Degradation of Trichloroethylene in Groundwater Using Iron Catalyzed Calcium Peroxide Systems

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Abstract. The application of calcium peroxide (CaO_2) 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 CaO_2 and $Na_2S_2O_8$ 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 CaO_2/ 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 CaO_2 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 CaO_2.Studies have shown that CaO_2 can slowly release H_2O_2 ($0.47gH_2O_2/gCaO_2$), and the release rate is controllable, and the repair effect is more significant than that of H_2O_2[8-9], which has become an effective substitute for liquid H_2O_2.The equation of CaO_2 and water is as follows[10]:

$$CaO_2 + H_2O \rightarrow 1/2O_2 \uparrow + Ca(OH)_2 \downarrow \qquad （1）$$

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \downarrow \qquad （2）$$
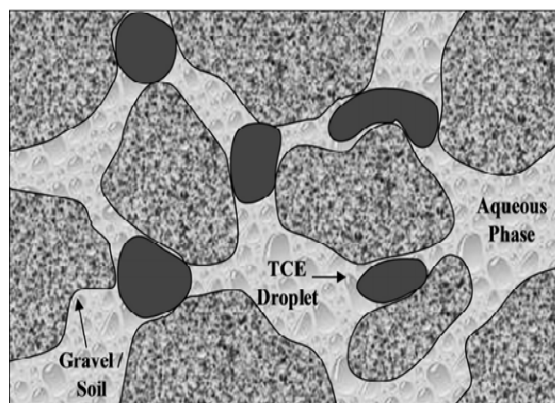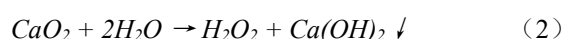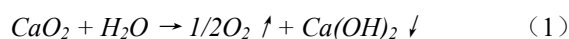

Fig.1. Distribution of DNAPL in the aquifer.

2 Experimental Part

2.1 Experimental reagents and instruments

2.1.1 Experimental reagents

The TCE and $Na_2S_2O_8$ used in this experiment were all produced by Tianjin Da Mao chemical reagent factory, CaO_2, trisodium citrate (TCD, China national pharmaceutical group), $FeSO_4 \cdot 7H_2O$, isopropanol, methanol, sodium chloride and anhydrous sodium sulfate (Tianjin Beilian Fine Chemical Co., Ltd).

2.1.2 Experimental instruments

Adjustable thermostatic shaker (ZWY-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[6], and the content of TCE 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 CaO$_2$ dosage on TCE removal rate

As can be seen from Figure 2, when the concentration of TCD-Fe^{2+} is fixed and the dosage of CaO$_2$ is changed, the degradation effect of TCE is different .When the dosage of CaO$_2$ increased from 0.96mmol/L (the ratio of CaO$_2$ to TCE was 6/1) to 3.84mmol/L (the ratio of CaO$_2$ 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 are that when CaO$_2$ meets water, it can produce H$_2$O$_2$, which is catalyzed by Fe^{2+} to produce HO · to degrade TCE. Studies have shown that the generation of H$_2$O$_2$ by CaO$_2$ conforms to the zero-order reaction kinetic model, and the amount of CaO$_2$ has no effect on release rate constant of H$_2$O$_2$, which should be paid attention to in engineering practice.

When the dosage of CaO$_2$ continued to increase to 4.8mmol/L (the ratio of CaO$_2$ to TCE was 30/1), the removal rate did not increase but slowed down, and the final removal rate within 180min was 97.0%.The reason may be that excessive H$_2$O$_2$ reacts with OH· produced by a large amount of CaO$_2$ (formula 3 and formula 4), which reduces the content of OH· and thus reduces the removal rates[7].

$$OH · + H_2O_2 \rightarrow H_2O + HO_2^- \qquad （3）$$

$$OH · + OH · \rightarrow H_2O_2 \qquad （4）$$
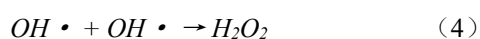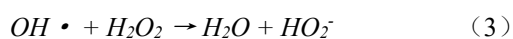
When the dosage of CaO$_2$ increased from 2.88mmol/L to 3.84mmol/L, the degradation effect of TCE did not increase significantly. For the sake of engineering economy, the dosage of CaO$_2$ in subsequent experiments was 2.88mmol/L.
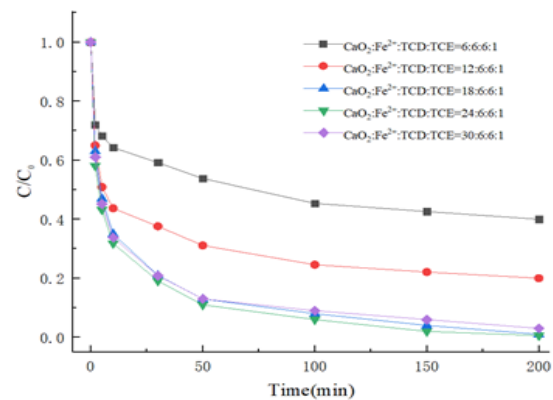

Fig.2. Effect of CaO$_2$ dosage on TCE removal rate （[TCE]$_0$=0.16mmol/L,[TCD-Fe^{2+}]$_0$=0.96mmol/L , pH=7）

3.2 Study on the degradation effect of TCE based on CaO$_2$ Fenton system

As can be seen from Figure 3, TCE was not effectively degraded when CaO$_2$ was added alone, and the removal rate was less than 6%.This indicates that although CaO$_2$ in water can slowly produce H$_2$O$_2$, the removal effect of H$_2$O$_2$ alone is not outstanding, indicating that the generation of its free radicals needs to be activated .This is consistent with the conclusion that H$_2$O$_2$ cannot remove refractory pollutants alone [8].

In the H$_2$O$_2$/TCD-Fe^{2+}/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 H$_2$O$_2$ dissolves to form O$_2$ under neutral conditions .In the actual in-situ remediation of soil and groundwater, the half-life of liquid H$_2$O$_2$ is usually only a few minutes to a few hours [9], which makes the instability of H$_2$O$_2$ in the underground environment the maximum limit in the application of ISCO. Under the condition of neutral pH value[10,11], disproportionation is the main loss form of H$_2$O$_2$. It consumes H$_2$O$_2$ without producing OH·, and the released O$_2$ gas will block the pores around the injection well, promoting the volatilization of pollutants [12,13], resulting in secondary pollution.

In the CaO$_2$/Fe^{2+}/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 Fe^{3+} under neutral conditions, which also limited the application of Fenton reagent under neutral conditions .In the CaO$_2$/TCD/Fe^{2+}/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 Fe^{2+} chelation in the system .On the one hand, TCD chelates Fe^{2+} to form relatively stable complexes. Although these complexes can catalyze Fenton-like reactions [14], their activity is weaker than

that of free state Fe^{2+}[15].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].
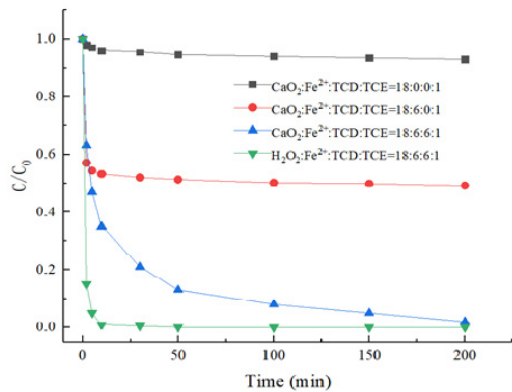

Fig.3. Study on the degradation effect of TCE based on CaO_2 Fenton system
（[TCE]$_0$=0.16mmol/L, [CaO_2]$_0$=2.88mmol/L , [TCD-Fe^{2+}]$_0$=0.96mmol/L, pH=7）

3.3 Effect of Na₂S₂O₈ on TCE removal rate

As can be seen from figure 4, when the fixed TCD-Fe^{2+} concentration changes the dosage of $Na_2S_2O_8$, the removal effect of TCE is different .When the dosage of $Na_2S_2O_8$ increased from 0.8mmol/L (the molar ratio of $Na_2S_2O_8$ and TCE was 5/1) to 4.8mmol/L (the molar ratio of $Na_2S_2O_8$ and TCE was 30/1), the removal rate of TCE increased from 49.5% to 79% within 100min, indicating that the $SO_4^-\cdot$ produced by 0.8mmol/L Na2S2O8 was limited and only a small part of TCE could be degraded .With the increase of $Na_2S_2O_8$ concentration, the $SO_4^-\cdot$ produced increased, and the degradation rate of TCE gradually increased (formula 5).This indicates that sufficient $Na_2S_2O_8$ must be present in the system, as it is the source of sulfate radicals leading to TCE degradation .However, excessive amount of $Na_2S_2O_8$ may not lead to the doubling of degradation rate or even reduce the remission rate, mainly because excessive amount of $Na_2S_2O_8$ will react with $SO_4\cdot$ (equation 6,7)[17-18], which cannot promote the removal of TCE.
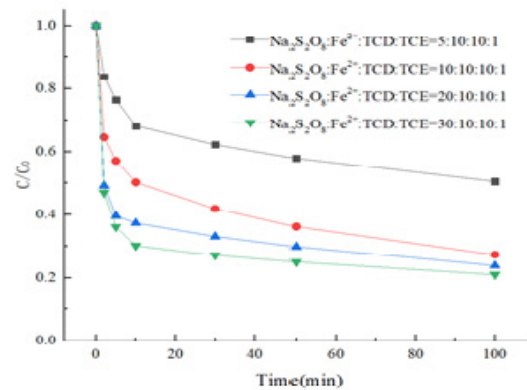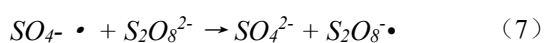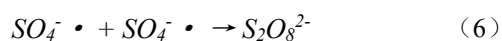
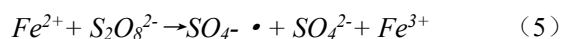$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4\text{-}\cdot + SO_4^{2-} + Fe^{3+} \qquad （5）$$

$$SO_4^-\cdot + SO_4^-\cdot \rightarrow S_2O_8^{2-} \qquad （6）$$

$$SO_4\text{-}\cdot + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8\cdot \qquad （7）$$

Fig.4. Effect of $Na_2S_2O_8$ on TCE removal rate
（[TCE]0=0.16mmol/L,[TCD-Fe2+]0=0.96mmol/L ,pH=7）

4 Conclusions

This paper mainly studied the Fe^{2+} CaO_2 or $Na_2S_2O_8$ 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 $Na_2S_2O_8$, improved utilization of CaO_2 and $Na_2S_2O_8$, 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.

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