Research Article

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Preparation of spherical aminopropyl-functionalized MCM-41 and its application in removal of Pb(II) ion from aqueous solution

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Abstract: Mesoporous silica microspheres were prepared by the polymerization-induced colloid aggregation (PICA) and pseudomorphic synthesis methods. The prepared microspheres have high specific surface area and MCM-41 type structure. In the PICA process, acidic silica sol was utilized as silica source and the effect of molar ration (formaldehyde/urea) was investigated. Moreover, the influences of reaction time and temperature were also studied. The specific surface area of porous and mesoporous silica microspheres were 186.4 m²/g and 900.4 m²/g, respectively. The materials were characterized by SAXS, FTIR, SEM, TEM and nitrogen sorption measurements. The prepared silica microspheres were functionalized by (3-Aminopropyl)triethoxysilane and then used to remove the lead from aqueous solution. The result indicates that the grafted silica microspheres have rapid adsorption capacity and good reproducibility. The adsorption data was fitted well with the Langmuir isotherm model, and the maximum adsorption capacities for MCM-41 silica microspheres were 102.7 mg/g.

Keywords: MCM-41, microspheres; aminopropyl groups; lead (II) ion adsorption

1 Introduction

The increasing amounts of heavy metals in water causes a serious damage to human health and ecological systems. The most abundant and harmful metals in the liquid effluents are Cr, Ni, Zn, Cu, and Cd, which are considered to be persistent, bioaccumulative and toxic substances [1–4]. The World Health Organization (WHO) proclaimed that the acceptable concentration of copper and lead in drinking water must be less than 2.0 mg/L and 0.05 mg/L, respectively [5]. In order to remove heavy metals from water, a wide variety of techniques such as ion exchange, reverse osmosis, nanofiltration, precipitation, coagulation or co-precipitation, electrodialysis, flotation, extraction, electrolysis and adsorption are available [6–8]. The adsorption technique is commonly used due to its simplicity, low-cost, reversibility, which can remove even trace quantities of metal ions from water [9]. For the adsorption processes, a variety of functional groups can be grafted or incorporated onto the surface of mesoporous channels to prepare highly effective adsorbents. The porous silica functionalized with various chelating agents have been widely applied as adsorbents, because of its high surface area, large uniform pores and tunable porous sizes. Moreover, it has good mechanical strength, high thermal stability, stability under a wide pH range and does not swell [10]. Thus, the developments of functionalized mesoporous adsorbents for removal of heavy metal ions using incorporated ligands with appropriate functional groups have attracted considerable interests [11]. The sol-gel silica functionalized with different organic reagents such as crown ether [12], 1,5-diphenylcarbazide and trialkyl phosphine oxides have been prepared and applied for removal of metals [13, 14]. In addition, polyamine-functionalized materials have been also studied due to their implication in anion removal, CO₂ capture, mobilization of biological molecules and basic catalysis of fine chemistry reactions [15–19].

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Since being prepared by a unique self-assembly process between surfactants and alkoxysilane in 1992, the mesostructured silica attracted considerable attentions because of its higher surface area, large uniform pores and tunable pore sizes [20–24]. The shape, size and structure of particles are all significant. In catalysis, control over particle size is important to transfer processes from batch experiments to continuous processes in order to avoid filter plugging by fine particles and to optimize mass transfer. In the drug delivery or galenic applications, the particle size of the host matrix is important to affect the drug or cosmetic action. For instance, particles with size of approximately 5 μm will penetrate into the skin pores and allow the diffusion of drugs or cosmetics inside the derm. Because of easily being retained at the surface of skin, the larger particles (0.5 mm to 1 mm) are required in pressure drop applications, such as in protective gas masks, where individuals must breathe or blow through a bed of particles. Thus, simultaneous and independent control of their textural and morphological properties remains a challenge. Several strategies have been investigated with the aim at producing spherical mesostructured silica with adjustable sizes. Among them, fluorine-promoted condensation, spray-drying of aerosol-generated microdroplets and of nanoparticles have been proven effective. However, particle coalescence has never been completely prevented, and the products exhibited broad size distributions [25–27].

Previously, Zhao *et al.* successfully prepared mesoporous silica particles by polymerization-induced colloid aggregation (PICA) [28]. These particles exhibited good chromatographic performance because of their large surface areas and good monodispersity. However, the pore structure is disordered and the pore size distribution is wide. In recent study, many researchers have successfully prepared the ordered mesoporous silica by pseudomorphic synthesis process [29–31]. First, a mild alkaline solution was used to slowly dissolve silica. Then the generated silicate was adsorbed on surfactant to form a hybrid surfactant/silicate mesophase without changing the morphology of the silica particles. Finally, silica particles with ordered mesoporous structure and initial morphology was obtained after calcination.

In the present work, porous silica microspheres (PSMs) were prepared by a sol-gel process coupled with the PICA method, and then the MCM-41 silica microspheres were synthesized by pseudomorphic synthesis process using the prepared PSMs. The effects of pH and stirring time in the PICA process as well as the amounts of NaOH and cetyl trimethyl ammonium bromide (CTAB) in the pseudomorphic synthesis process were investigated. The PSMs

and MCM-41 microspheres were functionalized with (3-Aminopropyl) triethoxysilane (APTES) under a hydrothermal condition, and then used as adsorbents for removal of lead ion from aqueous solutions [32]. Moreover, the adsorption capacities were determined using Langmuir adsorption model.

2 Experimental

2.1 Reagents

All reagents were used without further purification. Silica sol (25%), APTES (Aladdin), ammonium hydroxide (25%), EtOH (99.7%), urea (99%), formaldehyde solution (38%), sodium hydroxide (NaOH, 96%), CTAB (99%), HCl (38%) toluene (99.5%) and lead nitrate (99%) were received from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2 Preparation of silica sol and porous silica microspheres

Silica sol, urea and ultra-pure water were mixed in a 250 ml round-bottomed flask with a magnetic stirrer. The suspension pH was adjusted using HCl. After stirring for another 30 min, the mixed solution of formaldehyde and ultra-pure water was added into the above suspension with rapid stirring for a specific time and allowed to react in a water bath at 40°C for 1h without stirring. The suspension turned to white color and opaque at first, and then the white particles gradually sank to the bottom of flask. Then the reaction was terminated by adding a large amount of ultra-pure water. The solid particles were collected by filtration, washed with ultra-pure water and EtOH, and dried in a vacuum oven at 60°C for 12 h. The porous silica microspheres were obtained by calcining the solid particle with a staged heating process from 30 to 550°C, to burn off the polymer.

2.3 Pseudomorphic transformation of porous silica microspheres

The prepared PSMs, NaOH, CTAB and ultra-pure water were mixed in a flask at 90°C under magnetic stirring to form a suspension, which was then transferred to a PTFE-lined autoclave and reacted at 125°C for 10 h under static condition. The precipitate was recovered by filtration, washed with ultra-pure water and EtOH, and dried in

a vacuum oven at 60°C for 12 h. The MCM-41 silica microspheres were obtained after the polymer was burned off.

2.4 Modification of silica microspheres

The silica microspheres were rehydroxylated first by refluxing in 10% HCl for 12 h. The rehydroxylated silica microspheres was dispersed in toluene. Then APTES was added, and the suspension was refluxed for 24 h. The solid was recovered by filtration, and washed with toluene and EtOH, respectively. The NH₂-PSMs and NH₂-MCM-41 were obtained using PSM and MCM-41 silica microspheres, respectively.

2.5 Determination of the adsorption capacities and reusability

Lead (II) solution was prepared using a reagent grade lead nitrate to obtain a stock solution with the concentration of 800 mg/L. The solution was diluted by ultra-pure water to obtain desired solution for adsorption experiments. The silica adsorbents were dried at 100°C for 1 h in prior to the measurement of sample weight. The initial and final concentrations of lead ion in solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The pH of the initial solution was adjusted to 4.0 by adding NaOH or sulfuric acid solution in all adsorption experiments.

The adsorption experiments were performed as follows: The PSM (0.1 g) was placed with lead ion in solution (50 mL) to prepare the solution with different concentrations (50, 100, 200, 400, 600 and 800 mg/L, respectively) for adsorption isotherm study at 293 K, separately. The flasks were then transferred to an incubator shaker and vibrated at 140 rpm for 24 h to ensure adsorption equilibrium. All batch experiments were repeated thrice under the same conditions and all the data that appear in this article are based on the average values.

For regeneration of the adsorbent after adsorption experiments, the silica microspheres with adsorbed lead were added into a 20 mL HCl solution (pH 2.0) under stirring for 2 h, and then the adsorbent was recovered by centrifugation. For thorough desorption, the above process was repeated thrice. The extracted silica microspheres were subsequently washed with an alkaline solution for the regeneration of amino groups. Then, the regenerated adsorbent was obtained and used in a second cycle.

3 Results and discussion

3.1 Synthesis and characterization of porous silica microspheres

The silica source of silica microspheres is silica sol and affects the PSMs' formation is controlled by the amount of silica sol directly. The increasing amount of silica sol leads to higher content of silica in PSMs. Moreover, the solubility of silica sol is different when the addition of silica sol, and the reaction rate is different because of its influence on solute diffusion.

In this experiment, a series of silica gel microspheres were prepared by variation of the amount of silica sol at 12, 14, 16 and 18 g. The microspheres were characterized by scanning electron microscopy. The Figure 1 shows the SEM diagram of PSMs calcined with different amounts of silica sol under the identical conditions. It can be seen from the figure that when the amount of added silica sol is 14 g, the prepared microspheres exhibited the best sphericity. According to the reaction mechanism of PICA, if the amount of added silica sol is small, the silicon content is low in the prepared silica microspheres without a strong silica skeleton. Then, the surface of the microspheres collapses after being calcined at high temperature, and the particles deform, resulting in debris. With the increasing of silica sol dosage, the concentration of silica sol and the number of nucleation increase during the PICA process. When the amount of silica sol further increases, the particle size decreases, and the amount of silica microspheres is larger, even the particles are not completely spherical after agglomeration and precipitation, as shown in Figure 1(D). Under this preparation scale, 14 g of silica sol is the most suitable amount.

According to the reaction mechanism of PICA, temperature not only affects the polymerization rate of urea and formaldehyde, and the adsorption rate of silica particles by UF resin, but also affects the solubility of UF resin and the Brownian motion of silica particles. By calculating the average particle size D_i of n ($n > 100$) microspheres in the SEM images of the silicon microspheres under different pH conditions, the D_n and U values can be obtained by the following formula:

$$D_n = \sum n_i D_i / \sum n_i, \quad D_w = \sum n_i D_i^4 / \sum n_i D_i^3, \\ U = D_w / D_n$$

where, D_n is average particle size and U is width of the particle size distribution. The larger U value, the wider the particle size distribution, and the monodisperse mark is $U < 1.05$.

Figure 1: The SEM images of PSMs prepared at different silica sol addition, (A) 12g; (B) 14g; (C) 16g; (D) 18g

Figure 2: Influence of temperature on particle size (Dn) and particle size distribution (U)

The Figure 2 shows the effect of temperature on the particle size of PSMs. The diameter of the prepared PSMs were observed to increase obviously with the increase of temperature. In addition, the particle size distribution of PSMs is narrow and the monodisperse property is good in temperature range between 20°C and 40°C. When the temperature is less than 20°C or higher than 40°C, the particle size distribution will widen.

The Figure 3 shows the particle size distribution of PSMs prepared under different pH conditions. The preparation of PSMs by PICA is divided into two stages: nucleation and growth phases. During the nucleation phase, H^+ in the system can promote the polymerization process of urea formaldehyde and thus increase the nucleation rate. Therefore, when pH drops during the nucleation stage, the number of generated hybrid microspheres increases in the system, resulting in the decrease of the obtained particle

Figure 3: The particle size distributions of PSMs prepared at different pH

Figure 4: The SEM (A) and TEM (B) images of PSMs

Figure 5: Particle size distribution of PSMs

size. When pH is below 1.0 or above 2.1, the particle size of the PSMs becomes non-uniform.

When the pH above 2.1 in the system, urea formaldehyde polymerization rate is slow; thus, the nucleation time increases, which results in the formation of new nuclei during growth, that is, the second nucleation phenomenon,

Figure 6: Nitrogen sorption isotherm (A) and pore size distribution (B) of PSMs

Figure 7: The SEM images of porous silica microspheres prepared at different molar ratio of formaldehyde and urea, (A) 1; (B) 1.25; (C) 1.5; (D) 2

resulting in a number of peaks in the particle size distribution profile of the resulting microspheres.

The Figure 4 exhibits the SEM and TEM images of PSMs, which were successfully synthesized by the PICA method. The figure shows the PSMs were formed by accumulation of silica particles and the PSMs have good sphericity without any aggregation. The particle size distribution of PSMs is shown in Figure 5, in which the PSMs exhibited good monodispersity with average diameter of 3.76 μm . This finding corresponds to the SEM and TEM images.

The nitrogen sorption isotherm and pore size distribution are shown in Figure 6. The isotherm is a type IV curve with a hysteresis loop near the higher relative pressure $P/P_0 = 0.8$, indicating that the PSMs have large pore size and wide size distribution, which is corresponding to

the pore size distribution [28]. The PSMs have a pore structure with the pore diameter between 1 nm and 60 nm. The specific surface area, pore volume and average pore size are 186.4 m^2/g , 0.797 cm^3/g and 17.1 nm, respectively.

The Figure 7 shows the SEM images of PSMs prepared at different molar ratios of formaldehyde and urea. When the molar ratio is 1.25, the silica microspheres have good sphere and excellent dispersity. When the mole ratio is 1, the urea-formaldehyde resin mainly exists as a linear structure. The molecular chain easily moves in the system, and the resin is in contact with the silica particle molecular chain. On the other hand, a large number of secondary amino groups exist on the resin molecular chain, and the effect of secondary amino groups attract silicon hydroxyl groups that can enhance the adsorption between the resin and silica particle. Therefore, the rapid adsorption between the resin and silica particle will occur, the number of hybrid microspheres will increase and the diameter of silica microspheres will decrease. Moreover, the crosslinking structure of composite microspheres is reduced, which will cause the breakage after calcination. When the molar ratio of formaldehyde urea was 1.25, the polymerization rate of urea formaldehyde accelerated, the adsorption rate of silica particles and resin decreased, which led to a balance, and the hybrid microspheres maintained spherical shape at the growth stage. When the mole ratio between formaldehyde and urea was increased, the polymerization rate was further accelerated and the adsorption rate was further reduced, resulting in less silica particles adsorbed by the resin, the silica content in the hybrid microspheres reduced, and the silica microspheres shrank after calcination, the microspheres size become small. The surface of silica microspheres is very rough as shown in Figure 7.

Figure 8: SEM image and particle size distribution of ordered mesoporous silica microspheres

Figure 9: Nitrogen adsorption isotherm and pore size distribution of MCM-41 silica microspheres

When the molar ratio between formaldehyde and urea was further increased, the silica content in the hybrid microspheres reduced drastically and the structure became difficult to maintain and broke after calcination. Therefore, monodisperse silica microspheres can be prepared at the formaldehyde/urea molar ratio of 1.25.

3.2 Pseudomorphic synthesis and characterization of MCM-41 microspheres

To prepare ordered mesoporous silica microspheres (MCM-41 silica microspheres), the pseudomorphic synthesis method was used to rebuild the pore structure of PSMs. The Figure 8 shows the SEM image and particle size distribution of MCM-41 silica microspheres. The SEM image shows that the morphology of the silica microspheres was preserved after the pseudomorphic synthesis, while the particle size reduced and the agglomeration phenomenon was observed. This phenomenon is attributed to the fact that the silica slowly dissolved, then the generated silicate was immediately assembled with the surfactant dur-

ing the pseudomorphic synthesis. Thus, the pore size reduced, and the microspheres were slightly shrunk, resulting in the smaller particle size. Theoretically, when the silica dissolution rate is equal to the assembly rate, the silicate is immediately subjected to the assembly process to form the mesophase. The dissolved portion is immediately replaced by the mesophase, and the structure is successfully transformed to the MCM-41. However, in the reaction process, the generated silicate possibly assembled with the surfactant between the silica microspheres, resulting in agglomeration phenomenon with the particle size distribution widen.

From the Figure 9, the nitrogen adsorption isotherm is standard type IV, which implies that the PSMs were transformed to mesoporous material successfully after pseudomorphic synthesis [30]. The pore size distribution indicates the MCM-41 sample has uniform pore diameter of 3.20 nm. From Figure 10, the SAXS pattern of the PSMs sample has no diffraction peak at low angles, and the MCM-41 exhibits Bragg reflections, which are consistent with the hexagonal mesoporous structure of MCM-41 [33]. These observations demonstrate that the structure of PSMs was suc-

Figure 10: SAXS patterns of (A) MCM-41 and (B) PSM

Figure 11: SEM images of ordered mesoporous silica microspheres prepared under different temperature, (A) 100°C (B) 125°C (C) 150°C (D) 175°C

cessfully transformed into MCM-41 by pseudomorphic synthesis.

Pseudomorphic synthesis occurred in the pores of PSMs, which is the self-assembly process of the surfactants and the silicates. This method can transform amorphous silica microspheres into silica-surfactant mesostructures without changing the shape and size of the microspheres. The pseudomorphic synthesis process is controlled by the self-assembly rate and silica dissolution rate. Thus, the effect of temperature is crucial. A series of silica microspheres were prepared under different temperatures to illustrate the influence of temperature.

Figure 12: FT-IR spectra for unmodified and functionalized silica microspheres

Figure 13: EDS spectra of modified silica microspheres

3.3 Characterization of particles amine functionalized silica microspheres

The amine functionalized MCM-41 silica microspheres were prepared using APTES as the modifier in anhydrous toluene. The silica microspheres were heated at 150°C for 12 h to remove the physisorbed water before modification process. The Figure 12 shows the FT-IR spectra of unmodified and functionalized silica microspheres. The peaks around 1637 cm⁻¹ and 3447 cm⁻¹ correspond to the -OH stretching vibrations of silanol groups and the bending vibration of adsorbed water, respectively [34]. The vibration signals around 1109 cm⁻¹, 803 cm⁻¹ and 474 cm⁻¹ presented in all samples, which are corresponding to Si-O-Si bands and the condensed silica network [35, 36]. The stretching band at 2936 cm⁻¹ corresponds to C-H stretch-

ing in the propyl chain. The new peaks around 695 cm^{-1} , 1494 cm^{-1} and 1564 cm^{-1} were attributed to the characteristic absorption peaks of -NH_2 group as reported [35, 37]. The compositions of the modified MCM-41 silica microspheres were determined by EDS, which were shown in Figure 13. The strong N signal confirmed that -NH_2 groups were successfully grafted onto the microspheres surface. The FT-IR and EDS spectra indicate that the -NH_2 groups were successfully grafted on the surface of silica microspheres.

3.4 Adsorption capacity and reusability of amino-functionalization silica microspheres

In order to determine the adsorption capacity of NH_2 -MCM-41 adsorbent, the equilibrium adsorption isotherms were investigated and the Langmuir model was used to describe adsorption process. The formula describing the equilibrium adsorption capacity (Q_e , mg/g) is shown as follows:

$$Q_e = \frac{(C_0 - C_e) V_{Pb}}{w}$$

where, C_0 is the initial concentration and C_e (mg/L) is the equilibrium concentration of lead (II) in the solution, w (g) is the amount of adsorbent, and V_{Pb} (mL) is the initial volume of the lead (II) solution.

The Figure 14 displays the adsorption isotherms at 25°C for NH_2 -MCM-41. The isotherms show a sharp initial slope, which indicates the NH_2 -MCM-41 as adsorbent have excellent adsorption properties at low metal concentration. The isotherms are consistent with the Langmuir isotherm; thus, the Langmuir model was used to describe the adsorption process. The expression of Langmuir isotherm is as follows:

$$Q_e = \frac{b q_m C_e}{1 + b C_e}$$

where, q_m and b are the characteristic Langmuir parameters. q_m is the maximum adsorption quantity, which shows that the metal adsorbed on material to form a complete monolayer, and b is a constant related to the intensity of adsorption.

The Langmuir isotherms of lead ion adsorbed on MCM-41 are shown in Figure 15, in which the experimental data were successfully fitted by Langmuir model, and the regression coefficients of these two isotherms are 0.998. The results demonstrate that the type of lead ion adsorption on functionalized silica microspheres is monolayer fashion. From the Langmuir isotherms, the maximum adsorption capacity (q_m) of NH_2 -MCM-41 silica microspheres is 102.7

Figure 14: Adsorption isotherms of lead ions on the amino-functionalized MCM-41 adsorbent

Figure 15: Linearized Langmuir plots for lead ions on the amino-functionalized MCM-41 adsorbent

Figure 16: Adsorption capacities of amino-functionalized MCM-41 adsorbent after regeneration

mg/g, indicating that the silica microspheres have larger surface area with enough pore volume to support adsorption after pseudomorphic synthesis. The MCM-41 silica microspheres prepared by pseudomorphic synthesis were observed with excellent adsorption capacities after amino-functionalization.

The reusability is important to evaluate the property of an adsorbent. After the adsorption experiment, the silica microspheres could be regenerated by washing with HCl and alkaline solution, and then drying in a vacuum oven. The Figure 16 shows the adsorption capacities of NH₂-MCM-41 after a different number of cycles. The adsorption capacity decreased in the first cycle and then remained substantially constant. Given the presence of residual lead (II) in the pores of silica microspheres after the first cycle, the adsorption capacity decreased by 3% for NH₂-PSMs after several cycles, which indicates that the MCM-41 silica microspheres have excellent regeneration capacity and reusability.

4 Conclusions

The porous silica microspheres were synthesized by PICA method using acidic silica sol. The MCM-41 silica microspheres with large size of 3.27 μm and high specific surface area of 900.4 m^2/g were successfully prepared by the pseudomorphic synthesis process using the synthesized PSMs as primary particles. The amino functionalized silica microspheres have rapid adsorption capacity and superior reproducibility. The maximum adsorption capacity for MCM-41 silica microspheres was 102.7 mg/g. Therefore, the MCM-41 silica microspheres, presenting excellent adsorption capacity after amino-functionalization, can be used as adsorbent for removal of heavy metals from aqueous solutions.

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