Application of recyclable nano zero-valent iron encapsulated L-cysteine catalytic cylinder product for degradation of BTEX in groundwater by persulfate oxidation

Xuecheng Sun¹, Changzheng Cui¹, Chaoxiang Yang¹,² and Shuguang Lyu¹,²,*
¹State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China
²Department of Industrial Design, East China University of Science and Technology, Shanghai 200237, China
*Corresponding author. E-mail: lvshuguang@ecust.edu.cn

ABSTRACT

Benzene, toluene, ethylbenzene and xylene (BTEX) possess a negative impact on the environment and human beings due to their highly toxic and carcinogenic properties. In this study, persulfate (PS) activated by nano zero-valent iron (nZVI) coupled with chelated L-cysteine (L-cys) process was investigated for BTEX degradation in contaminated groundwater. BTEX degradation had a significant acceleration and improvement with the removal from 62.7 to 100% along with the increasing dosage of L-cys from 0.12 to 0.27 M in 24 h. Further, the compact nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder were successfully manufactured by encapsulating nZVI, and nZVI and L-cys together with additives of cement, river sand, stearic acid (SA) and zeolite. The SEM image, XRD patterns and FTIR spectra showed that the manufactured catalytic cylinder had a porous structure and encapsulated nZVI and L-cys successfully. Six successive cycles of BTEX degradation were completed and the degradation rate decreased gradually in each cycle. The catalytic activity of nZVI encapsulated L-cys catalytic cylinder was superior to nZVI catalytic cylinder in each cycle. The electron paramagnetic resonance (EPR) results indicated that HO• was the dominant active species in the BTEX degradation process. Benzoic acid (BA) scavenge experiments showed that L-cys could increase the yield of HO• in the PS/nZVI system. The HO• yields of PS/nZVI encapsulated L-cys catalytic cylinder system were 3.2 to 4.8 fold higher than those of the PS/nZVI catalytic cylinder system. The possible mechanisms of PS activation by nZVI encapsulated L-cys catalytic cylinder were supposed. Homogeneous Fenton reaction and heterogeneous catalysis on the nZVI surface are two co-existence mechanisms in the PS/nZVI encapsulated L-cys catalytic cylinder system. The findings of this study provide new insights into the mechanism of nZVI encapsulated L-cys catalytic cylinder activating PS, showing its potential applications for the remediation of groundwater.

Key words: BTEX, groundwater remediation, L-cysteine, nano zero valent iron, persulfate

HIGHLIGHTS

- PS/nZVI/L-cys system was applied to remediate BTEX contaminants.
- The compact nZVI encapsulated L-cys catalytic cylinder was successfully manufactured.
- Six successive cycles of BTEX degradation were completed.
- Two co-existence mechanisms in the PS/nZVI encapsulated L-cys catalytic cylinder system were investigated.
- PS/nZVI catalytic cylinder systems were recommended for BTEX-contaminated groundwater remediation.
1. INTRODUCTION

Gasoline fractions, particular benzene, toluene, ethylbenzene and xylene isomers (BTEX), are frequently introduced into soil and groundwater due to accidental spills and leakage from storage tanks (Boczka & Fernandes 2017; Mahmoud et al. 2018; Fedorov et al. 2020). BTEX possess a negative impact on the environment and human beings due to their highly toxic and carcinogenic properties (Ma et al. 2018; Sun et al. 2020a; Xia et al. 2020). Developing efficient and thoroughgoing BTEX-polluted groundwater remediation is an urgent scientific problem. Sulfate radical (SO₄⁻) based advanced oxidation processes (SR-AOPs) have been widely applied in removing organic pollutants (Hu & Long 2016; Ghanbari & Moradi 2017; Li et al. 2017, 2019b), in which persulfate (PS) is commonly used as the precursor of SO₄⁻ (Lee et al. 2020). SO₄⁻ has high redox potential (E₀ = 2.5–3.1 V), long half-life and high reactivity over a wide pH range (Song & Lee 2016). SO₄⁻ can be converted to hydroxyl radical (HO·) in aqueous solution so that SO₄⁻ and HO· co-exist frequently in PS-based AOPs systems (Lutze et al. 2015).

Ferrous ion (Fe²⁺), due to its relatively lower activation energy, is employed as the homogeneous activator and shows superior to thermal activation (Epold et al. 2015). Liang reported that the half-lives of BTEX degradation ranged from 3.0 to 23.1 days in the aqueous phase at PS/Fe²⁺/BTEX molar ratio of 20/5/1 (Liang et al. 2008). In the pH range of 5.0–8.5, the aniline degradation increased with increasing pH in a PS/Fe²⁺ system (Zhang et al. 2013); however, excessive Fe²⁺ can scavenge SO₄⁻ and HO· and the generated iron sludge requires additional treatment and disposal (Zhang et al. 2009). Zero valent iron (ZVI) can be used as a solid source of Fe²⁺ to overcome the disadvantages of Fe²⁺ (Wang et al. 2014; Cao et al. 2019; Sun et al. 2020b), in which nano zero-valent iron (nZVI) shows higher catalytic activity and is broadly used to activate PS due to its smaller particle size and larger specific surface area (Li et al. 2014). Jiang reported that 94% of benzene could be removed in 1 h at the PS/nZVI/benzene molar ratio of 10/5/1 (Jiang et al. 2020a). However, the heterogeneous reactions in the nZVI-water interphase play an important role in the removal of contaminants (Hussain et al. 2012). For instance, ZVI or nZVI, ferrous salts (Fe²⁺), ferric salts (Fe³⁺), and iron oxides are used as catalysts for activating PS to generate SO₄⁻ and HO· (Equations (1) and (2)) (Wang et al. 2016). Among them, nZVI has a rapid reaction rate to activate...
PS due to the huge specific area and strong activity (Li et al. 2014).

\[
\begin{align*}
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2+} \quad (1) \\
\text{Fe}^0 + 2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} &\rightarrow \text{Fe}^{2+} + 2\text{HO}^+ + 4\text{SO}_4^{2-} + 2\text{H}^+ \quad (2)
\end{align*}
\]

Fe\(^{2+}\) released continuously from nZVI corrosion is a dominant means for PS activation (Equation (3)). The reduction of Fe\(^{3+}\) by nZVI on the solid surface can promote the Fe\(^{2+}/\text{Fe}^{3+}\) redox cycles, which effectively suppress the formation of precipitation (Equation (4)).

\[
\begin{align*}
\text{Fe}^0 + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} \\
\text{Fe}^0 + 2\text{Fe}^{3+} &\rightarrow 3\text{Fe}^{2+}
\end{align*}
\]

In groundwater treatment, nZVI poses a challenge to its storage and transportation because of the rapid inactivation of chemical reactivity. Several strategies for preventing the oxidation of nZVI and controlling the release of Fe\(^{2+}\) were developed. Various solid supports were reported to encapsulate nZVI into the carriers such as activated carbon (Gosu et al. 2016), clay (Tandon et al. 2013), polyvinylpyrrolidone (Tian et al. 2020), and so on. But these studies only encapsulated the materials and no research has been done to encapsulate both nZVI and L-cys together. Besides, comparing to the above encapsulation materials, cement and river sand are relatively easily accessible and inexpensive materials. Cement products are inherently hydrophilic, porous and micro-cracked materials. Therefore, they usually cannot prevent the invasion and transportation of water (Liang et al. 2012). Cement and river sand are usually used as building materials, which also ensures that catalysts do not produce extra pollutants. Therefore, cement and river sand are the ideal encapsulation materials. Stearic acid (SA), a kind of phase change material, is the most commonly used encapsulation material due to its suitable melting temperatures, high energy storage abilities, and chemical inertness (Fu et al. 2018b).

An effective nZVI-based material should have the following advantages. The structure of the material should be porous to facilitate internal nZVI contact with the solution. nZVI-based material can slowly release nZVI to prolong its catalytic function. Support material should be easily recycled to reuse. The material of the carriers should be cheap and easy to process, given their economic applicability. Although various kinds of nZVI-based catalytic materials have been widely used in water treatment, the recycling and mechanisms of nZVI-based material for monoaromatic hydrocarbons degradation are still rare. In this study, employing cement, river sand, SA and zeolite as the components of the support materials for aiming to encapsulate nZVI and L-cys, nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder were successfully manufactured. The morphology and elemental status of the above two cylinders were characterized through SEM, XRD, and FTIR techniques. These catalytic cylinders and the pristine nZVI were used for activating PS to remove BTEX in the aqueous phase. The test for reuse of cylinders and the test using actual groundwater were carried out to evaluate these catalytic cylinders’ application. Further, the possible mechanism in the PS/nZVI catalytic cylinder system is hypothesized after detection of free radicals and release of iron ions.

2. METHODOLOGY

2.1. Materials
Benzene (C\(_6\)H\(_6\), 99.0%), toluene (C\(_7\)H\(_8\), 99.0%), ethylbenzene (C\(_8\)H\(_{10}\), 99.0%), xylenes (C\(_8\)H\(_{10}\), 99.0%), persulfate (Na\(_2\)S\(_2\)O\(_8\), 99.0%), stearic acid (C\(_{18}\)H\(_{36}\)O\(_2\), 98.0%) and zeolite (95.0%) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Tert-butanol (C\(_4\)H\(_{10}\)O, TBA, 99.0%), iso-propyl alcohol (C\(_3\)H\(_8\)O, IPA, 99.0%), ethanol (C\(_2\)H\(_6\)O, 99.5%), benzoic acid (C\(_7\)H\(_6\)O\(_2\), BA, 99.5%), 5,5-dimethyl-1-pyrroline N-oxide (C\(_6\)H\(_{11}\)NO, DMPO, 99.0%) and L-cysteine (C\(_3\)H\(_7\)NO\(_2\)S, L-cys, 99.0%) were supplied from Shanghai Lingfeng Reagent Co. Ltd (Shanghai, China). The nZVI (Fe, 99.0%) was purchased from Beijing Innochem Science and Technology Co. Ltd (Beijing, China). The Portland slag cement (325# slag cement) was purchased from Shanghai Cement Plant Co. Ltd (Shanghai, China). Yangzi river sand (diameter ≤ 1.0 mm) was supplied from Nanjing Sand Plant (Nanjing, China). All chemicals and materials were used as received without further purification. The ultrapure water that was used for preparing the BTEX-contaminated solution was supplied 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. The BTEX degradation test in the actual groundwater was carried out by replacing ultrapure water with actual groundwater.

2.2. Preparation of catalytic cylinders
Stearic acid (SA) was used as an embedding medium and dissolved in ethanol (m/v = 1/1.5). The powder of cement, river sand, and zeolite at the calculated ratio (m/m/m = 1/7/4) was added into the above ethanol solution and carefully stirred to uniformity. Two catalysts were manufactured by adding nZVI or nZVI with L-cys together (nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder). The ratio of ultrapure water and cement was controlled between 0.4 and 0.6 (m/m). The semi-solid compound was pressed into cylinders by a manual pressing machine. The size of the mold was fixed as diameter = 10.0 mm and height = 10.0 mm.

High-resolution transmission electron microscopy (TEM, JEM-2100 electron microscope operated at a condition of 80 kV accelerating voltage), X-ray diffraction (XRD) analysis with a Rigaku D/max diffractometer (2550VB/PC) with Cu Ka (λ = 0.154 nm) radiation, Fourier transform infrared spectroscopy (Thermo Nicolet 6,700, USA) were used to characterize the catalytic cylinder.

2.3. Experimental set-up
BTEX stock solutions (0.5 mM) were transferred into a series of 250 mL brown glass reactors and oscillated horizontally (100 rpm) by a biochemical incubator (SPX-250B-Z, Boxun Industrial Co. Ltd, Shanghai, China) at the temperature of 20 °C. The test started immediately after introducing the predetermined dosage of PS and catalytic agent. 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 GC coupling with a headspace auto-sampler, a flame ionization detector (FID), and an HP-5 column (30 m x 0.32 mm x 0.25 μm). The method detection limit (MDL) (or limit of detection (LOD)) for BTEX is 1.12 μg·L⁻¹, which was determined using a method in chapter one of ‘Test Methods for Evaluating Solid Waste, Physical/Chemical Methods’ (USEPASW-846). The recovery data of the standard BTEX solution at different concentrations maintained over 95%. The used catalytic cylinders were separated from the solution and dried in a vacuum oven (GHG, Heheng, Shanghai) for recyclability tests.

Benzoic acid (BA) was chosen as a probe to quantify the amount of HO• production. The production of p-hydroxybenzoic acid (p-HBA) by the reaction between BA and HO• has the conversion factor (5.87 ± 0.18) with the amount of HO• in the system (Xue et al. 2018). LC-MS with a reverse-phase Purospher RP-18, 5 μm, 4.6 x 250 mm column was used to detect the p-HBA. The column was eluted at isocratic mode for all experiments with a mobile phase composed of 70:30 (v/v) of methanol/phosphoric acid (1/1,000 v/v) at a flow rate of 0.8 mL min⁻¹. The column was thermostated at 40 °C. At 30 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 EPR (EMX-8/2.7, Bruker, U.S.) for the detection of ROSs. The DMPO-OH was monitored at the setting for the EPR spectrometer of center field (3,510.00 G), microwave frequency (9.79 GHz), and power (5.05 mW). The concentration of the ions in actual groundwater was determined by ion chromatography (ICS-1100, ThermoFisher, China). The total organic carbon (TOC) was determined using a TOC analyzer (LiquiTOC, Germany). The characteristics of the actual groundwater used in the tests are listed in Table S2. The absorbance of Fe²⁺ and total Fe were obtained by UV–vis spectrophotometer (type 2,802, Unico Corp, China). The pH value was determined by using a pH meter (STARTER 2,100).

The PS-based Fenton oxidation of BTEX was represented by pseudo-first-order kinetics (Equation (5)) (Wang 2008):

\[
\ln C_t = \ln C_0 - kt
\]

where, \(C_t\) represents the BTEX concentration at time \(t\), \(C_0\) the initial BTEX concentration, \(k\) the reaction rate coefficient and \(t\) the time.

The quality of data on BTEX degradation and radicals analyses was routinely monitored by analyzing blanks and repeated samples. To more accurately evaluate the treatment performance, composite samples were taken and analyzed.
3. RESULTS AND DISCUSSION

3.1. Performance of BTEX removal in the PS/nZVI/L-cys system

A comparison of BTEX removal rate in different PS-based Fenton systems at unadjusted pH (5.4–6.7) condition and 25 °C is shown in Figure 1. The BTEX removal rates were only 29.4%, 24.0%, 23.9% and 26.9%, respectively, when 0.12 M PS and 2.0 g/L nZVI were added simultaneously. However, when different dosages of L-cys were introduced into the system, the BTEX degradation had a significant acceleration and improvement. With an increase in dosage of L-cys from 0.12 to 0.36 M, BTEX removals in 24 h increased from 62.7%, 70.3%, 70.8% and 63.15 to 98.9%, 99.7%, 98.7 and 98.4%. Further increasing the dosage of L-cys to 0.72 M, the reaction terminated at 8 h and the BTEX were removed completely. It could be summarized that increasing the dosage of L-cys could effectively promote BTEX degradation.

The corrosion products of nZVI such as Fe3O4, Fe2O3, FeOOH and Fe8O8(OH)6SO4 were generated on the solid-liquid interface and acted as a physical barrier preventing the contact of nZVI and PS, which was the main reason why the PS activation was influenced (Kim et al. 2018). It is reported that two electron transmission pathways were proposed on passivated ZVI in the PS activation process: defect corrosion and semiconductor effect (Hou et al. 2021). The corrosion products generated randomly on the surface of nZVI contained defects such as grain boundaries or pits (Gao et al. 2018), then the electrons passed from ZVI to PS through these defects. In addition, most iron oxides and hydroxides are semiconductors (Hou et al. 2021). The Fermi energy of the ZVI is different from the iron oxide conduction band and the hydroxide shell (Ai et al. 2013). Therefore the electrons are delivered from the iron core to the corrosion products to the same Fermi energy levels (Batista & Friesner 2002). L-cys exhibits Fe-reducing activity owing to the functional sulphydryl group (–SH) (Lu et al. 2020; Ramos et al. 2020). Furthermore, L-cys can be adsorbed on the nZVI surface through amino, carboxyl and sulphydryl groups to generate L-cysteine-Fe complex (Karuppasamy et al. 2010; Ye et al. 2020). Meanwhile, the nZVI can be stabilized by L-cys thus decreasing the excitation state of the electron by forming an Fe-S bond, which means that the semiconducting material possesses delocalized electronic states close to the Fermi level (Bagbi et al. 2017). The acceleration and improvement on the BTEX removal after adding L-cys might sum up two reasons in this study. L-cys reduced corrosion products to increase the probability of defect generation and the electrons donated by nZVI. The L-cys-Fe complex served as the electron bridge to link the different levels of Fermi energy.

A series of comparative experiments were carried out to investigate the effect of L-cys dosage on the degradation of BTEX. Figure 2 displays the BTEX degradation in different initial L-cys dosages, and the rate constants and R-squared under different PS/nZVI/L-cys molar ratios are listed in Table S1. The BTEX degradation followed the pseudo-first-order kinetics for L-cys

**Figure 1** | BTEX removal performance in various PS-based Fenton systems under different PS/nZVI/L-cys molar ratios at 24 h ([BTEX] = 0.5 mM, [PS] = 0.12 M, [nZVI] = 2.0 g/L, unadjusted pH = 5.7 ± 0.3).
dosages tested in this study in 48 h. Deng reported that acetaminophen degradation strictly followed pseudo-first-order kinetics in PS/Fe$^0$ system (Deng et al. 2014). It was also reported that sulfamethazine degradation fitted pseudo-first-order reaction kinetics in the PS/nZVI system (Wu et al. 2019). However, the BTEX rate constants were increased from 0.0099 to 0.9018 M$^{-1}$ min$^{-1}$ when the L-cys dosage went up from 0 to 0.72 M. Under the same condition of L-cys dosage, the destruction rates for the four compounds were the same order of magnitude. Of interest, the BTEX degradation rate was heavily influenced by the L-cys dosage. When 0.72 M L-cys was introduced into the PS/nZVI system, the BTEX were completely degraded in 8 h. The different performances between non-L-cys and 0.72 M L-cys indicated that L-cys could improve nZVI utilization. The nZVI was applied as the source of Fe$^{2+}$ which could catalyze PS to generate SO$_4^{2-}$ and HO$. These radicals were the main reason for pollutant degradation (Sun et al. 2021). The yield of SO$_4^{2-}$ and HO$^-$ was one of the limiting factors for pollutant degradation (Wang & Jiang 2009). However, the corrosion products coated on the nZVI surface prevented the contact of inner nZVI with PS to generate more radicals. Therefore, L-cys presence increased the chance of internal iron contact with PS, hence increasing the yield of radicals in the system.

### 3.2. Characteristics of catalytic cylinder

Cement, river sand and SA were the excellent supports that were used as admixtures of porous material after cement hydration, setting and hardening. Therefore, in this study nZVI with/without L-cys were encapsulated in the supports as the main catalytic components with the zeolite as an additional additive. The microstructure of nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder characterized by SEM is presented in Figure 3(a) and 3(b). The SEM images revealed that the surface of the catalytic cylinder was porous and globular nZVI evenly distributed in the texture. Compared to nZVI catalytic cylinder, the particle aggregates of the nZVI-encapsulated L-cys catalytic cylinder were regular and relatively smooth. The X-ray diffraction patterns of the nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder are shown in Figure 3(c). It can be seen that the peak of iron (Fe, 20 peak at 44.7) was dominant. The peaks of quartz (SiO$_2$, 20 peak at 20.8) and aragonite (CaCO$_3$, 20 peak at 21.6) were also obvious. Closer observation of XRD patterns revealed that the peak of manganese sulfide (MnS, 20 peak at 27.3) could be found in the pattern of nZVI encapsulated L-cys catalytic cylinder, but not in the pattern of nZVI catalytic cylinder. The element S here was supplied by L-cys; therefore, L-cys was thoroughly added in the nZVI encapsulated L-cys catalytic cylinder.

The function groups in FTIR spectra are shown in Figure 4. There was no obvious difference between the spectra of the nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder. The catalytic cylinders exhibited stretching vibration...
Figure 3 | SEM images of (a) nZVI catalytic cylinder and (b) nZVI encapsulated L-cys catalytic cylinder, (c) XRD of nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder (unadjusted pH = 5.7 ± 0.3).
absorption peaks of C–H at 2,917.1 and 2,849.4 cm\(^{-1}\). Besides, a pronounced –OH peak appeared at 3,408 cm\(^{-1}\) in both FTIR spectra. It was proved that the SA reacted with calcium oxide in the cement and river sand (Li et al. 2019a). The absorption peaks of COO– based stretching vibration absorption at 1,473.2 cm\(^{-1}\) and C–O group at 1,082.8 cm\(^{-1}\) might come from SA, and the C–O...Fe bond formed by dehydration (Li et al. 2019b). According to the above characteristic results, the manufactured catalytic cylinder had a porous structure and encapsulated nZVI and L-cys. Meanwhile, the solid delivery system has the advantages of being recyclable and reusable.

**Recyclability of catalytic cylinder**

It has been confirmed that L-cys could accelerate and improve the catalytic activity of nZVI during the degradation of BTEX. To evaluate the catalytic activity of the nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder, a series of batch experiments of BTEX degradation were carried out. Keeping PS dosage constant (0.12 M), BTEX removal rates are recorded in Figure 5 when nZVI catalytic cylinder (system A, B, and C) and nZVI encapsulated L-cys catalytic cylinders (system D, E, and F) were set as 8.0, 28.0 and 56.0 g/L. Ignoring the quality loss during the production process, the iron contents of the nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder were 16.32% and 15.81% (w/w), respectively. The dosages of nZVI added into the systems were calculated as around 1.3, 4.5 and 9.0 g/L, respectively, when the nZVI catalytic cylinder and/or nZVI encapsulated L-cys catalytic cylinders were set as 8.0, 28.0 and 56.0 g/L, separately. It was obvious that increasing the dosage of the catalytic cylinders could improve the degradation of BTEX. The degradation efficiency of BTEX improved from 16.9%, 27.8%, 28.0%, 30.0% to 59.9%, 68.2%, 66.7%, 64.5%, respectively, when the dosage of nZVI catalytic cylinder increased from 8.0 to 56.0 g/L. The degradation efficiency of BTEX was 43.7%, 47.9%, 48.9%, 45.8% when the dosage of nZVI encapsulated L-cys catalytic cylinder was set as 8.0 g/L. Meanwhile, the complete removal of BTEX was obtained at the nZVI encapsulated L-cys catalytic cylinder dosage of 56.0 g/L. Thus, at the same dosage of the catalytic cylinder, the catalytic activity of nZVI encapsulated L-cys catalytic cylinder was superior to nZVI catalytic cylinder. It was attributed to the addition of L-cys since L-cys could accelerate and improve the catalytic activity of nZVI. In addition, rapid BTEX degradation was observed within 12 h, and the degradation of BTEX became much slower after 24 h. This may be due to the exhaustion of PS, or less BTEX, or the slower corrosion of nZVI. Therefore, the running time was set to 24 h in the recyclability tests.

To exploit the recyclability of the catalytic cylinders, the catalytic cylinders after each degradation cycle (24 h) were cleaned with ultrapure water and reused for a fresh batch of solution of BTEX of the same concentration (0.5 mM). Six successive cycles of BTEX degradation were conducted and the degradation rate of the 7th cycle was under 10%, which could be considered as the end of reuse because the removal rate was less than volatilization rate (Figure 6). It was shown that the degradation rate decreased gradually in each cycle and the catalytic activity of nZVI encapsulated L-cys catalytic cylinder was superior to nZVI catalytic cylinder in each cycle. This result was consistent with the batch BTEX degradation
Figure 5 | BTEX removal performance in (a) the system A ([nZVI catalytic cylinder] = 8.0 g/L), the system B ([nZVI catalytic cylinder] = 28.0 g/L), the system C ([nZVI catalytic cylinder] = 56.0 g/L) and (b) the system D ([nZVI encapsulated L-cys catalytic cylinder] = 8.0 g/L), the system E ([nZVI encapsulated L-cys catalytic cylinder] = 28.0 g/L), the system F ([nZVI encapsulated L-cys catalytic cylinder] = 56.0 g/L), ([PS] = 0.12 M, unadjusted pH = 5.7 ± 0.3).
Figure 6 | Recycle BTEX degradation experiments in (a) the system A ([nZVI catalytic cylinder] = 8.0 g/L), the system B ([nZVI catalytic cylinder] = 28.0 g/L), the system C ([nZVI catalytic cylinder] = 56.0 g/L) and (b) the system D ([nZVI encapsulated L-cys catalytic cylinder] = 8.0 g/L), the system E ([nZVI encapsulated L-cys catalytic cylinder] = 28.0 g/L), the system F ([nZVI encapsulated L-cys catalytic cylinder] = 56.0 g/L), ([PS] = 0.12 M).
experiments in PS/nZVI catalytic cylinder systems. The weight of cylinders lost was between 9.8 and 14.1% after 7 cycles with a small amount of material broken off and suspended in the solution. Several strategies have been reported to synthesize recyclable nZVI-based catalytic materials. The polyactic acid was used encapsulated nZVI in methyl orange decolorization and was recyclable up to 4 cycles for 60 h (Pandey & Saha 2020). nZVI nanoclusters were fabricated under the cetyltrimethylammonium bromide (CTAB) surfactant as a template and 8 successive cycles were observed in p-nitrophenol degradation (Shi et al. 2019). Nano-Fe encapsulated in hydrothermal carbon maintained removal efficiency for p-chlorophenol after 5 successive cycling experiments (Long et al. 2020). Compared with these encapsulated strategies, the supporting materials in this study were easier to obtain and produce, and inexpensive with more cycling runs.

Interaction of nZVI with L-cys
Detection of free-radicals
In order to identify the existence of radicals generated, the EPR experimental analysis was carried out by using DMPO as the spin-trapping agent and the results are shown in Figure 7. The EPR results indicated that HO· was produced in the four different systems but the spectrum peak intensity of SO₄²⁻ was very weak in the PS/nZVI and PS/nZVI/L-cys systems. L-cys increased the yield of both HO·and SO₄²⁻ significantly, thereby promoting the BTEX degradation. The presence of SO₄²⁻ provided multiple pathways for BTEX degradation; however, HO· remained the dominant radicals in the PS/nZVI and PS/nZVI/L-cys systems. Nevertheless, the role of SO₄²⁻ in the BTEX removal could not be ignored since SO₄²⁻ could be rapidly converted to HO· in aqueous systems (Equations (6) and (7)) (Watts et al. 2017):

\[
\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{HO}^* \tag{6}
\]
\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{HO}^* + \text{H}^+ \tag{7}
\]

Only the spectrum of HO· was observed in the PS/nZVI catalytic cylinder system and the PS/nZVI encapsulated L-cys catalytic cylinder system (Figure 7(b)). It meant that HO· was the dominant radical in the heterogeneous catalytic cylinder system. No SO₄²⁻ spectrum was observed, probably due to the SO₄²⁻ being too weak.

To further investigate the impact of L-cys on the yield of HO·, BA (10 mM) was used as a probe to quantify the amount of HO· and the results are shown in Figure 8. Rapid HO· accumulation was observed within the first 5 h in all tested PS-based Fenton-like systems and the production rate of HO· became slow in the remaining reaction time. The Fe²⁺ released from nZVI was sufficient and catalyzed PS rapidly to generate SO₄²⁻ and HO· at the beginning of the reaction. Since Fe³⁺ was quickly oxidized to Fe²⁺ in the initial reaction, the catalytic performance of the system decreased later (Chen et al. 2011). However, with the dosage of L-cys increasing to 0.72 M, the yield of HO· of the PS/nZVI system increased 9.8 fold. This result suggested that L-cys could increase the yield of HO· in the PS/nZVI system. The same rules were observed in the PS/nZVI catalytic cylinder system and PS/nZVI encapsulated L-cys catalytic cylinder system. Under the same dosage of catalytic cylinders, the HO· yield of the PS/nZVI encapsulated L-cys catalytic cylinder system was 3.2 to 4.8 fold higher than those of the PS/nZVI catalytic cylinder system. A reasonable explanation was that L-cys promoted the Fe³⁺/Fe²⁺ redox cycles to increase the catalytic capacity of the system, which will be discussed in detail in the next section. The accumulation of HO· could be measured in solutions within the catalytic cylinder systems, indicating that the systems had homogeneous Fenton reactions.

Release of iron ions
Iron species were analyzed to investigate the main role of L-cys in the PS/nZVI process. Fe³⁺ was not detected in the PS/nZVI, PS/nZVI/L-cys, PS/nZVI catalytic cylinder and PS/nZVI encapsulated L-cys catalytic cylinder systems. The concentrations of Fe²⁺ in the above different systems are summarized in Table 1. Herein, in the two non-L-cys systems, Fe²⁺ was not detected throughout the reaction. The concentration of Fe²⁺ was 1.226 mM at 24 h when the L-cys was added into the PS/nZVI system. Meanwhile, the concentration of Fe²⁺ was 0.067 mM when nZVI catalytic cylinder was replaced by nZVI encapsulated L-cys catalytic cylinder. Obviously, L-cys could improve the concentration level of Fe²⁺ in the PS/nZVI system. Reviewing the reports of other researchers (He et al. 2009; Li et al. 2016; Jiang et al. 2020b; Ye et al. 2020), the possible details of the iron cycle in the PS/nZVI/L-cys system could be summarized as follows: (1) Initially, Fe⁰ was corroded by H⁺ to release Fe²⁺; (2) Fe²⁺ activated PS producing SO₄²⁻ and HO· and the oxidation of Fe²⁺ to Fe³⁺; (3) the reduction of Fe³⁺ by nZVI on the solid surface and L-cys promoted the Fe³⁺/Fe²⁺ redox cycles, and the oxidation of L-cys to cystine at the same time; (4) the reduced Fe²⁺ continued to participate in the catalytic reaction into the Fe³⁺/Fe²⁺ redox cycles again.
Figure 7 | EPR spectrums of the (a) PS/nZVI/L-cys system at the different dosages of L-cys and (b) catalytic cylinder systems with/without L-cys ([BTEX] = 0.5 mM, [PS] = 0.12 M, [nZVI] = 2.0 g/L, [nZVI catalytic cylinder] = [nZVI encapsulated L-cys catalytic cylinder] = 56 g/L).
The X-ray diffraction patterns of the used nZVI catalytic cylinder and the used nZVI encapsulated L-cys catalytic cylinder are shown in Fig. S1. The peak of iron (Fe, 2θ peak at 44.7) was still dominant. Combined with the above results that no Fe$^{2+}$ was detected in the PS/nZVI catalytic cylinder system and the concentration of Fe$^{2+}$ in PS/nZVI encapsulated L-cys catalytic cylinder system being less than 0.067 mM, it could be inferred that heterogeneous Fenton oxidation was the dominant reaction in the PS/catalytic cylinder systems. The heterogeneous Fenton oxidation is partially carried out on the catalyst's surface and most heterogeneous Fenton oxidation requires external energy input such as UV light (Wang et al. 2010; Kerkez et al. 2014). The surface-generated ROSs by the nZVI mainly attack the adsorbed compounds such as by the Langmuir-Hinshelwood mechanism (He et al. 2016). That the iron ions were not detected in the PS/catalytic cylinder systems could be

Figure 8 | The production of HO• in different dosages of chemicals in (a) PS/nZVI/L-cys systems and (b) catalytic cylinder systems ([BA] = 10 mM, [HO•] = 5.87 × [p-HBA], [PS] = 0.12 M, [nZVI] = 2.0 g/L).
ascribed to the enrichment of BTEX at the surface. Xue et al. (2009) reported that pentachlorophenol might compete with H$_2$O$_2$ for magnetite surface sites. Similarly, BTEX adsorbed on the surface were preferentially degraded and replaced by BTEX in the solution.

Mechanisms of PS activation by nZVI encapsulated L-cys catalytic cylinder

Homogeneous Fenton reaction and heterogeneous catalysis on the nZVI surface are two co-existence mechanisms in the PS/nZVI encapsulated L-cys catalytic cylinder system. The encapsulated nZVI was corroded by H$^+$ from the hydrolysis of PS to produce Fe$^{2+}$. After that, Fe$^{2+}$ catalyzed PS to generate SO$_4^{2-}$ and HO$^-$ with the production of Fe$^{3+}$. Fe$^{3+}$ might be reduced by nZVI and L-cys to Fe$^{2+}$ again and completed the Fe$^{2+}$/Fe$^{3+}$ cycle.

The co-instantaneous heterogeneous Fenton reaction might have two possible explanations: defects corrosion effect and semiconductor effect. Due to the oxidation of PS, the corrosion products such as Fe$_3$O$_4$, Fe$^2$O$_2$, FeOOH and Fe$_8$O$_8$(OH)$_6$SO$_4$ coated the nZVI core, which prevented the transmission of electrons. However, L-cys reduction reaction made the corrosion defects improve the electron transport efficiencies from nZVI to PS. Besides, the Fermi energy of the oxides shell was more negative than the nZVI core. The L-cys-Fe bond made Fermi energy positive. In other words, L-cys-Fe played as an electron transport bridge to connect the nZVI core and PS and then PS was activated. The BTEX in the solution were attacked by SO$_4^{2-}$ and HO$^-$ to benzene-ring opening and decomposed further to CO$_2$ and H$_2$O finally.

Performance of BTEX removal in the actual groundwater

Effect of initial solution pH on BTEX degradation

To elucidate the influence of solution pH on PS/nZVI/L-cys and catalytic cylinder systems, control tests on the different dosages of L-cys and catalytic cylinders under different pH conditions on BTEX degradation were initially conducted (Fig. S2). In the PS/nZVI system, the removal rate of BTEX was from 44.9 to 52.1% at a pH of 3.0. The BTEX removal was less than 18.0% when the initial solution pH was 9.0. Therefore, pH had a significant impact on BTEX degradation in the PS/nZVI system and this was consistent with the results of other researchers (Pignatello et al. 2006; Xue et al. 2016). However, with the 0.12 M L-cys addition into the system, the BTEX removal surpassed 60% when the initial solution pH ranged from 3.0 to 9.0. It could be summarized that L-cys broadened the range of pH application of the PS/nZVI system. In the catalytic cylinder experiments, the same conclusion was obtained. 51.5% to 54% BTEX were removed in the PS/nZVI catalytic cylinder system under the range of pH 3.0 to 6.0. But only 7.1% to 10.1% BTEX were removed when initial pH was adjusted to 9.0. Better removal rates appeared in the PS/nZVI encapsulated the L-cys catalytic cylinder system. BTEX could be completely removed at pH 3.0 and surpassed 77.5% even with the pH adjusted to 9.0. In an oxidizing system, occurrence of iron species is primarily dependent upon pH. The increasing pH would cause iron activators to precipitate and prevent the reaction (Liang et al. 2009). Weak coordination may occur between Fe$^{3+}$ and the carboxyl group (–COOH) of L-cys. Thus, the lower formation of precipitation after adding L-cys to the system was the main reason for a broad pH range (Li et al. 2016).

The application of catalytic cylinder in the actual groundwater

In order to test the application of the above systems in actual groundwater, batch and cycle experiments were carried out using actual groundwater instead of ultrapure water. The characteristics of the actual groundwater used in experiments are listed in Table S2 and the batch and cycle experimental results are shown in Figure 9. BTEX removal rates in the PS/nZVI system were 20.3%, 19.0%, 20.5%, 20.3% in the actual groundwater compared with 29.4%, 24.0%, 23.8%, 26.9%
Figure 9 | BTEX removal performance in the actual groundwater in (a) the PS/nZVI system, (b) the PS/nZVI catalytic cylinder system, (c) the PS/nZVI encapsulated L-cys catalytic cylinder system ([BTEX] = 0.5 mM, [PS] = 0.12 M, [nZVI catalytic cylinder] = [nZVI encapsulated L-cys catalytic cylinder] = 56.0 g/L).
under the same condition in the ultrapure water. Meanwhile, BTEX removal rates in PS/nZVI/L-cys system decreased to 57.8%, 57.0%, 54.1%, 52.2% in the actual groundwater compared with the ultrapure water (complete degradation). The effect of these PS-based Fenton systems in actual groundwater deteriorated due to the high pH environment and high concentration of HCO₃⁻. The catalytic performance of the systems was reduced in high pH and the high concentration of HCO₃⁻ could scavenge HO⁻ (Fu et al. 2018a). Also, consumption of SO₄²⁻ caused by Cl⁻ was another possible reason (Gu et al. 2018). Continuously increasing the dosage of nZVI and L-cys to 4.0 g/L and 1.44 M, BTEX removal rate increased to 76.3%–80.1%. It was shown that the effect of water conditions on BTEX degradation in the PS/nZVI/L-cys system in actual groundwater could be remitted by increasing the dosages of nZVI and L-cys.

Four successive cycles and six successive cycles were completed in the PS/nZVI catalytic cylinder system and the PS/nZVI encapsulated L-cys catalytic cylinder system, respectively (Figure 9(b) and 9(c)). Compared with the ultrapure water experiment (see Figure 6), the PS/nZVI catalytic cylinder systems completed 2 cycles less and the BTEX removal rate decreased to 47.2%–85.6%. Although six cycles were completed in the PS/nZVI encapsulated L-cys catalytic cylinder system, the BTEX removal rate decreased to 15.6%–55.5%. It is apparent that PS activated by nZVI encapsulated L-cys catalytic cylinder had the ability to remediate BTEX in the actual groundwater. To achieve the ideal remediation performance, the dosages of the catalytic cylinder can be increased appropriately.

CONCLUSION

The PS/nZVI/L-cys system showed an efficient ability in the degradation of BTEX in both ultrapure water and actual groundwater. The BTEX degradation had a significant acceleration and improvement with the increasing dosage of L-cys. With an increase in dosage of L-cys from 0.12 to 0.27 M, BTEX removal in 24 h increased from 62.7%, 70.3%, 70.8% and 63.15 to 100%. Using cement, river sand, SA and zeolite as the additives to encapsulate nZVI and L-cys, nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder were successfully manufactured. The SEM image, XRD patterns and FTIR spectra showed that the manufactured catalytic cylinders had a porous structure and encapsulated nZVI and L-cys successfully. Six successive cycles of BTEX degradation were completed and the degradation rate decreased gradually in each cycle. The catalytic activity of nZVI encapsulated L-cys catalytic cylinder was superior to nZVI catalytic cylinder in each cycle. The EPR experimental results showed that HO⁻ were produced in the four different systems and the spectrum peak intensity of SO₄²⁻ was very weak in the PS/nZVI and PS/nZVI/L-cys systems. BA scavenge experiments showed that L-cys could increase the yield of HO⁻ in the PS/nZVI system. It also proved that the system had the homogeneous Fenton reaction. The analytical results of iron species showed that L-cys could improve the concentration level of Fe²⁺ in the PS/nZVI system. The possible mechanisms of PS activation by nZVI encapsulated L-cys catalytic cylinder were supposed. Homogeneous Fenton reaction and heterogeneous catalysis on the nZVI surface were two co-existence mechanisms in the PS/nZVI encapsulated L-cys catalytic cylinder system. It is confirmed that PS activated by nZVI encapsulated L-cys catalytic cylinder had the ability to remediate BTEX in actual groundwater. The effect of water conditions on BTEX degradation in PS/nZVI/L-cys system in actual groundwater could be reduced by properly increasing the dosages of nZVI and L-cys.

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).

DATA AVAILABILITY STATEMENT

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

REFERENCES


Li, H., Han, Z. T., Qian, Y., Kong, X. K. & Wang, P. 2019b In situ persulfate oxidation of 1,2,3-trichloropropane in groundwater of north China plain. *International Journal of Environmental Research and Public Health* 16 (15), 2752.


First received 27 May 2021; accepted in revised form 24 July 2021. Available online 6 August 2021