Removal of levofloxacin through adsorption and peroxymonosulfate activation using carbothermal reduction synthesized nZVI/carbon fiber

Weitong Tan\textsuperscript{a}, Yang Ruan\textsuperscript{a}, Zenghui Diao\textsuperscript{c}, Gang Song\textsuperscript{a}, Minhua Su\textsuperscript{a}, Li’an Hou\textsuperscript{a}, Diyun Chen\textsuperscript{b}, Lingjun Kong\textsuperscript{a,b, *}, Hongmei Deng\textsuperscript{a, **}

\textsuperscript{a} Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources, School of Environmental Science and Engineering, Guangzhou University, Guangzhou, 510006, China

\textsuperscript{b} Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, China

\textsuperscript{c} School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou, 510225, China

** Corresponding author. Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources, School of Environmental Science and Engineering, Guangzhou University, Guangzhou, 510006, China.

** Corresponding author.

\textit{E-mail addresses:} kongljun@gzhu.edu.cn (L. Kong), hmdeng@gzhu.edu.cn (H. Deng).

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1. Introduction

Levofloxacin (LEV) is a third-generation water-soluble fluoroquinolone antibiotic that is widely used to eradicate bacterial diseases (Mahmoud et al., 2020). LEV overuse increases the amount of LEV-containing wastewater released from pharmaceutical factories and hospitals, resulting in the formation of resistance genes as well as elevated endocrine disorder and cancer risks (Ma et al., 2019). LEV is refractory and nonbiodegradable owing to the high dissociation energy of the C–F bond in nature, which is difficult to break (Van Doorslaer et al., 2014; Zhong et al., 2021). Because the toxicity of halogen-containing organic molecules in aqueous environments has attracted considerable attention, investigations on LEV degradation should focus on breaking of the C–F bond. Advanced oxidation processes (AOPs) represent a promising approach to degrading refractory organic pollutants.

AOPs based on sulfate radicals (SO\textsubscript{4}\textsuperscript{•−}) have increasingly attracted attention for degrading recalcitrant organic contaminants in water due to their advantages of high redox potential (2.5–3.1 V), long lifetime (approximately 40 μs) (Li et al., 2018; Zhu et al., 2020), wide working pH range, and nonselectivity (Liu et al., 2018; Zhang and Wang, 2019). Generally, SO\textsubscript{4}\textsuperscript{•−} can be generated through peroxymonosulfate (PMS) activation by heat (Nie et al., 2014), UV radiation (Takdastan et al., 2018), catalysts (Furman et al., 2010), and ultrasound (Cai et al., 2015). Among these approaches, PMS activation using heterogeneous environmentally friendly catalysts is a benign and economic process (Ma.
Notably, iron, the fourth most abundant element in the Earth’s crust (Tanaka et al., 2019), is environmentally friendly and does not cause secondary pollution. Fe-based heterogeneous catalysts that can activate PMS to eliminate pollutants in wastewater have been widely discussed due to their low cost, low toxicity, and environment-friendly nature, among other advantages (Pang et al., 2019). In particular, zero valent iron (ZVI), owing to its favorable reduction potential and electron transformation ability, has been widely studied in the context of PMS activation to eliminate organic pollutants from wastewater (Liu et al., 2021). Cao et al. (2019) investigated PMS activation with ZVI for tetracycline degradation. Yang et al. (2018) used ZVI-montmorillonite for PMS activation to remove bisphenol. Ma et al. (2018) reported the PMS activation performance of nZVI in lignin-derived hydrochar for phenol removal. In a previous study, we achieved efficient PMS activation by using ZVI to degrade dyes in wastewater (Pang et al., 2019). Surface corrosion of ZVI limits the transformation of zero-valent iron to Fe$^{2+}$ or Fe$^{3+}$, further limiting the PMS activation efficiency. Therefore, nZVI, characterized by a large surface area and high reactivity, was developed to increase the PMS activation efficiency.

However, the instability and aggregation of nZVI due to its large surface area and strong magnetic interaction were the main issues limiting its further application (Zhang et al., 2020; Zhou et al., 2014). The large surface area and high reactivity of nZVI improved its ability to activate PMS, but these characteristics led to the unfavorable outcomes of agglomeration and oxidation. To overcome these limitations, various types of porous materials, such as montmorillonite (Zhang et al., 2013), resin (Du et al., 2014), mesoporous silica (Petala et al., 2013), and biochar (Dong et al., 2017) have been employed as nZVI supporters to avoid its agglomeration and maintain its ability to activate PMS. Among them, biochar has attracted considerable attention owing to its large specific surface area (Hao et al., 2021; Lyu et al., 2020), porous structure (Zhang and Wang, 2020), and oxygen-containing groups (Wang et al., 2020). Hence, biochar is among the most ideal supporters of nZVI (Wang et al., 2019). Biochar-supported nZVI has been widely synthesized using liquid phase reduction through the dropwise addition of sodium borohydride (NaBH$_4$) into a biochar and ferrate solution (Wang et al., 2017; Zhang, D.J. et al., 2019).

Biochar can be obtained through the carbonization of organic precursors in an inert atmosphere. Recently, the use of organic waste to prepare biochar has attracted considerable interest from the viewpoint of recycling resources. It is practical to use organic waste as precursors of biochar. Up to 562 million tons of waste cotton fiber is assumed to be generated in China, which accounts for 28% of the total textile waste in China (Xu et al., 2018). Waste cotton fibers can be converted to porous carbon fiber through carbonization, in which cotton fibers are decomposed into small organic molecules in a reducing atmosphere (Wanassi et al., 2017; Xia et al., 2020). In a previous study, we illustrated that nZVI can be obtained through the carbothermal reduction of iron-rich sludge, where the iron salt in the sludge can be reduced to ZVI in a reducing atmosphere (Kong et al., 2016). Thereafter, the preparation of graphite-supported nZVI through carbothermal reduction was reported, wherein graphite was immersed in an iron solution (Li et al., 2019).

We were inspired to explore a one-step carbothermal reduction process for the synthesis of carbon fiber (CF)-supported nZVI in the carbonization of waste cotton, wherein the porous CF may enhance the ability of nZVI to enrich pollutants through adsorption and the nZVI leads to efficient PMS activation. The enrichment of LEV on the CF surface through adsorption is hypothesized to facilitate LEV degradation by nZVI-activated PMS. The objective of this work was to synthesize a novel nZVI/CF by carbonizing for synergistic adsorption and degradation of LEV. In this work, cotton fiber was soaked into Fe(NO$_3$)$_3$·9H$_2$O solutions of various concentrations, and the solutions served as iron precursors. The synthesized nZVI/CF was characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) analyses. The iron concentration and morphology were adjusted by controlling the Fe$^{3+}$ solution concentration. The contribution of LEV enrichment through adsorption and PMS activation to LEV removal was investigated. The long-term stability of nZVI/CF was reported. This approach is expected to be a promising strategy for exploring the use of nZVI/CF to enrich and degrade LEV in the context of environmental decontamination.

2. Material and methods

2.1. Materials

Ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) was purchased from Sinopharm Chemical Reagent Co, Ltd. Levofloxacin (LEV), potassium monopersulfate triple salt (PMS), nitric acid (HNO$_3$), sodium hydroxide (NaOH) and zero-valent iron (ZVI) powder were purchased from Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). Cotton fiber was collected from solid waste transfer station in Guangzhou University, China. All solutions were prepared with ultra-pure water.

2.2. Synthesis of Fe based catalysts

The Fe based catalysts were prepared via the following procedure. Initially, 4 g cotton fiber were immersed in ferric nitrate solutions at concentrations of 0.03 M, 0.1 M, 0.3 M, and 0.6 M by stirring for 24 h. In this case, iron ions could be adsorbed onto the cotton fiber. The iron-soaked cottons were put in a natural environment to remove bulk water, and then further being dried at an oven under 60 °C for 12 h. The obtained iron cotton with different iron contents were filled into a ceramic ark and placed in a quartz tube of the programmed tube electrical furnace (LTKC-5-12, China). Firstly, the tube was purged with nitrogen to sweep residual air to obtain an inert atmosphere. Subsequently, the temperature was raised to 600, 700, 800, 900 °C with a heat rate of 5 °C/min, the iron cotton precursor was carbonized at the determined temperature for 2 h. Finally, the resulted materials were taken out after cooled to room temperature (Scheme 1). The resulted samples were named as nZVI/CF-T-s, in which the letters of T and s presented the carbonization temperature and iron concentration, respectively.

![Scheme 1. Schematic illustration of the preparation of nZVI/CF.](image-url)
2.3. Characterization

The chemical phase and surface morphology of nZVI/CF-T-s were observed by X-ray diffraction (XRD, PANalytical, PW3040/60, Holland) using Cu Kα at 40 kV and 40 mA in the range of 5°–80°. The micromorphology of nZVI/CF-T-s was characterized by a scanning electron microscope (SEM, Zeiss, Gemini 500, Germany). The concentration of LEV was determined using Shimadzu-2500 UV-visible spectrophotometer at 288 nm. The concentration of fluoride ion was determined using fluoride electrode (Thermo Orion, 9609BNWP, USA). The surface element composition and valence were determined by X-ray photoelectron spectroscopy (XPS) technology (Thermo Fisher Scientific, ESCALAB 250Xi, USA). The specific surface areas and pore structure are determined by fully automatic specific surface area and pore size test system (Micromeritics, ASAP, 2020, USA) at 77 K through a nitrogen adsorption-desorption method. To detect reactive radicals, electron paramagnetic resonance (EPR) was operated during the LEV degradation process using a spectrometer (Bruker, A300, Germany) with dimethyl-pyrroline-N-oxide (DMPO) as free radical tracer. Total organic carbon (TOC) was analyzed by a TOC analyzer (Shimadzu, TOC-L, JAPAN). The intermediate products were analyzed by liquid chromatography-mass spectrometry system (LC-MS, Thermo Fisher, Q-Exactive, USA).

2.4. Adsorption and degradation tests

All the adsorption and catalytic degradation experiments were performed in a series of 250 ml of conical flasks. Firstly, 100 ml of LEV of 10, 20, and 30 mg/L were poured into the conical flasks. The solution pH was adjusted by NaOH (0.1 M) and HNO₃ (0.1 M) solution to determine pH value. 20 mg catalysts were poured into the LEV solution to initiate the reaction. Then the mixtures were put into a constant temperature shaker at 25 °C. For the adsorption test, 5 ml of mixtures were taken out at each time interval, further being filtrated by 0.45 μm millipore membrane to remove the residual catalysts. The residual concentration of LEV was measured using a UV-visible spectrophotometer (Shimadzu, UV-2500, Japan) at 288 nm wavelength. For the catalytic degradation experiments, 1 mM PMS was added to the mixture solution to trigger the degradation reaction. At each determined time interval, 5 ml of mixtures were taken out and filtrated immediately for further analyzing the residual concentration of LEV. In this process, the concentration of fluoride ion in solution was measured by using fluoride electrode (Thermo Orion, 9609BNW, USA). The iron contents in nZVI/CF-900-s were measured by a flam atomic absorption spectrometer (Thermo Scientific, FAAS, iCE 3500 AA System, USA). To minimize the impact of errors, all the experimental tests were repeated three times.

3. Results and discussion

3.1. Characterization of nZVI/CF-T-s

Fig. 1 depicts the XRD patterns of nZVI/CF-T-s prepared through the carbothermal reduction of cotton fiber at 900 °C (JCPDS NO.06-0696) were observed at 2θ values of 44.8°, 53.5°, and 65.2°, and they were indexed to (1 1 0), (2 0 0), and (2 2 0), respectively (Ji et al., 2019). These results indicated that the carbonization temperature governed nZVI production. This finding is consistent with those of our previous works, in which nZVI was produced through carbothermal reduction at 900 °C (Zhang et al., 2019a, 2019b). In the cases of nZVI/CF-900-0.03, nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6, α-Fe (JCPDS NO.06-0696) was the main phase, confirming that nZVI can be produced through the carbothermal reduction of cotton fiber at 900 °C. However, the intensity of the diffraction peak of α-Fe for nZVI/CF-900-0.03 was low, whereas the intensities of the diffraction peaks of α-Fe for nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6 were similar. The low intensity of nZVI/CF-900-0.03 may be ascribed to the fact that it was immersed in a solution with a low iron concentration of 0.03 M.

Fig. 2 demonstrated that nZVI/CF-900-0.03, nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6 had different morphologies. Nanoparticles were dispersed on the CF surface of nZVI/CF-900-0.03. According to our XRD analysis, these nanoparticles were ascribed to nZVI. In the case of nZVI/CF-900-0.1, the ZVI nanoparticles started to agglomerate as the iron concentration of the immersion solution increased. In the case of nZVI/CF-900-0.3, nanoparticle agglomeration intensified when the iron concentration of the immersion solution was increased to 0.3 M, but internal gaps were observed. Nanoparticle agglomeration was observed even in the case of nZVI/CF-900-0.6. These results indicated that the increased iron concentration led to the agglomeration of ZVI nanoparticles. The narrow-scan XPS spectra of the Fe 2P peaks of nZVI/CF-900-0.3 are illustrated in Fig. 3. The peaks located at 706 and 718.6 eV represent the binding energies of nZVI, thus confirming the presence of nZVI. The calculated iron concentrations of nZVI/CF-900-0.03, nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6 were 229.8, 679.4, 831.2, and 849.4 mg/g, respectively, as illustrated in Fig. 4a reported in Text S1. These results suggest that the amount of nZVI produced could be adjusted conveniently by controlling the iron concentration of the immersion solution. According to Fig. 4a, the iron concentrations of nZVI/CF-900-0.3 and nZVI/CF-900-0.6 were equal when the immersed iron concentrations were increased to 0.3 and 0.6 M. That is to say, the soaked iron on cotton fiber is saturated when
the iron concentration is 0.3 M. The nZVI content of nZVI/CF-900-0.6 is equal to that of nZVI/CF-900-0.3.

The N$_2$ adsorption and desorption isotherms of nZVI/CF-T-s are depicted in Fig. S1, and the pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method. According to the International Union of Pure Applied Chemistry classification, the N$_2$ adsorption-desorption isotherms of nZVI/CF-900-s are of type IV and have a typical H$_2$ hysteresis loop. At $P/P_0$ > 0.4, all of the samples exhibited rapid
adsorption owing to the filling of the mesopores (Table S1). The Brunauer–Emmett–Teller (BET) surface area was small due to the low micropore volume. Notably, the surface area of nZVI/CF-900-0.3 was larger than that of nZVI/CF-900-0.6, although they had similar iron concentrations. This was ascribed to the agglomeration of nZVI for nZVI/CF-900-0.6, as confirmed by SEM (Fig. 2).

### 3.2. Adsorption performance of nZVI/CF-T-s in relation to LEV

The adsorption performance levels of nZVI, CF-900, nZVI + CF-900, and nZVI/CF-900-0.3 in relation to LEV are presented in Fig. 4. Moreover, nonlinear fitted kinetic models (pseudo-first-order and pseudo-second-order) were used to evaluate the adsorption behaviors of LEV on nZVI, CF-900, nZVI + CF-900, and nZVI/CF-900-0.3. As illustrated in Fig. 4b and c and summarized in Table 1, the results obtained using the pseudo-second-order kinetic model had a good fit with the experimental data pertaining to the adsorption of LEV on nZVI/CF-900-0.3. CF-900 exhibited a good LEV adsorption capacity, and LEV adsorption on commercial Fe powder was negligible. These results indicated that the CF mainly contributed to LEV adsorption. However, nZVI + CF-900 exhibited a higher LEV adsorption efficiency than that of nZVI/CF-900-0.3, although they had similar carbon and Fe concentration. The main difference between nZVI + CF-900 and nZVI/CF-900-0.3 was in the microstructures of nZVI and carbon. In nZVI/CF-900-0.3, the nZVI was loaded onto the carbon surface, whereas in nZVI + CF-900, the nZVI and carbon were separate. The loaded nZVI occupied the carbon surface, which may have limited the ability of nZVI/CF-900-0.3 to adsorb LEV. This result further confirmed the adsorption of LEV on carbon. Then, LEV could be enriched on the carbon surface, and by extension, on the nZVI surface as well. Carbonization temperature had a positive effect on the LEV adsorption capacity of nZVI/CF-T-s. nZVI/CF-900-0.3 exhibited the highest adsorption capacity among the nZVI/CF-T-0.3 samples (Fig. 4d) because high-temperature carbonization facilitated LEV enrichment on CF through adsorption.

### 3.3. Reactivity of nZVI/CF-T-s for PMS activation

To explore the reactivity of nZVI/CF-T-s for PMS activation, the degradation efficiency of LEV was investigated, as shown in Fig. 5. The LEV degradation efficiency of the nZVI/CF-T-s/PMS system was considerably higher than that of the PMS-only system (8.66%), indicating that nZVI/CF-T-s played an important role in PMS activation for LEV degradation. In particular, the carbonization temperature greatly affected LEV degradation. nZVI/CF-900-0.3 exhibited the highest LEV removal efficiency of 93.83% within 60 min, whereas the LEV removal efficiencies of nZVI/CF-600-0.3, nZVI/CF-700-0.3, and nZVI/CF-800-0.3 were 9.7%, 17.7%, and 25.6%, respectively. Our evaluations of the LEV degradation kinetics of the PMS/nZVI/CF-T-0.3 systems are presented in the inset of Fig. 5a. As described in the figure, the LEV degradation kinetics fitted well with the pseudo-first-order kinetic

![Fig. 4](image-url)

**Fig. 4.** (a) The concentration of Fe in nZVI/CF-900-s; (b) pseudo-first-order and (c) pseudo-second-order adsorption kinetic models of nZVI, CF-900, nZVI + CF-900, nZVI/CF-900-0.3 to LEV; (d) adsorption capacity of LEV on nZVI/CF-T-s. Reaction conditions: [nZVI] = 0.16 g/L, [CF-900] = 0.04 g/L, [nZVI + CF-900] = 0.2 g/L, [nZVI/CF-900-0.3] = 0.2 g/L, [LEV] = 20 mg/L, T = 25 °C, initial pH = 7.0.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k1 (min⁻¹)</td>
<td>qe (mg/g)</td>
</tr>
<tr>
<td>nZVI</td>
<td>0.282</td>
<td>1.048</td>
</tr>
<tr>
<td>CF-900</td>
<td>0.194</td>
<td>58.660</td>
</tr>
<tr>
<td>nZVI + CF-900</td>
<td>0.237</td>
<td>47.649</td>
</tr>
<tr>
<td>nZVI/CF-900-0.3</td>
<td>0.352</td>
<td>18.977</td>
</tr>
</tbody>
</table>
model (-ln (C/C₀) = kt). The calculated kinetic rate constant of LEV degradation with nZVI/CF-600-0.3, nZVI/CF-700-0.3, nZVI/CF-800-0.3, and nZVI/CF-900-0.3 activation was 0.0039, 0.0151, 0.0177, 0.0716 min\(^{-1}\), respectively. nZVI/CF-900-0.3 achieved the strongest CMS activation for LEV degradation. Because iron oxides constituted the main phase in nZVI/CF-800-0.3, nZVI/CF-700-0.3, and nZVI/CF-600-0.3, although nZVI was the main active components in nZVI/CF-900-0.3, the strong reactivity of nZVI/CF-900-0.3 was ascribed to the presence of nZVI, which has been widely used for CMS activation in the degradation of organic pollutants (Pang et al., 2019). The leaching of Fe\(^{2+}\) through nZVI corrosion, as expressed in reaction Eq. (1), was observed, and this process could provide an electron and Fe\(^{2+}\) for CMS activation (Fig. S2). The electron and Fe\(^{2+}\) could combine with HSO\(_{5}^-\) to produce -SO\(_{4}^-\) and -OH, as shown in the reaction equation, whereas Fe\(^{3+}\) could react with HSO\(_{5}^-\) to produce -SO\(_{4}^-\) and Fe\(^{2+}\) (Eqs. (2)–(5)), resulting in an increased LEV degradation efficiency.

Fe\(^{0}\) → Fe\(^{2+}\) + 2e\(^-\) \hspace{1cm} (1)

Fe\(^{2+}\) + HSO\(_{5}^-\) → Fe\(^{3+}\) + SO\(_{4}^-\) + OH\(^-\) \hspace{1cm} (2)

Fe\(^{3+}\) + HSO\(_{5}^-\) → Fe\(^{2+}\) + SO\(_{4}^-\) + H\(^+\) \hspace{1cm} (3)

HSO\(_{5}^-\) + e\(^-\) → SO\(_{4}^-\) + OH\(^-\) \hspace{1cm} (4)

HSO\(_{5}^-\) + e\(^-\) → SO\(_{4}^-\) + OH\(^-\) \hspace{1cm} (5)

The nZVI/CF-900-s samples with various iron concentrations were obtained by adjusting the concentration of the Fe(NO\(_{3}\))\(_{3}\)·9H\(_2\)O solution. The LEV removal efficiency achieved through nZVI/CF-900-0.03, nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6 activation was 48.18%, 61.54%, 93.83%, and 87.95%, respectively (Fig. 5b). The rate constant of LEV degradation achieved through nZVI/CF-900-0.03, nZVI/CF-900-0.1, nZVI/CF-900-0.3, and nZVI/CF-900-0.6 activation was 0.0208, 0.0263, 0.0716, and 0.0411 min\(^{-1}\), respectively. The LEV degradation efficiency and rate constant of nZVI/CF-900-0.3 activation was the highest, indicating that nZVI/CF-900-0.3 exhibited a higher reactivity for CMS activation than did nZVI/CF-900-0.1 and nZVI/CF-900-0.3. CMS activation for LEV degradation was enhanced as the Fe concentration increased. This result confirmed that nZVI played an important role in CMS activation for LEV degradation. Although the nZVI concentration of nZVI/CF-900-0.6 was similar to that of nZVI/CF-900-0.3, its reactivity for CMS activation was lower than that of nZVI/CF-900-0.3. nZVI/CF-900-0.6 was prepared through the immersion of cotton fiber in a 0.6 M iron solution. As shown in Fig. 4a, nZVI was agglomerated in nZVI/CF-900-0.6. The agglomerated nZVI could not efficiently activate CMS, which lowered the reactivity of CMS activation for LEV degradation.

To further confirm the reactivity of nZVI and carbon fiber in nZVI/CF-900-0.3 for CMS activation, a comparison of the CMS removal efficiencies of the nZVI/CF-900-0.3/PMS, CF-900/PMS, nZVI/PMS, nZVI + CF-900/PMS, and CMS-only systems is depicted in Fig. 5c. CF-900 had a slightly affected on CMS activation. During adsorption (Fig. S3), the CMS removal rate of CF-900 (39.83%) was 14.34% lower than that of CF-900/PMS (54.17%). This phenomenon can be ascribed to the fact that biochar produces persistent free radicals and electrons that react with CMS to produce -SO\(_{4}^-\) and -OH (Fang et al., 2014; Jiang et al., 2019; Li et al., 2019). In addition, the CMS removal rates of nZVI, CF-900, nZVI + CF-900, and nZVI/CF-900-0.3 during the adsorption process were 1.05%, 39.83%, 40.27%, and 19.25%, respectively. The CMS degradation efficiencies of the nZVI, nZVI + CF-900, and nZVI/CF-900-0.3 systems were up to 51.60%, 60.0%, and 93.83%, respectively, in the presence of CMS. The presence of nZVI strongly promoted CMS degradation by the nZVI/CF-900-0.3/PMS and nZVI + CF-900/PMS systems.
compared with that by the CF-900/PMS and PMS systems, thus confirming the efficient activity of nZVI in PMS activation. Although the nZVI/CF-900-0.3/PMS and nZVI + CF-900/PMS systems had similar nZVI concentrations, the nZVI/CF-900-0.3/PMS system exhibited significantly higher LEV degradation activity than the nZVI + CF-900/PMS system did, indicating that the synthesized nZVI/CF-900-0.3/PMS system is a preferable PMS activator to CF-900/nZVI. Because nZVI + CF-900 is a mixture of CF-900 and nZVI, its components became separated in the solution. CF-900 exhibited a favorable adsorption ability to remove LEV, and nZVI provided the PMS activation ability to degrade LEV. The nZVI + CF-900 system exhibited a higher LEV adsorption efficiency than did the nZVI/CF-900-0.3 system, as shown in Fig. S3. This result may be ascribed to the fact that CF-900 played an important role in LEV adsorption, whereas the micropores on the CF of nZVI/CF-900-0.3 were blocked by the nano-sized ZVI. LEV could have been concentrated around the CF-900 surface through adsorption in the nZVI + CF-900/PMS and nZVI/CF-900-0.3/PMS systems. Because free radicals were generated around the nZVI particles through PMS activation, these radicals were easily annihilated within several nanoseconds and could not attack the concentrated LEV around the CF-900 surface because the CF-900 and nZVI were separated in the nZVI + CF-900/PMS system (Xu et al., 2020). Once the nZVI was loaded on the CF in the nZVI/CF-900-0.3 system, the nZVI/CF-900-0.3 system not only exhibited advantages in enriching LEV through adsorption but also strongly activated PMS for LEV degradation, with an efficiency of 93.83%. This was ascribed to the fact that once the LEV molecules were enriched on the CF surface through adsorption, they were immediately degraded by the SO₄ and OH radicals. Thus, nZVI/CF-900-0.3 exhibited a preferable ability to remove LEV. Additionally, a high defluorination efficiency of 64.25% was observed for the nZVI/CF-900-0.3 system (Fig. S4), indicating that the fluorine could be released from small organic molecules, which could reduce the toxicity of the intermediate product. The TOC removal efficiency of the nZVI/CF-900-0.3 system was up to 48.61%, which was higher than the values reported in previous studies (Qi et al., 2018, 2020) (Fig. S5). The TOC removal efficiency is consistent with the defluorination ability, indicating that LEV mineralization leads to defluorination.

An evaluation of the effects of anions such as Cl⁻, NO₃⁻, HCO₃⁻, H₂PO₄⁻ on the LEV degradation efficiencies is depicted in Fig. 5d. The concentration of each anion was 10 mM. The results indicate that the influence of anions on the degradation efficiency of LEV has the following order: H₂PO₄⁻ > HCO₃⁻ > NO₃⁻ > Cl⁻. The LEV degradation efficiency decreased to 35.24% and the pH increased to 8.72 after the addition of H₂PO₄⁻. The alkaline solution may have inhibited the consumption of free radicals (Eqs. (19)-(22)) (Ma et al., 2020) Hydroxide is adsorbed on the surface of the catalyst under alkaline conditions, which induces a negative charge on the catalyst surface; this is conducive to the binding of a neutral or electron-rich form of LEV (Kaur et al., 2019). Moreover, the released Fe²⁺ could react with hydroxyl groups (OH⁻) in the alkaline solution to produce iron hydroxide, thus reducing PMS activation by Fe²⁺. Generally, OH⁻ is easily produced in acidic solutions through the Fenton reaction, but the degradation efficiency and kinetic constant rate are greatly reduced at a pH solution of >3.0. The excessive H⁺ could react with OH⁻ in the presence of electrons to form H₂O according to reaction Eq. (23) (Cai et al., 2020), leading to the consumption of electrons and OH⁻. Moreover, it has been widely reported that SO₄ can be consumed by H⁺ in an acidic solution (Eq. (24)) (Cai et al., 2020), leading to a decrease in the LEV degradation efficiency. Thus, SO₄ mainly contributed to LEV degradation. LEV degradation using PMS activated by nZVI/CF-900-0.3 could be achieved over a wide pH range, indicating that nZVI/CF-900-0.3 is promising for use in PMS activation in environmental remediation.

H₂PO₄⁻ + OH⁻ → H₂O + HPO₄²⁻, \( k = 2.0 \times 10^3 \ M^{-1} \ s^{-1} \) (9)
Cl⁻ + SO₄²⁻ → SO₄⁻ + Cl⁻, \( k = 1.3 \times 10^8 \ M^{-1} \ s^{-1} \) (10)
Cl⁻ + OH⁻ → ClO⁻, \( k = 3.4 \times 10^8 \ M^{-1} \ s^{-1} \) (11)
NO₃⁻ + SO₄²⁻ → SO₄⁻ + NO₃⁻, \( k = 5.2 \times 10^9 \ M^{-1} \ s^{-1} \) (12)
H₂PO₄⁻ + SO₄²⁻ → SO₄⁻ + H₂O + HPO₄²⁻, \( k = 1.2 \times 10^6 \ M^{-1} \ s^{-1} \) (13)
Cl⁻ + Cl⁻ → Cl₂⁻ (14)

An evaluation of the effects of PMS concentration, initial pH, nZVI/CF-900-0.3 dosage and LEV concentration on LEV degradation efficiency is depicted in Fig. 6b. Because PMS is a source of sulfate radicals, the addition of PMS promoted LEV degradation. Fig. 6a demonstrates the influence of PMS concentration on LEV degradation efficiency. Approximately 90.4%, 93.83% and 92.36% of LEV was degraded at the PMS concentrations of 0.5 mM, 1.0 mM, and 1.5 mM, respectively. The LEV degradation efficiency increased as the PMS concentration increased up to 1.0 mM, whereas it decreased when the PMS concentration reached 1.5 mM. Excessive PMS had a detrimental effect on LEV degradation due to the competitive reactions of free radicals, as shown in Eqs. (15)-(17) (Guan et al., 2011; Jiang et al., 2019; Takdastan et al., 2018). The generated SO₄ can strongly quench the LEV degradation activity of nZVI/CF-900-0.3 for PMS activation was the strongest under a neutral condition. In alkaline conditions, OH⁻ and SO₄ can react with hydroxide ions (OH⁻), thus causing the consumption of free radicals [Eqs. (19)-(22)] (Ma et al., 2020) Hydroxide is adsorbed on the surface of the catalyst under alkaline conditions, which induces a negative charge on the catalyst surface; this is conducive to the binding of a neutral or electron-rich form of LEV (Kaur et al., 2019). Moreover, the released Fe²⁺ could react with hydroxyl groups (OH⁻) in the alkaline solution to produce iron hydroxide, thus reducing PMS activation by Fe²⁺. Generally, OH⁻ is easily produced in acidic solutions through the Fenton reaction, but the degradation efficiency and kinetic constant rate are greatly reduced at a pH solution of >3.0. The excessive H⁺ could react with OH⁻ in the presence of electrons to form H₂O according to reaction Eq. (23) (Cai et al., 2020), leading to the consumption of electrons and OH⁻. Moreover, it has been widely reported that SO₄ can be consumed by H⁺ in an acidic solution (Eq. (24)) (Cai et al., 2020), leading to a decrease in the LEV degradation efficiency. Thus, SO₄ mainly contributed to LEV degradation. LEV degradation using PMS activated by nZVI/CF-900-0.3 could be achieved over a wide pH range, indicating that nZVI/CF-900-0.3 is promising for use in PMS activation in environmental remediation.

- SO₄²⁻ + SO₄⁻ → 2SO₃²⁻ or S₂O₅²⁻ (15)
- OH⁻ + OH⁻ → H₂O₂ (16)
- SO₄²⁻ + OH⁻ → HSO₄⁻ (17)
- HSO₄⁻ + SO₄²⁻ + H₂O → H₂O + SO₄²⁻ + 2H⁺ (18)
Fig. 6. Effects of reaction parameters on the degradation of LEV: (a) PMS doses (inset: pseudo-first-order rate constant of LEV under different PMS doses); (b) pH conditions (inset: pseudo-first-order rate constant of LEV under different pH conditions); (c) catalyst dosages (inset: pseudo-first-order rate constant of LEV under different catalyst dosages); (d) initial concentration (inset: pseudo-first-order rate constant of LEV under different initial concentration). Reaction conditions: [LEV] = 20 mg/L (if needed), [PMS] = 1 mM (if needed), [catalyst] = 0.2 g/L (if needed), T = 25 °C, initial pH = 7.0 (if needed).

\[
\begin{align*}
\cdot \text{SO}_4^– + \text{H}_2\text{O} &\rightarrow \text{HSO}_4^- + \cdot \text{OH} \\
\cdot \text{OH} + \cdot \text{OH} &\rightarrow \text{H}_2\text{O}_2 \\
\text{S}_2\text{O}_8^{2–} + \text{H}_2\text{O}_2 &\rightarrow 2\text{H}^+ + 2\text{SO}_4^{2–} + \text{O}_2 \\
\text{H}^+ + \cdot \text{OH} + \cdot \text{e}^- &\rightarrow \text{H}_2\text{O} \\
\text{H}^+ + \cdot \text{SO}_4^– + \cdot \text{e}^- &\rightarrow \text{HSO}_4^- 
\end{align*}
\]
(20–24)

The evolution of solution pH values after the reaction is displayed in Fig. S6. When the initial solution was acidic with a pH of 3.0, the final environment remained acidic (pH = 3.71). When the initial solution pH was 5.0, 7.0, and 9.0, the final pH values were 5.12, 5.14, and 5.13, respectively. A similar result was obtained by Jiang et al. (2019). One explanation was the buffering ability of biochar (Hu et al., 2018).

The LEV degradation efficiency increased to 89.34% after only 10 min as nZVI/CF-900-0.3 dosage increased from 0.1 to 0.3 g/L (Fig. 6c). As shown in the inset image, the k value increased with the nZVI content favoring high yields of free radicals through PMS activation, resulting in high LEV degradation efficiency. A comparison of the LEV degradation efficiency between the nZVI/CF/PMS systems and the reported system is presented in Table S2. And LEV degradation efficiency of 93.83% was achieved within 60 min in the case of the nZVI/CF-900-0.3/PMS system, which was the highest among the studied systems, especially at an initial LEV concentration and catalyst concentration of 20 ppm and 0.2 g/L, respectively. Although a removal efficiency of 89.4% was achieved with the CoFeO@CN system, the initial concentration was only 10 ppm (Pi et al., 2020). The nZVI/CF-900-0.3/PMS system benefited from its high LEV removal efficiency and low catalyst dosage compared with the tested system. The favorable results may be ascribed to the advantageous activity of nZVI/CF. In addition, an investigation of the influence of the initial LEV concentration on the LEV degradation efficiency is depicted in Fig. 6d, which indicates that 10 ppm LEV was almost removed within 40 min. As the LEV concentration was increased from 20 ppm to 30 ppm, the degradation efficiency decreased from 93.83% to 88.88%. The rate constants for LEV degradation at the concentrations of 10, 20, and 30 ppm was 0.0380, 0.0716, and 0.0211 min$^{-1}$, respectively.

Free radical quenching experiments were conducted, as depicted in Fig. 7, to identify the radicals generated during PMS activation by nZVI/CF-Ts. Ethanol (EtOH) and tert-butanol (TBA) were used as the free radical quenchers. EtOH has the capacity to quench ·SO$_4$ at a rate constant of 1.6–1.7 × 10$^7$ M$^{-1}$ s$^{-1}$, whereas TBA, which was used as an ·OH scavenger, displayed more advanced reactivity with ·OH (3.8–7.6) × 10$^8$ M$^{-1}$ s$^{-1}$) than with ·SO$_4$ (4–9.1) × 10$^6$ M$^{-1}$ s$^{-1}$) (Pi et al., 2020).

LEV degradation in the presence of EtOH and TBA is illustrated in Fig. 7a. When TBA was added into the mixed system of nZVI/CF-900-0.3/PMS, the LEV removal efficiency slightly decreased. However, the LEV removal efficiency was significantly inhibited to 28.67% within 60 min when 5 M EtOH was added to the system. ·SO$_4$ was the main radical that contributed to LEV degradation in the nZVI/CF-900-0.3/PMS system. The rate constants of $k_{\text{NO scavenger}}$, $k_{\text{(EtOH)}}$, and $k_{\text{(TBA)}}$ were calculated to be 0.0716, 0.0153, and 0.0393 min$^{-1}$, respectively (Fig. S7), confirming that both ·OH and ·SO$_4$ contributed to LEV degradation. The results of an EPR test are additionally displayed in Fig. 7b to confirm the produced radicals. When DMPO was added into the reactive solution in a typical ratio of 1:2:2:1 ($\alpha_M = \alpha_N = 14.8$), it confirmed the existence of ·OH. DMPO–SO$_4$ adducts ($\alpha_M = 0.78$, $\alpha_N = 1.48$, $\alpha_H = 9.6$, and $\alpha_N = 13.2$) and ·SO$_4$ (Ding et al., 2019; Li et al., 2019). The results further confirmed that although both ·SO$_4$ and ·OH were generated in the nZVI/CF-900-0.3/PMS system, the ·SO$_4$ mainly contributed to LEV degradation.
Fig. 7. (a) Effect of radical scavengers on LEV degradation (b) EPR test results in nZVI/CF-900-0.3/PMS systems. Reaction conditions: [scavenger] = 5 M, [LEV] = 20 mg/L, [PMS] = 1 mM, [catalyst] = 0.2 g/L, T = 25 °C, initial pH = 7.0.

Given that the stability of nZVI is important for its application, the stability of nZVI/CF-900-0.3 for PMS activation was measured, as shown in Fig. 8, after storage for 6 months. The stored nZVI/CF-900-0.3 system exhibited favorable PMS activation for LEV degradation, thus confirming its excellent long-term stability. This indicates that the nZVI embedded in the biochar micropores did not easily come into contact with air, which delayed the formation of an oxidation layer on the nZVI surface and preserved its high reactivity (Uzum et al., 2009; Wang et al., 2013). Moreover, the nZVI/CF-900-0.3 system exhibited strong magnetism, meaning that it could be separated easily using an external magnet (as shown in the inset of Fig. 8). The desirable long-term stability of the catalyst activity of nZVI/CF-900-0.3 can be ascribed to the electron-rich carbon that prevents the oxidation of nZVI. Thus, nZVI/CF-900-0.3 is promising system for use in environmental remediation applications.

3.4. Possible degradation pathways of LEV for nZVI/CF-900-0.3

To explore possible LEV degradation pathways, the intermediate products were detected using LC-MS. Several degradation intermediates of LEV in the nZVI/CF-900-0.3/PMS system were found, as summarized in Table S3. On the basis of these results, one of the degradation pathways of LEV in the nZVI/CF-900-0.3/PMS system was proposed (Scheme 2). First, LEV molecules (m/z = 362) are dehydrogenated to m/z 344 (Xu et al., 2017). Then, nonselective -SO₄ and -OH may attack piperazine nitrogen atoms, leading to the formation of m/z 336 through demethylation (Ma et al., 2019). The peak at m/z 279 was obtained by de-piperazinly of the product at a peak of m/z 336 (Xu et al., 2017). The peak at m/z 261 was produced through defluorination of the product corresponding to m/z 279 (Xu et al., 2017). Finally, all of the intermediate products were converted into other micromolecules of CO₂ and H₂O as the reaction time of the nZVI/CF-900-0.3/PMS system increased.

Thus, the strong catalytic performance of nZVI/CF-900-0.3 in activating PMS can be ascribed to the following mechanism: firstly, LEV molecules are absorbed and enriched on the nZVI/CF surface. Then, nZVI provides an electron and Fe²⁺ for activating PMS to generate -SO₄ and -OH. These radicals attack the LEV molecules, which are eventually transformed into smaller molecules.

4. Conclusion

In this study, nZVI/CF-900-0.3 was prepared with a one-step carbothermal reduction process in an inert gas atmosphere. nZVI was successfully supported on cotton carbon fiber. The resulting nZVI/CF-900-0.3 exhibited a high LEV degradation efficiency in the presence of PMS. Under a neutral condition, nearly 93.83% of the LEV with an initial concentration of 20 ppm was removed in the presence of nZVI/CF-900-0.3 with a dosage of 0.2 g/L and PMS concentration of 1 mM within 60 min. Both -SO₄ and -OH contributed to LEV degradation, but -SO₄ was the main component causing LEV degradation. Moreover, the proposed catalyst exhibited excellent long-term stability after storage for 6 months. Thus, we have provided a promising and stable nZVI/CF-900-0.3 synthesized through carbothermal reduction for eliminating LEV from the environment.

Credit author statement

Weitong Tan: Conceptualization, Methodology, Data curation, Investigation, Visualization, Writing - original draft preparation. Yang Ruan: Resources, Software, Writing - review & editing. Zenghui Diao: Writing - review & editing. Gang Song: Writing - review & editing. Minhua Su: Writing - review & editing. Li’an Hou: Writing - review & editing. Diyun Chen: Writing - review & editing. Hongmei Deng: English writing & editing. Lingjun Kong: Conceptualization, Data curation, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
the work reported in this paper.

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Appendix A. Supplementary data

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References


