

Degradation of tetracycline in water by activating peroxymonosulfate with nano zero-valent iron loading on nitrogen-containing biochar

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Abstract: To inhibit the agglomeration of nano zero-valent iron (Fe^0) during the reaction, Fe^0/NBC supported catalyst was prepared by loading Fe^0 on the surface of nitrogen-containing biochar (NBC), and characterized by X-ray diffractometer, specific surface area analyzer and scanning electron microscopy. Fe^0/NBC was applied to activate peroxymonosulfate (PMS) for the degradation of tetracycline (TC), and the results indicated that of 93.1% TC was removed after 120 min of reaction. Fe^0/NBC showed higher catalytic activity than that of pure Fe^0 and NBC. The effects of inorganic ions and natural organic matters on the catalytic performance of was investigated, and the produced reactive oxygen species in $\text{Fe}^0/\text{NBC}/\text{PMS}$ system were determined by radical quenching and electron paramagnetic resonance (EPR) tests. Stability experiments suggested Fe^0/NBC had a good reusability and showed good application prospect in the treatment of antibiotics in the wastewater.

Key words: Peroxymonosulfate; biochar; nano zero-valent; tetracycline; degradation

1. Introduction

Tetracycline antibiotics, a kind of broad-spectrum bacteriostatic agents for the treatment and prevention of potentially threatening infections, has been considered as emerging contaminants. Tetracycline antibiotics are unable to completely remove by conventional wastewater treatments due to their high biological toxicity and recalcitrance [1]. Thus, it is imperative to develop a highly efficient, economic and environmentally benign method for the degradation of tetracycline antibiotics.

Advanced oxidation processes (AOPs) have been regarded as one of the most effective approaches to degrade toxic organic pollutants in aqueous solution. Considerable scientific and technological interests have been paid on sulfate radical ($\text{SO}_4^{\bullet-}$) based AOPs, since $\text{SO}_4^{\bullet-}$ shows higher redox potential and longer half-time when compared to $\bullet\text{OH}$ [2, 3]. More powerful $\text{SO}_4^{\bullet-}$ generated via activating persulfate (PS) or peroxymonosulfate (PMS) can be exist in solution for longer time and oxidize more target organic contaminants [4]. Therefore, a large number of studies have focused on the formation of $\text{SO}_4^{\bullet-}$ to degrade antibiotics by activating PMS.

In this work, Fe^0/NBC supported catalyst was prepared by loading Fe^0 on the surface of nitrogen-containing biochar (NBC), and applied to activate PMS for tetracycline degradation. The experimental factors which influenced the degradation efficiency such as solution pH and

inorganic ions. The underlying mechanism involved in PMS activation by Fe^0 was elucidated in detail by radical scavenging experiment and Electron paramagnetic resonance (EPR). Moreover, cyclic degradation experiments were conducted to investigate the reusability and stability of Fe^0/NBC .

2. Experimental

2.1 Chemicals and materials

Tetracycline, PMS ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 4.5% active oxygen), were obtained from Shanghai Yien Chemical Technology Co. Ltd., China. NaOH, HCl, ethanol (EtOH), *tert*-butanol (TBA), *p*-benzoquinone (*p*-BQ), *L*-Histidine (*L*-H), humic acid (HA), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidone (TEMP) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents were of analytical grade and used as received without any further purification.

2.2 Preparation and Characterization of Fe^0/NBC

The corn cores were repeatedly washed three times with ultrapure water to remove dust and salt from the surface, dried at 80 °C for 24 h, and then grinded into powder. The above powders were placed in a tube furnace and pyrolyzed under the oxygen limited conditions for 3 h at

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500 °C. Then the obtained corn core biochar (BC) was stored in the centrifuge tube for further use. BC was modified by 10% $\text{NH}_3 \cdot \text{H}_2\text{O}$ and the nitrogen-containing biochar was named as NBC.

Fe^0/NBC was prepared via a liquid-reduction process according to the following procedure. A certain amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added into a three-necked flask and dissolved with 100 mL deionized water. After ultrasonic treatment for 10 min, 5 g NBC was added and N_2 was fed in the flask for protection. Then, excess NaBH_4 solution was dropwise added to the slurry under constant stirring. After completion of the addition, stirring was continued for 30 min and then Fe^0/NBC was obtained.

2.3 Tetracycline degradation experiment

The degradation of tetracycline in water was investigated in a 250 mL conical flask placed in an air bath vibrator with 200 rpm at a certain temperature. In each experiment, 100 mL of 20 mg/L tetracycline solution was added into the conical flask. Then PMS and solid catalysts were added to initiate the degradation process. Adsorption experiments in the absence of PMS were performed in the same system, under identical experimental conditions. At predetermined time intervals, 3 mL sample was taken, quenched with methanol, and filtered through a 0.22 μm membrane filter to remove the catalyst for further analysis. The concentration of tetracycline was measured at a wavelength of 357 nm using a 721 UV-vis Spectrophotometer (Shanghai Precision Scientific Instrument Co. Ltd., China) according to previous studies.

3. Results and discussion

3.1 Characterization

Fig. 1 shows the XRD patterns of Fe^0 , NBC and Fe^0/NBC . For the as-prepared Fe^0 , the significant peak at 44.6° was in good agreement with the specific diffraction peak of Fe^0 (JCPDS PDF#06-0696) [5]. Two peaks at 22° and 42° corresponded to the (002) and (101) lattice planes of the carbon materials. However, the characteristic diffraction peak of Fe^0 was not observed in the XRD pattern Fe^0/NBC , indicating that Fe^0 particles were small and well dispersed on the NBC surface.

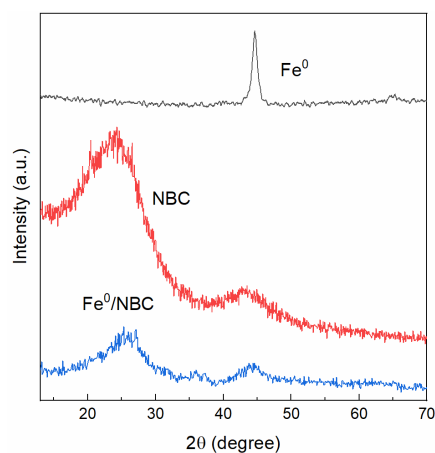


Fig. 1 XRD patterns of Fe^0 , NBC and Fe^0/NBC .

The specific surface area, pore volume and average pore size pore of Fe^0 , NBC and Fe^0/NBC determined by N_2 adsorption-desorption isotherms are listed in Table 1. The BET surface areas of Fe^0 , NBC and Fe^0/NBC were 0.5, 531 and 358 m^2/g , respectively. Moreover, Fe^0/NBC showed lower surface area and pore volume than that of NBC, which mainly be due to the Fe^0 particles penetrating into the pores of NBC.

Table 1 Specific surface area, pore volume and pore size of the catalysts

Catalysts	S/(m^2/g)	V/(cm^3/g)	d/nm
Fe^0	0.5	0.0014	13.4
NBC	531	0.425	3.2
Fe^0/NBC	358	0.287	6.7

3.2 Degradation of TC

The adsorption and catalytic performance of Fe^0 , NBC and Fe^0/NBC were investigated. As illustrated in Fig. 2, the adsorption quickly reached equilibrium within 60 min. The adsorption efficiency of Fe^0 , NBC and Fe^0/NBC were 9.6%, 18.9% and 15.2%, respectively. NBC showed the highest tetracycline removal, which mainly be attributed to the high specific surface area and rich pores (Table 1). Moreover, it was observed that single PMS had hardly any degradation effect towards tetracycline, implying that tetracycline cannot be oxidized by PMS without activation. The TC removal efficiency was 51.3% in the Fe^0/PMS system. When both NBC and PMS were added, the removal efficiency of CDX reached 71.2% in 120 min. Approximately 93.1% of TC was removed in the $\text{Fe}^0/\text{NBC}/\text{PMS}$ system, suggesting that loading Fe^0 on NBC surface promoted the catalytic performance for the activation of PMS.

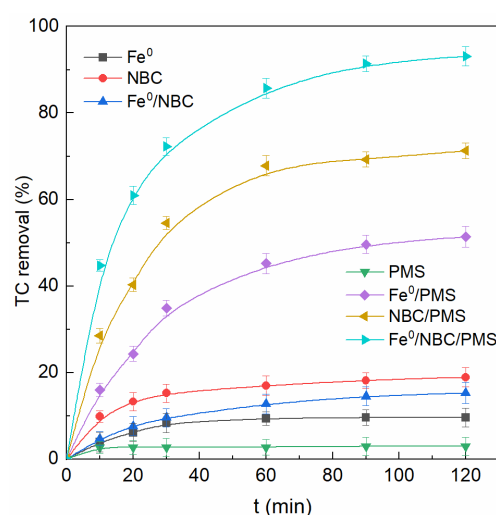


Fig. 2 Degradation of TC in different processes.

Water matrices, such as inorganic anions and natural organic matters are common components in natural waters and may affect the degradation of TC in the $\text{Fe}^0/\text{NBC}/\text{PMS}$ system. As shown in Fig. 3, the effect of Cl^- , HCO_3^- , SO_4^- , NO_3^- and humic acid (HA) on the TC removal was investigated. It was observed from that a slight inhibition effect was observed by the addition of Cl^- ,

$\text{SO}_4^{\cdot-}$ and $\text{NO}_3^{\cdot-}$. However, an obvious decrease in the degradation of TC was observed when $\text{HCO}_3^{\cdot-}$ was added. The reason for these results was that $\text{HCO}_3^{\cdot-}$ could undergo complexation with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ and form the less oxidative radicals [6]. In addition, the addition of HA also made the TC removal lower, since HA would compete with targeted pollutant for reactive radicals in solution and the deposit of HA on the surface of catalyst would lead to the deactivation of active sites [7].

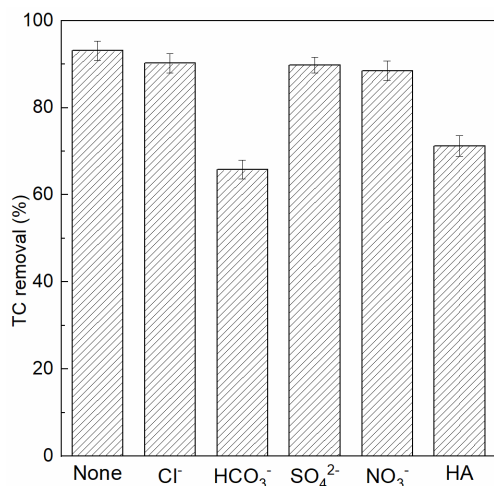


Fig. 3 Effect of Water matrices on the degradation of TC.

Since catalyst stability was a significant factor in practical application, the reusability of Fe^0/NBC was tested. As shown in Fig. 4, the degradation efficiency towards TC decreased from 93.1% of the first cycle to 90.5% third cycle. The decrease of activity may be caused by the occupation of active sites by intermediate products produced during the degradation process [8]. These results suggested the high reusability and stability of Fe^0/NBC for organic pollutants elimination.

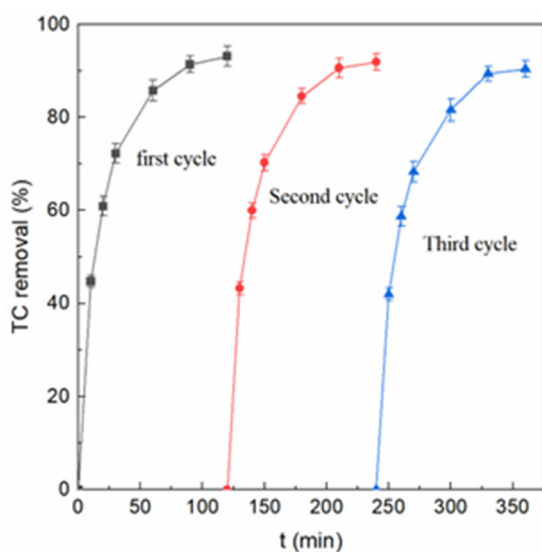


Fig. 4 Stability of Fe^0/NBC .

3.3 Determination of reactive oxygen species

The quenching experiments were conducted to investigate the other processes involved in the $\text{Fe}^0/\text{NBC}/\text{PMS}$ system and the results were presented in Fig. 5a. It was observed that the addition of either of the four chemical scavengers inhibited the degradation of tetracycline. When EtOH or TBA was added, the removal rate of tetracycline was decreased from 93.1% to 30.2% or 55.8%, respectively. When *p*-BQ, an effective quenchant for $\text{O}_2^{\cdot-}$, was added, the removal of tetracycline was markedly decreased to 36.8%. When L-Histidine (L-H), an effective quenchant for $^1\text{O}_2$, was added, the removal of tetracycline was markedly decreased to 30.6%. These results indicated $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ were produced during the reaction.

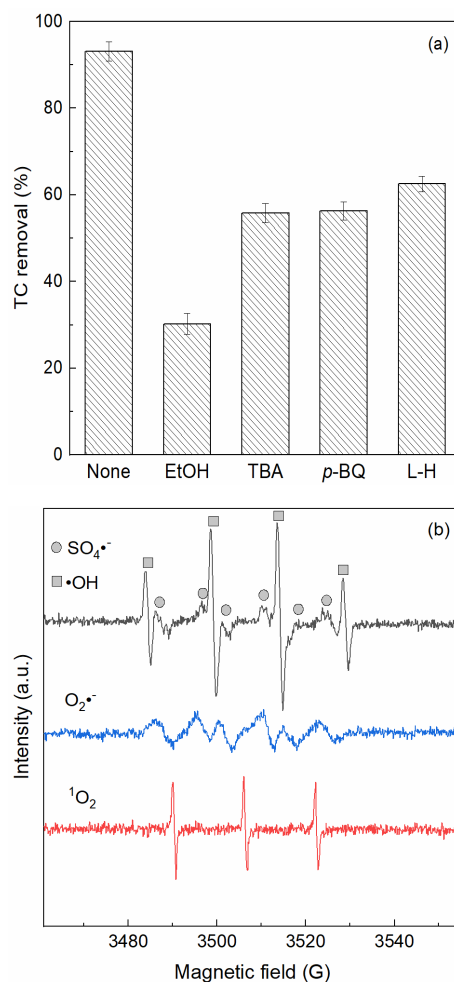


Fig. 5 (a) Quenching experiments; (b) EPR tests.

In order to further confirm the generation of these reactive oxygen species in $\text{Fe}^0/\text{NBC}/\text{PMS}$ system, EPR technique was performed. The typical EPR signals of $\text{DMPO}\text{-}\text{SO}_4^{\cdot-}$ and $\text{DMPO}\text{-}\cdot\text{OH}$ adduct were observed in Fig. 5b, suggesting that both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ were generated in $\text{Fe}^0/\text{NBC}/\text{PMS}$ system. $\text{O}_2^{\cdot-}$ was also trapped by DMPO, and the quartet characteristic EPR signals of $\text{DMPO}\text{-}\text{O}_2^{\cdot-}$ were observed. The production of $^1\text{O}_2$ was proved by the representative three-wire signals of $\text{TEMP}\text{-}^1\text{O}_2$. The above results were consistent with the free radical quenching experiments, which supported the production

of $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ participated in the degradation of TC.

4. Results and discussion

In the present study, Fe^0/NBC was fabricated and used to activate PMS for the removal TC in water. Fe^0/NBC exhibited superior catalytic performance than that of pure Fe^0 and NBC, allowing a TC removal efficiency of 93.9% with 120 min of reaction. Moreover, the mechanism of PMS activation by $\text{Fe}^0/\text{MnFe}_2\text{O}_4$ was investigated by quenching experiments and EPR tests. The production of $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ was confirmed in the $\text{Fe}^0/\text{NBC}/\text{PMS}$ system. Fe^0/NBC activating PMS may be a promising technique for the treatment of antibiotic wastewater.

Acknowledgments

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