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Research Article

Fabrication and Characterization of Manganese Ferrite Nanospheres as a Magnetic Adsorbent of Chromium

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Manganese ferrite nanospheres constructed by nanoparticles were synthesized in high yield via a general, one-step, and template-free solvothermal method. The product was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM). BJH pore-size distribution shows that the sphere-like manganese ferrite particle was a porous structure with a narrow pore-size distribution. The investigation of magnetic property of manganese ferrite nanospheres reveals that the saturation magnetization is high, which showes an excellent ability for magnetic removal of chromium in wastewater.

1. Introduction

Manganese ferrite is a kind of magnetic materials with cubic spinel structure which have been extensively used in various technological applications. The properties of manganese ferrite highly depend on the composition, morphology, and size, which are strongly connected with the preparation conditions. Up to now, various morphologies and sizes of manganese ferrite have been synthesized. For example, nanoparticles of MFe_2O_4 (M = Mn, Co, and Ni) with diameters ranging from 5 to 10 nm have been obtained through a solvothermal method [1]. Zhang et al. reported the preparation of octahedral-like $MnFe_2O_4$ crystallites fabricated using a TEA-assisted route under mild conditions [2]. A large number of high-purity $Mn_{1-x}Zn_xFe_2O_4$ nanocrystallites were synthesized and these nanocrystallites oriented aggregation to nanospheres [3]. Hollow spheres and colloidal nanocrystal clusters of $MnFe_2O_4$ with similar submicron scales have been synthesized controllably by a solvothermal method through simply adjusting the synthesis microenvironment [4].

Chromium (Cr(VI)), one of the most toxic heavy metals, is usually generated by the electroplating, metal finishing, leather tanning, dye, and textile industries. Trivalent chromium is less toxic than hexavalent chromium which is carcinogenic to living organism [5, 6]. Therefore, Cr(VI) should be removed from aqueous solution in order to protect human health. Adsorption is a simple and effective method in the removal of Cr(VI). Several kinds of materials were used as adsorbents for heavy metal ions, such as zeolite [6], active carbon [7, 8], boehmite [9], activated alumina [10], aluminum magnesium mixed hydroxide [11] and, chitosan [12]. These materials showed good performance for the removal of Cr(VI) from aqueous solutions. However, these kinds of adsorbents suffer from a common problem that it needs a next separation process from the solution, which will increase the operation cost. In order to avoid this problem, some researchers have find that magnetic materials can be a promising candidate to be easily separated from solution through a magnetic field [13, 14], which is convenient for the seperation of adsorbents from aqueous solution.

Magnetic adsorbent can provide a quick and effective route for magnetic seperation from an aqueous solution. Various applications have been carried out by using magnetic materials in environmental protection [15], catalytic chemistry [16], and drug delivery [17]. In this paper, the application of magnetic seperation technology was employed to solve environmental problem. Although nanoparticles usually showed a high surface area, the magnetic respond was low. In this case, nanospheres constructed by nanoparticles have a high surface area; at the same time, magnetization is high

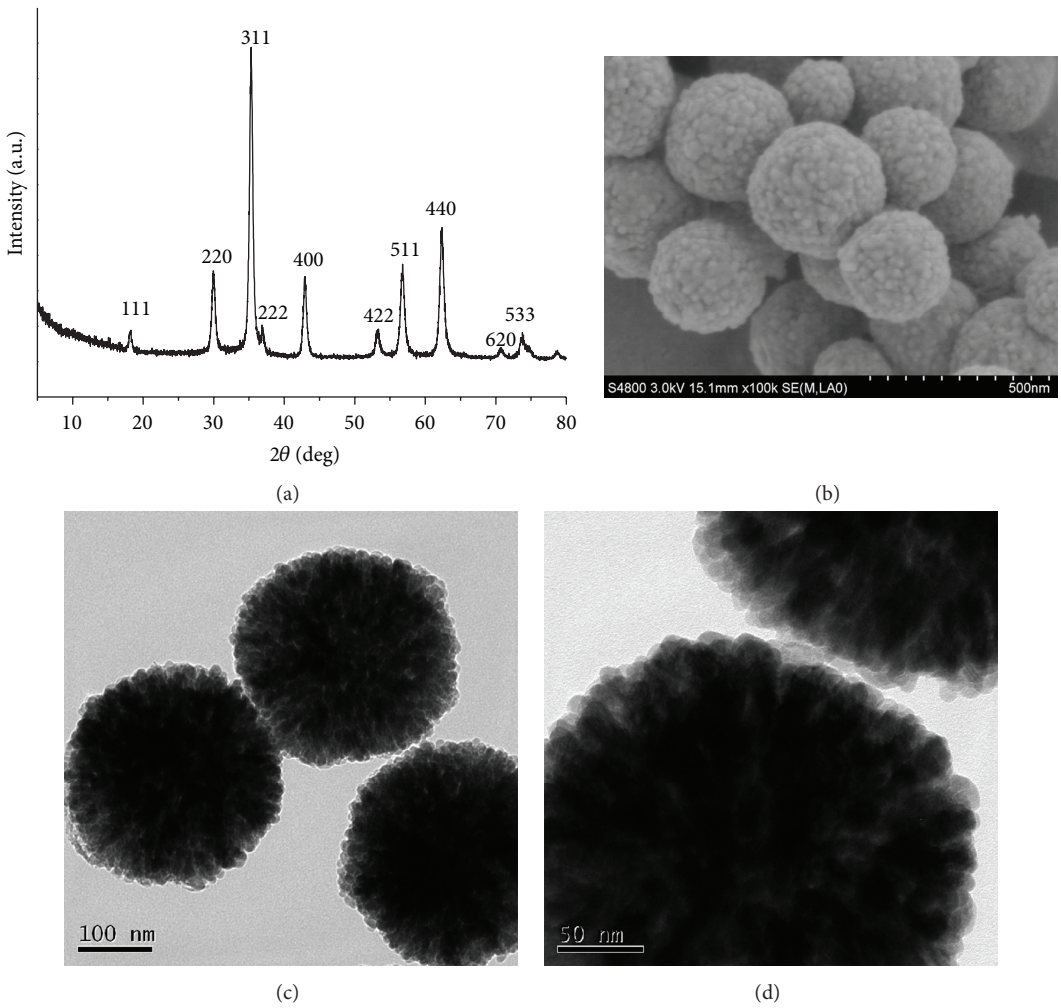


Figure 1: (a) XRD pattern, (b) SEM image, and (c)-(d) TEM images of manganese ferrite product prepared at 200°C for 24 h.

enough for separating the adsorbent from aqueous solution in a few seconds.

2. Experimental

2.1. Preparation of Manganese Ferrite Nanospheres. All reagents are analytically pure and used as-received without further purification. In a typical experiment, 4 mmol $FeCl_3 \cdot 6H_2O$ and 2 mmol $MnCl_2 \cdot 4H_2O$ were dissolved in 50 mL of ethylene glycol using magnetic stirring under room temperature. 5 mL ethanolamine was added to the above solution and followed by magnetic stirring to form a homogeneous solution. Then, this solution was transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 200°C for 24 h. After the autoclave was allowed to cool down to room temperature naturally, the solid products were collected by centrifugation, washed separately with distilled water and ethanol for several times, and then dried in an oven at 60°C before characterization and application.

2.2. Characterization. X-ray diffraction (XRD, Rigaku D/max 2500 VPC, Japan) was used to analyze the composition and crystal structure of the prepared products. The shapes of the products were characterized by transmission electron microscopy (TEM, JEM-1230, Japan) and scanning electron microscope (SEM, Hitachi S4800, Japan). N_2 adsorption and desorption isotherm was measured on a Micromeritics ASAP-2020 nitrogen adsorption apparatus (USA). Magnetic property data were collected with a quantum design physical property measurement system (PPMS). The absorption spectra of the solutions were obtained on a UNIC 7200 spectrophotometer (China).

2.3. Adsorption of Cr^{6+}. Adsorption experiments were carried out with a desk-type constant temperature oscillator (SHA-CA, China) at 25°C at a rate of 200 r/min. 0.1 g Mn ferrite adsorbent was added in 50 mL chromium(VI) solution (100 mg/L) prepared by dissolving required amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water. Chromium(VI) concentrations were measured by 1,5-diphenylcarbazide spectrophotometric method. The sorption kinetics was investigated. After shaking for various time intervals, the suspensions were separated with a magnet in a few seconds. The equilibrium concentrations of chromium

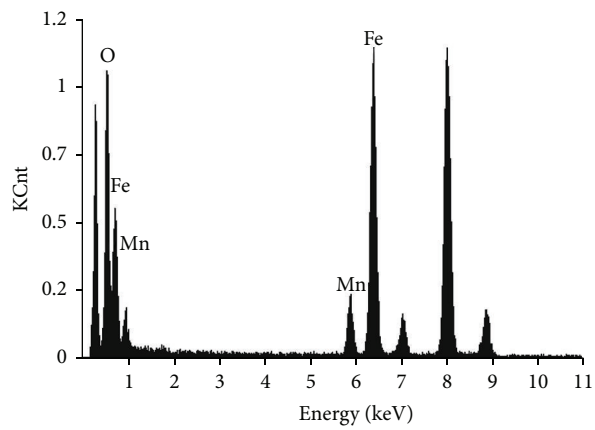


Figure 2: EDAX spectrum of manganese ferrite sample.

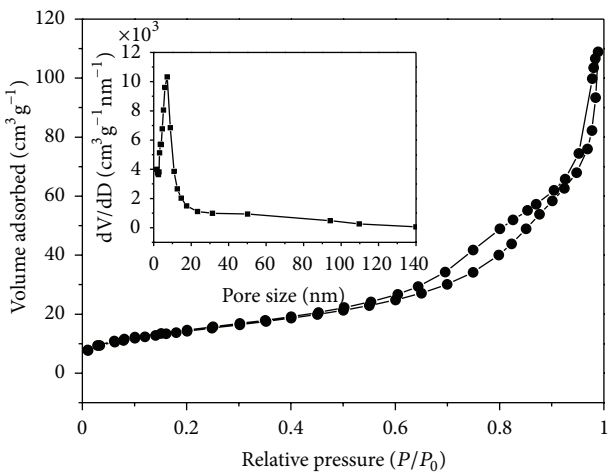
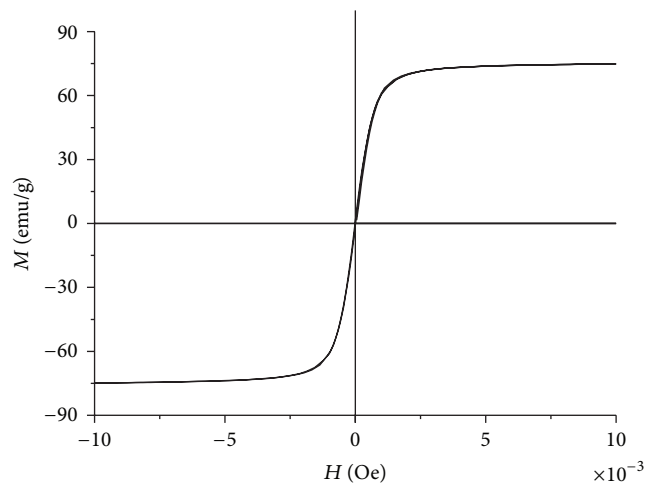
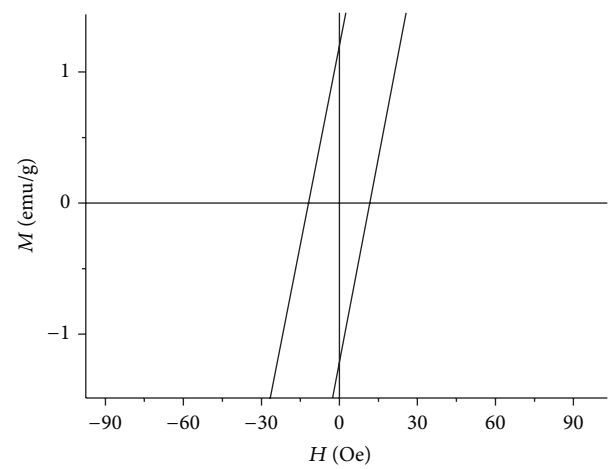


Figure 3: Nitrogen adsorption-desorption isotherms and the inset—the BJH pore-size distribution of manganese ferrite product prepared at 200°C for 24 h.



(a)



(b)

Figure 4: The magnetization hysteresis of manganese ferrite nanospheres at room temperature.

were determined at 540 nm using a 7200 spectrophotometer.

The removal percentage (R%) of chromium was calculated using the following equation:

$$(R\%) = \frac{C_i - C_e}{C_i} \times 100, \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of chromium.

3. Results and Discussion

The powder XRD pattern of the product synthesized at 200°C for 24 h using 5 mL ethanolamine is depicted in Figure 1(a). Crystalline nature can be derived from the appearance of sharp diffraction peaks in the XRD pattern prepared by the solvothermal method, which can be well indexed to a pure cubic phase of spinel manganese ferrite (JCPDS Card no. 38-0430). Morphology of the sample is studied by TEM and SEM. The SEM image of sample shows that the diameters of most of the spheres are in the range of 200–400 nm. The surface roughness demonstrates the formation of a ferrite sphere via the construction of nanoparticles (Figures 1(b) and 1(c)). Careful observation from an enlarged spheres, as shown in Figure 1(d), can further confirm the assembly of nanoparticles.

Figure 2 was the EDAX spectrum of the obtained manganese ferrite sample. The result shows that the as-prepared manganese ferrite nanospheres contained Fe, O and Mn, and no contamination element is detected. The atomic ratio of Fe : Mn is about 5.5, indicating that the chemical formula of the as-synthesized Mn ferrite is nonstoichiometric in nature.

Figure 3 shows the nitrogen adsorption-desorption isotherm and pore-size distribution curve of manganese ferrite nanospheres. Manganese ferrite nanospheres exhibit a type IV isotherm with an H3 type hysteresis loop, namely, typical hysteresis loops of mesoporous materials. Moreover, a sharp peak at 7 nm can be observed in the Barrett-Joyner-Halenda (BJH) pore-size distribution curve (the inset of Figure 3), which further demonstrates the existence of

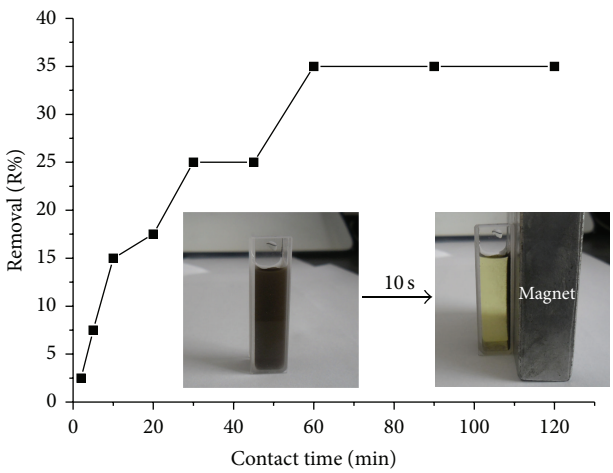


Figure 5: Effect of contact time on adsorption of chromium(VI). The inset is the photograph of seperation of manganese ferrite nanospheres from solution under an external magnetic field.

mesopores with a relatively narrow pore-size distribution. The Brunauer-Emmett-Teller-(BET-) specific surface area of manganese ferrite spheres is 52.39 m^2/g.

Figure 4 represents the magnetization curves measured at 300 K. As-prepared manganese ferrite nanospheres showed high magnetization performance. The magnetic saturation values reached 75 emu/g. As depicted in Figure 4(a), it is hard to see an obvious hysteresis loop at the full scale. In the close-up view (Figure 4(b)), the curve presents a very samll hysteresis loop with a remnant Mr of 1.2 emu/g and a coercivity Hc of 12Oe, denoting the ferromagnetic behaviour of the sample. This structural particle with high magnetization performance is supposed to be of great potential in magnetic seperation of chromium in wastewater.

The relationship between contact time and chromium adsorption onto Mn ferrite is shown in Figure 5. The adsorption increased from the beginning to 60 min, and the removal percentage increased to 35% at a contact time of 60 min. With a further increase in time, the adsorption approached to equilibrium in all the cases. The fast adsorption at the initial stage is probably due to the increased concentration gradient between the adsorbate in solution and adsorbate in adsorbent as there must be increased number of vacant sites available in the beginning. The attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of ferrite. As shown in the inset of Figure 5, manganese ferrite nanospheres were attracted toward the magnet within 10 s, demonstrating directly that manganese ferrite nanospheres could be easily separated from wastewater by applying a magnetic field.

4. Conclusion

In summary, the solvothermal method has been used to successfully synthesize manganese ferrite nanospheres with high magnetization. This approach developed a simple and efficient route to fabricate manganese ferrite nanospheres in large scale. The maximum saturation magnetization value of the product is 75 emu/g, which showed a magnetic manipulation of chromium in wastewater.

Acknowledgments

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