



Removal of Pb(II) from Water Using Nanoscale SBA-15

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Nanoscale SBA-15 molecular sieve was synthesized by hydrothermal method. The prepared material was characterized by powder X-ray diffraction and scanning electron microscopy. The fibrous grains with a diameter of 333 ± 5 nm were obtained. The prepared materials were modified with mercaptoethanol, mercaptoacetic acid, respectively and mercapto-modified functionalized SBA-15 (MP-SBA-15) were obtained. SBA-15, mercaptoethanol modified SBA-15 and mercaptoacetic acid modified SBA-15 were used as adsorbents, respectively to adsorb the Pb^{2+} in water. The effects of acidity, time and temperature on the efficiency of adsorption were studied and the optimum adsorptive conditions were confirmed. The results showed that the adsorptive effect on Pb^{2+} by the SBA-15 modified by mercaptoacetic acid is better than those by SBA-15 and the SBA-15 modified by mercaptoethanol. Its greatest adsorptive ratio reached 98.49 % when the pH was 6, temperature was 30 °C and adsorptive time was 50 min. Nitric acid, hydrochloric acid and acetic acid were used as desorbents and the effect of desorptive time on the efficiency of desorption was discussed. The results showed that 0.1 mol/L of nitric acid has a better desorptive ratio than those of hydrochloric acid and acetic acid. Its greatest desorptive ratio reached 77.38 % when desorptive time was 50 min.

Key Words: Pb(II), Nanoscale SBA-15 molecular sieve, Mercaptoacetic acid, Mercaptoethanol, Water.

INTRODUCTION

Researchers of Mobil Corporation published¹ a report claiming that they successfully synthesized an ordered mesoporous silica material in 1992. Release of this result set off an upsurge of studies of the syntheses of new type ordered mesoporous materials within the scope of world. As the pore diameters of the mesoporous materials are adjustable and the pore sizes distribution is narrow, makes the mesoporous materials be able to be used as the catalytic materials of fine chemical industry², the support materials of pharmaceutical industry³ and the catalytic materials for producing some special polymer materials⁴. However, as the thermal stability, hydrothermal stability and chemical stability of the mesoporous materials are relatively poor, this made these materials be suffered to a certainty in the applications of practical production. Zhao, Stucky and their co-worker successfully synthesized mesoporous molecular sieve by hydrothermal method^{5,6}. Synthesis of SBA-15 molecular sieve usually is to employ hydrothermal reaction method. The method is to use tetraethyl orthosilicate (TEOS) as silica source and triblock copolymer poly(ethylene glycol)-block-poly(propyl glycol)-block-poly(ethylene glycol) (EG₂₀PG₄₀EG₂₀, P123) as structure-directing agent and SBA-15 is obtained by stirring, crystalli-

zation and calcination. SBA-15 is an important member in mesoporous materials family and its component is majorly SiO₂. SBA-15 mesoporous material is highly ordered planar hexagonal phase, having 2-dimensional hexagonal channels. Its pore diameter size ranges between 4.6-30 nm and silica pore wall thickness can be between 3.1-6.0 nm. Pore wall is relatively thicker and between pore channels there is the connection of micropores. SBA-15 has large specific surface area, which is generally over the range of 700-1000 m²/g. It is just since SBA-15 molecular sieve has a relatively thicker pore wall, this makes it having higher chemical stability, thermal stability and hydrothermal stability compared with MCM-41. After removing template, SBA-15 has higher thermal stability and hydrothermal stability. The thermal stability of SBA-15 is higher than 900 °C and on its inner surface a large amount of silanol exist. Owing to the above numerous advantages, SBA-15 attracted more and more researchers' interests and has been become one of research hotspots during recent years.

Industry civilization brought the numerous advancement of science and technology, forcing the development of urbanization at full speed and by a long way enhancing people's living level. Nevertheless, environment breakage and pollution issue have already set in without expectation and aggravate as industrialization continuously goes deep into. Afterwards, the

global common harm of large area was formed, among which the pollution of heavy metals especially stood out even directly threatened the survival of human being. Lead now has become a pollutant that filtered to each corner of environments. Lead and its compounds have highly toxic action on many systems of a human body. Lead poisoning can cause belly angina, hepatitis, hypertension, outward neuritis, poisoning cephalitis, anaemia, neurasthenia, *etc.* Lead is a kind of accumulated poison. Mankind ingests lead by food chain and it is adsorbed by alimentary canal and respiratory tract. After adsorption, most parts accumulate in bones. The lead that accumulated in bones does not harm body. Poisoning depth majorly depends on the lead content in blood and tissue. If the lead content in blood exceeds 0.05-0.1 %, then poisoning symptom is brought. Nowadays, the American National Environmental Protection Bureau has decreased the lead content in drinking water to be 0.005 mg/L from previous 0.05 mg/L. However, adopting usual methods is difficult to effectively wipe off trace lead in water. To solve this issue looks especially important. People outspread extensive studies on the process of lead, *etc.*, heavy metals *via* various methods and there are majorly chemical precipitation method, adsorption method, ion-exchange method and process methods that are in virtue of absorption, accumulation, enrichment of microbiology or plants, *etc.* Among them, adsorption method is an important one. At present, commonly used adsorptive materials majority have fibre and resin. However, the regeneration cost of traditional adsorptive materials is high and the use process is complex, which is a bottleneck that restricts them to be widely applied to environmental domain. As some metal ions can make exchange with silanols on the surface of molecular sieve, thus the metal ions are made to be transplanted on outside surface of molecular sieve and they can also be adsorbed in pore channels. Worboys⁷ and Zhang *et al.*⁸, encapsulated Ag, Eu, Pt and Au metals, *etc.* into the pore channels of SBA-15 molecular sieve. In recent years, studies on the applications of zeolite molecular sieve materials to make ion exchange adsorption to wide off the heavy metal ions gradually caused people's attention. Wingenfelder *et al.*⁹, used amine-modified zeolite to adsorb Pb²⁺ in water and discussed the mechanism.

The synthesized mesoporous molecular sieve SBA-15 is a new type molecular sieve developed up lately. It has single hexagonal phase structure, distribution of a pore diameter of 2-5 nm, high specific surface area and high adsorptive capacity and it can avoid repollution to water body. As its pore diameter is uniform and the pore diameter size can be adjusted by adjusting synthesis conditions, excellent adsorptive selectivity and stability are pledged. The pore channels of SBA-15 are abundant and have excellent adsorptive ability, which makes SBA-15 have wide applied foreground. The clear, open and spacious structure of framework of mesoporous materials and bigger inner and outside specific surface area make them have unique adsorptive function. At the same time, nicer physical and chemical stability of molecular sieves make them have the excellent function of regeneration.

This study uses triblock copolymer poly(ethylene glycol)-block-poly(propyl glycol)-block-poly(ethylene glycol) (EG₂₀PG₄₀EG₂₀) 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 Pb²⁺ in water body, which has an important significance to harness of pollution water and the performance of SBA-15 adsorption. In this paper, optimum conditions of the adsorption of Pb²⁺ are studied in water body by SBA-15 and the modified SBA-15 materials and desorptive study is carried through and the application of SBA-15 mesoporous nanoscale molecular sieve is discussed to environmental harness. For the exploitation of new type heavy metal adsorbent, it is of reference value.

EXPERIMENTAL

Tetraethyl orthosilicate (TEOS, 98 %, Shanghai Company of Chemical Reagents, Chinese Medicine Group); poly-(ethylene glycol)-block-poly(propyl glycol)-block-poly(ethylene glycol) (EG₂₀-PG₄₀-EG₂₀, average molecular weight 5800, Aldrich); 2 mol L⁻¹ HCl (Beijing Beihua Fine Chemicals Corp., Ltd., China) solution; mercaptoacetic acid (C₂H₄O₂S, Sinopharm Chemical Reagent Co. Ltd., China); mercaptoethanol (C₂H₆OS, Tianjin Guangfu Fine Chemical Research Institute, China); absolute ethanol (Beijing Chemical Works, China); 1 mg/mL of Pb²⁺ standard stock solution: 0.1600 g of Pb(NO₃)₂ (Beijing Shiji Red Star Chemical Corp. Ltd., China) was dissolved in 100 mL of water and 1 mg/mL Pb²⁺ standard stock solution was obtained. Before use, 10 µg/mL of standard working solution was obtained by suitable dilution; 0.05 % (w/v) dibromo-*p*-methylsulfonazo (DBM-SA, Shanghai Changke Research Institute of Reagent, China) solution; 3 mol L⁻¹ H₃PO₄ (Beijing Chemical Plant, China) solution; 0.1 mol L⁻¹ HCl (Beijing Beihua Fine Chemicals Corp., Ltd., China) solution; 0.1 mol L⁻¹ HNO₃ (Beijing Chemical Plant, China) solution; 0.1 mol L⁻¹ CH₃COOH (Beijing Chemical Plant, China) solution; 0.1 mol L⁻¹ NaOH (Beijing Chemical Plant, China) solution.

Unless specially stated, all the reagents used in the experiments were of analytical grade. All the water used was deionized water.

Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5005 (Germany) diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$ and operating at 40 kV and 30 mA). Typically, the diffraction data were collected from 0.4-10° (2 θ) with a resolution of 0.02°. Scanning electron microscopic (SEM) photographs were determined on a JEOL JSM-5600L (Japan) scanning electron microscope. A 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China) equipped with 1 cm cells was employed in the determination of absorbance. A HJ-6A digital display constant temperature water-bath boiler (Jiangsu Jintan Ronghua Apparatus Manufacture Co., Ltd., China) was applied to the control of experimental temperature.

Procedures

Hydrothermal synthesis of SBA-15 molecular sieve: Mesoporous SBA-15 molecular sieve was prepared according to the reported method⁵. Under the acidic condition, the triblock copolymer, EG₂₀PG₄₀EG₂₀ was used as template and TEOS was used as silica source. In a typical synthesis, 2 g of the template was dissolved in 60 g of 2 mol L⁻¹ 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 placed 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 mesoporous silica SBA-15 white powder material obtained was calcined at 550 °C for 24 h to completely eliminate the template.

Surface modification of SBA-15 molecular sieve: 2 mL of mercaptoethanol and mercaptoacetic acid were taken and mixed with 20 mL of water, 20 mL of absolute ethanol, respectively, to prepare mixed solution. Two portions of 0.2 g of SBA-15 molecular sieve were weighed and placed in the above-stated mixed solution, respectively. After magnetic stirring for 48 h, the products obtained were filtered, one after another, washed by absolute ethanol, water and dried at room temperature. Mercapto-modified molecular sieves SBA-15 were obtained.

Plotting of the working curve of spectrophotometric determination¹⁰ of Pb²⁺: 0, 2.0, 3.2, 4.0, 4.8, 6.0 µg of Pb²⁺ were, respectively taken and added to six 10 mL calibrated flasks. To the above-stated 6 calibrated flasks were respectively added in turn 0.8 mL of 3 mol/L H₃PO₄ solution, 1.8 mL of 0.05 % (w/v) DBM-SA solution. Water was added to the mark and shaken well, placed for 10 min. Using a reagent blank as reference, the absorbance A of solution was measured at 630 nm by 1 cm cells to draw absorbance-concentration curve. Based on the data obtained in the experiments, a linear regression equation was calculated. The linear regression equation of analytical working curve for Pb²⁺ was: $A = 0.0311C + 0.0006$ (C: µg/10 mL), with a linear correlation coefficient of $\gamma = 0.9997$.

Procedure for the determination of Pb²⁺ concentration in solution by spectrophotometry: To 10 mL calibrated flasks, a definite amount of solution containing Pb²⁺ to be determined, 0.8 mL of 3 mol/L H₃PO₄ solution, 1.8 mL of 0.05 % (w/v) DBM-SA solution were added in turn. Water was used to dilute to the mark and shaken well, placed for 10 min. Using a reagent blank as reference, the absorbance (A) of colour solution was measured by 1 cm cells at 630 nm. Beer's law was obeyed over the concentration range of 0-0.8 µg/mL for Pb²⁺ and the Pb²⁺ concentration in the solution to be determined was figured out from the linear regression equation: $A = 0.0311C + 0.0006$ (C: µg/10 mL).

Studies of the adsorption of Pb²⁺ by unmodified SBA-15 molecular sieve

Effect of pH on the adsorptive effect of Pb²⁺: Six portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and placed in six beakers with a capacity of 100 mL. The pH values were adjusted to 1, 2, 3, 4, 5, 6, respectively. Six portions of 0.1 g of unmodified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20 °C and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. pH-adsorptive ratio curve was drawn.

Effect of temperature on the adsorptive effect of Pb²⁺: Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in

five beakers with a capacity of 100 mL. The optimum pH = 5 was adjusted. Five portions of 0.1 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 Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive ratio curve was drawn.

Effect of time on the adsorptive effect of Pb²⁺: Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken placed in five beakers with a capacity of 100 mL. The optimum pH = 5 was adjusted. Five portions of 0.1 g of unmodified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 30, 40, 50, 60 min at optimum temperature and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive ratio curve was drawn.

Adsorptive studies of Pb²⁺ by mercaptoethanol-modified SBA-15 molecular sieve

Effect of pH on the adsorptive effect of Pb²⁺: Six portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in six beakers with a capacity of 100 mL. The pH values were adjusted to 1, 2, 3, 4, 5, 6, respectively. Six portions of 0.1000 g of mercaptoethanol-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20 °C and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. pH-adsorptive ratio curve was drawn.

Effect of temperature on the adsorptive effect of Pb²⁺: Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in five beakers with a capacity of 100 mL. The optimum pH = 6 was adjusted. Five portions of 0.1 g of 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 Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive ratio curve was drawn.

Effect of time on the adsorptive effect of Pb²⁺: Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in five beakers with a capacity of 100 mL. The optimum pH = 6 was adjusted. Five portions of 0.1 g of mercaptoethanol-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 30, 40, 50, 60 min at optimum temperature and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive ratio curve was drawn.

Adsorptive studies of Pb²⁺ by mercaptoacetic acid-modified SBA-15 molecular sieve

Effect of pH on the adsorptive effect of Pb²⁺: Six portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and placed in six beakers with a capacity of 100

mL. The pH values were adjusted to 1, 2, 3, 4, 5, 6, respectively. Six portions of 0.1 g of mercaptoacetic acid-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 40 min at 20 °C and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. pH-adsorptive ratio curve was drawn.

Effect of temperature on the adsorptive effect of Pb²⁺:

Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in five beakers with a capacity of 100 mL. The optimum pH = 6 was adjusted. Five portions of 0.1 g of mercaptoacetic 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 Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Temperature-adsorptive ratio curve was drawn.

Effect of time on the adsorptive effect of Pb²⁺:

Five portions of 40 mL working solution whose Pb²⁺ concentration was 1 mg/mL were taken and respectively placed in five beakers with a capacity of 100 mL. The optimum pH = 6 was adjusted. Five portions of 0.1 g of mercaptoacetic acid-modified SBA-15 molecular sieves were accurately weighed, added to the above-stated samples, respectively, stirred for 20, 30, 40, 50, 60 min at optimum temperature and then filtered. The Pb²⁺ content in each filtrate was determined by the above-stated spectrophotometry and the adsorptive ratio was figured out. Time-adsorptive ratio curve was drawn.

Studies of desorption

Effect of nitric acid on desorption:

10 portions of 50 mL of 0.1 mol/L HNO₃ solution were taken and, respectively placed in 10 beakers with a capacity of 100 mL. 10 portions of the SBA-15 molecular sieves that adsorbed Pb²⁺ under the optimum conditions were taken and added to the above-stated solutions to be soaked for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 h. The soaked solutions were filtered. The Pb²⁺ content in each filtrate was determined by spectrophotometry and the adsorptive ratio was figured out. Time-desorptive ratio curve was drawn.

Effect of hydrochloric acid on desorption:

Ten portions of 50 mL of 0.1 mol/L HCl solution were taken and placed in ten beakers with a capacity of 100 mL. Ten portions of the SBA-15 molecular sieves that adsorbed Pb²⁺ under the optimum conditions were taken and added to the above-stated solutions to be soaked for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 h. The soaked solutions were filtered. The Pb²⁺ content in each filtrate was determined by spectrophotometry and the adsorptive ratio was figured out. Time-desorptive ratio curve was drawn.

Effect of acetic acid on desorption:

Ten portions of 50 mL of 0.1 mol/L CH₃COOH solution were taken and placed in ten beakers with a capacity of 100 mL. Ten portions of the SBA-15 molecular sieves that adsorbed Pb²⁺ under the optimum conditions were taken and added to the above-stated solutions to be soaked for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 h. The soaked solutions were filtered and the filtrates were held. The Pb²⁺ content in each filtrate was determined by spectrophotometry and the adsorptive ratio was figured out. Time-desorptive ratio curve was drawn.

Effect of acidity on desorption: The nitric acid, whose desorptive effect was the best in the above-stated solutions, was selected as desorptive agent. The concentrations of the solution as 0.01, 0.1, 1.0 mol/L were prepared, respectively. Three portions of the SBA-15 molecular sieves that adsorbed Pb²⁺ under the optimum conditions were taken and added to 50 mL of the above-stated solutions to be soaked for 8 h. The soaked solutions were filtered. The Pb²⁺ content in each filtrate was determined by spectrophotometry and the desorptive ratio was figured out. pH-desorptive ratio curve was drawn.

RESULTS AND DISCUSSION

Characterization of nanoscale SBA-15: The analytical results of powder XRD are shown as Fig. 1. From curve (a) it can be seen that for the SBA-15 prepared in the present study four diffraction peaks, which can be assigned to the peaks of (100), (110), (200) and (210) obtained from crystal face diffraction. The locations of these peaks are in agreement with those of SBA-15 molecular sieve^{5,6}, which proves that the sample prepared was SBA-15 molecular sieve. As is shown in curve (b), (c), for the mercaptoethanol-or mercaptoacetic acid-modified SBA-15 molecular sieve two diffraction peaks appear, which are respectively assigned to the characteristic peaks obtained from (100), (110) crystal face diffractions. These peaks are the characteristic ones of SBA-15 molecular sieve. The results show that the modified molecular sieves kept two-dimensional planar hexagonal channel structures and no situation of the

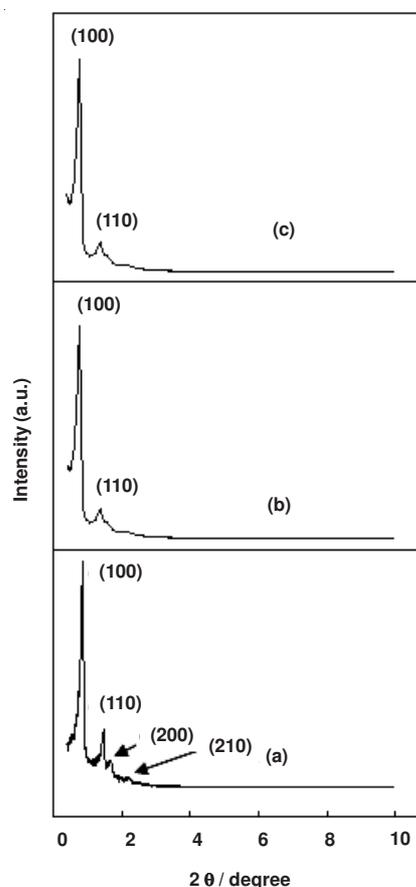


Fig. 1. XRD pattern of the sample: (a) SBA-15, (b) the SBA-15 modified by mercaptoethanol, (c) the SBA-15 modified by mercaptoacetic acid

collapse of frameworks occurred. The disappearance of (200) and (210) crystal face diffraction peaks shows that the crystalline degree and ordered degree of the modified materials decreased to some extent. In curve (a), for diffraction angle 2θ a stronger diffraction peak appears at 0.86° . In curve (b) and (c), for diffraction angle 2θ a stronger diffraction peak appears at 0.75° . The migration of the diffraction peaks shows that -SH has already entered the surface of molecular sieve or S atoms replaced the oxygen atoms in Si-O-Si.

Fig. 2 presents the SEM photographs of SBA-15 sample prepared in the experiment. It can be seen that the prepared sample presents fibriform structure and particle size distribution is homogeneous. By calculation of the diameters of the sample were obtained to be 333 ± 5 nm and crystalline particle length is 727 nm.

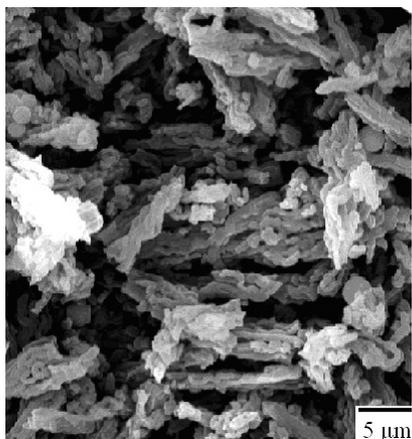


Fig. 2. SEM images of the sample

The modification mechanism of SBA-15 is shown as Fig. 3. Between the silanol in molecular sieve and the organic substance with mercapto-group a reaction occurred to introduce higher active mercapto-group into SBA-15 molecular sieve. As the internal and outside surfaces of SBA-15 have a large amount of silanols and as the reaction progressed, the amount of silanols for which the reaction occurred continuously increased. Accordingly, the active sites of SBA-15 increased and its adsorptive performance remarkably enhanced.

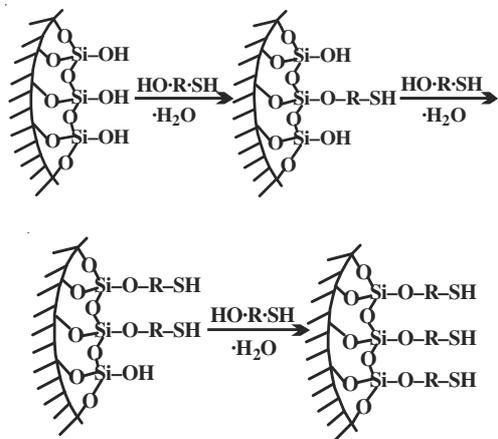


Fig. 3. Chemical reaction of SBA-15's modification (R = -COCH₂-, -CH₂CH₂-)

Adsorptive study of Pb²⁺ in water by SBA-15

Adsorption of Pb²⁺ by unmodified SBA-15: Fig. 4 presents a relationship curve between pH value and the adsorptive efficiency of Pb²⁺. From the figure, it can be seen that as pH value increased, the adsorptive efficiency of Pb²⁺ gradually enhanced. When pH value achieved 5, the adsorptive ratio achieved a maximum of 49.54%. At this time, the adsorptive amount of Pb²⁺ by SBA-15 was 198.16 mg/g. Afterwards, as pH value sequentially increased, the adsorptive efficiency of Pb²⁺ decreased. This is mainly because of the H⁺ in the solution and Pb²⁺ had a competitive adsorptive action. At low pH, the H⁺ concentration in the solution was more and the silanols in SBA-15 molecular sieve majorly combined with H⁺. At high pH, the H⁺ concentration in the solution was less and the silanols in SBA-15 molecular sieve combined with Pb²⁺.

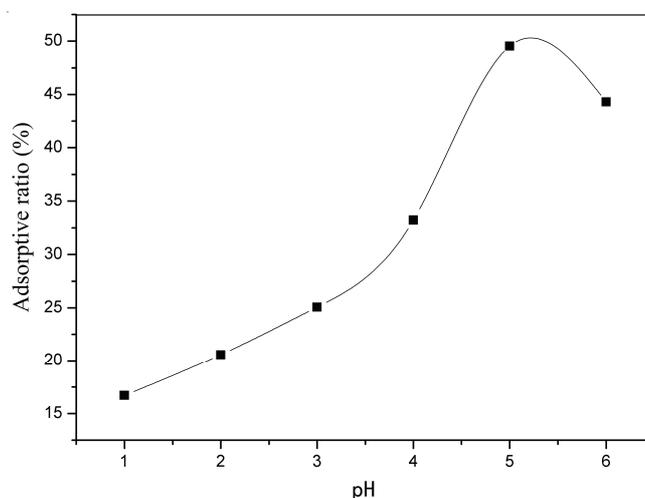


Fig. 4. Effect of pH on efficiency of the adsorption of Pb²⁺

Fig. 5 presents a relationship curve between temperature and the adsorptive efficiency of Pb²⁺. From the figure, it can be seen that as temperature increased, the adsorptive efficiency of Pb²⁺ gradually enhanced but the effect was not high. When the temperature achieved 35 °C, the adsorptive ratio achieved a maximum of 51.03%. Afterwards, as temperature sequentially increased, the adsorptive efficiency of Pb²⁺ decreased.

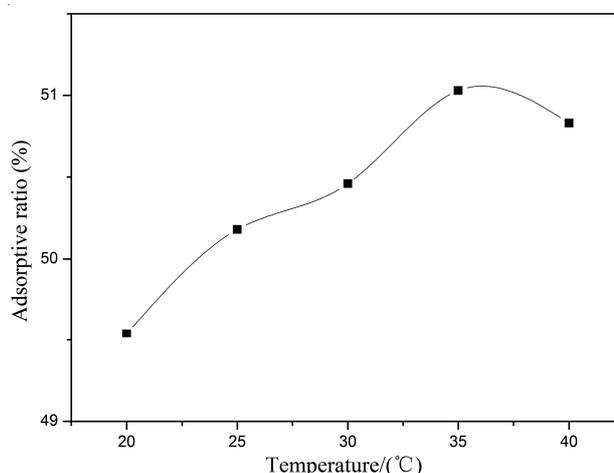


Fig. 5. Effect of temperature on efficiency of the adsorption of Pb²⁺

This is mainly because the H^+ in the solution and the moment of Pb^{2+} expedited when temperature increased. This made it more easily diffuse into the channels of SBA-15. However, when the temperature of solution was too high, the movement of Pb^{2+} was excessively active and the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive form again diffused out. On the contrary, the adsorptive ratio of Pb^{2+} was reduced.

Fig. 6 presents a relationship curve between time and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as time increased, the adsorptive efficiency of Pb^{2+} gradually enhanced. When time achieved 40 min, the adsorptive ratio achieved a maximum of 49.54 %. Afterwards, as time sequentially increased, the adsorptive efficiency of Pb^{2+} decreased a little. This is mainly attributed to that when the adsorptive time was too long, in the SBA-15 molecular sieve channels saturated the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive form began to desorb. Thus, the adsorptive ratio of Pb^{2+} was reduced.

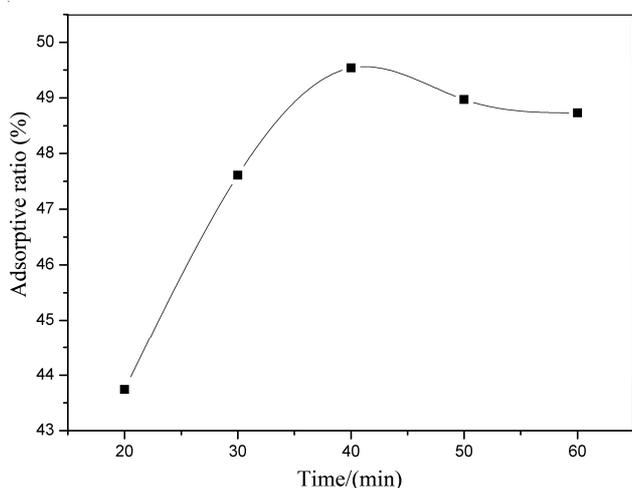


Fig. 6. Effect of time on efficiency of the adsorption of Pb^{2+}

Adsorption of Pb^{2+} by mercaptoethanol-modified SBA-15:

Fig. 7 presents a relationship curve between pH value and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as pH value increased, the adsorptive efficiency of Pb^{2+} gradually enhanced. When pH value achieved 6, the adsorptive ratio achieved a maximum of 83.03 %. At this time, the adsorptive amount of Pb^{2+} by mercaptoethanol-modified SBA-15 was 332.12 mg/g. Afterwards, as pH value sequentially increased, the adsorptive efficiency of Pb^{2+} instead decreased. This is mainly because the H^+ in the solution and Pb^{2+} had a competitive adsorptive action. When pH was low, the H^+ concentration in the solution was more and the silanols in the mercaptoethanol-modified SBA-15 molecular sieve combined with H^+ . When pH was more, the H^+ concentration in the solution was less and the silanols in the mercaptoethanol-modified SBA-15 molecular sieve majorly combined with Pb^{2+} .

Fig. 8 presents a relationship curve between temperature and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as temperature increased, the adsorptive efficiency of Pb^{2+} gradually enhanced but the effect was not significant. When the temperature achieved 30 °C, the adsorptive ratio

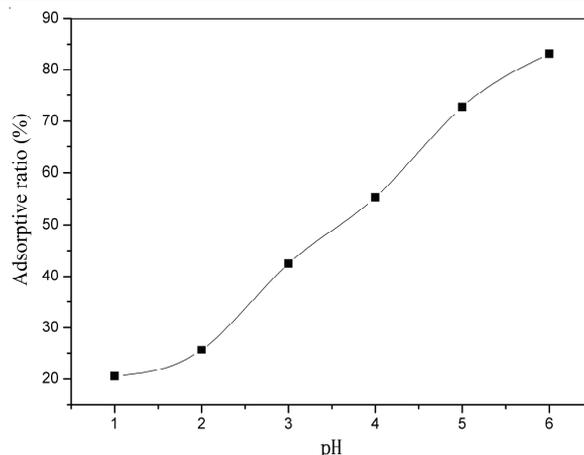


Fig. 7. Effect of pH on efficiency of the adsorption of Pb^{2+}

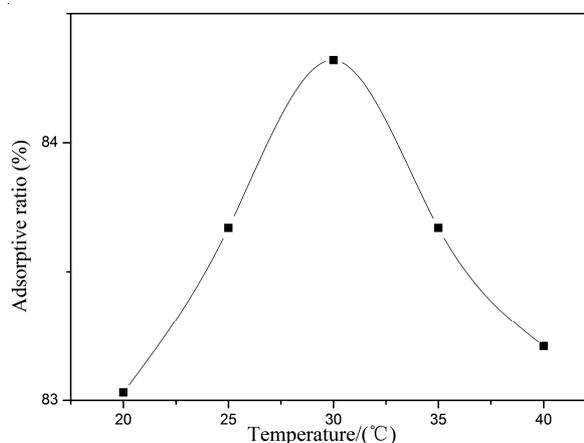


Fig. 8. Effect of temperature on efficiency of the adsorption of Pb^{2+}

achieved a maximum of 84.32 %. Afterwards, as temperature sequentially increased, the adsorptive efficiency of Pb^{2+} decreased. This is mainly because the H^+ in the solution and the moment of Pb^{2+} expedited when temperature increased. This made it more easily diffuse into the channels of SBA-15. However, when the temperature of solution was too high, the movement of Pb^{2+} was excessively active and the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive form again diffused out. Instead, the adsorptive ratio of Pb^{2+} was reduced.

Fig. 9 presents a relationship curve between time and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as time increased, the adsorptive efficiency of Pb^{2+} gradually enhanced. When time achieved 50 min, the adsorptive ratio achieved a maximum of 84.32 %. Afterwards, as time sequentially increased, the adsorptive efficiency of Pb^{2+} decreased a little. This is mainly attributed to that when adsorptive time was too long, in the SBA-15 molecular sieve channels saturated the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive form began to desorb, thus the adsorptive ratio of Pb^{2+} was reduced.

Adsorption of Pb^{2+} by mercaptoacetic acid-modified SBA-15: Fig. 10 presents a relationship curve between pH value and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as pH value increased, the adsorptive efficiency of Pb^{2+} gradually enhanced. When pH value achieved 6, the adsorptive ratio achieved a maximum of 98.49 %. At this time,

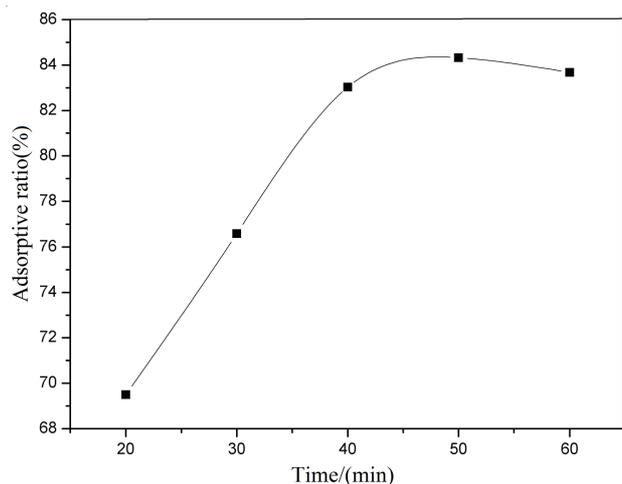


Fig. 9. Effect of time on efficiency of the adsorption of Pb^{2+}

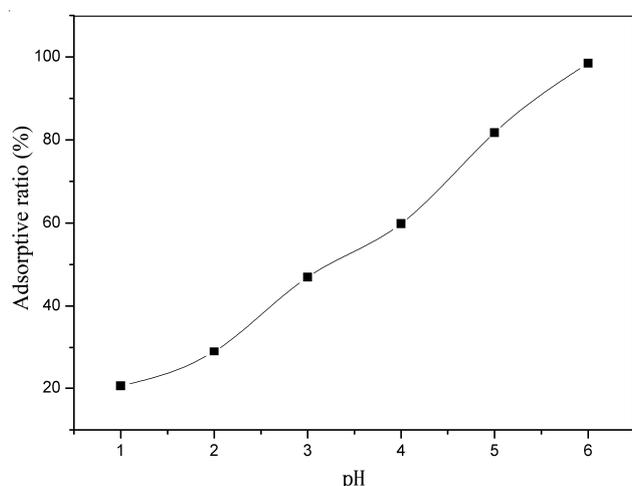


Fig. 10. Effect of pH on efficiency of the adsorption of Pb^{2+}

the adsorptive amount of Pb^{2+} by the mercaptoacetic acid-modified SBA-15 was 393.96 mg/g. Afterwards, as pH value sequentially increased, the adsorptive efficiency of Pb^{2+} decreased. This is mainly because the H^+ in the solution and Pb^{2+} had a competitive adsorptive action. When pH was low, the H^+ concentration in the solution was more and the silanols in the mercaptoacetic acid-modified SBA-15 molecular sieve combined with H^+ . When pH was high, the H^+ concentration in the solution was less and the silanols in the mercaptoacetic acid-modified SBA-15 molecular sieve majorly combined with Pb^{2+} .

Fig. 11 presents a relationship curve between temperature and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as temperature increased, the adsorptive efficiency of Pb^{2+} gradually enhanced but the effect was not high. When temperature achieved 30 °C, the adsorptive ratio achieved a maximum of 99.77 %. Afterwards, as temperature sequentially increased, the adsorptive efficiency of Pb^{2+} decreased. This is mainly because the H^+ in the solution and the moment of Pb^{2+} expedited when temperature increased. This made it more easily diffuse into the channels of SBA-15. However, when the temperature of solution was too high, the movement of Pb^{2+} was excessively active and the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive form again diffused out. Instead, the adsorptive ratio of Pb^{2+} was reduced.

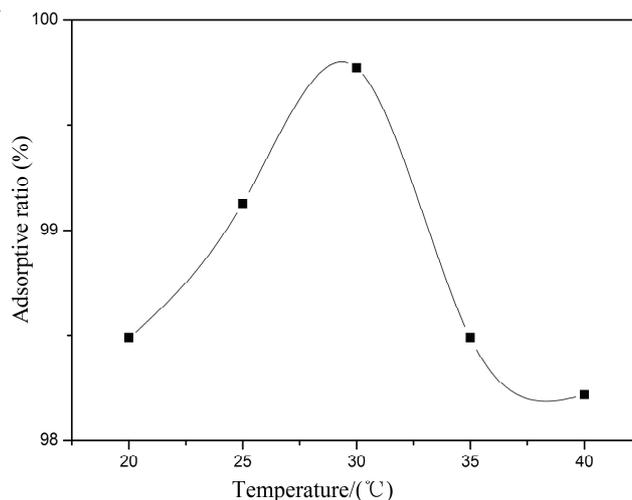


Fig. 11. Effect of temperature on efficiency of the adsorption of Pb^{2+}

Fig. 12 presents a relationship curve between time and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as time increased, the adsorptive efficiency of Pb^{2+} gradually enhanced. When time achieved 50 min, the adsorptive ratio achieved 98.49 %. Afterwards, as time sequentially increased, the adsorptive efficiency of Pb^{2+} decreased a little. This is mainly attributed to that when adsorptive time was too long, in the SBA-15 molecular sieve channels saturated the Pb^{2+} that existed in the channels of SBA-15 only in physical adsorptive began to desorb. Thus, the adsorptive ratio of Pb^{2+} was decreased.

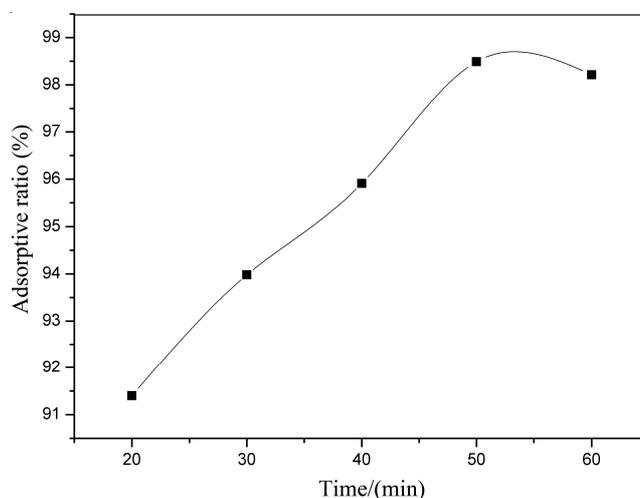


Fig. 12. Effect of time on efficiency of the adsorption of Pb^{2+}

Desorptive studies

Desorption by nitric acid: Fig. 13 shows the curve of relationship between time and the desorptive efficiency of Pb^{2+} using nitric acid as desorptive agent. From the figure, it can be seen that as time increased, the desorptive efficiency of Pb^{2+} gradually enhanced. This is mainly because the electron density of Pb^{2+} excessively concentrates and in outside surface there are vacant orbits. The complex, which Pb^{2+} and the mercapto-group in the modified SBA-15 molecular sieve formed, was not insufficiently stable. Under the condition that acidity was stronger, it is due to the competitive reaction between

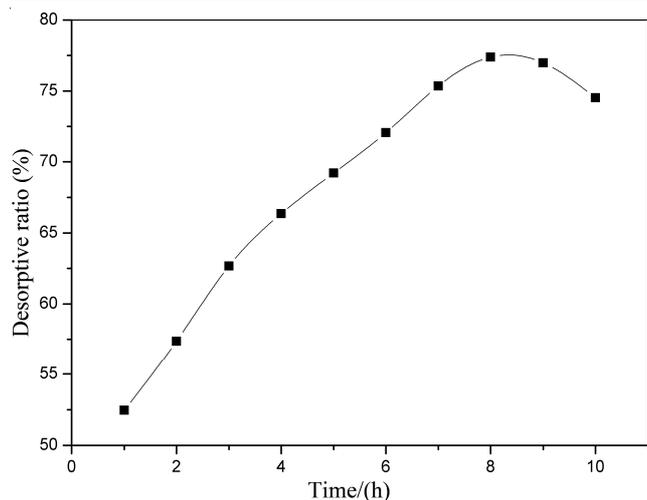


Fig. 13. Effect of time on efficiency of the desorption of Pb^{2+} using nitric acid as desorptive agent

H^+ in the solution and Pb^{2+} and the complex was destroyed. Thus, the concentration of Pb^{2+} in the solution gradually increased and desorptive ratio went up. When time reached 8 h, the desorptive ratio reached a maximum of 77.38 %. Afterwards, as time continuously increased, the desorptive efficiency of Pb^{2+} began to decrease. This may be because at too long desorptive time the desorbed Pb^{2+} in the solution again was adsorbed in SBA-15 in physical adsorption form, which resulted in the drop of Pb^{2+} concentration in the solution. Accordingly, the desorptive ratio of Pb^{2+} was reduced.

Desorption by hydrochloric acid: Fig. 14 shows the curve relationship between time and the desorptive efficiency of Pb^{2+} using hydrochloric acid as desorptive agent. From the figure, it can be seen that as time increased, the desorptive efficiency of Pb^{2+} gradually enhanced. This is mainly because the electron density of Pb^{2+} excessively concentrates and in outside surface there are vacant orbits. The complex, which Pb^{2+} and the mercapto-group in the modified SBA-15 molecular sieve formed, was not insufficiently stable. Under high acidity, it is due to the competition reaction between H^+ in the solution and Pb^{2+} and the complex was destroyed. Thus, the concentration of Pb^{2+} in the solution gradually increased and

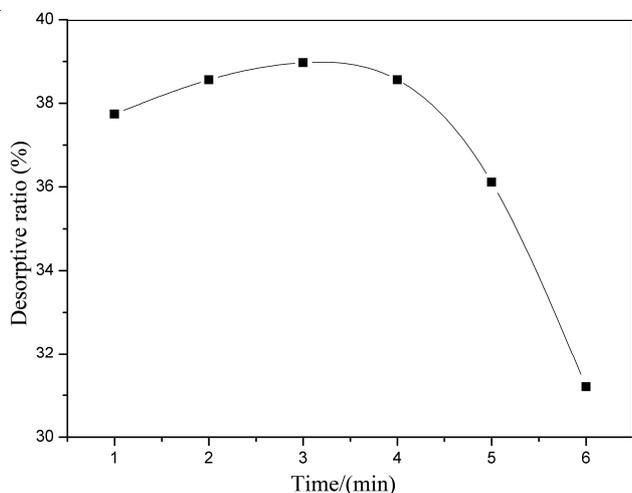


Fig. 14. Effect of time on efficiency of the desorption of Pb^{2+} using hydrochloric acid as desorptive agent

desorptive ratio went up. When time reached 3 h, the desorptive ratio reached a maximum of 38.97 %. Afterwards, as time continuously increased, the desorptive efficiency of Pb^{2+} began to decrease. This may be because at too long desorptive time the desorbed Pb^{2+} in the solution again adsorbed in SBA-15 in physical adsorption form, which resulted in the drop of Pb^{2+} concentration in the solution and accordingly the adsorptive ratio of Pb^{2+} was reduced.

Desorption by acetic acid: Fig. 15 shows the curve relationship between time and the desorptive efficiency of Pb^{2+} using acetic acid as desorptive agent. From the figure, it can be seen that as time increased, the desorptive efficiency of Pb^{2+} gradually enhanced. This is mainly because of the electron density of Pb^{2+} excessively concentrates and in outside surface there are vacant orbits. The complex formed with Pb^{2+} and the mercapto-group in the modified SBA-15 molecular sieve was not insufficiently stable. Under high acidity, it is due to the competitive reaction between H^+ in the solution and Pb^{2+} and the complex was destroyed. Thus, the concentration of Pb^{2+} in the solution gradually increased and the desorptive ratio went up. When time reached 3 h, the desorptive ratio reached a maximum of 56.95 %. Afterwards, as time continuously increased, the desorptive efficiency of Pb^{2+} began to decrease. This may be because at too long desorptive time the desorbed Pb^{2+} in the solution again was adsorbed in SBA-15 in physical adsorption form, which resulted in the drop of Pb^{2+} concentration in the solution. Accordingly, the adsorptive ratio of Pb^{2+} was reduced.

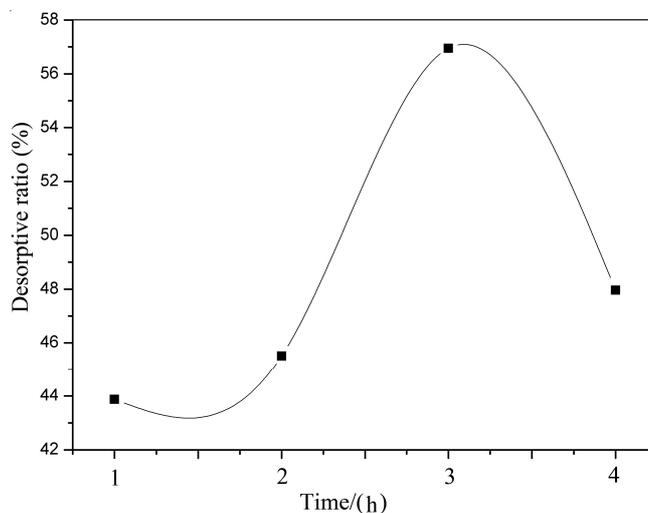


Fig. 15. Effect of time on efficiency of the desorption of Pb^{2+} using acetic acid as desorptive agent

Effect of the concentration of nitric acid on desorption: Fig. 16 shows a relationship curve between pH value and the adsorptive efficiency of Pb^{2+} . From the figure, it can be seen that as pH value decreased (pH 2 \rightarrow 1), namely nitric acid concentration increased, the adsorptive efficiency of Pb^{2+} gradually increased. When pH value reached 1, namely nitric acid concentration was 0.1 mol/L, the desorptive ratio was maximum of 75.38 %. Afterwards, as pH value continued to decrease (pH 1 \rightarrow 0), namely nitric acid concentration continued increase, on the contrary the adsorptive efficiency of Pb^{2+} decreased. This is mainly because the H^+ in the solution and Pb^{2+} have a

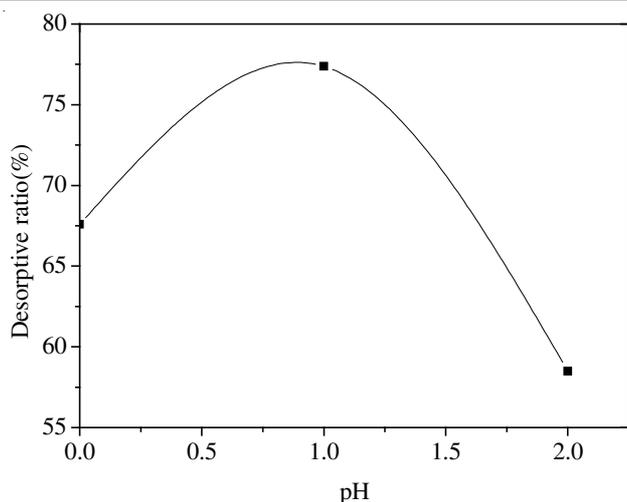


Fig. 16. Effect of pH on efficiency of the desorption of Pb^{2+}

competitive adsorptive action. When the acidity in solution was low, the H^+ concentration in the solution was less. The mercapto-group in the modified SBA-15 molecular sieve mainly combined with Pb^{2+} , the Pb^{2+} content in the solution was small and the desorptive ratio was low. As acidity strengthened and the Pb^{2+} content in the solution increased, the desorptive ratio became high. When acidity continued to increase, the H^+ concentration in the solution was excessively high, which may influence the internal structural arrangement of the modified SBA-15 molecular sieve adsorbing lead(II). Thus, the desorptive ratio decreased.

Application: Adsorption study on synthetic wastewater sample containing the following composition ($\mu\text{g/mL}$) of: K^+ (0.04); Pb^{2+} (0.01); Ni^{2+} (0.01); Fe^{3+} (0.1); NO_3^- (0.34); $Cr_2O_7^{2-}$ (0.02) was made by using the mercaptoacetic acid-modified SBA-15 under the optimum experimental conditions that pH value was 6, temperature was 30°C and adsorptive time was 50 min. The results showed that when the amount of the mercaptoacetic acid-modified SBA-15 was 0.1 g and the volume of the wastewater was 1 L, an average value of five elimination ratios (97.5, 97.3, 97.3, 97.1 and 97.3 %) of Pb^{2+} was 97.3 %. The results obtained were satisfactory.

Conclusion

In this paper, mesoporous molecular sieve SBA-15 was hydrothermally synthesized and mercapto-modified functionalization of it was made by using mercaptoacetic acid, mercaptoethanol, respectively. The adsorptive performance of the products towards Pb^{2+} was studied and the major results are as follows: the modified SBA-15 samples whose adsorptive performances are better were obtained and the adsorptive performance of the mercaptoethanol-modified SBA-15 was the best. When pH value was 6, temperature was 30°C and adsorptive time was 50 min, the adsorptive effect of mercaptoacetic acid-modified SBA-15 was the best and the adsorptive ratio reached 98.49 %. Nitric acid, hydrogen chloride and acetic acid were, respectively used to study the effect of desorptive time on desorption, indicating that when 0.1 mol/L nitric acid was used as desorptive agent, the desorptive effect was the best. When desorption was 8 h, the desorptive ratio was the highest and reached 77.38 %.

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