Degradation of Trichloroethylene in Groundwater Using Iron Catalyzed Calcium Peroxide Systems

Kegang Zhang¹, Xiaodong Wang¹,* Xiaohui Zhang¹, and Shengjie Peng¹

¹School of Civil Engineering and Architecture, University of Jinan, Jinan 250022, China

Abstract. The application of calcium peroxide (CaO₂) activated with ferrous ion chelate sodium citrate (TCD) to stimulate the degradation of trichloroethylene (TCE) was investigated. The experimental results show that the removal efficiency of TCE increases first and then decreases with the increase of CaO₂ and Na₂S₂O₈ dosage; the chelation ratio of Fe(II)/TCD, too much or too little, will affect the removal efficiency of TCE; when the molar ratio of CaO₂/Fe(II)/TCD/TCE is 18/6/6/1, the removal efficiency of TCE is the highest, reaching 97.99% within 200Min. The results demonstrated that the technique of CaO₂ activated with ferrous ion is a highly promising technique in in situ chemical oxidation (ISCO) remediation in TCE contaminated sites.

1 Introduction

Since the second half of the 20th century, TCE has been widely used as industrial solvent, household cleaner and metal degreaser[1]. However, due to improper disposal during production and use, as well as leakage from underground storage tanks[2], TCE has become one of the most common pollutants in soil and groundwater[3].

TCE as a human carcinogen and priority control pollutants persist in the environment (TCE, low viscosity, migration ability strong, can not only exists in the soil in the form of drops[4], also can through the gap to deeper soil aquifer[5] (Figure 1), such as in the soil half-life of about 0.5-1.5 years, in the groundwater can reach 4.5 years[6]) poses a serious threat to human health. There is evidence that long-term exposure to TCE may damage the human central nervous system, with major symptoms including nausea, facial numbness, dyskinesia and even death[7]. Therefore, in order to maintain the drinking safety of groundwater, it is necessary to study effective removal methods.

In recent years, more and more studies have been conducted on the oxidation of organic pollutants by CaO₂. Studies have shown that CaO₂ can slowly release H₂O₂ (0.47gH₂O₂/gCaO₂), and the release rate is controllable, and the repair effect is more significant than that of H₂O₂[8-9], which has become an effective substitute for liquid H₂O₂. The equation of CaO₂ and water is as follows[10]:

\[
\text{CaO}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 \uparrow + \text{Ca(OH)}_2 \downarrow \quad (1)
\]

\[
\text{CaO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{Ca(OH)}_2 \downarrow \quad (2)
\]

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).
Adjustable thermostatic shaker (ZBY-240), electronic analytical balance (BSA2201), pH meter (FE20), Gas chromatograph (7890B).

2.2 Experimental methods

All experiments in this part were static batch experiments, which were conducted in a 250ml headspace culture bottle and placed in a constant temperature culture shock box. A certain amount of samples was taken at a preset time point and the reaction was quickly stopped with methanol, Isopropanol and Trichloromethane and the content of HO· in the solution was determined. The experimental conditions were as follows: pH=7, the temperature was 25℃, the initial concentration of TCE was 21mg/L (0.16mmol/L), and the rotating speed of the constant temperature culture shock box was 165r/min.

3 Results and discussion

3.1. Effect of CaO₂ dosage on TCE removal rate

As can be seen from Figure 2, when the concentration of TCD-Fe²⁺ is fixed and the dosage of CaO₂ is changed, the degradation effect of TCE is different. When the dosage of CaO₂ increased from 0.96mmol/L (the ratio of CaO₂ to TCE was 6/1) to 3.84mmol/L (the ratio of CaO₂ to TCE was 24/1), the removal rate of TCE continued to increase, and the removal rate of TCE increased from 59.9% to 99.4% in the reaction time of 200min. The main reason is that when CaO₂ meets water, it can produce H₂O₂, which is catalyzed by Fe²⁺ to produce HO· to degrade TCE. Studies have shown that the generation of H₂O₂ by CaO₂ conforms to the zero-order reaction kinetic model, and the amount of CaO₂ has no effect on release rate constant of H₂O₂, which should be paid attention to in engineering practice.

When the dosage of CaO₂ continued to increase to 4.88mmol/L (the ratio of CaO₂ to TCE was 30/1), the removal rate did not increase but slowed down, and the final removal rate was 97.0%. The reason may be that excessive H₂O₂ reacts with OH· produced by a large amount of CaO₂ (formula 3 and formula 4), which reduces the content of OH· and thus reduces the removal rate.

\[
OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \tag{3}
\]

\[
OH\cdot + OH\cdot \rightarrow H_2O_2 \tag{4}
\]

When the dosage of CaO₂ increased from 2.88mmol/L to 3.84mmol/L, the degradation effect of TCE did not increase significantly. For the sake of engineering economy, the dosage of CaO₂ in subsequent experiments was 2.88mmol/L.

3.2 Study on the degradation effect of TCE based on CaO₂ Fenton system

As can be seen from Figure 3, TCE was not effectively degraded when CaO₂ was added alone, and the removal rate was less than 6%. This indicates that although CaO₂ in water can slowly produce H₂O₂, the removal effect of H₂O₂ alone is not outstanding, indicating that the generation of its free radicals needs to be activated. This is consistent with the conclusion that H₂O₂ cannot remove refractory pollutants alone.

In the H₂O₂/TCD-Fe²⁺/TCE system, the degradation efficiency of TCE reached 99% after 10min. However, a large number of micro-bubbles were produced in the reaction process of this system, and the main reason may be that H₂O₂ dissolves to form O₂ under neutral conditions. In the actual in-situ remediation of soil and groundwater, the half-life of liquid H₂O₂ is usually only a few minutes to a few hours, which makes the instability of H₂O₂ in the underground environment the maximum limit in the application of ISCO. Under the condition of neutral pH value, disproportionation is the main loss form of H₂O₂. It consumes H₂O₂ without producing OH·, and the released O₂ gas will block the pores around the injection well, promoting the volatilization of pollutants, resulting in secondary pollution.

In the CaO₂/Fe²⁺/TCE system, the degradation efficiency of TCE reached 42.9% after 2min of reaction, but the subsequent reaction was extremely slow, and the removal rate of TCE was 50.8% at 200min. The main reason for this phenomenon were the precipitation deactivation of Fe³⁺ under neutral conditions, which also limited the application of Fenton reagent under neutral conditions. In the CaO₂/TCD/Fe²⁺/TCE reaction system, the removal rate in the first 2 minutes was only 36.9%, but with the passage of reaction time, the reaction continued, and the final removal rate reached 97.99% within 200min. As can be seen from figure 3, the degradation trend of the above two reaction systems is significantly different, which may be caused by the addition of TCD to Fe²⁺ chelation in the system. On the one hand, TCD chelates Fe²⁺ to form relatively stable complexes. Although these complexes can catalyze Fenton-like reactions, their activity is weaker than
that of free state Fe\(^{2+}\). On the other hand, TCD chelating Fe\(^{2+}\) can prevent iron ion precipitation and maintain the active state of iron ion under neutral conditions. Meanwhile, the presence of chelating agent can make the reaction from Fe\(^{3+}\) to Fe\(^{2+}\) more likely to occur. Rastogi A et al. showed that until the end of the reaction, there was no iron precipitation in the system and all iron ions existed in the solution\(^{[16]}\).

**Fig.3.** Study on the degradation effect of TCE based on CaO\(_2\) Fenton system

\([\text{TCE}]_0=0.16\text{mmol/L}, \ [\text{CaO}_2]=2.88\text{mmol/L}, \ [\text{TCD-Fe}^{2+}]_0=0.96\text{mmol/L, pH}=7\)

### 3.3 Effect of Na\(_2\)S\(_2\)O\(_8\) on TCE removal rate

As can be seen from figure 4, when the fixed TCD-Fe\(^{2+}\) concentration changes the dosage of Na\(_2\)S\(_2\)O\(_8\), the removal effect of TCE is different. When the dosage of Na\(_2\)S\(_2\)O\(_8\) increased from 0.8mmol/L (the molar ratio of Na\(_2\)S\(_2\)O\(_8\) and TCE is 5/1) to 4.8mmol/L (the molar ratio of Na\(_2\)S\(_2\)O\(_8\) and TCE is 30/1), the removal rate of TCE increased from 49.5% to 79% within 100 min, indicating that the SO\(_4^2-\) production of Na\(_2\)S\(_2\)O\(_8\) was limited and only a small part of TCE could be degraded. With the increase of Na\(_2\)S\(_2\)O\(_8\) concentration, the SO\(_4^2-\) produced increased, and the degradation rate of TCE gradually increased (formula 5). This indicates that sufficient Na\(_2\)S\(_2\)O\(_8\) must be present in the system, as it is the source of sulfate radicals leading to TCE degradation. However, excessive amount of Na\(_2\)S\(_2\)O\(_8\) may not lead to the doubling of the degradation rate or even reduce the remission rate, mainly because excessive amount of Na\(_2\)S\(_2\)O\(_8\) will react with SO\(_4^2-\) (equation 6, 7)\(^{[17,18]}\), which cannot promote the removal of TCE:

\[
\begin{align*}
\text{Fe}^{2+} + \text{S}_2\text{O}_8^2- & \rightarrow \text{SO}_4^2- + \text{SO}_4^2- + \text{Fe}^{3+} \quad (5) \\
\text{SO}_4^2- + \text{SO}_4^2- & \rightarrow \text{S}_2\text{O}_8^2- \quad (6) \\
\text{SO}_4^2- + \text{S}_2\text{O}_8^2- & \rightarrow \text{SO}_4^2- + \text{S}_2\text{O}_8^2- \quad (7)
\end{align*}
\]

**Fig.4.** Effect of Na\(_2\)S\(_2\)O\(_8\) on TCE removal rate

\([\text{TCE}]_0=0.16\text{mmol/L}, \ [\text{TCD-Fe}^{2+}]_0=0.96\text{mmol/L, pH}=7\)

### 4 Conclusions

This paper mainly studied the Fe\(^{2+}\) CaO\(_2\) or Na\(_2\)S\(_2\)O\(_8\) single catalytic oxidation system and double degradation of aqueous solution of TCE oxidation system, specific to the following conclusion:

1. Adding chelating agent sodium citrate and Fe\(^{2+}\) to chelate to form Fe\(^{2+}\)-TCD can effective catalytic CaO\(_2\) and Na\(_2\)S\(_2\)O\(_8\), improved utilization of CaO\(_2\) and Na\(_2\)S\(_2\)O\(_8\), longer reaction time, increased the removal rate of TCE.

2. The best effect are achieved when the ratio of sodium citrate and Fe\(^{2+}\) is 1:1, while the removal effect of TCE is affected by either too high or too low ratio.

3. The phosphate buffer solution can better buffer the OH\(^-\) and H\(^+\) generated in the system, so as to maintain the system under neutral conditions and provide theoretical support for the actual underground environment restoration.

### References

1. Popat S C, Zhao K, Deshusses M A. Bioaugmentation of an anaerobic biotrickling filter for enhanced conversion of trichloroethene to ethene[J]. Chemical Engineering Journal, 183, 2012

2. Wu, X., Gu, X., Lu, S., Qiu, Z., Sui, Q., Zhang, X., Miao, Z., Xu, M. Strong enhancement of trichloroethylene degradation in ferrous ion activated persulfate system by promoting ferric and ferrous ion cycles with hydroxylamine. Sep. Purif. Technol. 147, 2015

3. Abdolnabi A. K. Optimal dynamic monitoring network design for reliable Tracking of Contaminant Plumes in an Aquifer System[D]. Dissertation of the degree of PhD, Dalhousie University, 2006: 1-10.

4. Lewis S, Lynch A, Bachas L, et al. Chelate-Modified Fenton Reaction for the Degradation of Trichloroethylene in Aqueous and Two-Phase Systems[J]. Environmental Engineering Science, 26 (4), 2009

5. Fountain J. C. Technology for Dense Non-aqueous Phase Liquid Source Zone Remediation [R]. Groundwater Remediation Technologies Analysis Center, TE-98-02, 1998.
6. Cui Yingjie. Experimental study on degradation of non-aqueous organic pollutants by Fenton technology [D]. Ocean University of China, 2008
7. Teel, A., Warberg, C., Atkinson, D., Watts, R. Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene[J]. Water Res. 35, 2001
8. Qian Y, Zhou X, Zhang Y, et al. Performance and properties of nanoscale calcium peroxide for toluene removal[J]. Chemosphere, 91(5), 2013.
9. Aronstein B N, Rice L E. Biological and integrated chemical-biological treatment of PCB congeners in soil/sediment-containing systems[J]. Journal of Chemical Technology and Biotechnology, 63(4), 1995
10. Northup A, Cassidy D. Calcium peroxide (CaO₂) for use in modified Fenton chemistry[J]. Journal of Hazardous Materials, 152, 2008.
11. Buxton G V, Greenstock C L, Helman W P, et al. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (•OH/-O•) in Aqueous Solution[J]. Journal of Physical and Chemical Reference Data, 17(2), 1988.
12. Ferrarese E, Andreottola G, Oprea I A. Remediation of PAH-contaminated sediments by chemical oxidation [J]. Journal of Hazardous Materials, 152(1), 2008
13. Kurniawan T A, Lo W H, Chan G.Y.S. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate[J]. Chemical Engineering Journal, 125(1), 2006
14. Environmental Security Technology Certification Program (ESTCP), Technology status review: in situ oxidation, ESTCP, Arlington, Virginia, USA, 1999.
15. Buda F, Ensing B, Gribnau M C M, et al. O₂ Evolution in the Fenton Reaction[J]. Chemistry–A European Journal, 9, 2003.
16. Watts R J, Foget M K, Kong S, et al. Hydrogen peroxide decomposition in model subsurface systems[J]. Journal of Hazardous Materials, 69(2), 1999.
17. Han D, Wan J, Ma Y, et al. Enhanced decolorization of Orange G in a Fe(II)-EDDS activated persulfate process by accelerating the regeneration of ferrous iron with hydroxylamine[J]. Chemical Engineering Journal, 256, 2014
18. Rastogi A, Al-Abed S R, Dionysiou D D. Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols [J]. Water Research, 43(3), 2009.