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Mechanism of PCE oxidation by percarbonate in a chelated Fe(II)-based catalyzed system

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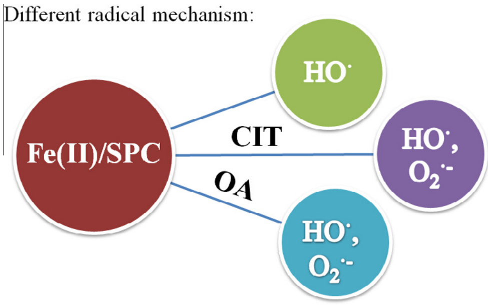
HIGHLIGHTS

- Perchloroethylene (PCE) is frequently detected in contaminated groundwater.
- PCE degradation by chelated Fe(II)-based catalyzed sodium percarbonate (SPC) was studied.
- Citric acid (CIT) and oxalic acid (OA) improved the PCE degradation performance.
- The main PCE degradation mechanism was through hydroxyl radical oxidation.
- $O_2^{\cdot -}$ participated in the degradation of PCE in CIT and OA modified system.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of chelated Fe(II)-based catalyzed sodium percarbonate (SPC) stimulating the degradation of perchloroethylene (PCE) in aqueous solution was investigated using six different chelating agents (CA), namely, citric acid monohydrate (CIT), oxalic acid (OA), L-ascorbic acid (ASC), ethylenediaminetetraacetic acid (EDTA), trisodium citrate 2-hydrate (CIT-Na_3), and EDTA-Na_2, at CA/Fe(II)/SPC/PCE molar ratios of 2/4/4/1, 4/4/4/1 and 8/4/4/1. The results indicated that the addition of CIT and OA significantly enhanced the PCE degradation. In addition, investigations using free radical probe compounds and radical scavengers revealed that PCE was primarily degraded by $HO^{\cdot}$ radical oxidation in Fe(II)/SPC, CIT/Fe(II)/SPC, and OA/Fe(II)/SPC systems and $O_2^{\cdot -}$ also participated in the degradation of PCE in CIT/Fe(II)/SPC and OA/Fe(II)/SPC systems. The intensity of $HO^{\cdot}$ detected by electron paramagnetic resonance (EPR) in CIT/Fe(II)/SPC and OA/Fe(II)/SPC systems indicated that the addition of CIT or OA indeed enhanced the continuous production of $HO^{\cdot}$ and enabled the intensity of $HO^{\cdot}$ to be more stable. The results demonstrated that CIT and OA significantly improved the PCE degradation efficiency by increasing the concentration of Fe(II) and maintaining the concentration of $HO^{\cdot}$ radicals in solution. In conclusion, chelated Fe(II)-based catalyzed SPC oxidation process shows enormous practical prospects for the remediation of PCE-contaminated groundwater because of the effectiveness without pre-adjusting the solution pH and complete mineralization in Fe(II)/SPC, CIT/Fe(II)/SPC and OA/Fe(II)/SPC systems.

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1. Introduction

Perchloroethylene (PCE) is a typical chlorinated solvent that is ubiquitously found in contaminated soil and groundwater; although it has been banned in several countries for decades, PCE is still a significant environmental problem in several countries due to its large-scale use in the past. The extensive utilization and improper disposal of chlorinated solvents have resulted in serious contamination of soils and groundwater worldwide. Therefore, the presence of such contaminants causes significant threats to groundwater resources. Because of their harmful characteristics, such as cytotoxicity, carcinogenicity, and persistence in groundwater environment, chlorinated solvents are one of the greatest threats to public health [1]. PCE has been classified as a possible carcinogenic compound according to the rules established by the United States Environmental Protection Agency (EPA). According to the Safe Drinking Water Act, the maximum contaminant level (MCL) of PCE has been regulated at 5 $\mu g\ L^{-1}$ [2].

Over the last few decades, researchers have made a great deal of effort to develop innovative and efficient technologies for remediating the soil and groundwater contaminated by chlorinated solvents. Biological technologies are usually accepted as the most cost-effective option for contaminated soil remediation and industrial wastewater treatment; however, the relatively longer treatment period limits their use in practical application. Instead, in situ chemical oxidation (ISCO) provides an approach for effectively degrading the biorefractive compounds. In the previous studies, ozone [3], potassium permanganate [4], persulfate [5], and Fenton reagents [6–8] all have been accepted as effective chemical oxidants for the remediation of contaminated soil and groundwater. Among the above-mentioned chemical oxidants, the Fenton reagent has attracted much attention because it is relatively environmental friendly and efficient in the remediation of organic contaminants. In the traditional Fenton system, the decomposition of H_2O_2 to hydroxyl radicals ($HO^{\cdot}$) induced by the Fe(II) is recognized as the main reaction mechanism [9]. $HO^{\cdot}$, which possesses a higher redox potential (2.76 V) than ozone (2.07 V), permanganate (1.68 V), and persulfate (2.01 V) [10], is a strong and relatively non-selective oxidant that is able to react with most organic compounds with a second-order rate constant exceeding $10^9\ M^{-1}\ s^{-1}$, even with highly halogenated compounds such as TCE, PCE, and polychlorinated biphenyls (PCBs) [11]. However, it is well known that the optimum pH condition for traditional Fenton reactions is in the range of 2–4 [12] and that the pH of natural groundwater is often near neutral or slightly alkaline. Therefore, lowering the pH artificially creates potential risks of unfavorable impacts on soil characteristics, and this approach goes against any subsequent biodegradation or recultivation [13]. In addition, under less acidic or alkaline conditions (pH > 6), the iron catalyst precipitates as ferric hydroxide ($Fe(OH)_3$) instead of generating $HO^{\cdot}$. Moreover, H_2O_2 is liable to decompose into oxygen and water and releases heat, which may lead to hazardous operational condition on site.

Numerous researchers have put forth significant efforts to develop novel treatment technologies to surmount the shortcomings of the traditional Fenton process and enhance the pollutants removal efficiency at neutral pH [14–16]. The chelate-based Fenton reaction, combining Fe(II) or Fe(III) with chelating agents (CA), can effectively stabilize and minimize non-specific loss of soluble iron. In one hand, this modified process has already been reported to reinforce the degradation of organic contaminants at neutral pH. For example, chelating agents, such as citrate (CIT) [17,18], humate [19], ethylenediaminetetraacetic (EDTA) [20], ascorbic acid (ASC) [21], oxalic acid (OA) [22], and cross-kinked chitosan [23], have been documented as efficient agents in modified Fenton or Fenton-like processes in the degradation of various contaminants. In the other hand, researchers are also engaged in finding alternative oxidants with similar oxidation capacity to hydrogen peroxide [24–28]. Sodium percarbonate ($2Na_2CO_3{\cdot}3H_2O_2$, SPC) salt has been considered as an alternative to liquid H_2O_2 because of its stability during handling, transportation, and storage. Compared with liquid H_2O_2, SPC is a solid powder which reduces the possibility of splashing and spilling during transportation and ensures the safety in application [29]. In recent years, SPC has been used as an alternative oxidant in ISCO practice [30]. SPC also possesses similar function as liquid H_2O_2 because when percarbonate is mixed with water, it releases free H_2O_2 in solution. Eqs. (1)–(3) show the relevant reactions in such Fenton-like process in the presence of ferrous iron [6]:

$$2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + OH^{-} + Fe^{3+} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \tag{3}$$

Compared with Fenton's reagent, SPC has many advantages: (1) it is applicable in a wide pH range; (2) the end products in SPC oxidizing organic compounds systems are usually carbon dioxide, water, and sodium carbonate, which occur naturally in groundwater; and (3) the decomposition products of SPC are non-toxic to microorganisms, making it compatible with the followed bioremediation. Therefore, chelated Fe(II) catalyzed SPC oxidation has an extensive practical prospect in the remediation of groundwater contaminated with chlorinated solvents.

So far, many studies based on advanced oxidation processes (AOPs) have focused on the remediation of groundwater and soil contaminated by PCE [31–35]. However, most of these studies were conducted by applying the conventional Fenton process. To the best of our knowledge, the chelated Fe(II)-based catalyzed SPC system has not been well studied yet. Our previous study documented that Fe(II)/SPC system is suitable for a wider pH range than the conventional Fenton system and that PCE was mainly degraded by hydroxyl radical oxidation, but the stability of Fe(II) remained a problem [36]. Therefore, the purpose of this work was to study the oxidative degradation of PCE with SPC and Fe(II) chelated by various chelating agents (CIT, OA, ASC, EDTA, trisodium citrate 2-hydrate ($CIT\text{-}Na_3$), and $EDTA\text{-}Na_2$). In order to investigate the mechanism of PCE degradation in various systems, the dominant free radicals in chelated Fe(II)-based catalyzed SPC system were studied by using free radical probe compounds and free radical scavengers to elucidate the PCE degradation performance. In this process, the dominant free radicals were further detected by electron paramagnetic resonance (EPR) to identify the main reactive species in PCE degradation. Furthermore, the mineralization of PCE during its degradation was assessed by measuring the Cl^{-} release rate using ion chromatography, and the intermediates were determined using gas chromatography/mass spectrometry (GC/MS). Finally, the PCE degradation mechanism in chelated Fe(II)-based catalyzed SPC system was proposed accordingly.

2. Materials and methods

2.1. Materials

The following reagents were purchased from Aladdin (Shanghai, China) and used without further purification: perchloroethylene (PCE, C_2Cl_4, >99.0%), carbon tetrachloride (CT, CCl_4, >99.5%), isopropyl alcohol ($(CH_3)CHOH$, >99.5%), nitrobenzene ($C_6H_5NO_2$, >99.0%), chloroform ($CHCl_3$, >99.0%), iron(II) sulfate heptahydrate