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One-step fabrication and characterization of hierarchical $MgFe_2O_4$ microspheres and their application for lead removal

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ABSTRACT

Nearly monodispersed hierarchical $MgFe_2O_4$ microspheres were prepared by a facile solvothermal method. The possible formation mechanism of the sphere-like $MgFe_2O_4$ was proposed. The presence of the EG, acetate ion and PEG played crucial roles and displayed significant synergistic effect in the formation of these microspheres. With relatively abundant mesopores, high specific surface area, excellent magnetic responsivity and redispersibility, the hierarchical $MgFe_2O_4$ microspheres were tested for their application in water treatment, and showed an excellent Pb(II) adsorption property with a maximum removal capacity of 113.7 mg/g. The adsorption isotherm and kinetics for Pb(II) onto the $MgFe_2O_4$ microspheres were also investigated. With high adsorption capacity and fast adsorption rate, the monodispersed hierarchical $MgFe_2O_4$ microspheres have the potential to be used as low-cost and efficient adsorbent materials for the removal of toxic metal ions from water. Also, this facile strategy may be extended to synthesize other metal oxides with hierarchical nanostructures, which may find many other applications due to their novel structural features.

1. Introduction

In recent years, hierarchical nanostructures have attracted considerable attention due to their unique properties and potential applications in adsorption [1,2,3,4], catalysis [5,6,7], drug delivery [8,9], supercapacitors [10,11,12], Lithium-Ion batteries [13,14,15] and sensors [16,17,18]. Till now, substantial efforts have been dedicated to develop methods for design and synthesis of various hierarchical nanostructures with great progress achieved. The most wide and simplest synthetic route to hierarchical nanostructures is generally considered to be self-assembly, in which low-dimensional building blocks, i.e., nanoparticles, nanofibers and nanofilms self-assemble into complex ordered nanostructures in a spontaneous process [19]. Complex metal oxides with various structures, such as nanowires [20,21,22], nanocubes [23], spheres [24,25], nanoboxes [26], urchin-like [27], flower-like [28,29] and nest-like [30] have been successfully synthesized by various methods, which have been extensively applied in diverse fields, especially used for water treatment [31,32,33], due to their effective performance, nontoxicity and low cost. However, the extensive use of toxic metal organic compounds in the synthesis process of the above as-mentioned complex metal oxides makes them detrimental to the environment to a certain extent and unsuitable for practical application. Therefore, it is very desirable to develop a facile, reliable and environment-friendly method to produce complex metal oxides with hierarchically nanostructures.

Heavy metal ions (e.g. Pb(II)) of water, are capable of having direct adverse impacts on human health and the environment when their concentrations are higher than permissible limits. Therefore, their efficient removal from water is of great importance. Among various removal technologies, adsorption technology is perhaps the most extensively used one because of its easy handling, low cost and high efficiency. As a basis for this technology, the intrinsic characteristic of the adsorbent materials is a key point for successful adsorption. However, there are still some challenges that restrict the adsorption approach, such as limited adsorption capacity and low adsorption rate, for traditional absorbents. Therefore, it is desirable to explore novel adsorbent materials for the removal of heavy metal ions with high adsorption capacity and fast

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adsorption rate. In recent years, using metal oxides as adsorbents for heavy metal ions removal has attracted much attention because of their high efficiency and low cost [34,35]. In particular, metal oxides with hierarchical nanostructures that are composed of nanometer-sized building blocks have many advantages in adsorption, such as high surface area and abundant active sites [36]. Hence, synthesis of hierarchical nanostructured metal oxides with low cost and excellent adsorption performance is urgently needed in water treatment.

Herein, we report a simple and economical method for large-scale synthesis of monodispersed hierarchical $MgFe_2O_4$ microspheres with designed chemical components and controllable morphologies by an ethylene glycol (EG)-mediated self-assembly process. To the best of our knowledge, there is limited knowledge about the preparation of the monodispersed hierarchical $MgFe_2O_4$ microspheres by a solvothermal method. The main objective of this work is to investigate the formation mechanism of the monodispersed hierarchical $MgFe_2O_4$ microspheres and the self-assembly process. Inspired by the hierarchical structure and high BET surface area, the as-prepared $MgFe_2O_4$ microspheres were used as adsorbent for Pb(II) removal in water treatment. Experiments results revealed that these $MgFe_2O_4$ microspheres exhibit superparamagnetic behavior with high saturation magnetization and an excellent adsorption performance for Pb(II) removal in water treatment. This work resulted in an important method for obtaining various monodisperse hierarchical microspheres, and provided an opportunity to further apply these promising materials.

2. Experimental section

2.1. Materials

All chemical reagents used in this study were purchased from Sinopharm Chemical Regent Beijing Co., Ltd., including magnesium acetate ($Mg(Ac)_2 \cdot 4H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium acetate ($NaAc \cdot 3H_2O$), polyethylene glycol (PEG; Mw = 20,000), ethylene glycol (EG) and lead nitrate ($Pb(NO_3)_2$). All of the reagents used are of analytical purity and used without further purification. Deionized water was used throughout the synthesis and treatment processes.

2.2. Synthesis of the $MgFe_2O_4$ microspheres

Nearly monodispersed hierarchical $MgFe_2O_4$ microspheres were synthesized by a simple hydrothermal method. In a typical synthesis process, 5 mmol $Mg(Ac)_2 \cdot 4H_2O$, 10 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 20 mmol $NaAc \cdot 3H_2O$ and 2 g PEG were dissolved in 70 mL EG to form a clear solution. After being ultrasonic for 1 h, the mixture was put into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 200 °C for 11 h in an electron oven, followed by a natural cooling to room temperature. After that, the resulting precipitates were harvested, and washed with deionized water and absolute ethanol several times by a centrifugation-redispersion process. Then the final products were dried in an oven at 60 °C for 24 h. Furthermore, in order to investigate the effect of acetate ion on products morphology, the $MgFe_2O_4$ microspheres without addition of acetate ion were synthesized by using $Mg(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3$ as precursors with other conditions unchanged.

2.3. Materials characterization

The morphology of the obtained products was observed by Hitachi S-4800 scanning electron microscope (SEM) operating at 10 kV. The transmission electron microscope (TEM) and High-resolution transmission electron microscopy (HR-TEM) were performed on JEOL JEM-2011 at an acceleration voltage of 200 kV. The phase and composition of the products were characterized by X-ray diffraction (XRD) using a Rigaku D/max 2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu Kα radiation ($\lambda = 1.5406$ Å), employing a scanning rate 0.02° s^{-1} in the 2θ ranging from 3 to 80°. The specific surface area was measured by nitrogen adsorption at 77 K (BET method) using an automated gas sorption analyzer (Quantachrome Instruments, autosorb-iQ). The pore size distributions were derived from the desorption branches using the barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed on ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. A Tensor 27 Fourier transform infrared spectroscopy (FTIR) was used to verify the presence of functional groups in the adsorbent. The magnetic property was characterized using a vibrating sample magnetometer (VSM, Lake Shore 7307) at room temperature.

2.4. Adsorption experiments

Pb(II) stock solutions were prepared by dissolving lead nitrate into deionized water. The working solutions for all experiments were freshly prepared from the stock solution. All adsorption experiments were carried out in a temperature controlled (at 25 ± 1 °C) shaker using 150 mL shaking flasks containing Pb(II) solution with different initial concentrations for a predetermined contact time at 200 rpm. Adsorption isotherms were conducted at 25 °C in the initial pH 7.0 ± 0.1, and the adsorbent dose was kept as 0.5 g/L for all the experiments. Adsorption experiments were carried out in duplicate and the average data were used to evaluate the adsorption performance. In our experiments, inductively coupled plasma mission spectroscopy (ICPE-9000, Shimadzu) was used to analyze the concentration of Pb(II), respectively. The adsorption capacity q_e (mg/g) was calculated by the following equation:

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

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of Pb(II), respectively; V (L) is the solution volume and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterizations of $MgFe_2O_4$ microspheres

3.1.1. SEM and TEM analysis

The morphology, shape and size of the $MgFe_2O_4$ microspheres are obtained by SEM and HRTEM analysis, as shown in Fig. 1. SEM image reveals that the obtained product consists of very uniform microspheres with hierarchical structures and a diameter of 200–250 nm (Fig. 1a). The higher-magnification (Fig. 1a, inset) SEM image indicates that the as-prepared $MgFe_2O_4$ have a sphere-like morphology and relatively rough surface. The composition of the $MgFe_2O_4$ microspheres is obtained from EDX spectrum, which is shown in Fig. 1b. The EDX spectrum of $MgFe_2O_4$ microspheres confirms the presence of Mg, Fe, C and O elements, and validates the purity of the material. To further investigate the elements distribution on the $MgFe_2O_4$ microspheres, elemental mapping characterization was carried out. Fig. 1c shows the elemental mapping spectrum of the $MgFe_2O_4$ microspheres corresponding to the region in Fig. 1a marked with a red box. The different color images shown in Fig. 1c indicate C, Fe, Mg and O-enriched areas of the sample, respectively. It is worth noting that the element of Fe and Mg are well dispersed on the surface of the $MgFe_2O_4$ microspheres.