Degradation of BTEX in groundwater by nano-CaO₂ particles activated with L-cysteine chelated Fe(III): enhancing or inhibiting hydroxyl radical generation

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ABSTRACT

The simultaneous oxidation performance of benzene, toluene, ethylbenzene, and xylene (BTEX) by nanoscale calcium peroxide particles (nCaO₂) activated with ferric ions (Fe(III)) and the mechanism of the enhancement of BTEX degradation by L-cysteine (L-cys) were investigated. The batch experimental results showed that the nCaO₂/Fe(III)/L-cys process was effective in the destruction of BTEX in both ultrapure water and actual groundwater. A proper amount of L-cys could enhance BTEX degradation due to the promotion of Fe(II)/Fe(III) redox cycles by the participation of L-cys, but an excessive presence of L-cys would cause inhibition. Adding 1.0 mM L-cys to the nCaO₂/Fe(III) system, the concentration of Fe(II) increased to 1.15 mM instantly. Simultaneously, the yield of HO• produced by the 1.0 mM L-cys-containing system was 0.066 mM at 180 min reaction, higher than that without L-cys (0.049 mM). When excess L-cys (5.0 mM) was added to the system, the amount of Fe(II) increased to 3.73 mM because excessive L-cys caused a large amount of Fe(III) in the system to be reduced. However, the yield of HO• decreased to 0.043 mM since excessive Fe(II) could conversely scavenge HO• to produce Fe(III) again. EPR tests and quenching results indicated that HO• was the dominant reactive species in the nCaO₂/Fe(III)/L-cys system. For the removal of BTEX, the optimal molar ratio of nCaO₂/Fe(III)/L-cys was 10.5/20/1 based on calculation by response surface methodology (RSM). Finally, the BTEX destruction pathway was proposed according to the detected intermediates by liquid chromatography–mass spectrometry (LC–MS).

Key words: BTEX, chemical oxidation, groundwater remediation, L-cysteine, nanoscale calcium peroxide particles

HIGHLIGHTS

- nCaO₂/Fe(III) system with L-cysteine (L-cys) was applied to remediate mixed contaminants.
- A suitable amount of L-cys promoted redox cycling (Fe(III) → Fe(II)).
- The mechanism of enhancing or inhibiting hydroxyl radical generation was investigated.
- Proposed BTEX destruction pathway in the nCaO₂/Fe(III)/L-cys system.
- nCaO₂/Fe(III)/L-cys system was recommended for BTEX-contaminated actual groundwater remediation.

INTRODUCTION

Mono-aromatic compounds (MACs), composed of one single benzene ring, exist in groundwater mainly as a result of accelerated industrialization (Dhanya 2019). Of these MACs, benzene, toluene, ethylbenzene, and xylenes (BTEX) are known to be relatively water-soluble and have carcinogenic and neurotoxic effects which can increase the risk of detrimental health effects (Stasik et al. 2015; Godin et al. 2020; Yang et al. 2020). It has been reported that BTEX are the most frequently detected aromatic hydrocarbons in contaminated groundwater in China, causing the rapid migration of BTEX pollution (Zhao et al. 2020). However, the groundwater in most MACs polluted sites is usually under anaerobic conditions where BTEX exhibits slower degradation kinetics and a more limited catabolic range in such environments (Stasik et al. 2015; Huang et al. 2017). Therefore, remarkable efforts are made toward in situ chemical oxidation (ISCO) to ensure BTEX degradation eventually to be broken off completely (Minetti et al. 2017; Ma et al. 2018; Xia et al. 2020).

Calcium peroxide (CaO₂), as an alternative oxidant for ISCO, has become a reassuring option in recent decades. CaO₂, compared with hydrogen peroxide (H₂O₂), has moderate longevity and can provide an aerobic condition for natural bacteria.
Most importantly, the released \( \text{H}_2\text{O}_2 \) from \( \text{CaO}_2 \) (the maximum amount of 0.47 g \( \text{H}_2\text{O}_2 \)/g of \( \text{CaO}_2 \)) can participate in the Fenton reaction and generate \( \text{HO}^+ \), which are the dominant radicals for the pollutant degradation under aqueous conditions \( \text{(Amina et al. 2018; Xue et al. 2018a, 2018b; Sun et al. 2019; Tang et al. 2020)} \). At the same time, hydroperoxy radical \( (\text{HO}_2^+) \), superoxide radical \( (\text{O}_2^-) \), singlet oxygen \( (^1\text{O}_2) \) and hydroperoxide anions \( (\text{HO}_2^-) \) can be generated as well in the \( \text{CaO}_2 \)-based Fenton system \( \text{(Ma et al. 2007; Zhang et al. 2015a, 2015b; Pan et al. 2018; Zheng et al. 2019)} \). These reactive/reductive species can occur simultaneously in the Fenton or Fenton-like process and exhibit a different oxidizing/reducing capacity for diverse organic pollutants because of the high selectivity of these reactive species, such as \( \text{O}_2^- \) and \( ^1\text{O}_2 \) \( \text{(Wang & Wang 2020)} \). This means that the oxidizing capacity of the combined Fenton-like process varies with the different target pollutants. Moreover, nanoscale \( \text{CaO}_2 \) \( (\text{nCaO}_2) \) was synthesized and displayed better dispersion and transportation ability than commercial \( \text{CaO}_2 \) from our previous study, owing to its smaller particle size and larger surface area \( \text{(Qian et al. 2013, 2016; Mosmeri et al. 2019; Ali et al. 2020; Sun et al. 2020)} \). Therefore, \( \text{nCaO}_2 \) has shown great perspective and attraction to scientists and engineers. \( \text{CaO}_2 \) similar to the Fenton process, can be activated by transition metals \( \text{(Lu et al. 2017)} \). Some researchers reported the application of \( \text{CaO}_2 \) activated with ferrous ion \( (\text{Fe(II)}) \) for the remediation of groundwater contaminated by trichloroethylene \( \text{(Zhang et al. 2015a, 2015b)} \), carbon tetrachloride \( \text{(Tang et al. 2018)} \), tetrachloroethene \( \text{(Jiang et al. 2019)} \), and benzene \( \text{(Xue et al. 2016)} \). \( \text{CaO}_2 \) can be also activated with ferric ion \( (\text{Fe(III)}) \) through spontaneous superoxide/perhydroxyl-driven reactions as well as the regeneration of \( \text{Fe(II)} \) in the process \( \text{(Zhang et al. 2017)} \). However, that \( \text{Fe(III)} \) precipitation as ferric hydroxide \( (\text{Fe(OH)}_3) \) at neutral pH does not re-dissolve limits the application of the \( \text{CaO}_2/\text{Fe(III)} \) system \( \text{(Zhou et al. 2017)} \). Chelating agents have been employed to overcome the above-mentioned limitation by researchers. For instance, citric acid \( (\text{CA}) \), tartaric acid \( (\text{TA}) \), oxalic acid \( (\text{OA}) \), glutamic acid \( (\text{Glu}) \), and ethylenediaminetetraacetic acid \( (\text{EDTA}) \) were introduced to the iron activation of the Fenton process to prevent iron precipitation and accelerate iron recycling \( \text{(Huang et al. 2016; Hu et al. 2018; Yuan et al. 2019; Bai et al. 2020)} \). \( \text{L-cysteine (L-cys)} \), a sulfur-containing non-phenolic amino acid, also exhibits \( \text{Fe(III)} \)-reducing activity owing to the actively functional sulfhydryl group \( (\text{–SH}) \) \( \text{(Lu et al. 2020; Ramos et al. 2020)} \). A rapid transformation from \( \text{Fe(III)} \) to \( \text{Fe(II)} \) in the presence of \( \text{L-cys} \) can happen, and at the same time the oxidation of \( \text{L-cys} \) to cystine \( \text{(Equation (1)) (Luo et al. 2016)} \). Furthermore, weak coordination may occur between \( \text{Fe(III)} \) and the carboxyl group \( (\text{–COOH}) \) of \( \text{L-cys} \) \( \text{(Li et al. 2016)} \).

\[
2\text{Fe(III)} + 2\text{HS–CH}_2–\text{CH–NH}_2 \rightarrow 2\text{Fe(II)} + 2\text{H}^+ \ + \text{COOH–CH}–\text{CH–S–S–CH}_2–\text{CH–NH}_3 \tag{1}
\]

However, \( \text{Luo et al. (2016)} \) reported that methylene blue removal increased with the concentration of \( \text{L-cys} \) up to 50 \( \mu \text{M} \), and its removal decreased with further increase in \( \text{L-cys} \) concentration. Similarly, the degradation of sulfadiazine in an \( \text{L-cys}-\text{Fenton} \) system increased with the increase of \( \text{L-cys} \) usage at the beginning and decreased with much more \( \text{L-cys} \) addition \( \text{(Lu et al. 2020)} \). The consumption of \( \text{HO}^+ \) with excessive \( \text{L-cys} \) might be the primary reason. In order to clearly understand the performance of \( \text{nCaO}_2 \) in the \( \text{L-cys}-\text{Fenton} \) reaction on composite pollutant removal and to reveal the mechanism of the role of \( \text{L-cys} \) in this system, in this article, the evaluation of an \( \text{nCaO}_2/\text{Fe(III)} \) system on \( \text{BTEX removal} \) was thoroughly investigated. The role of \( \text{L-cys} \) in the \( \text{Fe(III)}/\text{Fe(II)} \) cycle and the generation of \( \text{HO}^+ \) was confirmed. Finally, the application potential of the \( \text{L-cys}-\text{Fenton} \) system for \( \text{BTEX removal} \) in actual groundwater remediation implementation was demonstrated.

**METHODS**

**Materials**

\( \text{Benzenes (C}_6\text{H}_6, 99.0\%) \), toluene \( (\text{C}_8\text{H}_8, 99.0\%) \), ethylbenzene \( (\text{C}_9\text{H}_{10}, 99.0\%) \), xylenes \( (\text{C}_8\text{H}_{10}, 99.0\%) \), hydrogen peroxide \( (\text{H}_2\text{O}_2, 30\% \text{wt}) \), ferric sulfate \( (\text{Fe}_2(\text{SO}_4)_3, 99.0\%) \), calcium chloride \( (\text{CaCl}_2, 96\%) \), polyethylene glycol 200 \( (\text{PEG} 200, 99.0\%) \), ammonia \( (\text{NH}_3\text{H}_2\text{O}, 28\%) \), sulfuric acid \( (\text{H}_2\text{SO}_4, 98\%) \) and sodium hydroxide \( (\text{NaOH}, 96.0\%) \) were purchased from \( \text{Aladdin Reagent Co. Ltd (Shanghai, China)} \).\( \text{Tert-butanol (C}_4\text{H}_{10}\text{O, TBA, 99.0\%), benzoic acid (C}_7\text{H}_6\text{O}_2\text{, BA, 99.5\%), 5,5-dimethyl-1-pyrroline N-oxide (C}_6\text{H}_11\text{NO, DMPO, 99.0\% and L-cysteine (C}_6\text{H}_5\text{NO}_2\text{, L-cys, 99.0\% were supplied from Shanghai Lingfeng Reagent Co. Ltd (Shanghai, China). The ultrapure water was provided by a Milli-Q water purification} \)
system (Classic DI; ELGA, Marlow, UK). The actual groundwater from a well approximately 15 m deep below the surface (Songjiang, Shanghai, China) was used for preparing the actual BTEX contaminated solutions.

**Preparation of nCaO2**

Briefly, CaCl₂ was utilized as the precursor and H₂O₂ was added drop-by-drop in the presence of the surface stabilizer PEG 200. The detailed preparation method of nCaO₂ can be found in the Supplementary Material, Text S1.

**Experimental procedure**

BTEX stock solutions (0.5 mM) were transferred into a 250 mL glass reactor. A magnetic stirrer was used to mix the solution homogeneously and the temperature was controlled at 20 °C. The test started immediately after introducing the predetermined dosages of Fe(III) and nCaO₂. At the desired intervals, 2.5 mL samples were withdrawn and transferred into headspace vials containing 1.0 mL methanol. The vials were sealed immediately and then analyzed by a gas chromatograph (GC) instrument.

**Analytical methods**

BTEX were analyzed by a GC coupling with a headspace auto-sampler, a flame ionization detector (FID), and an HP-5 column (50 m × 0.32 mm × 0.25 μm) as described in the Supplementary Material (Text S2). Benzoic acid (BA) was chosen as a probe to quantify the production of HO⁻. The calculated production of p-HBA by the reaction of BA and HO⁻ has the conversion factor (5.87 ± 0.18) with the production of HO⁻ in the system (Xue et al. 2018a, 2018b).

The samples were extracted at 3 min after the start of the reaction for the analysis of intermediates during BTEX degradation. An amount of 150 mL ethyl acetate was mixed with 150 mL of the reaction solution and rested for 5 min. The top layer ethyl acetate mixed solution was condensed to 1.5 mL by a rotary evaporator (N-1300D; Eyela, Japan). The condensed solution was filtered by an organic-phase filter and tested by liquid chromatography–mass spectrometry (LC–MS) (Q-Exactive plus; ThermoFisher, China) (Supplementary Material, Text S2). At 3 min after the start of the reaction, 1.0 mL samples were withdrawn from the reactor and mixed with 1.0 mL DMPO (20.0 mM) for 1 min, then the mixed samples were analyzed by electron paramagnetic resonance (EPR) (EMX-8/2.7; Bruker, USA) for the detection of reactive oxygen species. The DMPO-OH was monitored at the settings for the EPR spectrometer of center field (3,510.00 G), microwave frequency (9.79 GHz), and power (5.05 mW). Total organic carbon (TOC) was determined by using a TOC analyzer (LiquiTOC, Germany). The BTEX degradation test in the actual groundwater was carried out by replacing ultrapure water with actual groundwater. The natural organic matter (NOM) of the actual groundwater was determined by ion chromatography (ICS-1100; ThermoFisher, China).

A central composite design (CCD) based on the response surface methodology (RSM) was used for the analysis of BTEX degradation performance. The dosages of nCaO₂ and Fe(III) were coded as X₁ and X₂. The initial concentration of L-cys was considered as X₃, 21 groups of experiments were tested. The ranges of both X₁ and X₂ were set from 1.0 to 20.0 mM and the range of X₃ was set from 1.0 to 10.0 mM.

**RESULTS AND DISCUSSION**

**Performance of BTEX removal in the nCaO₂/Fe(III)/L-cys system**

A series of comparative tests were carried out to estimate the performance of BTEX degradation in the nCaO₂/Fe(III)/L-cys system in order to investigate the L-cys chelating effect. The control tests for BTEX removal were conducted without nCaO₂ or Fe(III) under the same conditions and the results showed the BTEX volatilization rate was less than 5.0%. The removal of BTEX was below 8.0% when only nCaO₂ or Fe(III) existed. This means that nCaO₂ or Fe(III) alone was not available to degrade BTEX. In the nCaO₂/Fe(III)/L-cys system, rapid BTEX destruction was observed within 10 min, and the destruction became slower in the remaining reaction time. The reaction was terminated at 180 min in this test (Figure S1).

The performance of BTEX degradation in various systems is presented in Figure 1(a). As can be seen from Figure 1(a), the degradation efficiencies of BTEX were 19.7%, 17.6%, 21.6%, and 17.7%, respectively, when nCaO₂ and Fe(III) co-existed, but had a significant improvement (91.3%, 91.4%, 92.3%, and 86.6% degradation efficiencies) when 1.0 mM L-cys was introduced into the system. This means that nCaO₂ activated with Fe(III) could simultaneously degrade the combined BTEX pollutants, and L-cys could effectively improve the degradation capacity of the system on BTEX removal. The degradation efficiency of BTEX in the nCaO₂/Fe(II) system was higher than that in the nCaO₂/Fe(III) system. A possible explanation might be that...
Fe(III) reacted with H$_2$O$_2$ released from nCaO$_2$-producing HO$^\cdot$ radicals and Fe(II), and then Fe(II) catalyzed H$_2$O$_2$ to complete the Fenton reaction (Munoz et al. 2015). Matta et al. (2007) reported that minerals containing both Fe(III) and Fe(II) were more effective than Fe(III) oxides in the degradation of 2,4,6-trinitrotoluene. Giannakis et al. (2017) reported that Fe(II) salt was more efficient than Fe(III) on removing viruses from wastewater in the photo-Fenton process. L-cys chelate-Fe(III) presented outstanding catalytic performance. Under the same molar ratio conditions, BTEX had higher removal in the nCaO$_2$/Fe(III)/L-cys system than those in the nCaO$_2$/Fe(III) and nCaO$_2$/Fe(II) systems (70.8%, 72.8%, 76.1%, and 61.5% removal of BTEX in the nCaO$_2$/Fe(II) system). However, with the addition of L-cys from 1.0 to 10.0 mM, the degradation efficiency of BTEX declined from 91.3%, 91.4%, 92.3%, and 86.6% to 41.4%, 40.7%, 45.8%, and 28.6%, respectively (Figure 1(b)). Therefore, it could be summarized that a proper amount of L-cys promoted the pollutant degradation ability of the nCaO$_2$/Fe(III) system, but excessive L-cys inhibited BTEX degradation. The excessive L-cys could compete for HO$^\cdot$ with BTEX, leading to the decline of BTEX removal. This phenomenon of the consumption of HO$^\cdot$ by excessive L-cys was also reported in a sulfadiazine degradation system (Lu et al. 2020).

To investigate the effect of the initial nCaO$_2$ or Fe(III) concentration on BTEX degradation, we established response surface methodology (RSM) models (Figure 2). When the initial L-cys concentration constant was made 1.0 mM, the degradation of BTEX increased along with the increase of nCaO$_2$ and Fe(III) concentrations. However, the increasing rates of xylenes by nCaO$_2$ and Fe(III) were higher than the others. This means that the degradation efficiency of xylenes was influenced by the initial concentration of nCaO$_2$ and Fe(III) more sensitively than benzene, toluene, or ethylbenzene. Overall, the influence of the BTEX degradation of factors X$_1$ and X$_2$ was the same, and a better degradation efficiency could be achieved at the same nCaO$_2$ and Fe(III) concentration. Making nCaO$_2$ or Fe(III) constant and increasing another concentration could not contribute to a better BTEX degradation. This result was also reported in the nCaO$_2$/Fe(II) system on BTEX removal (Sun et al. 2020). As the concentration of L-cys changed from 1.0 to 10.0 mM, more nCaO$_2$ and Fe(III) were needed to achieve the same BTEX removal (Figure S2 in the Supplementary Material). It also confirmed that excessive L-cys inhibited the system degradation ability for BTEX. The optimal molar ratio of nCaO$_2$/Fe(III)/L-cys was 10.5/20/1 based on the calculation by RSM. In subsequent studies, the molar ratios of 10/10/2/1 and 10/10/10/1 of nCaO$_2$/Fe(III)/L-cys were chosen to represent low and high L-cys concentrations to investigate the role of L-cys in the system.

**Detection of free radicals in the nCaO$_2$/Fe(III)/L-cys system**

In order to authenticate the occurrence and production of dominant radicals in the nCaO$_2$/Fe(III)/L-cys system, EPR tests were carried out using DMPO as the spin-trapping agent and the results are presented in Figure 3. In the nCaO$_2$/Fe(III) system, Fe(III) could not react directly with H$_2$O$_2$ to produce HO$^\cdot$ and Fe(III) needs to be reduced to Fe(II) before reaction with H$_2$O$_2$ (Duesterberg et al. 2008; Fu et al. 2017). Therefore, the relative intensity of HO$^\cdot$ in the nCaO$_2$/Fe(III) system was weak at 50 min of reaction. The concentration of Fe(II) increased significantly at 60 min, which strongly supported HO$^\cdot$ production. However, the relative
Figure 2 | Response surface of (a) B, (b) T, (c) E, (d) X for nCaO₂ (X₁) and Fe(III) (X₂) ([L-cys] = 1.0 mM).

Figure 3 | EPR spectra of the (a) nCaO₂/Fe(III) system at the nCaO₂/Fe(III)/BTEX molar ratio of 10/10/1 and (b) nCaO₂/Fe(III)/L-cys system at the nCaO₂/Fe(III)/L-cys/BTEX molar ratio of 10/10/2/1 ([BTEX] = 0.5 mM).
intensity of HO• in the nCaO2/Fe(III)/L-cys system was kept strong from 5 to 60 min. This means that the Fe(II) concentration in the nCaO2/Fe(III)/L-cys system was high, in which Fe(II) could react with H2O2 and produce a large amount of HO• in a short time. There is a close relationship between the change of HO• and Fe(II)/Fe(III) redox cycles (Huang et al. 2020). It is deduced that the participation of L-cys promoted the Fe(II)/Fe(III) redox cycles in the nCaO2/Fe(III)/L-cys system.

In order to further investigate the production of HO• in the nCaO2/Fe(III)/L-cys system, BA (10 mM) was used as a probe to quantify the amount of HO• in the system. The production of HO• with the various dosages of nCaO2/Fe(III)/L-cys/BTEX was calculated and is listed in Figure 4. The results showed that HO• accumulated rapidly within 60 min of the reaction. In the presence of L-cys, the system produced HO• at the beginning of the reaction, which was due to the rapid reduction of Fe(III) into Fe(II) by L-cys. During the first 30 min, the HO• accumulation rate was fast but slowed down after 30 min. However, in the system without L-cys, HO• accumulated gradually after 20 min of reaction but there was no further production after 60 min. It was noteworthy that the yield of HO• produced in the 1.0 mM L-cys-containing system was 0.066 mM at 180 min reaction, higher than that without L-cys (0.049 mM). The yield of HO• decreased to 0.043 mM with increasing the dosage of L-cys to 5 mM, and this explained why excessive L-cys inhibited BTEX degradation. Excessive L-cys caused a large amount of Fe(III) in the system to be reduced while excessive Fe(II) could conversely scavenge HO• to produce Fe(III) again (Equation (2)) (Xue et al. 2016). It was also reported that the rapid production of HO• would undergo HO• extinction reaction (Equation (3)), which made it difficult for HO• to react with other organic compounds in the system and hence limited the effectiveness of pollutant degradation (Yang et al. 2014).

\[ \text{Fe}^{2+} + \text{HO}^{•} \rightarrow \text{Fe}^{3+} + \text{HO}^- \]  
(2)

\[ \text{HO}^{•} + \text{HO}^{•} \rightarrow \text{H}_2\text{O}_2 \]  
(3)

Effect of L-cys on Fe(III)/Fe(II) cycle in the nCaO2/Fe(III) system

Iron species in the nCaO2/Fe(III)/L-cys system were analyzed for understanding the effect of L-cys on the Fe(III)/Fe(II) cycle (Figure 5). In the system without L-cys (Figure 5(a)), a low concentration of Fe(II) (0.09 mM) was generated after 10 min and the maximum concentration of Fe(II) generated in the nCaO2/Fe(III) system was only 0.16 mM at 20 min of reaction. The change of Fe(III)/Fe(II) in the system could only explain why the system began to accumulate HO• after 20 min as mentioned above. The Fe(III) in the system could not directly react with H2O2 to produce HO• and it has to be reduced to Fe(II) (Equations (4) and (5)) (Duesterberg et al. 2008). Since the reaction rate constant of Equation (5) \( k_{\text{Fe(III),H}_2\text{O}_2} = 2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \) was smaller than that of Equation (4) \( k_{\text{Fe(II),H}_2\text{O}_2} = 7.6 \text{ M}^{-1} \text{ s}^{-1} \), the accumulative rate of HO• was slow before there was

**Figure 4** | The production of HO• with different dosages of chemicals in the nCaO2/Fe(III)/L-cys/BTEX system ([BA] = 10 mM, [HO•] = 5.87 \times [p-HBA], [BTEX] = 0.5 mM).
enough Fe(II) generation in the system (Li et al. 2020).

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} - \text{OOH}^{2+} + \text{H}^+ \quad (4)
\]

\[
\text{Fe} - \text{OOH}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^* \quad (5)
\]

However, by adding 1.0 mM L-cys into the nCaO2/Fe(III) system, the concentration of Fe(II) increased to 1.15 mM instantly. During the reaction, the concentration of Fe(II) was changed within the range of 0.07 mM to 0.19 mM. When excessive L-cys (5.0 mM) was added to the system, the amount of Fe(II) increased to 3.73 mM (Figure 5(c)), and was still maintained high during the subsequent reactions. The L-cys could reduce Fe(III) to Fe(II), and Fe^{2+}(L-cys) and Fe^{2+}(L-cys)\_2 complexes were generated simultaneously. The formations of Fe^{2+}(L-cys) and Fe^{2+}(L-cys)\_2 complexes could increase the concentration of Fe(II) and strengthen the catalytic performance because the catalytic effect of Fe(II) was stronger than that of Fe(III) (Jiang et al. 2020). In addition, after 180 min reaction, the total soluble iron concentration in the nCaO2/Fe(III) system was 2.53 mM (Figure 5(a)). However, the total iron concentration increased to 3.50 mM and 4.71 mM when the dosage of L-cys was 1.0 mM and 5.0 mM, respectively (Figure 5(b) and 5(c)), and this was simply due to less formation of precipitation after adding L-cys into the system (Ye et al. 2020).

Figure 5 | The distribution of iron species in the nCaO2/Fe(III)/L-cys/BTEX system at different nCaO2/Fe(III)/L-cys/BTEX ratios of (a) 10/10/0/1, (b) 10/10/2/1, and (c) 10/10/10/1 ([BTEX] = 0.5 mM).

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The mechanism of BTEX destruction

Tert-butanol (TBA) was selected as HO• scavenger to evaluate the dominant radicals in the nCaO2/Fe(III)/L-cys system due to TBA having a high reaction rate with HO• \( (k_{ HO} = 5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}) \) (Cai et al. 2020). The results showed that BTEX removal was significantly inhibited when TBA was added (Figure 6). BTEX removal at 180 min in the nCaO2/Fe(III)/L-cys system decreased from 91.3%, 91.4%, 92.3%, and 86.6% to 9.5%, 9.7%, 11.8%, and 9.1%, respectively, which, along with the EPR test results, indicated that HO• was the dominant reactive species in the nCaO2/Fe(III)/L-cys system.

The intermediates during BTEX degradation were analyzed by LC–MS and the possible BTEX destruction pathway is proposed in Figure 7. For the benzenoid compounds, the benzene-ring could be attacked by HO• to form various intermediate phenols (Gligorovski et al. 2015), such as C6H6O3 \((m/z = 126)\), C7H8O3 \((m/z = 140)\), and C8H9O3 \((m/z = 153)\). Further, HO• led to benzene-rings opening and formed short-chain alkanes and alkenes, such as C5H7O4 \((m/z = 131)\), C4H5O3 \((m/z = 101)\), and C3H5O3 \((m/z = 89)\). These intermediates and aromatic compounds were attacked by HO• and finally were completely mineralized. Since HO• are non-selective oxidation radicals, the reaction rate constants between organic compounds

Figure 6 | Effect of scavenger on BTEX degradation in the nCaO2/Fe(III)/L-cys system \([\text{BTEX} = 0.5 \text{ mM}, \text{TBA} = 100 \text{ mM}]\).

Figure 7 | Proposed BTEX destruction pathway in the nCaO2/Fe(III)/L-cys system.
containing intermediates and HO· are in a range of $10^9$–$10^{10}$ M$^{-1}$s$^{-1}$ (Xue et al. 2018a, 2018b). In this study, although BTEX removal exceeded 90% in the nCaO$_2$/Fe(III)/L-cys system, most intermediates in the reaction belonged to aromatic compounds. The toxicity during BTEX degradation and the related study need to be investigated in our future research.

**Performance of BTEX removal in the actual groundwater**

To investigate the effect of the nCaO$_2$/Fe(III)/L-cys system on BTEX removal in the actual groundwater, the tests were carried out using the actual groundwater instead of ultrapure water (Figure 8). The characteristics of the actual groundwater used in the tests are listed in Table 1. As to the results, only 12.1%, 13.4%, 15.6%, and 14.0% BTEX had been removed when nCaO$_2$ and Fe(III) existed at the nCaO$_2$/Fe(III)/BTEX molar ratio of 10/10/1. When 1.0 mM L-cys was added into the system, the removal rate of BTEX increased to 56.3%, 57.2%, 59.3%, and 53.2%, which was about 60% of the degradation rate compared with ultrapure water. The main reason was that the initial pH of the actual groundwater was nearly neutral (7.31 ± 0.2) and it had a strong buffer capacity which could maintain the pH without large change during the reaction. As the Fenton reaction is affected by the pH of the solution (Sarmento et al. 2016), the effect of initial solution pH on BTEX degradation was investigated and the results are shown in the Supplementary Material (Figure S3a). At pH 6.2, the system had the highest BTEX degradation efficiency and the degradation ability was inhibited under acidic and/or alkaline conditions. Besides, the existence of Cl$^-$, HCO$_3^-$, SO$_4^{2-}$ and the natural organic matter (NOM), humic acid (HA) being a typical NOM, were not conducive to the degradation of BTEX (Figure S3b). The results showed that HCO$_3^-$ had the most significant effect on BTEX removal.

**Figure 8** | BTEX removal performance in the actual groundwater in nCaO$_2$/Fe(III)/L-cys systems at various nCaO$_2$/Fe(III)/L-cys/BTEX molar ratios at 180 min ([BTEX] = 0.5 mM).

**Table 1** | Characteristics of the actual groundwater used in experiments

| Parameter               | Units     | Value           |
|-------------------------|-----------|-----------------|
| pH                      |           | 7.31 ± 0.2      |
| Total organic carbon (TOC) | mg L$^{-1}$ | 11.35 ± 0.5    |
| Cl$^-$ concentration    | mg L$^{-1}$ | 127.5 ± 1.2   |
| HCO$_3^-$ concentration | mg L$^{-1}$ | 91.3 ± 1.5    |
| NO$_3^-$ concentration  | mg L$^{-1}$ | 1.1 ± 0.1    |
| SO$_4^{2-}$ concentration | mg L$^{-1}$ | 62.7 ± 3.5    |
| Ca$^{2+}$ concentration | mg L$^{-1}$ | 126.0 ± 4.0   |
| Mg$^{2+}$ concentration | mg L$^{-1}$ | 27.3 ± 2.6    |
| BTEX concentration     | mg L$^{-1}$ | Not detected  |
BTEX degradation, with a 52.7% reduction in degradation efficiency. The inhibitory effect of HCO₃⁻ on BTEX degradation in the nCaO₂/Fe(III)/L-cys system could be speculated as being for two reasons: the increasing of the solution pH and the scavenging effect of HO· (Zhang et al. 2015a, 2015b). HA had little effect on BTEX degradation. Therefore, under the actual groundwater conditions, the degradation ability of the nCaO₂/Fe(III)/L-cys system was inhibited. Encouragingly, the removal rates of BTEX were promoted to 94.0%, 96.2%, 97.1%, and 94.3%, respectively, when the molar ratio of nCaO₂/Fe(III)/L-cys/BTEX increased to 40/40/8/1. Increasing the molar ratio of nCaO₂/Fe(III)/L-cys/BTEX was an effective way to overcome the adverse effects caused by the complex of the actual groundwater. The degradation efficiencies of BTEX were 81.8%, 83.3%, 84.8%, and 75.6%, respectively, when the nCaO₂/Fe(III)/L-cys/BTEX molar ratio was 20/20/4/1. Increasing the molar ratio to 40/40/8/1, the degradation efficiencies of BTEX increased to 94.0%, 96.2%, 96.9%, and 94.3%, respectively. Although the molar ratio of nCaO₂/Fe(III)/L-cys/BTEX doubled, the degradation efficiency only increased in the range of 12.1%–18.7%. Considering the remedial cost, the optimal ratio of nCaO₂/Fe(III)/L-cys/BTEX was set as 20/20/4/1 in the practical groundwater treatment. The agent cost of treating 1 m³ of groundwater was calculated to be $28.50 at the optimal molar ratio condition. The above results strongly demonstrated that the nCaO₂/Fe(III)/L-cys system has broad application prospects in the actual groundwater environment for BTEX removal.

CONCLUSION

In this study, BTEX removal in the nCaO₂/Fe(III)/L-cys system was performed and the results showed that the nCaO₂/Fe(III)/L-cys technique could be efficient in destruction of BTEX in both ultrapure water and actual groundwater. A proper amount of L-cys could promote the degradation ability of the nCaO₂/Fe(III) system because the participation of L-cys accelerated the Fe(III)/Fe(II) redox cycles, but excessive L-cys inhibited them. After adding 1.0 mM L-cys into the nCaO₂/Fe(III) system, the concentration of Fe(II) increased to 1.15 mM instantly. Simultaneously, the proper concentration of L-cys was conducive to the accumulation of HO·. The yield of HO· produced in the 1.0 mM L-cys-containing system was 0.066 mM, higher than that without L-cys (0.049 mM) at 180 min. When excessive L-cys (5.0 mM) was added to the system, the amount of Fe(II) increased to 3.73 mM, however, the yield of HO· decreased to 0.043 mM. Excessive L-cys caused a large amount of Fe(III) in the system to be reduced, and excessive Fe(II) could in turn scavenge HO· to produce Fe(III). The optimal molar ratio of nCaO₂/Fe(III)/L-cys/BTEX was 10.5/20/1 based on calculation by RSM. EPR tests and quenching results indicated that HO· was the dominant reactive species in the nCaO₂/Fe(III)/L-cys system. According to the detected intermediates by LC-MS, the BTEX destruction pathway was proposed. For these benzenoid compounds, the benzene-ring was attacked by HO· to form various intermediate phenols, and further HO· led to benzene-rings opening to form short-chain alkanes and alkenes and finally being completely mineralized. Under the actual groundwater conditions, the nCaO₂/Fe(III)/L-cys system has broad application prospects in the actual groundwater environment for BTEX removal. Considering the remedial cost, the optimal molar ratio of nCaO₂/Fe(III)/L-cys/BTEX was set as 20/20/4/1.

ACKNOWLEDGEMENTS

This study was financially supported by the National Key R&D Program of China (No. 2018YFC1803304) and the National Natural Science Foundation of China (No. 41977164).

ETHICAL APPROVAL

The authors confirm that this manuscript has not been previously published as a whole or part and it is not under consideration by any other journal.

CONSENT TO PARTICIPATE

All authors have approved the content and consent to submit it.

CONSENT TO PUBLISH

All authors have approved the content and consent to publish it.
AUTHORS’ CONTRIBUTIONS

Xuecheng Sun: Conceptualization, Methodology, Investigation, Writing – Original Draft, Meesam Ali: Validation, Formal analysis, Writing – Review & Editing, Changzheng Cui: Resources, Visualization, Shuguang Lyu: Conceptualization, Writing – Review & Editing, Supervision.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 24 March 2021; accepted in revised form 5 June 2021. Available online 17 June 2021