Effect of large pore size of multifunctional mesoporous microsphere on removal of heavy metal ions

Qing Yuan\textsuperscript{a}, Nan Li\textsuperscript{b}, Yue Chi\textsuperscript{b}, Wangchang Geng\textsuperscript{c}, Wenfu Yan\textsuperscript{d}, Ying Zhao\textsuperscript{a}, Xiaotian Li\textsuperscript{b,\textsuperscript{e}}, Bin Dong\textsuperscript{a,\textsuperscript{**}}

\textsuperscript{a} Institute of Nano-photonics, School of Physics and Materials Engineering, Dalian Nationalities University, Dalian 116600, China
\textsuperscript{b} Key Laboratory of Automobile Materials of Ministry of Education, School of Material Science and Engineering, Jilin University, Changchun 130012, China
\textsuperscript{c} Key Laboratory of Space Applied Physics and Chemistry of Ministry of Education, School of Science, Northwestern Polytechnical University, Xi’an 710072, China
\textsuperscript{d} State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

\textbf{HIGHLIGHTS}

- Synthesis of Large pore size of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@meso-SiO\textsubscript{2} core–shell microspheres.
- Large pore size of the microspheres is propitious to graft much more amino groups.
- Good adsorptive capability of the amino-functionalized Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@meso-SiO\textsubscript{2}.
- Magnetically recoverable property of the amino-functionalized Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@meso-SiO\textsubscript{2}.
- The multifunctional mesoporous microspheres can be regenerated by acid treatment.

\textbf{GRAPHICAL ABSTRACT}

A novel multifunctional microsphere with a large pore size mesoporous silica shell (ca. 10.3 nm) and a magnetic core (Fe3O4) has been successfully synthesized via a facile two-step sol–gel method. In the synthesis process, CTAB was first dissolved in water to form spherical micelles, then added to the mixture in which Fe3O4@SiO2 was dispersed in ethanol, next dropping TEOS to form Fe3O4@SiO2@CTAB/SiO2 composites. This approach helps to form mesoporous silica shell with a large pore size, which is propitious to the modification of much more amino groups in order to enhance the adsorption capacity of heavy metal ions. The metal-loaded multifunctional microspheres can be easily removed from aqueous solution by magnetic separation and regenerated easily by acid treatment.

\textbf{ABSTRACT}

Pore size of mesoporous materials is crucial for their surface grafting. This article develops a novel multifunctional microsphere with a large pore size mesoporous silica shell (ca. 10.3 nm) and a magnetic core (Fe3O4), which is fabricated using cetyltrimethylammonium bromide (CTAB) as pore-forming agents, tetraethyl orthosilicate (TEOS) as silicon source through a sol–gel process. Compared with small pore size mesoporous silica magnetic microspheres (ca. 2–4 nm), the large pore size one can graft 447 mg/g amino groups in order to adsorb more heavy metal ions (Pb\textsuperscript{2+}: 880.6 mg/g, Cu\textsuperscript{2+}: 628.3 mg/g, Cd\textsuperscript{2+}: 492.4 mg/g). The metal-loaded multifunctional microspheres could be easily removed from aqueous solution by magnetic separation and regenerated easily by acid treatment. The results suggest that the large pore size multifunctional microspheres are potentially useful materials for high effectively adsorbing and removing different heavy metal ions in aqueous solution.

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* Corresponding author. Tel.: +86 431 85168445; fax: +86 431 85168444.
** Corresponding author. Tel.: +86 411 87556959; fax: +86 411 87556959.
E-mail addresses: xiaotianli@jlju.edu.cn (X. Li), dong@dlnu.edu.cn (B. Dong).

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1. Introduction

Heavy metal pollution in water has attracted much attention due to its harmful influence on human life [1,2]. Therefore, the removal of heavy metal ions in wastewater is becoming increasingly important. Until now, various kinds of physical and chemical methods such as ion exchange [3], adsorption [4-5], chemical precipitation [6], reverse osmosis [7] and membrane process [8], etc. have been employed for separation of heavy metal ions from wastewater. Among the available methods, adsorption technology is the most promising and frequently used technique due to its simplicity, high efficiency, and low cost.

Since the discovery of M41S silica in 1992, mesoporous materials, due to their high surface areas, well-defined pore size, and tunable pore sizes, have been widely used in the field of adsorption of heavy metal ions [9-12]. In addition, magnetic particles can be easily removed from the reaction system by an external magnetic field. If the mesoporous structure and magnetic properties can be combined together, prepared nano-complexes with high specific surface area and the ability of magnetic recovery will be a major leap forward for practical application. So far, a number of articles have reported the synthesis of magnetic mesoporous silica microspheres [13-18]. For the adsorption of heavy metal ions like Hg2+, Pb2+, Cu2+, Cd2+, and so on, unmodified mesoporous silica materials have a little adsorption capacity [9-12]. At present, there are several kinds of modified methods. One is thiol-functionalized, which exhibited a high complexation affinity for Hg2+ [17,19,20], however, for Cu2+, Ni2+, Zn2+, and Cd2+, the amino-functionalized worked [21-24]. In this paper, we prepared a kind of novel Fe3O4@SiO2@meso-SiO2 microspheres. This sample has a larger pore size than that reported in the latest literatures [13-18], and the effect of pore size of the synthesized microspheres on the capability of heavy metal ions removal has been discussed.

2. Experimental

2.1. Chemicals

(3-aminopropyl)trimethoxysilane (APTMS) and Cetyltrimethylammonium bromide (CTAB) were purchased from Sigma–Aldrich. Other chemicals were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd. All chemicals were directly used as received without any further purification.

2.2. Methods

2.2.1. Synthesis of Fe3O4 microspheres

The magnetic particles were synthesized through a solvothermal reaction according to the method reported by Zhao et al. [25] with some modification. In a typical procedure, 1.08 g of FeCl3·6H2O was first dissolved in 20 mL of ethylene glycol under magnetic stirring until the solution became clear. Then 1.8 g of NaAc was added to this solution and stirred for another 1 h. Afterwards, 0.25 g trisodium citrate was added. When the mixed solution was stirred for 5 h to form a homogeneous dispersion, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL. The autoclave was sealed and heated at 200 °C for 10 h and naturally cooled to room temperature. The black particles were collected with the help of a magnet, followed by washing with ethanol and deionized water several times, and then dried under vacuum at 60 °C overnight for further use.

2.2.2. Synthesis of Fe3O4@SiO2 microspheres

The interlayer of SiO2 was prepared through a simple sol–gel process [26]. Briefly, 0.1 g as-prepared Fe3O4 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. To the solution, 0.4 mL of tetraethyl orthosilicate (TEOS) was added dropwise. After stirring for 6 h, the products were collected and washed with ethanol and deionized water, and finally dried under vacuum at 60 °C for 8 h.

2.2.3. Synthesis of Fe3O4@SiO2@meso-SiO2 microspheres

0.1 g as-prepared Fe3O4@SiO2 particles were first evenly dispersed in 60 mL ethanol by ultrasonication, and then added 1.2 mL concentrated ammonia solution (28 wt%) to form solution A. Next, 0.3 g CTAB was dispersed in 80 mL H2O under constant magnetic stirring to form solution B. Afterwards, solution B was mixed with solution A under vigorous stirring for 6 h. To the solution, 0.43 mL of 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. The products obtained are referred to as Fe3O4@SiO2@meso-SiO2–R1 sample. For comparison, in the step of synthesis of Fe3O4@SiO2@CTAB@SiO2 microspheres, CTAB was directly added to the Fe3O4@SiO2 solution rather than dissolved in water to form spherical micelles in order to prepare mesoporous SiO2 complex with the channel perpendicular to the magnetic nuclear surface named as Fe3O4@SiO2@meso-SiO2–R2 sample.

2.2.4. Synthesis of amino-functionalized Fe3O4@SiO2@meso-SiO2 microspheres

0.2 g as-made Fe3O4@SiO2@meso-SiO2 particles were dispersed in 50 mL toluene by ultrasonication, and then dropping 4 mL 3-aminopropyltrimethoxysilane (APTMS). The mixture was refluxed at 110 °C with continuous stirring for 24 h. The resulting functionalized Fe3O4@SiO2@meso-SiO2 composites were recovered by a magnet followed by washing with ethanol and acetone several times and then dried at 60 °C under vacuum for 12 h. The products obtained are referred to as Fe3O4@SiO2@meso-SiO2–NH2 samples.

2.3. Characterizations

The size and morphology of the products were characterized by a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance Diffractometer with CuKα radiation (λ = 1.5418 Å). The porosity of the products was measured at 77 K by the nitrogen adsorption–desorption isotherm and BJH methods on a Micromeritics ASAP 2020 M volumetric adsorption analyzer. Infrared (IR) spectra were taken on a Perkin–Elmer series with a resolution of 4 cm−1. The −NH2 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).

2.4. Adsorption equilibrium experiments

In order to test the heavy metal ions removal ability of the synthesized adsorbent, a set of adsorption experiments was carried out by stirring 50 mg of Fe3O4@SiO2@meso-SiO2–NH2 samples in 50 mL of a single metal ions solution for 2 h at room temperature. The aqueous systems selected were Pb2+, Cu2+ and Cd2+, and the metal salts used were nitrates in all cases. The initial concentration of the
heavy metal ions is varied from 20 mg/L to 1200 mg/L. When the adsorption process reached equilibrium, the adsorbent was separated using a magnet and the supernatant was collected. The final metal concentration was determined by atomic absorption spectroscopy (AAS). The equilibrium adsorption capacity of adsorbent was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e) \times V}{M} \]  

(1)

where \( q_e \) is the equilibrium adsorption capacity of adsorbent (mg/g), \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of the adsorbates (mg/L), \( M \) is the mass of adsorbent (g), and \( V \) is the volume of the metal ions solution (L).

2.5. Adsorption Isotherm models

In order to optimize the usage of adsorbents, it is important to establish the most appropriate isotherm. In our work, two isotherm models were tested.

The Langmuir model [27] is the most widely used two-parameter equation. It is assumed that adsorption takes place at specific homogeneous sites within the adsorbent as well as monolayer sorption, and each site can accommodate only one molecule or atom. The saturated adsorption capacity can be represented by the following expression:

\[ q_e = \frac{K_L \cdot C_e}{1 + a_L \cdot C_e} \]  

(2)

where \( q_e \) is the solid-phase adsorbate concentration at equilibrium (mg/g), \( C_e \) is the adsorbate concentration in the aqueous phase at equilibrium (mg/L), \( K_L \) (L/g) and \( a_L \) (L/mg) are the Langmuir isotherm parameters.

The Freundlich equation [28] can be applied to nonideal sorption on heterogeneous surfaces as well as multi-layer sorption and is expressed by the following equation:

\[ q_e = K_F \cdot C_e^n \]  

(3)

where \( q_e \) is the solid-phase adsorbate concentration at equilibrium (mg/g), \( C_e \) is the adsorbate concentration in the aqueous phase at equilibrium (mg/L), \( K_F \) (L/g) is the Freundlich parameter and \( n_F \) is the heterogeneity factor.

2.6. Adsorption kinetics

In order to study the effect of contact time, the adsorbed amount of heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}) versus time on the synthesized multifunctional microspheres was investigated and the initial metal ion concentration was all selected as 400 mg/L. A weighed adsorbent 50 mg was mixed with 50 mL pollutant solution. The suspension was shaken for different periods of time (from 0 to 120 min). Every five minutes, sample was taken and the concentration of metal ions in solution was measured after centrifugation by AAS. The adsorption ability of adsorbent at time t, \( q_t \) (mg/g), was calculated by the following equation:

\[ q_t = \frac{(C_0 - C_t) \times V}{M} \]  

(4)

where \( C_0 \) and \( C_t \) (mg/L) are the concentrations of adsorbates initially and at time t, respectively. \( M \) is the mass of adsorbent (g) and \( V \) is the volume of the adsorbate (L).

To analyze the adsorption rate of copper ions, two common kinetic models: the pseudo-first-order and pseudo-second-order equations were investigated, respectively.

The pseudo-first-order kinetic model is given in the lineal form as [29]:

\[ \ln(q_e - q_t) = \ln q_e - k_1t \]  

(5)

where \( q_e \) and \( q_t \) are the adsorbed amounts of metal ions at equilibrium and at time t, respectively, expressed as mg/g; \( k_1 \) is the rate constant of pseudo-first-order adsorption, expressed as min^{-1}.

The pseudo-second-order kinetic model is given in the lineal form as [30]:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(6)

where \( k_2 \) is the rate constant of second-order adsorption, expressed as g mg^{-1} min^{-1}. Experimental data were entered into Eqs. (5) and (6), which model is more close to fit the experimental data, the one is the kinetic model of our adsorption process.

2.7. Effect of solution pH

A sample of Fe3O4@SiO2@meso-SiO2-NH2 (50 mg) was added to 50 mL of 400 mg/L each heavy metal ion solution at different pH value varied from 2 to 8 using 1 M HCl or NaOH. These samples were stirred for 2 h, and then adsorbents were removed by a magnet. The supernatant was also tested by AAS. The percent of removed metal ions by adsorbent was calculated by the following equation:

\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]  

(7)

where R is the removal efficiency of the metal ions, \( C_0 \) and \( C_e \) is the initial and equilibrium concentration of the adsorbate (mg/L), respectively.

3. Results and discussions

3.1. Characterization of the multifunctional mesoporous microspheres

3.1.1. Morphology analysis

The synthetic strategy is designed and presented in Scheme 1. Fig. 1 shows the SEM and TEM images of the Fe3O4@SiO2@meso-SiO2 and Fe3O4@SiO2@meso-SiO2-NH2 composites. As seen in Fig. 1 (a, d), two kinds of Fe3O4@SiO2@meso-SiO2 particles both possess monodispersed spherical morphology with a uniform particle size distribution of ca. 470 nm. TEM of Fe3O4@SiO2@meso-SiO2-R1 sample shown in Fig. 1b clearly exhibits Fe3O4 core (average
diameter of ca. 190 nm), SiO₂ intermediate layer (mean thickness of ca. 45 nm) and a spherical pore morphology mesoporous SiO₂ shell (mean thickness of ca. 95 nm). Fe₃O₄@SiO₂@meso-SiO₂-R₂ sample (Fig. 1e) has the same hierarchical structure as Fe₃O₄@SiO₂@meso-SiO₂-R₁. However, the channel of the mesoporous SiO₂ shell existed in Fe₃O₄@SiO₂@meso-SiO₂-R₂ is perpendicular to the magnetic nuclear surface as shown in the inset of Fig. 1e. Under the same magnification as shown in Fig. 1b and Fig. 1e, we can easily conclude that the pore size of Fe₃O₄@SiO₂@meso-SiO₂-R₁ microparticle is much larger than that of Fe₃O₄@SiO₂@meso-SiO₂-R₂. When the two kinds of Fe₃O₄@SiO₂@meso-SiO₂ microspheres were modified with amino groups, the morphology of the microparticles was not changed and the mesoporous structure still existed as seen in Fig. 1(c and f). Large pore size is very beneficial for the surface modification of materials. Also the pore structure of silica shell may create large surface area and provide the opportunity to adsorb heavy metal ions.

3.1.2. Porosity and Pore size

Low-angle XRD patterns of the two kinds of Fe₃O₄@SiO₂@meso-SiO₂ microspheres before and after amino-modified all exhibit a single and strong diffraction peak between 2θ=2° and 3° as seen in Fig. 2A, indicating the presence of mesostructure. Compared with Fe₃O₄@SiO₂@meso-SiO₂-R₁ (a), the diffraction peak of Fe₃O₄@SiO₂@meso-SiO₂-R₂ (c) shifts to higher angle, illustrating that the pore size of Fe₃O₄@SiO₂@meso-SiO₂-R₁ is larger than that of Fe₃O₄@SiO₂@meso-SiO₂-R₂. Due to the grafting of amino groups, the diffraction peaks of Fe₃O₄@SiO₂@meso-SiO₂-NH₂ (b, d) also shift to higher angle and become weaker compared with that of unmodified ones (a, c). N₂ adsorption-desorption isotherms (Fig. 2B) of the four samples show representative type-IV curves with H₁-type hysteresis loops, suggesting well-uniform mesopores. The pore size distributions as shown in Fig. 2C clearly confirm a narrow curve. From the structural data of the four samples as seen in Table 1, all the values of the amino-modified microparticles are lower than that of the unmodified ones. This is probably due to the introduction of the amino-group, which is in consonance with the results obtained from the XRD analysis.

3.1.3. IR spectra

FTIR measurements were performed for Fe₃O₄@SiO₂@meso-SiO₂-R₁ and Fe₃O₄@SiO₂@meso-SiO₂-R₁-NH₂ samples as shown

![Scheme 1. Synthesis route of Fe₃O₄@SiO₂@meso-SiO₂-R₁-NH₂ microsphere and its use for heavy metal ions removal.](image)

![Fig. 2. XRD (A), N₂ adsorption-desorption isotherms (B) and the pore size distributions (C) of the Fe₃O₄@SiO₂@meso-SiO₂-R₁ (a), Fe₃O₄@SiO₂@meso-SiO₂-R₁-NH₂ (b), Fe₃O₄@SiO₂@meso-SiO₂-R₂ (c) and Fe₃O₄@SiO₂@meso-SiO₂-R₂-NH₂ (d) microspheres.](image)

**Table 1**

<table>
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<tr>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>BET surface area (m²/g)</th>
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<td>3.8</td>
<td>0.35</td>
<td>283</td>
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<td>2.3</td>
<td>0.29</td>
<td>365</td>
<td>[14]</td>
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<td>2.1</td>
<td>0.29</td>
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<td>[15]</td>
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<td>[16]</td>
</tr>
<tr>
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<td>1.20</td>
<td>882</td>
<td>[17]</td>
</tr>
<tr>
<td>2.5</td>
<td>0.66</td>
<td>913</td>
<td>[18]</td>
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<tr>
<td>2.2</td>
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<td>0.51</td>
<td>365</td>
<td>Fe₃O₄@SiO₂@meso-SiO₂-R₁-NH₂ (This work)</td>
</tr>
</tbody>
</table>
in Fig. 3. All spectra present the typical Si—O—Si bands of the inorganic framework: symmetric vibration modes around 800 cm$^{-1}$ and asymmetric stretching vibration around 1080–1100 cm$^{-1}$ [31]. The absorption peak of the Si—OH bands at 960 cm$^{-1}$ in Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$ turns into a shoulder upon functionalization, indicating that the aminosilane groups are substituting surface silanols. The presence of organic groups is confirmed by the CH$_2$ or CTAB templates around 2800–3000 cm$^{-1}$ region, broad N—H stretching bands superimposed to those of water, in the 3000–3500 cm$^{-1}$ range [32]. The observed bands at 1635, 1560 cm$^{-1}$ are ascribed to the $\delta$OH of adsorbed water and $\delta$N—H of free or protonated amino groups, respectively [33]. The presence of large N—H vibrations is typical of N-containing species with a strong H-bonding interaction with the pore surface [34,35]. Amino groups are equilibrated with ammonium-silanolate pairs, as demonstrated by the presence of the bending bands of the protonated and unprotonated species [36]. All these results show that amino groups have been successfully grafted to the pore surface of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$ microspheres. As shown in Table 1, compared with other synthesized magnetic mesoporous microspheres [13–18], our sample has a high surface area and pore volume which makes it adsorb enough APTMS, a larger pore size which enhances the loading of amino groups [37]. In our work as shown in Table 1, the pore volume and surface area of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 are quite close to these of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R2 sample, but the pore size of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 is much larger than that of Fe3O4@SiO2@meso-SiO2—R2. According to the CHNS elemental analysis, the determined −NH$_2$ loading is ca. 447 mg/g for Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 and for Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R2 is ca. 129 mg/g.

3.1.4. Magnetic property

Magnetization curves of the Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 and Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres exhibit near-zero coercivity and remanence, suggesting a superparamagnetic nature as shown in Fig. 4. The saturation magnetization strength of them is 38.7 and 35.6 emu/g, respectively. It should be noted that although the magnetization saturation value of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ is lower than that of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 due to the grafting of amino-group, it still shows strong magnetization, which suggests its suitability for magnetic separation and targeting [38]. Upon placement of a magnet beside the vial, Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres were quickly attracted to the side of the vial within 60 s, leaving the solution transparent (Fig. 4, inset), and the particles can be well redispersed again by shaking or ultrasonic vibrating.

3.2. Adsorption studies of the multifunctional mesoporous microspheres

3.2.1. Adsorption isotherms for different heavy metal ions

First, Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ sample was used as an adsorbent to assess its adsorption capacity toward different heavy metal ions of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$. Fig. 5 displayed the adsorption isotherms of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ on the Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres under varied initial metal ions concentration, respectively. As shown in this figure, the equilibrium adsorption amount depended on the heavy metal ion concentration at equilibrium, and gradually increased with the equilibrium concentration increased. The maximum adsorption capacity for Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ was 880.6, 628.3 and 492.4 mg/g, respectively, which is much higher than that reported in literature [39–45] as compared in Table 2. From the reported literatures [12,21–24], we know that the removal of heavy metal ions is derived from the complexation between the metal ions and surface amino groups. The more amino groups the mesoporous materials

![Fig. 3](image3.png) IR spectra of (a) Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 and (b) Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres.

![Fig. 4](image4.png) The magnetic hysteresis loop of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1 and Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres at room temperature. The inset is the separation process of the Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres by a magnet.

![Fig. 5](image5.png) Adsorption isotherm of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$—R1-NH$_2$ microspheres toward different heavy metal ions.
Table 2
Comparison of adsorption capacity (mg/g) for Pb2+, Cu2+, Cd2+ on Fe3O4@SiO2@meso-SiO2-NH2 microsphere with other magnetic absorbents.

<table>
<thead>
<tr>
<th>Magnetic adsorbent</th>
<th>Adsorption capacities (mg/g)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Amino-functionalized Fe3O4@SiO2 magnetic nanomaterial</td>
<td>Pb2+: 76.7</td>
<td>[39]</td>
</tr>
<tr>
<td>Magnetic Fe3O4 baker’s yeast biomass</td>
<td>Cu2+: 29.9</td>
<td>[40]</td>
</tr>
<tr>
<td>Fe3O4-SiO2-polyl(1,2-diaminobenzene) sub-micron particles</td>
<td>Cd2+: 22.5</td>
<td>[41]</td>
</tr>
<tr>
<td>Xanthate-modified magnetic chitosan</td>
<td>Pb2+: 88.2</td>
<td>[42]</td>
</tr>
<tr>
<td>Magnetic porous ferropinol MnFe3O4</td>
<td>Cu2+: 40.7</td>
<td>[43]</td>
</tr>
<tr>
<td>Pectin–iron oxide magnetic nanocomposite adsorbent</td>
<td>Pb2+: 65</td>
<td>[44]</td>
</tr>
<tr>
<td>Amine-functionalized Fe3O4 nanoparticles</td>
<td>Pb2+: 76.9</td>
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<td>Cu2+: 34.5</td>
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<td>Pb2+: 69</td>
<td>This work</td>
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</table>

3.2.2. Adsorption kinetics for different heavy metal ions

Fig. 6 shows the adsorption kinetics of Fe3O4@SiO2@meso-SiO2-R1-NH2 microspheres toward Pb2+, Cu2+, and Cd2+ at room temperature, respectively. As seen in Fig. 6a, the adsorption equilibrium of every heavy metal ion was almost attained within ca. 30 min accompanied by a two-stage kinetic behavior: the initial rapid adsorption within the first 10 min and a second stage with a much lower adsorption rate during 10–30 min. This can be related to the large number of vacant mesopore-grafted amino sites which are available for adsorption of heavy metal ion during the initial adsorption stage. After that, heavy metal ions have to traverse father and deeper into the micropores encountering much larger resistance, which results in slowing down the adsorption rate [46]. The results show that most of the Pb2+, Cu2+, and Cd2+ can be removed within 30 min at which the adsorption amount qt calculated by Eq. (4) is 395.1, 379.5 and 363.5 mg/g, respectively, and after this period, the concentration of the supernatant levels off and the uptake of the heavy metal ion remains almost unchanged with the increasing contact time, which indicates that all adsorption sites have been almost saturated. The adsorption kinetic data were processed to explore the possibility of intra-particle diffusion using the Weber–Morris equation [47]:

\[ q_t = k_d t^{1/2} + c \]  

where \( k_d \) is the rate constant of intra-particle diffusion and \( c \) is the film thickness. If the experimental data fit the linear behavior of Eq. (8), it can be concluded that the adsorption process is controlled by intra-particle diffusion only. If the deviation exists, it suggests that two or more steps influence the whole adsorption process. As seen in Fig. 6b, the plot of \( q_t \) versus \( t^{1/2} \) is not linear over the whole time range, indicating that the adsorption is at least a two-step process. The first step is the intra-particle diffusion and the second one can be attributed to the pore diffusion.

The kinetic experimental data have been further tested by the pseudo-first-order and pseudo-second-order models describing by Eqs. (5) and (6), respectively shown in Fig. S2 and the corresponding kinetic adsorption parameters are exhibited in Table 4. As seen in Table 3, compared with the correlation coefficient \( R^2 \) of the pseudo-first-order model, the value of \( R^2 \) of the pseudo-second-order model is more closed to 1, suggesting that the adsorption process can be accurately described by the pseudo-second-order model.
model, which implied that the heavy metal ions adsorption onto Fe3O4@SiO2@meso-SiO2-R1-NH2 microspheres may take place through a chemical process involving valence forces through sharing or exchange of electrons [48].

3.2.3. Effect of pH and Regeneration

The initial solution pH is an important factor affecting the adsorption of heavy metal ions. The pH of every kind of the heavy metal ions solution was measured around 6.2 and the percentage of removed heavy metal ions R reached to ca. 98.8%, 94.9% and 90.9% for Pb2+, Cu2+, and Cd2+ as shown in Fig. 7a. When the pH decreased from 6 to 2 adjusted by 1 M HCl, all the values of R for the three kinds of heavy metal ions dropped sharply. When the pH increased from 6 to 8 adjusted by 1 M NaOH, all the values of R increased slightly. The results show that the adsorption capacity of Fe3O4@SiO2@meso-SiO2-R1-NH2 microspheres toward the heavy metal ions is strong under the near-neutral circumstance and poor under the strong acidic circumstance. This is really because that the modified amino groups are protonated at low pH, passivating adsorption sites and hence suppressing metal adsorption [49–51]. So neutral and slightly alkaline conditions are favorable for Pb2+, Cu2+, and Cd2+ adsorption, in which the aminofunctionalized Fe3O4@SiO2@meso-SiO2-R1 microspheres showed exceptional binding ability toward them. Based on the above analysis, we adopted the method of acid treatment to regenerate our adsorbent. The used Fe3O4@SiO2@meso-SiO2-R1-NH2 microspheres were put into 1 M HCl solution shaking by ultrasonication for 1 h, then washed with deionized water several times in order to reuse in the next cycle. Fig. 7b showed the five cycles of the same adsorbent for Pb2+, Cu2+, and Cd2+. As can be seen, although the percentage of each metal ion removal may drop slightly during every cycle, it still maintained a high adsorption capacity, indicating that the Fe3O4@SiO2@meso-SiO2-R1-NH2 microsphere possess excellent chemical stability and reusability. Plus it has the feature of magnetic recovery. All these make the Fe3O4@SiO2@meso-SiO2-R1-NH2 microsphere can be used as a good performance adsorbent applied in the field of heavy metal ions removal.

4. Conclusions

In summary, a novel multifunctional mesoporous sphere was successfully fabricated. The sphere has a core–shell structure with a magnetic Fe3O4 core, a non-porous silica interlayer and a mesoporous silica shell with a large pore size ca. 10.3 nm. Compared
with small pore size mesoporous silica magnetic microspheres (ca. 2–4 nm), the large pore size ones can graft much more amino groups in order to adsorb more heavy metal ions (Pb²⁺, Cu²⁺, Cd²⁺). The adsorption process on the grafted large pore size microspheres was well described by the Langmuir model, and the equilibrium can be almost attained within ca. 30 min. After acid treatment, the as-synthesized adsorbent can be regenerated and reused in the next cycle with good chemical stability. The magnetism possessed by the adsorbent make it removed easily from the reaction system. Therefore, the large pore size microspheres can be applied as an excellent performance adsorbent in the field of heavy metal ions removal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.11561/j.jzhazmat.2013.03.035.

References


