



# Carbothermal preparation of porous carbon-encapsulated iron composite for the removal of trace hexavalent chromium



Linzhou Zhuang<sup>a</sup>, Qihan Li<sup>a</sup>, Jiasheng Chen<sup>a</sup>, Beibei Ma<sup>a</sup>, Shuixia Chen<sup>a,b,\*</sup>

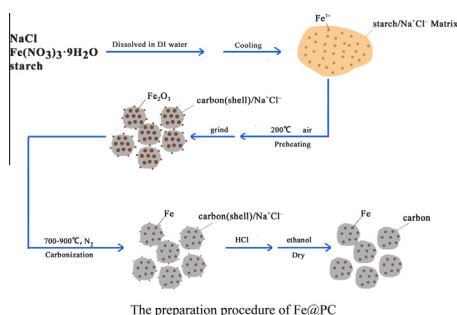
<sup>a</sup>PCFM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China

<sup>b</sup>Materials Science Institute, Sun Yat-Sen University, Guangzhou 510275, PR China

## HIGHLIGHTS

- A carbothermal preparation method of porous carbon-encapsulated iron (Fe@PC) was established.
- Fe@PC with strong magnetism and good regeneration ability showed high Cr(VI) removal efficiency.
- Effect of pore structure and surface chemistry of Fe@PC on its Cr(VI) removal ability was studied.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Porous carbon-encapsulated iron (Fe@PC) composite was prepared through carbothermal reduction of  $\text{Fe}(\text{NO}_3)_3$  and starch. The porous carbon could envelop iron and protect it from being oxidized, while iron endow the composite with ferromagnetism, so that Fe@PC can be easily recovered by an external magnetic field. The prepared material was used to remove trace Cr(VI) in polluted water. The Cr(VI) removal process of Fe@PC, which highly depended on both microporous structure and reducing groups, was significantly affected by the preparation conditions and solution *pH*. At 25 °C, Fe@PC-750 could remove 99.5% Cr(VI) from simulated wastewater containing  $5.00 \text{ mg L}^{-1}$  Cr(VI) with an initial *pH* of 7, and the residual concentration of Cr(VI) was as low as  $0.02 \text{ mg L}^{-1}$ . The XPS analysis results confirmed that Cr(VI) could be reduced to Cr(III) after being adsorbed, and the elevation of *pH* would enhance the reduction ability of Fe@PC. The Fe@PC composite with high Cr(VI) removal efficiency, strong magnetic property and desirable regeneration ability can be practically applied in the removal of trace heavy metal pollutants from wastewater.

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## 1. Introduction

Hexavalent chromium (Cr(VI)), which is widely used in electroplating, leather tanning, metal finishing and many other chemical industries, is a commonly identified contaminant in soils and

\* Corresponding author at: Materials Science Institute, Sun Yat-Sen University, Guangzhou 510275, PR China.

E-mail address: [cescsx@mail.sysu.edu.cn](mailto:cescsx@mail.sysu.edu.cn) (S. Chen).

ground water [1,2]. Owing to its carcinogenicity, toxicity and mobility, Cr(VI) has caused many serious environmental problems, therefore it should be removed from wastewater before discharge [3–5]. The tolerance limit for total Cr is  $0.1 \text{ mg L}^{-1}$ , recommended by the United States Environmental Protection Agency [6].

To date, a variety of technologies have been employed in the Cr(VI) removal from wastewater, including electro-deposition [7], membrane filtration [8], ion exchange [9] and chemical precipitation [10]. Although these methods are efficient for Cr(VI) removal,

many of them are not widely applied due to their disadvantages, including incomplete metal removal and high cost. Adsorption is one efficient alternative technique for treating wastewater laden with heavy metals [11], for which selecting a practical and affordable adsorbent is the critical step. Because of their abundant micropores and huge specific surface areas, activated carbon (AC) and activated carbon fiber (ACF) present high adsorption capacities [12], and thus they have been widely applied in the complete removal of organic pollutants from the air and water. Moreover, as the reducing groups on the surface of AC and ACF can effectively reduce Pt(IV), As(V), Fe(III) to lower valence ions and Pd(II), Ag(I), Au(III) ions to metallic elements, they are also used in the recovery of noble metals and removal of heavy metals from wastewater [13–16]. Though AC and ACF show good adsorption performance for organic pollutants, they can hardly reduce the concentration of metal ions to ppb level when used in the removal of metallic pollutants such as Cr(VI) [17–19].

In this study, porous carbon-encapsulated iron (Fe@PC) composite was fabricated through a facile carbothermal reduction method. The economic and water-soluble starch was chosen as the carbon precursor. The prepared material was subjected to Cr(VI) removal test, and to clarify this removal process, the influencing factors, including carbonization temperature, carbonization time and solution pH, were comprehensively studied. Based on the results, a Cr(VI) removal mechanism was further proposed. Due to its low cost, complete removal ability and easy recovery, Fe@PC can be considered as a desirable adsorbent for efficient removal of heavy metal ions from the wastewater.

## 2. Materials and methods

### 2.1. Material preparation

15.0 g soluble starch (AR), 2.0 g sodium chloride (AR, NaCl) and 5.0 g ferric nitrate nonahydrate (AR,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) were firstly dissolved in 60 mL deionized water. Next, the formed yellow gel was dried and preheated at 200 °C for 8 h, the resulted pre-oxidized carbonaceous material was denoted as Fe@PC-200. It was then heated at a rate of 5 °C  $\text{min}^{-1}$  to a preset temperature (700–900 °C) in a  $\text{N}_2$  atmosphere and kept a certain period of time for carbonization and activation. After being cooled in flowing  $\text{N}_2$ , the sample was washed with diluted hydrochloric acid to thoroughly remove the external Fe and iron oxide. The obtained product, porous carbon-encapsulated iron particle, was denoted as Fe@PC-X (X is in the range of 700–900 °C,  $d_p < 106 \mu\text{m}$ ). All reagents were purchased from Guangzhou Chemical Reagent Factory, Guangzhou, China, and used without further purification.  $\text{CO}_2$  and  $\text{N}_2$  were obtained from Guangzhou Gas Company, Guangzhou, China.

### 2.2. Characterization

Powder X-ray diffraction (XRD, D8 ADVANCE, BRUKER Textile Technologies GmbH & Co., KG, Germany) was employed to analyze the chemical composition of Fe@PC. Each profile was collected in the  $2\theta$  angle between 10° and 80°, at a step width of 0.12° and by counting 10 s at each step.

Scanning electron microscope (SEM, S4800, Hitachi, Japan) was used to observe the morphology and microstructure of Fe@PC, and the energy dispersive spectrum (EDS) mapping was applied to investigate its detailed elemental distribution.

Nitrogen adsorption–desorption measurements were performed at 77.35 K with an automatic gas adsorption instrument (ASAP2020, Micromeritics Corp., USA) at the range of relative pressure from  $10^{-6}$  to 1.

Magnetic Property Measurement System (MPMS XL-7, QUANTUM DESIGN, USA) was applied to the investigation of magnetic properties of the particles.

X-ray photoelectron spectroscopy (XPS, ESCALab 250, USA) was employed to assess the chemical state and surface composition of the materials.

The concentration of Cr(VI) was determined with a flame atomic absorption spectrometer (AAS, Z-2000, Hitachi, Japan).

### 2.3. General procedure of Cr(VI) removal by Fe@PC

#### 2.3.1. Static adsorption

A batch test was used for measuring the Cr(VI) removal efficiency of prepared Fe@PC. 0.1 g Fe@PC was dispersed into 50 mL  $\text{K}_2\text{Cr}_2\text{O}_7$  solution with certain Cr(VI) concentrations, and then shaken in a rotary shaker with a speed of 140 rounds per minute for 90 min. The Cr(VI) concentration in the residual solution was determined with AAS.

#### 2.3.2. Dynamic adsorption

0.4 g adsorbents was added into 200 mL Cr(VI) solution of 5.0  $\text{mg L}^{-1}$  and shaken at a speed of 140 rounds per minute. A certain amount of solution was taken from the adsorption system at defined time intervals for the analysis of Cr(VI) residual concentration.

#### 2.3.3. Continuous adsorption in a fixed bed

In the continuous adsorption test, 1.0 g Fe@PC was packed into a glass column with a diameter of 1 cm and a bed depth of around 4 cm, and Cr(VI) solution of 5.0  $\text{mg L}^{-1}$  was allowed to flow through the fixed-bed using a peristaltic pump, with a constant flow rate of 2.5  $\text{mL min}^{-1}$ . A certain amount of effluent was collected at regular intervals for the analysis of Cr(VI) residual concentration.

## 3. Results and discussion

### 3.1. Preparation and characterization of Fe@PC

In the preparation procedure of Fe@PC,  $\text{Fe}(\text{NO}_3)_3$  is applied as the iron source, and starch as the carbon source, while NaCl serves as a solid spacer to prevent the particles from agglomeration. After carbothermal reduction, the iron oxide was reduced to elementary iron and covered with a carbonaceous layer. Fe@PC-750 had an irregular and porous surface (Fig. 1a), whose specific surface area reached up to 378.71  $\text{m}^2 \text{g}^{-1}$  (with a micropore surface area of 232.72  $\text{m}^2 \text{g}^{-1}$  determined by *t*-plot method and a mesopore surface area of 153.41  $\text{m}^2 \text{g}^{-1}$  determined by *BJH* method) and pore volume to 0.17  $\text{cm}^3 \text{g}^{-1}$ . EDS mapping was further applied to investigate the elemental distribution throughout the Fe@PC-750 particles. The images corresponding to the C K-edge signals and Fe K-edge signals are shown in Fig. 1(b and c), respectively. As the external Fe species had been completely removed by the HCl solution, the remained Fe was believed to highly distribute in the internal of the bulk particles, instead of being attached to the extra carbon shell, and not accessible from the outside. It also confirmed that the carbon layer could protect Fe particles from harsh conditions.

The crystalline structures of Fe@PC-200 and Fe@PC-750 were both characterized by XRD. The strong peak at  $2\theta = 25^\circ$  was associated with the C(200) plane, while the weak one at  $2\theta = 44^\circ$  with the C(101) plane [20]. Aside from these two peaks, the diffraction pattern of Fe@PC-200 also showed peaks at  $2\theta = 30.2, 35.7, 43.0, 53.7, 57.2,$  and  $62.5^\circ$ , which could be indexed to 220, 311, 400, 422, 511 and 440 Bragg reflections of  $\text{Fe}_3\text{O}_4$  [21]. When the carbonization temperature was raised to 750 °C, these peaks ascribed to  $\text{Fe}_3\text{O}_4$  disappeared, and instead a strong peak that ascribed to the

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