



## SBA-15 for Effective Removal of Mercury(II) from Aqueous Solution

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Because of its good structural function, excellent hydrothermal stability, steady framework structure, easily modified interior surface and certain wall thickness with easily blended element, SBA-15 has a bright applied foreground in various domains, such as adsorption-separation, environment, catalysis and light, electricity, magnetism, *etc.* Molecular sieve SBA-15 was prepared by hydrothermal method in this paper. By means of X-ray diffraction and scanning electron microscopy, the products were characterized. The modified SBA-15 were prepared by surface modification method with mercaptoethanol and thioglycolic acid. The pre-modified and post-modified materials were used as sorbents to evaluate the effects of acidity, temperature and time on the adsorption of  $Hg^{2+}$ . The adsorptive experimental results showed that the optimum adsorbent was the SBA-15 obtained by the modification of thioglycolic acid. The optimal adsorptive conditions were: pH = 5, temp. 20 °C and the adsorptive time was 50 min. The experimental results indicated that the best desorbent was 0.1 mol/L HCl. The highest rate of desorption of 75.05 % could be reached at the desorption of 2 h.

**Key Words:**  $Hg^{2+}$ , SBA-15, Surface modification, Mercaptoethanol, Thioglycolic acid, Adsorption, Water body.

### INTRODUCTION

In 1992, Beck and Kresge *et al.*<sup>1,2</sup> of Mobil Corporation firstly used surfactant as template to synthesize a novel ordered mesoporous silica materials-M41S, which is the first breakthrough and leap. This kind of new mesoporous materials has the advantages that the pore diameter size is homogeneous, the arrangement is regular and ordered, the pore diameter can be continuously adjustable over the range of 2-10 nm and the materials have very high specific surface area, *etc.* However, due to their poor stability, the application of the materials is restricted. Zhao *et al.*<sup>3,4</sup> used triblock non-ionic type surfactant P123 to synthesize a new type silica mesoporous molecular sieve SBA-*n* series, among which SBA-15 is especially dramatical. It not only carried forward the advantages of MCM-41, but also has its excellent structural performance: (1) regular pore channel structure, presenting 2-dimensional hexagonal form; (2) very narrow pore diameter distribution and pore diameter can generally be continuously adjustable over 5-30 nm; (3) large specific surface area, which can reach 1000 m<sup>2</sup>/g; (4) compared with MCM-41, SBA-15 has better hydrothermal stability; (5) SBA-15 has stable framework structure, easily modified inner surface, definite wall thickness and the physical and chemical performance of easily adulterated amorphous framework composition. Therefore, SBA-15 has a prodigious development foreground in numerous domains

such as adsorption, separation, catalysis, chemical industry, biological technology, environment and optics, electricity, magnetism, *etc.*

Due to diversity of the chemical form of heavy metals, the complexity of environmental behaviour and harmful ponderance, it has been paying attention by the circles of water process at all times. There are many methods of processing heavy metal wastewater. According to harness process of the change of the chemical forms of metals, they can be sorted as reported by Peters *et al.*<sup>5</sup> and Wang<sup>6</sup>: chemical form change method and chemical form no-change method. According to process means, they can be sorted as physical method, chemical method, physical chemical method and biological chemical method, *etc.* Among them, a little more used method is as follows: adsorption method, which can selectively remove the heavy metal ions in waste water. The removed metal ions can not transfer into environment to work more execrable impact. However, due to the own toxic characteristic of mercury such as the reasons that volatility is strong, toxicity is strong, biological cumulative character is strong and composition of the industrial castoff containing mercury is complex, *etc.*, traditional adsorptive technique can not effectively harness the dangerous castoff containing mercury. Thus studies of the materials that have strong adsorption performance to mercury and applications to the pollution harness of mercury in waste water are an important approach and technical challenge.

## EXPERIMENTAL

Zeolite-A<sup>7</sup> and fargite<sup>8</sup> have already been applied to the adsorptive studies of Pb<sup>2+</sup> and Pb<sup>2+</sup>, Cd<sup>2+</sup>, respectively. MCM-41<sup>9</sup> has also been used in the discussion of the adsorption of Pb<sup>2+</sup>. Compared with the zeolite molecular sieves above-used, mesoporous material SBA-15 has a series of advantages that the pore channel structure is regular, specific surface area is big and surface energy is high, *etc.*, having great applied value in the aspect of dealing with the pollution of heavy metal mercury by adsorption method. In order to enhance the adsorption performance of mesoporous material SBA-15, scientific circles are devoted to the process of taking up with the modification aspect of its surface. As the surface of mesoporous materials SBA-15 is in unsaturated state and has surface energy, this makes it have the tendency of the spontaneous adsorption of foreign ions or molecules to reduce the surface energy. Its detailed approach is majorly that from water the proton are associated or the use of hydroxyl balances chemical force, which resulted in the surface hydroxylation of synthetic material. Thus, on the surface of the SBA-15 synthesized by hydrothermal method quite quantitative silanols exist. The surface of mesoporous silica material SBA-15 contains three kinds of silanol bonds, namely, free silanol bond, double hydroxyl silanol bond and association silanol bond, among which the former two have higher activity of chemical reactions. However, hydration silanol bond has not chemical activity and can not arise chemical reaction. The silanol having chemical activity is a base of the surface chemical modification of mesoporous material. Introducing active site into channels or framework by forming the bonds of surface silanol bond and active component can endure SBA-15 many excellent performances. SBA-15 mesoporous molecular sieve has larger specific surface area on structure and its surface has many -Si-OH, which makes Hg<sup>2+</sup> be able to exchange the H<sup>+</sup> in -Si-OH on surface and reaches a goal of the adsorption of Hg<sup>2+</sup>. In each point of adsorptive location, two Hg<sup>2+</sup> can be adsorbed. However, if by using surface modification -SH will be modified to the surface of SBA-15 and by using a strong chelated action between -SH and heavy metal ions: one mercapto-group can adsorb six Hg<sup>2+</sup>, this can make the adsorptive ability of SBA-15 be extremely largely enhanced.

This paper is just about base on ascendant properties of the adsorptive performance of mesoporous molecular sieve SBA-15 and uses triblock copolymer poly(ethylene glycol)-block-poly(propyl glycol)-block-poly(ethylene glycol) (EG<sub>20</sub>PG<sub>40</sub>EG<sub>20</sub>) as template under acidic condition and uses tetraethyl orthosilicate (TEOS) as silica source to synthesize SBA-15 and makes it modification process by using mercaptoethanol, mercaptoacetic acid, respectively. The modified SBA-15 molecular sieve is applied to the adsorptive study of Hg<sup>2+</sup> in water body. In this article the optimum conditions of the adsorption of Hg<sup>2+</sup> in water body by SBA-15 and the modified SBA-15 materials are studied and the desorptive study was made. The application of SBA-15 mesoporous nanoscale molecular sieve and its modified materials were discussed to environmental harness. For the exploitation of new type heavy metal adsorbent, it has an important value.

Poly(ethylene glycol)-block-poly(propyl glycol)-block-poly(ethylene glycol) (EG<sub>20</sub>-PG<sub>40</sub>-EG<sub>20</sub>, average molecular weight 5800, Aldrich); tetraethyl orthosilicate (TEOS, 98 %, Shanghai Company of Chemical Reagents, Chinese Medicine Group, China); 2 mol/L of hydrochloric acid (Beijing Chemical Plant, China) solution; mercaptoethanol (C<sub>2</sub>H<sub>6</sub>OS, Tianjin Guangfu Fine Chemical Research Institute, China); thioglycollic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>S, Sinopharm Chemical Reagent Co. Ltd, China); absolute ethanol (Beijing Chemical Works, China); mercury nitrate [Hg(NO<sub>3</sub>)-0.5H<sub>2</sub>O, Chemical Reagent Works of Taixing City, China]; 2-(5-bromo-2-pyridineazo)-5-diethylaminophenol (5-Br-PADAP, Shanghai Jingchun Reagent Co. Ltd., China): 5 × 10<sup>-4</sup> mol/L; NH<sub>3</sub>-NH<sub>4</sub>Cl buffer solution (pH = 9.26): equal volumes of 0.1 mol/L NH<sub>3</sub>·H<sub>2</sub>O (Beijing Chemical Works, China) and 0.1 mol/L NH<sub>4</sub>Cl (Plant of Reagent, Economy and Trade Company of Liaoning Medicine, China) solution were mixed to obtain the NH<sub>3</sub>-NH<sub>4</sub>Cl buffer solution of pH = 9.26. Sodium laurylsulfate (SLS, Sinopharm Chemical Reagent Co. Ltd., China): 10 g/L; 0.1 mol/L NaOH (Beijing Chemical Plant, China) solution; 0.1 mol/L of HCl (Beijing Chemical Plant, China) solution; 0.1 mol/L of HNO<sub>3</sub> (Beijing Chemical Plant, China) solution; 0.1 mol/L HAc (Beijing Chemical Plant, China) solution. Unless specially stated, all the reagents used were of analytical grade. The water was deionised water.

Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5005 diffractometer (Germany) using CuK<sub>α</sub> radiation (λ = 1.5418 Å and operating at 40 kV and 30 mA). Typically, the diffraction data were collected from 0.4-10° (2θ) with a resolution of 0.02°. A Jeol JSM-5600L scanning electron microscope (Japan) was used to measure the shape and size of sample particles. A HJ-6A digital display constant temperature water-bath boiler (Jiangsu Jintan Ronghua Apparatus Manufacture Co. Ltd., China) was employed to the control of experimental temperature. A 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China) equipped with 1-cm cells was applied to the determination of absorbance.

### Procedures

**Synthesis of SBA-15:** Mesoporous SBA-15 molecular sieve was prepared according to the reported procedure<sup>4</sup>. Under the acidic condition, the reported triblock copolymer, EG<sub>20</sub>PG<sub>40</sub>EG<sub>20</sub>, was used as template and TEOS was used as silica source. In a typical synthesis, 2.0 g of the template was dissolved in 60 g of 2 mol L<sup>-1</sup> hydrochloric acid and 15.0 g of deionized water, then 4.25 g of TEOS was added, stirred for 24 h at 40 °C. The mixture was aged in a Teflon-liner autoclaves treated at 100 °C for 48 h. The product was filtered and washed with deionized water and dried at room temperature. The obtained mesoporous silica SBA-15 white powder material was calcined at 550 °C for 24 h to completely eliminate the template.

**Modification of SBA-15:** Two kinds of modification agent, mercaptoethanol and thioglycollic acid, were, respectively used to modify SBA-15 molecular sieve to prepare functionalized materials SBA-15. The detailed experimental steps are as follows: 2 mL of the modification agent and 0.2 g of SBA-15 molecular sieve were placed in 40 mL of ethanol

aqueous solution (volume ratio was 1:1) and reacted for 48 h under magnetic stirring at room temperature. The reacted mixture was filtered, washed with ethanol and water, respectively and dried at room temperature.

**Working curve of spectrophotometric determination of mercury(II)<sup>10</sup>:** In a  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer medium of pH = 9.26 in the presence of an anionic surfactant SLS,  $\text{Hg}^{2+}$  was determined with 5-Br-PADAP. The maximum absorption wavelength was at 562 nm and the linear range of working curve was 0-35  $\mu\text{g}/25\text{ mL}$ . By calculation, the standard working curve of  $\text{Hg}^{2+}$  was obtained to be:  $A = 0.4030 C (\mu\text{g}/\text{mL}) + 0.0086$ , with a correlation coefficient of  $\gamma = 0.9990$ .

**Procedure of the adsorption of  $\text{Hg}^{2+}$  by SBA-15:** In the present experiment, the effect of pH, temperature and time are investigated on the adsorption of  $\text{Hg}^{2+}$  by SBA-15 and accordingly the optimum pH, optimum temperature and optimum time are obtained for the adsorption of  $\text{Hg}^{2+}$  by SBA-15.

**Effect of pH on the adsorptive effect of  $\text{Hg}^{2+}$ :** Six portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 6 beakers with a capacity of 100 mL. The pH values were respectively adjusted to 1, 2, 3, 4, 5, 6 using 0.1 mol/L  $\text{HNO}_3$  and 0.1 mol/L NaOH solution. Six portions of 0.1000 g of unmodified SBA-15 molecular sieves were accurately weighed, respectively added to the above-stated samples, stirred for 40 min at 20 °C and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the above spectrophotometric method and the adsorptive ratio was worked out. pH-adsorptive rate curve was drawn. The adsorptive optimum pH value was obtained.

**Effect of temperature on the adsorptive effect of  $\text{Hg}^{2+}$ :** Five portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken in 5 beakers with a capacity of 100 mL. The optimum pH value was, respectively adjusted. Five portions of 0.1000 g of unmodified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20, 25, 30, 35 and 40 °C and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive rate curve was drawn. The adsorptive optimum temperature was obtained.

**Effect of time on the adsorptive effect of  $\text{Hg}^{2+}$ :** Five portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 5 beakers with a capacity of 100 mL. The optimum pH value and optimum temperature were, respectively adjusted. Five portions of 0.1000 g of unmodified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 25, 30, 35 and 40 min at optimum pH value and optimum temperature and then filtered. The filtrates were held. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive rate curve was drawn. The adsorptive optimum time was obtained.

**Procedure for the adsorptive studies of  $\text{Hg}^{2+}$  by mercaptoethanol-modified SBA-15:** In the present experiment, the effect of pH, temperature and time are investigated on the adsorption of  $\text{Hg}^{2+}$  by mercaptoethanol-modified SBA-15 and accordingly the optimum pH, optimum temperature and optimum time for the adsorption of  $\text{Hg}^{2+}$  by SBA-15 were obtained.

**Effect of pH on the adsorptive effect of  $\text{Hg}^{2+}$ :** Six portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 6 beakers with a capacity of 100 mL. The pH values were, respectively adjusted to 1, 2, 3, 4, 5, 6 using 0.1 mol/L  $\text{HNO}_3$  and 0.1 mol/L NaOH solution. Six portions of 0.1000 g of mercaptoethanol-modified SBA-15 molecular sieves were accurately weighed, respectively added to the above-stated samples, stirred for 40 min at 20 °C and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the spectrophotometric method and the adsorptive rate was worked out. pH-adsorptive rate curve was drawn. The adsorptive optimum pH value was obtained.

**Effect of temperature on the adsorptive effect of  $\text{Hg}^{2+}$ :** Five portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 5 beakers with a capacity of 100 mL. The optimum pH value was, respectively adjusted. Five portions of 0.1000 g of the mercaptoethanol modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20, 25, 30, 35 and 40 °C and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive rate curve was drawn. The adsorptive optimum temperature was obtained.

**Effect of time on the adsorptive effect of  $\text{Hg}^{2+}$ :** Five portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 5 beakers with a capacity of 100 mL. The optimum pH value and optimum temperature were, respectively adjusted. Five portions of 0.1000 g of the mercaptoethanol-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 25, 30, 35 and 40 min at optimum pH value and optimum temperature and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive rate curve was drawn. The adsorptive optimum time was obtained.

**Procedure for the adsorptive studies of  $\text{Hg}^{2+}$  by thioglycolic acid-modified SBA-15:** In the present experiment, the effect of pH, temperature and time are investigated on the adsorption of  $\text{Hg}^{2+}$  by the thioglycolic acid-modified SBA-15 and accordingly the optimum pH, optimum temperature and optimum time for the adsorption of  $\text{Hg}^{2+}$  by SBA-15 were obtained.

**Effect of pH on the adsorptive effect of  $\text{Hg}^{2+}$ :** Six portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 6 beakers with a capacity of 100 mL. The pH values were, respectively adjusted to 1, 2, 3, 4, 5, 6 using 0.1 mol/L  $\text{HNO}_3$  and 0.1 mol/L NaOH solution. 6 portions of 0.1000 g of thioglycolic acid-modified SBA-15 molecular sieve were accurately weighed, respectively added to the above-stated samples, stirred for 40 min at 20 °C and then filtered. The  $\text{Hg}^{2+}$  content in each filtrate was determined by the spectrophotometric method and the adsorptive ratio was worked out. pH-adsorptive rate curve was drawn. The adsorptive optimum pH value was obtained.

**Effect of temperature on the adsorptive effect of  $\text{Hg}^{2+}$ :** Five portions of 40 mL working solution whose  $\text{Hg}^{2+}$  concentration was 1 mg/mL were taken and respectively placed in 5



beakers with a capacity of 100 mL. The optimum pH value was, respectively adjusted. Five portions of 0.1000 g of the thioglycollic acid-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20, 25, 30, 35 and 40 °C and then filtered. The Hg<sup>2+</sup> content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive rate curve was drawn. The adsorptive optimum temperature was obtained.

**Effect of time on the adsorptive effect of Hg<sup>2+</sup>:** Five portions of 40 mL working solution whose Hg<sup>2+</sup> concentration was 1 mg/mL were taken and respectively placed in 5 beakers with a capacity of 100 mL. The optimum pH value and optimum temperature were, respectively adjusted. Five portions of 0.1000 g of the thioglycollic acid-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 25, 30, 35 and 40 min at optimum pH value and optimum temperature and then filtered. The Hg<sup>2+</sup> content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive rate curve was drawn. The adsorptive optimum time was obtained.

**Procedure for the desorption experiment of Hg<sup>2+</sup> for thioglycollic acid modified-SBA-15 sample:** The experimental effects of three kinds of desorptive agents, 0.1 mol/L HNO<sub>3</sub>, 0.1 mol/L HCl, 0.1 mol/L AcOH, on the desorption of Hg<sup>2+</sup> adsorbed by the thioglycollic acid modified-SBA-15 were investigated to educe the optimum desorptive agent.

**Preparation of desorptive experimental material:** A suitable amount of thioglycollic acid modified-SBA-15 molecular sieve was accurately weighed and placed in a definite amount of the standard solution of Hg<sup>2+</sup> with concentration of 1 mg/mL. Adjusting pH = 5, adsorption was made for 50 min at 20 °C. It was filtered to obtain the sample A for desorption.

**Desorptive experiment of the Hg<sup>2+</sup> adsorbed by thioglycollic acid modified-SBA-15 using 0.1 mol/L nitric acid:** Eight portions of 50 mL of 0.1 mol/L HNO<sub>3</sub> were taken. Eight portions of a suitable amount of the sample were accurately weighed, respectively placed in the HNO<sub>3</sub> to be soaked for 1, 2, 3, 4, 5, 6, 7 and 8 h and then filtered. The Hg<sup>2+</sup> content in them was determined by the spectrophotometric method and desorptive rate was worked out. Desorptive time-desorptive rate curve was drawn. The optimum desorptive time was educed.

**Desorptive experiment of the Hg<sup>2+</sup> adsorbed by thioglycollic acid modified-SBA-15 using 0.1 mol/L hydrochloric acid:** Six portions of 50 mL of 0.1 mol/L HCl were taken. Six portions of a suitable amount of the above A sample were accurately weighed, respectively placed in the above HCl to be soaked for 1, 2, 3, 4, 5 and 6 h and then filtered. The Hg<sup>2+</sup> content in them was determined by the spectrophotometric method and desorptive rate was worked out. Desorptive time-desorptive rate curve was drawn. The optimum desorptive time was educed.

**Desorptive experiment of the Hg<sup>2+</sup> adsorbed by thioglycollic acid modified-SBA-15 using 0.1 mol/L acetic acid:** Four portions of 50 mL of 0.1 mol/L AcOH were taken. Four portions of a suitable amount of the above A sample were accurately weighed, respectively placed in the above HCl to

be soaked for 1, 2, 3 and 4 h and then filtered. The Hg(II) content in them was determined by the spectrophotometric method and desorptive rate was worked out. Desorptive time-desorptive rate curve was drawn. The optimum desorptive time was educed.

**Effect of the acidity of hydrochloric acid on the desorptive experiment of the Hg<sup>2+</sup> adsorbed by thioglycollic acid modified-SBA-15:** 50 mL of 0.01, 0.1 and 1 mol/L HCl were taken and respectively placed in 3 beakers with a capacity of 100 mL. Three portions of a suitable amount of the above-stated sample A were accurately weighed, respectively, placed in the above-stated beakers and soaked for 2 h. The above-stated mixed solutions were, respectively filtered. The Hg<sup>2+</sup> content in each filtrate was determined by the spectrophotometric method and the adsorptive rate was worked out. The acidity of desorptive agent-adsorptive rate curve was drawn. The optimum adsorptive acidity was educed.

## RESULTS AND DISCUSSION

**Powder X-ray diffraction (XRD):** The analytical results of XRD of the samples (Fig. 1) show that for the SBA-15 molecular sieve prepared four diffraction peaks (curve a) occur

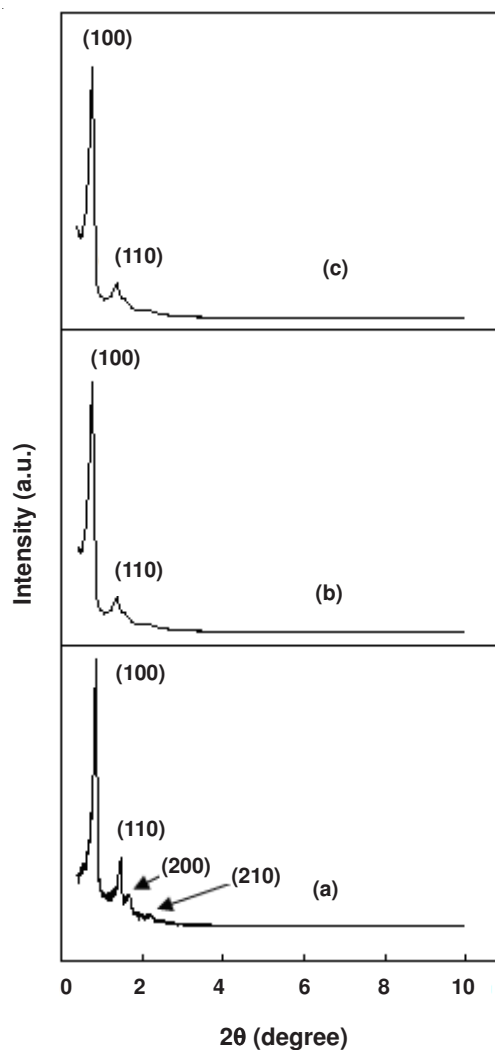


Fig. 1. XRD pattern of the samples: (a) SBA-15; (b) mercaptoethanol modified SBA-15; (c) thioglycollic acid modified SBA-15

and the peaks can be assigned to the diffraction peaks obtained by (100), (110), (200) and (210) crystal diffraction, indicating the SBA-15 molecular sieve was successfully prepared. For mercaptoethanol- or thioglycollic acid-molecular sieve sample two diffraction peaks (curve b, c) appear, which can be assigned to (100), (110) crystal face diffraction peaks, respectively. These are the characteristic diffraction peaks of SBA-15 molecular sieve<sup>3,4</sup>, showing that the modified molecular sieves remained two-dimensional planar hexagonal channel structures and no phenomenon of the collapse of framework appeared. The disappearance of (200) and (210) crystal face diffraction peaks shows that the crystalline degree and ordered degree of the modified materials decreased. In addition, the characteristic diffraction peaks of modified samples moved to smaller angle compared with those of unmodified SBA-15, showing that -SH has already gone into surface of the molecular sieves or S atoms substituted the oxygen atoms in Si-O-Si.

**Scanning electron microscopic (SEM) images:** SEM can well reflect the morphology of a sample and its size magnitude. For mesoporous materials, it is a very important means of characterization. From the SEM photographs (Fig. 2) it can be seen that the synthesized sample SBA-15 majorly presents fibriform shape and its particle diameter length is  $333 \pm 5$  nm.

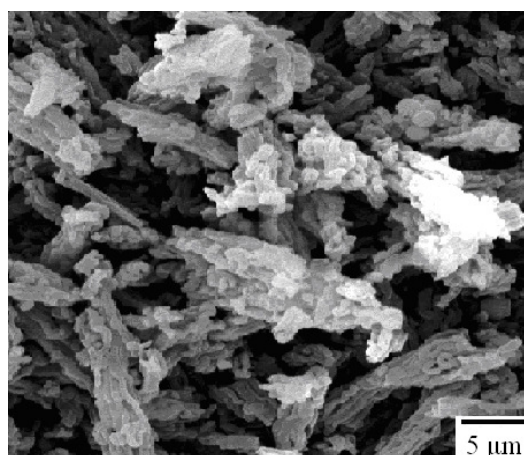


Fig. 2. SEM images of the sample

**Modification mechanism of SBA-15:** Modification mechanism of SBA-15 is shown as Fig. 3. It is *via* the modification agent mercaptoethanol and thioglycollic acid that react with the Si-OH of surfaces of mesoporous material SBA-15 to carry through dehydration reaction and to seriatim introduce mercapto-group into mesoporous material SBA-15.

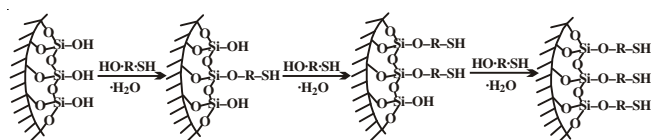


Fig. 3. Reaction mechanism (R = -COCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-)

### Adsorptive experimental results

**Results of the effect of pH value on the adsorption of Hg<sup>2+</sup>:** Based on the standard working curve of Hg<sup>2+</sup> obtained, the corresponding adsorptive rates of SBA-15, mercaptoethanol-

modified SBA-15 and thioglycollic acid-modified SBA-15 at different pH were worked out (Fig. 4). It can be seen that under the same mass adsorptive materials and the same initial Hg<sup>2+</sup> concentration the adsorptive rates of three kinds of materials increased as pH value increased. It may be due to the adsorption of Hg<sup>2+</sup>. After high pH, neutralizing H<sup>+</sup> could decrease the competitive action of H<sup>+</sup>, which was advantageous to the adsorption of Hg<sup>2+</sup>. Whereas at pH = 5, the adsorptive rates of Hg<sup>2+</sup> by the mercaptoethanol-modified SBA-15 and the thioglycollic acid-modified SBA-15 have been achieved to be 90.39 % and 97.19 %, respectively and at pH = 6 precipitation had been complete and an adsorptive rate of 100 % was mainly due to the precipitation action of Hg(OH)<sub>2</sub> and not due to the adsorptive action of adsorption materials. Thus, the optimum pH of adsorptions for three kinds of materials were ascertained to be 5. Under the same pH of three kinds of materials, the adsorptive rates of Hg<sup>2+</sup> were also different and from strong to weak their adsorptive ability is in order: thioglycollic acid-modified SBA-15 > mercaptoethanol-modified SBA-15 > SBA-15. The reason is investigated and it may be that the adsorption of Hg<sup>2+</sup> by SBA-15 belongs to the comprehensive action result of ion exchange and physical adsorption. However, the adsorptions of Hg<sup>2+</sup> by the mercaptoethanol-modified SBA-15 and the thioglycollic acid-modified SBA-15 belong to a comprehensive action result of three kinds of action force, ion exchange, physical adsorption and chemical adsorption. Thus, their adsorptive drive forces consumedly reinforced and thereby their adsorptive rates were obviously enhanced. That the adsorptive rate by the thioglycollic acid-modified SBA-15 was higher than that by mercaptoethanol-modified SBA-15 is due to that the effect of SBA-15 modification by thioglycollic acid was better than that of SBA-15 modification by mercaptoethanol and more -S entered into the thioglycollic acid-modified SBA-15.

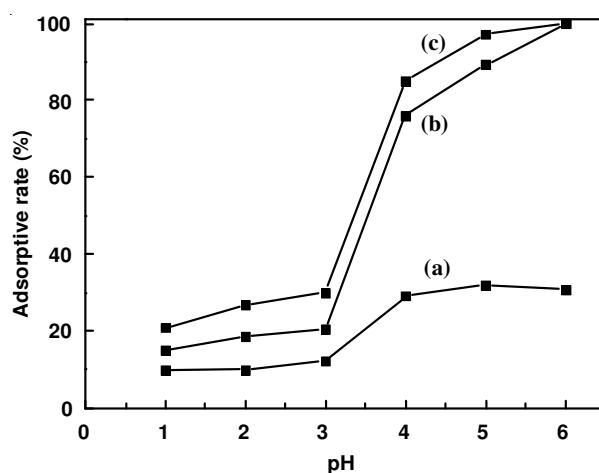


Fig. 4. Effect of pH on the adsorption of Hg<sup>2+</sup>: (a) SBA-15; (b) mercaptoethanol modified SBA-15; (c) thioglycollic acid modified SBA-15

### Results of the adsorptive effect of temperature on Hg<sup>2+</sup>:

Based on the standard working curve of Hg<sup>2+</sup> obtained, the corresponding adsorptive rates of SBA-15, mercaptoethanol-modified SBA-15 and thioglycollic acid-modified SBA-15 at different temperature were worked out as shown in Fig. 5. It

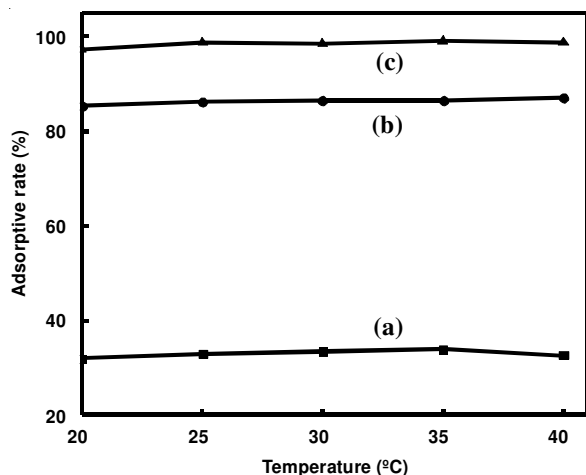


Fig. 5. Effect of temperature on the adsorption of Hg<sup>2+</sup>: (a) SBA-15; (b) mercaptoethanol modified SBA-15; (c) thioglycollic acid modified SBA-15

can be seen that the effects of temperature on the adsorptive performances of three kinds of adsorptive materials were not high. The reason may be due to the effect of temperature on adsorption has duality was caused. Firstly, when temperature increased, the thermal motion of Hg<sup>2+</sup> aggravated and in the solution vibration quickened. This made Hg<sup>2+</sup> more easily diffuse into the channels of adsorptive materials and made adsorptive rate increase as temperature increased. From it, a positive effect was caused. However, as non-ionic adsorption is exothermal reaction, thereby the increase in temperature is not disadvantageous to non-ionic exchange adsorption. This again made adsorptive rate decrease as temperature increased, causing negative effect. As two kinds of effects reciprocally counteracted, the variation of adsorptive rate was not high along with the change of temperature. At high temperature adsorption needs a large amount of energy consume, the optimum temperature was confirmed to be room temperature. From the figure, it can be deduced that at the same temperature the adsorptive ability of three kinds of adsorptive materials is in turn from strong to weak: thioglycollic acid-modified SBA-15 > mercaptoethanol-modified SBA-15 > SBA-15. The reason is investigated and it is the adsorptive drive forces of the thioglycollic acid-modified SBA-15 and the mercaptoethanol-modified SBA-15 are much more than that of SBA-15 itself. At the same time, it can once again illustrate the adsorptive effect using the thioglycollic acid-modified SBA-15 was better than that using the mercaptoethanol-modified SBA-15.

**Results of the adsorptive effect of time on Hg<sup>2+</sup>:** Based on the standard working curve of Hg<sup>2+</sup> obtained, the corresponding adsorptive rates of SBA-15, mercaptoethanol-modified SBA-15 and thioglycollic acid-modified SBA-15 at different temperature were worked out (Fig. 6). It can be seen that as time prolonged, all the adsorptive rates of three kinds of materials behaved ascending trend. However, when adsorptive rate achieved a definite value, it did not augment as time increased. At this time the adsorptive materials had already achieved saturation capacities and the adsorptive rates at this time were the largest ones. When time tend to increase, the adsorptive rates presented the trend of a little decrease. This might be the reason that desorption had already appeared.

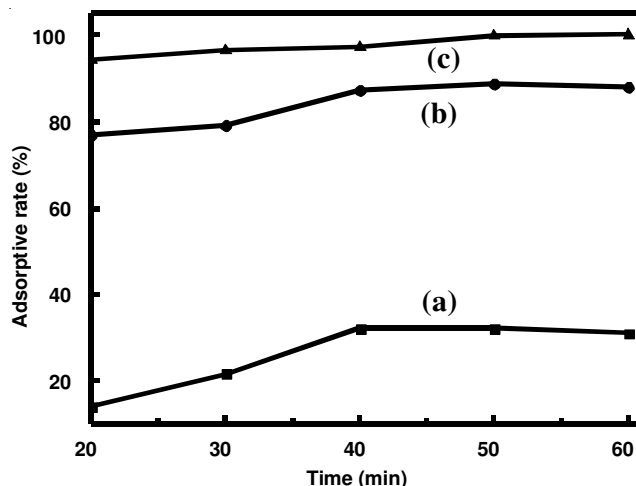


Fig. 6. Effect of time on the adsorption of Hg<sup>2+</sup>: (a) SBA-15; (b) mercaptoethanol modified SBA-15; (c) thioglycollic acid modified SBA-15

Therefore, the optimum desorptive time was confirmed to be 50 min. From the figure, it can be obtained that at the same time the adsorptive abilities of three kinds of adsorptive materials from strong to weak are in order: thioglycollic acid modified-SBA-15 > mercaptoethanol-modified SBA-15 > SBA-15. The reason may be due to the adsorptive drive forces of the thioglycollic acid modified-SBA-15 and the mercaptoethanol-modified SBA-15 are much more than that of SBA-15. At the same time, it is also proved that the adsorptive effect of the modification of SBA-15 using the thioglycollic acid is better than that of the modification of SBA-15 using the mercaptoethanol.

Thus, the thioglycollic acid-modified SBA-15 was selected as adsorptive material to study desorption.

#### Desorptive experimental results of the thioglycollic acid-modification post-adsorption Hg<sup>2+</sup> SBA-15 sample

The desorptive rate of the thioglycollic acid-modified SBA-15 adsorbing Hg<sup>2+</sup> using 0.1 mol/L HNO<sub>3</sub> at different time is shown as Fig 7. From the figure, it can be seen that as time prolonged, the desorptive rate was firstly gradually increased and then it decreased when reaching a definite value. It may be due to the reason that H<sup>+</sup> replaced Hg<sup>2+</sup> of the surface of adsorber and desorption occurred was a slow process. A

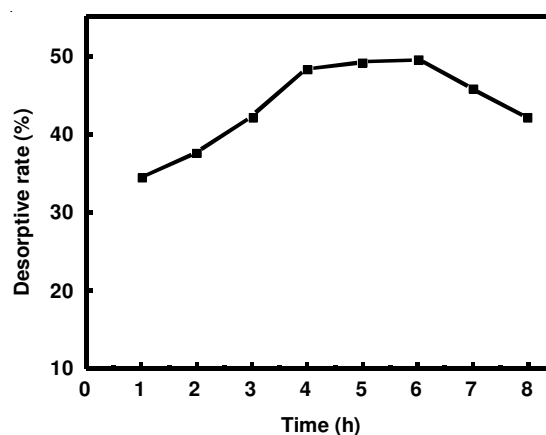


Fig. 7. Effect of time on desorptive impact

desorptive equilibrium to be reached needs a definite time. Thus, before the equilibrium is arrived, the desorptive rate is ascending. However, after the equilibrium is reached, as the desorbed  $\text{Hg}^{2+}$  again is adsorbed, this makes desorptive rate be reduced a little. Among them, at 6 h a maximum desorptive rate of 49.51 % was achieved.

The desorptive rate of the thioglycollic acid-modified SBA-15 adsorbing  $\text{Hg}^{2+}$  using 0.1 mol/L HCl at different time is shown in Fig. 8. From the figure, it can be seen that as time prolonged, the desorptive rate was firstly gradually increased and then it decreased when reaching a definite value. Among them, at 2 h a maximum desorptive rate of 75.05 % was achieved. It may be due to the reason that  $\text{H}^+$  replaced  $\text{Hg}^{2+}$  of the surface of adsorber and desorption occurred was a slow process. A desorptive equilibrium to be reached needs a definite time. Thus, before the equilibrium is arrived, the desorptive rate is ascending. However, after the equilibrium is reached, as the desorbed  $\text{Hg}^{2+}$  again is adsorbed, this makes desorptive rate be reduced a little.

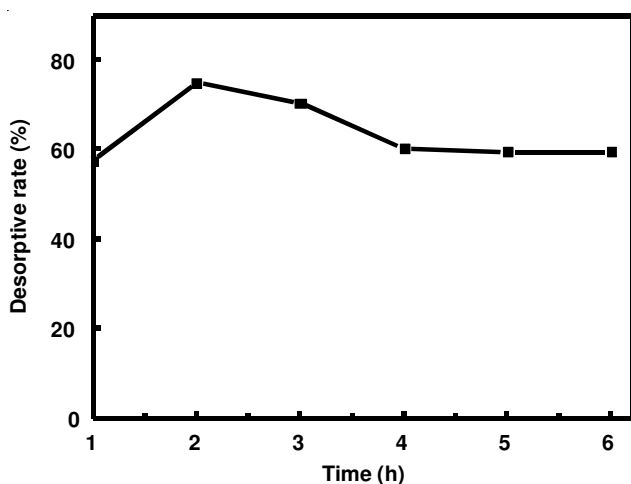


Fig. 8. Effect of time on desorptive impact

The desorptive rate of the thioglycollic acid-modified SBA-15 adsorbing  $\text{Hg}^{2+}$  using 0.1 mol/L AcOH at different time is shown in Fig. 9. From the figure, it can be seen that as time prolonged, the desorptive rate was firstly gradually increased and then it decreased when reaching a definite value. It may be due to the reason that  $\text{H}^+$  replaced  $\text{Hg}^{2+}$  of the surface of adsorber and desorption occurred was a slow process. A desorptive equilibrium to be reached needs a definite time. Thus, before 3 h, the desorptive rate was ascending. However, after 3 h, as the desorbed  $\text{Hg}^{2+}$  again is adsorbed, this makes desorptive rate be reduced a little. Among them, at 3 h a maximum desorptive rate of 44.21 % was achieved.

To sum up the above results, the optimum desorptive agent was 0.1 mol/L HCl. Among the three, the desorptive agent of 0.1 mol/L HCl can accomplish the desorption within the shortest time and the desorptive rate is the largest. In addition, its desorptive reason is investigated as follows: (1) In process of desorption, after acid was added, a large amount of hydrogen ions were immediately introduced. They would cause a competition with the metal cation. As the concentration of hydrogen

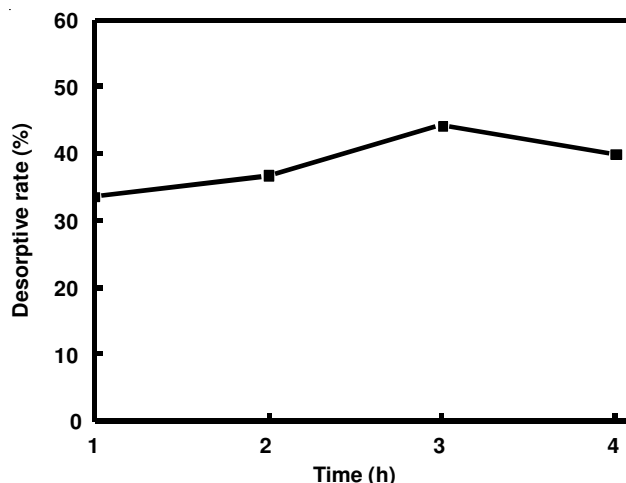


Fig. 9. Effect of time on desorptive impact

ions was consumedly higher than that of the heavy metal ions, the surface groups of the adsorber were occupied by hydrogen ions or hydronium ions and accordingly the desorption of the metal ions of surface of the adsorber was made to occur. The metal ions recurred into aqueous solution in cationic form; (2) As the addition of acid shall destroy some surface of adsorber, the original raised or cupped place was changed to be smooth and thereby some structure of adsorber was changed. The metal ions were desorbed out of the surface of adsorber.

The desorptive rates of the thioglycollic acid-modified SBA-15 adsorbing  $\text{Hg}^{2+}$  under different acidity by using optimum desorptive agent HCl was figured out based on the standard working curve of  $\text{Hg}^{2+}$  obtained and they are presented in Table-1. From the Table, it is observed that the optimum desorptive acidity is 0.1 mol/L HCl. That acidity is too high or acidity is too low is not advantageous to the progress of desorption. Its reason is investigated as follows: acidity concentration is low, the amount of  $\text{H}^+$  is small and the replacement ability for  $\text{Hg}^{2+}$  is low, thus the desorptive rate is low. Too high acidic concentration can also result in the changes of mechanical intensity, physical and chemical properties, etc., of adsorber itself and the process of desorption is also disadvantageous.

Acidity of hydrochloric acid (mol / L)	0.01	0.1	1
Desorptive rate (%)	49.91	75.05	44.33

## Conclusion

The present work successfully performed and obtained mesoporous SBA-15 nanoscale molecular sieve and its length was  $333 \pm 5$  nm. The adsorptive performance of the mercaptoethanol- or the thioglycollic acid-modified SBA-15 towards  $\text{Hg}^{2+}$  has high extent raise compared with that of the unmodified SBA-15 and the adsorptive performance using the thioglycollic acid-modified SBA-15 is better than that using the mercaptoethanol-modified SBA-15. This is mainly due to more -SH entered SBA-15 using thioglycollic acid-modification. Thus, it can be deduced that the best adsorptive agent was thioglycollic acid-modified SBA-15. The best desorptive effect



agent for the thioglycollic acid-modified SBA-15 adsorbing  $\text{Hg}^{2+}$  was 0.1 mol/L HCl and its desorptive rate was reached 75.05 %.

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