
- [8]. kang N, Lee DS, Yoon J, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, *Chemosphere* 47 (2002) 915–924. [PubMed: 12108698]
- [9]. Northup A, Cassidy D, Calcium peroxide (CaO₂) for use in modified Fenton chemistry, *J. Hazard. Mater.* 152 (2008) 1164–1170. [PubMed: 17804164]
- [10]. Zhang X, Gu X, Lyu S, Miao Z, Xu M, Fu X, Qiu Z, Sui Q, Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion, *J. Hazard. Mater.* 284 (2015) 253–260. [PubMed: 25463240]
- [11]. Xue Y, Gu X, Lyu S, Miao Z, Brusseau ML, Xu M, Fu X, Zhang X, Qiu Z, Sui Q, The destruction of benzene by calcium peroxide activated with Fe(II) in water, *Chem. Eng. J.* 302 (2016) 187–193. [PubMed: 28943778]
- [12]. Zhang X, Gu X, Lyu S, Miao Z, Xu M, Fu X, Qiu Z, Sui Q, Application of calcium peroxide activated with Fe(II)-EDDS complex in trichloroethylene degradation, *Chemosphere* 160 (2016) 1–6. [PubMed: 27351899]
- [13]. Zhang X, Gu X, Lyu S, Miao Z, Xu M, Fu X, Danish M, Brusseau ML, Qiu Z, Sui Q, Enhanced degradation of trichloroethene by calcium peroxide activated with Fe(III) in the presence of citric acid, *Front. Env. Sci. Eng.* 10 (2016) 502–512. [PubMed: 28959499]

- [14]. Zhang X, Gu X, Lyu S, Brusseau ML, Xu M, Fu X, Qiu Z, Sui Q, Application of ascorbic acid to enhance trichloroethene degradation by Fe(III)-activated calcium peroxide, *Chem. Eng. J.* 325 (2017) 188–198. [PubMed: 29104449]
- [15]. Teel AL, Watts RJ, Degradation of carbon tetrachloride by modified Fenton's reagent, *J. Hazard. Mater.* 94 (2002) 179–189. [PubMed: 12169420]
- [16]. Xu M, Gu X, Lyu S, Fu Z, Sui Q, Miao Z, Zang X, Wu X, Degradation of carbon tetrachloride in aqueous solution in the thermally activated persulfate system, *J. Hazard. Mater.* 286 (2015) 7–14. [PubMed: 25544995]
- [17]. Oturan MA, Pimentel M, Oturan N, Sires I, Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment, *Electrochim. Acta* 54 (2008) 173–182.
- [18]. Kavitha V, Palanivelu K, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere* 5 (2004) 1235–1243.
- [19]. Kwan CY, Chu W, The role of organic ligands in ferrous-induced photochemical degradation of 2,4-dichlorophenoxyacetic acid, *Chemosphere* 67 (2007) 1601–1611. [PubMed: 17239922]
- [20]. Rossetti G, Albizzati E, Alfano O, Decomposition of formic acid in a water solution employing the photo-Fenton reaction, *Ind. Eng. Chem. Res.* 41(2002) 1436–1444.
- [21]. Farias J J, Albizzati E, Alfano O, Kinetic study of the photo-Fenton degradation of formic acid: Combined effects of temperature and iron concentration, *Catal. Today* 144 (2009) 117–123.
- [22]. Grcic I, Obradovic M, Vujevic D, Koprivanac N, Sono-Fenton oxidation of formic acid/formate ions in an aqueous solution: from an experimental design to the mechanistic modeling, *Chem. Eng. J.* 164 (2010) 196–207.
- [23]. Rosso J, Bertolotti S, Braun A, Mártire D, Gonzalez M, Reactions of carbon dioxide radical anion with substituted benzenes, *J. Phys. Org. Chem.* 14 (2001) 300–309.
- [24]. Buxton GV, Greenstock CL, Helman WP, Ross AB, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}-$) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (2009) 513–886.
- [25]. Gara PD, Bucharsky E, Worner M, Braun AM, Martire DO, Gonzalez M, Trichloroacetic acid dehalogenation by reductive radicals, *Inorg. Chem. Acta* 360 (2007) 1209–1216.
- [26]. Mora VC, Rosso JA, Roux GCL, Martire DO, Gonzalez MC, Thermally activated peroxydisulfate in the presence of additives: a clean method for the degradation of pollutants, *Chemosphere* 75 (2009) 1405–1409. [PubMed: 19285704]
- [27]. Xu M, Gang X, Lyu S, Miao Z, Zang X, Wu X, Qiu Z, Sui Q, Degradation of carbon tetrachloride in thermally activated persulfate system in the presence of formic acid, *Front. Environ. Sci. Eng.* 10 (2016) 438–446.
- [28]. Gu X, Lyu S, Fu X, Qiu Z, Sui Q, Guo X, Carbon dioxide radical anion-based UV/S₂O₈²⁻/HCOOH reductive process for carbon tetrachloride degradation in aqueous solution, *Sep. Purif. Technol.* 172 (2017) 211–216.
- [29]. Ren H, Hou Z, Han X, Zhou R, Highly reductive radical CO₂ $\bullet^-$ deriving from a system with SO₄ $\bullet^-$ and formate anion: Implication for reduction of Cr(VI) from wastewater, *Chem. Eng. J.* 309 (2017) 638–645.
- [30]. Jiang W, Tang P, Lyu S, Zhang X, Qiu Z, Sui Q, Enhanced reductive degradation of carbon tetrachloride by carbon dioxide radical anion-based sodium percarbonate/Fe(II)/formic acid system in aqueous solution, *Front. Environ. Sci. Eng.* 12 (2018) 1–10.
- [31]. Bolobajev J, Trapido M, Goi A, Improvement in iron activation ability of alachlor Fenton-like oxidation by ascorbic acid, *Chem. Eng. J.* 281 (2015) 566–574.
- [32]. Jiang W, Tang P, Lyu S, Xue Y, Zhang X, Qiu Z, Sui Q, Comparative studies of H₂O₂/Fe(II)/formic acid, sodium percarbonate/Fe(II)/formic acid and calcium peroxide/Fe(II)/formic acid processes for degradation performance of carbon tetrachloride, *Chem. Eng. J.* 344 (2018) 453–461.
- [33]. Teel AL, Watts RJ, Degradation of carbon tetrachloride by modified Fenton's reagent, *J. Hazard. Mater.* 94 (2002) 179–189. [PubMed: 12169420]

- [34]. Tachikawa T, Tojo S, Fujitsuka M, Majima T, Direct observation of the one-electron reduction of methyl viologen mediated by the CO₂ radical anion during TiO₂ photocatalytic reactions, *Langmuir* 20 (2004) 9441–9444. [PubMed: 15491173]
- [35]. Tamura H, Goto K, Yotsuyanagi T, Nagayama M, Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III), *Talanta* 21 (1974) 314–318. [PubMed: 18961462]
- [36]. Aristova NA, Leitner N, Piskarev IM, Degradation of formic acid in different oxidative processes, *High Energ. Chem.* 36 (2002) 197–202.
- [37]. Baba Y, Yatagai T, Harada T. Hydroxyl radical generation in the photo-Fenton process: Effects of carboxylic acids on iron redox cycling, *Chem. Eng. J.* 277 (2015) 229–241.
- [38]. Waite TD, Morel F, Photo reductive dissolution of colloidal iron oxide: Effect of citrate, *J. Colloid Interf. Sci.* 102 (1984) 121–137.
- [39]. Miao Z, Gu X, Lyu 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.* 275 (2017) 53–62.
- [40]. Perissinotti LL, Brusa MA, Grela MA, Yield of carboxyl anion radicals in the photocatalytic degradation of formate over TiO₂ particles, *Langmuir* 17 (2001) 8422–8427.
- [41]. Villamena FA, Locigno EJ, Rockenbauer A, Hadad CM, Zweier JL, Theoretical and experimental studies of the spin trapping of inorganic radicals by 5,5-Dimethyl-1-Pyrroline N-Oxide (DMPO). 1. Carbon dioxide radical anion, *J. Phys. Chem. A* 110 (2006) 13253–13258. [PubMed: 17149843]
- [42]. Liu X, Zhong J, Fang L, Wang L, Yao M, Shao Y, Li J, Zhang T, Trichloroacetic acid reduction by an advanced reduction process based on carboxyl anion radical, *Chem. Eng. J.* 303 (2016) 56–63.
- [43]. Franch MI, Ayllón JA, Peral J, Domènech X, Photocatalytic degradation of short-chain organic diacids, *Catal. Today* 76 (2002) 221–233.
- [44]. Li K, Stefan MI, Crittenden JC, Trichloroethene Degradation by UV/H₂O₂ advanced oxidation process: Product study and kinetic modeling, *Environ. Sci. Technol.* 41 (2007) 1696–1703. [PubMed: 17396662]
- [45]. Itoh N, Kutsuna S, Ibusuki T, A product study of the OH radical initiated oxidation of perchloroethylene and trichloroethylene, *Chemosphere* 28 (1994) 2029–2040.
- [46]. Watts RJ, Teel AL, Chemistry of modified Fenton's reagent (catalyzed H₂O₂ propagations–CHP) for in situ soil and groundwater remediation, *J. Env. Eng.* 131 (2005) 612–622.
- [47]. Neta P, Huie RE, Ross AB, Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 1027–1284.

Fig. 1. CT degradation by the Fe(II)/CP/FA process: (a) the molar ratios of Fe(II)/CP/FA from 2/2/2/1 to 12/12/12/1 ($[CT]_0 = 0.13$ mM); (b) the influence of the dosage of FA ($[CT]_0 = 0.13$ mM, $[Fe(II)] = [CP] = 1.56$ mM).

Fig. 2.

The comparative transformation of Fe²⁺ and Fe³⁺ during the degradation of CT in the Fe(II)/CP process: the effect of FA and CIT ([CT]₀ = 0.13 mM, [Fe(II)] = [CP] = [FA] = [CIT] = 0.78 mM)

Fig. 3.
The influence of the dosage of CIT on CT degradation in the Fe(II)/CP/FA process ($[CT]_0 = 0.13$ mM, $[Fe(II)] = [CP] = [FA] = 1.56$ mM).

Fig. 4. The simultaneous degradation of CT, PCE, and TCE in the CP-based modified Fenton system. ($[CHs]_0 = 0.13$ mM, $[Fe(II)] = [CP] = [FA] = [CIT] = 1.56$ mM)

Fig. 5.

The influence of (a) the dosage of FA and (b) the dosage of CIT on the simultaneous degradation of CT, PCE, and TCE in the CP-based modified Fenton system. (with $[CHs]_0 = 0.13$ mM and initial $[Fe(II)] = [CP] = 1.56$ mM in (a) and (b), while only initial $[CIT] = 1.56$ mM in (a) and only initial $[FA] = 1.56$ Mm in (b)).

Fig. 6. EPR spectra of samples from (a) Fe(II)/CP/FA process ($[FA] = 1.56 \text{ mM}$), (b) Fe(II)/CP/FA/CIT process ($[FA] = 1.56 \text{ mM}$, $[CIT] = 1.56 \text{ mM}$), (c) Fe(II)/CP/FA/CIT process ($[FA] = 15.6 \text{ mM}$, $[CIT] = 1.56 \text{ mM}$) and (d) Fe(II)/CP/FA/CIT process ($[FA] = 156 \text{ mM}$, $[CIT] = 1.56 \text{ mM}$). (The initial $[Fe(II)]$ and $[CP]$ for (a)~(d) are 1.56 mM)

Fig. 7. The effect of scavengers on the simultaneous degradation of CT, PCE, and TCE in Fe(II)/CP/FA/CIT process. ($[\text{CHs}]_0 = 0.13\sim 0.15$ mM, $[\text{Fe(II)}] = [\text{CP}] = [\text{FA}] = [\text{CIT}] = 1.56$ mM)

Fig. 8.

Cl⁻ release and dechlorination of CHs in the CP/Fe(II)/FA/CIT process. ([CHs]₀ = 0.13~0.15 mM, [Fe(II)] = [CP] = [FA] = [CIT] = 1.56 mM)

Fig. 9.

The degradation of CT, PCE, and TCE by the Fe(II)/CP/FA/CIT process in groundwater: (a) $[\text{CHs}]_0 = 0.13\sim 0.15$ mM, $[\text{Fe(II)}] = [\text{CP}] = [\text{FA}] = [\text{CIT}] = 1.56$ mM, (b) $[\text{CHs}]_0 = 0.13\sim 0.15$ mM, $[\text{Fe(II)}] = [\text{CP}] = [\text{FA}] = [\text{CIT}] = 3.12$ mM.

Table. 1

Reactions involved in CP/Fe(II) system in the presence of formic acid and citric acid.

No.	Reactions	Rate constants ($M^{-1} s^{-1}$)	Reference
1	$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + HO^- + Fe^{3+}$	76	[7]
2	$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet$	2.7×10^7	[8]
3	$HO_2\bullet \rightarrow O_2\bullet^- + H^+$	$1.58 \times 10^5 s^{-1}$	[8]
4	$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2$	-	[9]
5	$HCOOH + HO\bullet \rightarrow H_2O + HCO_2\bullet$	1.3×10^8	[23]
6	$HCOOH \leftrightarrow COOH^- + H^+$	3.5×10^9	[24]
7	$COOH^- + HO\bullet \rightarrow H_2O + CO_2\bullet^-$	3.2×10^9	[23]
8	$COOH^- + H\bullet \rightarrow H_2 + CO_2\bullet^-$	2.1×10^8	[23]
9	$HCOOH + h\nu \rightarrow H\bullet + HCO_2\bullet$	-	[23]
10	$HCO_2\bullet \leftrightarrow CO_2\bullet^- + H^+$	-	[23]
11	$[CO_2\bullet^- \dots CO_2\bullet^-] \rightarrow C_2O_4^{2-}$	$4 \times 10^7 s^{-1}$	[36]
12	$H_2O + CO_2\bullet^- \rightarrow HCO_2^- + HO\bullet$	-	[43]
13	$CO_3^{2-} + HO\bullet \rightarrow CO_3\bullet^- + OH^-$	3.9×10^8	[47]
14	$CO_3\bullet^- + CO_2\bullet^- \rightarrow CO_2 + CO_3^{2-}$	5.0×10^7	[47]

Table. 2

Degradation performance of CHs in CP-based modified Fenton processes.

Experimental conditions	CP/Fe(II)/CHs = 12/12/1	CP/Fe(II)/FA/CHs = 12/12/12/1	CIT/CP/Fe(II)/FA/CHs = 12/12/12/12/1
	CT / PCE / TCE	CT / PCE / TCE	CT / PCE / TCE
CHs removal simultaneously	11.0% / 61.1% / 90.5%	66.5% / 41.7% / 74.3 %	81.7% / 79.4% / 96.1%
Dechlorination separately ^a	- / - / -	49.6% ^c / - / -	84.5% / 90.1% / 99.2%
Dechlorination simultaneously ^b	- / - / -	- / - / -	71.8%
pH(initial/final)	4.52 / 6.65	3.14 / 5.17	2.92 / 3.07

^a: The dechlorination was measured with individual contaminant;^b: The chloride ions detected came from CT, PCE and TCE at the same time;^c: The data came from reference [32].