Published in final edited form as:

Water Air Soil Pollut. 2017 December ; 228: .

Kinetic and thermodynamic studies of chlorinated organic compound degradation by siderite-activated peroxide and persulfate

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Abstract

The efficacy of two oxidant systems, iron-activated hydrogen peroxide (H_2O_2) and iron-activated hydrogen peroxide coupled with persulfate ($\text{S}_2\text{O}_8^{2-}$), was investigated for treatment of two chlorinated organic compounds, trichloroethene (TCE) and 1,2-dichloroethane (DCA). Batch tests were conducted at multiple temperatures (10–50 °C) to investigate degradation kinetics and reaction thermodynamics. The influence of an inorganic salt, dihydrogen phosphate ion (H_2PO_4^-), on oxidative degradation was also examined. The degradation of TCE was promoted in both systems, with greater degradation observed for higher temperatures. The inhibition effect of H_2PO_4^- on the degradation of TCE increased with increasing temperature for the iron-activated H_2O_2 system but decreased for the iron-activated hydrogen peroxide-persulfate system. DCA degradation was limited in the iron-activated hydrogen peroxide system. Conversely, significant DCA degradation (87% in 48 hours at 20 °C) occurred in the iron-activated hydrogen peroxide-persulfate system, indicating the crucial role of sulfate radical ($\text{SO}_4^{\cdot-}$) from persulfate on the oxidative degradation of DCA. The activation energy values varied from 37.7 to 72.9 kJ/mol, depending on the different reactants. Overall, the binary hydrogen peroxide-persulfate oxidant system exhibited better performance than hydrogen peroxide alone for TCE and DCA degradation.

Keywords

Advanced oxidation; Chlorinated organic compounds; Phosphate; Activation energy

1 Introduction

Chlorinated organic compounds, such as carbon tetrachloride (CT), dichloroethene (DCE), trichloroethene (TCE), tetrachloroethene (PCE), and 1,2-dichloroethane (DCA), are

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ubiquitous contaminants in soil, groundwater, and industrial wastewater (Moran et al. 2007; Pham et al. 2009; Salman et al. 2015). Extensive efforts have been made for cleanup of soil and groundwater contaminated by chlorinated compounds and other recalcitrant organic constituents. Pump-and-treat methods are costly and involve treatment of enormous volumes of groundwater. *In situ* chemical oxidation (ISCO) is an effective alternative method for treatment of sites contaminated by chlorinated organic compounds (Brusseau et al. 2011; Deng et al. 2014; Furman et al. 2010; Innocenti et al. 2014; Liu et al. 2014; McKenzie et al. 2015; Watts et al. 1990; Watts and Teel 2006). Ozone, permanganate, hydrogen peroxide (H_2O_2), and persulfate ($\text{S}_2\text{O}_8^{2-}$) are commonly used oxidation reagents.

Despite numerous successful applications, limitations to ISCO effectiveness remain. For example, some contaminants are recalcitrant to standard ISCO applications (Siegrist et al. 2001). Activated hydrogen peroxide and activated persulfate have received increased attention for treatment of recalcitrant contaminants (Ahuja et al. 2007; Chawla and Fessenden 1975; Ciotti et al. 2009; Fang et al. 2013; Hayon et al. 1972; Miller et al. 2012; Rokhina et al. 2009; Yuan et al. 2012), including use in combined-oxidant approaches. Prior research has shown for example that oxidant decomposition rates and radical generation rates are moderated in binary oxidant systems, thus overcoming the drawbacks of using hydrogen peroxide or persulfate alone (Block et al. 2004; Huang et al. 2013; Ko et al. 2012; Yan et al. 2013, 2015). In addition, for field applications, the overall remediation efficiency of ISCO may be significantly influenced by the presence of inorganic salts in groundwater (De Laat and Le 2005, 2006; Riga et al. 2007; Yan et al. 2016). Therefore, the influence of inorganic ions on ISCO processes should be examined for each approach.

While there have been numerous studies focused on ISCO treatment, limited research has explored reaction thermodynamics for the activated hydrogen peroxide and the activated binary hydrogen peroxide-persulfate oxidant systems. In this study, oxidation of TCE and DCA is examined at several temperatures. Iron, through the use of siderite, a common sedimentary mineral, is employed as the activation reagent (Huang et al. 2013; Yan et al. 2013, 2015). Phosphate is chosen as a representative inorganic ion to explore its inhibition effect on oxidation. The impact of selected common ions on the effectiveness of the activated binary hydrogen peroxide-persulfate system has been reported (Yan et al., 2016).

2 Materials and Methods

Experiments were conducted using batch reactors. The degradation of TCE and DAC in the two activated systems, siderite activated-hydrogen peroxide (designated as SO) and siderite activated-hydrogen peroxide combined with persulfate (designated as STO), at different temperatures was tested. The existing form of phosphate in aqueous phase varies under different pH conditions, and the most abundant species under weak acid condition (pH~3) is dihydrogen phosphate ion (H_2PO_4^-). Therefore, the impact of H_2PO_4^- on TCE degradation in the SO and the STO systems was also evaluated in this study.

2.1 Chemicals

All chemical stock solutions used in this study were prepared using ultrapure (filtered, distilled, deionized) water from a Millipore system (Millipore Model Milli-Q Academic

A10). Siderite was obtained from the Wuhan Iron and Steel (Group) Corporation, China. Hydrogen peroxide (H_2O_2 , ~30 wt. % in water), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%), trichloroethene (TCE, >99% purity), sodium phosphate monobasic (NaH_2PO_4 , 99% purity), 1,2-dichloroethane (DCA, ~99.8% purity) were purchased from Beijing Chemical Works.

The following reagent concentrations were used for all of the experiments. Oxidant concentrations were selected based on the results of previous studies employing persulfate and H_2O_2 (Yan et al. 2013, 2015). For TCE, 10 μL of pure TCE was added to each vial for the relevant experiments. This quantity is equivalent to 11.15 mM (1,500 mg/L) in solution. This equivalent concentration exceeds the aqueous solubility of TCE, reflecting the presence of TCE liquid. DCA: 5 mM (495 mg/L), $\text{Na}_2\text{S}_2\text{O}_8$: 6.3 mM (1,500 mg/L), H_2O_2 : 150 mM (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 Experiment Setup

Batch experiments (in triplicate) were conducted with 20 mL borosilicate vials fitted with PTFE septum caps. Experiments were conducted to examine TCE or DCA degradation alone, and multiple temperatures (10, 20, 30, 40, and 50 °C) were used for the thermodynamic study. The blank control group contained only contaminant and ultrapure water. This group was used to evaluate the influence of volatilization and other mass-loss processes during the experiment. The siderite control group contained contaminant, siderite, and water. This control was used to determine whether the siderite sorbed or otherwise influenced TCE or DCA. The reaction group was created by adding the reagents in the following order: siderite, ultrapure water, persulfate (if the group contained), contaminant, and hydrogen peroxide. The vials were immediately capped after the addition of all the reagents.

After preparation, the vials were stored in an air bath to maintain constant temperature. The experiments were conducted for 48 hours. At each time-point, 5 mL of isopropanol solution were added to the selected vials to quench the reaction. The samples were immediately analyzed as described below.

2.3 Analytical Methods

TCE and DCA were analyzed using gas chromatography (Agilent GC6820, USA) with a headspace autosampler, a FID detector and a 30 m $\times$ 0.53 mm DB-5 capillary column (film thickness was 1.5 μm). The temperature of injector and detector was 187 and 250 °C respectively. For TCE detection, the initial oven temperature was 40 °C and heated at a rate of 10 °C/min to a final temperature of 140 °C. For DCA detection, holding the initial oven temperature 40 °C for 1 minute, and then heated at a rate of 30 °C/min to a final temperature of 120 °C, hold final temperature for 2 minutes.

3 Results and Discussion

3.1 Effect of Temperature on TCE Degradation

The control tests for TCE and DCA in ultrapure water (Fig. 1) and ultrapure water + siderite (SI Fig. S1) show minimal TCE mass loss during the experiment. Conversely, approximately 10% DCA loss was observed in the presence of siderite.

The temperature effect on TCE degradation in the SO and the STO systems was investigated at temperatures varying from 10 to 50 °C. The results indicate that greater TCE degradation was achieved for higher temperatures (Fig. 1a and b). These results are anticipated based on the impact of higher temperatures on diffusive mixing, pH, and activation. As observed in Figure 2, the pH was lower at higher temperatures for the STO system (Fig. 2). Lower pH favors the hydrogen peroxide-persulfate-based oxidation process. Furthermore, heat enhances oxidant activation. Therefore, higher temperatures enhanced the magnitude of degradation (Deng et al. 2014).

The radical generation mechanisms in the SO and STO systems has been delineated in our previous studies (Yan et al. 2015). For the SO system, the decomposition rate of hydrogen peroxide is rapid in the first 2 hours of the reaction, resulting in high production of HO· at the beginning of the reaction, followed by a period of reduced decomposition rate. Therefore, a two-stage kinetic reaction process was identified: the rapid-stage (first 2 hours of the reaction) and the slow-stage (reaction after 2 hours). In the STO system, the existence of persulfate slowed the decomposition rate of hydrogen peroxide (Yan et al. 2015). Thus a single first-order rate equation was applied to the entire reaction period. Pseudo-first-order reaction rate constants for TCE degradation under multiple temperatures are presented in Table 1.

The rate constants obtained from the data were applied to the Arrhenius equation Eq. (1) and (2) to calculate the activation energy (E_a , kJ/mol).

$$k = Ae^{-E_a/RT} \quad (1)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

where k is the rate constant, A is the Arrhenius constant, R is the ideal gas constant (0.0083 KJ/mol·K), and T is the absolute temperature (K). The activation energy can be calculated from the slope of the $\ln K \sim 1/T$ relationship (Eq. (2), Fig. 3). The activation energy for the SO system (rapid-stage, slow-stage) and the STO system were 37.7, 60.8, and 72.9 kJ/mol, respectively. For the SO system, the activation energy of the slow-stage was almost two times larger than for the rapid-stage. This is related to the relative amounts of hydrogen peroxide available in the two stages. For the STO system, although the existence of persulfate slightly increased the energy barrier of the reaction compared to the traditional

Fenton-like reaction (the SO system), it significantly decreased the decomposition rate of hydrogen peroxide (Yan et al. 2013). Thus, it takes longer to deplete oxidant in the STO system, compared with the SO system. In the STO system, as the reaction proceeded, the heat released from hydrogen peroxide decomposition acted as an internal energy source to promote the reaction, which enhanced the contaminant degradation efficiency. Dichloroacetic acid and formic acid were reported as TCE degradation byproducts in our previous work (Yan et al. 2015).

3.2 The Influence of Phosphate on TCE Degradation Thermodynamics

The influence of H_2PO_4^- on the degradation of TCE in the SO and the STO systems under multiple temperatures was tested (Fig. 4a and b). The results illustrate that increasing the temperature leads to higher TCE degradation in the presence of H_2PO_4^- within the temperature range used herein.

For the SO system, the presence of H_2PO_4^- had minimal impact on TCE degradation under low temperature condition (10 °C). As the temperature increased, the degradation of TCE was inhibited in the presence of H_2PO_4^- compared to the reaction without H_2PO_4^- . The H_2PO_4^- in the system could complex with Fe^{2+} , leading to the conversion of iron species (Eq. (3) and (4)) (Ratanatamskul et al. 2010).

$\text{FeH}_2\text{PO}_4^+$ may still have the potential to activate hydrogen peroxide. However, $\text{FeH}_2\text{PO}_4^{2+}$ has limited ability to activate hydrogen peroxide. Therefore, the overall activation ability decreased. Moreover, the competition between the organic contaminant and H_2PO_4^- in reaction with $\text{HO}\cdot$ could also decrease the degradation efficiency.

For the STO system, the inhibition effect of H_2PO_4^- was present under all temperatures. Greater inhibition was observed at lower temperatures. The results are likely caused by a greater relative impact of radical scavenging by the salt at lower temperature due to the lower amount of radicals produced.

The results illustrate that the SO and the STO systems exhibited different inhibition mechanisms under different temperatures. Therefore, a low (10 °C) and a high (40 °C) temperature were selected to explore the mechanism of the temperature-dependent inhibition in the SO and the STO systems. Fig. 5a and b show TCE degradation in single and binary oxidant systems with the existence of H_2PO_4^- under two temperatures. At 10 °C, the STO system was more sensitive to the existence H_2PO_4^- . The oxidation ability of the STO system was strongly inhibited, resulting TCE degradation efficiency lower than the SO system. At 40 °C, the influence of H_2PO_4^- on the STO system became minimal. However, the SO system exhibited strong inhibition. The results reveal that H_2PO_4^- inhibits the degradation

by consuming the generated radical. Different from the SO system, oxidant decomposition and radical generation are relatively slow in the STO system. Under low temperature, the degradation efficiency of the STO system was limited by the limited decomposition ability of persulfate. In addition, the reduced inhibition effect as increasing the temperature reveals the important role of resultant $\text{SO}_4^{\cdot-}$ in the STO system.

3.3 Effect of Temperature on DCA Degradation

The DCA degradation in the SO and STO systems under different temperatures was investigated (Fig. 6a and b). Fig. 6a indicates that the SO system had limited DCA degradation, as compared to the control group. In addition, temperature has minimal influence on DCA degradation in the SO system. For the STO system, raising the temperature leads to greater DCA degradation (Fig. 6b), similar to TCE. More than 95% DCA was degraded within 48 hours at 20 °C and above. Mass balance calculations, based on measured DCA and Cl^- concentrations, show 100% Cl balance, indicating no degradation product accumulated.

The DCA exhibited significantly different degradation behavior in the SO and the STO systems. The results indicate that the activated-hydrogen peroxide process (Fenton-like process) has very limited ability for DCA degradation. The addition of only a small amount of persulfate improves the degradation efficiency significantly. The results of a previous study showed that most hydrogen peroxide was decomposed at the beginning of the reaction in the SO system (Yan et al. 2015). However, the reaction rate between DCA and $\text{HO}^{\cdot}$ is limited compared to the self-quenching rate of $\text{HO}^{\cdot}$, which will be further discussed in the next section. Furthermore, the addition of persulfate could reduce hydrogen peroxide decomposition rate and produce $\text{SO}_4^{\cdot-}$, and thus improve the degradation. In addition, the solution pH should also influence degradation efficiency. During the experiment, the pH of the SO system was ~7, and the pH of the STO system was ~3 (Fig. S2). Under low pH condition, more ferrous ion would dissolve into solution from the siderite (Fig. S2), therefore enhancing the activation activity. Therefore, DCA degradation mechanisms are different between the SO and the STO systems.

A first-order rate equation was applied, and pseudo-first-order reaction rate constants for DCA degradation under multiple temperature conditions in the STO system are shown in Table 2. The activation energy can be calculated from the slope of $\ln K \sim 1/T$ relationship (Eq. (2), Fig. 7). The calculated activation energy for DCA degradation in the STO system was 62.3 kJ/mol.

3.4 The Performance of the Iron-Activated Advanced Oxidation Under Different Contaminant Condition

Based on the results above, TCE and DCA had different degradation efficiencies in the SO system. TCE is an unsaturated chlorinated aliphatic hydrocarbon, whereas DCA is a saturated chlorinated aliphatic hydrocarbon. Different structure might influence the degradation pathway. The reaction rate constant of $\text{HO}^{\cdot}$ and TCE is $(3.3\text{--}4.3) \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$ (Eq. (3)).

The self-quenching rate constant of $\text{HO} \cdot$ is $\sim 5.3 \times 10^9 \text{ mol}^{-1}\text{s}^{-1}$ (Eq. (4)) (Chen et al. 2001).

The reaction between DCA and $\text{HO} \cdot$ is reported (Eq. (5) and (6)) (Randazzo et al. 2011), and the reaction rate constant is $\sim 2 \times 10^8 \text{ mol}^{-1}\text{s}^{-1}$ (Lal et al. 1988; Minakata et al. 2009).

The self-quenching rate constant of $\text{HO} \cdot$ is almost the same as the reaction rate constant of TCE and $\text{HO} \cdot$, but over one order of magnitude larger than the reaction rate constant of DCA and $\text{HO} \cdot$. Therefore, the SO system is generally effective for treating certain amount of TCE but not effective for degrading DCA.

The degradation efficiencies of TCE and DCA were almost the same in the STO system, which was also proved by the similar activation energy. The points of zero charge (PZC) of siderite is 5.3 ± 0.1 . The STO system has pH ~ 3 . Acidic condition prevents the adsorption and thus improve the effectiveness of degradation. Furthermore, the STO system is superior to the SO system for DCA treatment might also contributed by the production of $\text{SO}_4^{\cdot -}$, and the sustainable release of radicals.

4 Conclusion

This study investigated TCE and DCA degradation performance by the SO and the STO systems under multiple temperature conditions. TCE degradation efficiency was higher in the STO system than the SO system under all of the experiment temperature conditions. Higher temperature resulted in higher TCE degradation efficiency. For the SO system, the TCE degradation kinetic and thermodynamic parameters were identified by two stages, due to the hydrogen peroxide decomposition behavior. The activation energy for TCE removal in the SO system (first 2 hours, after 2 hours reaction) and the STO system were 37.7, 60.8, and 72.9 kJ/mol, respectively. The higher activation energy of the STO system caused by the higher energy needed for the decomposition of persulfate. The H_2PO_4^- had a temperature-dependent inhibitory effect on the SO and the STO systems. For the SO system, the H_2PO_4^- had minimal impact on TCE degradation under low temperature condition (10 °C) but exhibited increased influence as temperature increased. The STO system exhibited the opposite tendency, illustrating the different reaction mechanism between the two systems.

Minimal amount of DCA was degraded in the SO system at the various temperatures. However, the DCA degradation efficiency was significantly enhanced in the STO system. The calculated activation energy for DCA removal in the STO system was 62.3 kJ/mol. These results show the binary activated hydrogen peroxide-persulfate system has a strong potential to oxidize chlorinated aliphatic hydrocarbons and good application prospects for *in situ* treatment of groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) (40972162), the project from the Beijing Higher Education Young Elite Teacher Project (granted to X.Y. Guan), the National Institute of Environmental Health Sciences Superfund Research Program (P42 ES04940), and the Strategic Environmental Research and Development Program (ER-2302).

Appendix A. Supplementary Data

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

Abbreviations

SO	siderite-catalyzed hydrogen peroxideoxidant
STO	siderite-catalyzed binaryoxidants (hydrogen peroxide and persulfate)

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Fig. 1. TCE degradation under different temperatures a) the SO system (siderite-catalyzed hydrogen peroxide oxidant); b) the STO system (siderite-catalyzed hydrogen peroxide and persulfate)

Fig. 2.
The pH change during TCE degradation under different temperatures for the STO system

Fig. 3. The activation energy for TCE degradation a) first 2 hours of reaction for the SO system; b) after 2 hours of reaction for the SO system; c) entire reaction period for the STO system

Fig. 4.
The effect of H_2PO_4^- on TCE degradation under different temperatures a) the SO system; b) the STO system

Fig. 5.
The impact of H_2PO_4^- on TCE degradation in the SO and STO systems under different temperatures a) 10 °C; b) 40 °C

Fig. 6.
DCA degradation under different temperatures a) the SO system; b) the STO system

Fig. 7.
The activation energy for DCA degradation in the STO system

Table 1

Kinetic equations for TCE degradation in different oxidation systems

System	Reaction Period	Temperature (°C)	Regression equation	R ²	k _{obs} ^a (h ⁻¹)
SO ^b	Rapid-stage	10	$y = -0.076x + 0.014$	0.90	0.076
SO	Rapid-stage	20	$y = -0.123x - 0.016$	0.95	0.123
SO	Rapid-stage	30	$y = -0.208x - 0.054$	0.83	0.208
SO	Rapid-stage	40	$y = -0.362x - 0.089$	0.85	0.362
SO	Rapid-stage	50	$y = -0.533x - 0.087$	0.93	0.533
SO	Slow-stage	10	$y = -0.011x - 0.161$	0.93	0.011
SO	Slow-stage	20	$y = -0.018x - 0.237$	0.98	0.018
SO	Slow-stage	30	$y = -0.044x - 0.311$	0.95	0.044
SO	Slow-stage	40	$y = -0.116x - 0.420$	0.99	0.116
SO	Slow-stage	50	$y = -0.242x - 0.496$	0.98	0.242
STO ^c	Entire reaction	10	$y = -0.034x + 0.025$	0.90	0.034
STO	Entire reaction	20	$y = -0.104x + 0.014$	0.94	0.104
STO	Entire reaction	30	$y = -0.361x + 0.212$	0.92	0.361
STO	Entire reaction	40	$y = -0.899x + 0.304$	0.96	0.899
STO	Entire reaction	50	$y = -1.383x + 0.221$	0.93	1.38

^ak_{obs} is the pseudo first-order rate constant^bSO: siderite-catalyzed hydrogen peroxide oxidant^cSTO: siderite-catalyzed binary oxidants (hydrogen peroxide and persulfate)

Table 2

Kinetic equations for DCA degradation in the STO system

Temperature (°C)	Regression equation	R ²	k _{obs} ^a (h ⁻¹)
10	y = -0.034x + 6.198	0.92	0.034
50	y = -0.197x + 6.333	0.92	0.197
30	y = -0.380x + 6.279	0.99	0.380
40	y = -0.723x + 6.299	0.99	0.723
50	y = -1.035x + 5.983	0.89	1.035

^ak_{obs} is the pseudo first-order rate constant