

QING ZHOU ZHAI¹, WEI-HUA HU¹, XIAO-YU GUO¹

ADSORPTIVE PERFORMANCE OF MCM-41 TOWARDS Hg(II) IN WATER. ADSORPTION AND DESORPTION STUDIES

MCM-41 mesoporous material was prepared under a standard conditions by using cetyltrimethylammonium bromide as a structure-directing agent and tetraethyl orthosilicate as silica source from the liquid phase at 80 °C. Powder X-ray diffraction and scanning electron microscopy used to characterize the product, showed that the MCM-41 material had an average particle size of 110 nm. The synthesized material was used to investigate the effects of acidity, adsorption time, the concentration of Hg²⁺, adsorbent dosage and temperature on the adsorption of Hg²⁺. The results showed that the optimal adsorptive conditions were: pH 5.0, $m_{\text{(MCM-41)}}/m_{\text{Hg}^{2+}}$ 6.67, temperature 20 °C and contact adsorption time 60 min, for the initial Hg²⁺ concentration of 1.0 mg/cm³. The maximum adsorptive amount of Hg²⁺ was 56.48 mg Hg²⁺/g MCM-41. The results of the desorptive effect of three desorption agents such as HCl, HNO₃ and HAc showed that the best desorbent was HCl at the concentration of 0.10 mol/dm³. The highest desorption efficiency was 77.21% for the desorption time 2 h.

1. INTRODUCTION

Mercury and its compounds belong to highly toxic substances, whose accumulating in the body can cause systemic poisoning. Severe cases can lead to death and endanger the health of the offspring. Its toxicity showed damage of intracellular enzyme system protein thiol. Capacity of mercury enrichment is high through food chain up to tens thousand times, and once water body is polluted then it is very difficult to recover [1]. In recent years, heavy metal pollution in drinking water, mainly with mercury, is increasing. Water processing methods can be divided into physical, chemical, physico-chemical and biochemical ones [2–4]. For a long time, the adsorption method has been one of the most important water treatment methods, widely used in various water supply and wastewater treatment. The process is generally very quick, adding other agents is

¹Research Center for Nanotechnology, South Campus, Changchun University of Science and Technology, 7186 Weixing Road, Changchun 130022, Jilin Province, P.R. China, corresponding author Q.-Z. Zhai, e-mail: zhaiqingzhou@163.com

not needed and adsorbents used at present have large specific surface areas and high adsorption capacities. Therefore, using the adsorption method to remove pollutants from water has the advantages of high efficiency, high speed, strong adaptability and easy operation etc. Activated carbon can remove some heavy metal ions from wastewater, but the cost of activated carbon is expensive and the regeneration is complex. It is not suitable for processing the wastewater with the pollutants of high concentration, which limits its application [5].

In 1992, MCM-41 mesoporous molecular sieve was first synthesized by the American Mobil Company [6, 7]. This material, characterizing by regular hexagonal one-dimensional pore structure with large specific surface area (higher than $700 \text{ m}^2/\text{g}$), adjustable pore size and high adsorption capacities expected to be used in the field of chemical industry, medicine, catalysis, separation, environment technology etc., MCM-41 molecular sieve is one of members of a new family of mesoporous molecular sieves and opened up a new era of mesoporous materials. In 2001 Cai et al. [8] for the first time synthesized nanometer MCM-41. Mesoporous materials have been used for adsorption of biological molecules such as proteins [9–13]. Nanomaterials, due to the small particle size, often exhibit special properties of small size effect, surface effect. Nano MCM-41 has an open pore structure, narrow pore size distribution and very high specific surface area and pore volume, with potential as heavy metal purification materials.

In this paper, nano MCM-41 was prepared by the hydrothermal method, powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the prepared powders. By using its superiority in the adsorption performance, nano MCM-41 was used for adsorption of Hg^{2+} in water. The optimum conditions for the adsorption of Hg^{2+} have been established and desorption of the material was studied.

2. EXPERIMENTAL

Reagents. Unless specially stated, all the reagents used in the experiments were of analytical grade. Deionised water was used. Reagents for the synthesis of MCM-41 were tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd, China), cetyltrimethylammonium bromide (CTMAB, Changzhou Xinhua Research Institute for Reagents, China) and sodium hydroxide (Beijing Chemical Reagent Plant, China).

Mercury nitrate was obtained from the Chemical Reagent Works of Taixing City, China. Mercury stock standard solution ($3 \text{ g}/\text{dm}^3$), prepared from a readymade mercury nitrate (Taixing Chemical Reagent Factory, China), was used to prepare experimental mercury solutions of concentrations ranging from 0.5 to $3 \text{ g}/\text{dm}^3$. Mercury working solutions were prepared just before use by appropriate dilutions of the stock solution. $0.1 \text{ mol}/\text{dm}^3$ nitric acid and $0.1 \text{ mol}/\text{dm}^3$ sodium hydroxide solutions were used for adjusting the initial pH of solutions.

Apparatus. Powder X-ray diffraction (XRD) analysis experiments were made on a D5005 X-ray diffractometer (Siemens, Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), an operating voltage (tube voltage) of 30 kV and an operating current (tube current) of 20 mA. The scans were taken from $2\theta = 0.4^\circ$ to 10° . Environmental scanning electron microscopic (ESEM) images were taken on a PHILIPS XL30 field-emission environmental scanning electron microscope (Netherlands) instrument. A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) equipped with 1-cm cells was employed in the determination of mercury [14]. 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. MCM-41 was prepared according to the procedure described by Cai et al. [8]. A 1.0 g of CTMAB was dissolved in 480 cm^3 of deionized water at 80°C under vigorous stirring until the solution became homogeneous. To this solution were added 3.5 cm^3 of NaOH solution ($2 \text{ mol}\cdot\text{dm}^{-3}$) with stirring. After the solution became homogeneous, 5.0 cm^3 of TEOS was slowly dropped, giving rise to a white slurry. Then the reaction mixture was kept at 80°C for 2 h with stirring. The resulting solid product was filtered, extensively washed with deionized water for three times and dried in air at room temperature to obtain the as-synthesized materials. The CTMAB surfactant molecules were then removed by calcination of the as-synthesized material at 550°C in air for 4 h to obtain a white parent powder of MCM-41.

The concentration of mercury in the sample was analyzed using a spectrophotometer by forming a complex with 2-(5-bromo-2-pyridineazo)-5-diethylaminophenol 5-Br (PADAP) in the presence of dodecyl sodium sulfate at a wavelength of 562 nm [14]. A linear range of working curve for the determination of mercury using the present method was $0\text{--}1.4 \text{ }\mu\text{g}\cdot\text{cm}^{-3}$ and the sensitivity of the method, i.e., apparent molar absorption coefficient at 562 nm was $8.26\times 10^4 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Effect of the initial pH of solution on the adsorption process: Six portions of 30 cm^3 of $1 \text{ mg Hg}^{2+}/\text{cm}^3$ standard solution were placed into 100 cm^3 beakers. pH was adjusted to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, respectively, using $0.1 \text{ mol}/\text{dm}^3 \text{ HNO}_3$ and $0.1 \text{ mol}/\text{dm}^3 \text{ NaOH}$. Then 0.20 g of MCM-41 was added to each beaker and under magnetic stirring, adsorption was occurred for 60 min. Then each sample was centrifuged at 8000 rpm for 10 min and the concentration of Hg^{2+} in the supernatant was determined. Its adsorption efficiency was calculated and the optimum pH of adsorption was determined.

The adsorption efficiency and adsorption capacity may be calculated from the following equations:

$$E_e = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where E is the adsorption efficiency, Q_e is the adsorption capacity [mg/g], V is the volume of the solution [cm³], C_0 and C_e are the Hg²⁺ concentrations [mg/cm³] at the beginning and after reaching equilibrium, respectively, W is the weight of adsorbent [g].

Effect of initial Hg²⁺ concentration on the adsorption process: Seven portions of 30 cm³ of 0, 0.50, 1.0, 1.5, 2.0, 2.5, 3.0 mg Hg²⁺/cm³ standard solution were placed into 100 cm³ beakers. pH was adjusted to 5.0. 0.20 g of MCM-41 was added to each sample. After adsorption of Hg²⁺, its concentration was determined by the procedure described above, and adsorption efficiency of Hg²⁺ was calculated.

Effect of MCM-41 adsorbent dosage. Six portions of 30 cm³ of 1.0 mg Hg²⁺/cm³ standard solution were placed into 100 cm³ beakers. Their pHs were adjusted to 5.0. Samples of 0.050, 0.10, 0.15, 0.20, 0.25, 0.30 g of MCM-41 were weighed and added to the above stated samples, respectively. Then Hg²⁺ ions were adsorbed and adsorption efficiencies were determined as above, to obtain the optimum adsorbent MCM-41 dosage.

Effect of adsorption contact time on the adsorption process: At room temperature (20±1 °C), six portions of 30 cm³ of 1.0 mg Hg²⁺/cm³ standard solution were placed in six 100 cm³ beakers and adjusted to pH 5.0. 0.20 g of MCM-41 was added to each sample. After adsorption at room temperature for 30, 45, 60, 90, 120, 150 min, respectively, concentration of Hg²⁺ was determined and the efficiency of Hg²⁺ adsorption was calculated in order to obtain the equilibrium time.

Effect of temperature: Five portions of 30 cm³ of 1.0 mg Hg²⁺/cm³ standard solution were placed into 100 cm³ beakers. pH of each solution was adjusted to 5.0 and 0.20 g of MCM-41 was added. After adsorption of Hg²⁺ for 60 min under magnetic stirring at 20, 25, 30, 35, 40 °C, the adsorption efficiency was calculated in order to determine the optimum temperature of adsorption.

Desorption study of Hg²⁺. 0.20 g of MCM-41 was weighed and placed in a 30 cm³ of 1.0 Hg²⁺mg/cm³ standard solution. pH was adjusted to 5.0. After 60 min adsorption under magnetic stirring at room temperature (20±1 °C), the sample was centrifuged for 10 min at 8000 rpm. Then the supernatant was discarded and (MCM-41)-Hg composite material A was obtained.

In order to study effects of HCl, HNO₃, acetic (HAc) acids on Hg desorption in the (MCM-41)-Hg composite material, six portions (50 cm³) of 0.10 mol/dm³ solutions of every acid under examination were placed in a 100 cm³ beaker and 0.20 g of A was added to each

beaker to be soaked for 1, 2, 3, 4, 5, 6 h at room temperature (20 ± 1 °C) and then filtered. The supernatant samples were taken and the concentrations of Hg^{2+} were determined. Desorption efficiency was calculated and the optimum desorption time was obtained.

$$\text{Desorption efficiency} = \frac{A}{B} \times 100\% \quad (3)$$

where A , B are the amounts of mercury desorbed and loaded on the adsorbent, respectively.

Effect of hydrogen chloride concentration on desorption efficiency: Samples of 50 cm^3 of 0.01, 0.1, and 1.0 mol HCl/dm^3 , were taken and placed in 100 cm^3 beakers, and 0.2 g of A was added to each beaker. The solutions were soaked for 2 h, filtered and the filtrates were retained. Then the Hg^{2+} concentrations were determined, desorption efficiencies calculated and the optimum desorption acid concentration was obtained.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF MCM-41 ADSORBENT

Scanning electron microscopy (SEM) can well reflect the sample morphology, surface structure, size, degree of order, etc. Figure 1 shows the SEM image of MCM-41. It can be seen that the sample showed spherical particles, regular shape and the average particle diameter was 110 nm. MCM-41 is a mesoporous material, whose pore morphology and size can be observed from the transmission electron microscopy (TEM). Figure 2 shows the MCM-41 adsorbent TEM image. The sample presents a hole honeycomb structure and the average pore diameter is 3.5 nm. The small-angle X-ray diffraction (XRD) pattern for MCM-41 is shown in Fig. 3. The hexagonally arranged pore channels of mesoporous material MCM-41 represented by (100), (110), (200) and (210) diffractions existed in the sample, which is in accordance with the results reported by Cai et al. [8]. This shows that the adsorbent preparation was successful.

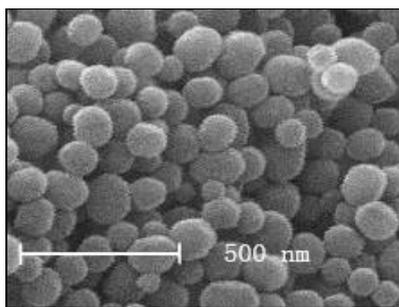


Fig. 1. SEM image of the sample

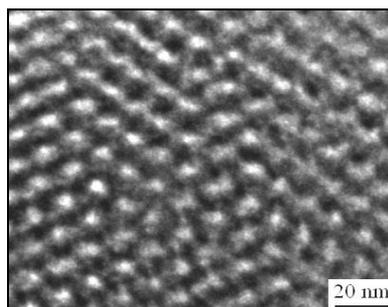


Fig. 2. TEM image of the sample

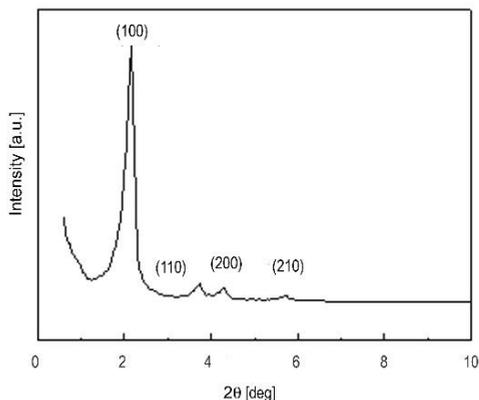


Fig. 3. XRD pattern of the sample

3.2. EFFECT OF THE INITIAL pH ON Hg^{2+} ADSORPTION

Figure 4 shows the effect of solution initial pH value on mercury (II) adsorption on MCM-41. As can be seen, the rate of Hg^{2+} adsorption by MCM-41 increased with the increase of pH value (pH = 1.0–5.0). The reason lies in that the adsorption of mercury ion by the material is always accompanied by the release of H^+ . After pH is increased, hydrogen ion can be neutralized and the competitive effect of hydrogen ion can be reduced, being advantageous to the adsorption of Hg^{2+} by the material.

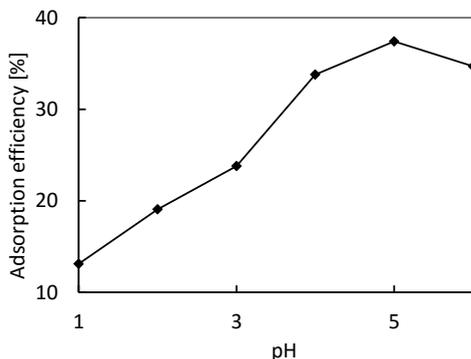


Fig. 4. Effect of pH on the adsorption efficiency of Hg^{2+} , temperature 20 °C, $[\text{Hg}^{2+}] = 1.0 \text{ mg/cm}^3$, 0.20 g MCM-41, contact time 60 min

MCM-41 displayed maximum adsorption efficiency of Hg^{2+} for pH ranging from 4.0 to 6.0. Thus, pH = 5.0 was selected as the optimum value. For a variety of SiO_2 materials, the isoelectric points are 0.5–3.7 [15, 16]. The isoelectric point of MCM-41 is 3.42–3.77 [17]. For pH = 5.0, MCM-41 surface is negatively charged, which is advantageous to the adsorption with positively charged Hg^{2+} .

3.3. EFFECT OF MCM-41 DOSAGE AND $\text{Hg}(\text{II})$ INITIAL CONCENTRATION ON ADSORPTION

The increase of the amount of MCM-41 could increase the removal rate of Hg^{2+} (Fig. 5) due to increase of the number of adsorption sites of Hg^{2+} . Upon increase of the

MCM-41 amount (0–0.20 g), the adsorption capacity of MCM-41 for Hg^{2+} increased. When 0.20 g of MCM-41 was used, the adsorption capacity was maximum, reaching 56.48 mg/g. When MCM-41 amount was further increased (0.20–0.50 g), the adsorption capacity presented a decreasing trend and reduced to 36.08 mg/g. In this experiment, the optimum value of 0.20 g MCM-41 was selected.

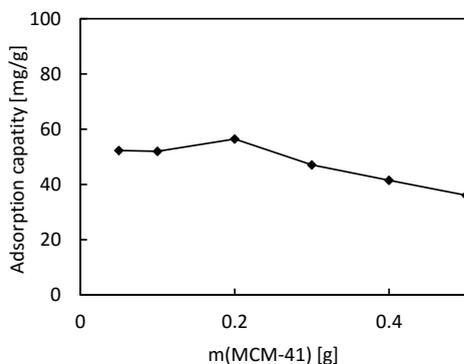


Fig. 5. Effect of the amount of MCM-41 used on the adsorption of Hg^{2+} ; pH 5.0, $[\text{Hg}^{2+}]$ 1.0 mg/cm^3 , contact time 60 min, temperature 20 °C

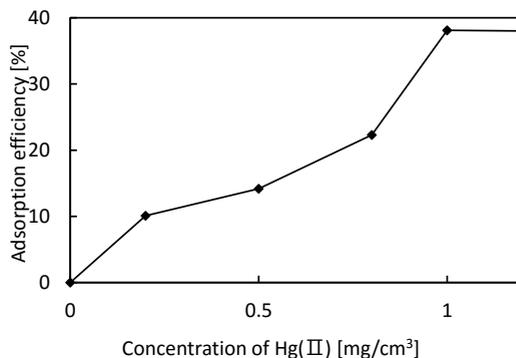


Fig. 6. Effect of initial Hg^{2+} concentration on the adsorption efficiency; pH 5.0, 0.20 g MCM-41, contact time 60 min, temperature 20 °C

The experimental results indicated that percentage of mercury removal as a function of initial concentration (0–1.0 mg/cm^3) with 0.20 g of sorbent (pH 5.0 and adsorption time 60 min) increased with the increase of mercury(II) concentration and the adsorption capacity also increased (Fig. 6). MCM-41 has good ability to remove Hg^{2+} from aqueous solutions.

3.4. EFFECT OF CONTACT TIME ON THE ADSORPTION OF Hg^{2+}

Effect of contact time is an important factor affecting the adsorption efficiency. The experiments showed (Fig. 7) that within the initial 60 min rapid adsorption of mercury(II)

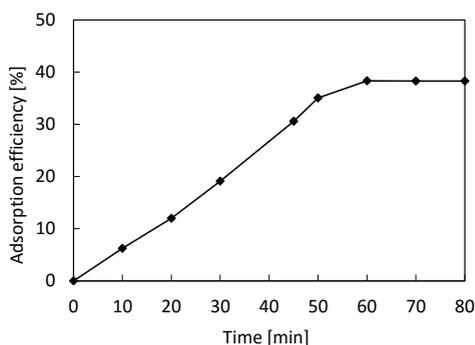


Fig. 7. Effect of contact time on Hg(II) adsorption efficiency; $[\text{Hg}^{2+}]$ 1.0 mg/cm^3 , 0.20 g MCM-41, pH 5.0, temperature 20 °C

was observed and then the adsorption slowed down until the equilibrium was reached. At the beginning of the process, a large amount of available vacant surface sites on the surface of MCM-41 were present which gradually decreased. Mercury(II) was not strongly adsorbed due to the repulsive forces between solute molecules on the adsorbent surface and inside the aqueous phase. In the following experiments, it was assumed that after 60 min the, equilibrium could be achieved.

3.5. EFFECT OF TEMPERATURE ON THE ADSORPTION OF Hg^{2+}

The effect of temperature on the adsorption of mercury(II) onto MCM-41 is shown in Fig. 8. The effect of temperature on the adsorption of mercury(II) by MCM-41 is not great, probably due to opposite factors influencing the process.

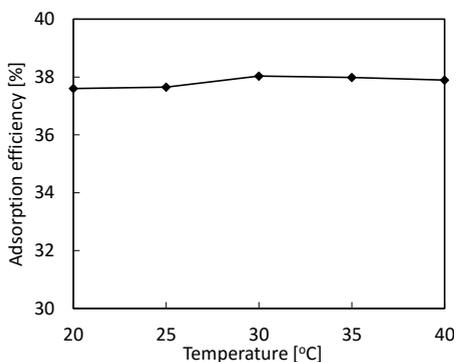


Fig. 8. Effect of temperature on the adsorption of Hg^{2+} ; $[\text{Hg}^{2+}]$ 1.0 mg/cm³, 0.20 g MCM-41, pH 5.0, contact time 60 min

Firstly, when temperature is increased, the thermal motions of Hg^{2+} ions become faster and they more easily diffuse into the channels of the adsorbent. The adsorption efficiency increases. However, as exchange reaction of silanol on MCM-41 with Hg^{2+} is the exothermal one, thereby the increase in temperature decreases its rate and adsorption efficiency. These two opposite effects cause weak dependence of the reaction efficiency on temperature. Considering that high temperature adsorption needs a large amount of energy, the optimum temperature seems to be room temperature 20 ± 1 °C.

The adsorption studies showed that the optimum conditions for the adsorption of Hg^{2+} by MCM-41 are determined as follows: pH 5.0, $m_{(\text{MCM-41})}:m_{\text{Hg}^{2+}} = 6.67$, temperature 20 °C and contact adsorption time 60 min, for the initial Hg^{2+} concentration of 1.0 mg/cm³. At this time, the maximum adsorptive amount of Hg^{2+} is 56.48 mg (Hg^{2+})/g of MCM-41.

3.6. DESORPTION STUDY

Desorption of Hg(II) from MCM-41 Hg(II) loaded was performed by three various acids such as hydrochloric acid, nitric acid and acetic acid (Fig. 9). For the desorption with hydrochloric acid, a maximum desorption efficiency was reached after 2 h and it was 77.21%; for the desorption with nitric acid, a maximum desorption rate was reached

at 6 h and it was 49.55%; for the desorption with acetic acid, a maximum desorption rate was reached at 3 h and it was 45.03%.

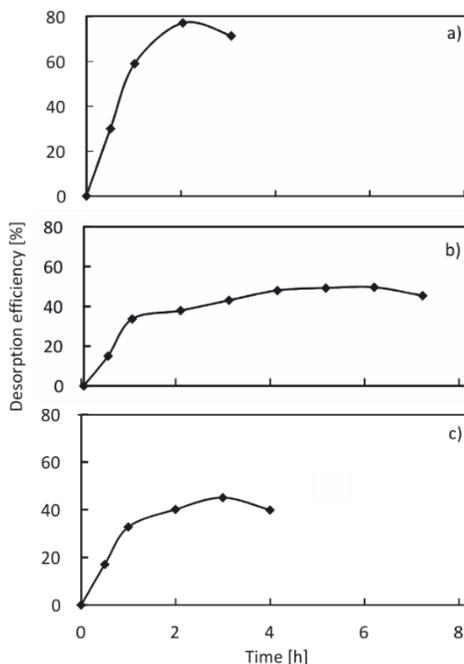


Fig. 9. Effect of desorbing agent a) HCl, b) HNO₃, c) HAc on time dependence of the desorption efficiency

The desorbing effect of HCl is the strongest one. In the process of desorption, after the acid was added, numerous hydrogen ions were immediately introduced. They would cause a competition for the metal cations. As the concentration of hydrogen ions became drastically higher than that of the heavy metal ions, the surface groups of the adsorbent were occupied by hydrogen ions or hydronium ions and accordingly desorption of the Hg²⁺ ions occurred. In addition, as the addition of acid destroyed some adsorbent's surface which made it more smooth, metal ions might desorb from the surface of adsorbent.

Table 1

Effect of the concentration of HCl on the desorption rate

[HCl] [mol/dm ³]	Desorption rate [%]
0.01	50.13
0.05	61.09
0.10	77.21
0.50	59.93
1.0	48.52

The effect of hydrogen chloride concentration on desorption has been presented in Table 1. The optimum desorption acidity was 0.10 mol HCl/dm³. Too high or too low acidity is not advantageous to desorption progress. When the acid concentration is low, the concentration of H⁺ is small and the replacement ability for Hg²⁺ is low, so the desorption efficiency is lower. Too high acid concentration also can result in the changes of mechanical intensity, physical and chemical properties of adsorbent leading to decrease in desorption efficiency.

4. CONCLUSIONS

Mesoporous MCM-41 with average particle diameter of 110 nm was successfully prepared by the liquid phase method. The optimal conditions of adsorption of Hg²⁺ by MCM-41 were determined. The adsorption capacity of MCM-41 towards Hg²⁺ can reach 56.48 mg Hg²⁺/g (MCM-41). The agent with best desorptive effect was HCl with the concentration of 0.1 mol/dm³. The highest desorption efficiency reached 77.21% after the process lasting 2 h.

ACKNOWLEDGEMENTS

The authors thank the Natural Science Foundation of Jilin Province, P.R. China for the financial support under Project No. 20090548, KYC-JC-XM-2009-040.

REFERENCES

- [1] TANG N., CHAI L.Y., MIN X.B., *Research development in the treatment of mercury-containing waste water*, Ind. Water Treatment, 2004, 24 (8), 5.
- [2] ZHENG H., *The actuality and trend of heavy metals wastewater treatment technology*, Guangdong Chem. Ind., 2009, 36 (10), 134.
- [3] WU J., LI Q.B., DENG X., LU Y.H., *Research advances in bioadsorption of heavy metals*, Ion Exchange. Adsorption, 1998, 14 (2), 180.
- [4] WANG J., *New technology for treatment of water pollution in Japan*, Advances. Environ. Sci., 1996, 4 (1), 75.
- [5] YANG J., QIN Z.F., CHEN S.Y., PENG S.Y., *Dynamic study on activated carbon adsorption of lead ion in water*, Environ. Chem., 1997, 32 (5), 423.
- [6] BECK J.S., VARTULI J.C., ROTH W.J., LEONOWICZ M.E., KRESGE C.T., SCHMITT K.D., CHU C.T.W., OLSON D.H., SHEPPARD E.W., MCCULLEN S.B., HIGGINS J.B., SCHLENKER J.L., *A new family of mesoporous molecular sieves prepared with liquid crystal templates*, J. Am. Chem. Soc., 1992, 114, 10834.
- [7] KRESGE C.T., LEONOWICZ M.E., ROTH W.J., VARTULI J.C., BECK J.S., *Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism*, Nature, 1992, 359 (22), 710.
- [8] CAI Q., LUO Z.S., PANG W.Q., FAN Y.W., CHEN X.H., CUI F.Z., *Dilute solution routes to various controllable morphologies of MCM-41 silica with a basic medium*, Chem. Mater., 2001, 13 (2), 258.
- [9] LI Y.J., ZHOU G.W., XU H.Y., QIAO W.T., WANG Y.Y., *Progress in enzyme immobilization on mesoporous materials and their modified materials*, Chemistry, 2009, 4, 326.

-
- [10] LV Y.J., LI P.J., GUO Y.L., WANG Y.Q., LU G.Z., *Immobilization of enzymes on mesoporous materials*, Prog. Chem., 2008, 20 (7/8), 1172.
- [11] LI Y.J., ZHOU G.W., XING F.Q., *Influence of immobilized enzyme in the mesoporous material*, Appl. Chem. Ind., 2006, 37 (6), 688.
- [12] HUDSON S., COONEY J., MAGNER E., *Proteins in mesoporous silicates*, Angew. Chem. Int. Ed., 2008, 47, 8582.
- [13] HARTMANN M., *Ordered mesoporous materials for bioadsorption and biocatalysis*, Chem. Mater., 2005, 17(18), 2577.
- [14] LIU J.H., HUANG C.X., HUANG Y., *Spectrophotometric study on the reaction of 5-Br-PADAP with mercury(II) in the presence of surfactant*, Phys. Test. Chem. Anal., 1999, 35B (5), 218.
- [15] PARKS G.A., *The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxocomplex systems*, Chem. Rev., 1965, 65, 177.
- [16] SONG S.W., HIDAJAT K., KAWI S., *Functionalized SBA-15 materials as carriers for controlled drug delivery: influence of surface properties on matrix-drug interactions*, Langmuir, 2005, 21 (21), 9568.
- [17] DEERE J., MAGNER E., WALL J.G., HODNETT B.K., *Mechanistic and structural features of protein adsorption onto mesoporous silicates*, J. Phys. Chem. B, 2002, 106, 7340.