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

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ABSTRACT

Benzene, toluene, ethylbenzene and xylene (BTEX) possess a negative impact on the environment and human being 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\textsuperscript{•} 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\textsuperscript{•} in the PS/nZVI system. The HO\textsuperscript{•} yields of PS/nZVI encapsulated L-cys catalytic cylinder system were 3.2 to 4.8 folds higher than those of 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 had been investigated.
- PS/nZVI catalytic cylinder systems were recommended for BTEX-contaminated groundwater remediation.
1. INTRODUCTION

Gasoline fraction, particular benzene, toluene, ethylbenzene and xylene isomers (BTEX), is frequently introduced into soil and groundwater due to the accidental spills and leakage from storage tanks (Boczkaj & Fernandes 2017; Mahmoud et al. 2018; Fedorov et al. 2020). BTEX possess a negative impact on the environment and human being due to the 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 (SO₄²⁻) based advanced oxidation processes (SR-AOPs) have been widely applied in removing organic pollutants (Hu & Long 2016; Ghanbari & Moradi 2017; Li et al. 2017, 2019a, 2019b), in which persulfate (PS) is commonly used as the precursors of SO₄²⁻ (Lee et al. 2020). SO₄²⁻ has high redox potential (E₀ = 2.5–3.1 V), long half-life and high reactivity over a wide pH range (Song & Lee 2016). SO₄²⁻ can be converted to hydroxyl radical (HO•) in the aqueous solution so that SO₄²⁻ 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 PS/Fe²⁺ system (Zhang et al. 2013), however, excessive Fe²⁺ can scavenge SO₄²⁻ 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, 2020b). 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⁺), iron oxides are used as catalysts for activating PS to generate SO₄²⁻ 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).

\[
\begin{align*}
Fe^{2+} + S_2O_8^{2-} &\rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{+} \\
Fe^0 + 2S_2O_8^{2-} + 2H_2O &\rightarrow Fe^{2+} + 2HO^+ + 4SO_4^{2-} + 2H^+ 
\end{align*}
\] (1) (2)

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

\[
\begin{align*}
Fe^0 + S_2O_8^{2-} &\rightarrow Fe^{2+} + 2SO_4^{2-} \\
Fe^0 + 2Fe^{3+} &\rightarrow 3Fe^{2+} 
\end{align*}
\] (3) (4)

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), etc. But these studies only encapsulated the materials and no research had 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, 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%) zeolite (95.0%), were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Tert-butanol (C\(_4\)H\(_{10}\)O, TBA, 99.0%), iso-propl 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) were supplied from Nanjing Sand Plant (Nanjing, China). All chemicals and materials were used as received without further purification. The ultrapure water which 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, zeolite at the calculated ratio (m/m/m = 1/7/4) were added into the above ethanol solution and carefully stirred to uniform. 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 high = 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 × 0.32 mm × 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 the chapter one of ‘Test Methods for Evaluating Solid Waste, Physical/Chemical Methods’ (USEPASW-846). The recovery data of the standard BTEX solution maintained over 95%. The used catalytic cylinders were separated from the solution and dried in 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 × 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 method 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 an ion chromatography (ICS-1100, ThermoFisher, China). The total organic carbon (TOC) was determined by using a TOC analyzer (LiquiTOC, Germany). The characteristics of the actual groundwater used in the tests were 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 were represented by the pseudo-first-order kinetics (Equation (5)) (Wang 2008):

\[ \ln C_t = \ln C_0 - kt \] (5)

In which \( C_t \) 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 about 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 was 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, Fe₂O₂, 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 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 sulfhydryl group (–SH) (Lu et al. 2020; Ramos et al. 2020). Furthermore, L-cys can be adsorbed on the nZVI surface through amino, carboxyl and sulfhydryl 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 Fe-S bond, which meant that the semiconducting material possesses delocalized electrons 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. 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 displayed the BTEX degradation in different initial L-cys dosages, and the rate constants and R-squared under different PS/nZVI/L-cys molar ratios were listed in Table S1. The BTEX degradation followed the pseudo-first-order kinetics for

![Figure 1](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.252/917736/ws2021252.pdf)

**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).
L-cys dosages tested in this study in 48 h. Deng reported that acetaminophen degradation strictly followed pseudo-first-order kinetics in PS/Feº 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 performance 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 Fe²⁺ which could catalyze PS to generate SO₄²⁻ and HO·, and these radicals were the main reason for pollutant degradation (Sun et al. 2021). The yield of SO₄²⁻ 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 could use as admixture 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 was presented 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 nZVI encapsulated L-cys catalytic cylinder were regular and relatively smooth. The X-ray diffraction patterns of nZVI catalytic cylinder and nZVI encapsulated L-cys catalytic cylinder were shown in Figure 3(c). It can be seen that the peak of iron (Fe, 2θ peak at 44.7) was dominant. The peaks of quartz (SiO₂, 2θ peak at 20.8) and aragonite (CaCO₃, 2θ peak at 21.6) were also obvious. Closer observation of XRD patterns revealed that the peak of manganese sulfide (MnS, 2θ 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 were shown in Figure 4. There was no obvious difference between the spectra of 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 $pH = 5.7 \pm 0.3$).
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, 2019b). 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. 2019a, 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 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), BETX removal rates were 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 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).
Iron species were analyzed to investigate the main role of L-cys in PS/nZVI process. The Fe\(^{3+}\) release of iron ions spin-trapping agent and the results are shown in Figure 7. The EPR results indicated that HO\(^{•}\) in order to identify the existence of radicals generated, the EPR experimental analysis was carried out by using DMPO as the detection of free-radicals interaction of nZVI with L-cys 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 SO\(_4^{•−}\) was very weak in the PS/nZVI and PS/nZVI/L-cys systems. L-cys increased the yield of both HO\(^{•}\) and SO\(_4^{•−}\) significantly, thereby promoting the BTEX degradation. The presence of SO\(_4^{•−}\) 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 SO\(_4^{•−}\) in the BTEX removal could not be ignored since SO\(_4^{•−}\) could be rapidly converted to HO\(^{•}\) in aqueous systems (Equations (6) and (7)) (Watts et al. 2017):

\[
\text{SO}_4^{•−} + \text{OH}^− \rightarrow \text{SO}_4^{2−} + \text{HO}^{•}
\]  
(6)

\[
\text{SO}_4^{•−} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2−} + \text{HO}^{•} + \text{H}^+
\]  
(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 radicals in the heterogeneous catalytic cylinder system. No SO\(_4^{•−}\) spectrum was observed probably due to the SO\(_4^{•−}\) 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 were 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 Fe\(^{2+}\) released from nZVI was sufficient and catalyzed PS rapidly to generate SO\(_4^{•−}\) and HO\(^{•}\) at the beginning of the reaction. Since Fe\(^{3+}\) was quickly oxidized to Fe\(^{2+}\) 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 folds. This result suggested that L-cys could increase the yield of HO\(^{•}\) in the PS/nZVI system. The same rules were observed in PS/nZVI catalytic cylinder system and PS/nZVI encapsulated L-cys catalytic cylinder system. Under the same dosage of the catalytic cylinder, the HO\(^{•}\) yields of PS/nZVI encapsulated L-cys catalytic cylinder system was 3.2 to 4.8 folds higher than those of PS/nZVI catalytic cylinder system. A reasonable explanation was that L-cys promoted the Fe\(^{3+}/\text{Fe}^{2+}\) redox cycles to increase the catalytic capacity of the system, which would 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 PS/nZVI process. The Fe\(^{3+}\) 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 Fe\(^{2+}\) in the above different systems were summarized in Table 1. Herein, in the two non-L-cys systems, Fe\(^{2+}\) was not detected throughout the reaction. The concentration of Fe\(^{2+}\) was 1.226 mM at 24 h when the L-cys was added into the PS/nZVI system. Meanwhile, the concentration of Fe\(^{2+}\) 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 Fe\(^{2+}\) in the PS/nZVI system. Reviewing the reports of other researchers (He et al. 2009; Li et al. 2016; Jiang et al. 2020a, 2020b; Ye et al. 2020), the possible details of iron cycle in the PS/nZVI/L-cys system could be summarized as follow. (1) Initially, Fe\(^{0}\) was corroded by H\(^+\) to release Fe\(^{2+}\); (2) Fe\(^{2+}\) activated PS producing SO\(_4^{•−}\) and HO\(^{•}\) and the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\); (3) The reduction of Fe\(^{3+}\) by nZVI on the solid surface and L-cys promoted the Fe\(^{3+}/\text{Fe}^{2+}\) redox cycles, and the oxidation of L-cys to cystine at the same time; (4) The reduced Fe\(^{2+}\) continued to participate in the catalytic reaction into the Fe\(^{3+}/\text{Fe}^{2+}\) redox cycles again.
Figure 7 | EPR spectrums of the (a) PS/nZVI/L-cys system at the different dosage 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 were 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 was less than 0.067 mM, it could be inferred that the 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 Langmuir-Hinshelwood mechanism (He et al. 2016). That the iron ions were not detected in the PS/catalytic cylinder systems could be ascribed

Figure 8 | The production of HO• in different dosage of chemicals in (a) PS/nZVI/L-cys systems and (b) catalytic cylinders systems ([BA] = 10 mM, [HO•] = 5.87 × [p-HBA], [PS] = 0.12 M, [nZVI] = 2.0 g/L).
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 Fe$^{2+}$/Fe$^{3+}$ cycle.

The coinstantaneous 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 to improve the electron transport efficiencies from nZVI to PS. Besides, the Fermi energy of oxides shell was more negative than 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 would become activated. The BTEX in the solution were attacked by SO$_4^{2-}$ and HO$^-$ to benzene-rings 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. 31.5% 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 the initial pH was adjusted to 9.0. Better removal rates appeared in PS/nZVI encapsulated L-cys catalytic cylinder system. BETX could be completely removed at pH 3.0 and surpassed 77.5% even the pH adjusted to 9.0. In an oxidizing system, the occurrence of iron species was 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 less formation of precipitation after adding L-cys into 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 were listed in Table S2 and the batch and cycle experimental results were shown in Figure 9. BTEX removal rates in PS/nZVI system were 20.3%, 19.0%, 20.5%, 20.3% in the actual groundwater comparing with 29.4%, 24.0%, 23.8%, 26.9% Table 1 | The concentration of Fe$^{2+}$ in different systems (mM)

| Time (h) | PS/nZVI system | PS/nZVI/L-cys system | PS/nZVI catalytic cylinder system | PS/nZVI encapsulated L-cys catalytic cylinder system |
|----------|----------------|----------------------|---------------------------------|---------------------------------|
| 0        | 0.00           | 0.00                 | 0.00                            | 0.00                            |
| 6        | 0.00           | 0.148                | 0.00                            | 0.00                            |
| 12       | 0.00           | 0.368                | 0.00                            | 0.015                           |
| 18       | 0.00           | 0.771                | 0.00                            | 0.037                           |
| 24       | 0.00           | 1.226                | 0.00                            | 0.067                           |

Note: [PS] = 0.12 M, [nZVI] = 2.0 g/L, [L-cys] = 0.12 M, [nZVI catalytic cylinder] – [nZVI encapsulated L-cys catalytic cylinder] = 56 g/L.
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 were decreased to 57.8%, 57.0%, 54.1%, 52.2% in the actual groundwater comparing with the ultrapure water (complete degradation). The effect of these PS-based Fenton systems in actual groundwater had deteriorated due to the high pH environment and high concentration of HCO$_3^-$ could scavenge HO$^•$ (Fu et al. 2018a). Also, consumption of SO$_4^{2-}$ 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 PS/nZVI/L-cys system in actual groundwater could be remitted by increasing the dosages of nZVI and L-cys.

The 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)). Comparing 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 SO$_4^{2-}$ 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 Fe$^{2+}$ 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 the 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.

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DATA AVAILABILITY STATEMENT

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

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