

Fe-MOF Derived Ferrous Hierarchically Porous Carbon Used as EF Cathode for PFOA Degradation

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Abstract

Pentadecafluorooctanoic acid (PFOA) is environmentally persistent, bioaccumulative, globally distributed and dangerous to human beings. Thus, the degradation of PFOA with effective method remains further exploration. Here, an Electro-Fenton (EF) system was studied for efficient PFOA degradation, and where a new composite material ferrous hierarchically porous carbon (FHPC) prepared by high temperature activation of MIL-100 (Fe) was applied as the cathode, and 81.4% PFOA (Initial 50 mg/L) elimination was achieved at a low potential of -0.4 V (pH = 7, 3 h). With the increasing of the activated temperature, the catalytic ability of the materials is decreasing because the reduced surface area reduced and the iron nanoparticles size enlarged. Moreover, the H_2O_2 and the $\bullet OH$ were also detected to confirm the dominating contribution of Electro-Fenton mechanism in the PFOA degradation. Thus, this material could be used in efficient heterogeneous EF technology for PFOA elimination.

Keywords

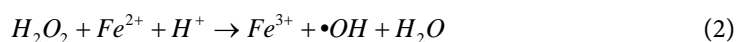
PFOA, Ferrous Hierarchically Porous Carbon, Electro-Fenton, Degradation

1. Introduction

Recently, PFOA received extensive concern because of its persistence, bioaccumulation, wide use and potential toxicity, such as endocrine disrupting effects, neurotoxicity, and developmental toxicity [1] [2]. However, it is resistant to traditional advanced oxidation technologies by reason of the stable bond of C-F (154 kcal/mol) [3]. Thus, an efficient degradation technique is urgently needed.

The Electro-Fenton (EF) system is a potential method for the PFOA degrada-

tion result from its numerous advantages. Firstly, the rapidly generated hydroxyl radical ($\bullet\text{OH}$), one of the most powerful oxidants ($E^\circ = 1.9 - 2.7 \text{ V}$) can rapidly degrade the electron-rich organic compounds. Secondly, the in situ production of H_2O_2 can avoid the risks associated with handling, transport and storage of H_2O_2 . Simultaneously, Fe^{2+} can be electro reduced at the cathode. The general mechanism of EF can be described as follows:



The heterogeneous catalysis can not only promote the electro production of H_2O_2 from O_2 , but also decompose the H_2O_2 in situ by the fixed iron particles. Nevertheless, the majority of heterogeneous catalysis has a lot of problems like dissolution, agglomeration and shedding [4] [5], so a new heterogeneous catalysis with the properties of high-efficiency, stability and easy fabrication is explored.

2. Materials and Methods

2.1. Preparation of FHPC Electrode

MIL-100(Fe) was prepared according to the previous reported by Liu Z M et al. [6]. Fe^0 , 1,3,5-BTC (Trimesic Acid), HF, HNO_3 and H_2O was mixed with a molar ratio of 1.0:0.67:2.0:0.6:277, then the mixture was transferred into a Teflon-lined stainless steel bomb and reacted at 160°C for 12 h. The synthesized MIL-100(Fe) crystals were activated at different temperature (600°C , 700°C , 800°C) under Ar for 1 hour, to get the ferrous hierarchically porous carbon (FHPC-600, FHPC-700, FHPC-800,). To prepare electrodes, 20 mg FHPC was dispersed in 4.95 mL water and 50 μL 5 wt% Nafion solution, then the suspensions were spin-coated onto carbon paper (HCP330N) with a catalyst loading of $1.4 \text{ mg}/\text{cm}^2$.

2.2. Electrochemical Experiments

The EF degradation of PFOA (50 mg/L) was performed in a single-compartment cell with a batch mode. The FHPC (working area of 10.0 cm^2) and Pt plate ($1 \text{ cm} \times 2 \text{ cm}$) were used as the cathode and anode, respectively. 0.05 M Na_2SO_4 were added as electrolyte. High-purity oxygen was fed into the cell at 0.45 L/min. The solution pH was 7. A constant potential of -0.4 V was applied on the cathode during the EF degradation of PFOA. As contrast, PFOA removal by electrosorption (ES) and electrocatalysis (EC) was conducted under N_2 atmosphere (to inhibit H_2O_2 production). Before PFOA degradation, the generation of H_2O_2 and $\bullet\text{OH}$ were detected in the same system without PFOA.

2.3. Analytical Methods

The H_2O_2 concentration was measured by flow-injection chemiluminescence method [7]. Luminol was diluted to 650 μM by 0.1 M Na_2CO_3 solution (left to sit

for 24 h), adjusting the pH to 10.15 by HCl and spiking with Co^{2+} to 0.06 mM. The prepared luminol solution and the diluted sample were proportionally injected into chemiluminescence system (MIP-B) to get the chemiluminescent signal.

The generated $\bullet\text{OH}$ was detected by EPR with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent at room temperature. Added 200 ppm DMPO, the solution was sampled by a 50 μL capillary tube. After analysis, the signal of DMPO-OH was recorded.

The concentration of PFOA in the E-Fenton degradation process was analyzed by liquid chromatography-Triple Quadrupole mass spectrometer (Agilent 1100-6410) equipped with a C18 column (2.1 mm \times 100 mm \times 3.5 μm), and the mobile phase was acetonitrile and 10 mM ammonium acetate with a flow rate of 0.25 mL/min. The gas temperature of the mass spectrometer is 300, while the capillary voltage is 4 kV.

3. Result and Discussion

The morphologies of the FHPC were investigated by SEM. **Figures 1(A)-(C)** shows that the crystal shape of the activated materials are octahedral, the same with the MIL-100 (Fe) precursor. Implying the retained framework with a hierarchically porous structure, and the HRSEM images **Figures 1(a)-(c)** reveal iron nanoparticles emerged in the porous carbon matrix, and the nanoparticle size of the FHPC enlarges with the increasing of the activated temperature.

XRD was applied to distinguish the iron specie in the FHPC. As **Figure 2** shown, the XRD spectrums of FHPC activated in different temperature have characteristic peaks centered at 44.6, 65.0 and 82.3 degrees, respectively, which are corresponding to zero-valent iron. However, from the Raman spectroscopy (**Figure 2**), we found the existence of $\alpha\text{-Fe}_2\text{O}_3$ in the FHPC by the characteristic peaks located in 225, 498, 247, 293, 299, 412 and 613 cm^{-1} , confirming the coexistence of Fe^0 and $\alpha\text{-Fe}_2\text{O}_3$, and with the increasing temperature, the signal of $\alpha\text{-Fe}_2\text{O}_3$ enhances while the signal of C recedes, which reflects the increased Fe/C ratio resulting from the decomposition of the organic chain. Moreover, the two

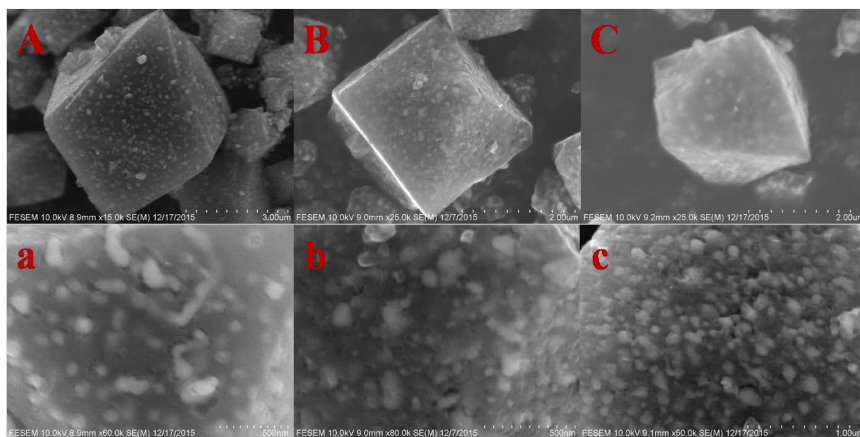


Figure 1. SEM of the FHPC-600 (A), FHPC-700 (B) and FHPC-800 (C). HRSEM of the FHPC-600 (a); FHPC-700 (b) and FHPC-800 (c).

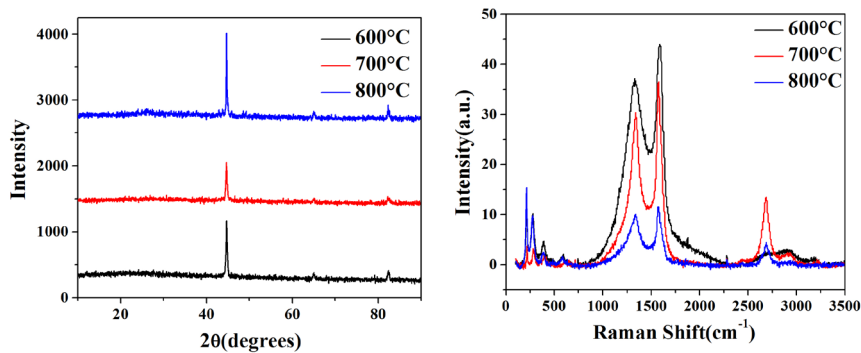


Figure 2. XRD and Raman of the FHPC-600, FHPC-700 and FHPC-800.

peaks located at 1340 cm^{-1} (D band) and 1570 cm^{-1} (G band) associated with disordered-induced and graphitic carbon. Abundant disordered-induced has been reported as active site for promoting H_2O_2 generation from O_2 reduction in the FHPC [8].

Surface area and porosity are two important characteristics of the catalysis, thus the nitrogen adsorption–desorption isotherms were applied. As **Table 1** shown, when the activation temperature increases, the specific surface area and porosity decreases, because of the enlarged iron nanoparticles fill the porous space.

Application of the FHPC in E-Fenton Catalysis to Degrade PFOA

Figure 3 shows that the PFOA removal rate of the FHPC-600 is 81.4% at 3 h ($\text{pH} = 7$, $V = -0.4\text{ V}$), by contrast, the FHPC-700 and the FHPC-800 is 69.4% and 45.3% at the same reaction time, respectively, and the kinetic constant (**Figure 3**) for PFOA degradation of FHPC-600 is 0.54 h^{-1} , which decreases to 0.39 h^{-1} of FHPC-700 and 0.18 h^{-1} of FHPC-800. These results indicate that the higher surface area and smaller iron nanoparticles size can efficiently enhance the catalytic ability, and the FHPC-600 was used in the following experiments.

Considering the porosity of the FHPC and the anodic oxidation of Pt, the electrosorption (ES) caused by the cathode and electrocatalysis (EC) caused by the anodic efficiency were tested. The removal efficiency is about 28.3% in total for ES and EC (**Figure 4**), and the corresponding kinetic constant is 0.18 h^{-1} (**Figure 4**), implying the dominant position of the EF oxidation in phenol degradation.

It is well-known that the concentration of H_2O_2 produced is a key parameter for evaluating the performance of Electro-Fenton, however, with the present of ferrous species which can quickly decompose H_2O_2 , it is difficult to quantify the real yield of H_2O_2 , thus the accumulative concentrations of electrogenerated H_2O_2 were measured. As **Figure 5** shown, after approximately 60 min reaction, the accumulated H_2O_2 did not increase and reached a steady state (7.09 mmol/L). In this steady state, H_2O_2 was generated and consumed at the same rate.

The generation of $\bullet\text{OH}$ in the EF system can also reflect the efficiency of Elec-

tro-Fenton. As the EPR spectra shown (**Figure 5**), the 4-fold peak with a ratio of 1:2:2:1 is the characteristic peak of $\bullet\text{OH}$, and the 4-fold characteristic peak ap-

Table 1. Surface area and pore volume of the FHPC activated in different temperatures.

	Activated Temperature		
	600°C	700°C	800°C
Surface Area (m^2/g)	255.8	206.0	158.4
Pore Volume (cm^3/g)	0.408	0.337	0.265

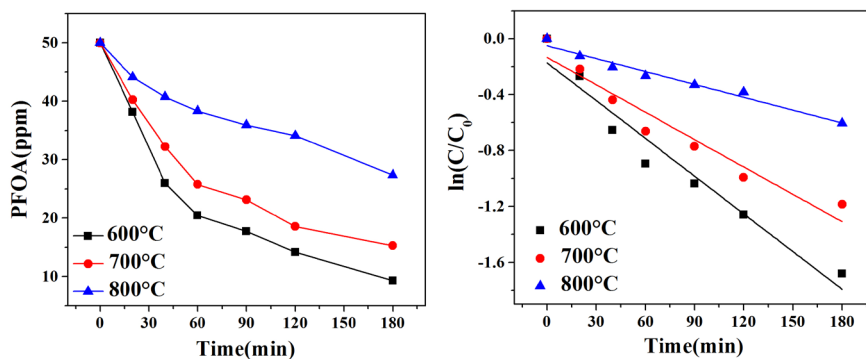


Figure 3. PFOA concentration and plots of $\ln(C/C_0)$ as a function of time during PFOA removal by FHPC-600, FHPC-700 and FHPC-800 (-0.4 V and pH 7).

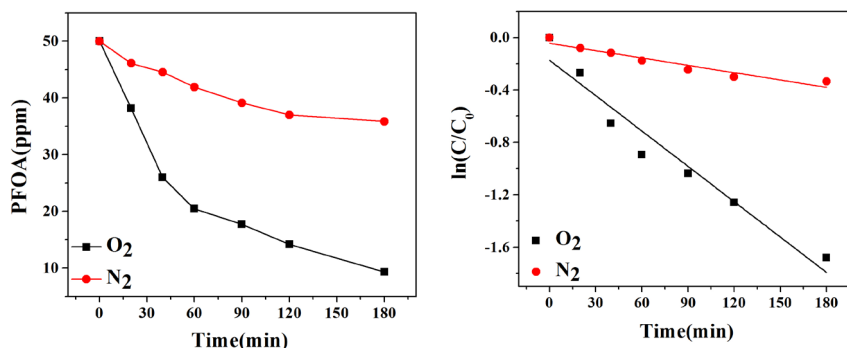


Figure 4. PFOA concentration plots of $\ln(C/C_0)$ as a function of time during PFOA removal by Electro-Fenton (-0.4 V, pH 7), electrocatalysis and electrosorption. Electrocatalysis and electrosorption was conducted under N_2 .

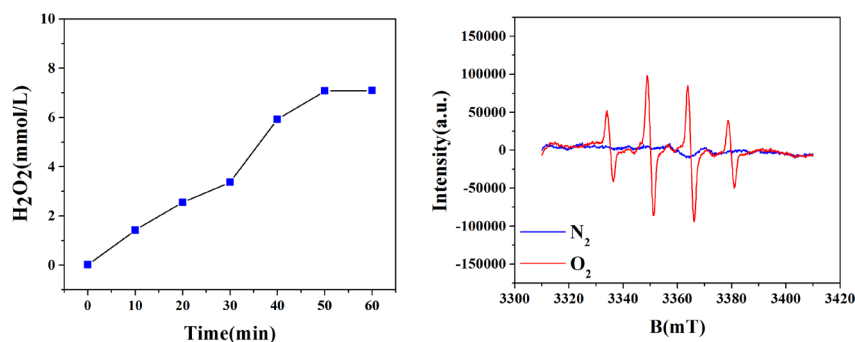


Figure 5. H_2O_2 concentration as a function of time produced by FHPC-600 without PFOA (-0.4 V, pH 7), and $\bullet\text{OH}$ signal of the solution in different atmosphere.

peared when the system fed with oxygen, but did not appear under N₂ atmosphere. These results indicate the reaction mechanism is Electro-Fenton.

Acknowledgements

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