



# Adsorption Studies of Heavy Metal Ions on Mesoporous Aluminosilicate, Novel Cation Exchanger

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## ABSTRACT

Mesoporous aluminosilicates, have been prepared with various mole ratios of Si/Al and Cethyltrimethylammonium bromide (CTAB). They have been characterized by XRD, nitrogen adsorption/desorption measurements, FT-IR and thermogravimetry. Adsorption behavior of heavy metal ions on this adsorbent have been studied and discussed. The results show that incorporation of aluminum ions in the framework of the mesoporous MCM-41 has transformed it into an effective cation exchanger. The  $K_d$  values of several metal ions have been increased. Separation of Sr(II)–Ce(III), Sr(II)–U(VI) and Cd(II)–Ce(III) has been developed on columns of this novel mesoporous cation exchanger.

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## 1. Introduction

Zeolites (aluminosilicates) are crystalline microporous silica based solids, which are used extensively in adsorption and catalytic processes. The main limitation of microporous zeolitic materials is their low surface area and pore size (<20 Å) and therefore their adsorption capacity is also low. Hence, there has been an ever-growing interest in enhancing the pore size of the zeolitic materials from micropore to mesopore range. Mesoporous materials have been found useful in separation science, due to their high surface area and selective behavior towards some elements [1,2]. Incorporation of certain elements such as Ce, Sn and Zr into the framework of mesoporous molecular sieves has transformed them into more effective adsorbents [3–5]. Many synthesized mesoporous aluminosilicate have been used as catalyst in organic reactions [6–13], but only few studies have been reported on their use as adsorbents [14]. We report here the synthesis and characterization of mesoporous aluminosilicate with different mole ratio of Si/Al. Adsorption behavior of radionuclides and toxic metal ions on this adsorbent has been studied and discussed. Separation of Sr(II)–Ce(III), Sr(II)–U(VI) and Cd(II)–Ce(III) has been developed on columns of this novel adsorbent.

## 2. Experimental

### 2.1. Reagents

All the chemicals used were of analytical grade from Merck, except Cethyltrimethylammonium bromide (CTAB) which was supplied by Aldrich (U.K.).

### 2.2. Apparatus

A Philips X'pert powder diffractometer system with Cu-K $\alpha$  ( $\lambda = 1.541 \text{ \AA}$ ) radiation was used for X-ray studies. XRD analysis was performed from  $1.5^\circ$  to  $10.0^\circ$  ( $2\theta$ ) at a scan rate of  $0.02^\circ$  ( $2\theta$ )  $s^{-1}$ . Nitrogen adsorption studies were made with a Quantachrome NOVA 2200e instrument. Nitrogen adsorption/desorption isotherms of the adsorbents were determined at 77 K and specific surface area by applying the BET equation to the isotherm [15]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [16]. FT-IR spectra were recorded using a Bruker FT-IR spectrophotometer of model Vector-22 by a standard KBr disc technique. Thermogravimetric analysis was performed on a Rheometric Scientific model STA-1500 instrument. The thermogravimetric analysis of various samples was performed from ambient temperature to  $900^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . Quantitative determinations of inorganic ions were carried out

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using an inductively coupled plasma–optical emission spectroscope (ICP–OES) of Varian Turbo Model 150–Axial Liberty. A waterbath shaker of model CH–4311 (Infors AG) was used in determination of distribution coefficients.

### 2.3. Preparation of mesoporous aluminosilicates

Four different samples of mesoporous aluminosilicate were prepared by mixing sodium silicate as silicon source, aluminum nitrate as aluminum source. In a typical synthesis, 0.6 g CTAB was dissolved in 23 g of demineralized water, the mixture 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 of mixture was adjusted to 9 by adding sulphuric acid (2 M). Then for preparing four materials with different ratios of Si/Al solutions of  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  containing 0.45, 0.22, 0.11 and 0.06 g in 50 mL demineralized water for mole ratios 10, 20, 40 and 80 respectively were added dropwise to obtain the particular material. The stirring was continued for 4 h. A bulky white gelatinous precipitate was formed. The resulting gel was transferred to a Teflon vessel and was left for 24 h at room temperature. Then the product was filtered, washed thoroughly with demineralized water and then dried at 50 °C for 12 h. A small portion of this material was calcined at 540 °C for 6 h. The material was digested in 0.1 M  $\text{HNO}_3$  for 24 h and then washed demineralized water.

The samples prepared were labeled as follows:  $\text{Al}_x\text{MCM-41}$  where  $x$  indicated the Si/Al molar ratio and MCM-41 (Mobile crystalline Material) indicated hexagonal ordered mesoporous silicate. In order to study the effect of addition of aluminum in these types of materials, a sample only with silica in the framework was also prepared under the same conditions and it was marked as Si–MCM-41.

### 2.4. Composition

A 250 mg (dry mass) amount of sorbet samples was dissolved in 10 mL hot 4 M NaOH. The solution was cooled and diluted. The amounts of aluminum and silicon were determined by ICP technique.

### 2.5. Distribution coefficients

The batch equilibrium method was used to determine the distribution coefficient as follows:

$$K_d = \left[ \frac{A - B}{B} \right] \times \frac{V}{m}$$

where  $A$  and  $B$  are the initial and final concentration ( $\text{mg L}^{-1}$ ) of solution,  $V$  is the volume of initial solution in mL, and  $m$  is the mass of the adsorbent in grams. A weighed amount of the adsorbent (200 mg) was shaken for 5 h at  $25 \pm 1$  °C in a polyethylene bottle containing 20 mL of the metal ion solution of  $1.2 \times 10^{-4}$  M. The concentrations ( $\text{mg L}^{-1}$ ) of the solution before and after equilibration

were measured by ICP technique. Standard deviation of  $K_d$  values were checked by five determinations and were <10%.

## 2.6. Separation of metal ions

### 2.6.1. Cadmium and cerium ions

A slurry of 0.5 g of Al80MCM-41 in  $\text{H}^+$  form was poured in a glass column with length 20 mm and inner diameter 8 mm. A mixture of 0.5 mL of the cadmium (0.005 M) and 0.25 mL of cerium (0.005 M) in 3.25 mL of the demineralized water was added to the column. The cadmium was eluted by demineralized water through the column. The cerium was sorbed on the column and cadmium passed into the effluent. The cerium was later eluted with 0.1 M  $\text{HNO}_3$ . The flow rate of effluents was maintained at  $0.2 \text{ mL min}^{-1}$  using a peristaltic pump until the metal ions were completely eluted from the column and the effluents were collected in 3 mL fractions.

### 2.6.2. Strontium and cerium ions

All the conditions were same as in the separation of cadmium and cerium ions.

### 2.6.3. Strontium and uranium ions

All the conditions were same as in the separation of cadmium and cerium ions.

## 3. Results and discussion

The mode of preparation has a significant effect on the size and shape of the cavities, pore volume and surface area of the adsorbent as given in Table 1. Four different samples of modified mesoporous aluminosilicate were prepared with various mole ratios of Si/Al. CTAB is used as the structure directing agent in the formation of supramolecular assembly of surfactant molecules rather than the conventional single molecule-templated structures [17]. In the liquid crystal templating (LCT) mechanism, Beck et al. [18] have proposed that silicate condensation is not the dominant factor in the formation of the structure. The structure is defined by organization of the surfactant molecules into micellar liquid crystals which serve as templates for the formation of the MCM-41 structure [18]. The structure of mesoporous materials can be altered by varying the surfactant/ $\text{SiO}_2$  mole ratio. For formation the mesoporous MCM-41, surfactant/ $\text{SiO}_2$  mole ratio should be <1.0 [18]. In this work, the surfactant/ $\text{SiO}_2$  mole ratio was 0.12.

The XRD patterns of the synthesized mesoporous aluminosilicates are presented in Fig. 1. All samples produce relatively well-defined XRD patterns, with one major peak along with two small peaks identical to those of MCM-41 materials [18,19]. The nitrogen adsorption–desorption isotherms and corresponding pore size distribution of the mesoporous aluminosilicates are given in Fig. 2. The nitrogen adsorption–desorption isotherms show a typical IV-type adsorption profile consisting of a step condensation behavior due to the formation of mesopores. Table 1 shows the specific surface area,

**Table 1**  
Synthesis and properties of mesoporous aluminosilicates.

Sample	Condition of synthesis		XRD $d_{100}$ (Å)	Unit cell parameter <sup>a</sup> ( $a_0$ ) (Å)	Pore volume ( $\text{cc} \cdot \text{g}^{-1}$ )	BET surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Pore diameter (Å)	
	Si/Al mole ratio							
	Added	Found						
Al10MCM-41	10	16.4	5.6	38.3	42.3	0.73	792	24.4
Al20MCM-41	20	19.7	6.7	35.7	41.3	0.67	834	21.8
Al40MCM-41	40	32.0	7.2	34.8	40.2	0.73	913	24.4
Al80MCM-41	80	37.2	7.8	32.8	37.9	0.79	1006	21.7
Si–MCM-41	–	–	9.6	31.8	31.8	0.74	1120	21.7

<sup>a</sup> Calculated from the equation  $a_0 = 2d_{100}/\sqrt{3}$ .

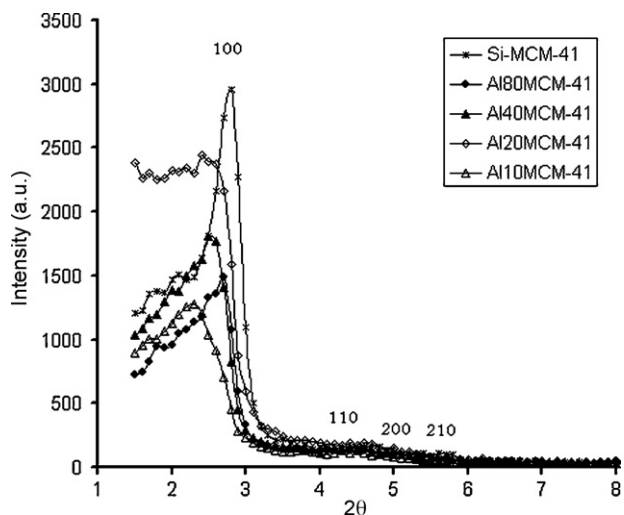


Fig. 1. XRD patterns of the synthesized mesoporous aluminosilicates.

pore volume and pore diameter of the unmodified and modified adsorbents.

The FT-IR spectra of the samples recorded in Fig. 3 ( $400\text{--}1300\text{ cm}^{-1}$ ) is similar to vibrations of the framework structure of zeolites [20]. The peak in region  $960\text{--}970\text{ cm}^{-1}$  is generally considered as a proof for the incorporation of the heteroatom into the framework [21].

The thermogram of the uncalcined Al80MCM-41 sample recorded in Fig. 4 shows three steps of weight loss up to  $900^\circ\text{C}$ . The steps can be distinguished as  $35\text{--}150$ ,  $150\text{--}300$ ,  $300\text{--}550^\circ\text{C}$ . The weight loss is  $\sim 7.0\%$  in the first step and is due to desorption of physisorbed water held in the pores. The weight loss during the second step ( $\sim 28.0\%$ ) is mainly associated with oxidative decomposition of templates. In the last step, the weight loss ( $\sim 5.0\%$ ) is mainly due to the condensation of silanol groups. The thermograms of the other samples are similar to the Al80MCM-41 sample.

The distribution coefficients of the metal ions on this adsorbent (Table 2) show good affinity of this material for a number of ions such as Ce(III), Cr(III), Fe(III), Te(IV), Tl(I), La(III), U(VI) and Th(IV) in water. On the basis of the results recorded in Table 2 it may be inferred that the mesoporous aluminosilicate behaves as a suitable adsorbent for a number of ions (Al10MCM-41 for Fe(III), Th(IV), Tl(I), La(III), U(VI) and Zr(IV), Al20MCM-41 for Th(IV) and U(VI),

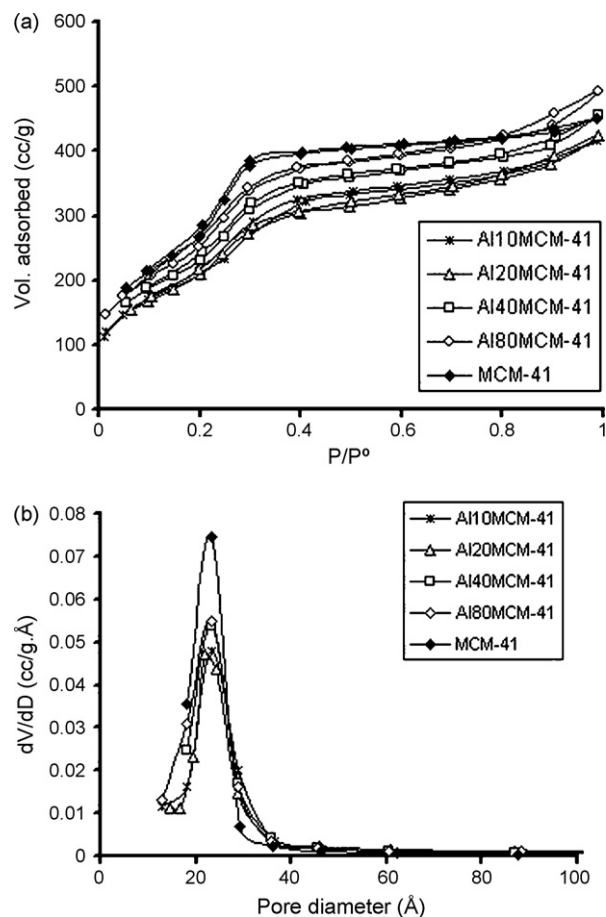


Fig. 2. (a) Nitrogen adsorption/desorption isotherm and (b) Pore size distribution of the synthesized mesoporous aluminosilicates.

Al40MCM-41 for Ce(III) and Te(IV), Al80MCM-41 for Ce(III), Cr(III), Te(IV) and Tl(I)). The  $K_d$  values for the many metal ions have been increased after incorporation of Al ions in the framework of the mesoporous MCM-41. It may be due to the fact that, in mesoporous aluminosilicate, the framework exhibits negative charges as a consequence of the incorporation of trivalent aluminum atoms instead of tetravalent silicon. Therefore mesoporous aluminosilicate can act as an inorganic cation exchanger. On the other hand, the meso-

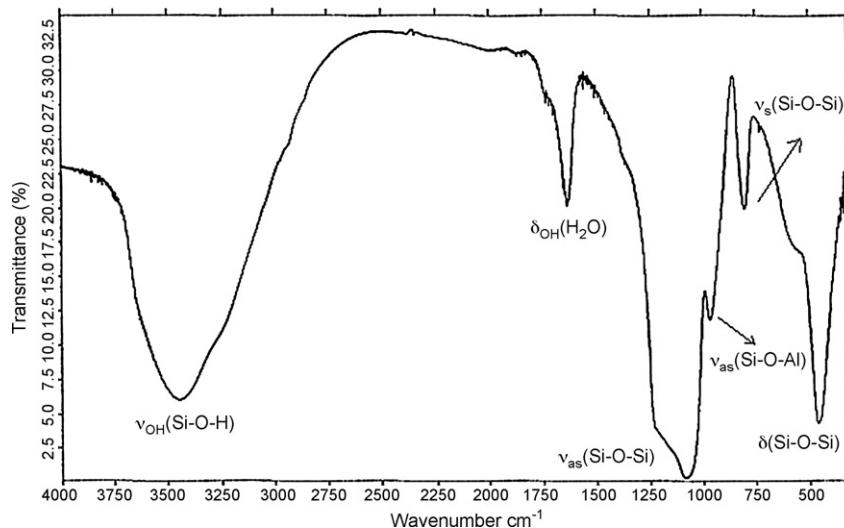


Fig. 3. FT-IR spectrum of the Al80MCM-41 sample.

**Table 2**  
Distribution coefficients of radionuclides and metal ions on mesoporous aluminosilicate:  $K_d$  value (mL/g) for different samples.

Compounds	pH <sup>a</sup>	Samples				
		Si-MCM-41	Al10MCM-41	Al20MCM-41	Al40MCM-41	Al80MCM-41
Ba(NO <sub>3</sub> ) <sub>2</sub>	5.8	94	1023	1484	564	337
Cd(NO <sub>3</sub> ) <sub>2</sub>	5.5	38	1260	1093	8	7
Ce(NO <sub>3</sub> ) <sub>3</sub>	5.7	35	4503	3574	>10 <sup>4</sup>	>10 <sup>4</sup>
Co(NO <sub>3</sub> ) <sub>2</sub>	5.6	23	773	843	401	203
Cr(NO <sub>3</sub> ) <sub>3</sub>	2.5	13	1151	282	2829	>10 <sup>4</sup>
(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5.5	5	16	11	576	107
CsNO <sub>3</sub>	2.0	8	401	71	1120	227
Cu(NO <sub>3</sub> ) <sub>2</sub>	5.6	504	839	842	940	263
Fe(NO <sub>3</sub> ) <sub>3</sub>	4.0	4762	>10 <sup>4</sup>	2712	150	73
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	1.9	413	185	264	2154	508
Pb(NO <sub>3</sub> ) <sub>2</sub>	4.6	1301	381	763	50	26
RbNO <sub>3</sub>	4.9	19	1059	467	564	337
Sr(NO <sub>3</sub> ) <sub>2</sub>	6.0	27	1474	1159	8	7
TeO <sub>2</sub>	1.9	18	38	16	>10 <sup>4</sup>	>10 <sup>4</sup>
Th(NO <sub>3</sub> ) <sub>4</sub>	2.4	2048	>10 <sup>4</sup>	>10 <sup>4</sup>	401	203
TiNO <sub>3</sub>	5.3	44	>10 <sup>4</sup>	7758	2829	>10 <sup>4</sup>
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	4.0	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	576	107
Ni(NO <sub>3</sub> ) <sub>2</sub>	5.5	35	1139	980	1120	227
La(NO <sub>3</sub> ) <sub>3</sub>	5.4	20	>10 <sup>4</sup>	3800	940	263
YCl <sub>3</sub>	5.8	25	2920	1754	7	6
Na <sub>2</sub> WO <sub>4</sub>	4.9	10	28	N.A.	150	73
Zn(NO <sub>3</sub> ) <sub>2</sub>	5.5	16	298	420	2154	508
ZrOCl <sub>2</sub>	4.5	>10 <sup>4</sup>	>10 <sup>4</sup>	3281	50	26
Sm(NO <sub>3</sub> ) <sub>3</sub>	2.2	2	123	99	564	337

N.A. = Negligible adsorption.  
<sup>a</sup> Equilibrium pH.

**Table 3**  
Comparison of distribution coefficients ( $K_d$ ) of some metal ions on modified mesoporous aluminosilicates with that on other mesoporous adsorbents [3–5].

Sample	Metal ions									
	Cr(III)	Ce(III)	Fe(III)	Th (IV)	La(III)	Ti(I)	Y(III)	Te(IV)	Ni(II)	Cd(II)
Si-MCM-41	13	35	4762	2048	20	44	25	18	35	38
Mesoporous zirconium silicate	22	96	–	>10 <sup>4</sup>	–	24	–	2944	–	102
Mesoporous cerium (IV) silicate	36	180	–	>10 <sup>4</sup>	–	6	–	>10 <sup>4</sup>	–	77
Mesoporous Sn(IV) silicate	159	530	–	>10 <sup>4</sup>	–	62	–	132	–	340
Modified mesoporous aluminosilicates	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	2920	>10 <sup>4</sup>	1139	1260

porous aluminosilicate 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 elements. It may be explained by the characterization of hard-soft acid–base.

The comparison of distribution coefficients of radionuclides and metal ions on modified mesoporous aluminosilicate with other modified mesoporous adsorbents reported [3–5] (Table 3) shows the high sorption of Ce(III), Cr(III), Fe(III), Te(IV), Ti(I), La(III) and Th(IV) on modified mesoporous aluminosilicates, therefore this

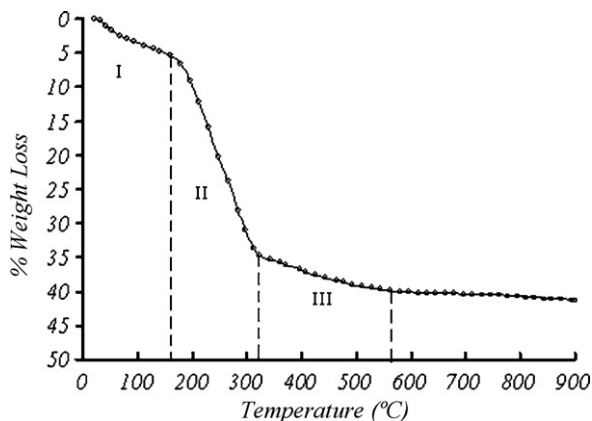


Fig. 4. Thermogram of the Al80MCM-41 sample.

modified adsorbent can be used for their removal from aqueous systems.

The utility of this adsorbent has been demonstrated by achieving separations of great analytical significance. For example Sr(II) was separated from Ce(III) and U(VI) (Figs. 5 and 6). Here Ce(III) and

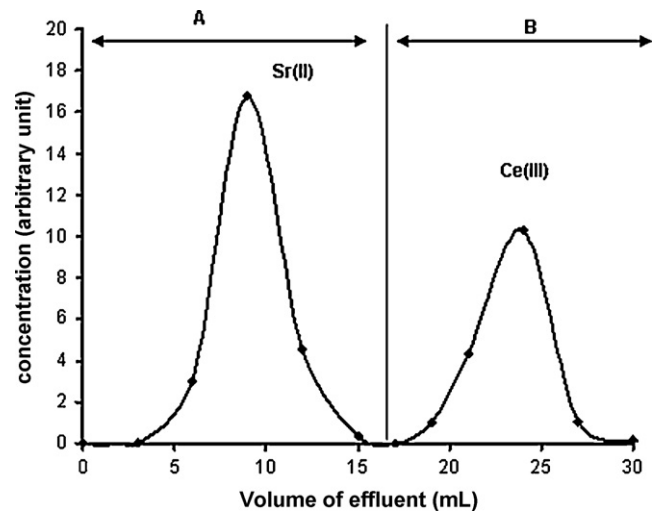


Fig. 5. Elution curve of separation of Sr(II)–Ce(III). (a) Demineralized water, (b) 0.1 M HNO<sub>3</sub>, Flow rate 0.2 mL min<sup>-1</sup>.

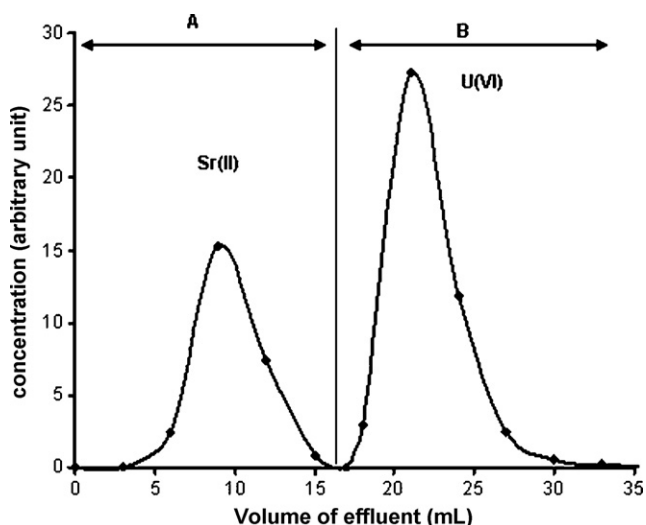


Fig. 6. Elution curve of separation of Sr(II)–U(VI). (a) Demineralized water, (b) 0.1 M HNO<sub>3</sub>, Flow rate 0.2 mL min<sup>-1</sup>.

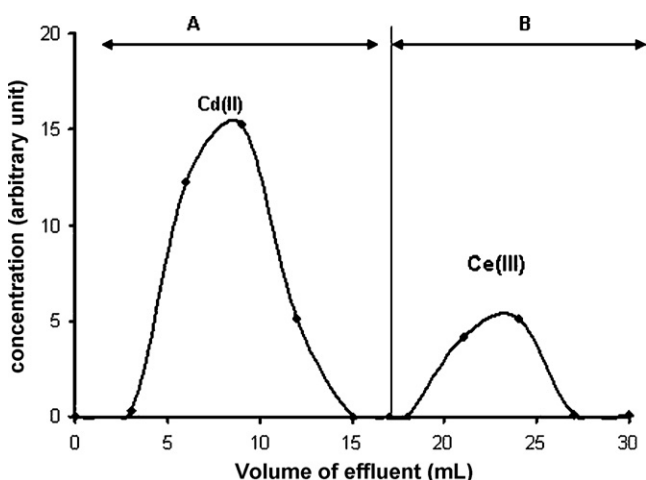


Fig. 7. Elution curve of separation of Cd(II)–Ce(III). (a) Demineralized water, (b) 0.1 M HNO<sub>3</sub>, Flow rate 0.2 mL min<sup>-1</sup>.

U(VI) are highly adsorbed on the column at acidic pH (Table 2) due to their hard–hard interaction with Si–OH groups present in the pores, while Sr(II) is passed through the column due to low  $K_d$  value. Later, by using 0.1 M nitric acid solution, Ce(III) and U(VI) are eluted from the columns. Similarly the separation of Cd(II)–Ce(III) has been performed with simple eluents (Fig. 7).

#### 4. Conclusions

Modified mesoporous aluminosilicates (with Si/Al mole ratios of 10, 20, 40 and 80) with high thermal stability and high surface area and pore volumes have been synthesized. The results show that mesoporous aluminosilicate behaves as a good adsorbent for elements, such as Ce(III), Cr(III), Fe(III), Te(IV), Ti(I), La(III), U(VI), Th(IV) and Zr(IV). The prepared materials show high potential to

be used as new promising adsorbent in removal of heavy metal ions from wastewaters.

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