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Synthesis of functionalized mesoporous silica and its application for Cu(II) removal

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ABSTRACT

The amine-grafted and mercapto-grafted SBA-15 mesoporous silica were synthesized successfully via hydrothermal method. These functionalized mesoporous silica were prepared by direct co-condensation and post-synthesis grafting processes and then used as adsorbents to remove the Cu^{2+} from the simulated water. The obtained mesoporous adsorbent was characterized by X-ray diffraction, nitrogen adsorption–desorption analysis, Fourier transform infrared spectroscopy, transmission electron microscopy, and scanning electron microscopy. The experimental results showed that mesoporous materials can be grafted functional groups successfully without significant change of the hexagonal mesostructure after the functionalization process, but the adsorption capacity of copper ions was greatly enhanced and the adsorption amount was up to 99.68%. Compared with post-synthesis grafting processes, because the direct co-condensation templating agent was not completely removed which affects the adsorption capacity. It was demonstrated that the functionalized mesoporous silica could be used as a promising adsorbent for removing and recovering heavy metal ions in water.

Keywords: Functionalized; Mesoporous silica; Adsorbent; Heavy metal ions

1. Introduction

As a result of industrial activities, heavy metal ions have been continuously emitted into the environment caused severe problems to the environment and human health because they are usually toxic and very reactive with proteins [1–5]. The Cu^{2+} is one of the toxic heavy metal ions and is normally produced by electroplating, smelting, and alloy manufacturing industries. Cu^{2+} will be accumulated in the liver and lead to liver toxicity up to a certain amount by excessive intake of Cu^{2+} to the human body. Traditional methods for Cu^{2+} removal from wastewater include chemical precipitation, ion exchange, liquid membrane, electrolysis, and adsorption using activated carbon. However, all these methods are often ineffective or costly, especially for removing heavy metal ions from dilute solutions [6].

SBA-15 is one of the mesoporous molecular sieves with ordered pore distribution, high surface area, and pore volume [7]. It has controllable structure and composition which makes it suitable for a wide range of application in adsorption [8]. However, the adsorption capacity of the SBA-15 is low and the high density of

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silanol groups on the pore wall is beneficial to the introduction of functional groups [9]. Therefore, the chemical modification of these materials has been documented as an effective method to improve their natural adsorption capacity.

The functionalization method of synthesis of novel absorbent would affect adsorption capacity which has been scarcely reported. In this study, functionalized mesoporous silicas which were used as adsorbent for Cu^{2+} removal have been conducted comparative studied on synthesis methods and functional reagents. The effect of contact time in affecting the sorption onto the mesoporous silica has also been investigated.

2. Experimental

2.1. Reagents and materials

All chemical reagents used in this study are of analytical grade and purchased from Guoyao Chemical Reagent Co., Ltd, except MPTMS (3-mercaptopropyltrimethoxysilane) and APTES (3-aminopropyltriethoxysilane) which were purchased from Wuhan University Silicone New Material Co., Ltd (Hubei, China). Nitrate copper was used to prepare the metal ion solutions. No further pH adjustments of these solutions were made.

2.2. Synthesis of functionalized mesoporous silica

A typical synthetic procedure used to obtain mesoporous silica SBA-15 from TEOS (tetraethyl orthosilicate), P123 (triblock copolymer, $EO_{20}PO_{70}EO_{20}$, Mav = 5,800), HCl, H_2O, and ethanol in relative ratios. After 8.07 g P123 was dissolved in 200 mL deionized water. 41.7 mL concentrated hydrochloric acid was added and vigorously stirred at 40℃ for 1 h. Then, 18.32 mL TEOS was slowly added and stirred at 40℃ for further 1 h. Then 1.72 mL MPTMS (3-mercaptopropyl trimethoxy silane) or 1.70 mL APTES (3-aminopropyl triethoxysilane) was added and vigorously stirred at 40℃ for another further 20 h. After reaction, the produced mixtures were transferred into a beaker and static crystallization aged at room temperature for 2 days. After recovered by filtration, the solid product was refluxed in ethanol (200 mL ethanol per 1.5 g solid produce) for 6 h at 65℃ to extract the surfactant templates. The powder was collected by filtration, washed with deionized water, and dried at 80℃. The produced amine-grafted or mercapto-grafted mesoporous silica materials were named as SBA-N-1 and SBA-SH-1 corresponding to organic chains containing amino and mercapto functional groups, respectively. In a typical synthesis procedure which described above was followed, 3 g SBA was dispersed in the mixture of 90 mL ethanol and 9 mL MPTMS or APTES. The mixture was stirred and refluxed under 80℃ for 6 h. The powder was collected by filtration, washed with deionized water, and dried at 80℃. The amine-grafted and mercapto-grafted mesoporous silica materials were denoted as SBA-N-2 and SBA-SH-2, respectively. The standard mesoporous silica was denoted as SBA.

2.3. Characterization

The X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (HZG41B-PC) using Cu Kα radiation at a scan rate of $0.05^\circ\ 2\theta s^{-1}$. The Brunauer–Emmett–Teller (BET) specific surface areas (SBET) and porous structures of the samples were characterized using a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). Specific surface area was determined by applying the BET equation to the isotherm. Mesopore size distribution was calculated using the adsorption branch of the isotherm and the Barrett–Joyner–Halenda (BJH) formula. Scanning electron microscopy (SEM) was performed by an S-4800 Field Emission SEM (FESEM, Hitachi, Japan) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was tested using a JEM-2100F electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectrum of KBr powder-pressed pellets was collected by a Shimadzu IRAffinity-1 FTIR spectrometer in the frequency range of 4,000–500 cm^{-1}.

2.4. Preparation of Cu^{2+} metal ion solutions and adsorption analysis studies

0.5 mmol L^{-1} of Cu^{2+} stock solution was prepared by dissolving nitrate copper in distilled water. Batch process was employed to study the adsorption of Cu^{2+} from aqueous solutions onto the mesoporous silica. Standard and blank solution was prepared and treated in the same way as the functionalized silica. Adsorption experiments were done in three replicates. The uptake of Cu^{2+} by the mesoporous silica was calculated from the differences between the initial amount in the loaded sample and that remaining in the eluate. To study the effect of contact time factor, the adsorbent (SBA-N-1, SBA-N-2, SBA-S-1, or SBA-S-2) was added to 100 mL Cu^{2+} solutions at the same temperature, respectively. After reaching the equilibrium, the mixtures were filtered through Whatman No. 50 filter papers, and the concentration of the remaining heavy metal ions was determined by flame atomic

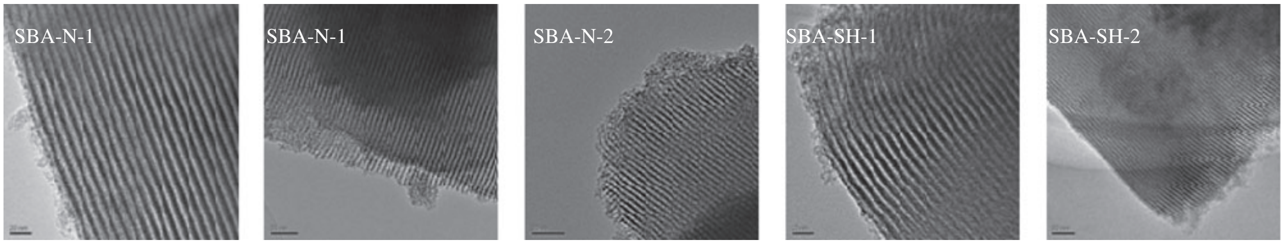

Fig. 1. TEM images of the materials of the mesoporous silica.

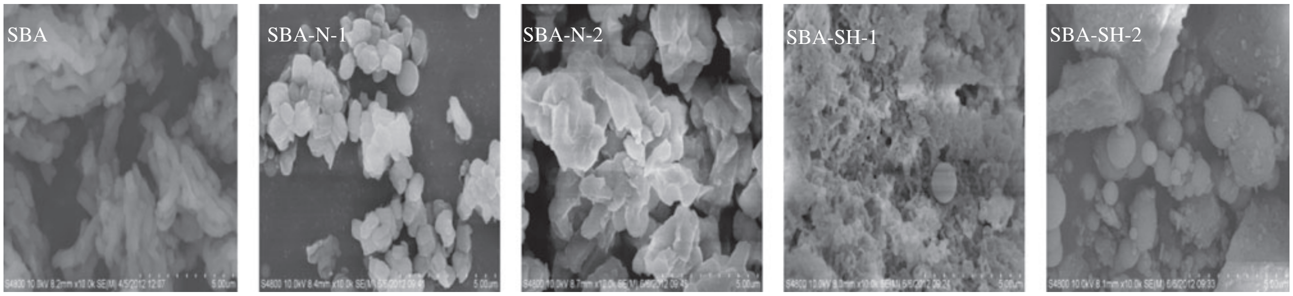

Fig. 2. Scanning electron micrograph (SEM) of the materials of the mesoporous silica.

absorption spectroscopy. The initial metal ion concentration is 0.5 mmol L^{-1}. The adsorption time was ranged from 5 to 360 min under continuous stirring. The removal percentage of Cu^{2+} ($R\%$) and the amounts of Cu^{2+} (q) adsorbed on material were calculated using Eqs. (1) and (2), respectively.

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q(mg \cdot g^{-1}) = \frac{(C_0 - C_e) \times M \times V}{m} \tag{2}$$

where C_0 is the initial Cu^{2+} concentration (mmol L^{-1}), C_e is the Cu^{2+} concentration at equilibrium (mmol L^{-1}), V is the volume of the solution (L), M is the molar mass of the Cu (64 g mol^{-1}), and m is the amount of the adsorbent used (g).

3. Results and discussion

3.1. Adsorbent characterization

The standard and functionalized mesoporous silica was investigated by TEM and SEM measurement, and the representative images are shown in Figs. 1 and 2. From Fig. 1, all the samples show highly ordered two-dimensional hexagonal mesostructure. Noticeably, mesoporous silicas after grafted by the organic functional groups maintain long range orderings as the parent SBA-15. The center-to-center distance of adjacent channels is about 10 nm. Average pore size of SBA-15 analyzed by BJH pore size distribution is 6.65 nm, so the wall thickness is 3.35 nm. The SEM images show that part of the porous silica has a loose, short rod shape with the length diameter ratio of 5. After grafting process, the quantity of both small pores and larger pores decreases, particle agglomeration intensifies and the particle surface becomes rougher. This is

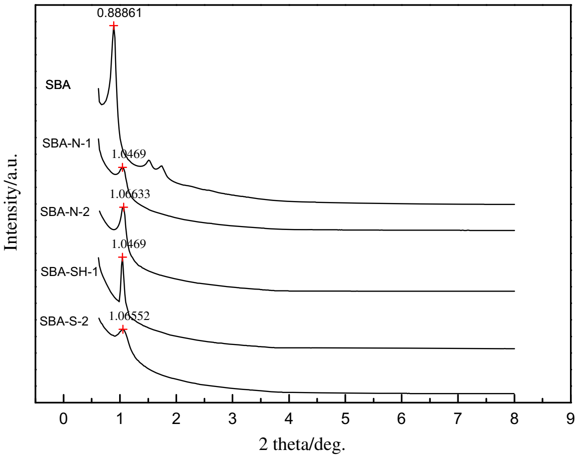

Fig. 3. Low-angle XRD of the materials of the mesoporous silica.

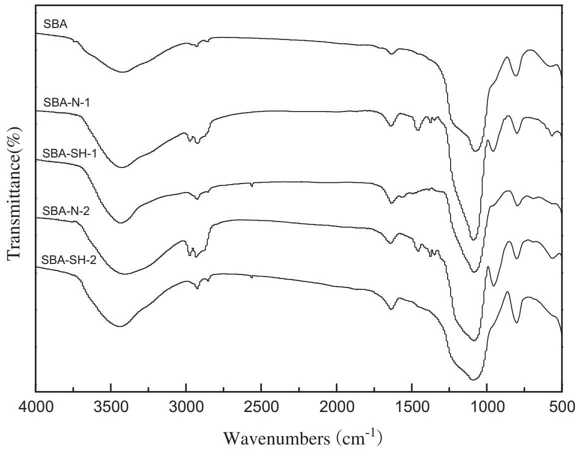

Fig. 4. FTIR spectrum of the materials of the mesoporous silica.

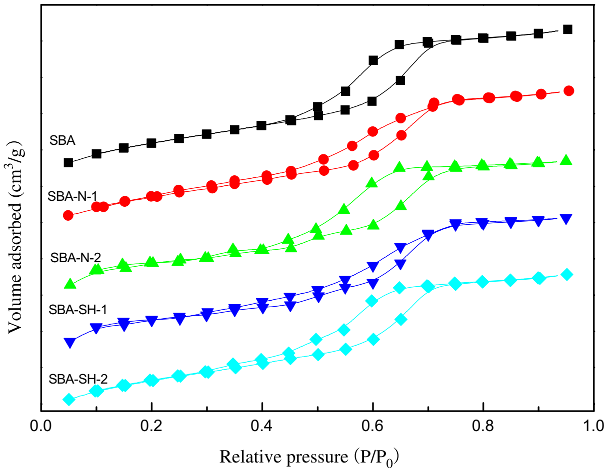

Fig. 5. The nitrogen adsorption–desorption isotherms of the mesoporous silicas.

probably because the grafted functional groups block some of the small pores.

The low-angle XRD patterns of all the functional adsorbents show a clear diffraction peak (100) at 0.89˚, 1.05˚, 1.07˚, 1.05˚, 1.07˚ for the SBA, SBA-N-1, SBA-N-2, SBA-SH-1, and SBA-SH-2, respectively. After grafting functional groups, the intensity of the (100) reflection decreases dramatically due to the reduced scattering contrast between the silica wall and the pore network as well as a reduction of pore volume by the relatively large functional groups [10]. All the functional samples have a XRD pattern similar to that of the standard silica, but with a slight peak shift to higher angles, indicating a decreasing dimension of the repetitive structure. The peaks for SBA-N-1 and SBA-SH-1 occur at the same angles similar to that of SBA-N-2 and SBA-SH-2, indicating no significant change of the structure (Fig. 3).

The bonding of the functional groups to the surface is through reaction with surface silanol groups. Fig. 4 shows the FTIR spectra for each of the samples. For the SBA sample, a sharp absorption band is identified at 3410 cm^{-1} due to hydrogen-bonded SiOH groups [11]. This band is better defined by functionalization. The isolated silanol groups [12] which belong to the amine functional materials are not observed. New features can also be seen at 2,700–2,900 cm^{-1} and 1625 cm^{-1} which can be assigned to C–O and C–OH stretches of the ethoxy group. There are some other feature bands at around 1590, 1550, and 1460 cm^{-1} which can be assigned to –NH$_2$, confirming that the amino groups have been grafted successfully [13]. The mercapto-functionalized materials show attenuation of

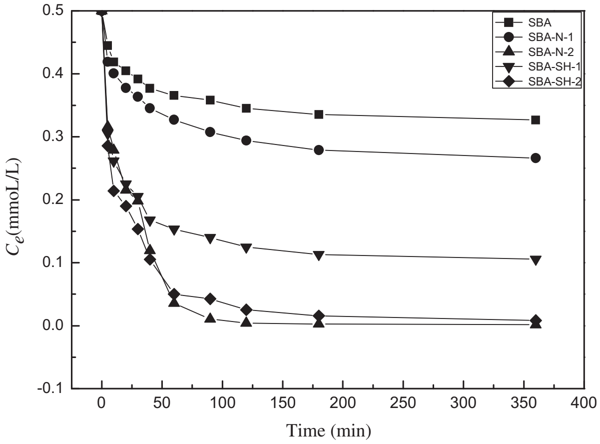

Fig. 6. The concentration change of the Cu^{2+} with the adsorption time.

Table 1
Physical properties of the mesoporous silicas

	SBA	SBA-N-1	SBA-N-2	SBA-SH-1	SBA-SH-2
Surface area (m^2 g^{-1})	838.2	545.5	786.4	550.7	779.6
Pore volume (cm^3 g^{-1})	0.870	0.545	0.7542	0.553	0.757
Pore size (nm)	4.3	2.9	4.2	3.0	4.2

Table 2
The removal percentage (*R*) and adsorbed amounts (*q*) of the mesoporous silica materials

	C_0 (mmol L^{-1})	m (mg)	C_e (mmol L^{-1})	q (mg g^{-1})	R (%)
SBA	0.5	100	0.3654	8.6141	34.70
SBA-N-1	0.5	100	0.3270	11.0705	46.79
SBA-N-2	0.5	100	0.0358	29.7119	99.68
SBA-SH-1	0.5	100	0.1535	22.1746	78.86
SBA-SH-2	0.5	100	0.0499	28.8034	98.32

the hydrogen-bonded Si–OH groups at 3,440 cm^{-1}, and the characteristic bands for mercapto groups are around 2,560–2,620 cm^{-1}, so we conclude that mercapto groups have been successfully grafted onto the mesoporous silica [14].

The nitrogen adsorption–desorption isotherms of the mesoporous silicas are shown in Fig. 5, respectively. Fig. 5 reveals that the nitrogen adsorption–desorption isotherms are all in accordance with the type-IV curve, which is the characteristic of the mesoporous materials . After the addition of new functional groups, the inflection position shifted slightly toward lower relative pressures and the volume of nitrogen adsorbed decreased, which was also indicative of a reduction in pore size. The inflection position of SBA-N-1 and SBA-SH-1 displayed the lowest relative pressure (0.4) indicating that the templating agents are not completely removed which is good agreement with the FTIR results.

The BET measurement was performed for each sample. Table 1 shows the porosity date. The pore size of the mesoporous silica decreased after functionalization because of the existence of organic functional groups in the mesopore channels. The surface area, pore volume, and pore size of the functionalized adsorbents were all lower than the non-functionalized sample.

3.2. *Copper metal adsorption*

Preliminary experiments were carried out to determine the time of equilibrium for adsorption. Fig. 6 shows the typical time profiles of metal ion concentration (C_e) for adsorption of copper metal ions. It shows that more than 75% of metal ion adsorption was completed within 10 min and the equilibrium was reached after 60 min. Table 2 clearly shows that the equilibrium adsorption capacity of heavy metal ions on functionalized mesoporous silica was larger than the SBA-15. The adsorption experiments of Cu^{2+} were conducted in order to investigate the activity and the location of the amino and mercapto functional groups that introduced into mesoporous silica via the direct co-condensation and post-synthesis grafting methods comparatively. All materials were tested under similar conditions. The result shows that functionalizing was an effective way to improve the equilibrium adsorption capacity of heavy metal ions, and the post-synthesis grafting methods are much better because the template removal is more easier and completely.

4. Conclusions

In summary, amine-grafted and mercapto-grafted SBA-15 were prepared successfully by direct co-condensation and post-synthesis grafting processes. The hexagonal mesostructure was not significantly changed and the adsorption capacity of copper ions was greatly enhanced after being functionalized new organic functions as chelating agents of the even more active. The adsorption capacity of the direct co-condensation functionalized material was affected to a certain extent since the template agent was removed incompletely, but adsorption capacity of functionalized mesoporous silica was greater than the pure mesoporous silica. It is seen that functionalization is a useful tool for improving the performance of an adsorbent. Consequently, this functionalized silica material can be a promising material for removing and recovering heavy metal ions in water.

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