Materials Letters 159 (2015) 64–67

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Porous hematite microflowers toward the adsorption of organic pollutants from water

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ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form
11 June 2015
Accepted 22 June 2015
Available online 24 June 2015

Keywords:
Microstructure
Porous materials
Hematite
Wastewater treatment

ABSTRACT

Porous flower-like hematite microstructures assembled with porous nanosheets were prepared by thermal decomposition of a precursor which was obtained using $FeCl_3 \cdot 6H_2O$, urea, and polyvinylpyrrolidone (PVP) in the solvent of ethylene glycol (EG) via a simple solution method. Because of the high specific surface area and porous structure, such α-Fe_2O_3 microflowers showed excellent adsorption performances for the Congo red in wastewater treatment with a maximum removal capacity of 628.9 mg/g. The adsorption rate and adsorption isotherm were also investigated, and were well represented by the Langmuir model. These hematite flowers may hold great potential as environmentally friendly dye adsorbent candidate in decontamination of water.

1. Introduction

In the past decades, organic dyes have been widely used in textile, dyeing, paint, paper and pulp, and so on. Synthetic origin and complex molecular structures make these organic dyes more stable and difficult to be degraded, and therefore living organisms have received increasing threatens [1]. The adsorption process has been developed for the dye removal in the wastewater treatment. Several types of materials including activated carbon, fly ash, and nature clays were suitable for the removal of organic pollutants [2,3]. Transition metal oxides were also used for environmental protection in recent years due to their rich valence states, vast surface areas, and variable electronic structures [4–6]. Among them, the n-type semiconductor of α-Fe_2O_3 with band gap of 2.1 eV, is the most stable iron oxide under ambient conditions and is widely used in catalysts, pigments, and water treatment as well [7–10].

Up to now, iron oxide nanostructures including nanoparticles, cubes, wires, and tubes have been extensively investigated for use in wastewater treatment. However, its practical application is greatly hindered because of slow charge transfer, a short hole diffusion length and a high probability of electron–hole recombination [11]. Some work demonstrated that hollow structures could effectively alleviate the above mentioned drawbacks since they often exhibited a high light harvesting efficiency and a fast motion of charge carriers [12]. In addition to the hollow structures, porous structures have also been considered as a promising candidate for dye removal and photocatalysis. For example, Li et al. reported the template-free fabrication of 3D iron oxide hierarchical nanostructures through a self-assembly process using a galvanic-cell reaction at room temperature, and these Fe_2O_3 nanomaterials could selectively remove neutral dyes from wastewater with much higher capacities than those of conventional Fe_2O_3 nanoparticles [13]. Zhu et al. prepared hierarchical flowerlike α-Fe_2O_3 hollow spheres, which had a high removal capacity for Congo red (195 mg/g) [14]. Li et al. prepared flower-like Fe_3O_4 microspheres through ultrasound-assisted hydrothermal method, and the sample had a removal capacity of 40 mg/g to Congo red [15]. In order to realize the practical application of such adsorbent, the difficulty is to prepare samples with the same shape and uniform size, and sometimes requires accurate control of experimental parameters. Hence, it is necessary to develop a facile and feasible approach for the fabrication of porous structures.

Previously we reported that novel flowerlike hematite microstructures composed of many porous nanosheets were synthesized by a PVP-assisted process [16]. Herein, we applied these hematite flowers in wastewater treatment, and adsorption experiments indicated that the Fe_2O_3 flowers exhibited outstanding performance with 628.9 mg/g of adsorption capacity toward Congo red. The adsorption rate and adsorption isotherm are also investigated.

2. Experimental section

The preparation of the flowerlike α-Fe_2O_3 microstructures assembled with porous nanosheets is the same as that we reported

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http://dx.doi.org/10.1016/j.matlet.2015.06.081
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previously [16]. typically, 1.2 g of $FeCl_3 \cdot 6H_2O$, 2.7 g of urea, and 2.5 g of PVP were dissolved in 100 mL of EG, and then the mixture was transferred into a three-necked flask and heated at 197 °C for 6 h. Finally, the green precursor was collected, rinsed with ethanol for several times, and dried at 60 °C. The as-synthesized precursor was placed into a furnace and heated in oxygen atmosphere to 450 °C, and maintained for 3 h to obtain α-Fe_2O_3.

To estimate the adsorption capacity of the α-Fe_2O_3 flowers, the initial concentrations of Congo red were varied in the range of 400–1000 mg/L, and the dosage of α-Fe_2O_3 flowers was kept at 0.3 g/L. The adsorption rate of α-Fe_2O_3 flowers was obtained by monitoring the concentration of Congo red at various intervals when the initial Congo red concentration was 40 mg/L. The UV–vis adsorption spectra were recorded in the wavelength range of 300–600 nm.

XRD pattern was recorded on a Bruker D8 focus diffractometer with Cu Ka radiation. The morphologies were observed with a FEI Nova Nano 630 scanning electron microscope. Fourier-transforming infrared absorption spectrum was performed with a Nicolet IS50 FTIR spectrometer in the range of 4000–400 cm^{-1} at room temperature. The UV–vis absorption spectra were recorded on a 4802 UV–vis double beam spectrophotometer. The specific surface area was calculated by the Brunauer–Emmer–Teller (BET) method.

3. Results and discussion

Fig. 1a shows the SEM images of α-Fe_2O_3 microstructures, in which a large amount of perfect flowers with size of 2–3 μm could be observed. The flowers were assembled by many nanosheets radiating from the core. The magnified view (Fig. 1b) showed that the sheet possessed many pores, suggesting the porous structures. The phase purity was investigated by XRD technique, and the result was shown in Fig. 1c. All the diffraction peaks could be indexed as α-Fe_2O_3 (JCPDS 33-0664). No other impurities including hydroxide, maghemite, and magnetite were detected, suggesting that the obtained α-Fe_2O_3 was rather pure. The specific surface area of the sample was investigated by N_2 adsorption–desorption measurement at 77 K, which revealed a typical type-IV sorption isotherm with a distinct hysteresis loop (Fig. 1d). It suggests the presence of mesopores, which is consistent with the SEM observation. The pore size (the curve not shown here) is mainly in the range of 5–11 nm. As a result, a relatively high BET surface area of 73.9 m^2/g is obtained. Such self-organized porous structures with a high specific surface area should be interesting as adsorption material for organic pollutant removal in wastewater treatment.

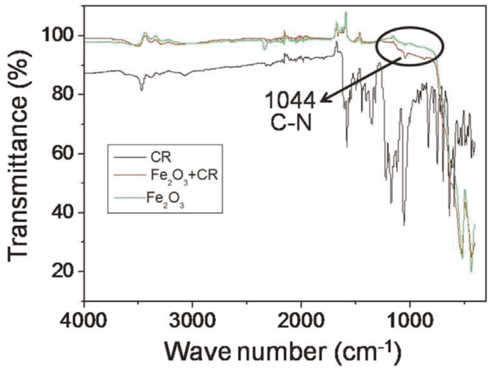

Fig. 2. The FTIR spectra of Fe_2O_3 flowers, Fe_2O_3 flowers attached with Congo red (CR), and pure CR, respectively.

These α-Fe_2O_3 flowers were applied to water treatment, and its adsorption capacity for Congo red was investigated. In order to further confirm whether the Congo red was attached to the surface of α-Fe_2O_3, FTIR spectrum was used to explore the change of the samples before and after dye adsorption. Fig. 2 shows the FTIR spectra of Fe_2O_3 flowers, Fe_2O_3 flowers attached with Congo red (CR), and pure CR, respectively. The green and red curves were belonged to those of before and after adsorption, in which we

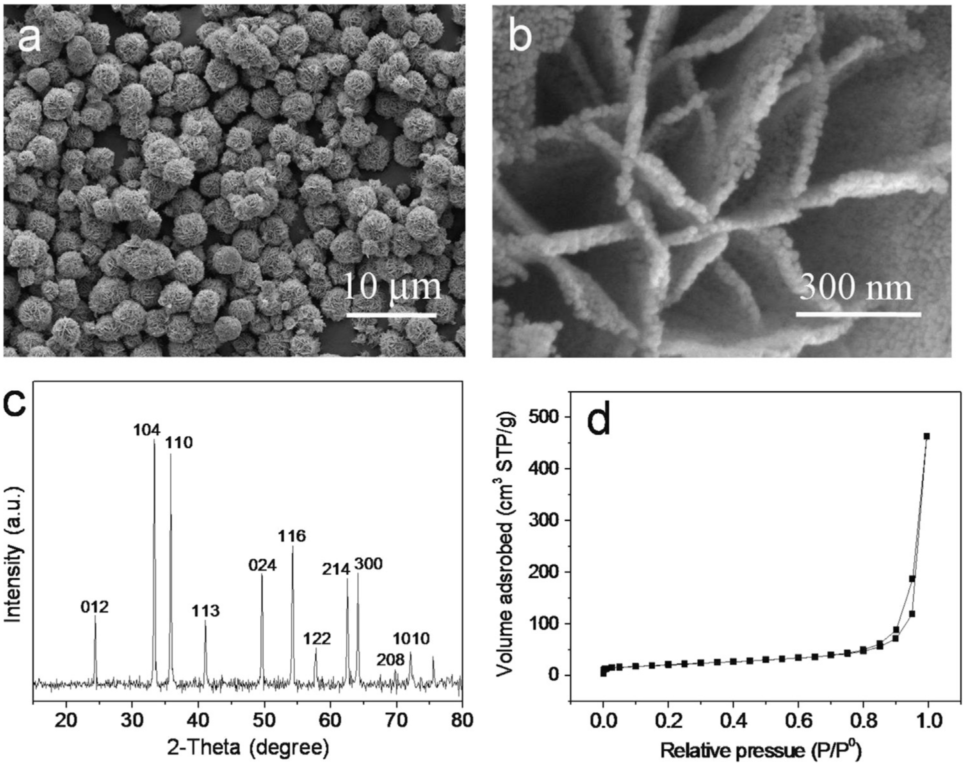

Fig. 1. (a and b) SEM images, (c) XRD pattern, and (d) N_2 adsorption–desorption isotherm plot of α-Fe_2O_3 microflowers.