Journal of Alloys and Compounds 678 (2016) 179–184

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Efficient removal of Cr(VI) by magnetically separable $CoFe_2O_4$/activated carbon composite

Wenmei Qiu, Dan Yang, Jingcai Xu*, Bo Hong, Hongxiao Jin, Dingfeng Jin, Xiaoling Peng, Jing Li, Hongliang Ge, Xinqing Wang**

College of Materials Science and Engineering, Zhejiang Province Key Laboratory of Magnetism, China Jiliang University, Hangzhou, PR China

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
18 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Composite materials
Magnetic properties
Cr(VI) adsorption

ABSTRACT

Owing to the unique microporous structure and high specific surface area, activated carbon (AC) could act as a good carrier for functional materials. In this paper, $CoFe_2O_4$/AC composite was prepared by a facile hydrothermal method for the adsorption of Cr(VI) in wastewater. The results indicated that $CoFe_2O_4$ nanoparticles embedded in the AC pores decreased the carbon surface area. However, The Cr(VI) adsorption capacity of $CoFe_2O_4$/AC was more effective than the initial AC. The magnetic properties of $CoFe_2O_4$/AC indicated it could be separated and retrieved easily by an outer magnet after Cr(VI) adsorption. The effects of solution pH, temperature and initial Cr (VI) concentration on the Cr(VI) adsorption of AC and $CoFe_2O_4$/AC were investigated. The Cr(VI) adsorption was pH dependent and found to be maximum at pH = 2.0. It was effective Cr(VI) adsorption with increasing temperatures. The standard free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were evaluated. The kinetic parameters of Langmuir and Freundlich isothermal equation were analyzed, and the Freundlich kinetic model was feasible to describe the Cr(VI) adsorption process in $CoFe_2O_4$/AC composite. According to these results, it was efficient removal of Cr(VI) with $CoFe_2O_4$/AC composite and magnetically separable easily by an outer magnet after Cr(VI) adsorption.

1. Introduction

In recent years, heavy metals effluents have become a serious environmental problem attracting much more attention to develop and implement various methods for removing toxic heavy metals pollutants from water [1]. The chromium (Cr), a typical heavy metal, has been widely used in metal cleaning and plating baths, painting, tannery and fertilizer industries [2,3]. Cr in wastewaters mainly exists in two stable oxidation states, Cr(VI) and Cr (III). Cr(VI) is 300 times more toxic than Cr(III) due to that acute exposure to Cr(VI) could cause lung cancer, kidney disease, dermatitis, irritation to eyes and respiratory tracts, gastrointestinal disorders etc [4]. According to the US Environmental Protection Agency (USEPA), the maximum contaminant concentration for Cr(VI) in domestic water supplies is no more than 100 μg/L [5]. Therefore, it is urgent to develop effective methods for removal of Cr(VI). A lot of conventional treatment techniques such as membrane separation [6], electrocoagulation [7], sedimentation [8], precipitation [9], activated sludge [10] and adsorption/filtration [11,12] have been used to remove Cr(VI). Among all these methods, adsorption technique is the most widely used method due to its cost-effective and operational simplicity. As a versatile adsorbent material, activated carbon (AC) has been used in a wide range of applications [13–15]. In the effluent treatment field, AC has been proven to be a successful adsorbent for removal of organic and inorganic contaminants from wastewater. However, AC is difficult to separate, retrieve and regenerate when it is exhausted. Filtration, the traditional method for separating powdered AC, could cause blockage of filters and loss of AC. And these sorbents had been traditionally discarded with the process sludge, resulting in the secondary pollution [16,17]. To overcome the disadvantages of powdered AC for difficult separating, magnetically separable AC composite, an effective and low-cost adsorbent, has attracted a lot of attention recently. Manpreet et al. [18] reported synthesis of magnetic $MgFe_2O_4$ nanoparticles loaded on activated charcoal for effective removal of Cr (VI) by sol-gel method. Nguyen et al. [19] prepared magnetic Fe_2MO_4 (M:Fe, Mn)/AC by impregnating method for

---

* Corresponding author.
** Corresponding author.
E-mail addresses: xujingcai@cjlu.edu.cn (J. Xu), wxqnano@cjlu.edu.cn (X. Wang).

http://dx.doi.org/10.1016/j.jallcom.2016.03.304
0925-8388/© 2016 Elsevier B.V. All rights reserved.

catalytic activity in heterogeneous Fenton oxidation of methyl orange. Shao et al. [20] employed $MnFe_2O_4$/activated carbon magnetic composite by coprecipitation method for removal of the tetracycline. Feng et al. [21] synthesized $NiFe_2O_4$/AC nanocomposites by the hydrothermal method for degradations of the model pollutants of MB, rhodamine B, and malachite green. Wei et al. [22] studied the selective adsorption of Cr (VI) from the wastewater with $NiFe_2O_4$/AC by co-sedimentation method. Up to now, most work have used paramagnetic oxides which possess the suitable saturation magnetization (Ms) and very small coercive force (Hc) as the magnetic sources in the magnetic AC composite, and few magnetic sources were implanted into AC to maintain the adsorptive performance, which led to a weak magnetic response with Ms of several emu g^{-1}.

$CoFe_2O_4$ with the spinel structure exhibits excellent Ms, suitable Hc, chemical stability and regulated free metal and organic matter concentration in soil or water through adsorption reactions [23]. Therefore, combining the advantages of AC and $CoFe_2O_4$ nanoparticles would exhibit excellent adsorptive properties with highly effective recovery by the magnetic separation technique. What's more, $CoFe_2O_4$ with a suitable Hc, could act as a micro-magnet, which could absorb the micro magnetic pollutants in the solution [24]. It has been reported magnetic $CoFe_2O_4$/AC nanocomposites were synthesized by one-step refluxing route and $CoFe_2O_4$ nanoparticles with the diameter of 14–20 nm were deposited on the surface of AC [25], while the deposited $CoFe_2O_4$ nanoparticles were not immobilized and not suitable for the absorbent in wastewater. In this work, as few $CoFe_2O_4$ as possible with higher Ms were anchored into the micropores of AC to improve the adsorptive performance of magnetic $CoFe_2O_4$/AC composite. The as-prepared samples were characterized and discussed by x-ray diffraction (XRD), thermal gravity analysis (TGA), differential scanning calorimetry (DSC), surface area and porosity analyzer (ASAP) and vibrating sample magnetometer (VSM). Additionally, the effectiveness on Cr(VI) removal of $CoFe_2O_4$/AC composite was deduced and investigated.

2. Experimental

2.1. Materials

Commercial carya peels based activated carbon (100 meshes) was provided by Changnan Activated Carbon Co., LTD. (Zhejiang, China). All other chemicals, including cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], sodium hydroxide (NaOH), hydrochloric acid [HCl], potassium dichromate [$K_2Cr_2O_7$], and 1,5-diphenylcarbazide, purchased from Hangzhou Chemical Co., LTD. (Zhejiang, China) were analytic grade. All solutions were prepared with deionized water.

2.2. Preparation of $CoFe_2O_4$/AC magnetic composite

$CoFe_2O_4$/AC magnetic composite were prepared by a facile hydrothermal method, the detailed process was showed as the following [24]. First, a certain amount of AC were added into 100 mL deionized water, which dissolved $Co(NO_3)_2 \cdot 6H_2O$ (0.005 mol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.01 mol) at room temperature. The mole ratio of Co^{2+}:Fe^{3+}:AC was 1:2:150. After vigorous stirring for 24 h, 6 mol/L NaOH solution was added dropwise to keep the pH value to 12. The mixture solution was laid into a reaction kettle and hydrothermal treated at 150 °C for 12 h. After cooling, the prepared magnetic composite was washed with distilled water repeatedly until the pH value reaches 7, which was then separated from water by an outer magnet and dried in the oven at 105 °C.

2.3. Characterization of $CoFe_2O_4$/AC magnetic composite

The phase structure of $CoFe_2O_4$/AC composite was characterized by an XRD diffractometer (DX2700 China) with the Cu-Kα radiation (λ = 1.54051 Å, step 0.02°) at 40 kV and 30 mA. Pyrolysis process (TGA/DSC) of the prepared composite was tested by a thermal balance instrument (SDT Q600, TA) in air with a heating rate of 5 °C/min. BET surface area, pore diameter, and pore volume were carried out by a surface analyzer (ASAP 2020 USA) with N_2 as the adsorbate at −196 °C. The magnetic properties of the prepared samples were measured by a vibrating sample magnetometer (VSM: LakeShore-7407, up to 2 T) at room temperature.

2.4. Batch adsorption experiments

Adsorption experiments for Cr(VI) with AC and $CoFe_2O_4$/AC were carried out in a temperature-controlled shaker. 0.2 g AC or $CoFe_2O_4$/AC were put into glass vessels containing 50 mL of Cr(VI) solution with different initial concentrations (50, 100 and 150 mg/L), temperatures (298, 318 and 338 K) and pH (2–11), respectively. After equilibration, AC was separated with cellulose filter paper and $CoFe_2O_4$/AC was separated with an outer magnet form the solution. The residual Cr(VI) concentrations were determined by spectrophotometer (Shimadzu UV-3600) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm. The equilibrium adsorption capacity was calculated using the Equation (1) [26]:

$$q_e(mg/g) = \frac{(C_0 - C_e)V}{M} \tag{1}$$

Where q_e (mg/g) was the equilibrium adsorption capacity, C_0 (mg/L) and Ce (mg/L) were the initial Cr(VI) concentration and the Cr(VI) concentration after adsorption with AC or $CoFe_2O_4$/AC, V (L) was Cr(VI) solution volume, M (g) was the mass of AC or $CoFe_2O_4$/AC.

3. Results and discussion

3.1. Characteristics of AC and CoFe2O4/AC

3.1.1. XRD patterns of AC and $CoFe_2O_4$/AC

Fig. 1 presented the XRD patterns of the initial AC and $CoFe_2O_4$/

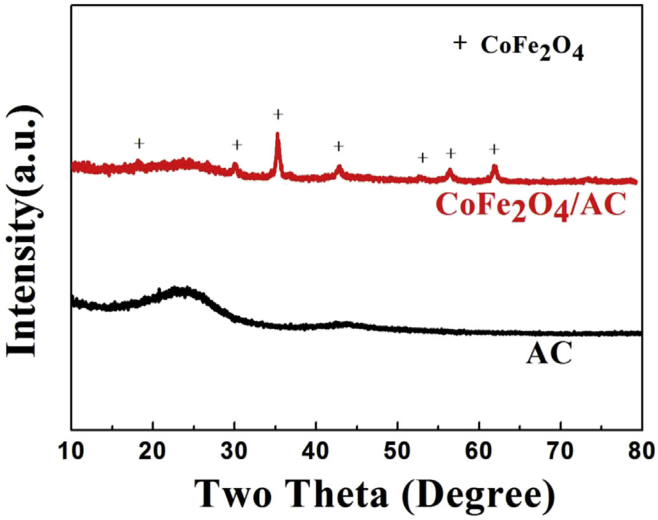

Fig. 1. XRD patterns of AC and $CoFe_2O_4$/AC composite.