

Removal of trichloroethylene in groundwater with two oxidants: siderite catalyzed hydrogen peroxide and sodium persulfate

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ABSTRACT

Trichloroethylene (TCE), a widely used solvent, is often determined in groundwater and is one of biologically refractory organic contaminants. The aim of the study is to use a new chemical oxidation method to degrade TCE source pollution in groundwater. Fenton-like reactions (hydrogen peroxide catalyzed by iron minerals generates hydroxyl radicals) and sodium persulfate activation (sodium persulfate activated by heat/iron minerals to produce sulfate radicals) have strong oxidative capacity to degrade a wide range of organic contaminants. In this work, hydrogen peroxide and/or sodium persulfate catalyzed by siderite (designated as STO, SO, PO systems, respectively) degrading TCE in groundwater were investigated. Removal rates of TCE in STO, SO, and PO systems were 100%, 57%, 20%, respectively. The order of TCE removal rates is in agreement with that of hydroxyl radicals generated in the systems, indicating that hydroxyl radicals play a critical role in removing TCE. No by-product except CO₂, Cl⁻ and H₂O generated as final products in the STO system suggests that TCE was near completely mineralized. The results show that the STO is an effective method to treat TCE contaminated source in groundwater.

Key words | hydroxyl radicals, *in situ* chemical oxidation, radical, source pollution

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NOTATION

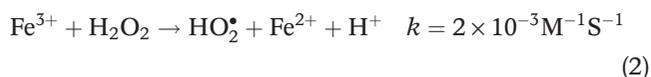
STO	Siderite catalyzed two oxidants (hydrogen peroxide and persulfate)
SO	Siderite catalyzed hydrogen peroxide oxidant
PO	Siderite catalyzed persulfate oxidant
PRB	Permeable reactive barriers
TCA	Trichloroethane
VC	Vinyl chloride
DCEs	Cis-1, 2-dichloroethylene and 1,1-dichloroethylene
DNAPL	Dense non-aqueous phase liquid
TCE	Trichloroethylene
SOM	Soil organic matter
ISCO	<i>In situ</i> chemical oxidation

INTRODUCTION

Trichloroethylene (TCE) as a good organic solvent is widely used in metal degreasing and clothes dry cleaning, and is a common pollutant determined in groundwater of many developed and developing countries (Folkard 1986). It exists in the groundwater usually as dense non-aqueous phase liquid (DNAPL), which slowly dissolves into groundwater (forming a contaminated source). TCE and its biological metabolic intermediates (such as trichloroethane (TCA), vinyl chloride (VC), cis-1, 2-dichloroethylene and 1,1-dichloroethylene (DCEs)) have been considered as potential carcinogenic, teratogenic and mutagenic substances (Lock & Reed 2006). The problem of TCE

contamination poses a significant threat to public drinking water safety.

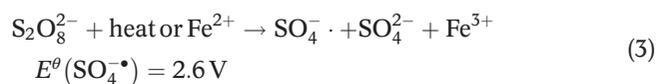
The most common *in situ* technologies include air sparging, bioremediation, chemical treatment, permeable reactive barriers (PRB), and multi-phase extraction. Bioremediation and air sparging account for more than half of all *in situ* groundwater treatment projects, but in recent years bioremediation and chemical treatment have become more common. For the biologically refractory organic compounds, chemical treatment is typically applied as an aggressive technology that requires a relatively short treatment time to achieve clean-up goals (US EPA 2007). *In situ* chemical oxidation (ISCO) is an effective and rapid method used to treat environmental contaminants in soil and/or groundwater. Fenton's reagent (forms of hydrogen peroxide and ferrous ions) which generates hydroxyl radicals (HO•) with a strong oxidative ability is commonly used in ISCO. Fenton reactions can be described as follows (Walling 1975):



However, Fenton reactions proceed rapidly and hydrogen peroxide decomposes quickly, releasing an excessive amount of heat and gas that may threaten the structural stability of the groundwater and soil, as well as the safety of indigenous biology (Mecozzi *et al.* 2006). In order to control the process and intensity of Fenton reactions, chelators such as citrate, phosphate and cyclodextrin were commonly used to chelate ferrous ions in the solution to regulate the free ferrous ions which can catalyze hydrogen peroxide decomposition (Watts *et al.* 2007; Seol & Javandel 2008; Smith *et al.* 2009). However, the price of the chelators is generally much more expensive than hydrogen peroxide (three to six times). In 1990, Tyre and coworkers found naturally occurring iron minerals can also catalyze hydrogen peroxide to generate HO•. The types of reactions are referred to as Fenton-like reactions (Tyre *et al.* 1991). Fenton-like reactions are relatively

milder than Fenton reactions. Another problem arises that the removal efficiency of TCE by Fenton-like reactions is much lower than that by Fenton reactions. The comparison of the Fenton reactions to degrade TCE and the Fenton-like reactions was conducted by Smith and coworkers (Smith *et al.* 2009), who found that the Fenton reactions and the Fenton-like reactions removed 78 and 25% of TCE, respectively.

Sodium persulfate as a new oxidant has been used to degrade refractory pollutants in ISCO (Crimi & Taylor 2007). Sodium persulfate is more stable than hydrogen peroxide. It can be transported a longer distance in groundwater. Furthermore, sodium persulfate is cheaper than hydrogen peroxide. Thus, the remediation will be less costly if it is used together with hydrogen peroxide. Sodium persulfate can be activated by heat or transition metals to produce the sulfate radical (SO₄•⁻) (Equation (3)) with oxidative ability just after HO• ($E^\theta(\text{OH}\cdot) = 2.7\text{V}$) (Huie *et al.* 1991; Anipsitakis & Dionysiou 2004).



Hydrogen peroxide mixed with sodium persulfate was used successfully to degrade chloride solvents (TCE, DCEs, etc.) by FMC (Block *et al.* 2004). The US EPA (Jack Riggensbach *et al.* 2009) has remediated an approximately 280 m² field site contaminated with chlorinated solvent by injecting 0.7% Fe-EDTA catalyzed 10.6% of sodium persulfate 42,750 L, 8.4% hydrogen peroxide 7,250 L, 6% of potassium permanganate 2,500 L into the wells, respectively. The final pollutant concentrations were below the limit of detection or the safe dose levels. However, potassium permanganate will plug porosity of groundwater and affect mass transfer (Siegrist *et al.* 2002). The usage of siderite catalyzed hydrogen peroxide and sodium persulfate to remove TCE can avoid the use of potassium permanganate and obtain the same good removal efficiency.

This study is aimed at examining siderite catalyzed hydrogen peroxide and/or sodium persulfate to degrade TCE DNAPL. The yield of hydroxyl radicals was quantified and the reaction mechanism of TCE degraded was investigated.

METHODS

Chemicals

Siderite (FeCO_3) was purchased from steel institution of Wuhan Iron and Steel (Group) Corporation, China. The particle size of the siderite was less than 0.088 mm. Hydrogen peroxide (30%), TCE, benzoic acid, sulfuric acid, sodium thiosulfate, sodium persulfate, potassium iodide, isopropanol were obtained from Beijing Chemical Plant. All chemicals were analytical grade and used as received.

Experimental methodology

Experimental design

All experiments were performed in 20 mL borosilicate vials fitted with PTFE septum caps. **SO system:** The vials of the first set were added 0.1267 g of siderite, followed by 5 mL of deionized water, and then 10 μL of pure TCE (>99%) was injected to the bottom of the solution (TCE existed as DNAPL), subsequently a pulse input of 5 mL of 0.3 $\text{mol}\cdot\text{L}^{-1}$ hydrogen peroxide and then they were capped immediately. **Siderite alone system:** The constituents added in the second set of vials were similar to the first set except that 5 mL of deionized water was used to replace hydrogen peroxide. **Hydrogen peroxide alone system:** Without adding any siderite, the other reagents in the third set were the same as the first set. **Control system:** The fourth set was added 10 μL of pure TCE and 10 mL of deionized water for monitoring the loss of TCE by volatilization throughout the experiment.

PO system: The same amount of siderite as mentioned above was added into the vials of the fifth set, 7 mL of deionized water and 3 mL of 0.021 $\text{mol}\cdot\text{L}^{-1}$ sodium persulfate were added (the adding volume was set according to the previous experiment), and then the same amount of TCE was injected into the bottom of the solution and capped. **Persulfate alone system:** Without adding any siderite, the other components of the sixth set were the same as the fifth set.

STO system: The same amount of siderite was added into the vials of the seventh set, 2 mL of deionized water and 3 mL

of 0.021 $\text{mol}\cdot\text{L}^{-1}$ sodium persulfate were added, and then the same amount of TCE was injected into the bottom of the solution, and 5 mL of hydrogen peroxide was added and the vials were capped. The initial concentration of sodium persulfate in PO and STO systems was 0.0063 $\text{mol}\cdot\text{L}^{-1}$.

At each time point interval, triplicates from each system were injected 5 mL of isopropanol to stop TCE from reaction with oxidants and the residual TCE was analyzed.

Hydroxyl radical production

The quantities of all components in the major systems above (PO, SO, STO systems) were magnified 10 times except that the deionized water was replaced by 50 mL of scavenger benzoic acid (concentration of 9 $\text{mmol}\cdot\text{L}^{-1}$, according to the literature (Lindsey & Tarr 2000)). As for the STO system, the concentrations of hydrogen peroxide and sodium persulfate were multiplied by two to decrease the added volume. All the systems contained 50 mL of benzoic acid solution and the total volume of the solution of each system was 100 mL.

Analysis

The remaining TCE and by-product of TCE degradation were analyzed using the methods provided in this study (Huang *et al.* 2010). Concentrations of hydrogen peroxide and sodium persulfate were monitored by iodometric titration with 0.1 $\text{mol}\cdot\text{L}^{-1}$ sodium thiosulfate (Schumb & Stratterfield 1955). For the STO system, the concentrations of oxidants determined were the sum of the two oxidants. The iron ions were analyzed using phenantroline method. The silver nitrate titration method was used to determine the amount of chlorides released from TCE. The yield of hydroxyl radicals in the above systems were quantified with the method described by Lindsey & Tarr (2000).

RESULTS AND DISCUSSION

TCE degradation

The loss of TCE in the control system over the period of the experiment was less than 15%. The removal rates of TCE in

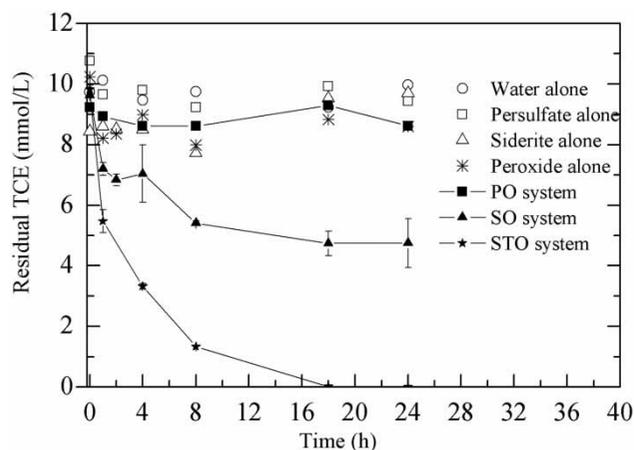


Figure 1 | TCE degradation in the SO, PO, STO systems and their comparative systems.

the SO, PO, STO systems were 57%, 20%, 100%, respectively (Figure 1). When hydrogen peroxide, sodium persulfate or siderite was used alone, the removal of TCE was far lower than when they were used together. These

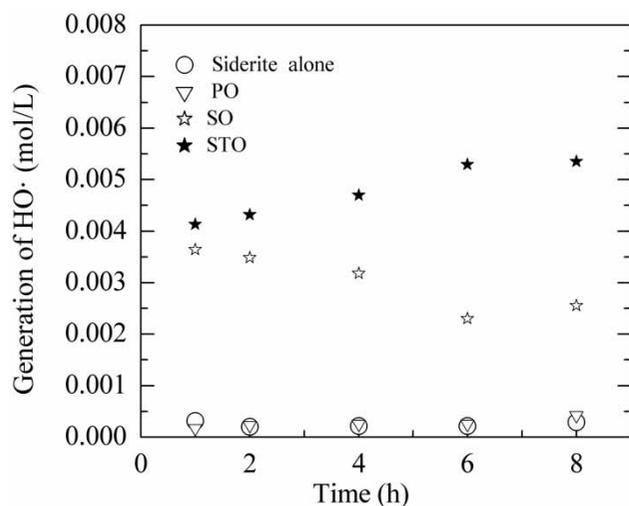


Figure 2 | Generation of HO[•] in the SO, PO, STO systems and their comparative systems.

results indicate that oxidative radicals produced in PO, SO, STO system were in an increasing order.

Reaction mechanism

Hydroxyl radical generation

The mechanism of Fenton reactions involving radicals (such as HO[•], O₂^{-•}, and HO₂[•]) has been proposed in the study (Haber & Weiss 1934). However, the lives of these radicals are very short; the quantitative determination each of them is difficult. Therefore, the primary radical was quantified in this research. According to Equations (1)–(3), HO[•], O₂^{-•}, HO₂[•], and SO₄^{-•} could be produced in SO and STO systems. Since the initial concentration of sodium persulfate added in the STO system was an order of magnitude lower than that of hydrogen peroxide, the yield of SO₄^{-•} could be negligible. HO₂[•] is a weak oxidant and O₂^{-•} a reducing agent unreactive with most organic compounds (Smith *et al.* 2009). Thus, HO[•] was the primary radical in the SO and the STO systems. Benzoic acid was used as a probe to capture HO[•]. The reaction produces *p*-hydroxyl benzoic acid and other derivatives. Per mole of *p*-hydroxyl benzoic acid produced needs 5.87 ± 0.18 moles HO[•] reacted (Lindsey & Tarr 2000). The amount of HO[•] formation in the comparative systems is shown in Figure 2.

The production of HO[•] in the STO system was 5.35×10^{-3} mol, the highest amount among the systems, which is consistent with the largest of TCE removed in the system. The results imply that TCE was degraded mainly through a hydroxyl radical oxidation mechanism. On the contrary, there was few HO[•] produced in the siderite alone system and in the PO system. This can explain the observation that little TCE was degraded in the two systems.

Table 1 | Concentrations of constituents in the SO and STO systems initial and after the oxidation process

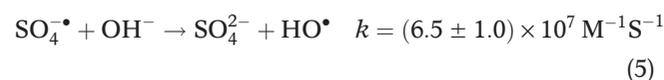
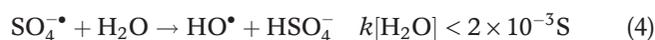
	Initial reaction (mmol·L ⁻¹)						After reaction (mmol·L ⁻¹)					
	Oxidant	TCE	pH	Fe ²⁺	Fe ³⁺	Cl ⁻	Oxidant	TCE	pH	Fe ²⁺	Fe ³⁺	Cl ⁻
SO	150.	11.15	8.40	0.0098	0.020	0	35.0	4.83	5.99	0.00	1.35	7.0
STO	161.0	11.15	2.76	0.015	0.012	0	70.1	0	3.38	1.05	1.43	20.35
SO ^a	150	11.15	2.75	0.017	0.012	0	60.3	3.13	2.50	0.86	0.51	11.30

Note: SO^a system, by adding acid or base at concentrations as high as 3 mol L⁻¹ for neglecting the volume added.

Effect of sodium persulfate

The TCE removed and Cl^- released in the STO system were much more than that in the SO system (Table 1). The difference between the two is that the SO system had one oxidant (hydrogen peroxide) and the STO system had two oxidants (hydrogen peroxide and sodium persulfate) and that the pH value found in the SO system was much higher than that in the STO system (Table 1). To demonstrate the effect of sodium persulfate on degrading TCE, we performed additional experiments at which the pH values and the composition were the same as the STO system except that sodium persulfate was absent (SO^a system).

The Cl^- release in the SO^a system was slightly higher than that in the SO system. Whereas, the Cl^- release in the SO^a systems was much less than that in the STO system, which is evidence that the sodium persulfate rather than pH has an important effect on hydrogen peroxide degradation of TCE. Sodium persulfate will produce $\text{SO}_4^{\cdot-}$ under reaction (3), and $\text{SO}_4^{\cdot-}$ will produce $\text{HO}\cdot$ via reaction (4) and (5) (Hayon *et al.* 1972; Chawla & Fessenden 1975).



Evidence of TCE degradation

There was not any other by-product generated during the oxidation process in the STO system except oxygen (possibly produced by hydrogen peroxide decomposition), carbon dioxide and chloride (Figure 3 and Table 1). The chloride balance of TCE in SO and STO systems was 58.0 and 60.8%, respectively (chloride balance = the amount of chloride release / (3 * the amount of TCE removed), which was calculated according to the data in Table 1). The reason as to why the chloride balance in the two systems did not reach 100% may be due to TCE loss by volatilization. Theoretically, TCE degraded into CO_2 , Cl^- , and H_2O is possible via a series of transformation, such as the hydroxyl radical electrophilic addition with TCE, the carbon-carbon single bond break, O_2^- and other reactive oxygen species

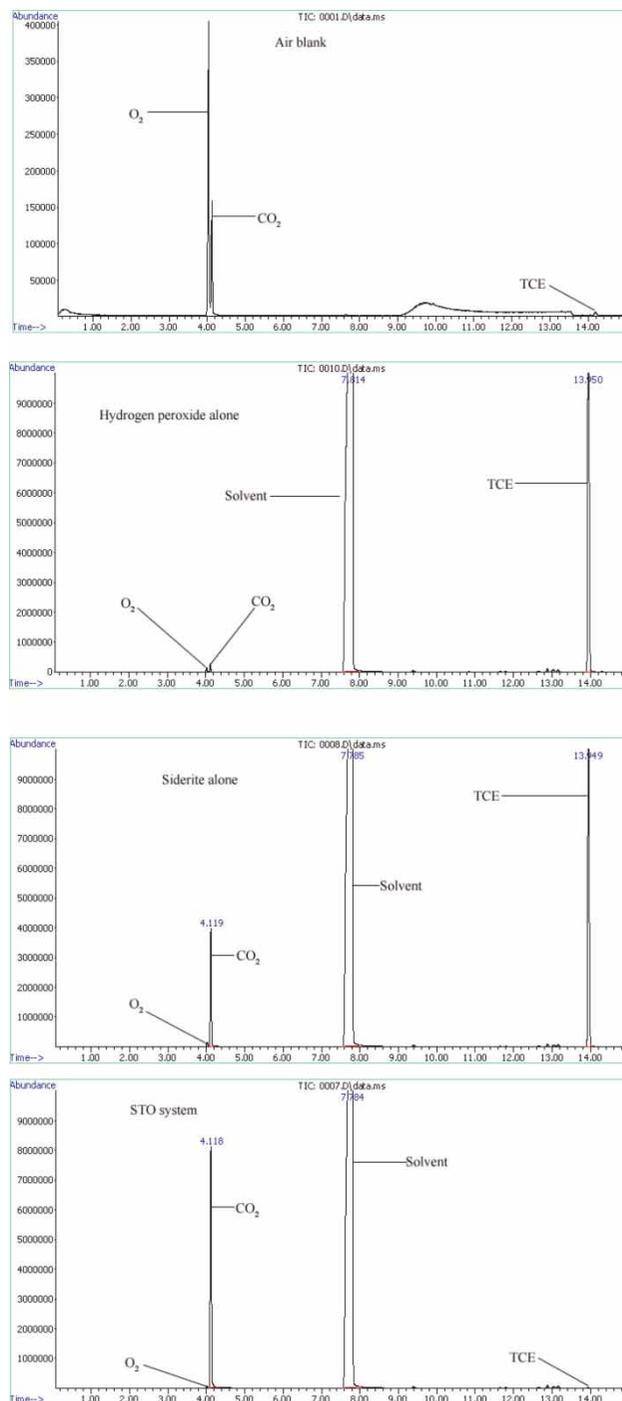


Figure 3 | Final products of TCE degradation with the STO system, the solvent is isopropanol.

nucleophilic substitution Cl , and then dehydration reaction. This TCE degradation mechanism will be proven until intermediates of TCE degradation are detected. However, another tool (gas chromatography-mass spectrometry) was

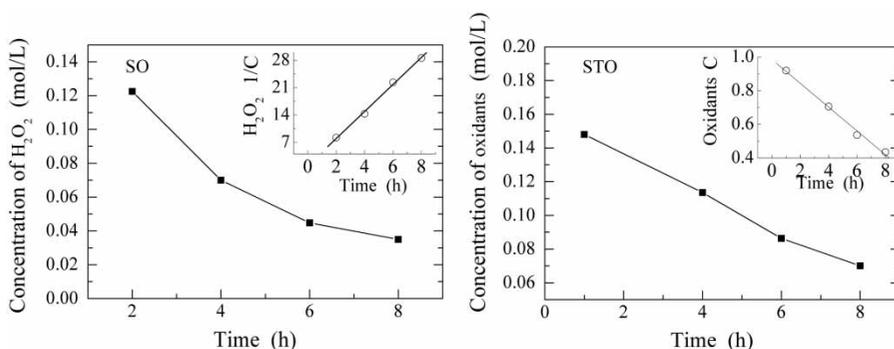


Figure 4 | Decomposition of the oxidants in the SO and STO systems.

used to provide evidence for no intermediates of TCE (such as TCA, DCEs or VC) were generated in the systems. Thus, the determinations of intermediates of TCE transformation need further study.

pH effect on oxidants decomposition

Hydrogen peroxide decomposition in the SO systems and the STO system is shown in [Figure 4](#). The data of hydrogen peroxide decomposition in the SO system can be modeled using the second-order kinetics with a R^2 greater than 0.96 and a reaction rate constant k of $0.0004 \text{ M}^{-1}\text{S}^{-1}$, half-life of 3.06 h. Whereas, the decomposition of hydrogen peroxide and sodium persulfate in the STO system obeys the zero-order kinetics with a R^2 greater than 0.99, k of $3 \times 10^{-6} \text{ MS}^{-1}$ and with a half-life of 7.4 h. The half-life of the two oxidants (primary hydrogen peroxide) in the STO system increases by a factor of 2 as compared to the half-life of hydrogen peroxide in the SO system. The result shows that hydrogen peroxide decomposed in the STO system much slower than that in the SO system, which possibly results from the effect of pH. In acidic pH, hydrogen peroxide will have a longer life time than in neutral and basic pH under the same catalyst ([Barreiro *et al.* 2007](#)). Furthermore, the TCE degraded in the STO system was much faster than that in the SO system. Thus, the results suggest that most of hydrogen peroxide decomposition in the SO system directly produces oxygen and water without formation of OH^\cdot .



The matrix effect except pH on the treatment of pollutants by ISCO has been greatly discussed in the literature. The chloride ions, carbonate may quench the free radicals and decrease the removal efficiency ([Liang *et al.* 2006](#)). The adverse effect of chlorine ion, bromine ion, carbonate ion ($\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$) on the UV/ H_2O_2 degradation of pollutants was in a decreasing order: carbonate, bromide, chloride ions ([Grebel *et al.* 2010](#)). In addition, humic substances in the soil and groundwater inhibit the removal of pollutants ([Lipczynska-Kochany & Kochany 2008](#)). However, soil organic matter (SOM) does not affect hydrogen peroxide to produce hydroxyl radicals at pH 3, while in the neutral conditions, the SOM reduced the hydrogen peroxide decomposition rate and increased the formation rate of hydroxyl radicals ([Bissey *et al.* 2006](#)), indicating SOM will promote the removal of pollutants at neutral pH. Soil organic carbon content was also observed as having no effect on the degradation of dieldrin pesticides and hexadecane ([Tyre *et al.* 1991](#)). In short, when applying the STO method in the treatment of pollutants in the real environment, the above factors should be considered.

CONCLUSIONS

Siderite catalyzed hydrogen peroxide and/or sodium persulfate producing hydroxyl radicals resulted in TCE removed in the SO and STO system. The TCE removed was significantly greater in the STO system than that in the SO system, indicating that the sodium persulfate plays an important role in enhancing degradation of TCE. The sodium persulfate in

STO participated in formation of hydroxyl radicals and accelerated TCE degradation. This STO method is a potential alternative for treatment of recalcitrant contaminants in source pollution of groundwater. It is recommended that STO is combined with bioremediation. Since STO degrades the pollutants quickly, the toxicity of pollution zone can be largely reduced and subsequently suitable to bioremediation. The matrix effect on this method to treat contaminants needs further study.

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