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Simultaneous removal of benzene, toluene, ethylbenzene and xylene (BTEX) by CaO_2 based Fenton system: Enhanced degradation by chelating agents

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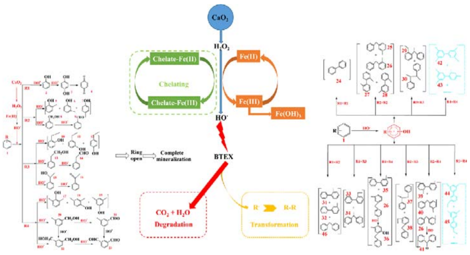
GRAPHICAL ABSTRACT



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ABSTRACT

Most of the calcium peroxide (CaO_2) based Fenton oxidation studies focus on the individual pollutant degradation. In this study, the simultaneous oxidation of benzene, toluene, ethylbenzene, and xylene (denoted as BTEX) by CaO_2 based Fenton system was demonstrated. It was observed that BTEX removal increased with increasing molar ratios of CaO_2/Fe(II)/BTEX. In the case of CaO_2/Fe(II)/BTEX molar ratio of 5/5/1, BTEX removal were 35% in the ultrapure water and 15% in the actual groundwater. In the case of CaO_2/Fe(II)/BTEX molar ratio of 40/40/1, BTEX removal were elevated to 98% in the ultrapure water and 88% in the actual groundwater. Chelating Fe(II) agents, such as citric acid (CA), oxalic acid (OA), and glutamic acid (GA), significantly enhanced the destruction of BTEX. When the molar ratio of Fe(II)/CA, Fe(II)/GA, and Fe(II)/OA was 10/20 while fixing CaO_2/Fe(II)/BTEX molar ratio of 10/10/1, the enhancements in BTEX removal were 60%, 32%, and 72%, respectively. In terms of BTEX removal, OA chelated Fe(II) was demonstrated to be most effective in the CaO_2/Fe(II)/BTEX system. Based on TOC analysis, the transformation effect was confirmed. The transformation products of BTEX were determined and oxidation pathways were proposed, in which $HO^{\cdot}$ was mostly responsible to the parent compounds mineralization.

1. Introduction

BTEX refers to the aromatic components (usually benzene, toluene, ethylbenzene, and xylenes) that were frequently found in gasoline. Given that gasoline is stored in underground tanks, faulty installation or inadequate operation/maintenance may result in undetected soil and

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groundwater contamination with high potential for dispersion of the unnoticed dissolved contaminant [1]. Bioremediation is considered as one of the most economical options for groundwater remediation. However, time constraints and other environmental requirements, such as temperature, dissolved oxygen, and pH, make groundwater bioremediation restricted to some extent.

Advanced oxidation processes (AOPs) are promising alternative remediation techniques [2]. Among AOPs, Fenton and Fenton-like reactions are appealing due to their high oxidation capacity. Fenton reaction produces hydroxyl radicals ($HO^{\cdot}$) through the hydrogen peroxide (H_2O_2) decomposition catalyzed by ferrous ion (Fe(II)). The mechanism for Fenton reaction is very complex and still not very clear. The well-known conventional Fenton mechanism involves the following reactions (Eqs. (1)–(5)) [3,4]:

$$H_2O_2 + Fe(II) \rightarrow HO^- + HO^{\cdot} + Fe(III) \tag{1}$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}\ (HO_2^{\cdot} \leftrightarrow O_2^{\cdot-} + H^+) \tag{2}$$

$$HO_2^{\cdot} + Fe(III) \rightarrow H^+ + O_2 + Fe(II) \tag{3}$$

$$HO_2^{\cdot} + Fe(II) \rightarrow HO_2^- + Fe(III) \tag{4}$$

$$HO^{\cdot} + Fe(II) \rightarrow HO^- + Fe(III) \tag{5}$$

The reaction between H_2O_2 and Fe(II) initiates the chain reactions. Eqs. (1)–(3) form the reaction chain without oxidation of organic compounds, and Eqs. (4) and (5) serve as the chain termination reaction. $HO^{\cdot}$ is a powerful oxidant and can efficiently react with many organic contaminants [5,6]. Fenton reaction can, therefore, be applied to remediate various contaminated soils and groundwater. However, instability of liquid H_2O_2 in the subsurface limits the application of Fenton reaction in groundwater remediation. Thus, a stable H_2O_2 source is a critical requirement for oxidative degradation of organic contaminants in soils and groundwater.

Calcium peroxide (CaO_2) has been considered as an alternative solid source of H_2O_2 (Eq. (6)) [7], which can then participate in Fenton reaction (Eq. (1)). The released H_2O_2 could degrade contaminants directly or through the generation of $HO^{\cdot}$ and other active species (such as $O_2^{\cdot-}$) [8]. Significantly, CaO_2 could produce H_2O_2 over a wide pH range, and the maximum conversion factor for calculating H_2O_2 released from CaO_2 is 0.47 [7].

$$2H_2\ O + CaO_2 \rightarrow Ca(OH)_2 + H_2O_2 \tag{6}$$

CaO_2 has been used in removing some toxic and persistent pollutants. For instance, CaO_2 has been applied to destruct the endocrine-disrupting compounds [9], oxidize the cable insulating oil [10], treat the 2,4,6-trinitrotoluene (TNT) [11], toluene [12], and other pollutants [13,14]. The degradation of refractory organic contaminants using CaO_2 alone is relatively slow [9–14]. Recent research has shown that the activation of CaO_2 by Fe(II) could degrade single contaminant in a short time. The CaO_2/Fe(II) system has been used to treat trichloroethylene (TCE) [15,16], benzene [17,18] contamination. Most of CaO_2 based Fenton oxidation studies focused on the individual pollutant degradation, few research focused on BTEX mixture pollutants destruction. Though CaO_2 alone has been employed in biodegradation as the oxygen supplier to enhance BTEX pollutants remediation [19–21], the biodegradation requires long remediation time and strict environmental conditions. Thus it is essential to evaluate the treatment performance of mixed pollutants in the CaO_2/Fe(II) system. Since BTEX is frequently detected in contaminated sites, we tested the BTEX mixture destruction performance in the CaO_2/Fe(II) system in this study.

In general, an initially rapid incomplete pollutant decay is observed in the CaO_2/Fe(II) system. This may occur due to excess of Fe(II) in the system, which quickly consumes the reactive species $HO^{\cdot}$ (Eq. (5)). Additionally, the applicability of Fenton process would be limited by the accumulated Fe(III) as the result of ferric hydroxide ($Fe(OH)_3$) formation. Various approaches have been considered in Fenton process to avoid the initially rapid incomplete pollutants decay in the system [2,22]. Some of the approaches use iron-bearing minerals, such as goethite [23], nano zero-valent-iron [24], or iron (II) phthalocyanine [25], to guarantee a slow Fe(II) release. Another approach is the use of Fe(II)-chelating agents, an attractive alternative for diminishing the loss of soluble iron by avoiding its precipitation and regulating Fenton reaction efficiency. For example, citric acid (CA) [26–28], oxalic acid (OA) [27,29], glutamic acid (GA) [30], have been widely investigated to regulate Fe(II) or Fe(III) in Fenton reaction and diminish the loss of soluble Fe(II) iron ions.

The present study was conducted with the aim of extending CaO_2 based Fenton system application in degrading BTEX mixture. To demonstrate the CaO_2/Fe(II) system performance and investigate the function of Fe(II)-chelating agents, the following researches have been conducted in order to: (1) identify the optimal treatment conditions (including chemical dosages and reaction time) for the maximum reduction of BTEX in the CaO_2/Fe(II) oxidation system; (2) test the effects of chelating agents (ChA) on BTEX reduction in the CaO_2/ChA/Fe(II) system; (3) quantify BTEX destruction performance in the CaO_2/Fe(II) oxidation system by developing mathematical expressions; and (4) propose BTEX destruction mechanism in the tested system. The overall significance of this study is expected to provide the scientific basis for efficient BTEX mixture treatment in contaminated groundwater by means of the CaO_2/Fe(II) oxidation technique.

2. Experiments

2.1. Materials and analytical methods

All the chemicals used in the experiments are listed in Supplementary Material (Text S1).

BTEX concentration was measured by a gas chromatography (Agilent 7890A) equipped with a headspace auto-sampler (Agilent 7697A), a flame ionization detector (FID), and a HP-5 column (30 m × 0.32 mm × 0.25 μm) as described in Supplementary Material (Text S2). The intermediates formed during BTEX destruction were identified using the GC/MS (Focus DSQ) (Supplementary Material, Text S2). Benzoic acid (BA) and p-hydroxybenzoic acid (p-HBA) were analyzed by a HPLC (Shimadzu LC-20AT) coupled with UV–vis detector (SPD-20A) and an auto-sampler (SIL-20A) (Supplementary Material, Text S2) [31]. The concentration of the available Fe(II) was determined at 396 nm followed the treatment with 1,10-phenanthroline [32], and the total iron was analyzed using an atomic absorption spectrometer (AAS) instrument (novAA). The H_2O_2 concentration was determined at 410 nm by spectrophotometric method [33]. The dissolved oxygen (DO) was measured using DO meter (YSI 5100). Total organic carbon (TOC) was determined by a TOC analyzer (Liquid TOC). The solution pH was recorded by a PB-10 pH meter (Sartorius) equipped with a pH/ATC electrode (Sartorius), and all the initial and final pH values are listed in Table S1.

2.2. Experimental design

The initial BTEX concentration was set at 0.5 mM (B: 39 mg/L; T: 46 mg/L; E: 53 mg/L; X: 53 mg/L). The temperature in all experiments was controlled at 20 ± 0.5 °C. The predetermined dosage of ferrous sulfate was added into the 250 mL reactor, subsequently with a predetermined CaO_2 added. Reactor was stirred at a constant speed, and 2.5 mL samples were transferred to headspace vials for GC analysis at the determined time intervals. Control experiments with absence of CaO_2 and/or Fe(II) were carried out in parallel and no significant loss of BTEX from volatilization was found (data given in Supplementary Material, Fig. S1). All the experiments were replicated and the averaged data were reported in the results. Preliminary tests confirmed the primary reactive species in this system (Supplementary Material, Text S3 and Fig. S2). Production of $HO^{\cdot}$ was quantified by measuring