Chemical Engineering Journal 253 (2014) 456–463

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

A new approach for one step synthesis of magnetic carbon nanotubes/diatomite earth composite by chemical vapor deposition method: Application for removal of lead ions

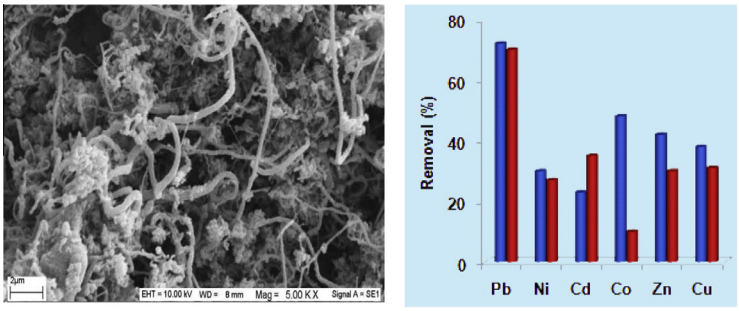
Hassan Alijani [a], Mostafa Hossein Beyki [b], Zahra Shariatinia [a,*], Mehrnoosh Bayat [b], Farzaneh Shemirani [b]

[a] Department of Chemistry, Amirkabir University of Technology, P.O. Box 159163-4413, Tehran, Iran
[b] School of Chemistry, University College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran

HIGHLIGHTS

- Carbon nanotubes were synthesized on diatomite by chemical vapor deposition method.
- A one step and simultaneous approach was used for synthesis of magnetic composite.
- Characterization by FT-IR, XRD, TEM, SEM, TGA, VSM, BET and Raman spectroscopy.
- Prepared material was used as a magnetic sorbent for lead uptake from water sample.
- The maximum Langmuir monolayer capacity of 60 mg g^{-1} was measured for lead ions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 4 May 2014
Accepted 5 May 2014
Available online 27 May 2014

Keywords:
Carbon nanotube
Chemical vapor deposition
Diatomite earth
Heavy metals

ABSTRACT

In this research, a one step and facile approach was used for the synthesis of magnetic multiwalled carbon nanotubes on the surface of diatomite earth as a substrate by chemical vapor deposition (CVD) of methane. The prepared composite was characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM, SEM), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), N_2 adsorption – desorption measurement (BET) and Raman spectroscopy analyses. This new material combines the advantages of carbon nanotubes and diatomite in one material. The composite exhibited superparamagnetic properties and was used as a magnetic separable sorbent for adsorption of metal ions from aqueous media. The acid activated sorbent showed fast adsorption kinetic within 10 min and maximum Langmuir monolayer capacity of 60 mg g^{-1} for lead ions. The thermodynamic parameters, ΔH, ΔS and ΔG were calculated from temperature-dependent adsorption data indicating adsorption of Pb^{2+} ions onto the composite material is a spontaneous process. The results suggest that this sorbent is a suitable material for the removal and solidification of metal ions from polluted environmental samples.

* Corresponding author. Tel.: +98 21 64542766; fax: +98 21 64542762.
E-mail address: shariati@aut.ac.ir (Z. Shariatinia).

http://dx.doi.org/10.1016/j.cej.2014.05.021
1385-8947/

1. Introduction

Environmental pollution with some heavy metals such as lead, cobalt, copper and zinc is a worldwide problem. Most of these metals have toxic and carcinogenic characteristics and they threaten human health and aquatic environment seriously when enter into water and food chain. Hence, recent studies have mainly focused on exploring novel adsorbents with fast adsorption rate, large adsorption capacity, and high adsorption selectivity for hazardous metal ions [1–3]. Carbon-based materials especially carbon nanotubes (CNTs) typify a class of significantly and widely used engineering adsorbents because of their extraordinary mechanical, electrical, thermal, and structural properties [4–6]. There have been many methods for the production of carbon nanotubes with metallic or semi-conducting properties [7]. The most common methods used for the production of nanotubes are arc discharge [8], laser vaporization [9], and chemical vapor deposition (CVD) which allows the location and orientation of nanotubes to be controlled with a large degree of precision. Moreover, CNTs can be synthesized on the surfaces of different substrate materials such as organic polymers and porous inorganic particles to create high performance catalysts and adsorbents [10]. The role of substrate is to disperse the catalyst active phase and prevent metal nanoparticles from aggregating into large clusters, resulting in smaller particles suitable for CNTs growth [11].

Among many substrate materials such as alumina, titana, nanoclay and etc., diatomite earth has many useful features. It is the fossilized remnants of diatoms, tiny planktonic algae, residing in all of the earth's waters which are mainly composed of amorphous hydrated silica (SiO_2-nH_2O) [12,13]. It has a low-cost and is readily available as a mineral with highly developed porous structure which can be used as a functional filter, thermal insulator and catalyst. Diatomite and CNT are widely employed in different applications; therefore their composite material could be of high interest for environmental remediation through dynamic or static procedures [14–18]. However, separating and recycling of this composite material turn out to be a challenge when the adsorbent is made into nanoscale for enhancement of the adsorption efficiency. Consequently, considerable attention has recently been focused on the application of magnetic separation as a simple, quick and effective technique for collecting the solid mass from aqueous solutions [19–21].

Different approaches such as blending, microgel template, hydrothermal and co-precipitation methods have been used to generate magnetic diatomite or CNT composite. Although above works are useful to synthesize the target nanocomposite, the conventional methods have several disadvantages such as the requirement of additives, long period of time for synthesis of CNT and MNPs by discrete method and the presence of two iron sources which is not economic. Considering these aspects, we have developed a new method for preparation of a magnetic CNT-diatomite composite. In fact, the catalytic activity of iron supported on diatomite and its role for production of magnetic carbon nanotubes (MCNTs) has been investigated. Diatomite support was prepared using aluminum nitrate and diatomite by impregnation method and the CNT was synthesized on the surface of diatomite as a substrate. The prepared composite, which exhibits superparamagnetic properties, has potential applicability in lithium ion battery, environmental remediation, and as a catalyst. Herein, the prepared composite was activated with HNO_3 solution and used as a magnetic separable sorbent for removal of lead ions from aqueous media. The influences of time, temperature and other effective parameters on adsorption of Pb^{2+} ions from water samples were investigated and the results indicated that the new sorbent has a high potential for uptaking heavy metals in order to reduce their hazardous impact on ecosystem.

2. Experimental

2.1. Reagents and solutions

Diatomite earth sample was obtained from Kamel Abad-Azerbaijan-I.R. Iran. It was dispersed in 100 mL distilled water by magnetic stirring and then it was kept constant until some solid impurities were dispersed. The particles were separated with filter paper and dried at 100 °C for 8 h. Methanol, acetic acid, sodium acetate and $Fe(NO_3)_3{\cdot}9H_2O$ were of analytical grade and supplied from Merck (Darmstadt, Germany). Standard solutions of lead ions (1000 mg L^{-1}) were prepared by dissolving $Pb(NO_3)_2{\cdot}5H_2O$ in minimum amount of HNO_3 and then diluted to an appropriate volume with distilled water. The pH adjustment was performed with acetate buffer solution (0.1 mol L^{-1}). All the glassware were cleaned by soaking in diluted HNO_3 or HCl and rinsed with distilled water prior to use.

2.2. Instruments

A Varian model AA-400 atomic absorption spectrometer (Varian, Musgrave, Australia), equipped with a deuterium lamp background and a hollow cathode lamp was used for determination of lead ions. All measurements were carried out in a peak height mode. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP. The specific surface area and pore size distributions were calculated by the Brunauer–Emmett–Teller (BET) method and Barret–Joyner–Halenda (BJH) model on the desorption branch, respectively. Thermogravimetric analysis (TGA) was carried out in PerkinElmer Pyris Diamond instrument from ambient temperature to 1000 °C, using a ramp rate of 10 °C/min. Micro-Raman spectra were recorded using a Renishaw system 1000 spectrometer, equipped with Leica DMLM microscope, a 25 mW diode laser (782 nm), and a Peltier-cooled CCD detector. A digital pH-meter (model 692, Herisau, metrohm, Switzerland), equipped with a glass-combination electrode was used for the pH adjustment. Separation was assisted using a strong neodymium–iron–boron ($Nd_2Fe_{12}B$) magnet (1.31 T). Fourier transform infrared spectra (FT-IR) were measured with Equinox 55 Bruker with ATR method over the wavelength range of 400–4000 cm^{-1}.

2.3. Preparation of substrate

Diatomite–alumina composite was prepared by impregnation method. In a typical route, appropriate amount of diatomite was dispersed in 100 mL distilled water, 0.1 g of $Al(NO_3)_3{\cdot}9H_2O$ was added and the solution was stirred at 80 °C for 13 h. Solid mass was separated with filter paper and dried at 100 °C for 8 h, then calcined at 500 °C for 2 h. In order to prepare catalyst with different loadings of Fe^{3+} ions (1–5% w), appropriate amounts of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 100 mL of methanol and 1.0 g of substrate was added to the solution. The final mixture was stirred for 2 h and then the solvent was evaporated by rotary evaporator and finally dried at 200 °C for 2 h. The final product was calcined at 600 °C for 6 h.

2.4. Synthesis of CNTs on substrate surface

A fixed bed flowed reactor was used for synthesis of CNTs. The reactor which was composed of a ceramic boat containing 0.1 g of the catalyst was placed in a horizontal quartz tube with an external diameter of 50 mm, an internal diameter of 46 mm and a length of about 880 mm. After purging with argon for 30 min, the methane