



Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion



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HIGHLIGHTS

- CaO₂ is applied to stimulate the degradation of trichloroethylene activated with Fe(II).
- TCE degradation performance hinges on the dosage of CaO₂ and Fe(II) as well as pH.
- The primary reactive oxygen species are HO• and O₂^{-•} in CaO₂/Fe(II) system.
- The inhibitive effect of anions on TCE degradation ranks SO₄²⁻ < NO₃⁻ < Cl⁻ < HCO₃⁻.

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ABSTRACT

The application of calcium peroxide (CaO₂) activated with ferrous ion to stimulate the degradation of trichloroethylene (TCE) was investigated. The experimental results showed that TCE could be completely degraded in 5 min at a CaO₂/Fe(II)/TCE molar ratio of 4/8/1. Probe compound tests demonstrated the presence of reactive oxygen species HO• and O₂^{-•} in CaO₂/Fe(II) system, while scavenging tests indicated that HO• was the dominant active species responsible for TCE removal, and O₂^{-•} could promote TCE degradation in CaO₂/Fe(II) system. In addition, the influences of initial solution pH and solution matrix were evaluated. It suggested that the elevation of initial solution pH suppressed TCE degradation. Cl⁻ had significant scavenging effect on TCE removal, whereas HCO₃⁻ of high concentration showed favorable function. The influences of NO₃⁻ and SO₄²⁻ could be negligible, while natural organic matter (NOM) had a negative effect on TCE removal at a relatively high concentration. 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.

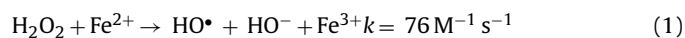
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1. Introduction

The contamination of soil and groundwater by chlorinated organic compounds has been a significant public health and environmental concern due to their harmful characteristics such as high carcinogenicity, toxicity, and flammability [1]. Trichloroethylene (TCE) is a typical chlorinated solvent widely used in metal degreasing, electronics processing, dry cleaning, electroplating, and organic synthesis [2]. The widespread occurrence of TCE in groundwater has been a significant threat to human health and the environment. TCE is ranked number 16 of the 275 substances on the Agency

for Toxic Substances and Disease Registry (ATSDR) Priority List of Hazardous Substances and has been found in at least 861 of 1428 hazardous waste sites on the National Priorities List (NPL) identified by the USEPA, and targeted for long-term federal clean-up [3].

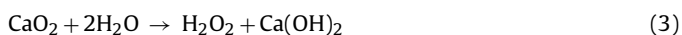
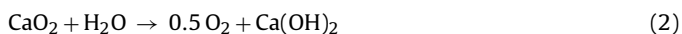
Chemical oxidation processes with ozone [4], permanganate [5], persulfate [6,7], percarbonate [8], and Fenton's reagent [9–11] have been extensively studied to remediate the soil and groundwater contaminated by chlorinated organic compounds. Among various oxidants, Fenton's reagent has attracted much attention due to its low environmental impacts and high reactivity for the removal of organic contaminants. Fenton process is known as the reaction between hydrogen peroxide (H₂O₂) as an oxidant and ferrous ions as a catalyst to produce highly active species, mainly hydroxyl radical (HO•) with a high oxidation potential (2.76 V) [12].



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HO• generated from Fenton process is a stronger oxidant than ozone (2.07 V), permanganate (1.68 V), and persulfate (2.01 V) [13], and can oxidize most target organic compounds with higher degradation rates non-selectively. Depending on the catalyst type and the dosage used, various suites of other reactive species may be generated through Fenton's propagation reactions, including perhydroxyl radicals (HO₂•), superoxide radical anions (O₂^{-•}), and hydroperoxide anions (HO₂⁻), which promote free chain radical reactions [14,15]. However, Fenton process is strongly dependent on the solution pH. The optimum pH for Fenton process is found to be around 3. Besides, H₂O₂ is found to be unstable and has a short life-time after injected into the subsurface in soil and groundwater remediation [16]. Subsequent problems are the precipitation of Fe(II) to Fe(OH)₃ at near-neutral pH, leading to problems of injection-well plugging and lose of catalyst [17].

Calcium peroxide (CaO₂) is one kind of oxygen release compound which can slowly decompose to release oxygen when dissolved in water (Eq. (2)). It is not only widely used in agricultural planting, aquaculture, and foodstuff keeping, but also widely applied in sterilization, sewage treatment as an oxygen intensifier and bleach [18,19]. In recent years, CaO₂ is found to be a more effective source of H₂O₂ than liquid H₂O₂ for in situ remediation [20,21]. At a large pH range, CaO₂ can dissolve in water to form H₂O₂ and Ca(OH)₂, liberating a maximum of 0.47 g H₂O₂/g CaO₂ (Eq. (3)). CaO₂ has the advantage of keeping reaction for relatively long time and reducing disproportionation. Therefore, it can be considered as a solid form of H₂O₂, which has better effect in remediation of contaminated soil and groundwater than liquid H₂O₂ [20].



Some researchers reported the application of CaO₂ to replace liquid H₂O₂ in the remediation of soil contaminated by polycyclic aromatic hydrocarbons (PAHs) [21], 2,4,6-trinitrotoluene (TNT) [22], and total petroleum hydrocarbons (TPHs) [23], with significant contaminant removal efficiency. Besides, CaO₂ was also used as an activator for other oxidants such as persulfate [24]. Northup and Cassidy investigated the CaO₂ dissolution to yield H₂O₂ at various pH conditions and the degradation performance of perchlorethylene (PCE) in modified Fenton system [20].

However, so far the study on the application of CaO₂ in removing chlorinated hydrocarbons did not provide much information in details. Particularly, the chemical mechanisms in the process have not been elucidated clearly, and the dominated reactive oxygen radicals responsible for contaminant removal had not been identified yet. Therefore, the objectives of this study were (1) to investigate the degradation performance of TCE in CaO₂/Fe(II) system, (2) to identify the main reactive oxygen species responsible for TCE degradation using reaction-specific probe compounds and free radical scavenging agents, (3) to evaluate the influence of the initial solution pH, effects of solution matrix, such as Cl⁻, HCO₃⁻, NO₃⁻, SO₄²⁻ and natural organic matter (NOM), on TCE degradation performance, (4) to determine the mineralization of TCE during its degradation to elucidate the TCE oxidation pathway.

2. Materials and methods

2.1. Materials

Analytical grade calcium peroxide (75% CaO₂, 25% Ca(OH)₂), trichloroethylene (TCE, 99.0%), humic acid (HA, fulvic acid > 90%) were purchased from Aaladdin Reagent Co. Ltd. (Shanghai, China). Carbon tetrachloride (CT, 99.5%), methanol (CH₃OH, 99.9%), sodium chloride (NaCl, 99.5%), sodium bicarbonate (NaHCO₃,

99.5%), sodium nitrate (NaNO₃, 99.0%), sodium sulphate (Na₂SO₄, 99.0%), *n*-hexane (C₆H₁₄, 97%), and ferrous sulfate heptahydrate (FeSO₄·7H₂O, 99.5%) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). 1,10-Phenanthroline monohydrate (C₁₂H₈N₂·H₂O, 98%), hydroxylamine hydrochloride (NH₂OH·HCl, 99.0%), *tert*-butyl alcohol ((CH₃)₃OH, TBA, 99.0%), trichloromethane (CHCl₃, 99.0%) and nitrobenzene (NB, 99.0%) were purchased from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). Ultrapure water from a Milli-Q water process (Classic DI, ELGA, Marlow, UK) was used for preparing aqueous solutions.

2.2. Experimental procedures

All experiments were conducted in a 250 mL jacketed cylindrical glass reactor with a constant temperature of 20 ± 0.5 °C using a thermostat circulating water bath. A magnetic stirrer was used to ensure the uniformity of contaminants. Stock solution of TCE was prepared by allowing the pure non-aqueous phase liquid TCE to equilibrate with Milli-Q water under gentle stirring in the dark and then diluted to the desired concentration. After the chemicals participated in the reaction except for CaO₂ (for instance, TCE, ferrous sulfate, etc.) were dissolved in the reactor, reaction was started by adding desired CaO₂ dosage. Samples were withdrawn at desired time intervals and immediately quenched with *n*-hexane before analysis of TCE. In order to identify the reactive oxygen species generated during the reaction, probe tests were conducted in accordance with TCE degradation procedure and TCE was instead of by NB (HO• probe) [25,26], or CT (O₂^{-•} probe) [11,27]. Furthermore, to evaluate the contribution of the reactive oxygen species to TCE degradation, TBA (HO• scavenger) [26] and CHCl₃ (O₂^{-•} scavenger) [11] as radical scavengers had been applied in the experiments to observe TCE degradation changes. All experiments were conducted in duplicate and the mean values were reported. The standard deviations in all experiments were in the range of 0.012–0.045. Control tests were carried out in parallel without CaO₂ addition under each experimental condition. The initial pH of solution in all experiments was unadjusted except in the tests for investigating the influence of solution pH.

2.3. Analytical methods

Aqueous samples (1 mL) of TCE, CT, or NB were analyzed, following extraction with hexane (1 mL) for 3 min using a vortex stirrer and standing for 5 min for separation. Extracts containing TCE were analyzed using a gas chromatograph (Agilent 7890A, Palo Alto, CA, USA) equipped with an electron capture detector (ECD), an autosampler (Agilent 7693), and a DB-VRX column (60 m length, 250 μm i.d., and 1.4 μm thickness). The temperatures of the injector and detector were 240 and 260 °C, respectively, and the oven temperature was kept at a constant temperature of 75 °C. A 1-microliter (1 μL) sample was injected into the gas chromatography (GC) at a split ratio of 20:1. Extracts containing CT were determined in accordance with TCE analysis procedure with the exception that the oven temperature was constant at 100 °C. Extracts containing NB were quantified by flame ionization detector (FID) equipped with a HP-5 column (30 m length, 250 μm i.d., and 0.25 μm thickness). The injector, detector, and oven temperatures were set at 250 °C, 300 °C, and 175 °C, respectively. The amount of sample injected was 1.0 μL with a split ratio of 5:1. Chloride anions were analyzed by ion chromatography (Dionex ICS-1000, Sunnyvale, CA, USA). The concentrations of ferrous ion (Fe(II)) and total iron ions (Fe(II), and Fe(III)) were determined using the 1,10-phenanthroline method [28]. The pH was measured by a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

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