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Chemical-Template Synthesis of Micro/Nanoscale Magnesium Silicate Hollow Spheres for Waste-Water Treatment

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Abstract: Micro/nanoscale magnesium silicate hollow spheres were synthesized by using silica colloidal spheres as a chemical template in one pot. The hollow spherical structure, consisting of well-separated nanoscale units, was microscale as a whole and could be easily handled in solution. The as-synthesized magnesium silicate hollow spheres with large specific surface area showed availability for the removal of organic and heavy-metal ions efficiently from waste water. Importantly, the micro/nanoscale magnesium silicate hollow spheres that had adsorbed organic pollutants could be regenerated by calcination and used repeatedly in pollutant removal. Magnesium silicate hollow spheres synthesized by a scaled-up chemical template method may have potential applications in removing cationic dyes and heavy-metal ions from waste water.

Keywords: microporous materials · nanostructures · silicates · water treatment

Introduction

Removal of pollutants such as weakly biodegradable dyes and heavy-metal ions from water is very important for the protection of our environment[1–4] because the disposal of effluents including organic pollutants and heavy-metal ions into natural water resources causes damage to the aquatic environment and humans. For example, most dyes have a high tinctorial value and less than 1 ppm of dye produces an obvious coloration in water, and some heavy-metal ions, even in small amounts, can cause severe physiological and health effects. To date, various treatments for the removal of dyes and heavy-metal ions have been investigated, including electrochemical methods,[5] adsorption,[6–10] chemical coagulation,[11,12] photodegradation,[13–15] and biodegradation.[16] Among these methods, the adsorption process is an attractive treatment, especially if the adsorbent is inexpensive, readily available, highly efficient, easy to use, environmentally friendly, and so on. Up to now, many adsorbents have been tested to remove pollutants from aqueous solutions. Among them, activated carbon is regarded as an effective but expensive adsorbent due to its high costs of manufacturing and regeneration. In recent years, there has been an upsurge of interest in the utilization of silicate clay minerals in environmental studies for their special surface properties. A silicate such as sepiolite is a good adsorbent for organic and metal-ion species because it exhibits the features of environmental friendliness, high specific surface area, high porosity, and surface activity.[8,9] The use of silicates as adsorbents has so far focused more on natural minerals and on improving their adsorption performance by physical and chemical treatments. However, less attention has been paid to the synthesis and investigation of nanostructured artificial silicates, which may exhibit excellent performance in waste-water treatment.

Nanostructured-material-based technologies are promising for environmental remediation. Hierarchical nanostructured materials can avoid aggregation and maintain high specific surface areas; these factors are important in enhancing the accessibility of adsorbates to reactive sites.[17] Micro/nanoscale hollow colloidal particles represent a promising type of nanomaterial, and the special structure makes hollow spheres with low density, high specific surface areas, void properties, and so on; these spheres have proven to be excellent in widespread applications, including lithium-ion batteries, catalysis, sensors, drug delivery, and controlled

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drug release.[18–21] Until now, synthesized silicates, especially silicate hollow spheres with large surface areas, have rarely been reported. In this paper, we report a simple technique to synthesize hierarchical magnesium silicate hollow spheres with large surface areas by using a chemical template. Our previous work has shown that silica colloidal spheres can release silicate ions in ammonia solution and can be used as chemical templates.[22] Herein, the chemical-template-synthesized magnesium silicate hollow sphere presents a porous surface with a morphology and structure similar to sepiolite. Applied in waste-water treatment, the as-prepared porous magnesium silicate hollow spheres show good adsorption ability in the removal of cationic dyes and heavy-metal ions from the model waste water. Magnesium ions in water are not harmful to the environment, so the prepared magnesium silicate hollow spheres could be used as an environmentally benign and efficient adsorbent.

Silica colloidal spheres have often been used as one of the important physical templates for the preparation of core/shell structures, and the corresponding hollow spheres could be obtained by dissolving the silica core in alkaline solution.[23,24] However, little attention has been paid to the dissolution properties of silica in alkaline conditions. In this paper, we report that silica colloidal spheres were employed as the chemical template (the source of silicate ions) to synthesize magnesium silicate hollow spheres by a facile hydrothermal strategy. As illustrated in Figure 1, silica colloidal spheres are dispersed first into an alkaline solution containing magnesium chloride, ammonia, and ammonia chloride. The silica chains can be broken by hydroxide ions, so silicate-ion groups are generated in alkaline solution at high temperature.[25] The silicate ions released from the silica templates react with magnesium ions to form magnesium silicate particles in situ around the silica cores (Figure 1, step a). In the following process, with gradual release of the silicate ions from the silica colloidal spheres, all of the magnesium ions are transformed into the magnesium silicate shell, and the silica/magnesium silicate core/shell structure is formed (Figure 1, step b). Finally, after the remaining silica core has been dissolved completely under the original alkaline conditions at high temperature, the well-structured magnesium silicate hollow sphere is thus obtained (Figure 1, step c).

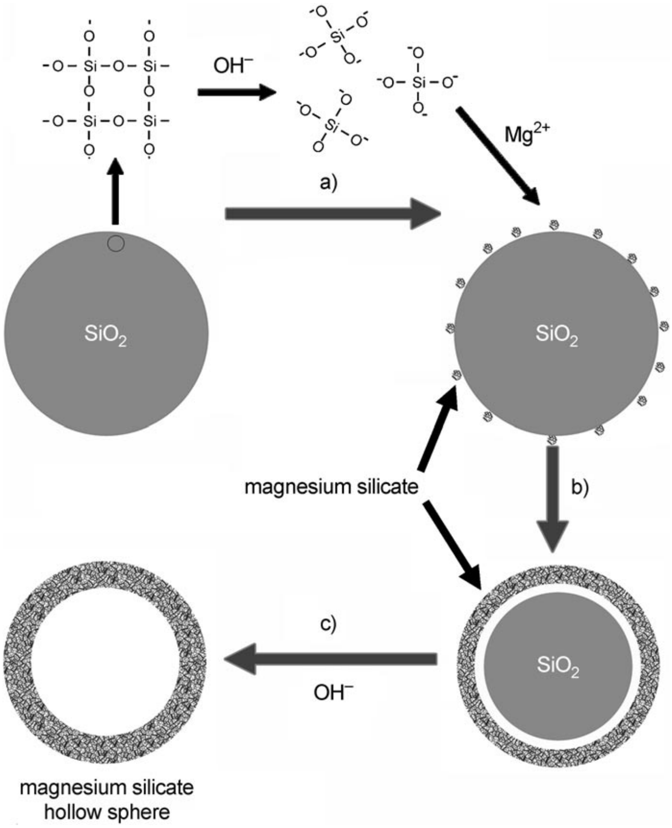

Figure 1. Schematic illustration of the preparation of magnesium silicate hollow spheres: a) on the surface of silica spheres, silicate ions are released from the silica colloidal sphere through the breaking of silicon–oxygen chains by hydroxide ions and react with magnesium ions to generate magnesium silicate particles around the silica colloidal sphere; b) the magnesium silicate particles aggregate to form a shell around the silica colloidal sphere as the reaction proceeds; c) the magnesium silicate hollow sphere is obtained by the dissolution of the silica core under alkaline conditions.

Results and Discussion

The final product synthesized according to the above procedure was characterized by X-ray diffraction (XRD); all peaks show the characteristics of magnesium silicate hydroxide hydrate (reported data: JCPDS no. 03-0174) from the relative XRD pattern (Figure S1a in the Supporting Information) and can be identified as representing a talc structure with the ideal chemical formula of $Mg_3Si_4O_{10}(OH)_2$. The results (Figure S1b in the Supporting Information) of the energy dispersive X-ray (EDX) analysis confirmed that the product consisted of magnesium, silicon, and oxygen elements. The morphology of the as-prepared product was characterized by scanning electron microscopy (SEM) and transmitting electron microscopy (TEM). As shown in Figure 2a, the final product was composed of large uniform and spherical particles. The magnified image of a single spherical particle in Figure 2b reveals that the surface of the spherical particles is rough, porous, and bestrewn with a large amount of thin lamellae. The TEM image (Figure 2c) illustrates that the magnesium silicate spheres had a hollow structure, with an obviously black edge and darkish center; the shell was uniformly about 50 nm in thickness. The surface presents needle-like structures at first glance. Actually, observation of the SEM and TEM images indicates that the final porous magnesium silicate hollow sphere was composed of large, narrow, and nanoscale lamellae (Figure 2d). The observed needle-like structures were proposed to arise from the black edges of tilted nano-scale lamellae, which were partially or completely parallel to the electron beam.

In order to understand the formation process, time-dependent experiments were carried out. As shown in Figure 3a, the silica colloidal spheres are uniform with a diameter of

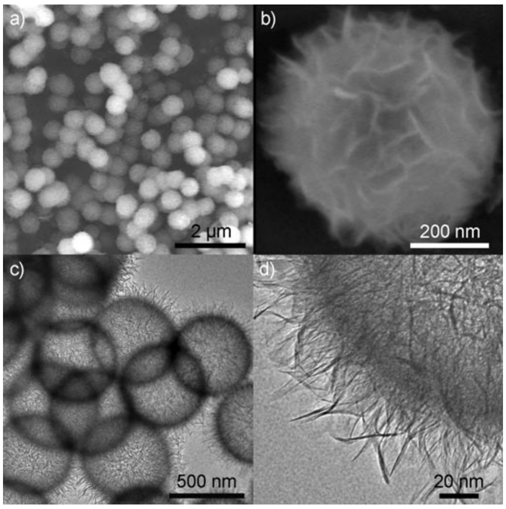

Figure 2. Morphologies of magnesium silicate hollow spheres synthesized at 140°C for 12 h. a and b) SEM images of the sample; c and d) TEM images of the sample.

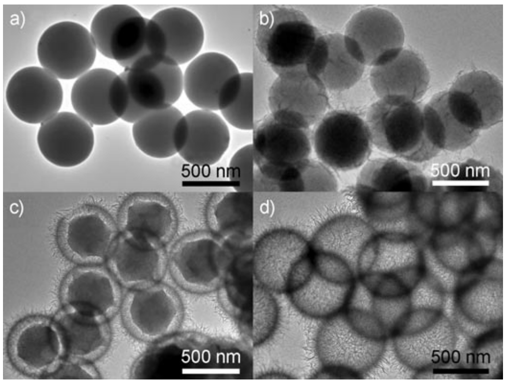

Figure 3. TEM images of the synthesis of magnesium silicate hollow spheres at 140°C at different times in the reaction: a) 0 h; b) 0.5 h; c) 3 h; d) 12 h.

500 nm and a smooth surface at the initial stage. After 0.5 h of the reaction, the surface became rough with some particles (Figure 3b), which indicated that the silica colloidal spheres were partially dissolved by the hydroxy ions. When the reaction time was prolonged to 3 h, because the hydroxy ions persistently broke the silicon–oxygen chains of the silica colloidal spheres and the silicate ions generated continually reacted with magnesium ions to form magnesium silicate particles, thin and complete silicate shells around the remaining silica cores were formed, as shown in Figure 3c. The inner silica colloidal spheres present irregular morphology, which indicates that they were gradually etched. The shell kept growing until all of the magnesium ions had been transformed into magnesium silicate particles. After 12 h, the remaining silica cores had completely dissolved to leave the void structure (Figure 3d). Obviously, if the amount of magnesium ions in the initial precursor solution was increased, magnesium silicate hollow spheres with thicker shells could be obtained (Figure S2 in the Supporting Information).

In our experiment, ammonia was chosen to provide the hydroxide ions based on the ionization balance of ammonia. For the magnesium ions, ammonia chloride was a necessary additive in the precursor solution; otherwise, magnesium hydroxide was formed and deposited in the precursor ammonia solution, and large irregular particles with few spherical particles were obtained (Figure S3a in the Supporting Information). The possible process is as follows. The magnesium ions react with the hydroxide ions to form magnesium hydroxide in ammonia solution. Thus, the concentration of magnesium ions decreases in the solution, especially around the silica colloidal spheres, based on the deposition and dissolution balance [Eq. (1)].[26]

$$\mathrm{Mg^{2+} + 2\,NH_3 \cdot H_2O \rightleftharpoons Mg(OH)_2 + 2\,NH_4^{+}} \qquad (1)$$

When a large amount of silicate ions were generated from the silica colloidal spheres under alkaline conditions at high temperature and there were few magnesium ions around the silica colloidal spheres to react with the silicate ions, then superfluous silicate ions generated from the silica colloidal spheres would diffuse into the solution and lead gradually to the nucleation of magnesium silicate; thus, irregular magnesium silicate particles formed in the ammonia solution without addition of ammonia chloride. When the amount of ammonia chloride was increased, in accordance with Equation (1), more magnesium ions would exist and react with the silicate ions and then grow into the magnesium silicate shell around the silica colloidal spheres; meanwhile, the amount of irregular particles would decrease, as proved by the images in Figure S3b–d in the Supporting Information. If the amount of ammonia chloride was increased to 10 mmol in the present experiment, uniform and pure spherical particles formed. All these results proved that the introduction of ammonium ions restrained the formation of magnesium hydroxide, in accordance with Equation (1). Thus, enough ammonia chloride would prevent the magnesium ions from forming magnesium hydroxide and would promise the generation of magnesium silicate particles on the surface of the silica colloidal spheres.

The formation of nanoscale magnesium silicate lamellae in the final hollow spheres was investigated. According to the XRD results, the synthesized magnesium silicate belongs to the talc structure. Talc is composed of three ‘infinite’ layers formed by the sharing of oxygen ions at three corners of the silica tetrahedron (Figure S4a in the Supporting Information); a layer of octahedral-coordinated magnesium/hydroxide ions holds two layers of tetrahedral-coordinated silicon/oxygen ions together as a three-layer sheet. This ‘sandwich-like’ three-layer unit is electrically neutral on the basal plane, so the crystal is held together by Van der Waals forces acting across adjacent tetrahedral layers.[27] As a result of this structure, the generated magnesium silicate tends to grow in the form of a lamellar structure. Thus, the as-prepared magnesium silicate hollow spheres were composed of narrow nanoscale lamellae with a large amount of edges and faces. The edges of talc (Figure S4a in the Supporting Information) consisting of broken bonds exist in the form of Si–OH groups.[28] When the magnesium silicate hollow spheres were put in water, the surface Si–OH groups adsorb/dissociate hydrogen ions, which results in positive, negative, or uncharged sites, depending on the pH value of the solution. The isoelectric point of the as-prepared magnesium silicate hollow spheres in deionized water without any additives was measured at a pH value of about 3. Thus, the magnesium silicate hollow spheres show a negative charge in deionized water.

Silicate materials such as sepiolite have always been used as efficient adsorbents due to their charged surface. In this case, the adsorption performance of porous magnesium silicate hollow spheres was investigated in model waste water. Methylene blue (MB), a common cationic dye in the textile industry, was chosen as a model organic pollutant in the adsorption experiments. The adsorption ability of the as-prepared magnesium silicate hollow spheres was investigated. A certain amount of magnesium silicate hollow spheres (20 mg) was mixed with MB solutions (40 mL) of different concentrations at room temperature, with no other additive present. After several hours, the magnesium silicate hollow spheres were deposited at the bottom of the bottles under gravitation, and the solution was characterized by UV/Vis absorbance spectroscopy (Figure 4) and recorded by digital camera (inset of Figure 4). From the inset color photos, it can be seen that MB solutions below 75 mgL^{-1} (samples 1–3) were clear and colorless, which indicates that the MB was almost all adsorbed by the magnesium silicate hollow spheres; this result corresponds to the absorbance curves of the samples (curves 1–3) in Figure 4. These observations indicated the high adsorption performance of the prepared magnesium silicate hollow spheres.

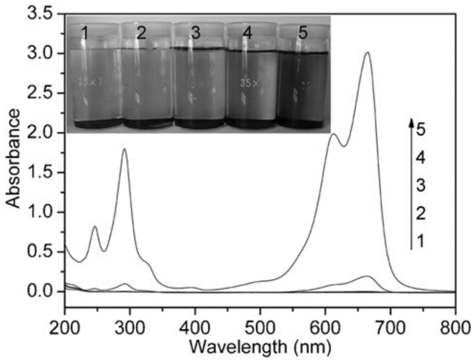

Figure 4. UV/Vis absorbance spectra and photo (inset) of magnesium silicate hollow spheres (20 mg) in solution (40 mL) with MB concentrations of 1) 25, 2) 50, 3) 75, 4) 100, and 5) 125 mgL^{-1}, respectively.

To determine the adsorption rate, the adsorption of the cationic MB dyes onto the magnesium silicate hollow spheres was studied as a function of contact time. The contact time between the adsorbate and the adsorbent is of great importance in waste-water treatment by adsorption. A rapid uptake of adsorbates and the establishment of equilibrium in a short period signifies the efficiency of an adsorbent for use in waste-water treatment.[8] The effect of contact time on the adsorption of MB dyes by the magnesium silicate hollow spheres was studied for a period of 80 min with an initial dye concentration of 75 mgL^{-1} at room temperature and the solution pH value. When 20 mg of as-prepared magnesium silicate hollow spheres were added into 40 mL of MB solution, more than 90 % of the MB in the solution could be removed in less than 10 min, as illustrated in Figure 5. No significant variation in the residual dye concentration was detected after 30 min of contact time. The above results primarily show that the magnesium silicate hollow spheres could be used as a fast and efficient adsorbent.

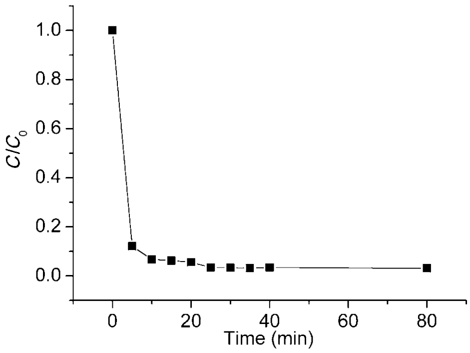

Figure 5. Relationship between the adsorption rate and time for the adsorption of MB by the as-prepared magnesium silicate hollow spheres. C_0 (in mgL^{-1}) is the initial concentration of MB solution and C (in mgL^{-1}) is the concentration of MB in the solution at different intervals during the adsorption.

The detailed relationship between the removal ability of a material and the concentration of the contaminant solution can be illustrated by an adsorption isotherm. Figure 6 shows the adsorption isotherm of MB for the as-prepared magnesium silicate hollow spheres. The Langmuir adsorption model was employed for the adsorption analysis. Such a model was

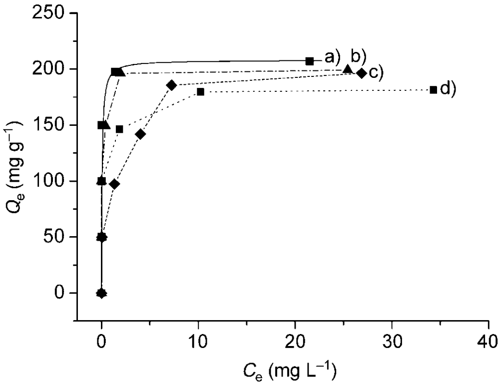

Figure 6. Adsorption isotherm of MB on a) the new as-prepared magnesium silicate hollow spheres or those that have been regenerated b) once, c) twice, or d) three times, respectively.

used to represent the relationship between the amount of MB adsorbed at equilibrium (Q_e in mg g^{-1}) and the equilibrium solute concentration (C_e in mg L^{-1}), as described by Equation (2),[17] in which Q_m (in mg g^{-1}) is the maximum adsorption capacity, corresponding to complete monolayer coverage, and b is the equilibrium constant (in L mg^{-1}).

$$Q_e = Q_m b C_e / (1 + bC_e) \qquad (2)$$

As shown in Figure 6 (line a), the experimental data fit the Langmuir adsorption isotherm well. The maximum adsorption capacity of the as-prepared magnesium silicate was found to be 207 mg g^{-1} for MB, which is much higher than the adsorption capacity of the treated sepiolite (60 mg g^{-1}) under the same conditions[8] and indicates a better adsorption performance of the as-prepared magnesium hollow spheres. After adsorption of MB, the magnesium silicate hollow spheres could be regenerated by combustion at 400 °C in air for 4 h, and the regenerated magnesium silicate hollow spheres still exhibit good adsorption performance, as shown in curves b–d in Figure 6. The removal of pollutants in water by the magnesium silicate hollow spheres is not limited to MB; other cationic dyes, such as methyl violet (MV), can also be removed effectively, as seen from the adsorption isotherm with an adsorption capacity of 180 mg g^{-1}, which is larger than the adsorption capacity of sepiolite (68 mg g^{-1}; Figure S5 in the Supporting Information).[8]

The as-prepared magnesium silicate hollow spheres were also used as absorbents to remove heavy-metal ions. Lead ions were selected as an example. The adsorption isotherm was obtained by using the above method, and the adsorption data fitted the Langmuir adsorption isotherm well, as shown in Figure 7. Most lead ions could be removed at low concentrations, and the maximum adsorption capacity of the as-prepared magnesium silicate hollow spheres reached about 300 mg g^{-1} for lead ions, which was several times higher than that of acid-treated sepiolite with an adsorption capacity of 94 mg g^{-1} at room temperature.[9] The adsorption of metal ions onto magnesium hollow spheres could also be extended to other metal ions, like copper ions (Figure S6 in the Supporting Information).

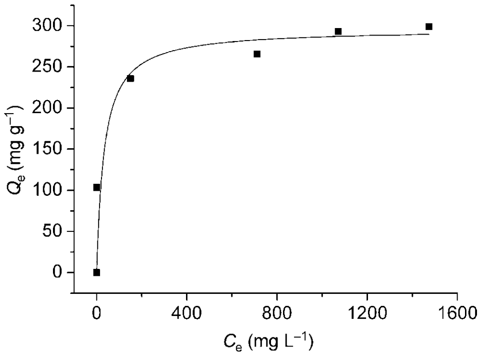

Figure 7. Adsorption isotherm of lead ions on the as-prepared magnesium silicate hollow spheres at room temperature.

If compared with those for the sepiolite adsorbent, the above results show that the as-prepared magnesium silicate hollow spheres are promising micro/nanostructures for the removal of weakly biodegradable pollutants and toxic metal ions from waste water. The high adsorption performance was explained as follows. As we know, the sepiolite was an attracting adsorbent due to its special structure, which is formed by alternation of blocks and tunnels that grow up in the microfiber direction; the blocks have the talc structure illustrated in Figure S4b in the Supporting Information.[6] In this case, the magnesium silicate hollow spheres were composed of narrow and nanoscaled lamellae. When a structural comparison was made between sepiolite and the synthesized magnesium silicate hollow spheres, we found that the separate narrow and nanoscaled lamellae of the magnesium silicate hollow spheres could be seen as the blocks of sepiolite and the space between lamellae could be seen as the tunnels in sepiolite (Figure S4b in the Supporting Information). Thus, a single magnesium silicate hollow sphere seemed to be a big "sepiolite" particle. The nitrogen adsorption and desorption isotherm and corresponding BET pore-size distribution are shown in Figure 8. The isotherm is identified as type IV, which is characteristic of mesoporous materials. The BET calculation for the pore-size distribution, derived from desorption data, reveals a narrow distribution for the as-prepared magnesium silicate hollow spheres centered at 3–5 nm (inset of Figure 8). The BET specific surface area of the as-prepared magnesium silicate hollow spheres calculated from the nitrogen isotherm is 521 m^2 g^{-1}, which is larger than that of sepiolite or sepiolite under chemical and heat treatment (maximum BET surface area of around 340 m^2 g^{-1});[8,9] on the other hand, the size of the pores between the lamellae was larger than that of tunnels, which favors the fast diffusion of dye molecules. Thus, the porous structure of the artificial magnesium silicate hollow spheres increased the amount of surface active adsorption sites and enhanced the adsorption capacity and rate greatly. When it is considered that natural sepiolite often needs to be activated with complex physical and chemical processes for high adsorption performance, these artificial magnesium silicate hollow

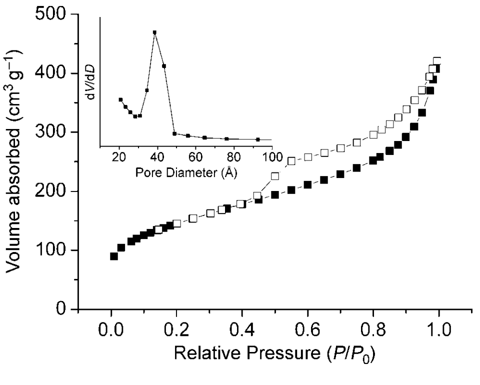

Figure 8. N_2 adsorption/desorption isotherm for the magnesium silicate hollow spheres. Inset: pore-size distribution curve obtained from the desorption data.

spheres prepared by a facile hydrothermal method provide another potential efficient absorbent due to their advantageous structure.

Conclusion

In summary, we demonstrated that micro/nanoscale magnesium silicate hollow spheres were facile to synthesize by using silica colloids as chemical templates in a hydrothermal process. The growth mechanism and conditions were studied in detail. The silica colloidal spheres were the source of silicate ions, which then react with magnesium ions to generate a magnesium silicate layer around the remaining silica colloidal spheres in situ. The as-prepared magnesium hollow spheres exhibited a large surface area and show excellent adsorption capability in the removal of organic pollutant dyes and toxic metal ions, and these results indicate that this type of silicate hollow spheres may be potential adsorbents for the removal of other toxic pollutants from water. This synthesis technique could be extended to fabricate magnesium silicate hollow structures on a large scale by using industrial amorphous silica powder and could contribute to environment remediation in the future.

Experimental Section

Preparation of the magnesium silicate hollow spheres: Monodispersed silica colloidal spheres were prepared according to the process developed by Stöber et al.[29] At room temperature, magnesium chloride (0.75 mmol, analytical reagent grade) and ammonia chloride (10 mmol, analytical reagent grade) were dissolved in deionized water (30 mL), and ammonia solution (1 mL, 28 %) was added. Silica colloidal spheres (0.1 g) were dispersed homogeneously in deionized water (20 mL). The above two solutions were mixed until homogeneous and then transferred into a Teflon autoclave (70 mL) and heated to a temperature of 140 °C for 0–12 h in a heating oven. After cooling of the reaction mixture to room temperature, the white precipitate was collected by centrifugation and washed with deionized water until the pH value was 7. After the residue was dried in an oven at 100 °C for 4 h, the magnesium silicate hollow spheres were obtained. In order to investigate the precursors affecting the growth of the magnesium silicate hollow spheres, the amount of magnesium chloride and ammonia were increased to 1.5 mmol and 1.2 mL, respectively; in addition, the amount of ammonia chloride was changed from 0 to 10 mmol while the other parameters were unchanged.

Characterization: The products were analyzed by X-ray diffraction, in a 2θ range from 10 to 80°, by using CuKα radiation (Philips X′pert diffractometer). The morphologies of the as-prepared products were studied by field-emission scanning electron microscopy (FESEM, Sirion 200 FEG) and field-emission transmission electron microscopy (FETEM, JEOL-2010, 200 kV) with an energy-dispersive X-ray analyzer (EDX, OXFORD, Link ISIS). The isoelectric point of the final product was determined by using a zeta-potential analyzer (Zetasizer 3000HSa). The surface area of the samples was determined by nitrogen adsorption (Micrometerics ASAP 2020) by using the five-point BET isotherm.

Water-treatment experiment: For the adsorption of organic pollutants, methylene blue (MB) was used as the model, and MB solutions of different concentrations were prepared. The as-prepared magnesium silicate hollow spheres (20 mg) were used as the adsorbent. After the adsorbent was wetted by a drop of ethanol, the MB solutions with different concentrations (40 mL) were added. The magnesium silicate hollow spheres were dispersed homogeneously in the MB solution by ultrasonication for 1 min and then left for a specified time (10 h) until the solid and liquid separated naturally under gravitation. A UV/Vis spectrophotometer (CARY-5E) was used to determine the concentration of MB in the remaining solution by standard spectrophotometric methods at $\lambda = 664$ nm. The adsorption isotherm of MB was obtained by varying the initial MB concentrations at room temperature. The adsorption isotherm of methyl violet was obtained in a similar way. For the adsorption of heavy-metal ions, lead and copper ions were used as the models, and metal-ion solutions of different concentrations were prepared. In the heavy-metal-ion removal experiments, the as-prepared magnesium silicate hollow spheres (20 mg) were used as the adsorbent. After the hollow spheres were wetted by a drop of ethanol, the metal-ion solutions with different concentrations (40 mL) were added. The magnesium silicate hollow spheres were dispersed homogeneously in the mixed solution by ultrasonication for 1 min and then leftt for a specified time (10 h) until the solid and liquid separated naturally under gravitation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Atomscan Advantage) was used to measure the concentration of metal ions in the remaining solution. The adsorption isotherm was obtained by changing the initial metal-ion concentrations at room temperature.

Acknowledgements

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