

Adsorption of Cadmium and Chromium in Water Body by SBA-15

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Nanoscale SBA-15 molecular sieve was synthesized by hydrothermal method and modified with ethylenediamine tetraacetic acid. The prepared materials were characterized by powder X-ray diffraction and scanning electron microscopy. The modified SBA-15 was used as sorbents to adsorb the heavy metal ions Cd²⁺ and Cr⁶⁺ in water body. The effects of pH, temperature and adsorption time on the efficiency of adsorption were studied and the optimum adsorptive conditions were confirmed. The results showed that the adsorptive effect of the material is the best and adsorptive ratio reaches 99.0 % when the pH is 4, temperature is 35 °C and adsorption time is 0.5 h.

Key Words: Adsorption, Cadmium, Chromium, SBA-15 molecular sieve, EDTA, Water body.

INTRODUCTION

Zhao *et al.*¹ prepared mesoporous molecular sieve SBA-15 using poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) hydrophilic triblock copolymer as template. SBA-15 mesoporous molecular sieve was a highly ordered planar hexagonal with two-dimensional hexagonal pores. The diameter of pore varies over the range of 4.6-30 nm. And the wall thickness of silica pore was between 3.1-6.0 nm with microporous connecting the pores. SBA-15 has large specific area *ca.* 700-1000 m² g⁻¹. After the template was removed, SBA-15 has better thermal stability more than 900 °C and higher hydrothermal stability. Its internal surface has lots of Si-OH. Because of these superiorities, mesoporous silica material, synthesized by block copolymer which served as structure directing agent, has become a hot domain in recent years.

Mesoporous molecular sieve SBA-15 not only has large surface area, uniform pore size distribution, large adjustable pore size and thicker wall, but also has good mechanical and chemical stability. Thus, it could have potential usage in several fields such as catalysis, separation, biology and nanomaterials. Song *et al.*² made use of the properties that mesoporous molecular sieve SBA-15 has high specific

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area, homogeneous distribution nanoscale pores and within a fixed range the pores can be adjusted and used different pore diameter SBA-15 as carriers to fix pig pancreas lipase (PPL), observing the effect of the pore size on the activity of the fixed PPL. The results of study indicated that in certain range the pore size of SBA-15 has obvious effect on the activity of fixed PPL and the activity is the best at 8 nm pore size. Liu *et al.*³ has already prepared large-surface and 2D (dimensional)-hexagonal-structure mesoporous SBA-15 and characterized its structure by transmission electron microscopy and nitrogen adsorption. By taking advantage of static-electrical technology, Ru(bpy)₃²⁺ was fixed on the mesoporous SBA-15 taking negative electricity on the surface. Then the mesoporous SBA-15, in which Ru(bpy)₃²⁺ was fixed, was modified to the surface of Pt-C electrode. The electrochemical luminescent action of the fixed Ru(bpy)₃²⁺ was studied. The electrode had fine stability in continuous scan. The large pores of SBA-15 are in favour of the conveyance of reagent in the channels and further reaction. With increase of reactant increased content, nanowires of various materials with 1D (dimensional)-structure were prepared in the channels one after the other. Yang *et al.*⁴ prepared nanowires of Ag having the diameter of 5-6 nm by decomposing AgNO₃ at the high-temperature in the one-dimensional ordered pores of SBA-15. Adopting similar method, Stucky *et al.*⁵ utilized SBA-15 to synthesize nanowires of Pt, Ag and Au.

At present, the domain where molecular sieves are used as adsorbent to adsorb heavy metal ions in the sewage has been primarily explored by the researchers. Chen⁶ used the novel modified zeolite to deal with electroplating wastewater which contains nickel ion and researched the influence of the mass of zeolite, temperature and the reaction time to wipe off nickel ion from electroplating wastewater. Zhan *et al.*⁷ studied the adsorption behaviour of zeolite-A towards heavy metal ions in water body and found that within a suitable and the defined range of time the longer adsorption time lasts, the higher adsorption ratio is. Zhang *et al.*⁸ used mercapto-modified mesoporous silica MCM-41 (MP-MCM-41) to adsorb Pb²⁺ ion in water and studied the influence on the extent of adsorption under different conditions. They reported that MP-MCM-41 have an extensive application prospect in selective adsorption for Pb²⁺ ion and -SH in the MP-MCM-41 and the Pb²⁺ probably formed into chelate compound. Marek *et al.*⁹ compared the natural zeolite with synthetic zeolite and pointed out the deflection of natural zeolite and the advantage of synthetic zeolite. It was indicated that the adsorptive capacity of natural zeolite differs a lot for the reason that the size of its inner passage is not homogeneous and the adsorptive ability difference is distinguish. Especially, the natural zeolite is of complex constitute and easily introduces external pollutant during the adsorption of heavy metal ions. Thus, its application to wastewater treatment is limited. In the mean while, the synthetic zeolite overcame its disadvantage. Its pure structure avoids the water being polluted again. Its homogeneous pore size which can be adjusted by changing synthetic conditions ensures the satisfactory adsorptive capacity. Perez-Quintanilla *et al.*¹⁰ took two different functionalized ways of homogeneous method and heterogeneous

method and obtained a few kinds of SBA-15 materials. They used the materials as adsorbents to purify wastewater (pH 6) that contains Hg(II) at room temperature. The results revealed that the mesoporous silica synthesized by homogeneous method showed stronger adsorptive capacity towards Hg(II) and the greatest extent of adsorption was 0.24 ± 0.02 Hg(II) mmol/g.

In recent years, with the development of industrialization, the environment was destroyed more seriously. Environmental treatment has become an urgent issue. Environmental treatment mainly includes air and water source treatment. Heavy metal elements present in water (such as Cd, Cr) did great harm to human body. Therefore, the adsorption of heavy metal elements in water and management is a priority in today's environmental treatment.

Since some metal ions can exchange with the Si-OH on the surface of molecular sieve, so metal ions can migrate to the external surface of the molecular sieve and they can also be adsorbed in the pores. Zhai and Wang have prepared the La-(SBA-15)¹¹, La-(nanometer MCM-41)¹² composites by liquid phase graft. Someone¹³ has also prepared Ru-(SBA-15) composites through Ru³⁺ exchanging with hydroxyl in the SBA-15 molecular sieve. Similar approaches¹⁴⁻¹⁷ have also been used to assemble the Ag, Eu, Pt, Au and other metals to the SBA-15 molecular sieve pores. Thus, nano-mesoporous molecular sieve can be considered as adsorbent for the adsorption of heavy metals in the environment.

As the nanoscale molecular sieve has the unique pore structure characteristics and large specific surface, so it has great potential application in the adsorption, separation and environmental governance. At present, the research on the use of nanoscale molecular sieve as the adsorbent to adsorb the harmful heavy metals in the environment is not reported. Taewook *et al.*¹⁸ modified the SBA-15 molecular sieve with imidazole at first, then used it as the adsorbent for Pb²⁺ and proved its validity. Zhang *et al.*¹⁹ found that the SBA-15 molecular sieve modified with alkyl sulfide to Hg²⁺ has a strong adsorption capacity and selectivity. Wingenfelder *et al.*²⁰ have used sodium zeolite modified with mercaptoethylamine to adsorb the Pb²⁺ in water and explained the mechanism.

The aim of the present study is to prepare mesoporous molecular sieve SBA-15 by hydrothermal synthesis using the triblock copolymer as a structure-directing agent and modified SBA-15 with EDTA. The modified nanoscale molecular sieve is used to adsorb certain heavy metals such as Cd, Cr in environment. The optimum adsorptive conditions for Cd²⁺ and Cr⁶⁺ are established. The application of the nanoscale mesoporous molecular sieve to environmental governance is explored.

EXPERIMENTAL

Tetraethyl orthosilicate (TEOS, 98 %, Fluka); poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EG₂₀-PG₄₀-EG₂₀, the average molecular weight is 5800, Aldrich); 2 mol/L hydrochloric acid (Beijing Chemical Reagent Plant, China) prepared from conc. hydrochloric acid by suitable dilution

(Beijing Beihua Fine Chemical Co., Ltd, China); EDTA (ethylenediamine tetraacetic acid, Tianjin Third Chemical Reagent Factory, China); CrO₃ (Tianjin Third Chemical Reagent Factory, China); Cd(CH₃COO)₂·2H₂O (Sinopharm Chemical Reagent Co., Ltd); NaOH (Beijing Chemical Reagent Plant, China). All chemicals used were of analytical grade and the water used was deionized water.

Power X-ray powder diffraction (XRD) patterns were collected on a D5005 diffractometer (Siemens, Germany) using Cu-K_α radiation with $\lambda = 1.5418 \text{ \AA}$ and operating at 30 kV and 20 mA. Scanning electron microscopy (SEM) images were recorded on JEOL JSM-5600L SEM instrument. The content determination of heavy metal was carried out on a TAS-990 atomic absorption spectrophotometer.

Preparation of mesoporous SBA-15 molecular sieve: Mesoporous SBA-15 molecular sieve was synthesized by hydrothermal method¹. Under the acidic condition, the triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EG₂₀-PG₄₀-EG₂₀) was used as the template and tetraethyl orthosilicate as silica source. 2.0 g of the EG₂₀-PG₄₀-EG₂₀ was dissolved in 15 g of deionized water and 60 g of 2 mol/L hydrochloric acid solution. After the template was completely dissolved under magnetic stirring, 4.25 g of tetraethyl orthosilicate was slowly dropped, stirred for 24 h at 40 °C. The mixture was transferred into a Teflon-liner autoclave treated at 100 °C for 2 days. The crystallized product was filtered and washed with deionized water and dried at room temperature. The obtained material was calcined at 550 °C for 24 h to decompose the template and obtain a white powder, mesoporous SBA-15 molecular sieve.

Modification of the SBA-15 molecular sieve

Preparation of saturated EDTA solution: The concentration of the solution was 0.5 g/L.

Modification of the SBA-15 molecular sieve by EDTA: Take a certain amount of SBA-15 molecular sieve powder accurately and then add it to the saturated EDTA solution. After magnetic stirring for 48 h, filter, wash and drying it. Then, the modification of the SBA-15 molecular sieve by EDTA can be achieved.

The purpose to modify SBA-15 is to increase its efficiency in adsorbing heavy metals by EDTA modification as EDTA is a very good complexing agent and one EDTA molecule can complex four metal ions.

Modified SBA-15 molecular sieve's adsorption for heavy metal

Effect of pH on the adsorptive impact

Effect of pH on the adsorptive impact of Cd²⁺: (1) Take an exact amount of 0.2371 g of Cd(CH₃COO)₂·2H₂O. Achieve 1 g/L of working solution of Cd²⁺ after the dissolution of it in 50 mL ionized water and put the solution in a volumetric flask of 100 mL and dilute the solution to the mark with water for application. (2) Taking 6 portions of Cd²⁺ working solution, each of which contains 2 mL Cd²⁺ solution with the concentration of 1 g/L. Put these portions separately in 6 beakers with a capacity of 100 mL. The pH values are adjusted to 1, 2, 3, 4, 5, 6, respectively.

(3) Taking 6 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1 g, add them separately into the aqueous sample mentioned above. The adsorptive reaction is lasted for 40 min at the temperature of 30 °C. (4) Remain the filtrate after the filtration. Use atomic absorption spectrometry to measure the content of Cd^{2+} in the filtrate. After the calculation of the adsorptive rate, the pH-adsorptive rate curve was drawn.

Effect of pH on the adsorptive impact of Cr^{6+} : (1) Take an exact amount of 0.1923 g CrO_3 . Achieve working solution of the concentration of 1 g/L Cr^{6+} after the dissolution of it in 50 mL of 2 mol/L hydrogen chloride solution. Put the solution in volumetric flask with the capacity of 100 mL for application. (2) Taking 6 portions of Cr^{6+} working solution, each portion contains 2 mL of Cr^{6+} solution with the concentration of 1 g/L. Put these portions separately in 6 beakers of 100 mL capacity. The pH values are separately adjusted to 1, 2, 3, 4, 5, 6. (3) Taking 6 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1 g, add them separately into the aqueous sample mentioned above. The adsorptive reaction is lasted for 40 min at the temperature of 30 °C. (4) Remain the filtrate after the filtration. Use atomic absorption spectrometry to measure the content of Cr^{6+} in the filtrate. After the calculation of the adsorptive rate, the pH-adsorptive rate curve was drawn.

Effect of temperature on adsorptive impact

Effect of temperature on the adsorptive impact of Cd^{2+} : (1) Take an exact amount of 0.2371 g of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Achieve working solution of the concentration of 1 g/L Cd^{2+} after the reagent was dissolved in 50 mL of 2 mol/L hydrogen chloride solution. Put the solution in a volumetric flask of 100 mL capacity and then dilute it to a 100 mL calibrated flask for application. (2) Taking 5 portions of Cd^{2+} working solution, each portion contains 2 mL of Cd^{2+} solution with the concentration of 1 g/L. Place these portions separately in 5 beakers of 100 mL capacity. The pH values are adjusted to 4. (3) Taking 5 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1 g. Add them separately into the aqueous sample mentioned above. The adsorptive reaction is lasted for 40 min at 20, 25, 30, 35 and 40 °C. (4) Keep the filtrate after filtration. Use atomic absorption spectrometry to measure the content of Cd^{2+} in the filtrate. After the calculation of the adsorptive rate, the pH-adsorptive rate curve was drawn.

Effect of temperature on the adsorption of Cr^{6+} : (1) Take an exact amount of 0.1923 g of CrO_3 . Achieve working solution concentration of 1 g/L Cr^{6+} after the dissolution of it in 50 mL of 2 mol/L hydrogen chloride solution. Put the solution in volumetric flask with the capacity of 100 mL and dilute it to the mark for application. (2) Taking 5 portions of Cr^{6+} working solution, each portion contains 2 mL of Cr^{6+} solution with the concentration of 1 g/L. Place these portions separately in 5 beakers 100 mL capacity. The pH values are adjusted to 4. (3) Taking 5 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1 g, add them separately

into the aqueous sample mentioned above. The adsorptive reaction is left for 40 min at 20, 25, 30, 35 and 40 °C. (4) Keep the filtrate after filtration. Use atomic absorption spectrometry to measure the content of Cr⁶⁺ in the filtrate. After the calculation of the adsorptive rate, the pH-absorptive rate curve was drawn.

Time-adsorptive rate curve

Time-adsorptive rate curve of Cd²⁺: (1) Take an exact amount of 0.2371 g Cd(CH₃COO)₂·2H₂O. Achieve working solution whose concentration of Cd²⁺ is 1 g/L after it was dissolved in 50 mL of ionized water and then put the solution in volumetric flask with capacity of 100 mL and dilute the solution to the mark for application. (2) Taking 12 portions of Cd²⁺ working solution, each of which contains 2 mL of Cd²⁺ solution with the concentration of 1 g/L. Put these portions separately in 12 beakers with the capacity of 100 mL. The pH values are adjusted to 4. (3) Taking 12 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1000 g. Add them separately into the aqueous sample mentioned above. The adsorptive reaction is lasted for 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70 min at the temperature of 35 °C. (4) Remain the filtrate after filtration. Use atomic absorption spectrometry to measure the content of Cd²⁺ in the filtrate. After the calculation of the adsorptive rate, the pH-absorptive rate curve was drawn.

Time-adsorptive rate curve of Cr⁶⁺: (1) Take an exact amount of 0.1923 g of CrO₃. Achieve working solution for which the concentration of Cr⁶⁺ is 1g/L after the dissolution of it in 50 mL of 2 mol/L hydrogen chloride solution and put the solution in 100 mL volumetric flask and dilute it to the mark for application. (2) Taking 12 portions of Cr⁶⁺ working solution, each of which portion contains 2 mL of Cr⁶⁺ solution with the concentration of 1 g/L. Put these portions separately in 12 beakers 100 mL capacity. The pH values are adjusted 4. (3) Taking 12 portions of exact amount of SBA-15 molecular sieve, each of which contains 0.1 g. Add them separately into the aqueous sample mentioned above. The adsorptive reaction is left for 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70 min at 35 °C. (4) Keep the filtrate after filtration. Use atomic absorption spectrometry to measure the content of Cr⁶⁺ in the filtrate. After the calculation of the adsorptive rate, the pH-absorptive-rate curve was drawn.

RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD) analysis: The EDTA modified SBA-15 sample was analyzed by powder XRD and the result is shown in Fig. 1. It can be seen¹ that the sample has a strong diffraction peak at 0.90° corresponding to the (100) peak of SBA-15. The two weaker peaks appeared correspond to (110) and (200) diffraction peaks of SBA-15. These are typical well-ordered two-dimensional (2D) hexagonal (p6mm) mesostructure characteristic diffraction peaks. After the SBA-15 was modified by EDTA, the framework of the sample was remained good ordered property and the sample has good high crystallization degree.

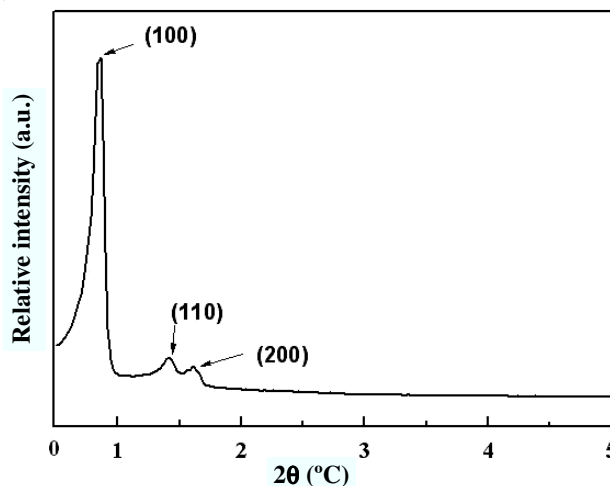


Fig. 1. XRD pattern of the modified SBA-15 molecular sieve

Scanning electron microscopic (SEM) image: Fig. 2 shows the SEM images of the modified SBA-15. It can be known from Fig. 2 that the modified SBA-15 sample consists of wheat-like macrostructures aggregated together. The crystalline form of the sample was nearly equiaxed granular crystals and uniform in shape with a calculated average particle size of 333 nm.

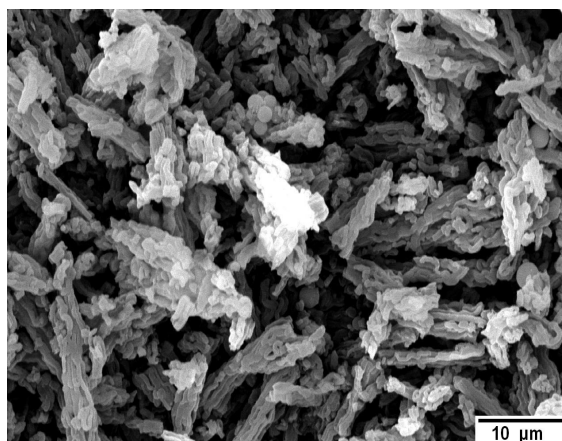


Fig. 2. SEM images of the modified SBA-15

Influence of pH on adsorptive effect

Influence of pH on the adsorptive impact of Cd^{2+} : The relationship curve between pH value and the adsorptive efficiency of Cd^{2+} is presented in Fig. 3. From the figure it can be seen that with the increase in pH value, Cd^{2+} adsorptive efficiency gradually increases. When the pH reaches 4, the adsorptive efficiency reaches

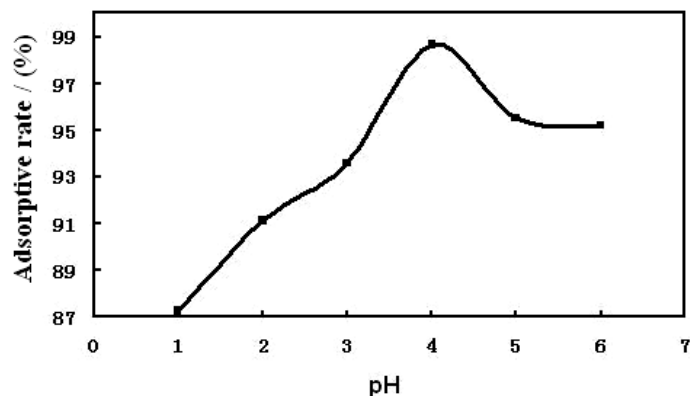


Fig. 3. Influence of pH on the adsorptive efficiency of Cd^{2+}

the maximum of 98.6 %. As the pH value further increases, Cd^{2+} adsorption efficiency decreases on the contrary. This is mainly because H^+ in the solution and Cd^{2+} have competitive adsorptive effect. With reducing the concentration of H^+ , the metal ions have more adsorptive opportunities^{7,8}. However, when the solution pH value is too large, concentration of OH^- in the solution becomes larger. A large number of OH^- and Cd^{2+} can generate precipitation compounds to block the SBA-15 pores, which accordingly reduces the efficiency of Cd^{2+} adsorption.

Influence of pH on the adsorptive impact of Cr^{6+} : The relationship curve between pH value and adsorptive efficiency of Cr^{6+} is shown in Fig. 4. From the figure it can be seen that with the increase in pH value, the adsorptive efficiency of Cr^{6+} gradually increases. When pH value reaches 4, the maximum is achieved as 98.7 %. Afterwards, as pH value further increases, the adsorptive efficiency of Cr^{6+} decreases. This is mainly because H^+ in the solution and Cr^{6+} have competitive adsorptive effect. With reducing the concentration of hydrogen ions, the metal ions have more adsorptive opportunities^{7,8}.

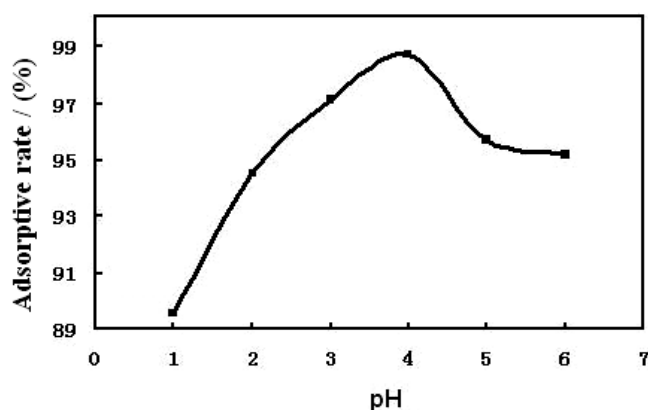


Fig. 4. Influence of pH on the adsorptive efficiency Cr^{6+}

Influence of temperature on the adsorptive impact

Influence of temperature on the adsorptive impact of Cd^{2+} : The relationship curve between temperature and adsorptive efficiency of Cd^{2+} is presented in Fig. 5. From the figure, it is clear that with the increase in temperature, the adsorptive efficiency of Cd^{2+} gradually increases, but the effect is little. When the temperature reaches 35 °C, the maximum is attained to be 98.8 %. Then, as the temperature continues to increase, the adsorptive efficiency of Cd^{2+} decreases on the contrary. This is mainly because when the temperature raises, Cd^{2+} vibration in the solution accelerates and this makes it more easily to diffuse to the SBA-15 molecular sieve pores. However, when the solution temperature is too high, Cd^{2+} movement is too active. This made the Cd^{2+} , which only existed in the form of physical adsorption in SBA-15 channels, once again diffused out. Accordingly, the adsorptive efficiency of Cd^{2+} was reduced.

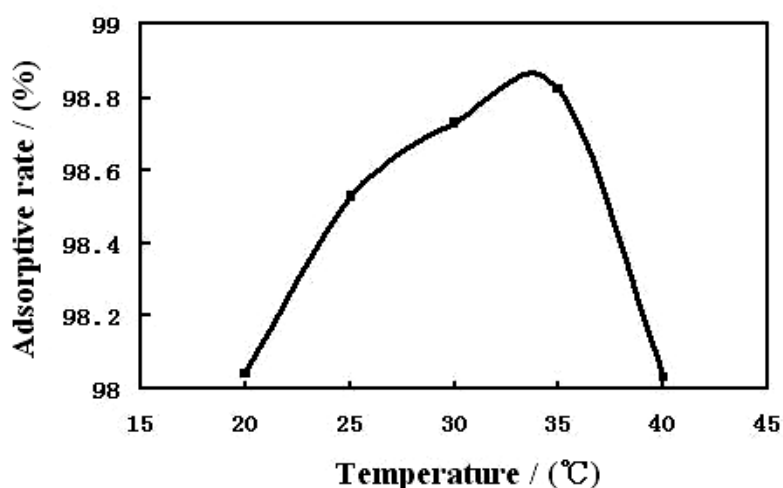


Fig. 5. Influence of temperature on the adsorptive efficiency of Cd^{2+}

Influence of temperature on the adsorptive impact of Cr^{6+} : The relationship curve between temperature and adsorptive efficiency of Cr^{6+} is presented in Fig. 6. From the figure it can be seen that with increase in the temperature, Cr^{6+} adsorption efficiency gradually increases, but the effect is little. When the temperature reaches 35 °C, the maximum attained is 98.6 %. As the temperature further increases, the adsorptive efficiency of Cr^{6+} decreases. This is mainly because the temperature rises, vibration of Cr^{6+} in the solution speeds up and this makes it more easily to diffuse to the SBA-15 molecular sieve pores. But when the solution temperature is too high, Cr^{6+} movement is too active. Thus, the Cr^{6+} , which only existed in the form of physical adsorption in SBA-15 channels, once again diffused out. Thereby, the adsorptive efficiency of Cr^{6+} was reduced.

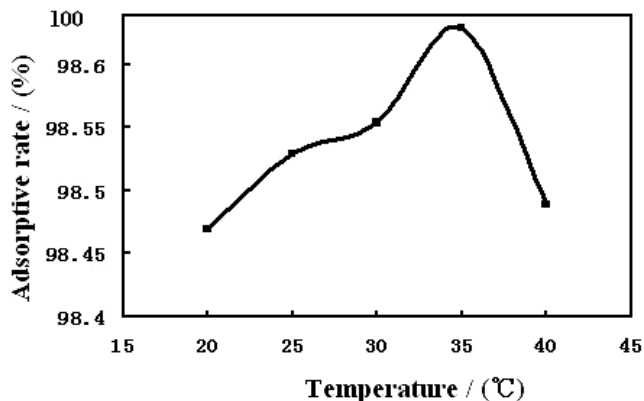


Fig. 6. Influence of temperature on the adsorptive efficiency of Cr⁶⁺

Impact of time on the adsorptive efficiency

Impact of time on the adsorptive rate of Cd²⁺: Fig. 7 presents the relationship curve between time and Cd²⁺ adsorption efficiency. From the figure it can be seen that the Cd²⁺ adsorptive efficiency increases gradually with the increase in temperature. When the time reaches 0.5 h, the maximum reached is 99.0 %. Afterwards, as time continues to extend, the adsorptive efficiency of Cd²⁺ decreases. This is mainly because at too long adsorptive time Cd²⁺ that only belonged to physical adsorption and existed in the adsorptive saturated SBA-15 molecular sieve pores began to be desorbed. Thereby, the efficiency of Cd²⁺ adsorption was decreased.

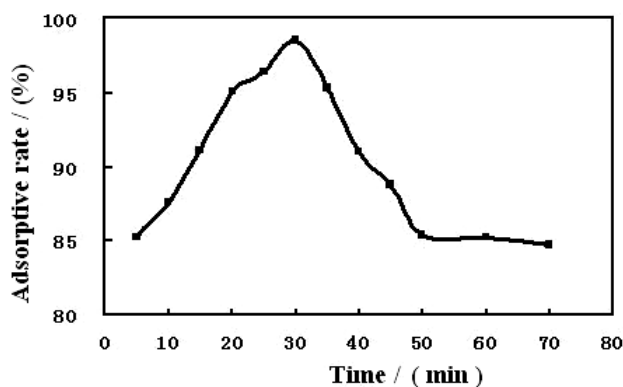


Fig. 7. Influence of time on the adsorptive efficiency of Cd²⁺

Impact of time on the adsorptive rate of Cr⁶⁺: Fig. 8 presents the relationship between time and Cr⁶⁺ adsorption efficiency. Fig. 8 shows that with the increase in temperature the adsorptive efficiency of Cr⁶⁺ increases gradually. When the time reaches 0.5 h, the maximum obtained is 98.0 %. Afterwards, as time continues to prolong, the adsorptive efficiency of Cr⁶⁺ decreases. This is mainly because at too

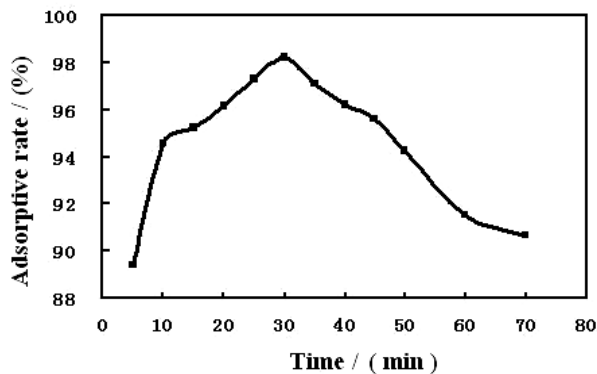


Fig. 8. Influence of time on the adsorptive efficiency of Cr^{6+}

long adsorptive time Cr^{6+} that only belonged to physical adsorption in the adsorptive saturated SBA-15 molecular sieve pores began to be desorbed. Thus, the efficiency of Cr^{6+} adsorption was decreased.

Conclusion

The EDTA modified SBA-15 molecular sieve can be used as the adsorbent of Cd^{2+} and Cr^{6+} in water and it is expected to be used in waste water treatment. The optimum adsorptive conditions were defined. The highest adsorptive efficiency of Cd^{2+} and Cr^{6+} can reach 98.6 and 98.7 % at pH = 4, respectively. At 35 °C, the highest adsorptive efficiency of Cd^{2+} and Cr^{6+} can reach 98.8 and 98.6 %, respectively. When the adsorptive time is 0.5 h, the highest adsorptive efficiency of Cd^{2+} and Cr^{6+} reaches 99.0 and 98.0 %, respectively.

ACKNOWLEDGEMENT

The authors are grateful to the financial support from Jilin Provincial Science and Technology Department, China. The grant number was 20090548 (KYC-JC-XM-2009-040).

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(Received: 28 May 2010; Accepted: 5 August 2010) AJC-8961