



Short communication

A facile preparation of hierarchical dendritic zero-valent iron for Fenton-like degradation of phenol



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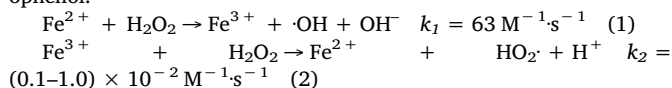
Dendritic Fe⁰
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Removal rate
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ABSTRACT

A simple, low-cost and high-efficient electrodeposition method was used to prepare three-dimensional hierarchical dendritic zero-valent iron (Fe⁰) with large specific area as heterogeneous Fenton-like catalyst. 35 ppm of phenol was removed up to 90% in 15 min in 50 mL Fe⁰/H₂O₂ solution with Fe⁰ = 100 mg/L, pH = 4.0 and H₂O₂ = 6.0 mmol/L. In the second or third run, the phenol removal efficiency still could reach ~70% in 60 min. This study illustrates that dendritic Fe⁰ has a great potential in the fields of wastewater treatment containing persistent organic pollutants.

1. Introduction

Presently, Fenton system with Fe²⁺/H₂O₂ is considered as a powerful advanced oxidation technique for the removal of various organic pollutants in wastewater [1–3]. However, one serious problem is that the regeneration of Fe²⁺ is very difficult. In addition, Fe³⁺ is easily precipitated as Fe(OH)₃ sludge, which reduces the degradation efficiency and causes secondary pollution, as shown in Eqs. (1)–(2). Therefore, various effective approaches were proposed by employing zero valent iron (Fe⁰) to replace Fe²⁺ catalyst for activating H₂O₂ [4–9] due to the tremendous redox potential of Fe⁰ [6,10]. Lu et al. [11] hydrothermally fabricated Fe-Fe₂O₃ core-shell nanowires, which could degrade more efficiently rhodamine B than Fe^{II} in an electro-Fenton system. Li et al. [12] fabricated Fe@C particles which presented high catalytic activity and excellent stability in the degradation of 4-chlorophenol.



However, the nanoscale Fe⁰ in air or an aqueous environment always faces surface passivation and aggregation, where both appear as the main drawbacks for the catalytic degradation of organic pollutants [6,7,10].

In this work, a three-dimensional hierarchical dendritic Fe⁰ with micro-nano structure was prepared by the electrodeposition method. Meanwhile, Fenton-like catalytic activity of the dendritic Fe⁰ was also investigated and degradation mechanisms were discussed in detail. The prepared dendritic Fe⁰ presents a very promising potential for the practical application of removal of refractory organic pollutants.

2. Experimental

The dendritic micro-nano structure Fe⁰ was prepared by electrodeposition. The electrolyte was composed of 0.5 mol/L FeSO₄·7H₂O and 50 mL/L ethanol. The current density was 1.6 A/dm² and the electrodeposited time was 20 s. The electrodeposited product was collected and washed by deionized water and anhydrous ethanol for 3 times. At last, the product was dried in a vacuum at 333 K.

The phenol removal experiments were carried out at 303 K and the original phenol solution of 50 mL contained 35 mg/L phenol. The pH of the solution was adjusted by 0.01 mol/L H₂SO₄. The Fe⁰ sample was added into the solution and dispersed by ultrasound for 10 s. The reaction was initiated once a given amount of H₂O₂ were added in the phenol solution under vigorous mechanical stirring.

3. Results and discussion

3.1. Structure and composition of Fe⁰

The structure of the fresh dendritic Fe⁰ and that of the used Fe⁰ was characterized by TEM/HR-TEM images as shown in Fig. 1. It is indicated (Fig. 1a) that dendritic Fe⁰ possesses a typical three-level structure (primary structure in several micrometers, secondary structure in about 1 μm and tertiary structure in about 100 nm) and each dendrite is about 10 μm long and 3 μm wide. The HRTEM image (Fig. 1) shows that the spacing of crystal planes is 0.203 nm, corresponding to the (110) of α-Fe. Furthermore, the growth of dendrite Fe⁰ mainly followed the [110] crystal orientation during the deposition process. After the degradation test of phenol, the spent Fe⁰ basically maintains

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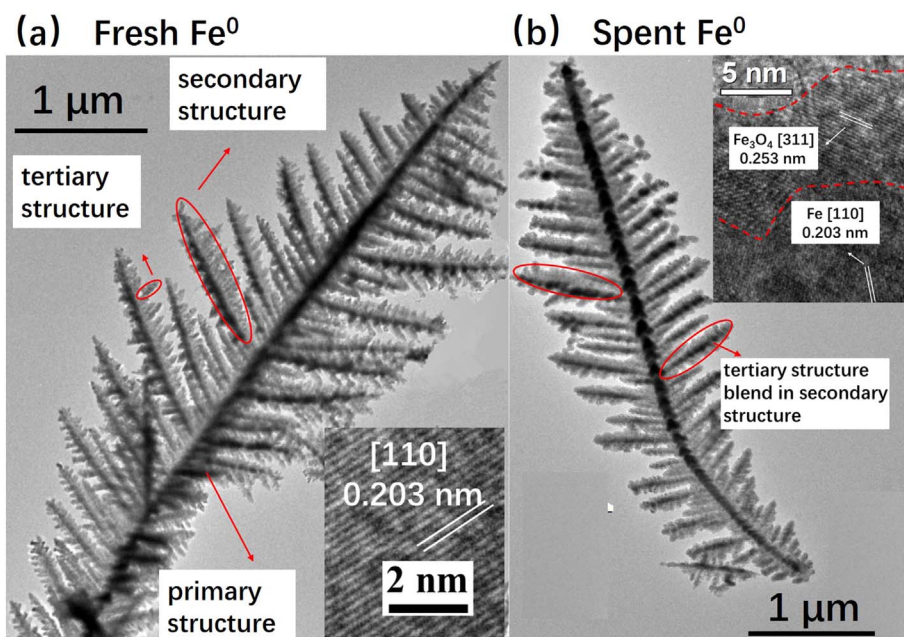


Fig. 1. TEM and HR-TEM images of the fresh Fe^0 catalyst (a) and the spent Fe^0 catalyst (b) after phenol degradation reaction.

the dendritic structure, but the tertiary structure becomes large and even blends in a secondary structure, leading to the decrease of specific surface area of Fe^0 . This could be confirmed by the BET analysis results shown in Fig. S1. The surface area (S_{BET}) of the fresh Fe^0 ($41 \text{ m}^2/\text{g}$) was larger than that of the spent Fe^0 ($32 \text{ m}^2/\text{g}$). However, it is important to note that both of them were higher than those of other Fe^0 reported in the literature as reported in Table S1 [13–16]. In addition, the HR-TEM morphology (Fig. 1) exhibited another striation interval with 0.253 nm , corresponding to the (311) crystal plane of Fe_3O_4 , which suggests that Fe_3O_4 is formed on the surface of Fe^0 sample during the degradation process. The formation of Fe_3O_4 was the main reason of the decrease of specific surface area.

XRD and XPS analyses were employed to analyse the composition of dendritic Fe^0 sample before and after the degradation test and results are shown in Figs. 2 and 3. The fresh Fe^0 (Fig. 2) is composed of $\alpha\text{-Fe}$ (JCPDS 89–7194) with three X-ray diffraction peaks corresponding to the planes of (110), (200) and (211). As for the spent Fe^0 sample after the degradation test, another small weak diffraction peak was detected, corresponding to the (311) plane of Fe_3O_4 , result that is consistent with the HR-TEM analysis. Therefore, both HR-TEM and XRD indicated that

a small amount of Fe_3O_4 was formed during the Fenton-like reaction.

Based on the XPS spectra shown in Fig. 3, the Fe 2p spectra of fresh Fe^0 presents two strong peaks (711.1 eV and 724.8 eV) corresponding to Fe_3O_4 and two tiny peaks (706.8 eV and 720.6 eV) corresponding to Fe^0 . These results indicate that the fresh Fe^0 surface was oxidized slightly in the air atmosphere. The O 1s spectra of fresh Fe^0 exhibits two peaks at 531.5 eV and 530.0 eV , which are ascribed to H–O and Fe–O [19]. In addition, there is a peak of 284.6 eV observed in C 1s spectra derived from sample's contamination. As for the XPS spectra of spent Fe^0 , Fe 2p spectra presents two main peaks at 711.5 and 724.9 eV [17,18] which could be assigned to Fe_3O_4 and no peak corresponding to Fe^0 was detected, which further illustrates that a dense Fe_3O_4 layer was formed on the surface of Fe^0 sample. Furthermore, Fig. 1b shows that the crystallized Fe_3O_4 layer is about 10 nm thick, which was enough to influence the detection of inner Fe during XPS analysis. O1s spectra of the spent Fe^0 could be fitted into three peaks located at 530.0 , 531.5 and 533.1 eV , which are attributed to Fe–O [19], H–O and C–O [20], respectively. Furthermore, the C 1s spectra of the spent Fe^0 displayed carbon atoms existed in different chemical states: sp^2C , sp^3C , C–H, C–O, C=O and COOH on the surface of Fe^0 catalyst after Fenton-like reaction, which might be related to the degradation products of phenol. It was reported [21–24] that the existence of sp^3C could prove that the phenyl rings are broken, and those of C=O and COOH groups correspond to the typical degradation products, such as benzoquinone, maleic acid, oxalic acid and acetic acid due to the oxidation of phenol. The latter gave rise to the decrease of pH value of the Fenton-like system from the initial value of 4.0 to 3.6 after degradation reaction.

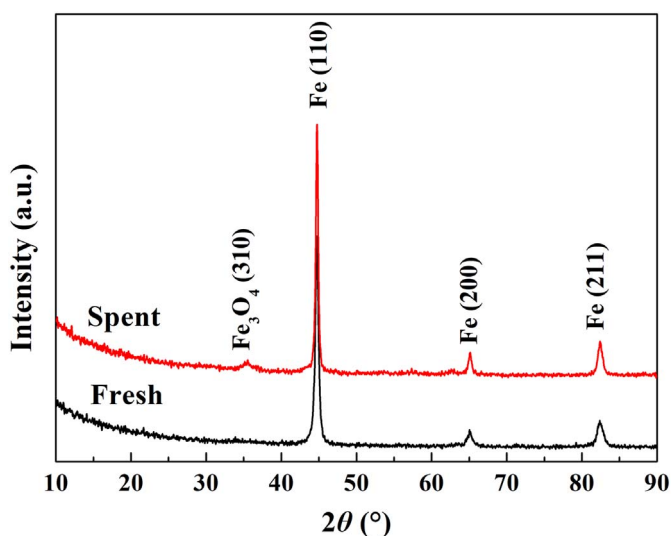


Fig. 2. Powder XRD patterns of the fresh and spent Fe^0 catalyst.

3.2. The removal rates of phenol in Fenton-like dendritic $\text{Fe}^0 / \text{H}_2\text{O}_2$ system

Fig. 4 shows the effects of pH, H_2O_2 dosage, Fe^0 content and cycle number on the removal efficiency of phenol in the Fenton-like system. The relevant leached Fe concentration results are presented in Fig. S2. The solution pH plays a significant role in the degradation reaction. When the pH is 4.5 or 5.0, there is not an obvious phenol removal and under $\text{pH} = 4.0$, over 90% of phenol is removed in 15 min. As the pH value decreased to lower than 3.5, the degradation rate is improved greatly, and within 2 min more than 90% of phenol is removed. Based on Fig. S2, it could be inferred that leached Fe concentration is mainly controlled by the pH of the system and not by the H_2O_2 dosage or catalyst content. Clearly, the decrease of pH value was beneficial to the

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