



Amino-functionalized magnetic mesoporous microspheres with good adsorption properties

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ABSTRACT

An amino-functionalized magnetic mesoporous microsphere was fabricated by a colloidal chemical method and using cationic surfactants (CTAB) as structure-directing agents. The prepared nanocomposite microspheres were mesoporous and magnetizable, with a diameter of ca. 480 nm, a high surface area of 474 m²/g, a pore size of 2.1 nm, and a saturation magnetization of 36.0 emu/g. As an adsorbent, these multifunctional microspheres showed excellent adsorptive capability toward heavy metal ions (Pb²⁺, Cu²⁺, Cd²⁺) and the adsorption capacity was as high as 289.7 mg/g (1.40 mmol/g) for Pb²⁺, 196.5 mg/g (3.09 mmol/g) for Cu²⁺ and 154.2 mg/g (1.37 mmol/g) for Cd²⁺. The amino-functionalized magnetic mesoporous microsphere can be easily removed from solution by an external magnetic field and regenerated easily by acid treatment. These results suggest that this kind of nanocomposites is a potentially useful material for effectively adsorbing and removing the heavy metal ions in aqueous solution.

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1. Introduction

Heavy metal ions removal from aqueous solution is one of the major problems on wastewater treatment because they can not only have toxic and harmful effects on organism living in water, but also accumulate throughout the food chain to affect human beings [1,2]. These pollutants are present in water from industrial applications, including mining, refining and production of textiles, paints and dyes [3,4]. Many techniques, such as ion exchange [5], reverse osmosis [6], precipitation [7], adsorption [8], membrane process [9], etc., have been applied on removal of heavy metal ions. Among them, adsorption is the most promising and frequently used technique due to its low cost, easy application and superior efficiency [10–14].

With the increase in environmental pollution, there is a growing demand in developing novel adsorbents to remove heavy metal ions efficiently from wastewater. A good adsorbent should have the features of strong affinity to target adsorbate and a large surface area with more binding sites. Mesoporous silica, owing to its uniform pore structure, a large surface area and well-defined pore size, fully meets this requirement and has been widely used in the techniques of adsorption and separation [15–17]. However, the unmodified mesoporous silica has a little adsorption capacity

toward heavy metal ions [15–17]. Thus, the functionalization of ordered mesoporous silica is very important. So far, there are several kinds of modified methods. One is thiol-functionalized, which exhibited a high complexation affinity for Hg²⁺ [18–20], however, for Cu²⁺, Ni²⁺, Zn²⁺, and Cd²⁺, the amino-functionalized worked [21–23]. As a development in the area, some magnetic mesoporous microspheres consisting of a magnetic core and mesoporous shell have been prepared [24–27]. It provides the advantage for the recovery and separation of the sample by applying a magnetic field. The integration of functionalized groups in the mesoporous shell with a magnetic core has undoubtedly of great potential application prospect.

In this paper, an amino-modified magnetic mesoporous microsphere has been synthesized and used as an adsorbent to remove the heavy metal ions. The effects of metal ions concentration, contact time, and solution pH were studied in order to analyze the adsorption kinetics and determine the equilibrium time. Langmuir and Freundlich isotherms were applied to the experimental equilibrium data in order to explain the adsorption mechanism.

2. Experimental

2.1. Synthesis of Fe₃O₄ microspheres

The magnetic particles were synthesized via a solvothermal method as described previously [28]. Briefly, 1.08 g FeCl₃·6H₂O

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was first dissolved in 20 mL ethylene glycol under magnetic stirring until the solution became clear. Then 1.8 g NaAc was added by stirring for another 1 h. Subsequently, 0.25 g trisodium citrate was added. When the mixed solution was stirred at 50 °C to form a homogeneous dispersion, the mixture was transferred to an autoclave which was kept at 200 °C for 10 h under static condition. The black particles were collected with the help of a magnet, followed by washing with ethanol and deionized water, and then dried at 60 °C overnight for further use.

2.2. Synthesis of $Fe_3O_4@SiO_2$ microspheres

The SiO_2 coating Fe_3O_4 spheres could be processed at room temperature by a modified Stöber method [29]. In a typical procedure, 0.1 g as-prepared Fe_3O_4 particles were dispersed in a mixture of ethanol (40 mL), deionized water (10 mL), and concentrated ammonia solution (28 wt%, 1.2 mL) by ultrasonication for 1 h. Then, 0.4 mL tetraethyl orthosilicate (TEOS) was added dropwise. After stirring for 4 h, the products were collected and washed with deionized water, and then dried at 60 °C for further use.

2.3. Synthesis of $Fe_3O_4@SiO_2@meso-SiO_2$ microspheres

0.1 g as-made $Fe_3O_4@SiO_2$ particles were first evenly dispersed in 140 mL ethanol by ultrasonication, and then added 80 mL H_2O , 1.2 mL concentrated ammonia solution (28 wt%) and 0.3 g CTAB under constant stirring for 6 h. To the solution, 0.43 mL TEOS was added dropwise. After mechanical agitation for 6 h, the obtained particles were separated with a magnet and washed with deionized water. Finally, the purified samples were re-dispersed in 100 mL of acetone and refluxed at 85 °C for 48 h to remove the CTAB template. The extraction was repeated three times. Then the resulting powders were washed with water and dried at 60 °C overnight.

2.4. Synthesis of amino-functionalized $Fe_3O_4@SiO_2@meso-SiO_2$ microspheres

0.2 g as-made $Fe_3O_4@SiO_2@meso-SiO_2$ particles were dispersed in 50 mL toluene by ultrasonication. Next, 4 mL 3-aminopropyltrimethoxysilane (APTMS) was added. The mixture was refluxed at 110 °C with continuous stirring for 24 h and then recovered by a magnet followed by washing with ethanol several times. The products obtained were dried at 60 °C under vacuum overnight and named as $Fe_3O_4@SiO_2@meso-SiO_2-NH_2$ sample.

2.5. Characterizations

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance Diffractometer with $Cu_{K\alpha}$ radiation

($\lambda = 1.5418 \text{ \AA}$). FT-IR spectra were obtained on a Perkin-Elmer series with a resolution of 4 cm^{-1} using the KBr pellet technique. The size and morphology of the samples were inspected using a field emission scanning electron microscope ((FE-SEM Hitachi S-4800). Transmission electron microscopy (TEM) was obtained from a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. Nitrogen adsorption/desorption analysis was measured using a Micromeritics ASAP 2020 M apparatus. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using the data between 0.05 and 0.35. The $-NH_2$ content in the final solid products was determined on CHNS Elemental Analyzer. Magnetization measurements were performed on a superconducting quantum interference device (SQUID) magnetometer at 300 K. The concentrations of metal ions in the solutions were measured by atomic absorption spectroscopy (AA-6800 Japan).

2.6. Adsorption experiments

In a typical adsorption procedure, 50 mg of the as-prepared $Fe_3O_4@SiO_2@meso-SiO_2-NH_2$ was added into 50 mL of a single metal ions solution for 2 h at room temperature. The aqueous systems selected were Pb^{2+} , Cu^{2+} and Cd^{2+} , and all used were nitrates. Effects of adsorption isotherms (initial concentration: 10–400 mg/L), kinetics time (0–120 min), pH (2.0–8.0) were studied. When the adsorption process reached equilibrium, the adsorbent was separated by a powerful magnet and the residual heavy metal ions in the solution were determined by atomic absorption spectroscopy (AAS).

3. Results and discussions

3.1. Characterization of the amino-modified magnetic mesoporous microspheres

Fig. 1 shows the SEM and TEM images of the $Fe_3O_4@SiO_2@meso-SiO_2-NH_2$ composites. As seen in Fig. 1a, amino-modified $Fe_3O_4@SiO_2@meso-SiO_2$ particles possess monodispersed spherical morphology with a uniform particle size distribution of ca. 480 nm. TEM of Fig. 1b clearly exhibits Fe_3O_4 core, SiO_2 intermediate layer and the mesoporous SiO_2 shell with the channel perpendicular to the magnetic nuclear surface, indicating that the introduction of amino-group may not destroy the mesoporous structure of the outer SiO_2 shell.

To confirm the existence of mesoporous structure, the $Fe_3O_4@SiO_2@meso-SiO_2$ microspheres before and after amino-modified were examined by low-angle XRD as shown in Fig. 2A. As can be seen, the two samples both exhibit a single and strong diffraction peak around $2\theta = 2.5^\circ$, indicating the presence of mesostructure. Due to the grafting of amino groups, the diffraction

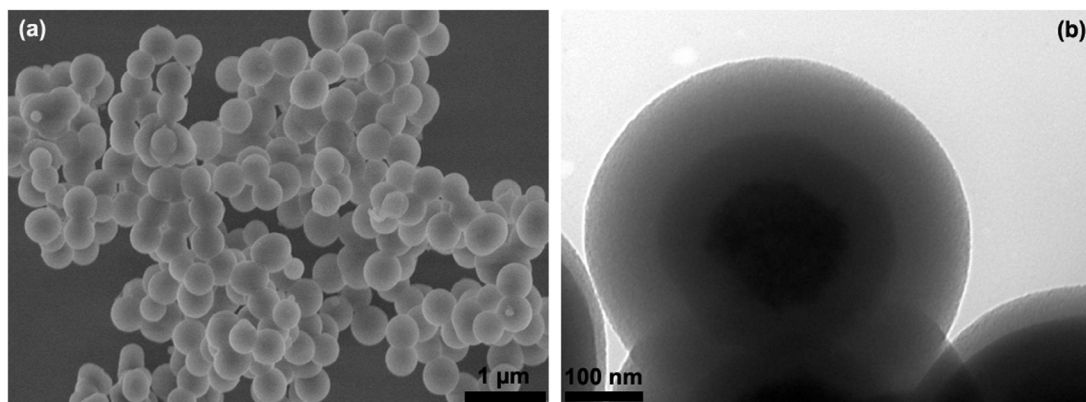


Fig. 1. SEM (a) and TEM (b) of the $Fe_3O_4@SiO_2@meso-SiO_2-NH_2$ composites.

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