Preparation of amino-functionalized Fe_3O_4@$mSiO_2$ core-shell magnetic nanoparticles and their application for aqueous Fe^{3+} removal

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HIGHLIGHTS

- Magnetic core-shell Fe_3O_4@$mSiO_2$-NH_2 adsorbent was prepared and its tunable removal efficiency for Fe^{3+} was studied.
- The adsorption process follows the pseudo-second-order model and the Langmuir model.
- A two-stage adsorption process of Fe_3O_4@$mSiO_2$-NH_2 for Fe^{3+} was developed to explore the adsorption mechanism.
- Fe_3O_4@$mSiO_2$-NH_2 could be effectively regenerated after adsorption and the removal efficiency has little change.

GRAPHICAL ABSTRACT
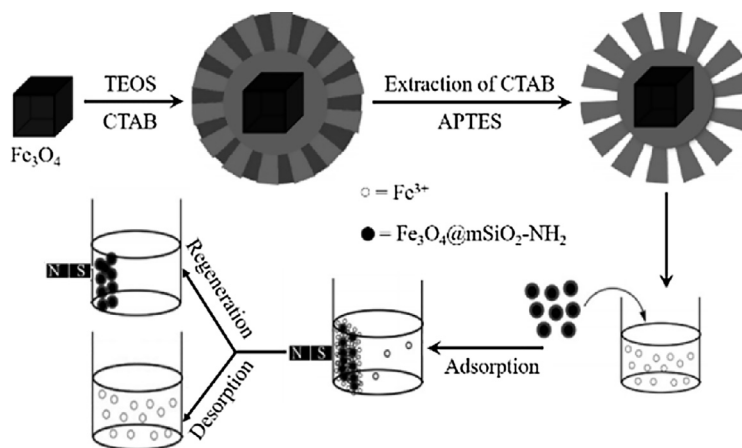
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ARTICLE INFO

ABSTRACT

Fe_3O_4 nanoparticle with magnetic properties and nanoscale features has provoked wide research interest and great potential application. Herein, a modified Stober and template-removing method was adopted to prepare magnetic mesoporous silica nanoparticles (MSNs), comprising a Fe_3O_4 core and a mesoporous silica shell. The shell was functionalized by amino-groups with tunable removal efficiency for aqueous heavy metals ions. Structural and magnetic properties were characterized by XRD, SEM, FT-IR, vibrating sample magnetometer (VSM) and BET (Brunauer-Emmertt-Teller) techniques. Also, the adsorbing efficiency for heavy metal ions was measured by UV–vis spectrometry. Results revealed that the pure magnetite is cubic with a side length of $40 − 70$ nm, while the silica-coated magnetite is spherical with a diameter of 220–260 nm. The mesoporous silica shell has an average pore size of 2.6 nm and a high surface area of $675 \text{ m}^2 \cdot \text{g}^{-1}$, which lead to a large adsorption capacity for Fe^{3+} (up to 20.66 mg of Fe per g of adsorbent). Moreover, rapid magnetic separation and regeneration of as-prepared adsorbent were achieved

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conveniently. The distinctive structure and the heavy metal ions removal property of magnetic nanocomposites reflect their prospective application in water treatment.

1. Introduction

Recently, direct discharge of trade effluents and solid waste into water has resulted in rapid elevation of heavy metals. Heavy metals not only induce severe contamination of the environment but also bring about great threats to human and aquatic organisms due to their high toxicity, hard metabolism and prone bioaccumulation. So far, many methods, including ion-exchange [1], chemical precipitation, reverse osmosis and membrane process [2], have been developed for the removal of heavy metal ions in water. However, these traditional methods still have many deficiencies such as complicated process, high cost, secondary pollution and recycling difficulty.

In view of the concept of sustainable development, the reasonable design and facile preparation of novel multifunctional adsorbents with more active sites and less secondary pollution and toxicity have become one of the most urgent issues. The emergence of adsorption materials [3] provides a better way to realize the effective removal of heavy metals due to the low cost, high efficiency and easy regeneration features of such materials. Mesoporous silica nanoparticle with high surface area and feasibility and diversity in surface modification [4] is the most appropriate adsorption material for the removal of heavy metal ions. However, mesoporous nanoparticles are difficult to be recycled in practical application because they are easy to aggregate due to the ultrafine size. To solve this problem, magnetic particles can be loaded in mesoporous particles to achieve rapid separation and recovery by magnetic separation. Current researches mainly focus on optimizing the integration of magnetic and non-magnetic materials to improve the magnetization and enhance the absorption/recovery efficiencies of such materials. Moreover, there are also existing researches on such core-shell magnetic nanoparticles as biocatalyst [5–7].

Furthermore, the removal ability of mesoporous nanoparticles for the heavy metal ions can be improved by modifying the chemical groups on the surface. The surface hydroxyl groups on the SiO_2 coating shell provide abundant reaction sites for the amino functionalization of magnetic composites by covalent interaction. Because of the strong metal chelating capability of amino groups, the functionalized mesoporous nanoparticles are more advantageous and effective in removing various types of heavy metal ions, e.g., Cu^{2+}, Co^{2+}, Pb^{2+}, Cr^{6+}, and Fe^{3+} from aqueous solutions [8–11]. Besides, the amino-functionalized adsorbents can be easily regenerated by the proton displacement of metal ions in acid treatment. The most typical magnetic adsorbents are iron oxides based materials which are susceptible to be damaged under acidic condition. Mesoporous SiO_2 could serve as a desirable shell material to protect the inner magnetite core [12–15] due to its inertness to various reaction mediums and the ability to maintain stable state under acidic condition. Therefore, the amino-functionalized mesoporous core-shell type magnetic and environmentally friendly nanoparticle (i.e., $Fe_3O_4@mSiO_2$-NH_2) without secondary pollution in the process of adsorption and regeneration is able to compensate the shortcomings of bared and organic modified nanoparticles and recently has been researched for applications of heavy metal ions removal.

In this work, the amino-functionalized magnetic composite, $Fe_3O_4@mSiO_2$-NH_2, was first prepared. Then, the heavy metal ion (Fe^{3+}) removal efficiency of this composite in aqueous solution was investigated. The adsorption capacity, adsorption kinetics and reusability of the as-prepared adsorbent were further studied in detail. The present work will be beneficial for determining the operating conditions, achieving the optimal adsorption function and understanding the adsorption mechanism.

2. Materials and experimental methods

2.1. Materials

Ion(III)acetylacetonate (97%), oleic acid (90%), benzyl ether (98%), tetraethyl orthosilicate (TEOS) (98%), acetone (99.5%), ethanol (99.9%), hexane (95%), N,N-Diisopropylethylamine (99.5%), N^1-(3-Trimethoxysilylpropyl)diethylenetriamine, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ammonium persulfate were purchased from SIGMA-ALDRICH. Cetyltrimethylammonium bromide (CTAB), ammonium hydroxide, nitric acid and potassium thiocyanate were obtained from DAEJUNG CHEMICALS & METALS CO. LTD. Hydrochloride acid was obtained from DUKSAN PURECHEMICAL CO. LTD. All chemicals were used without further purification.

2.2. Preparation of $Fe_3O_4@mSiO_2$-NH_2 nanoparticles

2.2.1. Preparation of oleic acid modified Fe_3O_4 nanoparticles
Oleic acid modified Fe_3O_4 nanoparticles were synthesized by the thermal decomposition method. In a typical synthesis protocol, the mixture of ion(III)acetylacetonate (0.002 mol), oleic acid (0.004 mol) and benzyl ether (0.054 mol) was prepared and degassed at room temperature for 15 min, and then the obtained mixture was heated to 290 °C with a heating rate of 10 °C/min under vigorous magnetic stirring and N_2 protection. Finally, the reaction mixture was kept at 290 °C for 1 h, and then cooled down to room temperature. The resultant solution was centrifuged after the addition of acetone to precipitate Fe_3O_4 nanoparticles. The obtained deposition was repeatedly rinsed for three times using hexane and magnetically recovered, then re-dispersed in chloroform.

2.2.2. Preparation of core-shell $Fe_3O_4@mSiO_2$ (MSNs)
The obtained oleic acid modified Fe_3O_4 nanoparticles were then coated with mesoporous silica through three steps. First, hydrophilic CTAB-Fe_3O_4 nanoparticles were prepared by the phase transfer process. Fe_3O_4 nanoparticles obtained in Section 2.2.1 (15 mg in 0.5 mL chloroform) were added to an aqueous CTAB solution (20 mL, 54.8 mM), then the mixture was stirred for 1.5 h to produce a homogenous microemulsion. The microemulsion was then heated to 70 °C for 30 min to evaporate the chloroform and to induce ligand exchange [16]. Second, the synthesis of the core-shell $Fe_3O_4@mSiO_2$ (MSNs) was performed via the modified Stober method [17] with CTAB serving as the soft template. As-prepared CTAB-Fe_3O_4 nanoparticles (30 mg) were added to a mixture of CTAB (0.3 g), water (80 mL) and ethanol (40 mL) and then dispersed by sonication for 1 h. Ammonium hydroxide (0.67 mL) and TEOS (1 mL) were added in sequence during the sonication process. Finally, the as-synthesized MSNs were washed three times with ethanol. The CTAB was extracted from the pores in MSNs by the solvent-extracting method and the obtained MSNs were stored in DI water.