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Benzene depletion by Fe^{2+}-catalyzed sodium percarbonate in aqueous solution

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HIGHLIGHTS

- Effective degradation of benzene is achieved by Fe^{2+}-catalyzed SPC.
- The primary reactive oxygen species is $HO^{\cdot}$ in SPC/Fe^{2+} system.
- Fe^{2+}-catalyzed SPC oxidation is suitable for alkalescent conditions.
- Effective Fe^{2+}-catalyzed SPC oxidation of benzene in real groundwater is achieved.

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ABSTRACT

In this study, the chemical oxidation of benzene by Fe^{2+}-catalyzed sodium percarbonate (SPC) was conducted. The effects of various factors, such as the SPC/Fe^{2+}/benzene molar ratio, temperature, order of the reagent addition, solution matrix including the presence of anions (Cl^-, HCO_3^-, SO_4^{2-} and NO_3^-) and natural organic materials (NOM), and the initial solution pH, were thoroughly investigated. The experimental results showed that benzene can be completely degraded (<0.01 mg/L) in 20 min with a SPC/Fe^{2+}/benzene molar ratio of 10/10/1 at 20 °C, indicating the effectiveness of Fe^{2+}/SPC oxidation for benzene removal. The degradation of benzene is significantly influenced by the SPC/Fe^{2+}/benzene molar ratio as well as the order of the reagent addition, but less affected by the temperature. HCO_3^- and NOM have significant scavenging effects on benzene degradation, whereas Cl^- has a slightly expediting effect at low concentration and a scavenging effect at high concentration. Meanwhile, the influences of SO_4^{2-} and NO_3^- are negligible at the tested ionic strength ranges. The degradation of benzene was not apparently inhibited at pH 9.0. This result indicated that Fe^{2+}-catalyzed SPC oxidation is suitable for alkalescent conditions which is superior to the conventional Fenton process. Hydroxyl radical ($HO^{\cdot}$) has been confirmed as the predominant species responsible for benzene degradation by using free radical probe compounds tests, $HO^{\cdot}$ scavengers tests and electron paramagnetic resonance (EPR) analysis. In addition, an amazing effective Fe^{2+}-catalyzed SPC oxidation of benzene in actual groundwater was achieved, indicating that Fe^{2+}-catalyzed SPC oxidation is a highly promising technique for the remediation of benzene-contaminated groundwater.

1. Introduction

The contamination of groundwater and soils by toxic and biorefractory organic compounds remains a widespread problem even after several decades of remediation efforts. BTEX (benzene, toluene, ethylbenzene and xylenes) are constituents of fossil fuels that are widely used in industrial processes. BTEX are frequently detected contaminants of groundwater and soils because of discharge from factories and leachate from gas storage tanks or landfills [1]. The slow dissolution of BTEX often results in a contaminated plume of groundwater. The concentration of contaminants found in groundwater can vary from several μg/L to over hundreds of mg/L. Because these water-soluble chemicals (aqueous solubility at 25 °C for BTEX; 22.4, 5.8, 1.43 and 1.65 mM (o-xylene), respectively) may be dispersed in the environment, their occurrence may present a threat to human and ecosystem health because of their toxicity [2]. For example, these chemicals may cause neurological damage according to the previous reference, and hence they are listed as US EPA priority pollutants [1,2]. Of

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the BTEX components, benzene is especially toxic and is categorized as a carcinogen by the US National Toxicology Program though ethylbenzene is also possibly carcinogenic to humans. Therefore, the maximum contaminant level of benzene has been regulated at 5 $\mu g L^{-1}$ under the Safe Drinking Water Act [1,2].

Although remediation by natural attenuation (RNA) is considered the most economical approach for the treatment of BTEX-contaminated soils and groundwater, more active technologies may be necessary when there are conditions under which RNA is inadequate. Compared to RNA and other conventional treatment technologies, including pump and treat, phytoremediation and bioremediation, in situ chemical oxidation (ISCO) is a more popular and effective method for the remediation of groundwater and soils contaminated by BTEX because of its strong degradation capability and high treatment efficiency. For ISCO, several chemical oxidative reagents, including ozone (O_3), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) combined with Fe(II) (Fenton's reaction), and sodium persulfate, are injected into groundwater or soil to degrade contaminants into less toxic substances [3–5]. O_3 is a strong oxidant (E^0 = 2.07 V vs. SHE) that reacts selectively with electron-rich moieties [3]. However, O_3 is only sparingly soluble in water (~40 mg/L) and thus its practical application may be limited by low delivery rates [3]. $KMnO_4$ (E^0 = 1.68 V vs. SHE), as a strong and relatively soluble and stable oxidant, has received considerable attention and has been frequently used in remediation projects because of its ease of use and persistence in the environment [4]. Unfortunately, the strong selectivity of $KMnO_4$ (e.g., toward unsaturated moieties) limits its broad application [4]. Compared with the two oxidative reagents mentioned above, H_2O_2 has not only higher solubility but also a high oxidation potential (E^0 = 1.78 V vs. SHE) and, therefore, can degrade organic contaminants non-selectively [5]. Meanwhile, the catalyzed decomposition of hydrogen peroxide (H_2O_2) by Fe(II) to form hydroxyl radicals ($HO^{\cdot}$), commonly known as Fenton's reagent, has attracted much more attention due to its strong and non-selective oxidation ability in the degradation of organic contaminants [6].

$HO^{\cdot}$, with a redox potential of 2.70 V, is a strong oxidant that can react with most organic contaminants such as TCE, BTEX, and polychlorinated biphenyls (PCBs) at nearly diffusion-controlled rate with a second-order rate constant > $10^9 M^{-1} s^{-1}$ [7]. However, the persistence of $HO^{\cdot}$ generated by Fenton's reaction is rather low even though they are very powerful and hence H_2O_2 can be consumed during transport through the soil and aquifer before reaching contaminants in some cases [8]. It is also well known that the reaction pH needs to be controlled at approximately 3.0 when using the Fenton's reagent for the treatment of contaminated groundwater, and the iron catalyst is easily precipitated to ferric hydroxide ($Fe(OH)_3$) with increasing solution pH [9]. So the practical effects of this technology will be limited because the pH of natural groundwater is often near neutral or slightly alkaline.

Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$, SPC), as an adduct of 32.5% hydrogen peroxide and 67.5% sodium carbonate (based on weight) [10], has recently been used as another oxidant for ISCO [11]. Compared with liquid H_2O_2, SPC comes in a solid form that can be used as a dry carrier of H_2O_2 and as a granulated powder is easier to transport. Meanwhile, SPC can also lead to the development of well-known Fenton-like chemistry by disassociating to hydrogen peroxide and sodium carbonate when mixed with water, as shown in Eq. (1), and it offers many of the same functional benefits as liquid H_2O_2. In comparison to the Fenton's reaction, SPC can effectively oxidize many water impurities due to the effectiveness in a wider pH range. In addition, the production of carbon dioxide, water and sodium carbonate in the reaction of SPC with organic compounds is not of environmental concern they exist in natural groundwater. Moreover, SPC is non-toxic to microbes, making it compatible with the following bioremediation. Therefore, Fe^{2+}-catalyzed SPC oxidation might be a highly promising technique for BTEX contaminated groundwater remediation:

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

To date, there have been many researchers focusing on the remediation of groundwater and soils contaminated by BTEX [12,13]. Besides, some researchers reported the application of SPC to replace liquid H_2O_2 in the remediation of soil or groundwater contaminated by chlorinated aromatic hydrocarbons [14], trichloroethylene [15] and polycyclic aromatic hydrocarbon (PAHs) [11], with significant contaminant removal efficiency. However, to our best knowledge, there are a paucity of literatures related to the degradation of BTEX by Fe^{2+}-catalyzed SPC system (SPC/Fe^{2+}). In this study, benzene, one of the known carcinogenic compounds in BTEX, was selected as the target compound. The degradation performance of benzene in the SPC/Fe^{2+} system was investigated for the first time. Batch tests were conducted to evaluate the influence of remediation conditions, such as the dosages of Fe^{2+} and SPC, order of the reagent addition, anions (Cl^-, HCO_3^-, SO_4^{2-} and NO_3^-), natural organic materials (NOM) and initial solution pH on the efficiency of SPC/Fe^{2+} process for the degradation of benzene in aqueous solution. In order to investigate the benzene degradation mechanisms, free radical scavengers and free radical probe compounds were used to explore the dominant free radicals, and the electron paramagnetic resonance (EPR) was tested to verify the dominant free radicals. Finally, benzene removal in actual groundwater was also tested to assess its potential application in real remediation processes.

2. Materials and methods

2.1. Materials

The following reagents were obtained from Aladdin (Shanghai, China): benzene (C_6H_6, 99.7%), carbon tetrachloride (CCl_4, CT, 99.5%), isopropyl alcohol ($(CH_3)CHOH$, IPA, 99.5%), methanol (CH_3OH, 99.8), nitrobenzene ($C_6H_5NO_2$, NB, 99.0%), chloroform ($CHCl_3$, CF, 99.0%), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.0%), sodium nitrate ($NaNO_3$, 99.0%), sodium chloride (NaCl, 99.5%), sodium sulfate (Na_2SO_4, 99.0%), sodium bicarbonate ($NaHCO_3$, 99.5%). Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$, SPC, 98%) was purchased from Acros Organics (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Sigma (Shanghai, China). Humic acid (HA, fulvic acid >90%, was used instead of NOM in this study as fulvic acid is one of the main fractions of dissolved organic matter in nature with high solubility), potassium biphthalate ($C_8H_5KO_4$, 99.0%), 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$, 98%), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, HH, 99.0%) were purchased from Shanghai Jingchun Reagent Ltd. Co. (Shanghai, China). H_2SO_4 (0.1 M) or NaOH (0.1 M) was used for solution pH adjustment. All of the reagents were used as received. Ultrapure water from a Milli-Q water process (Classic DI, ELGA, 102 Marlow, U.K.) was used to prepare aqueous solutions. The actual groundwater (see Table 1) from a site in Minhang, Shanghai, China, were collected from a well approximately 10 m

Table 1
Characteristics of groundwater.

Parameter	Value
pH	6.5
Total organic carbon (TOC, mg/L)	50.4
Cl^- concentration (mg/L)	64.1
HCO_3^- concentration (mg/L)	678.6
NO_3^- concentration (mg/L)	21.5
SO_4^{2-} concentration (mg/L)	398.2