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Synthesis, Ion Exchange Properties, and Applications of Amorphous Cerium(III) Tungstosilicate

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Abstract: A novel hetropolyacid-based cation exchanger cerium(III) tungstosilicate was synthesized in amorphous form by mixing tungstosilisic acid (TSA) solutions to cerium(III) nitrate solutions at different Ce:TSA ratios. The materials were precipitated from the liquid phase by raising the pH of the solutions using sodium hydroxide. The produced ion exchange powders were characterized using powder X-ray diffractometry, thermogravimetry, infrared spectrometry, inductively coupled plasma and atomic absorption elemental analysis. The materials which were dried at 50°C were found to be stable in water, dilute acids, alkaline solutions, and high temperature up to 1000°C. The Ion exchange properties of the synthesized samples were studied by measuring the distribution coefficients (K_d) for 29 metal ions in demineralized water and nitric acid media. On the basis of K_d values, some quantitative separations such as Co^{2+}-Pb^{2+}, Cr^{3+}-Zr^{4+}, and Mo^{6+}- W^{6+} are achieved on their columns.

Keywords: cerium(III) tungstosilicate, distribution coefficients, hetropolyacids, inorganic ion exchanger, separation

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INTRODUCTION

Since the classical work of Amphelt, a great deal of interest has been taken on synthesis and characterization of new inorganic ion exchangers due to their excellent high selectivity with respect to a certain element or group of elements, good kinetics of sorption, high chemical stability, resistance to oxidation, good mechanical properties and stability at elevated temperature (1–5). The development of inorganic ion exchangers to take advantage of its properties in the removal and separation of heavy toxic metal ions such as chromium, lead, copper, iron and cobalt from aqueous media (which are generated into public sewages, rivers, sea and on land owing to the increasing use of them in many industries) is always of interest.

The different types of inorganic ion exchangers and their applications in diverse fields have been described in detail in a book by Clearfield (2). Amongst these materials, hydrous oxides, salts of heteropolyacids, and insoluble ferrocyanides are worthy of mention (6–8) and hetropolyacids-based inorganic ion exchangers are the most important classes of these materials that have been reported in the literatures (9–19). These types of materials exhibit improved properties over the simple salt of the metals and other conventional inorganic ion exchanger. One of the outstanding features of these materials is that the selectivity may be enhanced by varying the composition of the ion exchange materials (17).

Cerium based ion exchangers are known to be stable thermally and to possess good ion exchange capacity in a comparative study under identical conditions of synthesis (20,29). Also among the inorganic ion exchanger compounds, which have been used by rare earth elements in their structures, the cerium element has gained much attention due to its high relative abundance of cerium in comparison with other rare earth elements (5,30,31), so the synthesis of a new inorganic ion exchanger based on cerium is worthwhile.

Some insoluble acid salts based on cerium such as silicate, selenite, molybdate, tungstate, antimonite, vanadate, arsenite, hydrous oxide and molybdophosphate have been reported (10,20–29). However, no studies have been made on cerium tungstosilicate ion exchanger in this field in the literature.

In continuation of our work on the development of inorganic ion exchangers (10,11), in this paper we present the synthesis, ion exchanger behavior, characterization, chemical stability and analytical application of cerium(III) tungstosilicate.

EXPERIMENTAL

Chemical and Reagents

All the chemicals and reagents used were of Analytical Grade obtained from E. Merck or Fluka.

Apparatus

Bruker Spectrometer (Vector 22) was used for IR studies. pH measurements were made with a Schott CG841 pH-meter (Germany). Thermogravimetric analysis was performed on a thermobalance (PL-STA 1500, PL Thermal Science). The quantitative determinations of inorganic ions were carried out using an inductively coupled plasma ((ICP) Varian Turbo Model 150-Axial Liberty) and atomic absorption spectrometer (AAS Model, Spectra AA-220 Varian). X-ray diffraction studies were made with a Philips diffractometer (model PW 1130/90) and Waterbath shaker (model CH-4311, Infors AG) was used in determination of distribution coefficients of elements.

Synthesis of Cerium(III) Tungstosilicate

Three samples of cerium(III) tungstosilicate were synthesized by adding gradually tungstosilicic acid (TSA) solutions to cerium(III) chloride solutions under varying conditions given in Table 1. While the reaction mixture was thoroughly stirred with a magnetic stirrer at room temperature (20°C), the pH of system was increased slowly by adding NaOH to desired final pH for completion of precipitation formation. The solution mixture was stirred for 30 minutes and was then refluxed at 85–90°C for 24 hours. The resulting precipitate was decanted and washed five times with demineralized water, filtered by suction and dried at 50°C for 24 hours. Finally to obtain the samples into H^+ form, they were soaked in 0.1 M nitric acid, rewashed by demineralized water in order to remove the excess of acid and was again dried at 50°C.

Determination of Ion Exchange Capacity (IEC)

The ion exchange capacity of each sample was determined by the column process taking 1 g of ion exchanger samples (in H^+ form) into a column

Table 1. Synthesis and properties of cerium tungstosilicate

		Conditions of synthesis		Properties		
No.	Sample code	Concn. of reagents[a] (M)	Mixing volume ratio, Ce:TSA	Fainal pH	Composition molar ratio Ce:W:Si	Cation-Exchange Capacity (meq/g)
1	CTS-11	0.025	1:1	6.2	11.92, 53.28, 10.00	0.48
2	CTS-21	0.025	2:1	5.6	12.40, 49.10, 9.08	0.42
3	CTS-31	0.05	2:1	4.8	12.99, 48.00, 8.52	0.35

pH = pH of the reaction mixture; meq/g = ion exchange capacity as milliequivalent per gram of the ion exchanger.

[a] solution of Cerium(III) Chloride and tungstosilicic acid (TSA).

with a glass wool support, 100 mL of 1 M KCl solution was used as eluant, maintaining a very slow flow rate (0.2 mL/min). The effluent was titered against a standard NaOH solution to determine the total H^+ ions released. Table 1 shows the ion exchange capacity values of samples.

Composition

250 mg portions of each sample were dissolved after heating in 50 mL hot 4 M NaOH and after separation, the residue was dissolved in 20 mL 3 M HNO_3 solution by heating. Both the solutions were diluted and their elements were determined by inductively coupled plasma and atomic absorption spectrometer (32).

Distribution Coefficients

The distribution coefficients (K_d) for different metal ions were determined in aqueous solution by batch operation (33). 200 mg of ion exchangers in H^+ form were kept in 20 mL of 1.2×10^{-4} M metal ion solution at 25°C±1°C for 5 hours, with intermittent shaking to attain equilibrium. Blank solutions were prepared without the ion exchanger, having the same concentration of metal ions. This solution was treated in the same way as above. The solution was then filtered and metal ions were determined using ICP or AAS methods (32). The K_d values were calculated by the following equation;

$$K_d = [(I - F)/F] \cdot V/W(mLg^{-1})$$

Where I and F are the initial and final concentration (ppm) of metal ions in the solution phase, V is volume of initial solution in mL, and W is the dry mass of the ion exchanger in grams. Standard deviation for K_d values were checked by two determinations and were <10%.

Chemical Stability

The chemical stability of the samples was assessed in two mineral acids (HCl and HNO_3), sodium hydroxide base and organic solvents such as ethanol, methanol, acetone, ether. A 50 mg (dry mass) amount of each inorganic ion exchanger were placed in 20 mL of the solvent of interest and kept for 24 hours with continues shaking at room temperature samples. When heated in conc. HNO_3 or aquaregia or 4 M NaOH solution for more than 20 minutes, they dissolve. The metal ions released from the ion exchangers were analyzed with ICP spectrometry. Detailed quantitative studies on the stability of the exchangers were made as reported earlier (34) in different solutions and the results are given in Table 3.

Infrared Absorption Spectra

Infrared spectra of samples were measured by the standard KBr disk method. The spectrum of sample CTS-31 in H^+ form is shown in Fig. 1.

Thermogravimetric Studies

The thermal analysis was performed with cerium(III) tungstosilicate samples in H^+ form. A 20-mg (dry mass) amount of each sample was analyzed for TGA with sample holder made up Al_2O_3 in atmosphere of N_2 at flow rate of 50 ml/min. The heating rate was maintained at 10°C/min. Each analysis was done by heating the samples up to 1000°C. The thermogram for sample CTS-31 in H^+ form is given in Fig. 2.

X-Ray Analysis

X-ray powder diffraction method using nickel-filtered Cu-K_α radiation at 298 K was used for X-ray studies of samples in H^+ form. The study was done between 4 and 75° 2θ values with step size of 0.05. XRD spectrum of CTS-31 is given in Fig. 3.

Table 2. Distribution coefficients of elements on cerium tungstosilicate: K_d value (ml/g) for different sample

	Samples								
	CTS-11			CTS-21			CTS-31		
Species	DMW	0.001 M HNO_3	0.1 M HNO_3	DMW	0.001 M HNO_3	0.1 M HNO_3	DMW	0.001 M HNO_3	0.1 M HNO_3
$Ba(NO_3)_2$	2478	862	69	3515	691	91	1178	294	12
$Sr(NO_3)_2$	493	152	9	1215	180	17	322	57	4
$Co(NO_3)_2$	53	21	N.A.	187	111	N.A.	99	37	5
$Cu(NO_3)_2$	960	580	8	926	498	12	477	213	7
$Pb(NO_3)_2$	4150	2915	18	$>10^4$	8017	7	5431	3140	11
$BiONO_3$	3300	2700	145	1701	1504	81	624	490	42
$TlNO_3$	4926	3559	21	4039	2819	109	2010	1517	46
$In(NO_3)_3$	334	259	12	2015	1859	49	891	756	11
$Cr(NO_3)_3$	134	21	N.A.	1067	818	36	1587	1163	109
Na_2CrO_4	N.A.	N.A.	38	N.A.	N.A.	N.A.	38	32	30

(*Continued*)

Table 2. Continued

	Samples								
	CTS-11			CTS-21			CTS-31		
Species	DMW	0.001 M HNO_3	0.1 M HNO_3	DMW	0.001 M HNO_3	0.1 M HNO_3	DMW	0.001 M HNO_3	0.1 M HNO_3
$(NH_4)_6Mo_7O_{24}$	198	91	5	334	217	24	401	330	45
Na_2WO_4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
$Th(NO_3)_4$	1930	1294	83	364	61	12	439	124	9
$UO_2(NO_3)_2$	956	374	34	347	107	9	394	169	11
$Zn(NO_3)_2$	400	289	29	546	352	17	281	127	6
$Cd(NO_3)_2$	764	271	9	653	391	3	502	137	1
$ZrOCl_2$	$>10^4$	$>10^4$	67	$>10^4$	2341	49	$>10^4$	$>10^4$	16
$HfOCl_2$	$>10^4$	2950	27	$>10^4$	244	20	$>10^4$	2153	7
$LiNO_3$	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
$NaNO_3$	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
KNO_3	86	4	N.A.	27	1	N.A.	21	1	N.A.
RbCl	299	18	6	220	15	2	159	12	N.A.
$CsNO_3$	604	120	31	671	93	22	477	115	16
YCl_3	1029	186	11	3300	309	9	1683	260	6
$La(NO_3)_3$	750	354	35	2416	529	91	1422	931	186
$Ce(NO_3)_3$	950	390	79	886	451	61	1867	1206	33
$Nd(NO_3)_3$	861	556	21	3978	3015	55	3019	1612	109
$Sm(NO_3)_3$	680	391	10	2397	1945	24	1721	1024	6
$Dy(NO_3)_3$	871	390	48	2574	1892	101	1694	1200	25

Table 3. Chemical stability of cerium tungstosilicate in different solutions; (Weight dissolved (mg) from 50 mg)

			CTS-11			CTS-21			CTS-31		
No.	Solvent (M)		Ce (mg)	W (mg)	Si (mg)	Ce (mg)	W (mg)	Si (mg)	Ce (mg)	W (mg)	Si (mg)
1		0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	HCl	0.5	4.18	4.37	0.86	4.20	7.72	0.80	4.85	8.63	0.77
3		1	4.98	5.00	0.94	4.71	10.25	0.86	5.11	11.38	0.85
4		4	6.14	5.87	1.12	6.07	10.48	0.93	6.52	11.62	0.87
5	HNO_3	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6		0.5	4.23	4.89	0.72	4.42	8.59	0.61	4.66	9.42	0.53
7		1	5.30	7.74	0.73	4.94	9.17	0.62	5.37	12.28	0.56
8		4	5.96	7.88	0.79	5.95	10.96	0.68	6.37	12.69	0.67
9	NaOH	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10		0.5	0.00	28.91	1.82	0.00	28.56	1.58	0.00	28.37	1.41
11		1	0.00	29.11	2.22	0.00	29.39	2.08	0.00	29.70	1.99
12		4	0.00	29.57	4.05	0.00	29.85	3.74	0.00	29.93	3.68

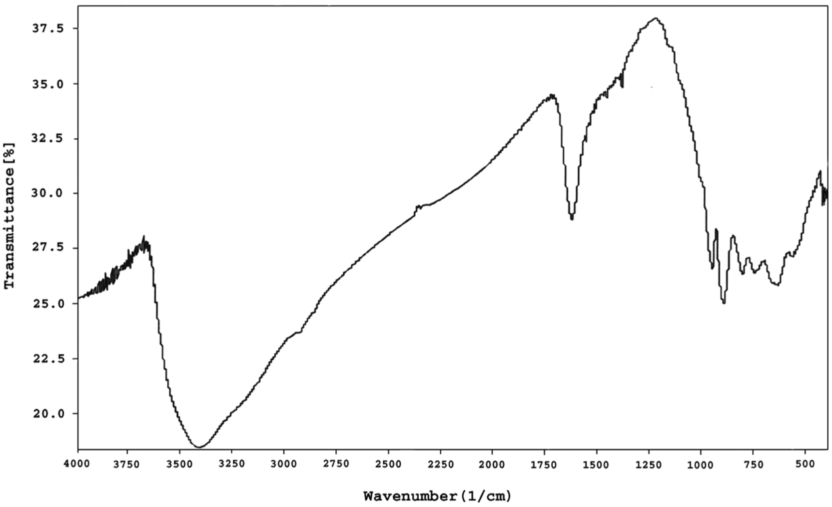

Figure 1. Infrared spectrum of cerium(III) tungstosilicate (CTS-31).

Binary Separation of Metal Ions

Important quantitative separations of metal ions were performed on column of titanium cerium(III) tungstosilicate. A 0.5 gram amount (dry mass) of CTP in H^+ form (mesh size 50–100 mm) was placed in glass

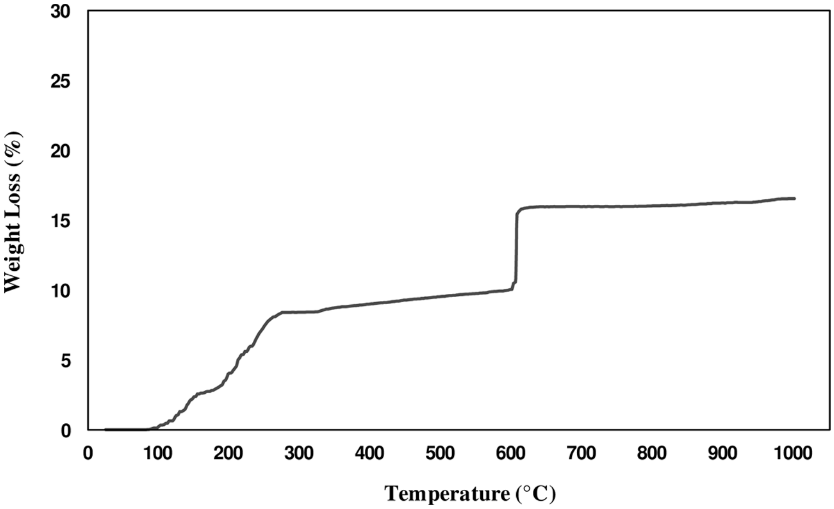

Figure 2. Thermogram of cerium(III) tungstosilicate (CTS-31).

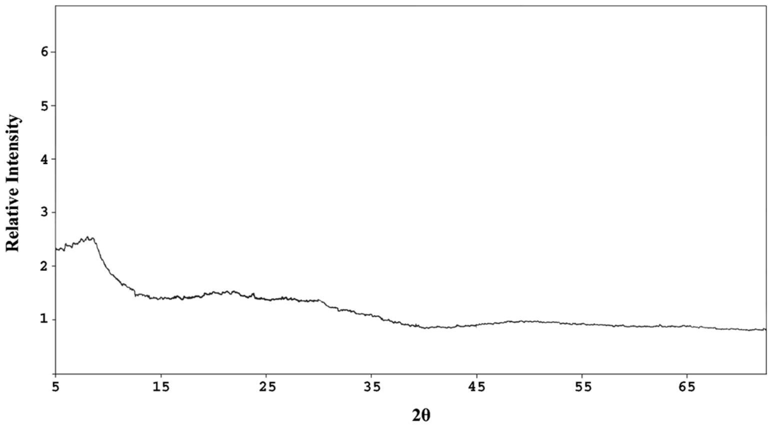

Figure 3. XRD spectrum of cerium(III) tungstosilicate (CTS-31).

column of inner diameter 6 mm with a glass wool support at the bottom. The column was washed thoroughly with demineralized water and the mixture of the two metal ions (Table 4) to be separated was then loaded by passing the mixture through the column at slow rate (maintaining a flow-rate of 0.18 ml/min). The column was washed with demineralized water so that the metal ions, which were not exchanged, could be removed. The metal ions adsorbed on the exchanger were then eluted with 0.1 M HNO_3 or NH_4Cl. The flow-rate of effluent was maintained at 0.18 ml/min until the metal ions were completely eluted out of the column. The effluents were collected in 2-ml fractions and determined by ICP or AAS in mind, the metal ion solutions were either concentrated or diluted as required so as to ensure detection.

Table 4. Separation of metal ions on cerium tungstosilicate at room temperature

No.	Metal ions separated	Amount loaded(μg)	Amount found(μg)	Total elution volume (ml)	Eluent used	The type of ion exchanger
1	W	460	460	42	H_2O	CTS-31
	Mo	240	235	106	0.1 M NH_4Cl	
2	Cr	130	130	14	H_2O	CTS-31
	Zr	228	225	18	0.1 M HNO_3	
3	Co	147	147	16	H_2O	CTS-11
	Pb	518	518	18	0.1 M HNO_3	

RESULTS AND DISCUSSION

The condition used for the preparation of the inorganic ion exchanger has considerable effect on the degree of hydration and the composition of the exchanger. These two factors are responsible for the shape and size of cavities inside the ion exchanger and for other properties of the exchanger resulting in unusual ion exchange behaviors (4,5,35). Three different samples of cerium(III) tungstosilicate have been prepared under varying conditions (Table 1). The result shows that the molar composition of cerium(III) tungstosilicate was found as Ce:W:Si about 1:4.5:1, which shows that anionic part is higher than cationic one. As it was observed earlier table 1 that anionic part contributed toward ion exchange capacity for this cation exchanger. Therefore, cerium(III) tungstosilicate showed relatively good ion exchange capacity.

The infrared spectrum of cerium(III) tungstosilicate is recorded in Fig. 1. On the basis of IR data, we can say that the peak between 2900 and 3500 cm^{-1} with the maximum at 3400 cm^{-1} is attributed to interstitial water molecules and OH groups while a sharper peak at 1600 cm^{-1} is probably due to the deformation vibration of free water molecules. The presence of several low and mid intensity bands in the region of 500–1000 cm^{-1} corresponds to metal-oxygen bonds, presumably in a polymeric compound (36,37), while the band at 900 cm^{-1} may be due to Si-O stretching vibration in cerium(III) tungstosilicate (38). This suggests that cerium tungstosilicate and tungstosilisic acid are quite different from each other regarding their structures.

The thermogram for sample CTS-31 recorded in Fig. 2 implies that the weight loss of the ion exchanger up to 280°C is due to the removal of free external water molecules. At higher temperatures (280–590°C), the gradual loss in weight (2%) is attributed to loss of coordinated water and hydroxyl groups. These losses follow the regular trend of inorganic ion exchangers (39). Further heating of the material from 590–610°C shows a more weight loss (5%) which is due to the removal of structure water condensation. The curve pattern shows that the ion exchanger is stable up to 1000°C. On the basis of the thermogram pattern recorded here it can be concluded that cerium tungstosilicate ion exchangers are more stable than other cerium ion exchangers (19–21).

Distribution coefficients of 29 metal ions have been studied using batch experiments. Furthermore the nature of the ion exchanger, various factors such as swelling, formation of complexes, nature of the chemical bond and solvent distribution may be responsible for the wide variation in the distribution coefficient values (40). The obtained values for K_d (given in Table 2) in demineralized water and nitric acid media show that the amorphous cerium(III) tungstosilicate is an useful and good cation

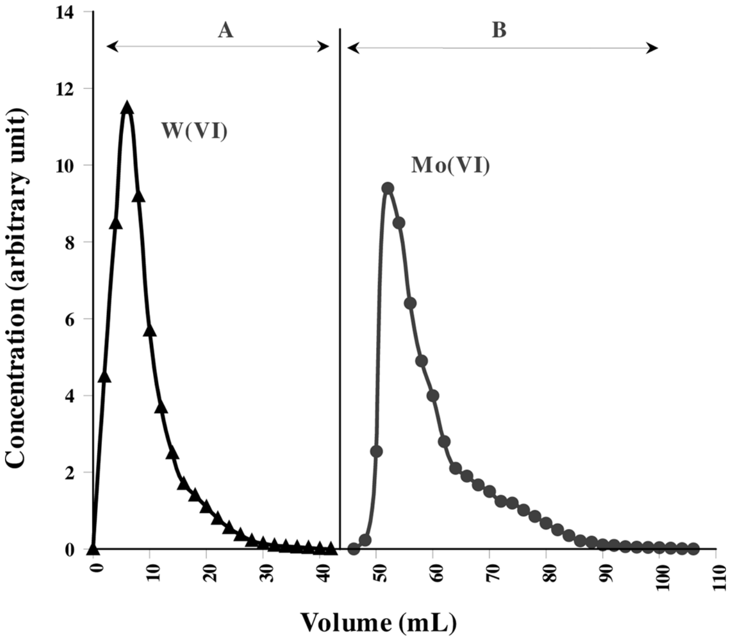

Figure 4. Elution curve of separation of W(VI)-Mo(VI). (a) Demineralized water, (b) 0.1 M NH_4Cl, Flow rate 0.18 mL/m.

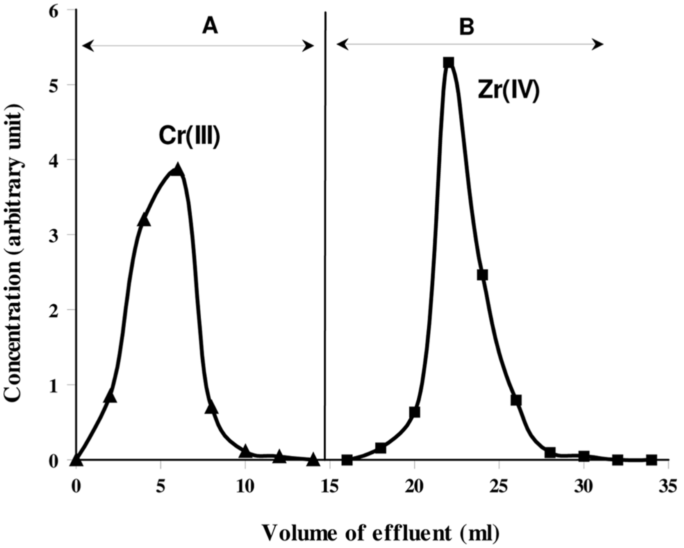

Figure 5. Elution curve of separation of Cr(III)-Zr(VI). (a) Demineralized water, (b) 0.1 M HNO_3, Flow rate 0.18 mL/m.

exchanger in the pH range 3–7, showing a high affinity for some cationic elements. It was observed that for most of the metals K_d values decreased with the increase in concentration of nitric acid. Low K_d values of the metal ions in high concentration of nitric acid are due to slower replacement of the metal ions in acidic media and competition of H_3O^+ ions with metal ions as expected.

Based on the K_d values of alkali metal ions in demineralized water, all the samples of cerium(III) tungstosilicate start to exchange the larger alkali metal cations (according to the bare ionic radius) at a pH between 5–6.5 and exhibit the following selectivity sequence.

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

Sorption behaviors of metal ions show a high selectivity of the elements such as Ba^{2+}, Bi^{3+}, Zr^{4+}, HF^{4+}, and especially Pb^{2+}, that indicating their importance in environmental studies, in demineralized water and 0.001 M nitric acid media. The selectivity determined how efficiently a certain element removed from other elements. On the basis of these data, three separations of metal ion pairs were performed. The separation of Co^{2+} from Pb^{2+}, Cr^{3+} from Zr^{4+}, and Mo^{6+} from W^{6+} have been achieved on the column of this ion exchanger (given in detailed in table 4 and show in Figs. 4–6 as a elution curves). The salient feature of the separation using

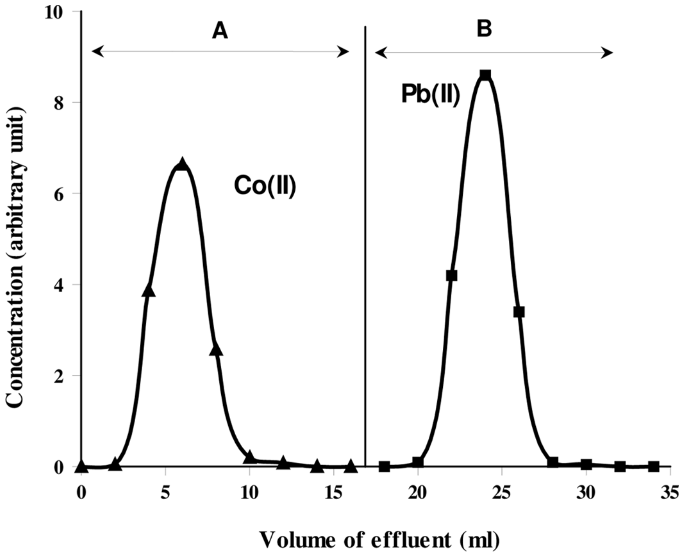

Figure 6. Elution curve of separation of Pb(II)-Co(II). (a) Demineralized water, (b) 0.1 M HNO_3, Flow rate 0.18 mL/m.

the column of amorphous cerium(III) tungstosilicate is the slight tailing which Lead to their sharpness in achieving the separation.

CONCLUSION

An amorphous cation-exchanger cerium(III) tungstosilicate was found to have high chemical and thermal stability, good ion-exchange capacity and selectivity for some toxic metal ions. The differential behavior of the exchanger towards metal ions showed the separation possibilities of metal ions of analytical interest from a given mixture. So this cation exchanger material can be conveniently utilized for the removal and isolation of toxic metal ions, released from the wastewater stream.

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