Asian Journal of Chemistry; Vol. 26, No. 18 (2014), 6261-6265

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17493

Research on Eliminating Hardness in Water by Mesoporous Material

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Received: 1 March 2014; *Accepted*: 5 May 2014; *Published online*: 1 September 2014; AJC-15894

Hardness in water, which judges the water quality, impacts greatly on the human health according to the relevant researches, appropriate treatment of corresponding high hardness water is urgently necessary. This paper reports the preparation of mesoporous silicon material by the application of sol-gel method, where the template was cetyltrimethyl ammonium bromide and the silicon source was tetraethoxysilane. Using X-ray diffraction, Fourier transform infrared spectroscopy and polarizing microscope, a series of corresponding researches on phase composition, chemical composition and microscopic crystal morphology of the synthetic mesoporous material were carried out. Its property of removing hardness in water was also tested by static adsorption experiments. The results show that the synthetic mesoporous material has certain absorption efficiency as to cope with the total hardness eliminating problem in water and which is advanced by high purity and low crystallinity.

Keywords: Mesoporous material, Total hardness, Adsorption, Water treatment.

INTRODUCTION

Nowadays, people are more and more concerned with the quality of the drinking water with the rapid development of industry and economy, it is necessary to treat wastewater prior to its discharge to the environment[1], thus apply more and more strict demands on the water treatment. Water that contains a large amount of Ca^{2+} and Mg^{2+} is called hard water, and in general, the total hardness of water is also the content of Ca^{2+} and Mg^{2+} namely[2]. Researchers demonstrate that urbanization has a significant impact on water chemistry composition of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, *etc*.[3]. Though these ions are essential micro-elements to the health of human, appropriate amount required. Overlarge hardness water intake will trigger them to act the other way around. Appropriate amount of ions can provide certain kind of nutrients, which will resist the volatilization of the potential poisons, however, incidences like gallstone and kidney stone trend to raise if people keep drinking high hardness water in a long time. But not only that, high hardness also influences industrial water[4], especially as to boiler water, whose thermal conductivity decrease dramatically because of the incrustation, which is also created by aforementioned high hardness and this process is pretty easy to happen under the circumstance of heat, undoubtedly, it causes serious fuel waste and financial loss.

So it is necessary to adopt appropriate measures to eliminate hardness in water, a lot of corresponding researches have been carried out, especially on adsorption method. Nevertheless, traditional adsorption method has some shortcomings like low adsorption capacity, or poor adsorption selectivity, *etc*. Mesoporous material, as a new type adsorption material, is featured by potential application in sorption, catalysis and separation, *etc*.[5]. In general, it can be divided into silicon-based mesoporous material and non-silicon-based mesoporous material, pure silicon mesoporous material includes structures like MCM, SBA, FSM, HMS, MSU and so on[6], whose property will be improved if charging some new ions and groups[7]. In regard to non-silicon-based mesoporous material, however, it encounters a series of difficulties in practical application due to its poor thermostability, low specific surface area and small pore volume[8,9]. But on the whole, mesoporous material has found an increasing wide utilization in the field of water treatment[10,11].

This paper introduces a new measure to eliminate the hardness in water, where the template was cetyltrimethyl ammonium bromide (CTAB) and the silicon source was tetraethoxysilane (TEOS). Modern analytical techniques like XRD, FTIR and polarizing microscope also participated the analysis[12].

EXPERIMENTAL

The experimental apparatuses were as follows: (1) X ray diffracmeter, Bruker D8 Advance, made by Germany. (2) Infrared spectrometer, FT-IR 550, made by Nicolet Magna Corporation. (3) Polarizing microscope, Coke A1, made by Carl Zeiss Group in Germany. (4) pH meter, pHS-25, made by Shanghai Xinrui Instruments and Meters Co., Ltd. (5) Digital thermostatic oscillator, SHA-BA, made by Jintan Precision Instrument Manufacturing Co., Ltd. (6) Electronic analytical balance, CP-512, made by Shanghai Jingtian Electronic Instrument Co., Ltd.

All of the the experimental reagents were analytical reagent and they were shown as follows: (1) cetyltri methyl ammonium bromide (CTAB), (2) tetraethoxysilane (TEOS), (3) ammonium hydroxide, (4) absolute ethyl alcohol, (5) hydrochloric acid, (6) EDTA (ethylene diamine tetraacetic acid), (7) eriochrome black T, (8) triethanolamine, (9) ammonium chloride, (10) magnesium sulfate and (11) calcium chloride.

General procedure

Mesoporous silicon material preparation: Dissolve 2 g of cetyltrimethyl ammonium bromide in distilled water accurately at 30 °C and dilute with distilled water to 180 mL, then charge absolute ethyl alcohol and continue stirring for 5 min, until the pH value of the solution is about 6-7. Use pipette to transfer certain amount of ammonium hydroxide (mass fraction is 25 %) into beaker and adjust pH to 10, then pipette a specified volume of tetraethoxysilane (TEOS) and instill slowly into beaker, continue stirring for 2 h. Until the solution presents viscous white gel state, then move it into the high-pressure crystallization kettle for the propose of crystallization, under 110 °C for 24 h. Afterwards, cool it to room temperature and conduct suction filtration process. Wash it by absolute ethyl alcohol firstly, then finally wash to neutral by distilled water. Transfer the generated white solid into crucible, then heat it under 120 °C. Next, cool it to room temperature, then move the crucible into muffle and warm it up to 550 °C at the speed of 5 °C/min, under the same condition, calcine it for 6 h to eliminate the template. Finally, the original powder of mesoporous silicon material can be obtained after cooling it to room temperature naturally. Reagent CATB consists of ammonium hydroxide, absolute ethyl alcohol and tetraethoxysilane, the specific composition flowchart is shown in Fig. 1.

Simulation schemes of different hardness in water: Hardness in one kind of water may differ from another, to simulate their similarities and differences, there puts different amount of calcium chloride into the same amount of ultrapure water, thus several water samples were created in order to configure multiple test schemes.

Total hardness test method in water: EDTA titration method, which conforms to national test standard in China, was applied in this test, it also stipulated that complexometric titration should be used to test the total hardness in water. In the ammonia-ammonium chloride buffered solution with pH equals 10, there take neriochrome black T as the indicator and titrated the amount of Ca^{2+} directly by EDTA standard solution. Eriochrome black T would combine with some Ca^{2+} and then formed wine red complexation firstly, but as EDTA instilled, which has stronger complex capacity and much easier to combine with Ca^{2+}, solution colour would turn into blue at titration end point[13].

Adsorption experiment: Charge certain amount of mesoporous powder into above simulation water sample, water's volume was 100 mL, then oscillate frequently with speed 120 r min^{-1} in 20 °C until adsorption equilibrium was attained. Based on concentration and dosage of the standard titration solution Na_2EDTA, equation for total amount of Ca^{2+} and Mg^{2+} is expressed as below[14]:

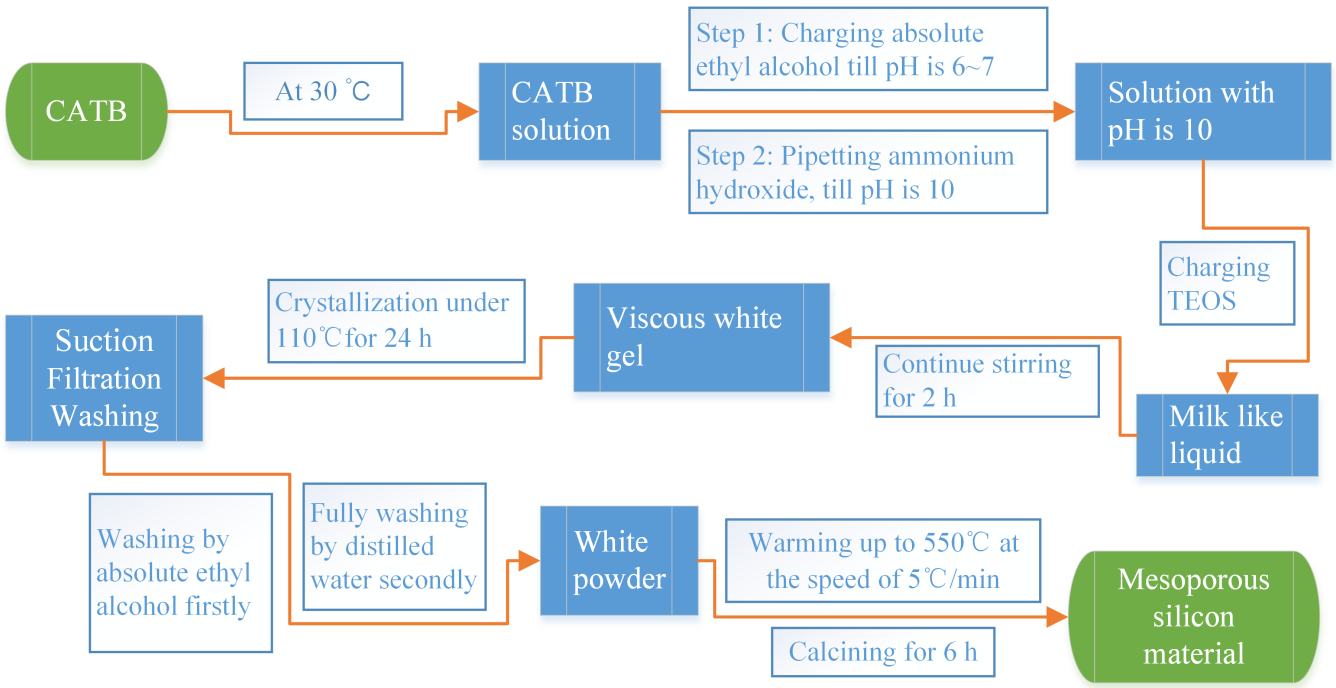

Fig. 1. Composition flowchart of mesoporous material

$$C = \frac{(V_1 - V_0) \times C_1 \times 100.09 \times 1000}{V}$$

where C is mass concentration of total hardness in water sample, mg/L; V_1 is consumption volume of solution Na_2EDTA by titrating water sample, mL; V_0 is consumption volume of solution Na_2EDTA by titrating blank water sample, mL; C_1 is amount-of-substance concentration of standard titration solution Na_2EDTA, mol/L; V is the volume of water sample, mL; 100.09 is atomic mass of calcium.

The equation for eliminating rate is shown as follows,

$$N = \frac{(C_0 - C)}{C_0} \times 100\ \%$$

where C_0 is initial hardness concentration of water sample and C is residual hardness concentration of water sample.

Regeneration experiment of adsorbent: Solid-to-liquid ratio of desorption and regeneration in adsorbent was 1 g/L, where desorption solution was sulfuric acid (amount-of-substance concentration is 1 mol/L). Adsorption experiment was carried out under room temperature and pH value was 2, charge 0.10 g mesoporous material into each water sample respectively, and the volume of water was 100 mL. Let the absorption sustain for 12 h, then filter out the adsorbent and stove it under 100 °C. Next, let adsorptive mesoporous material desorb by mixing it with the sulfuric acid (1 mol/L) under room temperature, with solid-to-liquid ratio was 1 g/L and duration was 12 h, in the end, reagent would come through filtration, washing and stoving consequently. Then repeat the aforementioned hardness adsorption experimentation.

RESULTS AND DISCUSSION

Characterization of mesoporous material: Diffraction analysis on powder by X-Ray diffraction (XRD): XRD is the most fundamental approach to characterize mesoporous material,whose diffraction pattern can denote a series of information, such as the degree of crystallinity, crystal structure and lattice parameters, *etc*. This experiment applied X-ray diffracmeter (typed by Bruker D8 Advance) to characterize the crystal structure, radiation of calcium and potassium of the sample, in diffracmeter, tube voltage was 40 KV and tube electric current was 30 mA. Characterize conditions were as follows: antiscattering slit (SS) was 0.17°, divergence slit (DS) was 0.17°, receiving slit (RS) was 0.15 mm, scanned area was 5°-70° and scanning speed was 0.2°/s.

Fig. 2 shows the XRD diffraction peak of the synthetic mesoporous material, it can be observed that a raised diffraction peak exists at 25° or so according to the diffraction pattern, which is coincide with MCM-41, a new type nanostructured material. Thus demonstrating that mesoporous structure made by this experiment is similar with MCM-41. So it can be concluded that mesoporous material also has hexagon mesoporous structure, however, with relative low degree of crystallinity. The hardness absorption in water mainly happens on the surface of the mesoporous material and whose adsorption property is mostly depended on the corresponding surface structure, so generally speaking, a mesoporous material with lower degree of crystallinity and smaller crystal particle, however, is capable of having larger adsorption capacity.

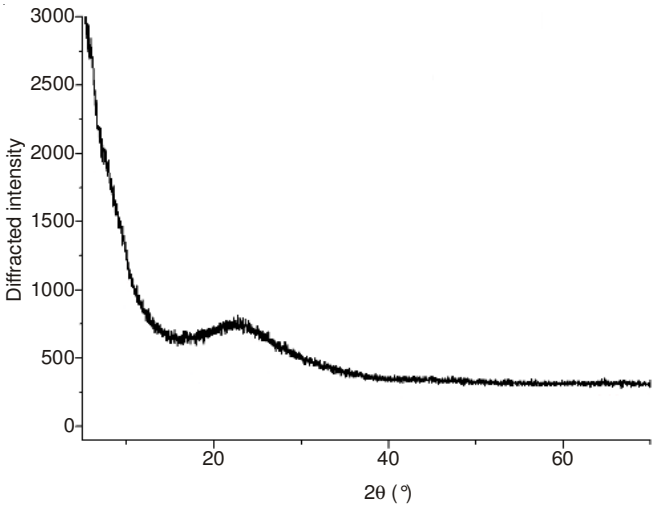

Fig. 2. XRD diffraction pattern of the synthetic mesoporous material

Infrared spectroscopic analysis (FT-IR): Infrared spectroscopy (IR) is aimed to analyze the mesoporous skeleton structure, surface hydroxyl group, surface acidity and catalytic performance[15].

Fig. 3 shows the infrared spectrogram of the synthetic mesoporous powder. It can be seen that the main affiliations of the absorbance peaks are as follows, peaks at 927.67, 802.71 and 619.78 cm^{-1} belong to Si-O-Si characteristic vibration peaks, while peaks at 927.67 and 802.71 cm^{-1} belong to Si-O-Si stretching vibration peaks, peak at 619.78 cm^{-1} belongs to Si-O-Si bending vibration peak, in other words, the prepared adsorbent possesses the skeleton structure of mesoporous silica.

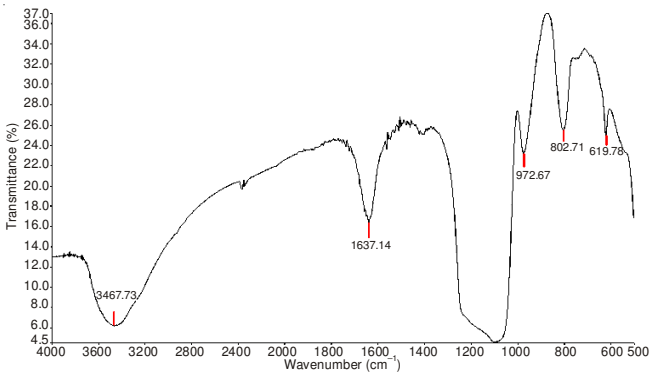

Fig. 3. Infrared spectra of the synthetic mesoporous material

Polarizing microscope: Polarizing microscope was used to measure the crystal length, crystal particle size, particle size distribution and observe agglomeration and corresponding distribution. Fig. 4 shows the photo of the synthetic mesoporous material, and it was taken by polarizing microscope. It can be observed that particle size of original mesoporous powder is less than a micro and its aperture is too small to be observed, it conforms to relevant specifications, and it also demonstrates that the synthesized mesoporous material is outstripped by low degree of crystallinity.

Relationship between adsorbent dosage and eliminating effects: Relationship between adsorbent dosage and eliminating rate is shown in Fig. 5 and from which it can be

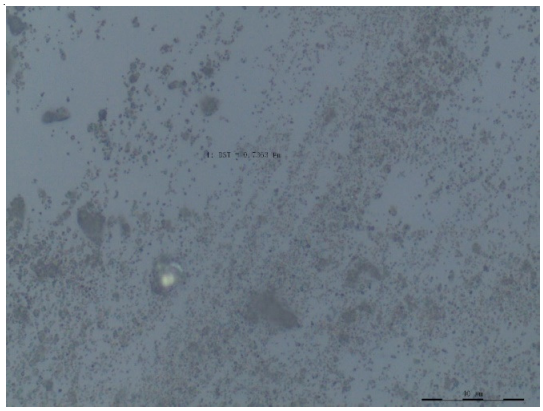

Fig. 4. Photo of the synthetic mesoporous material, taken by polarizing microscope

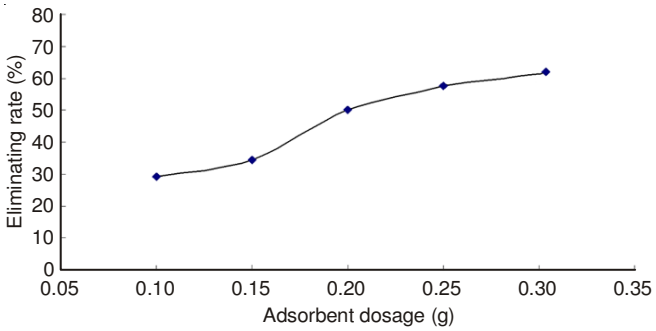

Fig. 5. Relationship between adsorbent dosage and eliminating rate

concluded that increasing the adsorbent dosage will add the eliminating rate dramatically. Nevertheless, the eliminating rate will reach a stable value under certain amount of adsorbent dosage, since the solution provides a large amount of adsorbate for adsorbent to adsorb when the dosage is relative low, namely the eliminating increase rate rises very fast. With continue increasing of the dosage, induced increase rate trends to mitigate, saturation adsorption of the synthetic material will be attained eventually, *i.e*. adsorption equilibrium, at this time, the eliminating rate almost keeps its constant value.

Test on adsorption kinetics curve: Adsorption kinetics curve is used to inspect the relationship between adsorption rate and adsorption equilibrium. It can be seen from curvilinear trend in Fig. 6 that the curve is almost horizontal when the absorption time is beyond 0.5 h and only few fluctuations show out, the baseline of the eliminating rate is 19 %. Additionally, some tiny decrease appears beyond 80 min, but in general, the adsorption equilibrium is almost reached after proceeding for 0.5 h.

Relationship between original pH value and eliminating effects: pH value is very important to the solution property and it also affects greatly on the materials in solution. This paper made specialized researches on the absorption efficiency of adsorbent under different original pH values, the result is shown in Fig. 7. The figure indicates that the eliminating rate trends to increase firstly and then decrease. The maximal eliminating rate is 29.5 % with relevant pH value 5. Overall, absorption capacity of the mesoporous material is influenced greatly by the pH value and the optical material can be obtained under the pH value is 5, this result meets with the reports of Morales *et al.*[16].

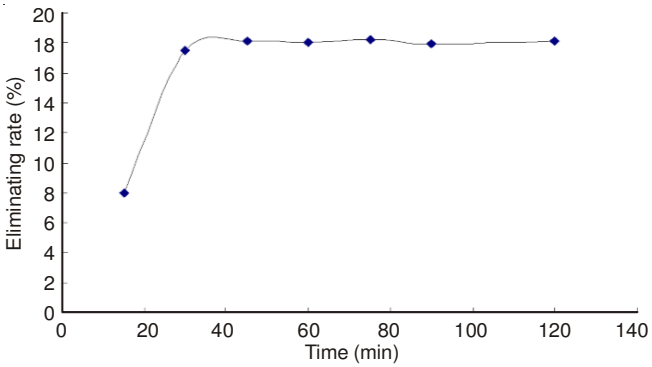

Fig. 6. Adsorption kinetics curve of the synthetic mesoporous material

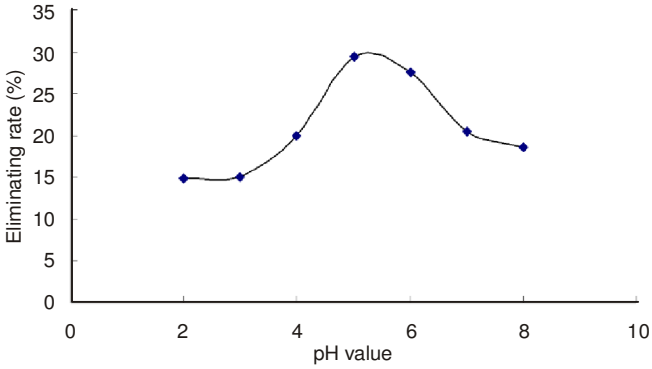

Fig. 7. Relationship between original pH value and eliminating effects

Relationship between original temperature and eliminating effects: Temperature is also a key factor that influences the absorption capacity of mesoporous material, so this paper conducted the experiment in regard to the relationship between temperature and eliminating rate (Fig. 8), where the eliminating rate is little influenced by temperature. Considering that total hardness in water reacts sensitively to temperature and some calcium ion will be transformed into precipitate if the temperature is higher than 50 °C, thus induce big error in test results. Finally it can be testified that the room temperature is preferably good and there is no need to take heating measure.

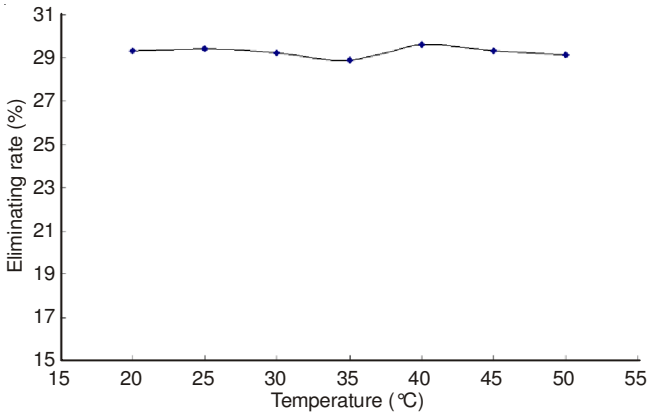

Fig. 8. Relationship between original temperature and eliminating effects

Relationship between initial concentration and eliminating effects: Fig. 9 shows the relationship between initial concentration and eliminating rate, there is no wonder that eliminating rate decrease dramatically with original concen-

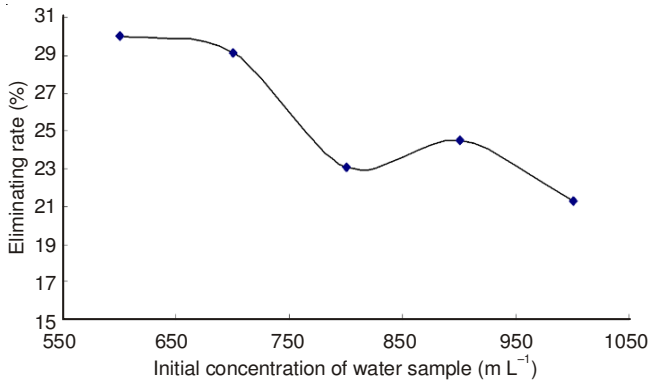

Fig. 9. Relationship between initial concentration in water sample and eliminating rate

tration increase of water sample, the optical eliminating rate is attained when the initial concentration of water sample is 600 mg/L. Because of the original useful quantity of total hardness, it provides abundant ions for adsorbent to absorb. But higher initial concentration in water induces higher initial quantity of ions, thus give rise to high adsorption capacity and this adsorption capacity shows rising trend with the increase of water concentration. But eventually, the eliminating rate will go from little to less because of the constant amount of adsorbent.

Conclusions

(1) Mesoporous silicon material was prepared successfully by the adoption of sol-gel method and the template was cetyltrimethyl ammonium bromide (CTAB), the silicon source was tetraethoxysilane (TEOS). Additionally, characterization conducted by XRD, FTIR and polarizing microscope testified that this material was partially ordered mesoporous SiO_2 and was featured by high purity and low degree of crystallinity.

(2) According to the total hardness absorption experiment conducted by prepared mesoporous SiO_2 and single factor analysis, then provided that the initial hardness in water was 600 mg/L, under such condition, maximal absorption capacity could be realized with absorption time is 0.5 h and absorption pH value is 5. In other words, optical effects could be obtained as to eliminating hardness in water.

(3) Though eliminating effects was not ideal enough for mesoporous, certain hardness eliminating capacity existed, this defect could be improved by modification. Such as importing amino group or mercapto group and adding ions that are excangeable with hardness ions in water.

(4) Prepared mesoporous material overcome many other adsorbent in high recovery rate according to the adsorption regeneration experiment, and that is another reason to choose mesoporous material as the most appropriate adsorbent.

ACKNOWLEDGEMENTS

This work was supported by Jiangsu Province Science and Technology support program (Grant No.BE2011648), the 111 Project (B12030) and National Natural Science Foundation of China (Grant No. 51274197)

REFERENCES

1. M. Masrournia, *Asian J. Chem*., **25**, 3867 (2013).
2. R.G. Srinivas and B.R. Ravichandra, *Res. J. Chem. Environ*., **17**, 25 (2013).
3. H.-B. Yang, M.-Z. Liu, H.-H. Chen, G.-P. He, X. Chen and D.-H. Cheng, *Asian J. Chem*., **26**, 1069 (2014).
4. A. Akgul, *Asian J. Chem*., **24**, 4771 (2012).
5. D. Tian and X. Zhao, *Asian J. Chem*., **22**, 4617 (2010).
6. C. Wang, S.J. Luo, Y.Q. Ren and H.X. Xi, *Chem. Eng*., **39**, 21 (2011).
7. G.K. Chuah, X. Hu, P. Zhan and S. Jaenicke, *J. Mol. Catal. Chem*., **181**, 25 (2002).
8. C. Lv, Y. Zhou, H. Li, M. Dang, C. Guo, Y. Ou and B. Xiao, *Appl. Surf. Sci*., **257**, 5104 (2011).
9. W. Zhan, Y. Guo, Y. Wang, Y. Guo and G. Lu, *J. Rare Earths*, **28**, 369 (2010).
10. J.J. Wei, M.H. Sui and L. Sheng, *Sichuan Environ*., **31**, 110 (2012).
11. L. Wang, H.P. Deng and J. Qi, *Mater. Rev*., **27**, 139 (2013).
12. Qi J. Y., Modern Analysis and Testing Technology, Tongji University Press, Shanghai (2006).
13. Tianjin Environment Monitoring Center, PRC PatentCN12473-11A. 2000.3.15 (2000).
14. Standard Examination Methods for Drinking Water-Organoleptic and Physical Parameters, PRC National Standard, GB/T 5750.4.7-2006, China Standards Press, Beijing (2006).
15. M.E. Davis, *Nature*, **417**, 813 (2002).
16. V. Hernández-Morales, R. Nava, Y.J. Acosta-Silva, S.A. Macías-Sánchez, J.J. Pérez-Bueno and B. Pawelec, *Micropor. Mesopor. Mater*., **160**, 133 (2012).