Published in final edited form as:

Chem Eng J. 2015 August 15; 274: 61–68. doi:10.1016/j.cej.2015.03.056.

Degradation of trichloroethene by siderite-catalyzed hydrogen peroxide and persulfate: Investigation of reaction mechanisms and degradation products

Ni Yan^{a,b}, Fei Liu^{a,*}, Qiang Xue^a, Mark L. Brusseau^b, Yali Liu^a, and Junjie Wang^c

^aBeijing Key Laboratory of Water Resources and Environmental Engineering/School of Water Resources and Environment, China University of Geosciences, Beijing 100083, PR China

^bHydrology and Water Resources Department, School of Earth and Environmental Sciences, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, United States

^cDevelopment Research Center of the Ministry of Water Resources, Beijing 100038, PR China

Abstract

A binary catalytic system, siderite-catalyzed hydrogen peroxide (H_2O_2) coupled with persulfate ($\text{S}_2\text{O}_8^{2-}$), was investigated for the remediation of trichloroethene (TCE) contamination. Batch experiments were conducted to investigate reaction mechanisms, oxidant decomposition rates, and degradation products. By using high performance liquid chromatography (HPLC) coupled with electron paramagnetic resonance (EPR), we identified four radicals (hydroxyl ($\text{HO}\cdot$), sulfate ($\text{SO}_4\cdot^-$), hydroperoxyl ($\text{HO}_2\cdot$), and superoxide ($\text{O}_2\cdot^-$)) in the siderite-catalyzed H_2O_2 - $\text{S}_2\text{O}_8^{2-}$ system. In the absence of $\text{S}_2\text{O}_8^{2-}$ (i.e., siderite-catalyzed H_2O_2), a majority of H_2O_2 was decomposed in the first hour of the experiment, resulting in the waste of $\text{HO}\cdot$. The addition of $\text{S}_2\text{O}_8^{2-}$ moderated the H_2O_2 decomposition rate, producing a more sustainable release of hydroxyl radicals that improved the treatment efficiency. Furthermore, the heat released by H_2O_2 decomposition accelerated the activation of $\text{S}_2\text{O}_8^{2-}$, and the resultant $\text{SO}_4\cdot^-$ was the primary oxidative agent during the first two hours of the reaction. Dichloroacetic acid was firstly detected by ion chromatography (IC). The results of this study indicate a new insight to the reaction mechanism for the catalytic binary H_2O_2 - $\text{S}_2\text{O}_8^{2-}$ oxidant system, and the delineation of radicals and the discovery of the chlorinated byproduct provide useful information for efficient treatment of chlorinated-solvent contamination in groundwater.

Keywords

Advanced oxidation; Chlorinated solvent; Radical identification; Byproduct

1. Introduction

The contamination of groundwater by chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and carbon tetrachloride continues to pose risk for both human health and the environment. Numerous studies have been conducted to

*Corresponding author. Tel.: +86 151 20086112; fax: +86 10 8232 1081. feiliu@cugb.edu.cn (F. Liu).

develop methods for effective remediation of soil, sediment, and groundwater contaminated by these compounds. *In-situ* chemical oxidation (ISCO), using reagents such as permanganate, hydrogen peroxide (H_2O_2), or persulfate ($\text{S}_2\text{O}_8^{2-}$), has become a prospective alternative method for remediation of sites contaminated by chlorinated aliphatic compounds. While ISCO has been very successful overall, limitations have been identified [1–3].

More recently, advanced oxidation methods, often comprising binary oxidant systems, have been investigated. Among many advanced oxidation processes (AOPs), catalyzed H_2O_2 coupled with $\text{S}_2\text{O}_8^{2-}$ has been shown to be effective for chlorinated solvent degradation [4–7]. H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ can be catalyzed to generate hydroxyl ($\text{HO}\cdot$), sulfate ($\text{SO}_4^{\cdot-}$), and additional radicals such as hydroperoxyl ($\text{HO}_2\cdot$) and superoxide ($\text{O}_2^{\cdot-}$) [8–13]. Both $\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$ have high oxidative capabilities ($E^0=2.7$ V for $\text{HO}\cdot$ and $E^0=2.6$ V for $\text{SO}_4^{\cdot-}$) to degrade chlorinated solvents, and $\text{SO}_4^{\cdot-}$ can convert into $\text{HO}\cdot$ [14, 15]. However, the function and conversion mechanisms among radicals remain unclear.

In this study, siderite is selected as the catalyst because it is often reported to be highly supersaturated in natural groundwater [16, 17], and many prior studies have shown that ferrous ion is an effective catalyst for Fenton and Fenton-like reactions [18–23]. Furthermore, it is used as a representative of the several iron-containing components typically present in sedimentary geomedial.

The radical reaction mechanism in the siderite-catalyzed H_2O_2 - $\text{S}_2\text{O}_8^{2-}$ system (designated as STO system) is poorly understood. For example, the specific radicals produced, how these radicals are generated, and how they react with TCE remain unclear. As is well known, the radical type and its catalytic performance directly affect contaminant removal efficiency. However, distinguishing various radicals and evaluating their reaction mechanisms is challenging, especially for binary oxidant systems. Another unknown for the STO system is the potential production of reaction intermediaries. The incomplete degradation of TCE may cause secondary pollution, and the detection of byproducts is a key way to confirm the degree of degradation and analyze the chlorine ion balance, which can help to understand the reaction mechanism.

Well-characterized probe molecules are often used to investigate the generation of $\text{HO}\cdot$ [24–26]. Benzoic acid (BA) is one of the most commonly used radical probes to measure $\text{HO}\cdot$ formation, and both BA and the reaction product hydroxybenzene acid can be measured by high performance liquid chromatography (HPLC). Electron paramagnetic resonance (EPR) spin-trapping has also been used, due to its excellent sensitivity and selectivity in the detection of free radicals [27–30]. The EPR technique is able to detect and identify radicals by measurement of spin-adducts formed by the radicals and spin traps in a magnetic field [28, 31–33]. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) is often used as a spin trap to identify oxygen-centered radicals [12, 13, 34–38].

The primary objectives of this study are to delineate the radicals generated from the STO system, to identify potential degradation byproducts, and to investigate reaction mechanisms, compared with the siderite-catalyzed H_2O_2 system (designated as SO system).

TCE is used as a model chlorinated solvent, as it is one of the most commonly detected dense non-aqueous phase liquid (DNAPL) contaminants in groundwater [39–41]. Experiments were conducted using batch reactors. HPLC combined with EPR spin-trapping methods were used to identify the radicals and their reaction mechanism for the degradation of TCE. In addition, ion chromatography (IC) was used to identify byproducts. The results were used to help illuminate the degradation pathway of TCE in this siderite catalytic system.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were prepared using ultrapure (filtered, distilled) water (Millipore Model Milli-Q Academic A10). Siderite was purchased from the Wuhan Iron and Steel (Group) Corporation, China. Hydrogen peroxide (H_2O_2 , ~30% solution), trichloroethene (TCE, >99% purity), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%), benzoic acid (>99.5%), *p*-hydroxybenzoic acid (>99.5%), and isopropanol (>99.7%) were obtained from the Beijing Chemical Plant. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 97%) was purchased from Sigma-Aldrich, Inc.

The following reagent concentrations were used for all of the experiments. For TCE, 10 μL of pure TCE was added to each vial for the relevant experiments. This quantity is equivalent to 11.15 mmol/L (1,500 mg/L) in solution. This equivalent concentration exceeds the aqueous solubility of TCE, reflecting the presence of TCE liquid. $\text{Na}_2\text{S}_2\text{O}_8$: 6.3 mmol/L (1,500 mg/L), H_2O_2 : 0.15 mol/L (5,100 mg/L), siderite: 11,450 mg/L. These oxidant concentrations are relatively low compared to typical concentrations used for field applications. Thus, these concentrations will produce conservative results.

2.2. HO $\cdot$ radical production

Experiments were conducted with 20 mL borosilicate vials fitted with PTFE septum caps. Two sets of controls were employed. The first one contained only 0.1145 g of siderite, 5 mL of 0.018 mol/L BA, and 5 mL of ultrapure water. This group was used to determine background HO $\cdot$ production. The second one contained 2 mL of 0.045 mol/L BA, 3 mL of 0.021 mol/L $\text{Na}_2\text{S}_2\text{O}_8$, and 5 mL of 0.30 mol/L H_2O_2 . This control group was used to determine if the oxidants alone, with no activation, could produce HO $\cdot$. Two experiment treatment groups were prepared. One group was prepared with 0.1145 g of siderite, 5 mL of 0.018 mol/L BA and 5 mL of 0.30 mol/L H_2O_2 . Another group contained 0.1145 g of siderite, 2 mL of 0.045 mol/L BA, 3 mL of 0.021 mol/L $\text{Na}_2\text{S}_2\text{O}_8$, and 5 mL of 0.30 mol/L H_2O_2 .

After preparation, the vials were maintained at 20 ± 1 °C in an air bath for the experiments. At each time-point, isopropanol solution was added to the sacrificed reactors to quench further oxidation. The target analytes, BA and *p*-hydroxybenzoic acid, were analyzed by HPLC.

2.3. Radical identification

Experiments were conducted with 100 mL borosilicate vials at 20 ± 1 °C, and were done in triplicate. Four control groups were used for the experiments. The first one contained only 0.5725 g of siderite and 50 mL of ultrapure water. The second one contained 25 mL of ultrapure water and 25 mL of 0.30 mol/L H_2O_2 . The third one contained 35 mL of ultrapure water and 15 mL of 0.021 mol/L $\text{Na}_2\text{S}_2\text{O}_8$. The fourth one contained 10 mL of ultrapure water, 15 mL of 0.021 mol/L $\text{Na}_2\text{S}_2\text{O}_8$, and 25 mL of 0.30 mol/L H_2O_2 . There were three experiment treatment groups. The constituents added in the three groups were the same as those used for the second, third, and fourth control groups, respectively, with the exception that 0.5725 g of siderite was added as a catalyst.

At each time-point, a 1 mL aliquot was collected and mixed with 100 μL of 500 mmol/L DMPO. The DMPO-adducts were analyzed using EPR spin trapping.

2.4. Detection of byproducts

Experiment (triplicate) conditions were the same as for section 2.2. The control group contained 0.1145 g of siderite, 10 mL of ultrapure water, and 10 μL of TCE, which was injected into the bottom of the vial. There were two experiment treatment groups. One group contained 0.1145 g of siderite, 5 mL of ultrapure water, and 10 μL of TCE, to which 5 mL of 0.30 mol/L H_2O_2 was added. Another group contained 2 mL of ultrapure water and 3 mL of 0.021 mol/L $\text{Na}_2\text{S}_2\text{O}_8$. Then, 10 μL of TCE and 5 mL of 0.30 mol/L H_2O_2 were added in sequence. At each time point, the reaction was quenched for the selected vials, the residual TCE was analyzed, and IC was used to investigate byproducts produced during the reaction.

2.5. Analytical methods

Siderite was analyzed before and after reaction in the STO system by x-ray diffraction (XRD) (Fig. S1). The results show that iron ions dissolved from the catalyst surface during the reaction. The dissolved iron data are shown in Fig. S2.

BA and *p*-hydroxybenzoic acid were analyzed by HPLC using a Shimadzu LC-20A with a 4.6×250 mm Inertsil® ODS-SP column (particle size was 5 μm). $\text{HO}\cdot$ was quantified referring to the method described by Lindsey and Tarr [42]. Samples were loaded onto a 2 μL loop. The elution gradient was water at pH 2.5 (A) and acetonitrile (B): 0–3 min 15% B, 3–13 min linear to 100% B. The mobile phase flow rate was 1 mL/min. BA and *p*-hydroxybenzoic was detected at 254 nm.

DMPO-adducts were analyzed using EPR (Bruker A300). The instrument settings were as follows: field sweep, 500 G; Microsoft power, 20 mW; modulation amplitude, 2.0 G; receiver gain, 6.3×10^5 ; time constant, 82 ms.

TCE was analyzed using gas chromatography (Agilent GC6820) with a headspace autosampler, a FID detector, and a $30 \text{ m} \times 0.53 \text{ mm}$ DB-5 capillary column (film thickness was 1.5 μm), using the external standard method for quantification. The temperature of injector and detector was 187 and 250 °C respectively. The initial oven temperature was 40 °C and heated at a rate of 10 °C/min to a final temperature of 140 °C.

The byproducts, chloride ion and sulfate ion, were analyzed using ion chromatography (Dionex ICS-2100) with a 4× 250 mm AS19 column. Samples were loaded onto a 250 μ L loop. The eluent was potassium hydroxide solution. The elution gradient was: 0–15 min, 8 mmol/L; 15–35 min, 8–45 mmol/L; 35–40 min, 8 mmol/L. The flow rate was 1.0 mL/min. It was necessary to filter the samples before injection to remove ferric ion and isopropanol.

Concentrations of hydrogen peroxide and sodium persulfate were monitored by using iodometric titration with 0.1 mol·L⁻¹ sodium thiosulfate [43]. For the STO system, the concentrations of oxidants determined were the sum of the two oxidants. The pH was measured for all samples, including the initial solutions. No buffer reagent was used for the experiments.

3. Results and discussion

3.1. Determination of hydroxyl radical and impact on TCE degradation

A critical aspect of these experiments that does not appear to have been discussed in prior research is the suitable BA concentration to employ when using it as a radical probe to measure HO· formation. Specifically, the radical trapping is incomplete if the BA concentration is too low. However, the preparation of high concentration BA solutions is not straightforward considering that it is a low-solubility organic compound. Hence, we explored the lowest suitable BA concentration that could provide robust results.

Hydroxyl radicals were determined from the measured *p*-hydroxybenzonic concentration [42]. The generation of radicals increased when the amount of BA increased from 1 mmol/L to 9 mmol/L, and then plateaued (Fig. S3). Thus, 9 mmol/L BA was selected as the initial probe concentration for subsequent experiments.

Fig. 1 shows the generation of radicals in the different systems. Control tests were conducted to determine HO· generation in the absence of catalyst. No measurable production was observed for the siderite-only group. A small amount of radical was produced initially for the H₂O₂·S₂O₈ group, after which no additional production was observed. The addition of the catalyst siderite greatly increased HO· generation for both the H₂O₂ and H₂O₂·S₂O₈ groups, which appeared to plateau by approximately eight hours.

The results show minimal TCE loss for the control (Fig. 2). TCE degradation efficiency in the different systems is in the following order from low to high: the non-catalyzed H₂O₂·S₂O₈ system (<10% TCE loss), the SO system (~50%), the STO treatment (essentially complete degradation). The pH changed from 8.44 to 5.99 in SO system in compared with 3.01 to 2.66 in STO system. These results clearly show the effectiveness of the binary oxidant system upon catalysis with siderite. The observation that TCE degradation continues as long as the system had HO· generation indicates that HO· contributes significantly to TCE transformation.

The STO system generated slightly more total radical than the SO system in the first several hours of the experiment. However, less TCE was degraded for the STO system during that period. In the SO system, the degradation of TCE primarily occurred in the first hour. Conversely, in the STO system, TCE was gradually degraded during the entire reaction

period. The results indicate that in the SO system, H_2O_2 decomposed quickly and released large amounts of $\text{HO}\cdot$ in a short time. Conversely, the release of $\text{HO}\cdot$ was a relatively slow and continuous process in the STO system.

Fig. 1 also illustrates that there was radical accumulation after 1 hour of reaction in the SO system. However, the degradation rate of TCE was very slow after 1 hour. If there had been $\text{HO}\cdot$ produced, there should have been concomitant TCE degradation. The explanation for this phenomenon was that $\text{HO}\cdot$ was not the primary radical produced in this period. BA can also react with $\text{HO}_2\cdot/\text{O}_2^{\cdot-}/\text{HO}_2^-$ as shown as Eq. (1)–(4), and summarized as Eq. (5). It is reported that $\text{HO}_2\cdot$ is a weak oxidant with low activity, and $\text{O}_2^{\cdot-}$ is a weak reductant [8], so their production and accumulation likely contributed minimally to TCE degradation [44].

In addition, the reaction rate constant for BA with $\text{HO}\cdot$ is $4.3 \times 10^9 \text{ M}^{-1}\text{S}^{-1}$ [45], and the quenching rate between two $\text{HO}\cdot$ is $5.2 \times 10^9 \text{ M}^{-1}\text{S}^{-1}$ [46]. These two reaction rates are much higher than the first-order reaction rate constant of TCE degradation ($6.0 \times 10^2 \text{ M}^{-1}\text{S}^{-1}$) [4]. Therefore, while the system apparently produced radicals, TCE removal was very slow due to the non-optimal radical composition.

3.2. Identification of different radicals

The STO system produces a variety of free radicals. EPR spin-trapping was used to distinguish different radicals, using DMPO as the spin trap. DMPO-radical adducts can be identified by their hyperfine coupling constant (Table 1) [29, 47–49].

The EPR spectra obtained from the DMPO experiments after 5 min reaction at $20 \pm 1^\circ\text{C}$ are presented in Fig. 3. These four-line signals showed DMPO-radical adducts in the different test systems. The results presented in Fig. 3b–d indicates the presence of DMPO-OH (peak height ratio was 1:2:2:1, $\alpha_{\text{N}} = 14.94 \text{ G}$, $\alpha_{\text{H}}^{\beta} = 14.87 \text{ G}$) in these oxidation systems. DMPO-OOH (12-line peak, $\alpha_{\text{N}} = 14.69 \text{ G}$, $\alpha_{\text{H}}^{\beta} = 11.46 \text{ G}$, $\alpha_{\text{H}}^{\gamma} = 1.33 \text{ G}$) could also be recognized when the spectra of Fig. 3b and d were amplified. The signal of DMPO-OOH was much weaker than that of DMPO-OH. This phenomenon is most likely due to the following two reasons. First, the generation of superoxide radical may be very small; second, the short half-life of DMPO-OOH. The decay of DMPO-OOH is shown as Eq. (6), where k_{decay} is $2.8 \pm 0.5 \times 10^3 \text{ M}^{-1}\text{S}^{-1}$ [50].

$$V_{\text{decay}} = nk_{\text{decay}}[\text{DMPO-OOH}]^2 \quad (6)$$

In addition, the results of previous research showed that DMPO-OOH can easily convert into DMPO-OH [51]. Therefore, the detected DMPO-OH signal may be, at least in part, the result of conversion from DMPO-OOH. The DMPO-OSO₃ signal was not detected in this reaction period. This is attributed to the fact that only a low concentration of DMPO-OSO₃ was produced in the beginning of the reaction, and that DMPO-OSO₃ is short-lived, and can decay into DMPO-OH [52, 53].

The peak intensity of the STO system was much stronger than that of the other two systems (Fig. 3). However, the HPLC results revealed that there was little difference in the amount of HO· produced between the STO and SO systems (Fig. 1). This suggests that part of the DMPO-OH signal was produced by transformation from other radicals. The production of O₂^{·-} was insignificant and can be ignored [8], and the short-lived DMPO-OSO₃ readily decays to form DMPO-OH. In total, these results suggest that the large disparity in peak intensities is due to the large quantity of SO₄^{·-} generated in the STO system. This is supported by the observation of significant production of sulfate (Fig. 4). The identification of different radicals is conducive to the further understanding of the free radical reaction mechanism.

3.3. The mechanism of radical generation

Fig. 5a illustrates the changes in the DMPO-OH signal intensity during the reaction in the SO and the STO systems. Within the first two hours of the reaction, the SO system decomposed more H₂O₂ than did the STO system (Fig. 5b). When the reaction in the SO system proceeded from the second to the fourth hour, the captured radicals had a slight decrease, but only a small amount of H₂O₂ decomposed in this time period. This shows that in the first two hours of the reaction, most of the generated hydroxyl radicals were quenched by the reactions denoted in Eq. (7) and (8) without being captured.

Therefore, the SO system will incur a waste of oxidants and thus reduced efficiency for TCE degradation. This is also a deficiency of the traditional Fenton-like reaction. Moderating the decomposition rate of the oxidant is one potential means to improve overall effectiveness.

The STO system can not only produce large amounts of hydroxyl radicals, but it also reduces the decomposition rate of the oxidants (Fig. 5). As seen from Fig. 5a, there were approximately twice as many radicals generated when adding S₂O₈²⁻ into the SO system. What's more, in the SO system, a fraction of H₂O₂ hydrolyzed or reacted with iron ions, leading to reduced formation of HO·, as shown by Eq. (9) and (10).

Hence, the addition of $\text{S}_2\text{O}_8^{2-}$ is helpful to reduce the waste of H_2O_2 caused by the reactions presented in Eq. (7)–(10), as discussed in [4].

In the first few hours of the reaction, less TCE was degraded in the STO system compared to the SO system, whereas the STO system generated slightly more total radical than the SO system as noted above. These results suggest that $\text{SO}_4^{\cdot-}$ ($E^0 = 2.6 \text{ V}$) rather than $\text{HO}^{\cdot}$ ($E^0 = 2.7 \text{ V}$) was the predominant radical in this period for the STO system, given the lower oxidation capacity of $\text{SO}_4^{\cdot-}$. This is consistent with the analysis of the EPR spin-trapping data above and the observed production of sulfate (Fig. 5), both of which support the conclusion that significant quantity of SO_4^{2-} was produced in the first few hours of the reaction for the STO system.

The use of hydrogen peroxide greatly enhanced the effectiveness of $\text{S}_2\text{O}_8^{2-}$. Non-catalyzed $\text{S}_2\text{O}_8^{2-}$ is stable under typical environmental conditions and is therefore a poor oxidant. Siderite catalysis of $\text{S}_2\text{O}_8^{2-}$ generates a very weak radical signal (Fig. 6), indicating $\text{S}_2\text{O}_8^{2-}$ decomposed at a very slow rate. However, in the H_2O_2 - $\text{S}_2\text{O}_8^{2-}$ system, more radicals were captured, and the $\text{S}_2\text{O}_8^{2-}$ decomposition rate increased, enhanced by the heat released during the decomposition of H_2O_2 .

3.4. Investigation of byproducts

In the STO system, Cl^- was released with the degradation of TCE (Fig. 7a). The production of Cl^- followed first-order kinetics (Fig. 7b). Cl^- was no longer produced when TCE was completely depleted. However, Cl^- concentration is imbalanced during the reaction, wherein the measured concentration was 35% less than the theoretical concentration of Cl^- production (3 times TCE concentration).

Indeed, the byproducts in the STO system are poorly understood. There was no chlorinated byproducts detected by gas chromatography-mass spectrometer (GC-MS) method [5]. The IC method was used herein to analyze for byproducts. Dichloroacetic acid and formic acid were detected as the byproducts in both the SO and the STO systems (Fig. 8). There was no other chlorinated byproduct (eg. chloroacetic acid and trichloroacetic acid) detected in either of these two systems.

The STO system produced more dichloroacetic acid compared with that of the SO system (Fig. 9), although the latter system had a relatively lower chlorine balance ratio. In addition, the amount of dichloroacetic acid did not increase once TCE was no longer degraded in the SO system or when TCE was completely degraded in the STO system, which suggests that dichloroacetic acid was directly converted from TCE's electrophilic addition reaction, as shown in Eq. (11).

Dichloroacetic acid accumulated and could not be removed during the reaction. Complete Cl^- balance still could not be attained when accounting for the Cl^- in dichloroacetic acid coupled with the detected Cl^- concentration at the end of the reaction (Table 2). Therefore, other chlorine-containing substances may be formed, and/or there may have been loss of other chlorinated volatile products, which needs further investigation.

4. Conclusions

The radicals formed and the operative mechanisms were investigated for the catalytic STO system, using HPLC and EPR spin-trapping methods. Four radicals $\text{HO}\cdot$, $\text{SO}_4^{\cdot-}$, $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$ were identified in STO system. Both $\text{HO}\cdot$ and $\text{SO}_4^{\cdot-}$ were effective radicals to oxidize TCE. The release of $\text{HO}\cdot$ was a relatively slow and sustainable process in the STO system, compared with that of the SO system. Under current experiment conditions, TCE was removed completely, for $\text{HO}\cdot$ was generated in the whole reaction period. However, in the SO system, a large amount of H_2O_2 was decomposed in the first 1 hour, resulting in an inefficient use of $\text{HO}\cdot$, and TCE could not be removed effectively in this system. $\text{SO}_4^{\cdot-}$ was mainly produced in the first 2 hours, and was the dominant effective radical in this period. Under catalytic conditions, $\text{S}_2\text{O}_8^{2-}$ could slow down the decomposition of H_2O_2 , and the heat released by the decomposition of H_2O_2 could also accelerate the decomposition of $\text{S}_2\text{O}_8^{2-}$, which overcomes the disadvantage of using one oxidant alone. Dichloroacetic acid, a chlorinated byproduct, was detected in the STO system, and it could not be degraded during the reaction. To our knowledge, this is the first report of a chlorinated byproduct in the STO system, which is an important element for analysis of chlorine balance and the understanding of the degradation mechanism. These results provide significant insights for efficient TCE removal in groundwater environment. More detailed work (such as detection of other byproducts) is in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was financially supported by the Fundamental Research Funds for the Central Universities (2652013024), National Natural Science Foundation of China (NSFC) (41172226), and the project from the China Geological Survey (1212011121171). The contributions of Dr. Brusseau were supported by the NIEHS Superfund Research Program (ES04940). We acknowledge Yanqing Zhao and Mengjiao Li for their help during the study.

Abbreviations

SO	siderite-catalyzed hydrogen peroxide oxidant
STO	siderite-catalyzed two oxidants (hydrogen peroxide and persulfate)

References

1. Tsitonaki A, Petri B, Crimi M, Mosbæk H, Siegrist RL, Bjerg PL. In situ chemical oxidation of contaminated soil and groundwater using persulfate: a review. *Crit Rev Environ Sci Technol*. 2010; 40:55–91.
2. Krembs FJ, Siegrist RL, Crimi ML, Furrer RF, Petri BG. ISCO for groundwater remediation: Analysis of field applications and performance. *Ground Water Monit Rem*. 2010; 30:42–53.
3. Brusseau M, Carroll KC, Allen T, Baker J, DiGuseppi W, Hatton J, Morrison C, Russo A, Berkompas J. Impact of in situ chemical oxidation on contaminant mass discharge: linking source-zone and plume-scale characterizations of remediation performance. *Environ Sci Technol*. 2011; 45:5352–5358. [PubMed: 21615133]
4. Yan N, Liu F, Huang W. Interaction of oxidants in siderite catalyzed hydrogen peroxide and persulfate system using trichloroethylene as a target contaminant. *Chem Eng J*. 2013; 219:149–154.
5. Huang W, Liu F, Yan N, Lu A, Chen H, Chen L, Wang F. Removal of trichloroethylene in groundwater with two oxidants: siderite catalyzed hydrogen peroxide and sodium persulfate. *Water Sci Technol: Water Supply*. 2012; 13:36–43.
6. Block, PA.; Brown, RA.; Robinson, D. Novel activation technologies for sodium persulfate in situ chemical oxidation. *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*; Monterey, CA. 2004;
7. Ko S, Crimi M, Marvin BK, Holmes V, Huling SG. Comparative study on oxidative treatments of NAPL containing chlorinated ethanes and ethenes using hydrogen peroxide and persulfate in soils. *J Environ Manage*. 2012; 108:42–48. [PubMed: 22658989]
8. Ciotti C, Baciocchi R, Tuhkanen T. Influence of the operating conditions on highly oxidative radicals generation in Fenton's systems. *J Hazard Mater*. 2009; 161:402–408. [PubMed: 18468791]
9. Ahuja DK, Bachas LG, Bhattacharyya D. Modified fenton reaction for trichlorophenol dechlorination by enzymatically generated H_2O_2 and gluconic acid chelate. *Chemosphere*. 2007; 66:2193–2200. [PubMed: 17166556]
10. Rokhina EV, Golovina EA, As H, Virkutyte J. ESR ST study of hydroxyl radical generation in wet peroxide system catalyzed by heterogeneous ruthenium. *Chemosphere*. 2009; 77:148–150. [PubMed: 19487011]
11. Miller CJ, Rose AL, Waite TD. Hydroxyl Radical Production by H_2O_2 -Mediated Oxidation of Fe (II) Complexed by Suwannee River Fulvic Acid Under Circumneutral Freshwater Conditions. *Environ Sci Technol*. 2012; 47:829–835. [PubMed: 23231429]
12. Fang G, Gao J, Dionysiou DD, Liu C, Zhou D. Activation of persulfate by quinones: free radical reactions and implication for the degradation of PCBs. *Environ Sci Technol*. 2013; 47:4605–4611. [PubMed: 23586773]
13. Yuan S, Mao X, Alshawabkeh AN. Efficient degradation of TCE in groundwater using Pd and electro-generated H_2 and O_2 : a shift in pathway from hydrodechlorination to oxidation in the presence of ferrous ions. *Environ Sci Technol*. 2012; 46:3398–3405. [PubMed: 22315993]
14. Hayon E, Treinin A, Wilf J. Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfite systems. SO_2^- , SO_3^- , SO_4^- , and SO_5^- radicals. *J Am Chem Soc*. 1972; 94:47–57.
15. Chawla OP, Fessenden RW. Electron spin resonance and pulse radiolysis studies of some reactions of peroxysulfate ($SO_4^{\cdot-1, 2}$). *J Phys Chem*. 1975; 79:2693–2700.
16. Jensen DL, Boddum JK, Tjell JC, Christensen TH. The solubility of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) in anaerobic aquatic environments. *Appl Geochem*. 2002; 17:503–511.
17. Teel AL, Ahmad M, Watts RJ. Persulfate activation by naturally occurring trace minerals. *J Hazard Mater*. 2011; 196:153–159. [PubMed: 21968122]
18. Teel AL, Warberg CR, Atkinson DA, Watts RJ. Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Res*. 2001; 35:977–984. [PubMed: 11235893]
19. Chen K, Kao C, Wu L, Surampalli R, Liang S. Methyl tert-butyl ether (MTBE) degradation by ferrous ion-activated persulfate oxidation: feasibility and kinetics studies. *Water Environ Res*. 2009; 81:687–694. [PubMed: 19691249]

20. Xu L, Wang J. Fenton-like degradation of 2, 4-dichlorophenol using Fe_3O_4 magnetic nanoparticles. *Appl Catal B: Environ.* 2012; 123–124:117–126.
21. Pinto IS, Pacheco PH, Coelho JV, Lorençon E, Ardisson JD, Fabris JD, de Souza PP, Krambrock KW, Oliveira LC, Pereira MC. Nanostructured $\delta\text{-FeOOH}$: an efficient Fenton-like catalyst for the oxidation of organics in water. *Appl Catal B: Environ.* 2012; 119–120:175–182.
22. Mitsika EE, Christophoridis C, Fytianos K. Fenton and Fenton-like oxidation of pesticide acetamiprid in water samples: Kinetic study of the degradation and optimization using response surface methodology. *Chemosphere.* 2013; 93:1818–1825. [PubMed: 23871596]
23. Rao Y, Qu L, Yang H, Chu W. Degradation of Carbamazepine by Fe (II)-Activated Persulfate Process. *J Hazard Mater.* 2014; 268:23–32. [PubMed: 24462988]
24. Zepp RG, Faust BC, Hoigne J. Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron (II) with hydrogen peroxide: the photo-Fenton reaction. *Environ Sci Technol.* 1992; 26:313–319.
25. Jen J, Leu MF, Yang TC. Determination of hydroxyl radicals in an advanced oxidation process with salicylic acid trapping and liquid chromatography. *J Chromatogr A.* 1998; 796:283–288.
26. Kwan WP, Voelker BM. Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environ Sci Technol.* 2003; 37:1150–1158. [PubMed: 12680668]
27. Cheng SA, Fung WK, Chan KY, Shen P. Optimizing electron spin resonance detection of hydroxyl radical in water. *Chemosphere.* 2003; 52:1797–1805. [PubMed: 12871746]
28. Kim J, Metcalfe I. Investigation of the generation of hydroxyl radicals and their oxidative role in the presence of heterogeneous copper catalysts. *Chemosphere.* 2007; 69:689–696. [PubMed: 17604820]
29. Rangelova K, Rice AB, Khajo A, Triquigneaux M, Garantziotis S, Magliozzo RS, Mason RP. Formation of reactive sulfite-derived free radicals by the activation of human neutrophils: An ESR study. *Free Radic Biol Med.* 2012; 52:1264–1271. [PubMed: 22326772]
30. Hernández-Alonso, MaD; Hungría, AB.; Martínez-Arias, A.; Fernández-García, M.; Coronado, JM.; Conesa, JC.; Soria, J. EPR study of the photoassisted formation of radicals on CeO_2 nanoparticles employed for toluene photooxidation. *Appl Catal B: Environ.* 2004; 50:167–175.
31. Robert R, Barbat S, Ricq N, Ambrosio M. Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterization of hydrogen peroxide. *Water Res.* 2002; 36:4821–4829. [PubMed: 12448525]
32. Duling DR. Simulation of multiple isotropic spin-trap EPR spectra. *J Magn Reson Series B.* 1994; 104:105–110.
33. Villamena FA, Merle JK, Hadad CM, Jay L. Superoxide radical anion adduct of 5, 5-dimethyl-1-pyrroline N-oxide (DMPO). 2. The thermodynamics of decay and EPR spectral properties. *J Phys Chem A.* 2005; 109:6089–6098. [PubMed: 16833946]
34. Finkelstein E, Rosen GM, Rauckman EJ. Spin trapping of superoxide and hydroxyl radical: practical aspects. *Arch Biochem Biophys.* 1980; 200:1–16. [PubMed: 6244786]
35. Zhou N, Qiu T, Yang-ping L, Yang L. Superoxide anion radical generation in the $\text{NaOH}/\text{H}_2\text{O}_2/\text{Fe}$ (III) system: a spin trapping ESR study. *Magn Reson Chem.* 2006; 44:38–44. [PubMed: 16302167]
36. Han SK, Hwang TM, Yoon Y, Kang JW. Evidence of singlet oxygen and hydroxyl radical formation in aqueous goethite suspension using spin-trapping electron paramagnetic resonance (EPR). *Chemosphere.* 2011; 84:1095–1101. [PubMed: 21561642]
37. Gabriel J, Baldrian P, Verma P, Cajthaml T, Merhautová V, Eichlerová I, Stoytchev I, Trnka T, Stopka P, Nerud F. Degradation of BTEX and PAHs by Co (II) and Cu (II)-based radical-generating systems. *Appl Catal B: Environ.* 2004; 51:159–164.
38. Yuan S, Liao P, Alshawabkeh AN. Electrolytic Manipulation of Persulfate Reactivity by Iron Electrodes for TCE Degradation in Groundwater. *Environ Sci Technol.* 2013; 48:656–663. [PubMed: 24328192]
39. Stroo HF, Leeson A, Marqusee JA, Johnson PC, Ward CH, Kavanaugh MC, Sale TC, Newell CJ, Pennell KD, Lebrón CA. Chlorinated ethene source remediation: Lessons learned. *Environ Sci Technol.* 2012; 46:6438–6447. [PubMed: 22558915]

40. U.S. Environmental Protection Agency (EPA). Edition of the Drinking Water Standards and Health Advisories. Washington, DC: 2009. EPA 822-R-09-011
41. U.S. Environmental Protection Agency (EPA). Support of Summary Information on the Integrated Risk Information System (IRIS). Washington, DC: 2011. Toxicological Review of Trichloroethylene (CAS No. 79-01-6). EPA/635/R-09/011F
42. Lindsey ME, Tarr MA. Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. *Chemosphere*. 2000; 41:409–417. [PubMed: 11057603]
43. Schumb, WC.; Satterfield, CN. Hydrogen peroxide. Wentworth, RL., editor. American Chemical Society, Rienholt Publishing; New York: 1955. p. 557-558.
44. Walling C. Fenton's reagent revisited. *Acc Chem Res*. 1975; 8:125–131.
45. Kwon BG, Kwon JH. Measurement of the hydroxyl radical formation from H_2O_2 , NO_3^- , and Fe(III) using a continuous flow injection analysis. *J Ind Eng Chem*. 2010; 16:193–199.
46. Masomboon N, Ratanatamskul C, Lu MC. Kinetics of 2, 6-dimethylaniline oxidation by various Fenton processes. *J Hazard Mater*. 2011; 192:347–353. [PubMed: 21645969]
47. Mottley C, Mason RP. Sulfate anion free radical formation by the peroxidation of (bi) sulfite and its reaction with hydroxyl radical scavengers. *Arch Biochem Biophys*. 1988; 267:681–689. [PubMed: 2850769]
48. Furman OS, Teel AL, Watts RJ. Mechanism of base activation of persulfate. *Environ Sci Technol*. 2010; 44:6423–6428. [PubMed: 20704244]
49. Fang GD, Dionysiou DD, Al-Abed SR, Zhou DM. Superoxide radical driving the activation of persulfate by magnetite nanoparticles: Implications for the degradation of PCBs. *Appl Catal B: Environ*. 2013; 129:325–332.
50. Dikalov S, Khramtsov V, Zimmer G. Determination of rate constants of the reactions of thiols with superoxide radical by electron paramagnetic resonance: critical remarks on spectrophotometric approaches. *Arch Biochem Biophys*. 1996; 326:207–218. [PubMed: 8611025]
51. Finkelstein E, Rosen GM, Rauckman EJ. Production of hydroxyl radical by decomposition of superoxide spin-trapped adducts. *Mol Pharmacol*. 1982; 21:262–265. [PubMed: 6285165]
52. Davies MJ, Gilbert BC, Stell JK, Whitwood AC. Nucleophilic substitution reactions of spin adducts. Implications for the correct identification of reaction intermediates by EPR/spin trapping. *J Chem Soc, Perkin Trans*. 1992; 2:333–335.
53. Zalibera M, Rapta P, Staško A, Brindzová L, Brezová V. Thermal generation of stable spin trap adducts with super-hyperfine structure in their EPR spectra: An alternative EPR spin trapping assay for radical scavenging capacity determination in dimethylsulphoxide. *Free Radic Res*. 2009; 43:457–469. [PubMed: 19353392]

Appendix A. Supplementary data

Supplementary data related to this article can be found at “Supporting Information” File.

Fig. 1.

The generation of radicals in different systems. The initial reaction conditions: siderite = 11.45 g/L, [BA] = 9 mmol/L, [H₂O₂] = 0.15 mol/L, [Na₂S₂O₈] = 6.3 mmol/L.

Fig. 2. TCE removal in different systems. The inset shows the complete experiment time. The initial reaction conditions: siderite= 11.45 g/L, [TCE] = 11.15 mmol/L, [H_2O_2] = 0.15 mol/L, [$\text{Na}_2\text{S}_2\text{O}_8$] = 6.3 mmol/L.

Fig. 3.

EPR spectra obtained from DMPO experiments after 5 min reaction at 20 ± 1 °C reaction temperature. The initial reaction conditions: siderite = 11.45 g/L (a), siderite = 11.45 g/L, [H₂O₂] = 0.15 mol/L (b), siderite = 11.45 g/L, [Na₂S₂O₈] = 6.3 mmol/L (c) and siderite = 11.45 g/L, [Na₂S₂O₈] = 6.3 mmol/L, [H₂O₂] = 0.15 mol/L (d).

Fig. 4.

Generation of sulfate ion in the STO system. The initial reaction conditions: siderite = 11.45 g/L, $[\text{Na}_2\text{S}_2\text{O}_8] = 6.3 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 0.15 \text{ mol/L}$.

Fig. 5. Changes of the DMPO-OH signal intensity during the reaction in the SO and the STO system (a) and oxidants remaining in the SO and the STO system (b). The initial reaction conditions: siderite = 11.45 g/L, $[\text{Na}_2\text{S}_2\text{O}_8] = 6.3 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 0.15 \text{ mol/L}$.

Fig. 6.

EPR spectra obtained from DMPO experiments. Siderite-catalyzed $\text{S}_2\text{O}_8^{2-}$ system after 1 h reaction (a), siderite-catalyzed $\text{S}_2\text{O}_8^{2-}$ system after 2 h reaction (b), STO system after 1 h reaction (c) and STO system after 2 h reaction (d). The initial reaction conditions: siderite = 11.45 g/L, $[\text{Na}_2\text{S}_2\text{O}_8] = 6.3 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 0.15 \text{ mol/L}$.

Fig. 7. Chloride ion generation and TCE removal in the STO system (a) and generation of chloride ion in the STO system was the first order reaction (b). The initial reaction conditions: siderite= 11.45 g/L, $[Na_2S_2O_8]$ = 6.3 mmol/L, $[H_2O_2]$ = 0.15 mol/L.

Fig. 8. IC spectrum of the SO system (a) and IC spectrum of the STO system (b). The initial reaction conditions: siderite = 11.45 g/L, [Na₂S₂O₈] = 6.3 mmol/L, [H₂O₂] = 0.15 mol/L.

Fig. 9.

The generation of dichloroacetic acid in the siderite-catalyzed systems. The initial reaction conditions: siderite = 11.45 g/L, $[\text{Na}_2\text{S}_2\text{O}_8] = 6.3 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 0.15 \text{ mol/L}$.

Table 1

Hyperfine coupling constant values of DMPO adducts

Adduct	a_N	a_H^{β}	$a_H^{\gamma 1}$	$a_H^{\gamma 2}$
HO·	14.9	14.9		
HOO·/O ₂ · ⁻	14.3	11.2	1.3	
SO ₄ · ⁻	13.7	10.1	1.42	0.75

Table 2

Chloride balance in different systems for all chlorine-containing substance

System	Cl ⁻ (mmol/L)	Removed TCE (mmol/L)	Chlorine Balance Ratio ^a (%)	Mineralization Ratio ^b (%)
SO	5.99	5.24	38.10	17.91
STO	21.66	11.15	64.75	64.75

$$^a \text{Chlorine Balance Ratio} = \frac{C_{Cl^-}}{3 \times TCE_{Removed}} \times 100\%$$

$$^b \text{Mineralization Ratio} = \frac{C_{Cl^-}}{3 \times TCE_{Total}} \times 100\%$$