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H. Sepehrian[ab]; R. Yavari[b]; S. Waqif-Husain[a]; M. Ghannadi-Maragheh[b]
[a] Department of Applied Chemistry, Chemistry Faculty, University of Tarbiat Moallem, Mofateh Avenue, Tehran, Iran [b] Jaber Ibn Hayan Research Laboratories, Nuclear science and Technology Research Institute, AEOI, Tehran, Iran

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Separation of Radionuclides on Mesoporous Zirconium Silicate: A Novel Sorbent

H. Sepehrian,[1,2] R. Yavari,[2] S. Waqif-Husain,[1] and M. Ghannadi-Maragheh[2]

[1]Department of Applied Chemistry, Chemistry Faculty, University of Tarbiat Moallem, Mofateh Avenue, Tehran, Iran

[2]Jaber Ibn Hayan Research Laboratories, Nuclear science and Technology Research Institute, AEOI, Tehran, Iran

Abstract: Five different samples of mesoporous zirconium silicate have been prepared with various mole ratios of Si/Zr and Cetyltrimethylammonium bromide (CTMABr) as template. XRD, nitrogen sorption, SEM, IR, thermogravimetry and sorption of radionuclides have been studied. Separation of Cs(I)-Mo(VI), Sr(II)-Mo(VI), Cs(I)-Th(IV), Sr(II)-Th(IV), and Tl(I)-Th(IV) have been developed on columns of this novel sorbent.

Keywords: Mesoporous, radionuclides sorption, zirconium silicate

INTRODUCTION

Since the synthesis of a group of new porous materials (1), there has been an increasing interest in the development of new porous solids owing to their wide applications in separation, purification, and catalytic processes (1,2). Many new mesoporous materials have been developed and successfully used in the removal of heavy metal ions from aqueous media (3–6). Recently some mesoporous materials have also been employed in the removal of radionuclides from waste streams (7–10). A new class of ordered mesoporous materials using surfactant micellar structures as templates has been employed for wide environmental applications

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Address correspondence to S. Waqif-Husain, Department of Applied Chemistry, Chemistry Faculty, University of Tarbiat Moallem, 49-Mofateh Avenue, Tehran-15614, IRAN. E-mail: syedwhusain@yahoo.com

(6,11–13). In this paper, we report the synthesis of mesoporous zirconium silicates under varying conditions, their properties, and sorption of radionuclides on these materials have been studied. Separation of Cs(I)-Mo(VI), Sr(II)-Mo(VI), Cs(I)-Th(IV), Sr(II)-Th(IV), and Tl(I)-Th(IV) have been developed on the columns of this sorbent.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical grade (E. Merck or Fluka). ^{131}Ba, ^{115}Cd, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{64}Cu, ^{203}Hg, ^{99}Mo, ^{86}Rb, ^{85}Sr, ^{232}Th, ^{204}Tl, $^{235+238}$U, ^{187}W, ^{65}Zn, and ^{95}Zr radioisotopes were supplied by the Nuclear Research Center, Atomic Energy Organization of Iran, except Cetyltrimethylammonium bromide (CTMABr) which was supplied by Aldrich (U.K.).

Apparatus

A Philips X'pert powder diffractometer system with Cu-Kα ($\lambda = 1.541$ Å) radiation was used for X-ray studies. Nitrogen sorption studies were made with a Quantachrome NOVA instrument and scanning electron micrograph was recorded using a Philips microscope XL30. FT-IR was obtained using a Bruker FT-IR spectrophotometer model Vector-22. Thermogravimetric analysis was performed on a Rheometric Scientific modal STA-1500. pH measurements were made with a Schott CG841 pH-meter (Germany). Quantitative determinations of inorganic ions were carried out using an inductively coupled plasma – optical emission spectrometry (ICP-OES) Varian Turbo Model 150-Axial Liberty. A Gamma spectrometer Model Ortec EG&G, HPGe high resolution, Coaxial, GMX detector coupled to a 4 k multichannel analyzer was used during the determination of distribution coefficients of radionuclides. A waterbath shaker model CH-4311 (Infors AG) was used in the determination of the distribution coefficients.

Preparation of Mesoporous Zirconium Silicate

Five different samples of mesoporous zirconium silicate were prepared by mixing sodium silicate as silicon source, zirconium oxychloride as zirconium source, and cetyltrimethylammonium bromide (CTMABr) as surfactant under non-thermal conditions. In a typical procedure, 0.6 g CTMABr was added in 23 g of demineralized water, this was stirred

for 15 min (140 rpm), after that 3 g of sodium silicate was added to the mixture and it was further stirred for 30 min. The pH value was adjusted at 9 by adding sulphuric acid (2 M). Then the solution of $ZrOCl_2 \cdot 8H_2O$ (0.45 g in 50 mL demineralized water) was added dropwise. The stirring was continued for 4 h. A bulky white precipitate was formed. It was filtered, washed five times with demineralized water, and dried in air oven at 50°C for 48 h. A small portion of this material was calcined at 600°C for 6 h. The material was digested in 0.1 M HNO_3 for 24 hours and then washed with demineralized water.

The samples prepared were having Si/Zr molar ratios: 10; 20; 40; and 80. They were marked as: ZrxMCM-41 where x indicated the Si/Zr molar ratio and MCM-41 (Mobile Crystalline Material) indicated hexagonal ordered mesoporous silicate. In order to study the effect of addition of zirconium in these types of materials, a sample only with silica in the framework was also prepared under the same conditions and it was denoted as Si-MCM-41.

Ion-exchange Capacity

One gram of sorbent sample in the H^+ form was placed in a glass column having glass wool at the base. Then 1 M KCl solution was passed slowly through this column by adjusting the effluent rate to 20 drops/min. The effluent was carefully collected in a 250 mL conical flask. The complete replacement of H^+ from sorbent by the K^+ of KCl was checked by pH meter. The collected acid was titrated with 0.1 M KOH solution and the ion-exchange capacity was calculated respectively (14).

Composition

250 mg (dry mass) amount of the sorbents were dissolved in 10 mL hot 4 M NaOH. The solutions were diluted and zirconium and silicon were determined by ICP-OES technique.

Distribution Coefficients

The batch equilibrium method was used to determine the distribution coefficients as following:

$$K_d = [(A_i - A_f)/A_f] \cdot V/m$$

Where A_i and A_f are the initial and final activity (cps) or concentration (ppm) of solution, V is the volume of the initial solution in mL, and m

is the mass of the sorbent in grams. A weighed amount of the sorbent (200 mg) was shaken for five hours at 25°C ± 1°C in a polyethylene bottle containing 20 mL of 1.2×10^{-4} M of the metal ion solution as a radionuclide or natural isotopes. The activities or concentration (ppm) of the solution before and after equilibration were measured by Gamma-spectrometry or ICP-OES technique. Standard deviation for K_d values were checked by two determinations and were $< 10\%$.

Chemical Stability

The chemical stability of mesoporous sorbents was studied in HCl, HNO_3, and in NaOH (Table 2). A 100 mg (dry) amount of each mesoporous materials was placed in 50 mL of the acidic or basic solution and were shaken for 24 hours at room temperature. The metal ions released from the mesoporous zirconium silicate were analysed by ICP-OES (15).

Separation of Metal Ions

Cesium and Molybdenum(VI) Ions

A slurry of 0.5 g of Zr10MCM-41 in H^+ form was poured in a glass column with an inner diameter of 8 mm. A 4.0 mL mixture containing 0.5 mL cesium solution (0.005 M) and 1.0 mL molybdenum solution (0.005 M) and demineralized water, was added to the column. The cesium ion was eluted with demineralized water through the column. The molybdenum was adsorbed on the column and was later eluted with 0.05 M NaOH solution. The flow rate of the effluent was maintained at 0.2 mL/min and the effluents were collected in 2 mL fractions.

Strontium and Molybdenum(VI) Ions

All the conditions were the same as in the separation of cesium and molybdenum.

Thallium(I) and Thorium Ions

A slurry of 0.5 g of Zr20MCM-41 in H^+ form was poured in a glass column with inner diameter of 8 mm. A 4.0 mL mixture containing 0.75 mL of thallium solution (0.005 M), 0.75 mL thorium solution (0.005 M) and demineralized water, was added to the column. Thallium was eluted with demineralized water while thorium was sorbed on the column and was

later eluted with 0.1 M HNO_3. The effluent with rate of 0.2 mL/min was collected in 2 mL fractions.

Cesium and Thorium Ions

All the conditions were same as in the separation of thallium and thorium, except that a slurry of 0.5 g Zr10MCM-41 in H^+ form was poured in a glass column. A 4.0 mL mixture of 0.5 mL of the cesium solution (0.005 M) and 1 mL of thorium solution (0.005 M) plus of demineralized water was added to the column.

Strontium and Thorium Ions

All the conditions were the same as in the separation of cesium and thorium.

RESULTS AND DISCUSSION

The properties of sorbents vary widely by changing the conditions of their preparation (16–18). The mode of preparation has a significant effect on the size and shape of the cavities inside the sorbent as given in Table 1. Five different samples of mesoporous zirconium silicate were prepared with various mole ratios of Si/Zr. The difference between added and found Si/Zr mole ratios may be due to the fact that less number of zirconium ions entered in the framwork of these compounds.

The ion-exchange capacity for H^+ ion recorded in Table 1 shows very low values. This may be due to the high affinity of anion of silicic acid (a weak acid) present in the pores of this sorbent, for the proton resisting its easy release. Therefore this sorbent behaves as a weak cation-exchanger.

XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) at a scan rate of 0.02° (2θ)/sec. The XRD patterns after the calcinations of synthesized zirconium silicate samples are presented in Fig. 1. The XRD patterns of samples show a strong diffraction at 2θ smaller than 3° along with presence of small peaks thus confirming the formation of the mesoporous materials (1,2).

Nitrogen sorption isotherms of the calcined samples were determined at 77 K and a specific surface area was determined by applying the BET equation to the isotherm (19). The pore size distribution was calculated using the adsorption branch of the isotherm and applying the Barrett-Joyner-Halenda (BJH) formula (20). The nitrogen sorption isotherms and corresponding pore size distribution of the

Table 1. Synthesis and properties of the mesoporous zirconium silicates

	Condition of preparation								
	Si/Zr mole ratio								
Sample	added	found	Gel, final pH	Ion-exchange Capacity (meq/g)	XRD d_{100} (Å)	unit cell parameter[a] (a_o) (Å)	pore volume (cc/g)	BET surface area (m^2/g)	Pore diameter (Å)
Zr10MCM-41	10	3.7	4.4	0.07	33.38	38.5	0.51	788	17.8
Zr20MCM-41	20	7.3	6.2	0.06	34.08	39.4	0.73	1019	17.8
Zr40MCM-41	40	13.7	7.1	0.05	34.89	40.3	0.86	1164	23.4
Zr80MCM-41	80	26.3	8.5	0.05	35.24	40.7	0.87	1088	17.9
Si-MCM-41	–	–	9.6	0.08	36.78	42.5	0.63	876	17.9

[a]Calculated from the equation $a_\circ = 2d_{100}/\sqrt{3}$.

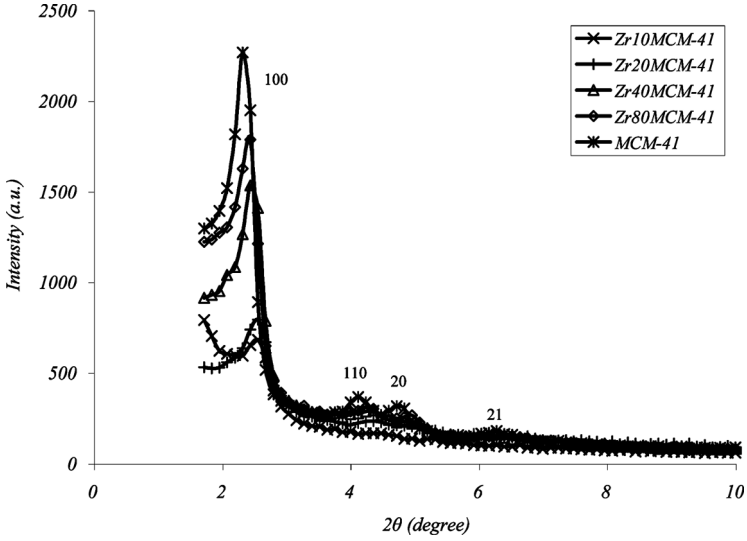

Figure 1. XRD patterns of the calcined mesoporous zirconium silicates.

synthesized zirconium silicates are given in Fig. 2. Table 1 shows the specific surface area, pore volume and pore diameter of all the samples. The nitrogen sorption isotherms show a typical IV-type adsorption profile consisting of a step condensation behavior due to the formation of mesopores.

The SEM image of mesoporous Zr10MCM-41 was taken using 2 minutes gold coat for high magnification and is shown in Fig. 3. The SEM image of mesoporous Zr10MCM-41 exhibits uniform spherical crystallites $\sim$0.4–0.8 μm in size.

Infrared spectra of these sorbents were measured by standard KBr disc technique. The FT-IR spectrum of Zr10MCM-41 sorbent recorded in Fig. 4 is closely similar to the mesoporous molecular sieves which also show a series of bands that are characteristics of the SiO_4 tetrahedral and its modification by introduction of metal ions (21–22). The spectrum shows five main absorption bands in the regions 3000–3700, 1055–1090, 960–970, 790–850, 440–465 cm^{-1}. The band in region 1055–1090 cm^{-1} is due to internal asymmetric stretching mode of SiO_4 (TO_4) skeleton, the strongest band in the spectra of silicates (23). The peak in region 960–970 cm^{-1} is generally considered as a proof for the incorporation of the heteroatom into the framework (24). Camblor et al. have proposed that the band at 960 cm^{-1} is due to the Si-O stretching vibrations of Si-OH groups present.

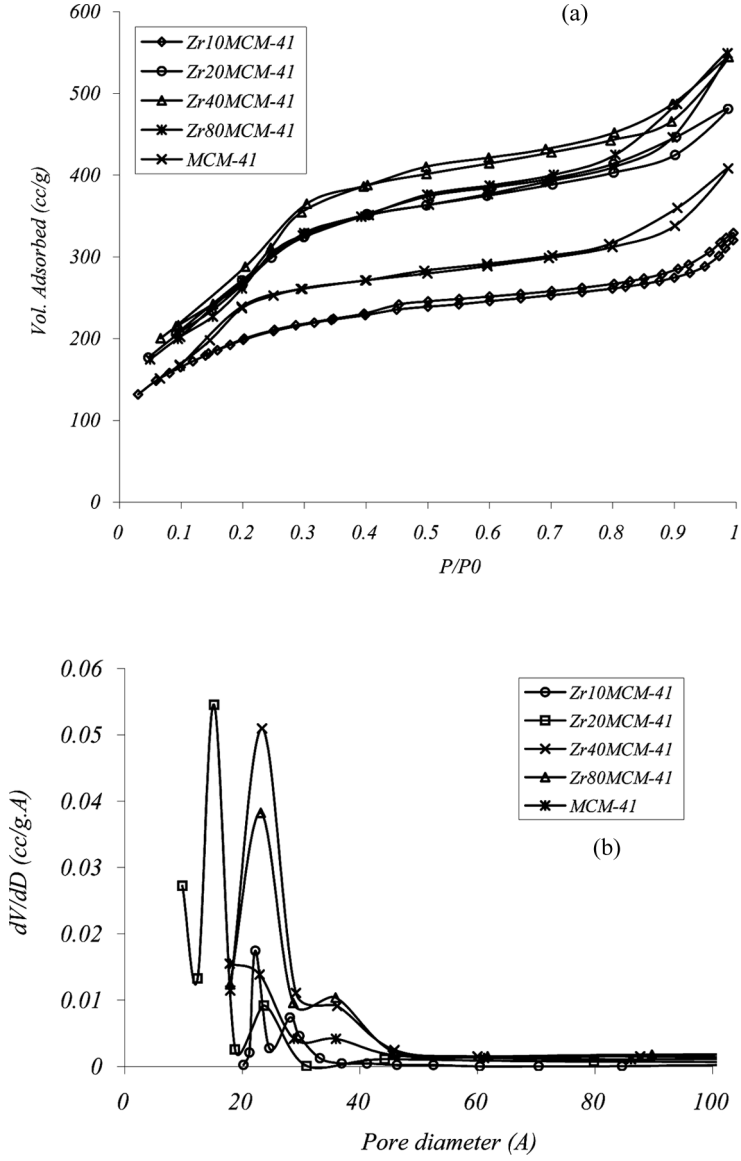

Figure 2. (a) Nitrogen adsorption/desorption isotherm and (b) Pore size distribution of the synthesized mesoporous zirconium silicates.

The thermogravimetric analysis of various sorbents was performed from ambient temperature to 900°C at a heating rate of 10°C/min. The thermograms of the sorbents are recorded in Fig. 5. The thermograms

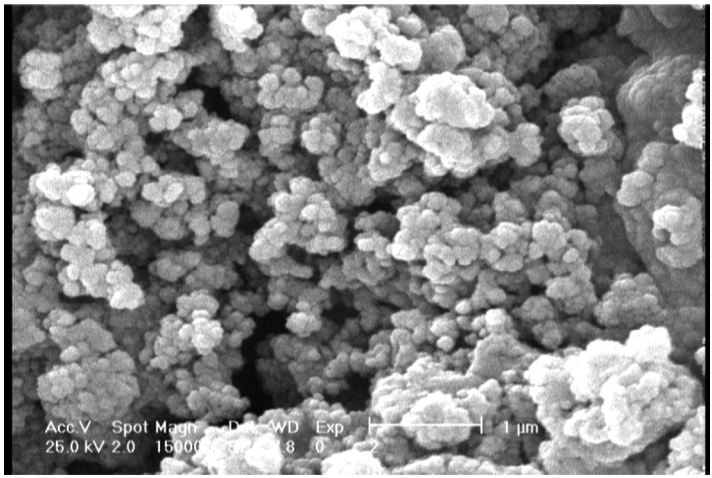

Figure 3. SEM image of Zr10MCM-41.

of the uncalcined samples show a gradual weight loss up to 900°C. The TGA curve of the samples show five steps of weight loss (35–130, 130–300, 300–380, 380–480, and 480–600°C). The weight loss is ~4.0% in the first step and is due to desorption of the physisorbed water held

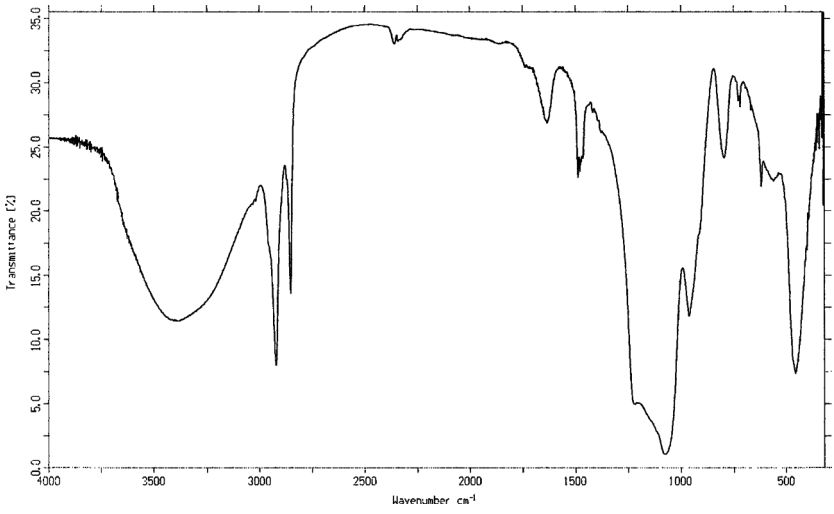

Figure 4. FT-IR spectrum of the Zr10MCM-41.

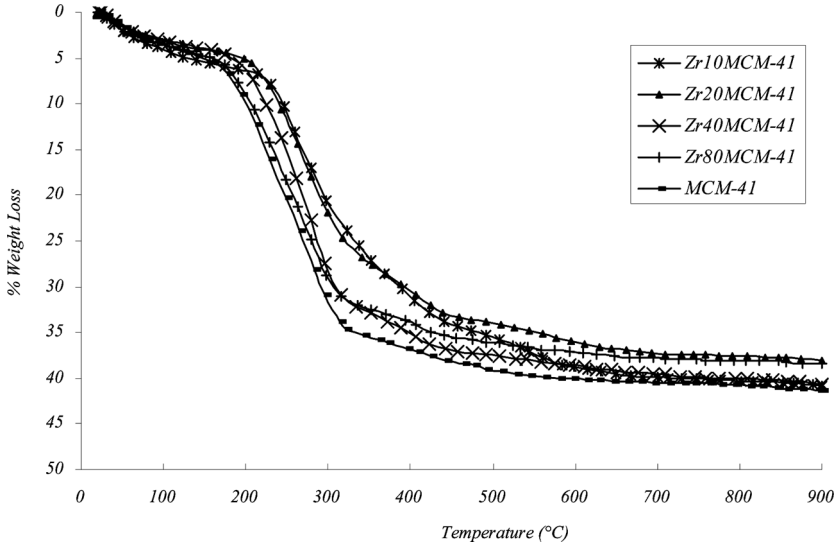

Figure 5. Thermograms of the synthesized mesoporous zirconium silicates (uncalcined).

in the pores. The weight losses in the second (~20.0%) and third (~7.0%) steps are mainly associated with oxidative decomposition of templates, in the fourth step, the weight loss (~7.0%) is due to removal of coke formed in the previous steps by the decomposition of templates. In the final step, the weight loss (~2.0%) is mainly due to water loss formed by the condensation of the silanol groups.

The chemical stability of mesoporous zirconium silicates (Table 2) show that all four samples are stable in water, dilute mineral acids. However, when heated in concentrated HCl, 4M HNO_3 and NaOH solutions, they gradually decompose. The distribution coefficients of the radionuclides on mesoporous zirconium silicates (Table 3) show that transition metal ions isomorphously substituted into the framework of mesoporous molecular sieve makes them more efficient sorbent for selective separations. The differences in the K_d values for different mesoporous zirconium silicates (with mole ratios 10, 20, 40, 80) may be due to the fact that their surface area, pore volume, and hydrophobic and hydrophilic character is modified by changing Si/Zr Zr mole ratios. On the basis of the results recorded in Table 2 it may be inferred that the mesoporous zirconium silicate behaves as a good sorbent, showing a high affinity for hard cations and also a weak uptake of soft cations, resulting in low K_d values for a number of

Table 2. Chemical stability of the synthesized mesoporous zirconium silicates

No.	Solvent	Zr10MCM-41		Zr20MCM-41		Zr40MCM-41		Zr80MCM-41	
		Zr released (mg/l)	Si released (mg/l)	Zr released (mg/l)	Si released (mg/l)	Zr released (mg/l)	Si released (mg/l)	Zr released (mg/l)	Si released (mg/l)
1	4 M HNO_3	23.48	8.62	42.61	10.15	20.73	8.80	9.49	9.89
2	2 M HNO_3	13.09	14.96	27.43	19.55	10.15	12.24	6.36	11.69
3	1 M HNO_3	5.72	17.20	12.21	19.93	4.34	15.84	2.20	12.15
4	4 M HCl	28.97	9.78	56.45	12.31	25.61	10.03	11.70	7.68
5	2 M HCl	15.60	16.76	27.09	17.31	12.78	14.90	7.49	12.00
6	1 M HCl	5.03	16.25	10.01	17.52	3.46	13.11	1.96	10.53
7	1 M NaOH	Dispersed	563	Dispersed	581	Dispersed	592	Dispersed	623
8	0.1 M NaOH	Dispersed	522	Dispersed	568	Dispersed	545	Dispersed	589
9	DMW	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 3. Distribution coefficients of radionuclides (and few ions) on mesoporous zirconium silicate: K_d value (mL/g) for different sorbents

		Samples				
Species	pH[a]	Si-MCM-41	Zr10MCM-41	Zr20MCM-41	Zr40MCM-41	Zr80MCM-41
$Ba(NO_3)_2$	6.5	257	277	139	63	98
$Cd(NO_3)_2$	1.3	256	25	24	73	102
$Ce(NO_3)_3$	5.0	166	31	56	96	81
$Co(NO_3)_2$	2.7	16	2.6	2.1	6.3	4.7
$Cr(NO_3)_3$	2.8	48	26	22	22	17
$CsNO_3$	6.3	32	N.A.	N.A.	10	32
$Cu(NO_3)_2$	3.0	473	123	32	105	199
$Hg(NO_3)_2$	1.2	N.A.	21	102	N.A.	12
$HfOCl_2$	1.2	$\geq 10^4$	$\geq 10^4$	$\geq 10^4$	$\geq 10^4$	1108
KCl	4.6	N.A.	N.A.	N.A.	N.A.	N.A.
NaCl	4.9	N.A.	N.A.	N.A.	N.A.	N.A.
$(NH_4)_6Mo_7O_{24}$	4.2	52	$\geq 10^4$	6325	364	92
$Pb(NO_3)_2$	2.7	37	40	23	25	30
$RbNO_3$	4.7	68	16	17	39	40
$Sr(NO_3)_2$	6.0	428	23	30	62	85
TeO_2	8.6	6.5	2944	1069	336	130
$Th(NO_3)_4$	3.7	$\geq 10^4$	$\geq 10^4$	$\geq 10^4$	$\geq 10^4$	$\geq 10^4$
$TlNO_3$	2.7	7.7	6.8	19	24	24
$UO_2(NO_3)_2$	4.4	3257	154	158	416	693
Na_2WO_4	5.6	7.7	6.8	19	24	24
$Zn(NO_3)_2$	3.0	211	16	21	101	103
$ZrOCl_2$	2.7	3711	671	732	372	209

N.A. = Negligible adsorption.
[a]pH of the tracer solution.

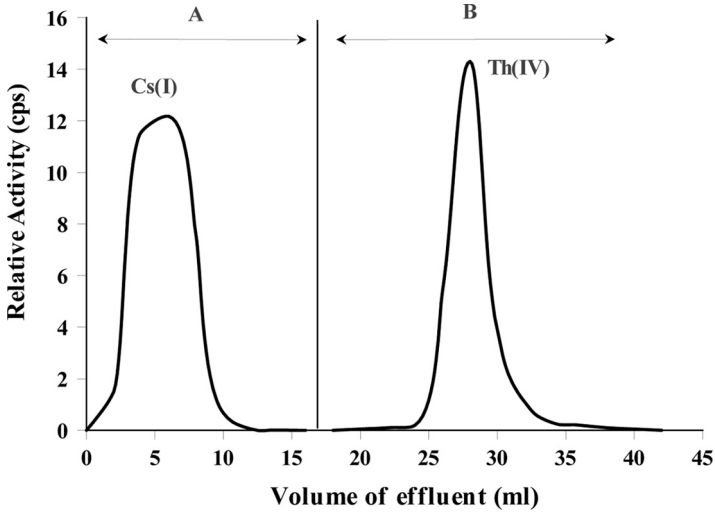

Figure 6. Elution curve of separation of Cs(I)-Th(IV). (a) Demineralized water, (b) 0.1 M HNO_3, Flow rate 0.2 mL/min.

elements. The utility of these sorbents have been demonstrated by achieving separations of great analytical significance. For example Th(IV) was separated from Cs(I), Sr(II) and Tl(I) (Figs. 6–8). Here Th(IV) is highly adsorbed on the column at acidic pH (Table 3) due to hard-hard interaction with Si-OH groups presentin the pores, while

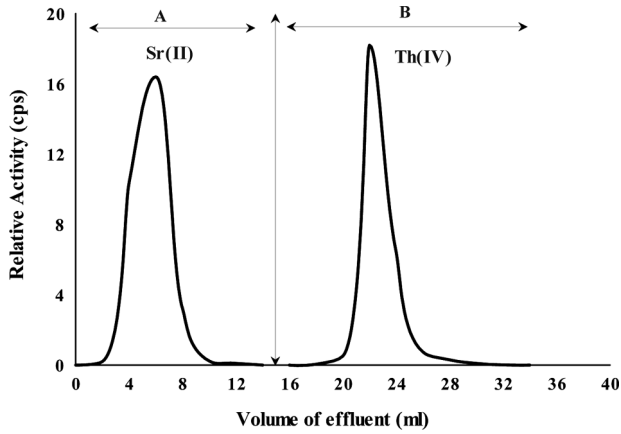

Figure 7. Elution curve of separation of Sr(II)-Th(IV). (a) Demineralized water, (b) 0.1 M HNO_3, Flow rate 0.2 mL/min.

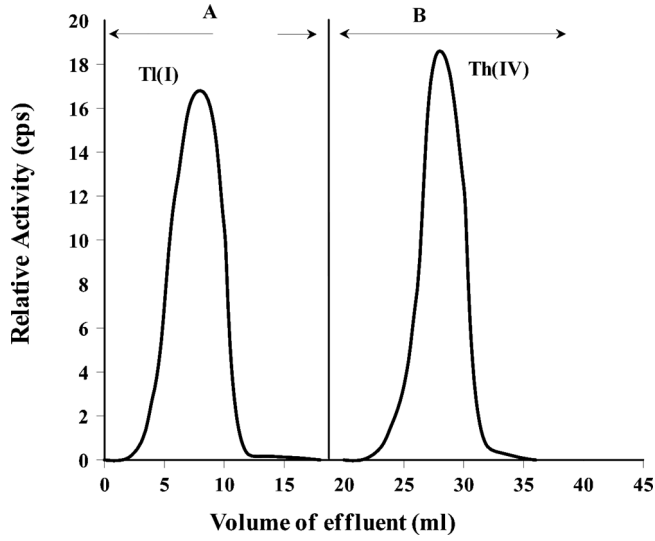

Figure 8. Elution curve of separation of Tl(I)-Th(IV). (a) Demineralized water, (b) 0.1 M HNO_3, Flow rate 0.2 mL/min.

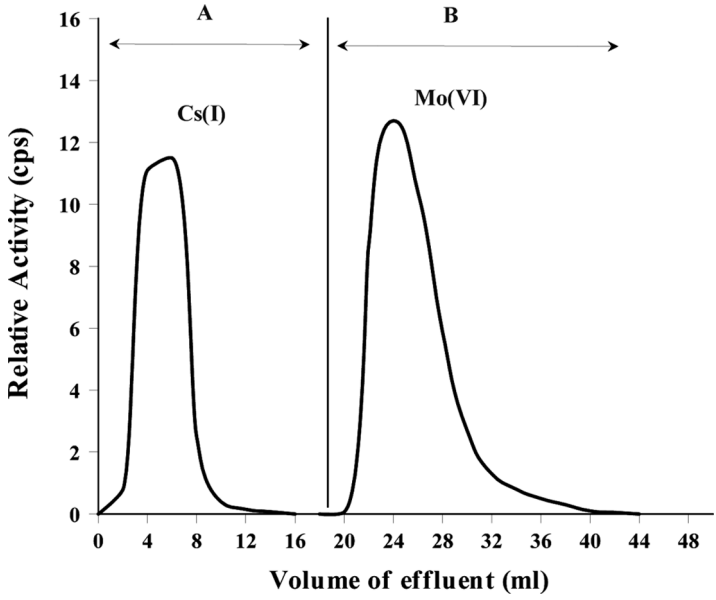

Figure 9. Elution curve of separation of Cs(I)-Mo(VI). (a) Demineralized water, (b) 0.05 M NaOH, Flow rate 0.2 mL/min.

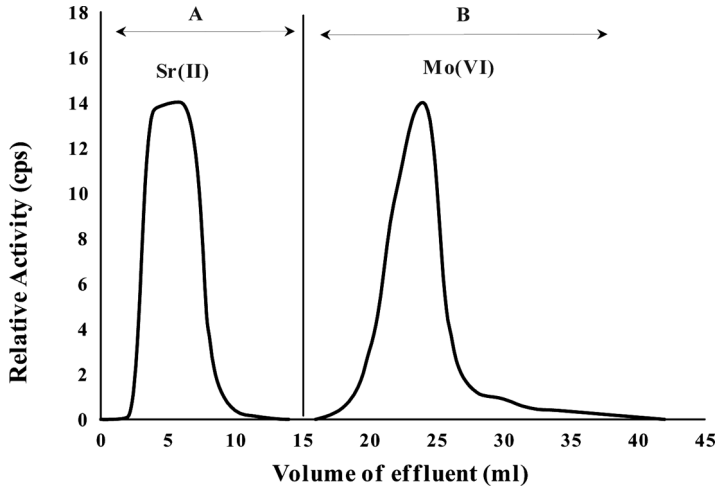

Figure 10. Elution curve of separation of Sr(II)-Mo(VI). (a) Demineralized water, (b) 0.05 M NaOH, Flow rate 0.2 mL/min.

Cs(I), Sr(II) and Tl(I) are passed through the column due to negligible K_d values. Later, by using an 0.1 M HNO_3 solution, Th(IV) is eluted from the columns. Similarly Mo(VI) was separated from Cs(I) and Sr(II) with simple eluents (Figs. 9 and 10).

In addition to the nature of the sorbent, various factors such as swelling, nature of the chemical bond, and solvent distribution may be responsible for the wide variation in the K_d values (17), which has provided new possibilities for the development of fast and selective methods of separation of radionuclides using mesoporous zirconium silicate as a new sorbent.

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REFERENCES

1. Kresge, C.T.; Leonowics, M.E.; Roth, W.J.; Vartuli, J.C.; Beck, J.S. (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*, *359*: 710.

2. Beck, J.S.; Vartuli, J.C.; Roth, W.J.; Leonowics, 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. (1992) A new family of mesoporos molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.*, *114*: 10834.
3. Liu, A.M.; Hidajat, K.; Kawi, S.; Zhao, D.Y. (2000). A new class of hybrid mesoporous materials with functionalized organic monolayers for selective adsorption of heavy metal ions. *Chem. Commun.*, *13*: 1145.
4. Olkhovyk, O.; Antochshuk, V.; Jaroniec, M. (2004) Benzoylthiourea-modified MCM-48 mesoporous silica for mercury(II) adsorption from aqueous solutions. *Colloids Surf. A: Physicochem. Eng. Aspects*, *236*: 69.
5. Yang, Q.; Liu, J.; Yang, J.; Zhang, L.; Feng, Z.; Zhang, J.; Li, C. (2005) Acid catalyzed synthesis of ordered bifunctionalized mesoporous organosilicas with large pore. *Micropor. Mesopor. Mater.*, *77* (2–3): 257.
6. Anbia, M.; Rofouei, M.K.; Husain, S.W. (2006) Synthesis of mesoporous lanthanum phosphate and its use as a novel sorbent. *Chin. J. Chem.*, *24*: 1026.
7. Lin, Y.; Fryxell, G.E.; Wu, H.; Engelhard, M. (2001) Selective sorption of cesium using self-assembled monolayers on mesoporous supports. *Environ. Sci. Technol.*, *35*: 3962.
8. Trens, P.; Russell, M.L.; Spjuth, L.; Hudson, M.J.; Liljenzin, J. (2002) Preparation of malonamide-MCM-41 materials for heterogeneous extraction of radionuclides. *Ind. Eng. Chem. Res.*, *41*: 5220.
9. Addleman, R.S.; Egorou, O.B.; O'Hara, M.J.; Busche, B.; Zemanian, T.S.; Fryxell, G.E. (2005) Preconcentration and assay of radionuclides with self assembled monolayers on mesoporous supports. *J. Radioanal. Nucl. Chem.*, *263* (1): 59.
10. Wellman, D.M.; Mattigod, S.V.; Parker, K.E.; Heald, S.M.; Wang, C.; Fryxell, G.E. (2006) Synthesis of organically templated nanoporous tin(II/IV) phosphate for radionuclide and metal sequestration. *Inorg. Chem.*, *45*, 2382.
11. Hudson, M.J.; Husain, S.W.; Anbia, M. (2005) Development of New Sorbents: I. Ordered Porous Phase of Titanium Phosphate. *J. Ir. Chem. Soc.*, *2* (1): 54.
12. Li, X.S.; Courtney, A.R.; Yantasee, W.; Mattigod, S.V.; Fryxell, G.E. (2006) Templated synthesis of mesoporous titanium phosphates for the sequestration of radionuclides. *Inorg. Chem. Commun.*, *9*: 293.
13. Anbia, M.; Rofouei, M.K.; Husain, S.W. (2005) Development of new adsorbents: II. sorption of toxic metals on mesoporous lanthanum silicate. *Or. J. Chem.*, *21*: 199.
14. Qureshi, M.; Husain, S.W. (1970) Synthesis of thorium molybdate and its use for the quantitative separation of iron(III) from zinc(II), cobalt(II), and copper(II). *J. Chem. Soc. A*, 1204.
15. Siddiqi, Z.M.; Pathania, D. (2003) Titanium(IV) tungstosilicate and titanium (IV) tungstophosphate: Two new inorganic ion exchangers. *J. Chromatogr. A*, *987* (1–2): 147.

16. Husain, S.W.; Rasheedzad, S.; Manzoori, J.L.; Jabbari, Y. (1982) Synthesis and ion exchange properties of lanthanum tungstate, A new inorganic ion exchanger. *Sep. Sci. Technol.*, *17* (7): 935.
17. Husain, S.W.; Ghannadi Marageh, M.; Rasheedzad, S. (1984) Synthesis and ion exchange properties of cerium(IV) selenite. *J. Radioanal. Nucl. Chem.*, *84* (2): 239.
18. Srivastava, S.K.; Singh, R.P.; Agrawal, S.; Kumar, S. (1977) Synthesis and ion-exchange properties of cerium(IV) molybdate. *J. Radioanal. Nucl. Chem.*, *40*: 7.
19. Brunauer, S.; Emmett, P.H.; Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.*, *60*: 309.
20. Barrett, E.P.; Joyner, L.G.; Halenda, P.P. (1951) The determination of pore volume and area distributions in porous substances. I. computations from nitrogen isotherms. *J. Am. Chem. Soc.*, *73* (1): 373.
21. Flanigen, E.M. (1976) *Intrazeolite Chemistry and Catalyst*, Pabo, J.A., eds.; AS Monograph Series 171; American Chem. Soc.; Washington, DC.
22. Chen, X.; Huang, L.; Ding, G.; Li, Q. (1997) Characterization and catalytic performance of mesoporous molecular sieves Al-MCM-41 materials. *Catal. Lett.*, *44*: 123.
23. Chen, C.-Y.; Burkett, S.L.; Li, H-X.; Davis, M.E. (1993) Studies on mesoporous materials II. Synthesis mechanism of MCM-41. *Microporous Mater.*, *2*: 27.
24. Camblor, M.A.; Corma, A.; Perez-Pariente, J. (1993) Infrared spectroscopic investigation of titanium in zeolites. A new assignment of the 960 cm^{-1} band. *J. Chem. Soc. Chem. Commun.*, 557.