Journal of Hazardous Materials 198 (2011) 282–290

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Removal of methylene blue from aqueous solution with magnetite loaded multi-wall carbon nanotube: Kinetic, isotherm and mechanism analysis

Lunhong Ai[a,b,*], Chunying Zhang[b], Fang Liao[a,b], Yao Wang[a,b], Ming Li[b], Lanying Meng[b], Jing Jiang[a,b,*]

[a] Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, China West Normal University, Shida Road 1#, Nanchong 637002, PR China
[b] College of Chemistry and Chemical Engineering, China West Normal University, Shida Road 1#, Nanchong 637002, PR China

ARTICLE INFO

Article history:
Received 19 May 2011
Received in revised form 1 October 2011
Accepted 13 October 2011
Available online 18 October 2011

Keywords:
Magnetite
Multi-walled carbon nanotubes
Adsorption
Methylene blue

ABSTRACT

In this study, we have demonstrated the efficient removal of cationic dye, methylene blue (MB), from aqueous solution with the one-pot solvothermal synthesized magnetite-loaded multi-walled carbon nanotubes (M-MWCNTs). The as-prepared M-MWCNTs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. The effects of contact time, initial dye concentration, and solution pH on the adsorption of MB onto M-MWCNTs were systematically studied. It was shown that the MB adsorption was pH-dependent. Adsorption kinetics was best described by the pseudo-second-order model. Equilibrium data were well fitted to the Langmuir isotherm model, yielding maximum monolayer adsorption capacity of 48.06 mg g^{-1}. FTIR analysis suggested that the adsorption mechanism was possibly attributed to the electrostatic attraction and π–π stacking interactions between MWCNTs and MB.

1. Introduction

Dyes are one of the most hazardous materials in industrial effluents which can cause severe health problems in human beings, since they exhibit high biotoxicity and potential mutagenic and carcinogenic effects [1,2]. Therefore, the removal of dye from colored effluents has attracted increasing attention. Several technologies including biological treatment, adsorption, coagulation/flocculation, chemical oxidation, membrane separation and ion exchange have been developed [3–8]. Among these methods, adsorption has been considered to be simple, highly efficient, and ease of operation. A wide range of materials have been reported for dye removal, including activated carbon, zeolite, clay, polymer, etc. [9–12]. In view of pollutant control at present, it is still indispensible for the development of new adsorbent materials with high adsorption capacities and removal efficiencies.

Recently, carbon nanotubes (CNTs) have attracted great interest as a new type of adsorbent for removing environmental pollutants (e.g. small molecules, heavy metal ions, radionuclides, and organic chemicals) [13], due to their remarkable features of the large specific surface area, hollow and layered structures. However, recovery of this kind of adsorbent usually needs the complicated and time-consuming filtration and/or centrifugation, thus limiting the reusability and increasing the regeneration cost. In this regard, many researchers have focused on combining CNTs and magnetic oxides to create a promising novel adsorbent that possesses adsorptive and magnetic dual functionalities [14–16], which opens new opportunities for the achievement of desirable adsorption capacity and effective magnetic separation. For example, Luan et al. synthesized CNTs/iron oxide composites by a chemical coprecipitation method with a high performance for the removal of Pb(II) and Cu(II) from water [17]. Gong et al. demonstrated chemical coprecipitation derived MWCNTs/iron oxide composites can efficiently remove cationic dye from aqueous solution [18]. Mishra and Ramaprabhu also employed chemical coprecipitation method to synthesize MWCNTs/magnetite composites for the removal of high concentration of arsenic and desalination of seawater [19]. However, to the best of knowledge, there is little report on the adsorption behavior of the solvothermally synthesized MWCNTs/magnetite composites.

In the present work, we have demonstrated a one-pot solvothermal route to prepare the magnetite (Fe_3O_4)-loaded multi-walled carbon nanotubes (M-MWCNTs) as an efficient adsorbent for the removal of cationic dye, methylene blue (MB), from aqueous solution. The effect of various parameters such as contact time, solution pH and initial dye concentration on the adsorption of MB onto M-MWCNTs was systematically studied. Adsorption isotherm, kinetic and mechanism were also evaluated. Furthermore, the resulting M-MWCNTs presented high magnetic sensitivity under an external magnetic field, providing an easy and efficient way for the separation of adsorbent from aqueous solution.

---

* Corresponding authors at: Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, China West Normal University, Shida Road 1#, Nanchong 637002, PR China. Tel.: +86 817 2568081; fax: +86 817 2224217.
E-mail address: ah_aihong@163.com (L. Ai).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.10.041

2. Experimental

2.1. Materials

$FeCl_3 \cdot 6H_2O$, sodium acetate (NaAc), ethylene glycol (EG), methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. All chemicals used in this study were of commercially available analytical grade. Multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port Ltd. Co. (Shenzhen, China). The detailed parameters supplied by the manufacturer are as follows: length: 5–15 μm; diameter: 20–40 nm; purity: ≥95%; ash: ≤0.2 wt%; amorphous carbon: <3%. MWCNTs were purified via being dispersed in concentrated nitric acid at 60 °C with constant stirring for 12 h, followed by filtering and washing with distilled water several times until the pH value reached neutral, and then filtered and dried in vacuum at 60 °C for further use.

2.2. Preparation of magnetite loaded MWCNTs (M-MWCNTs)

In a typical synthesis, 0.8 g purified MWCNTs were dispersed in 70 mL EG solution by ultrasonication for 30 min. Afterward, 1.6 g $FeCl_3 \cdot 6H_2O$ and 3.2 g NaAc were then added to EG solution at ambient temperature. After stirring for about 30 min, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 6 h followed by cooling to ambient temperature naturally. The black precipitate was centrifuged, washed with ethanol several times, and finally dried at 60 °C in a vacuum oven.

2.3. Characterization

The powder X-ray diffraction (XRD) measurements were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm). The morphology was observed with a JSM-6510 scanning electron microscope (SEM). The Fourier transform infrared (FTIR) spectroscopy was measured on Nicolet 6700 FTIR Spectrometric Analyzer using KBr pellets. A pHS-3C digital pH meter (Rex Instruments Factory, Shanghai, China) was employed for the pH measurements. The point of zero charge (pH_{PZC}) of the adsorbent was determined by the solid addition method. To a series of 100 mL conical flasks, 45 mL of 0.1 mol L^{-1} NaCl solution was transferred. The initial pH values (pH_i) of the solution were adjusted from 1.0 to 11.0 by adding either 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the NaCl solution. Then, 0.1 g of M-MWCNTs was added to each flask and the mixtures were agitated at 150 rpm. After 48 h, the final pH values (pH_f) of the solutions were measured. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave the pH_{PZC}.

2.4. Adsorption experiments

Batch adsorption experiments were carried out in a thermostated shaker with a shaking speed of 150 rpm using 100 mL Erlenmeyer flasks and conducted in duplicate. To study the adsorption isotherms, 0.02 g of M-MWCNTs were added into 50 mL of MB solutions of different initial concentrations (10–30 mg L^{-1}) at natural pH in flask, and agitated in a temperature-controlled shaker at 25 ± 1 °C for 120 min. The concentration of MB left in the supernatant solution was determined by using a UV–vis spectrophotometer (Shimadzu, UV-2550). The amount of MB adsorbed per unit mass of M-MWCNTs was calculated according to Eq. (1):

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of MB (mg L^{-1}), m is the mass of M-MWCNTs (g), and V is the volume of solution (L).

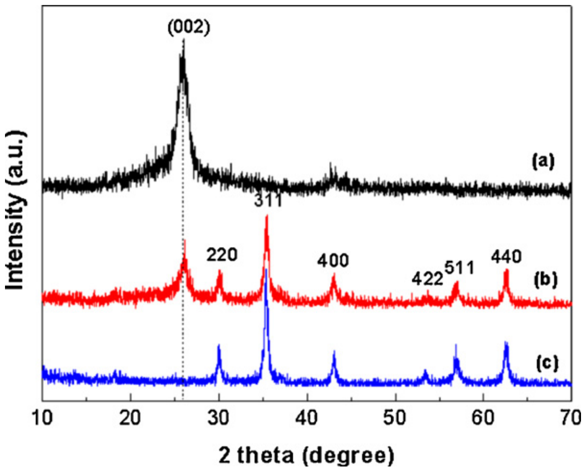

Fig. 1. XRD patterns of MWCNTs (a), M-MWCNTs (b) and Fe_3O_4 (c).

Batch kinetic experiments were carried out by mixing 0.02 g of M-MWCNTs to 50 mL of MB solution with a known initial concentration (10, 20 and 30 mg L^{-1}) at natural pH and agitated in a temperature-controlled shaker at 25 ± 1 °C for different time interval (5–280 min). The concentration of MB left in the supernatant solution was analyzed as above.

The effect of pH was performed by dispersion of 0.02 g of M-MWCNTs in 50 mL of MB solution of 20 mg L^{-1}. The initial pH of MB solution was adjusted to values in the range of 2.0–10.0 by the addition of 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. The suspensions were agitated in a temperature-controlled shaker at 25 ± 1 °C for 120 min. The concentration of MB left in the supernatant solution was analyzed as above.

2.5. Leaching test

To evaluate the stability of M-MWCNTs, the leaching of iron ions from M-MWCNTs at different pH levels was investigated. 0.02 g of M-MWCNTs was dispersed in 50 mL aqueous solution with pH ranging from 2.0 to 10.0 and agitated in a temperature-controlled shaker at 25 ± 1 °C for 280 min. The leached Fe concentration in the supernatant was determined by a WFX-120 atomic absorption spectroscopy (AAS, Rayleigh Analytical Instrument Corp., China).

3. Results and discussion

3.1. Characterization of the adsorbent

Fig. 1 shows the X-ray diffraction (XRD) patterns of MWCNTs, Fe_3O_4 and M-MWCNTs. As for MWCNTs (Fig. 1(a)), the strong diffraction peak at $2\theta = 25.8°$ can be indexed as the (0 0 2) reflection of the hexagonal graphite structure. After loading of Fe_3O_4 (Fig. 1(b)), besides the diffraction peak of MWCNTs, the new peaks at 2θ values of 18.2° (1 1 1), 30.0° (2 2 0), 35.3° (3 1 1), 42.9° (4 0 0), 53.4° (4 2 2), 56.9° (5 1 1), and 62.5° (4 4 0) are observed, which are consistent with the standard XRD data for the cubic phase Fe_3O_4 (JCPDS no. 89-4319) with a face-centered cubic (fcc) structure, indicating the coexistence of Fe_3O_4 and MWCNTs in the M-MWCNTs.