Application Sodium Percarbonate to Oxidative Degradation Trichloroethylene Contamination in Groundwater

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Abstract

Sodium percarbonate has been shown to oxidize a wide variety to organic and inorganic compounds in water under multiple conditions of environment. Compared to function with Fenton’s reagent, Sodium percarbonate is effective showed over an extensive pH range. In This study, therefore, was to discover the characteristics of peroxide process by using trichloroethenes (TCEs) as Standards compounds. The Results demonstrate that TCEs can be oxidized or dissolved by sodium percarbonate. When the molar ratios of $[\text{TCE}] / [\text{2Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2]$ ranged from 5 to 10, the oxidation or decomposition rate increased with increasing ratio. Even though the theoretical dosage of $[\text{TCEs}] / [\text{2Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2]$ even down to 0.5 for complete degradation of TCEs, it still needed, at least, 4 moles of $[\text{2Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2]$ to degradation this chemical dosage. This indicates that oxidation intermediates competed sodium percarbonate molecules with the parent TCEs. The primary pH has no obviously efficacy on TCEs decompose, because hydrogen-ions were conformation during the period of TCEs degradation.

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Introduction

TCEs are of special attention because of the potential risks that they constitute to human health as potential suspected carcinogens [1]; therefore these compounds have serious attention to regulatory levels. TCEs usually occur in the subsurface as local zones of residual zones Concentration or occasionally exist as Monomer products [2]. Because of TCEs in nature of low solubility in fluid, and exist in dense non-aqueous phase liquids persist in aquifers, especially provide a stable supply source of contaminants [4].
Chemical oxidation of TCE employed in studies included ozone (O$_3$), Fenton’s reagent (a mixture of H$_2$O$_2$ and Fe$^{2+}$) and Sodium Percarbonate (2Na$_2$CO$_3$•3H$_2$O$_2$). O$_3$ was the firstly used in water treatment applications, more than 100 years ago, and is commonly used in today. However, the half-life of O$_3$ limits its ability to migrate through soil over large distances. In Fenton process, hydroxyl radicals are generated by the reaction of hydrogen peroxide and ferrous ions to oxidize organic compounds. When using the Fenton’s reagent for the treatment of contaminated soil and groundwater, reaction pH needs to be controlled between from 2 to 4. Therefore, this technology is difficult to apply in the field of in-situ pre-treatment [5, 6].

The chemical oxidation of toxic and hazardous organic pollutants such as TCEs is often carried out by using single oxidants such as chlorine, ozone, UV radiation, hydrogen peroxide, etc. However, sometimes this decomposition may be difficult if these pollutants are present at high concentrations, or if they are especially refractory to the oxidants [7].

Sodium percarbonate is a free-flowing powder with a common name of solid hydrogen peroxide; It is an addition compound of sodium carbonate and hydrogen peroxide. Sodium Percarbonate has an active available oxygen content which is equivalent to 27.5% H$_2$O$_2$. It breaks down to oxygen, water and sodium carbonate upon decomposition. Sodium Percarbonate offers many of the same functional benefits as liquid hydrogen peroxide. It dissolves into water to release oxygen. In comparison to Fenton’s reagent, Sodium Percarbonate (2Na$_2$CO$_3$•3H$_2$O$_2$) can effectively oxidize many water impurities, and is also effective over a wide pH range. Reaction of 2Na$_2$CO$_3$•3H$_2$O$_2$ with organic compounds produces Carbon dioxide, water and a small amount of sodium carbonate, which is naturally present in soils. Therefore, the production of Carbon dioxide, water and a small amount of sodium carbonate is not of environmental concern. In addition, 2Na$_2$CO$_3$•3H$_2$O$_2$ is non-toxic to microbes, making it compatible with bioremediation, so no hazards environmental due to it breaks down to oxygen, water and sodium carbonate (soda ash) in environmental[2,7].

Many scholars investigated oxidation of TCEs by peroxide and obtained good results. Yan et al.[8] reported about their extensive kinetic studies of TCE oxidation by peroxide, and suggested that TCEs degradation is a second-order reaction. Yan et al.[9] also pointed out that the reaction involves several intermediate compounds. Other studies showed that the degradation rate of TCE by peroxide is influenced mainly by reactant concentration and temperature, and is independent of both ionic strength and pH[9, 10].

There are so many studies focusing on TCEs oxidation, but no literature is available reporting on the optimum dosage of 2Na$_2$CO$_3$•3H$_2$O$_2$. Therefore, this study was to investigate the effects of the molar ratio of [TCE]/[2Na$_2$CO$_3$•3H$_2$O$_2$] and pH on TCEs oxidation in aqueous phase. In addition, the extent of de-chlorination is also reported.

Analysis

Analysis of samples: Aqueous solution of TCEs (7.0 mL) was extracted with chloroform twice (30mL each times), and the above layers were collected, dried with Na$_2$SO$_4$, and evaporated to 1mL for the determination of the remains of TCEs with a flame ionization detector (FID) and HP-6890 column (15m×0.53mm×1.5μm), was used to determine TCE concentrations. For the analysis of TCEs in the extracts, a HP 6890 gas chromatograph equipped with a flame ionization detector and a capillary column. The carrier gas (N2: 99.999%) flow rate in the GC-ECD was 1.5mL min-1. The dried temperature was
about 200°C. The injection volume of extract was 2μL. Chloride was analyzed by using a DIONEX ion chromatograph (IC), equipped with a 4-mm The IonPac® AS14A anion-exchange column.

Recovery of PCBs: Sampled 7.0 mL PCBs solution (200μg•L⁻¹) were pretreated by the above described method, then detected by GC-FID and calculated the recovery of TCEs. Results showed that the recovery of TCEs was stabilized at the level of 90%-95%.

Methods

In headspace GC analysis, 25.0 mL of reaction mixture and 1.0 mL of PeCl (as internal standard for CK) saturated solution were filled into a 43.0 mL vial, which was then immediately sealed with a Thermo Scientific Mininert push-button valve. In turn, the sample filled vials were put into a water-bath with the temperature controlled at 70°C for 30 mins, allowing for complete volatilization of TCEs and PeCl. Following this, a volume of 500 μL of head-space gas mixture was withdrawn for GC analysis. The chloride was measured by IC analysis, and samples were filtered through 0.45μm glass fiber filters to remove the sodium carbonate micro particles [6, 8].

Results and Discussion

In general, effect of pH Peroxide can oxidize TCEs under acidic and alkaline conditions, but the oxidation efficiency is higher at lower pH value. Fig. 1 depicts the effect of initial pH on the oxidation of TCE.

![Fig. 1 Effect of initial pH on the oxidation of TCE. [TCEs]= 1×10⁻³M, [2Na₂CO₃•3H₂O₂]=2×10⁻³ M).](image)

Under the experimental conditions of [TCEs] =1×10⁻³M, [2Na₂CO₃•3H₂O₂]=2×10⁻³ M and initial pH = 5.0, 6.0, 7.0, 8.0 and 9.0, there was no significant difference for the oxidation ratios of TCEs. Yan et.al[8] have reported that pH did not affect TCEs oxidation by Peroxide, but change the species and concentration of oxidation intermediates. They also found that 90% of carbon dioxide was produced at acidic pH, and only about 60% was detected under alkaline conditions. In this study, although the initial pHs were 5.0, 6.0, 7.0, 8.0 and 9.0, after 60 mins of reaction time, the final pH of the reaction mixtures were below 2.8 (Table 1). There is no significant difference in TCEs oxidation at different initial pH value.

The equation of TCE oxidized by Sodium percarbonate is illustrated as below [9]:

\[
C₂HCl₃ + 2 • 2Na₂CO₃•3H₂O₂ → 2 Na₂CO₃ (l) + 3 Cl⁻ + H⁺ + 2 CO₂ (g) + 2Na⁺ \quad \text{Eq.(1)}
\]

CO₂ is generated from the reaction of TCEs oxidation, and H⁺ is then produced, leading to the reduction of pH. Peroxide can also react with water molecules to release OH⁻ (see Eq. (2)), but this is very slow,
compared with the amount of $H^+$ produced in TCEs oxidation. That is why the initial pH has no significant effect on TCE oxidation in this study.

$$2Na_2CO_3 \cdot 3H_2O_2 \text{ (aq) } + 2H_2O \rightarrow 3O_2 \text{ (g) } + 4CO_2 \text{ (g) } + 4OH^- \quad \text{Eq. (2)}$$

**Table 1** Variation of pH with time of TCE oxidation

| Time (min) | 5.00 | 6.0 | 7.00 | 8.0 | 9.00 |
|------------|------|-----|------|-----|------|
| 5          | 8.82 | 8.86 | 8.87 | 8.88 | 8.89 |
| 10         | 8.76 | 8.80 | 8.82 | 8.83 | 8.85 |
| 20         | 8.72 | 8.77 | 8.79 | 8.81 | 8.83 |
| 30         | 8.72 | 8.76 | 8.78 | 8.78 | 8.78 |
| 60         | 8.72 | 8.76 | 8.77 | 8.75 | 8.79 |

**Effect of [TCEs] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] reaction ratio**

In these experiments, the initial TCEs concentration was kept at $1.0 \times 10^{-3}$M. The ratios of [TCEs] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] were varied by changing the concentration of Peroxide. Fig. 2 shows the effect of [TCEs] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] ratio on the oxidation of TCEs. When the ratios of [TCEs] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] were 2.0, 1.0, 0.5 and 0.25, then 70%, 45%, 20% and 5% TCEs, respectively, were remaining in the reaction mixtures.

![Fig. 2 Effect of [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] on the oxidation of TCE at [TCEs] = 1×10-3M.](image)

Fig. 3 shows the results with $6 \times 10^{-4}$M initial TCE concentration, and the ratios of [TCE] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] were also 2.0, 1.0, 0.5 and 0.25. The remaining percentages of TCEs after 60 mins of reaction were 70%, 50%, 20% and 5%. By comparing Fig. 2 with Fig. 3, it can be illustrate that the oxidation of TCE depended on the ratio of [TCEs] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] under the experimental conditions. The complete oxidation of TCEs occurred at ratios of [TCE] / [2Na$_2$CO$_3$$\cdot$$3H_2$O$_2$] greater than 0.25. In other words, the concentration of sodium percarbonate has to be four times higher than that of TCEs. According to Eq. (1), one mole of TCE needs 2 moles of sodium percarbonate for complete oxidation. However, from the results obtained in Figs. 2 and 3, only 50-60% of TCEs was oxidized, as shown in Eq-(1). It is assumed that the oxidation intermediates competed with TCEs in capturing the sodium percarbonate molecules, leading to the inhibition of TCEs oxidation.
Conclusion

Experiments of TCEs oxidation by Sodium Percarbonate were carried out in this study. The initial rate of TCEs oxidation almost increased linearly with increasing the initial concentration of TCEs. The factors, pH and ratio of $[\text{TCEs}] / [2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2]$, affecting the reaction have been explored. Even the theoretical dosage of $[\text{TCE}] / [2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2]$ is 0.5 for complete degradation of TCEs, it still needed, at least, 4.0 moles of $2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2$ to decompose this chemical. This indicates that oxidation intermediates and the parent TCEs competed with Sodium percarbonate molecules. Initial pH has no significant effect on the TCEs oxidation, because hydrogen ions were released during the period of oxidation reaction.

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References

[1] Rachel H. Waldemer, Paul. G, Tratnyek Richard L. Johnson and James. T: Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products. Environ. Sci. Technol. 41(3), (2007), p. 1010-1015

[2] Kun-Chang Huang, George E. Hoag, Pradeep Chheda, Bernard A. Woody and Gregory M. Dobbs: Oxidation of chlorinated ethenes by potassium permanganate: a kinetics study. J. Hazardous Materials, 87 (2001), p. 155-169

[3] Alam S. Hasson and Ian W. M. Smith: Chlorine Atom Initiated Oxidation of Chlorinated Ethenes: Results for 1, 1-Dichloroethene (H2C=CCl2), 1, 2-Dichloroethene (HCIC=CCIH), Trichloroethene (HCIC=CCl2), and Tetrachloroethene (CI2C=CCl2). J. Phys. Chem. A, 103(13) (1999), p. 2031-2043

[4] D. Hunkeler, R. Aravena, B. L. Parker, J. A. Cherry, and X. Diao: Monitoring Oxidation of Chlorinated Ethenes by Permanganate in Groundwater Using Stable Isotopes. Laboratory and Field Studies Environ. Sci. Technol. 37(4) (2003), p. 798-804

[5] Yongkoo Seol and Franklin W. Schwartz: Phase-transfer catalysis applied to the oxidation of nonaqueous phase trichloroethylene by potassium permanganate. J. of Contaminant Hydrology. 44(2000), p. 195-201
[6] T.T. Tsai, C.M. Kao, T. Y. Yeh, S. H. Liang and H.Y. Chien: Application of surfactant enhanced permanganate oxidation and biodegradation of trichloroethylene in groundwater. 161(2009), p. 111-119

[7] Prasad K. Kakarla, Thomas Andrews, Richard S. Greenberg and David S. Zervas: Modified Fenton's processes for effective in-situ chemical oxidation-Laboratory and field evaluation, 12 (2002), p. 23-26

[8] Y. Eugene Yan and Frank W. Schwartz: Oxidative degradation and kinetics of chlorinated ethylenes by potassium permanganate. 37 (1999), p. 343-365

[9] K.C. Huang, G.E. Hoag, P. Chheda, B.A. Woody and G.M. Dobbs: Kinetic study of oxidation of trichloroethylene by Sodium Percarbonate. Environ. Eng. Sci. 16(4) (1999), p. 265-274

[10] Y. Eugene Yan and Franklin W. Schwartz: Kinetics and Mechanisms for TCE Oxidation by Permanganate. 34 (2000), p. 2535–2541