Chinese Chemical Letters 27 (2016) 795–800

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Original article

Magnetically separated and N, S co-doped mesoporous carbon microspheres for the removal of mercury ions

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 22 December 2015
Accepted 21 January 2016
Available online 2 February 2016

Keywords:
N, S co-doped mesoporous carbon microspheres
Magnetite
Adsorption
Mercury ion
Magnetic separation

ABSTRACT

Magnetically separated and N, S co-doped mesoporous carbon microspheres (N/S-MCMs/Fe_3O_4) are fabricated by encapsulating SiO_2 nanoparticles within N, S-containing polymer microspheres which were prepared using resorcinol/formaldehyde as the carbon source and cysteine as the nitrogen and sulfur co-precursors, followed by the carbonization process, silica template removal, and the introduction of Fe_3O_4 into the carbon mesopores. N/S-MCMs/Fe_3O_4 exhibits an enhanced Hg^{2+} adsorption capacity of 74.5 mg/g, and the adsorbent can be conveniently and rapidly separated from wastewater using an external magnetic field. This study opens up new opportunities to synthesize well-developed, carbon-based materials as an adsorbent for potential applications in the removal of mercury ions from wastewater.

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1. Introduction

Human activities, besides their contributions to the global civilization, also introduce considerable pollutants, such as heavy metals, organic compounds, and other hazardous materials, into the environment [1]. Heavy metal pollution of water through the discharge of industrial wastewater is a particularly intractable problem [2]. The high volatility of Hg and its compounds, and their toxicity, accumulative, and persistent features in the ecosystem as well as the biomagnifications along the food chain has been considered as a serious health threat to human beings [3]. Therefore, highly effective removal of mercury ions from wastewater has been a long-standing goal for industrial process and environmental remediation [4]. Many separation technologies have been utilized for effectively reducing mercury concentrations from wastewater, including chemical precipitation, adsorption, ion exchange, membrane separation, solvent extraction, and electrochemical treatment [5], *etc*. Among these separation processes, adsorption using functionalized adsorbents is considered to be one of the most common techniques due to the advantages of simplicity of operation, applicability toward dilute solutions and economical feasibility [6].

Porous carbons with large surface areas, suitable mechanical strength, and good acid and alkali resistance show important applications in pollutant removal. However, their adsorption of soft, heavy metals (*e.g.*, Hg) is usually limited because of their relatively inert surface (*i.e.*, lack of active functional groups). This shortage causes difficulties in the widespread use of porous carbon materials as acceptable adsorbents for the removal of mercury ions from wastewater. Therefore, it is important to modify or functionalize porous carbons by heteroatoms, such as sulfur and nitrogen, for finally achieving the modifications/adjustments in which efficient and effective adsorption of mercury becomes a reality [2c,2d,7]. In general, however, post-synthesis treatment suffers the disadvantage of unstable functionalized groups and relatively complicated preparation processes. Therefore, to prepare functionalized porous carbon materials using one-step synthesis process is a preferred choice [8].

On the other hand, the present carbon adsorbents are mainly powdered materials, which are difficult for efficient separation and recycling. Carbon micro- or nanospheres with regular morphology and adjustable porosity and diameter show enhanced mechanical strength and improved adsorption, separation, and recycling performance compared with carbon powders or flakes [9]. Furthermore, the common separation methods for adsorbents

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http://dx.doi.org/10.1016/j.cclet.2016.01.038
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from aqueous solution are precipitation, filtration, and centrifugation which are inconvenient, uneconomical, and inefficient. Magnetic materials could be conveniently separated from environmental water with an external magnetic field, exhibiting promising prospects for heavy metal removal [10]. For example, Peng *et al.* prepared carbon nanotube-iron oxide magnetic composites as an adsorbent for removal of aqueous Pb^{2+} and Cu^{2+} ions [10c]. Liu *et al.* developed humic acid coated Fe_3O_4 nanoparticles by a co-precipitation procedure for the removal of toxic Hg(II), Pb(II), Cd(II), and Cu(II) from water [10d].

Taking into account all the above-mentioned criteria, carbon-based materials with a combination of porous structure, regular functional groups, and a magnetic separation feature would represent innovative materials and are expected to be particularly suitable as sorbents. As a target toward that goal, herein, we demonstrate the synthesis of magnetically separated and N, S co-doped mesoporous carbon microspheres (N/S-MCMs/Fe_3O_4) for the removal of mercury ions. N/S-MCMs/Fe_3O_4 shows the advantages of high specific surface area, dual mesopore sizes, microspherical shape, sulfur and nitrogen heteroatoms, and superparamagnetic Fe_3O_4. N/S-MCMs/Fe_3O_4 has an Hg^{2+} adsorption capacity of 74.5 mg/g, and the adsorbent can be rapidly separated from the aqueous phase with an external magnetic field. This study highlights the great potential to fabricate well-designed, carbon-based adsorbents for the removal of aqueous mercury ions.

2. Experimental

100 mL of distilled water, 40 mL of ethanol, and 1.5 mL of 25 wt% ammonia solution were mixed under stirring. Then 2.0 g of tetraethyl orthosilicate (TEOS) was added into the mixed solution and stirred for 30 min to prepare silica nanoparticles. Into the solution, 1.0 g of resorcinol and 1.0 g of cysteine were added under stirring for 10 min. Then, 1.5 g of formaldehyde (37–40 wt%) solution was slowly added to the above mixed solution and stirred for 24 h at 30 °C. After that, the whole mixture was transferred to a Teflon autoclave at 100 °C for 24 h to fabricate SiO_2 nanoparticles embedded N, S co-doped polymer microspheres (N/S-PMs). N/S-PMs were subjected to thermal treatment at 550 °C for 4 h with a heating rate of 3 °C/min under N_2 flow, followed by etching SiO_2 template with 3 mol/L NaOH solution to prepare N, S co-doped mesoporous carbon microspheres (N/S-MCMs). For comparison, pure mesoporous carbon microspheres (MCMs) were also obtained using similar procedure without cysteine. Finally, $Fe(NO_3)_3$ $9H_2O$ and N/S-MCMs were mixed with a mass ratio of 1:2, and ethanol was added to dissolve ferric nitrate. The mixture was agitated by rotation at 200 ± 5 rpm in a rotator oscillator at r.t. for 24 h, followed by natural evaporation of ethanol. The sample was heated to 400 °C under N_2 atmosphere for 1 h to fabricate Fe_3O_4 and N/S-doped carbon microspheres (labeled as N/S-MCMs/Fe_3O_4). The samples were characterized by SEM, XRD, Raman spectra, XPS, N_2 adsorption, and a vibrating sample magnetometer.

The batch adsorption experiments of adsorbents were performed using $Hg(NO_3)_2$ as a model pollutant. In a typical experiment, 20 mg of as-prepared adsorbent was diluted with 50 mL of $Hg(NO_3)_2$ solution and the concentration of Hg^{2+} was varied from 10 mg/L to 50 mg/L (pH 6.0 ± 0.05). Kinetic study was conducted using 20 mg of adsorbent in contact with 50 mL $Hg(NO_3)_2$ solution (C_{Hg} = 50 mg/L). The solution was stirred by rotation at 200 ± 5 rpm at 25 °C until equilibrium was reached. Separate experiments were done using rotation time intervals from 10 min to 150 min. Before analysis, the suspension was separated using a 0.45 μm membrane filter, and the adsorption capacities of Hg^{2+} were measured using the supernatant. The concentrations of Hg^{2+} were determined using an atom absorption spectroscopy. The amounts of Hg^{2+} adsorbed (Q_e in mg/g) were calculated according to the following equation,

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where, C_0 and C_e are the initial and equilibrium concentrations of mercury ions (mg/L), respectively; V is the volume of mercury nitrate solution (L) and W is the weight of the adsorbent (g).

3. Results and discussion

Fig. 1 shows SEM images of MCMs, N/S-MCMs, and N/S-CMs/Fe_3O_4. MCMs exhibit regular spherical geometry with a uniform diameter of about 580 nm, as shown in Fig. 1a. The diameters of carbon-based microspheres are constant (Fig. 1b). Cysteine which provides N,S sources can be introduced into the carbon framework and does not affect the ethanol/water/ammonia system to generate polymer microspheres. After the introduction of Fe_3O_4 into the N/S-MCMs, the surface roughness and luster were altered (Fig. 1c).

Fig. 2 shows Raman spectra of MCMs, N/S-MCMs, and N/S-MCMs/Fe_3O_4. The spectra have a distinct pair of peaks located at about 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band). The D band is a typical characteristic of disordered graphite or crystal defects, and the G band is ascribed to an ideal graphitic lattice vibration mode with E_{2g} symmetry [11]. Additionally, the peak located at ~2700 cm^{-1} denotes G′ band, corresponding to undisturbed or highly ordered graphitic lattices [12]. In the Raman spectrum of N/S-MCMs/Fe_3O_4, three dominant Raman bands at about 360, 500, and 700 cm^{-1} reflect the E_g, T_{2g}, and A_{1g} mode of magnetite [13]. The $Fe(NO_3)_3$ $9H_2O$ in N/S-MCMs occurs a decomposition reaction to transfer into γ-Fe_2O_3 at a temperature of 350 °C [14], and then γ-Fe_2O_3 was transfer into Fe_3O_4 by carbothermal reduction, which matches the result obtained from XRD analysis (Fig. S1 in Supporting information).

The XPS spectrum of N/S-MCMs/Fe_3O_4, shown in Fig. 3a, exhibits signals for the binding energy of S 2p, C 1s, N 1s, O 1s, and Fe 2p. There are six peaks in N 1s spectrum (Fig. 3b) at the binding energy of 398.6, 400.0, 400.7, 401.2, 402.6, and 404.1 eV which are

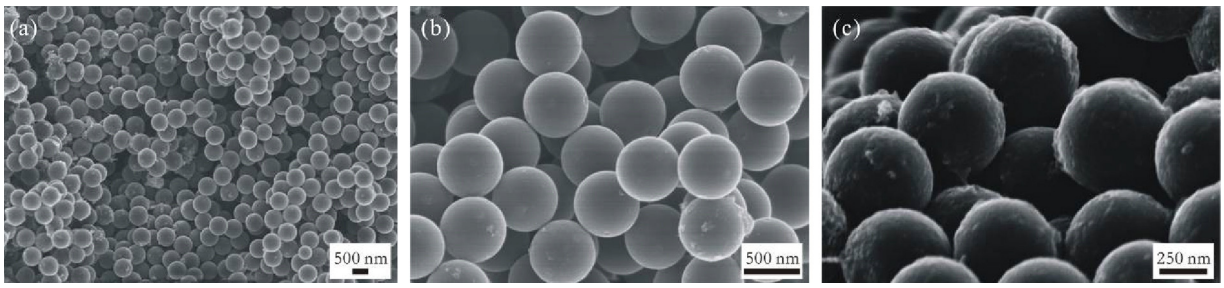

Fig. 1. SEM images of MCMs (a), N/S-MCMs (b), and N/S-CMs/Fe_3O_4 (c).

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