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Modified Mesoporous Cerium(III) Silicate: Synthesis, Characterization and Adsorption Studies of Heavy Metal Ions

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ABSTRACT

Modified mesoporous cerium(III) silicates, have been prepared with various mole ratios of Si/Ce (10, 20, 40, 80) by using cetyltrimethylammonium bromide (CTAB) as template and characterized by powder X-ray diffraction, N_2 adsorption-desorption measurment, SEM, FT-IR, thermogravimetry to confirm the mesoporous structure. Sorption behavior for 23 metal ions on this adsorbenthave been studied and discussed. Separation of Rb(I)–U(VI), Tl(I)–U(VI) and Co(II)–U(VI) have been developed on columns of this adsorbent.

Key words: Mesoporous, Cerium(III) Silicate, Adsorption Studies, Heavy Metal Ions.

INTRODUCTION

Indastrial activites such as electroplating, mining, metal processing, dyeing and textile produce wastewater contaminated with heavy metals[1]. The discharge of these untreated wastewater into natural water dodies cause serious environmental problems because metals tend to accumulate in living tissues throughout the food chain[2]. Synthesis of mesoporous adsorbents is accomplished using the methodology developed by scientists at Mobil Oil Research and Development[3]. Many new mesoporous materials have been developed and successfully used in removal of heavy metal ions and radionuclides from aqueous media[4-7]. The modification of the mesoporous materials by various functional groups has received much attention to adsorption and separation science[7-10]. The modification of MCM-41 by organic modifier is an expensive method, but modification by inorganic metal ions is a rapid, simple and inexpensive method. Transition metal ions isomorphously substituted into the framework of mesoporous molecular sieves make them more efficient catalysts for selective oxidations and as potential adsorbents for selective separations. Most of these modified mesoporous silicates were used as efficient catalysts for organic reactions, but inconsiderable studies have been reported for their use as adsorbents[12-14]. In our recent works, we reported the synthesis of modified MCM-41 by incorporation Ce(IV), Sn(IV) and Zr(IV) ions and their applications for removal of radionuclides from hazardous wastes[15-17]. Amorphous cerium(III) silicate as an ion-exchanger has been synthesized and its adsorption behavior for radionuclides has been studied[18]. In this paper, we report the synthesis and characterization of modified mesoporous cerium (III) silicates with different mole ratios of Ce/Si. Adsorption behavior of 23 metal ions and some radionuclides on these materials have been studied. Separation of Rb(I)–U(VI), Tl(I)–U(VI) and Co(II)–U(VI) have been developed on columns of this adsorbent.

EXPERIMENTAL

Materials and methods

All the chemicals used were of analytical grade (E. Merck or Fluka) except cetyltrimethylammonium bromide (CTAB) which was supplied by Aldrich (U.K.).

A Philips X'pert powder diffractometer system with Cu-Ka (l=1.541 Å) radiation was used for X-ray studies.XRD analysis was performed from 1.5(2è) to 10.0(2è) at a scan rate of 0.02(2è)/Sec. The Nitrogen adsorption-desorption studies were made with a Quantachrome NOVA 2200e instrument. Nitrogen adsorption isotherms of the adsorbents were determined at 77 K and the specific surface area by applying the BET equation to the isotherm[19]. The pore size distributions were calculated using the adsorption branch of the isotherms and the Barrett-Joyner-Halenda (BJH) formula[20]. The scanning electron micrographic image was recorded by using a LEO1455VP microscope. FT-IR was done using a Bruker FT-IR spectrophotometer 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 800 ºC at a heating rate of 10 ºC/min. pH measurements were made with a Schott CG841 pH-meter (Germany). Quantitative determinations of inorganic ions were carried out using an inductively coupled plasma (ICP) Varian Turbo Model 150-Axial Liberty. Waterbath shaker model CH-4311 (Infors AG) was used in determination of distribution coefficients.

Preparation of Mesoporous Cerium(III) Silicate

Four different samples of modified mesoporous cerium(III) silicate were prepared by mixing CTAB as the structure directing agent, sodium silicate as silicon source and cerium(III) nitrate as cerium source. In a typical procedure, 6 g CTAB was added in 230 g demineralized water, the solution was stirred for 15 min (140 rpm) after that 30 g sodium silicate was added and it was further stirred for 30 min. Then pH of the solution was adjusted at 9 using 2 mol.L^{-1} sulfuric acid. Then solution of $Ce(NO_3)_3.6H_2O$ (0.075, 0.15, 0.30 and 0.60 g in 50 mL demineralized water) was added dropwise. The stirring was continued for 4 h. A bulky white gelatinous precipitate was formed. It was filtered, washed five times with demineralized water and dried in air oven at 50 °C for 24 h. The surfactant was removed by acidic extraction in a solution of 7.5% v/v of HCl in ethanol at 50 °C for 5 h. The material was digested in 0.1 mol.L^{-1} HNO_3 for 24 h and then washed with demineralized water.

Samples were denoted as follows: CexMCM-41 where x indicated the Si/Ce molar ratio and MCM-41(Mobile Crystalline Material) indicated hexagonal ordered mesoporous silicate. In order to study the effect of addition of cerium 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

Distribution Coefficients

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

$$K_d = [(A_i – A_f)/A_f].V/m$$

Where A_i and A_f are the initial and final concentrations (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 five hours at 25±1 ÚC in a polyethylene bottle containing 20 mL of 1.2×10^{-4}mol.L^{-1} metal ion solution. The concentration (mg.L^{-1}) of the solution before and after equilibration were measured by ICP technique.

Standard deviation for K_d values were checked by five determinations and were<10%.

Separation of Metal Ions

Rubidium and Uranium: A slurry of 0.5 g of Ce80MCM-41 in H^+ form was poured into a glass column with the length 20 mm and inner diameter 8 mm. A mixture of 0.5 mL each of the rubidium (0.005 mol.L^{-1}) and uranium (0.005 mol.L^{-1}) in 4 mL of the demineralized water was added to the column. The column was eluted by demineralized water and 0.1 mol.L^{-1} HCl. The flow rate of effluents was maintained at 0.2 mL.min^{-1} by a peristaltic pump until the metal ions were completely eluted and the effluents were collected in 3 mL fractions.

Thallium and Uranium: All conditions were the same as in the separation of rubidium and uranium.

Cobalt and Uranium: All conditions were the same as in the separation of rubidium and uranium.

RESULTS AND DISCUSSION

The XRD patterns after calcinations of synthesized cerium(III) silicate samples are presented in Fig 1. All the samples produce relatively well-defined XRD patterns, with one major peak (100) along with two small peaks (110, 200) identical to those of MCM-41 materials[3]. The nitrogen adsorption-desorption isotherms and corresponding pore size distribution of the synthesized cerium(III) silicate 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, pore volume and pore diameter of the modified mesoporous cerium(III) silicate adsorbents.

The SEM image of mesoporous Ce10MCM-41 is shown in Fig 3, The SEM image of Ce10MCM-41 sample exhibits uniform spherical crystallites.

The FT-IR spectra of the samples recorded in Fig 4 (400-1300 cm^{-1}) are similar to vibrations of the framework structure of zeolites[20]. Similarly, mesoporous molecular sieves also show series of bands that are characteristics of the SiO_4 tetrahedral unit and its modification by introduction of metal ions. The peak in region 960-970 cm^{-1} is generally considered as a proof for the incorporation of the heteroatom into the framework[21].

The thermogram of the uncalcined Ce80MCM-41 sample recorded in Figure 5 showa three steps of weight loss up to 900 °C. The steps can be distinguished as 35-150, 150-300, 300-550 °C. The weight loss is ~ 7.0% in the first step and is due to desorption of physisorbed water held in the

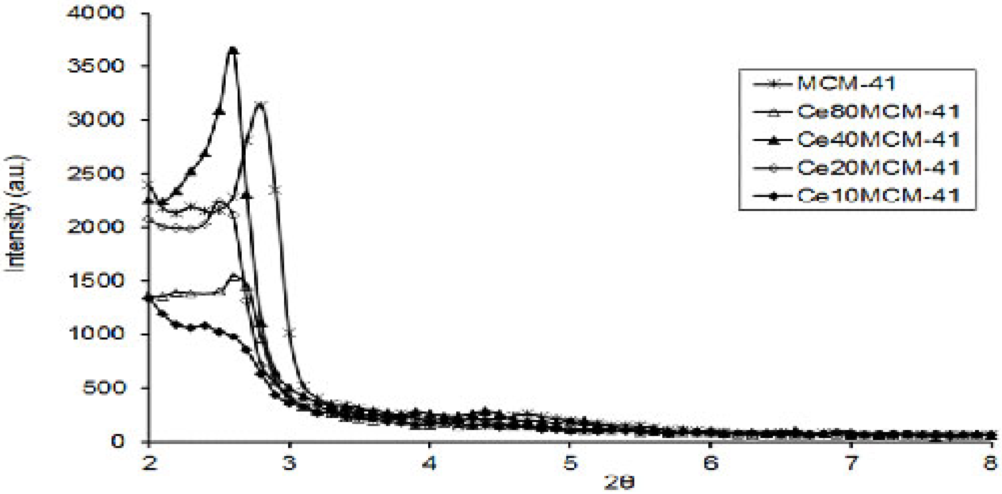

Fig 1. XRD patterns of the modified mesoporous cerium(III) silicates.

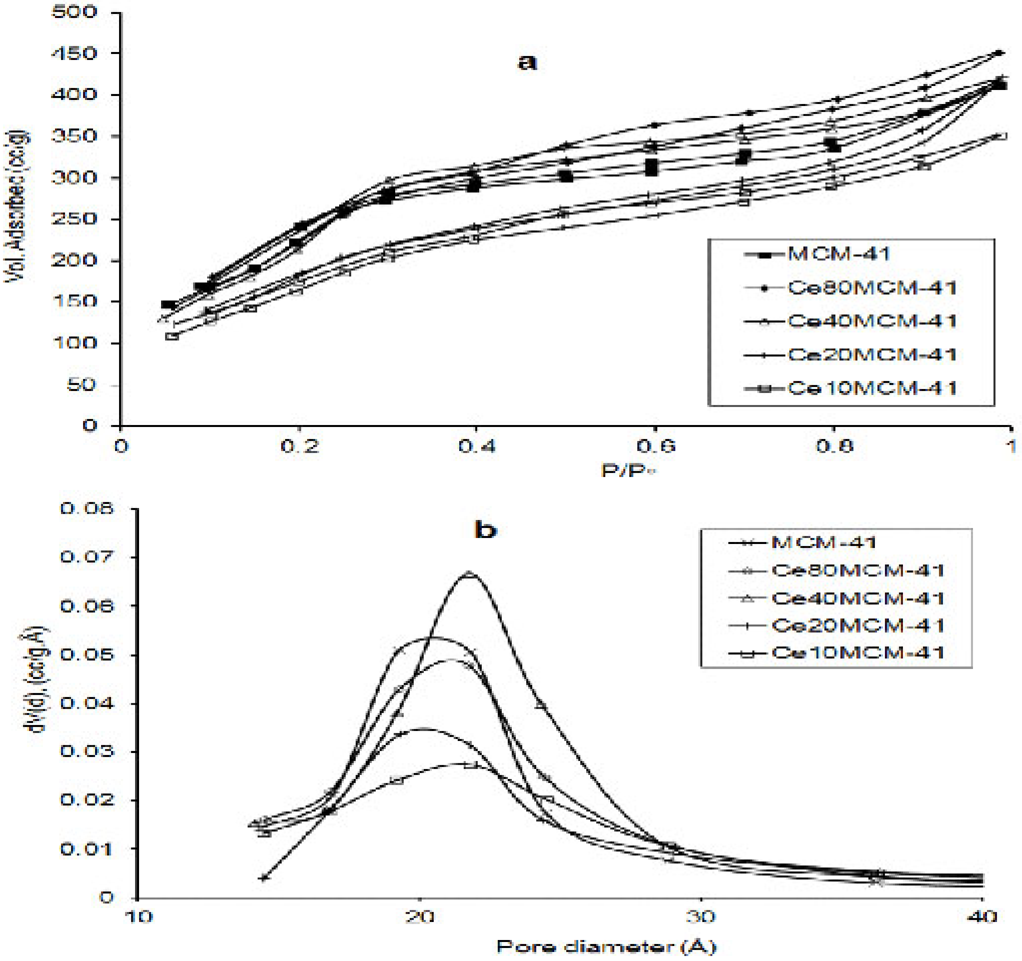

Fig 2. (a) nitrogen adsorption-desorption isotherms and (b) pore size distribution of the modified mesoporous cerium(III) silicates.

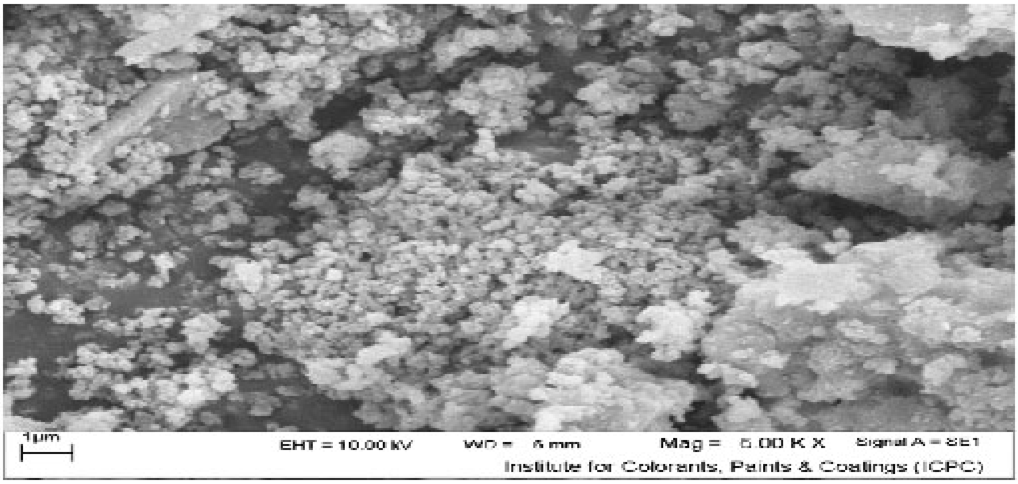

Fig 3. SEM image of the Ce10MCM-41 sample.

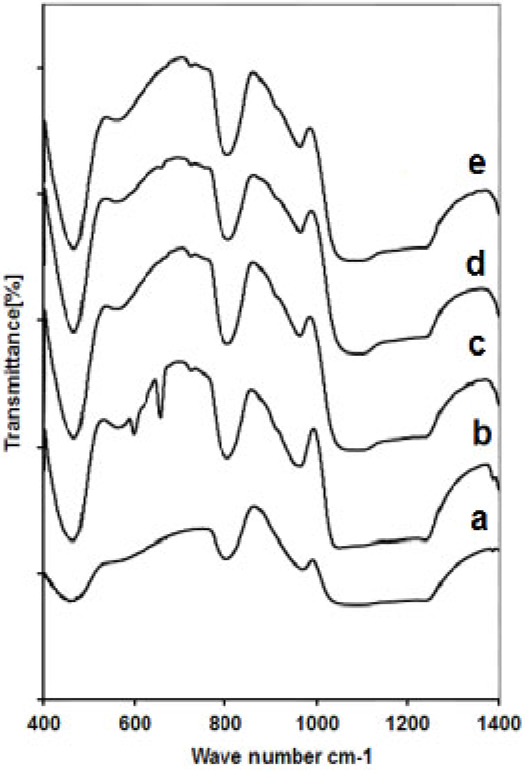

Fig. 4: FT-IR spectra of the modified mesoporous cerium(III) silicates (a) MCM-41 (b) Ce10MCM-41 (c) Ce20MCM-41 (d) Ce40MCM-41 (e) Ce80MCM-41.

pores. The weight losses in the second (~ 28.0 %) are mainly associated with oxidative decomposition of templates. In the last step, the weight loss (~5.0 %) is mainly due to the condensation of silanol groups. The thermograms of the other samples are similar to the Ce80MCM-41 sample.

The distribution coefficients of the metal ions on this adsorbent (Table 2) show good selectivity of this material for a number of ions in water. On the basis of the result recorded in Table 2 it may be inferred that the mesoporous cerium(III) silicate behaves as a good adsorbent, showing a high affinity for Ba^{2+}, Cr^{6+}, Hf^{4+}, Mo^{6+}, UO_2^{2+}, W^{6+} and Zr^{4+} ions.

The mesoporous cerium(III) silicates show high affinity for hard cations and also a weak affinity for 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 differences in Kd values for different mesoporous cerium(III) silicates (with mole ratios 10, 20, 40, 80) may be due to the fact that their surface areas, pore volumes and hydrophobic and hydrophilic characters are modified by changing Si/Ce mole ratios.

The comparison of percent adsorption of heavy metal ions on modified mesoporous cerium(III) silicate and amorphous cerium(III) silicate

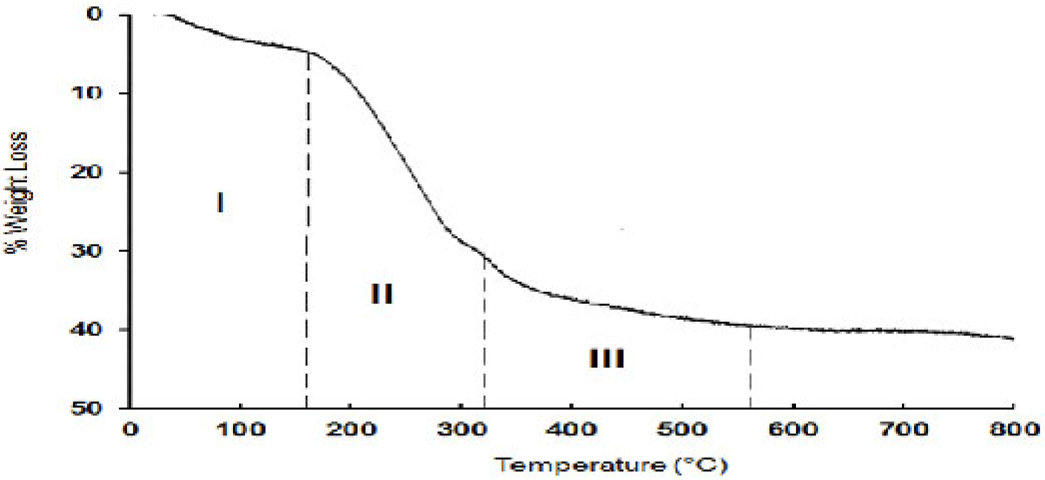

Fig. 5: Thermogram of the as-synthesized Ce80MCM-41 sample

Table 1 : Physical properties of modified mesoporous cerium(III) silicates.

Sample `	XRD d_{100} (Å)	Unit cell Parameter $^a(a_o)$ (Å)	Pore Volume (cc/g)	BET Surface Area (m^2/g)	Average Pore Diameter (Å)
Ce10MCM-41	34.3	39.6	0.59	657	19.1
Ce20MCM-41	37.5	43.3	0.68	721	18.6
Ce40MCM-41	36.0	41.6	0.75	916	19.3
Ce80MCM-41	36.2	41.8	0.77	918	18.6
Si-MCM-41	31.8	36.7	0.67	915	18.4

a.calculate from the equation $a_o \quad 2d_{100} \big/ \sqrt{3}$

Table 2 : Distribution Coefficients of metal ions on modified mesoporous cerium(III) silicate: K_d Value (mL/g) for different samples

Compounds	pH^a	Samples				
		Si-MCM-41	Ce10MCM-41	Ce20MCM-41	Ce40MCM-41	Ce80MCM-41
$Ba(NO_3)_2$	3.0	26	$\geq 10^4$	6	6	4
$Cd(NO_3)_2$	6.7	$\geq 10^4$	10	123	67	127
$Co(NO_3)_2$	3.7	10	2	N.A.	N.A.	N.A.
$Cr(NO_3)_3$	2.9	72	9	12	14	8
CrO_4K_2	5.6	N. A.	509	799	4035	2147
$CsNO_3$	2.8	32	N. A.	N. A.	2.0	N. A.
$Cu(NO_3)_2$	3.9	107	6	30	37	38
$Hg(NO_3)_2$	3.0	814	388	35	173	116
$HfOCl_2$	1.5	$\geq 10^4$	$\geq 10^4$	6388	$\geq 10^4$	7228
$Fe(NO_3)_3$	2.5	495	1202	860	1143	755
$(NH_4)_6Mo_7O_{24}$	5.5	19	3616	459	997	1108
$Pb(NO_3)_2$	6.2	1592	108	102	258	208
$RbNO_3$	2.3	28	N.A.	5	4	N.A.
$Sr(NO_3)_2$	4.0	T.A.	122	125	613	312
TeO_2	4.2	9	600	118	116	91
$Th(NO_3)_4$	3.4	5623	63	538	338	594
$Tl(NO_3)$	4.2	149	N.A.	8	15	8
$UO_2(NO_3)_2$	4.8	$\geq 10^4$	137	1345	8351	$\geq 10^4$
$Ni(NO_3)_2$	4.9	2369	10	37	107	70
$La(NO_3)_3$	2.6	24	3	4	2	4
Na_2WO_4	4.3	35	$\geq 10^4$	232	1211	$\geq 10^4$
$Zn(NO_3)_2$	5.6	364	N.A.	N.A.	23	8
$ZrOCl_2$	3.9	$\geq 10^4$	5905	71	2240	118

N.A. = Negligible adsorption, T.A. = Total adsorption, ^{a} equilibrium pH

Table 3: Comparison of distribution coefficient (K_d) of some metal ions on modified mesoporous cerium(III) silicates with that on amorphous cerium(III) silicate

	Metal ions							
Sample	**Cd^{2+}**	**Rb^{2+}**	**Th^{4+}**	**UO_2^{2+}**	**Sr^{2+}**	**Zr^{4+}**	**Zn^{2+}**	**Cs^{+}**
Amorphous cerium(III) silicate[15]	24	21	197	87	81	119	6	53
Modified mesoporous cerium (III) silicate	127	5	594	>10000	613	5905	23	2

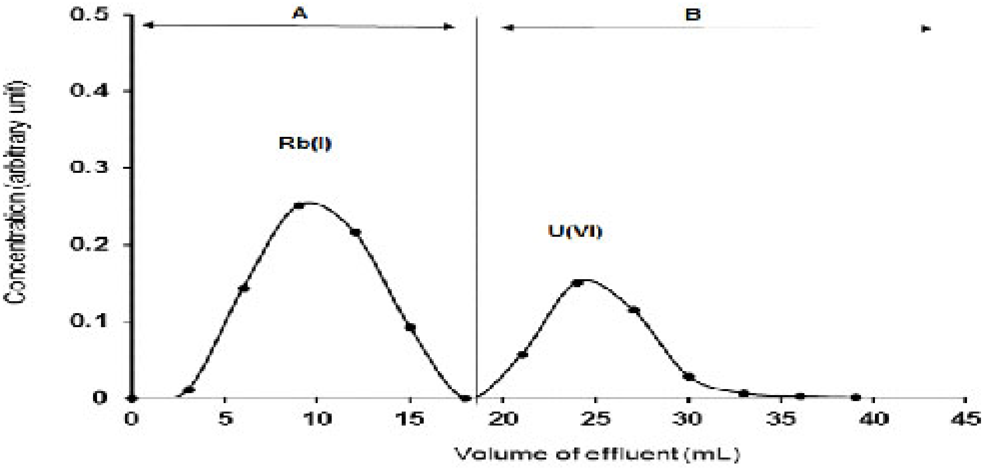

Fig. 6: Elution curve of separation of Rb(I)-U(VI). 1) Demineralized water, 2) 0.1 M HCl, Flow rate 0.2 mL/min

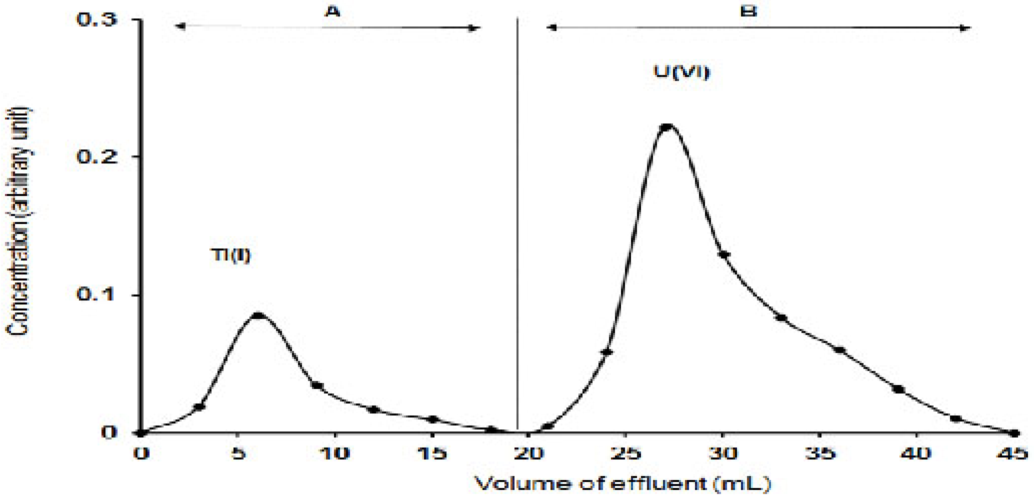

Fig. 7: Elution curve of separation of Tl(I)-U(VI). 1) Demineralized water, 2) 0.1 M HCl, Flow rate 0.2 mL/min

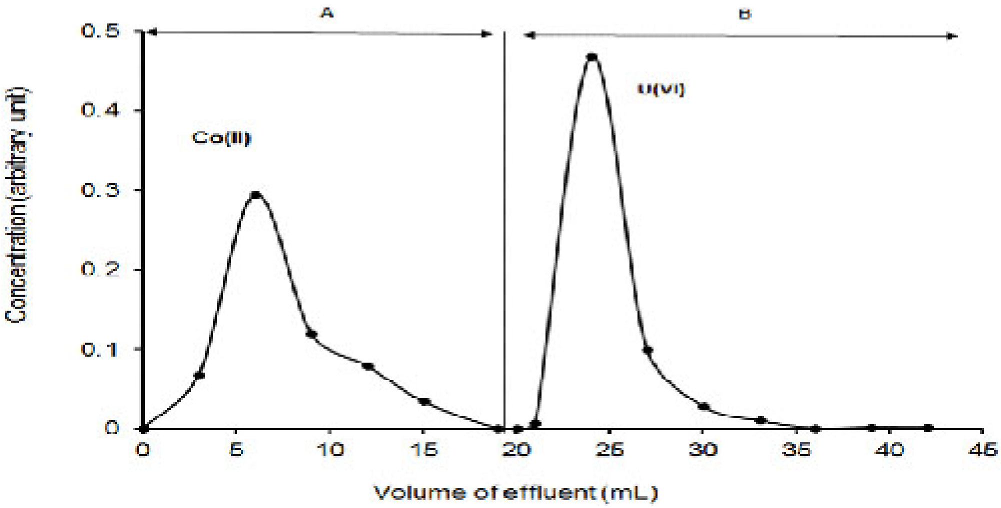

Fig 8. Elution curve of separation of Co(II)-U(VI). 1) Demineralized water, 2) 0.1 M HCl, Flow rate 0.2 mL/min.

reported earlier[12], (Table 3) show a more adsorption affinity of metal ions on modified cerium(III) silicate due to high surface area. Therefore this modified adsorbent can be used for their removal from aqueous systems.

The utility of this adsorbent has been demonstrated by achieving separation of great analytical significance. For example Rb(I) was separated from U(VI) (Fig 5). Here 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 Rb(I) is passed through the column due to low $K_d$value. Later, by using an 0.1 mol.L^{-1}HCl solution, U(VI) are eluted from their columns. Similarly the separation of Tl(I)-U(VI) and Co(II)-U(VI) have been performed with simple eluents (Figs 6,7).

CONCLUSION

A simple, rapid and low cost non-thermal method has been developed to synthesize cerium(III) incorporated mesoporous molecular sieves (with Si/Ce ratios of 10, 20, 40, and 80) with high thermal stability and high surface area and pore volumes. The distribution coefficients of the heavy metal ions on this sorbents show good selectivity of these materials for a number of ions in water. 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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