



Application of calcium peroxide activated with Fe(II)-EDDS complex in trichloroethylene degradation



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HIGHLIGHTS

- CaO₂ activated with Fe(II)-EDDS removed TCE efficiently at near neutral pH.
- EDDS prevented soluble iron from precipitation by forming complex.
- The dominant free radicals was HO• while O₂^{-•} promoted HO• generation.
- Cl⁻, HCO₃⁻ and humic acid inhibited CP/Fe(II)-EDDS performance on different levels.

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ABSTRACT

This study was conducted to assess the application of calcium peroxide (CP) activated with Fe(II) chelated by (*S,S*)-ethylenediamine-*N,N'*-disuccinic acid (EDDS) to enhance trichloroethylene (TCE) degradation in aqueous solution. It was indicated that EDDS prevented soluble iron from precipitation, and the optimum molar ratio of Fe(II)/EDDS to accelerate TCE degradation was 1/1. The influences of initial TCE, CP and Fe(II)-EDDS concentration were also investigated. The combination of CP and Fe(II)-EDDS complex rendered the efficient degradation of TCE at near neutral pH range. Chemical probe and scavenger tests identified that TCE degradation mainly owed to the oxidation of HO• while O₂^{-•} promoted HO• generation. Cl⁻, HCO₃⁻ and humic acid were found to inhibit CP/Fe(II)-EDDS performance on different levels. In conclusion, the application of CP activated with Fe(II)-EDDS complex is a promising technology in chemical remediation of groundwater, while further research in practical implementation is needed.

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1. Introduction

Chemical oxidation technologies possess high efficiency on organic contaminants destruction, and are widely applied in groundwater and soil remediation in the contaminated sites. Hydrogen peroxide (H₂O₂) is a common chemical oxidant with low cost and minor impact on environment. The combination of H₂O₂ and soluble ferrous ion (Fe(II)) is referred as Fenton's reagent which can decompose multitude organic compounds as generated hydroxyl radical (HO•) is recognized as a strong nonspecific oxidant (Buxton et al., 1988; Qiang et al., 2008). Moreover, several other free radicals are produced simultaneously such as perhydroxyl radicals

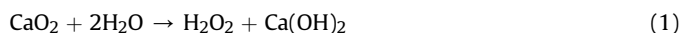
(HO₂•), superoxide radical anions (O₂^{-•}) and hydroperoxide anions (HO₂⁻), etc. resulting in a potential to destroy organic compounds via both oxidative and reductive ways (Che and Lee, 2011).

However, the lifetime of H₂O₂ is short after injected into the subsurface due to the disproportionation at neutral pH. Calcium peroxide (CaO₂, CP) is considered as a versatile and harmless solid source of H₂O₂ (Eq. (1)) (Northup and Cassidy, 2008). Different from liquid H₂O₂, CP presents as solid form and can be introduced into the contaminated zone in slurry form after mixed with water (Arienzo, 2000). The characteristics of CP make the preservation and transportation more convenient and the slow dissolution would also improve the persistence of oxidants and allow for more time for the reaction distribution in the subsurface. The liberation rate of H₂O₂ is controlled by CaO₂ dissolution, therefore CP can participate in the modified Fenton chemistry to avoid rapid depletion of oxidant and violent exothermic reaction. Arienzo

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(2000) found the excellent effectiveness of CP in the contaminated soil and water remediation with negligible damage on microorganisms which has been confirmed that the content of microbial biomass after the treatment by CP at low concentration did not lead to soil sterilization. Northup and Cassidy (2008) reported efficient degradation of tetrachloroethylene by CP activated with EDTA chelated Fe(III). PCB-containing electrical insulating oil was removed from contaminated soil efficiently by CP activated with natural soil catalyst (Goi et al., 2011).



Furthermore, the optimum pH (around 3) for conventional Fenton reaction is difficult to implement in subsurface due to the buffer capacity of groundwater and the incompatibility with bioremediation. To maintain soluble iron in solution at neutral pH range, modified Fenton process were conducted with the introduction of various chelating agents, such as ethylenediaminetetraacetic acid (EDTA), citric acid (CA) and (*S,S*)-ethylenediamine-*N,N*-disuccinic acid (EDDS) (Sherwood and Cassidy, 2014; Rastogi et al., 2009). As a structure isomer of EDTA, EDDS has the similar chemical structure with EDTA. Both of EDTA and EDDS can produce 4-anionic ligands upon deprotonating. However, EDDS can be readily biodegraded while EDTA is recalcitrant to biodegradation (Huang et al., 2013). Several researches have shown that EDDS compared favorably with EDTA in most cases with equivalent effectiveness in metal complexation (Jones and Williams, 2001; Meers et al., 2005). Therefore, EDDS is more suitable than EDTA to apply in groundwater remediation. Researches conducted in recent years confirmed that EDDS can conjugate with Fe(II) and Fe(III) to form stable complexes to extend the valid application range of Fenton processes (Wu et al., 2014; Zhou et al., 2014).

To our best knowledge, the application of Fe(II)-EDDS complex to activate CP in the removal of organic contaminants from groundwater has not been reported yet. Therefore it is much more encouraging to assess the competence of CP/Fe(II)-EDDS system for the degradation of contaminants in aqueous solution in this study while trichloroethylene (TCE) was selected as the target contaminant, since TCE has been reported as a most frequently detected hazardous organic contaminant in groundwater varied in a wide range from tens ppb to hundreds ppm at different contaminated sites according to local contamination (An et al., 2004; Dobaradaran et al., 2010; Liu et al., 2007; Travis and Doty., 1990). The contribution of generated free radicals to TCE degradation and the influences of solution matrix were specifically evaluated as well. It is anticipated that the outcomes of this study could provide a theoretical basis for the application of CP/Fe(II)-EDDS system in practice.

2. Experimental procedures and methods

2.1. Experimental procedures

TCE stock solution was prepared by dissolving pure non-aqueous TCE liquid in ultrapure water completely with gentle agitating and it was added to the reactor and diluted to the concentration of 0.15 mM in subsequent tests except in the tests for investigating the influence of TCE concentrations. A customized glass cylinder (250 mL) with two opens for dosing and sampling was used as reactor where a magnetic stirrer was used to maintain uniformity of reaction system. The temperature was held at 20 ± 0.5 °C by a thermostat circulating water bath (DC, Ningbo, China) and solution pH was maintained with 0.1 M phosphate buffer. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and EDDS of predetermined dosages were mixed in aqueous solution to prepare Fe(II)-EDDS complex freshly

before experiments. The reaction started with the addition of CP after all the chemicals except for CP were involved in the system homogeneously. Sampling were conducted for TCE analysis with gas chromatograph (GC) at determined time intervals. Control tests were carried out in parallel without addition of CP, which indicated that less than 6% TCE was volatilized during the entire experimental process. All experiments were performed in duplicate and the averaged data reported. Detailed information of chemicals used can be found in Text S1 in the Supplementary material.

2.2. Analytical methods

Aqueous samples (1.0 mL) were extracted with *n*-hexane (1.0 mL) and the organic phase was injected to GC for quantification (Agilent 7890A, Palo Alto, CA, USA). The specific conditions for the analyses in GC can be found in our previously published study (Zhang et al., 2015). Free ferrous ion (Fe(II)) was determined with 1,10-phenanthroline spectroscopically and total soluble iron was quantified with inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent 725 ES, Santa Clara, USA) (Tamura et al., 1974). H_2O_2 concentration in aqueous solution was quantified using titanium sulfate (Cohen et al., 1967). Solution pH was measured by a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

3. Results and discussion

3.1. TCE degradation in CP/Fe(II)-EDDS system

Fig. 1 shows TCE degradation performances by CP with the activation of Fe(II) and Fe(II)-EDDS complex at pH 6. Minor removal of TCE was observed due to the TCE volatilization in the individual application of CP, Fe(II) or Fe(II)-EDDS. About 72% of TCE was removed in CP/Fe(II) system within 10 min, whereas the degradation almost ceased in the following experimental period. This phenomenon was consistent with our previous study in which TCE degradation by CP/Fe(II) process without phosphate buffer also ended in 10 min (Zhang et al., 2015). In CP/Fe(II) system, CP dissolved in solution to release H_2O_2 and free Fe(II) was converted to Fe(III) rapidly accompanied by the generation of free radicals. Due to the precipitation of Fe(III) at pH 6 and the formation of iron-phosphate complexes in the presence of phosphate as buffer, the

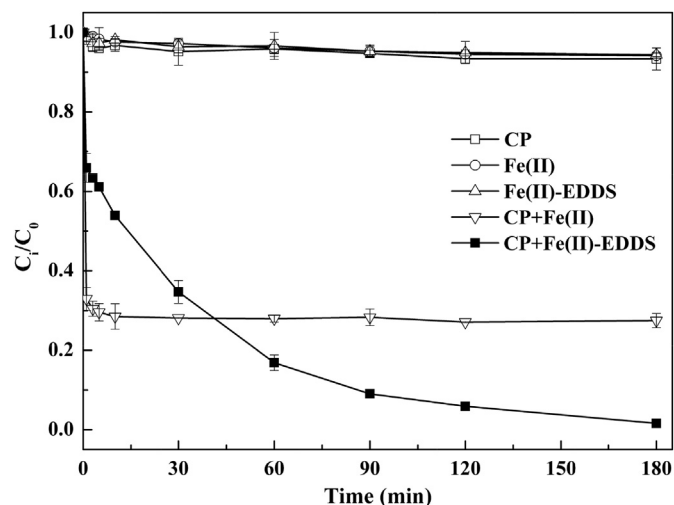


Fig. 1. TCE degradation in CP/Fe(II) and CP/Fe(II)-EDDS system. $[\text{TCE}]_0 = 0.15$ mM, $[\text{CP}]_0 = 2.25$ mM, $[\text{Fe(II)}]_0 = 0.75$ mM, $[\text{EDDS}]_0 = 0.75$ mM, pH = 6.0.

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