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Solid Phase Extraction, Preconcentration and Sequential Separation of U(VI), Th(IV), La(III) and Ce(III) by Octa-*O*-methoxy resorcin[4]arene based Amberlite XAD-4 Chelating Resin

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Abstract Amberlite XAD-4 was covalently linked with octa-*O*-methoxy resorcin[4]arene through - N=N- to form chelating resin, which has been duly characterized and successfully used for separation and preconcentration of rare-earth metal ions like U(VI), Th(IV), La(III) and Ce(III). Various physiochemical parameters like pH, flow rate, sorption capacity, breakthrough studies, distribution coefficient, preconcentration factor, concentration of eluting agents responsible for quantitative extraction of metal ions were optimized. The resin possessed good binding affinity towards U(VI), Th(IV), La(III) and Ce(III) under selective pH conditions and were quantitatively eluted with suitable eluants like HCl and HNO_3. Amount of metal ions was determined by spectrophotometry or inductively coupled plasma-atomic emission spectrometry. Fast exchange kinetics and good breakthrough capacity of the resin lead to effective separation of metal ions from their binary and ternary mixture by column method on the basis of pH and eluting agents. The resin could be reused for 8-10 cycles with recoveries of analytes higher than 98%. Proposed method having analytical data with the relative standard deviation (RSD) < 2%, reflect upon the reproducibility and reliability of the method which has been effectively used for separation and determination of U(VI), Th(IV), La(III) and Ce(III) ions from monazite sand and standard reference materials.

Keywords: *solid phase extraction, Amberlite XAD-4; Separation, Octa-O-methoxy resorcin[4]arene*

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1. Introduction

There is a considerable interest in new separation techniques for extraction of selective metal ions from the industrial effluents containing radioactive and waste hazardous elements [1,2]. In the nuclear industry, a large amount of solid and liquid waste containing uranium, thorium, is being generated during various processes like mining, fabrication of nuclear fuel, reprocessing of spent fuel, and waste management [3]. Uranium and thorium find extensive application as nuclear fuel in power, and their main sources are pitchblende, monazite sand and sea water. Both metal ions are known to cause acute toxicological effects in mammals, and their compounds are potential occupational carcinogens [4]. In the same way lanthanum and cerium are most commonly obtained from monazite sands and used as a catalyst for automobile and nuclear industries. Human beings exposed to cerium have experienced itching, sensitivity to heat and skin lesions and animals injected with large doses of cerium have died due to cardiovascular collapse [5,6,7]. Similarly, lanthanum solution injections cause hyperglycemia, low blood pressure, degeneration of the spleen and hepatic alterations, sometimes led to pneumoconiosis [5,6,7]. Recovery of these metal ions is a not easy task because of high acidic environment associated with them [8,9,10]. However, numerous methods have been described such as precipitation [11,12], ion exchange, electrolysis [13] etc., to remove dissolved metals from aqueous samples, but they suffer from disadvantages like poor removal competence, high cost, generation of secondary pollution and ineffectiveness towards the metal present at trace levels [14].

Solid phase extraction (SPE) has emerged as an excellent separation technique in view of immiscibility of resins with aqueous phase, low rate of physical degradation, recycling options and minimum release of toxic solvents [15,16]. It is commonly used technique for preconcentration/separation of trace and ultra trace amounts of inorganic and organic species with enhance sensitivity for separation from the analytical matrix, as it allows discriminatory binding of analyte to a solid support and subsequently eluted with a small volume of solvent. This technique has advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, environment friendly, flexibility and easier incorporation into automated analytical techniques [17,18,19]. Various procedures involving preconcentration of rare-earth elements employing a variety of materials such as silica gel [20], microcrystalline naphthalene [21], polyurethane foam [22], C18 cartridges [23], Alumina [24] Amberlite XAD resins [25-30] etc. can be found in literature. Among all Amberlite XAD, resin proves to be one of the best in series. Various chelating moieties, e.g., 4-(2-thiazolylazo) resorcinol [31], bicine [32], pyrogallol [33], *o-vanillin* semicarbazone [34], tiron [35], etc. have been impregnated or covalently linked on to Amberlite XAD to produce a insoluble solid sorbent for separation and preconcentration of metal ions from various matrices.

Calix[4]resorcinarenes which can be easily functionalized as per choice and expertise, holds a great potential for its complexation with various metal ions. As far as work on polymer supported calix[4]resorcinarenes is concerned, Merdivan et al. [36,37,38] have reported the use of calix[4]resorcinarene impregnated on Amberlite XAD for separation and preconcentration of rare earths.

Here, the use of octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 chelating resin for extraction, preconcentration and sequential separation of metal ions such as U(VI), Th(IV), La(III) and Ce(III) is described. Factors influencing the separation and preconcentration of the trace metal ions, such as pH of maximum extraction, concentration of eluting agents, flow rate, total sorption capacity, exchange kinetics, preconcentration factor, distribution coefficient, breakthrough capacity, resin stability, and effect of electrolytes have been investigated. The developed method has been applied in the determination of U(VI), Th(IV), La(III) and Ce(III) from monazite sand and standard reference materials.

2. Experimental Section

2.1. Materials

High-purity reagents from Sigma-Aldrich, Merck and Fluka were used in the preparations of all standard solutions. Amberlite XAD-4 with surface area 750 $m^2\ g^{-1}$, pore diameter 50Å and bead size 20–50 mesh was procured from Fluka. All glassware were washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with double distilled water before use. The pH was adjusted with the buffer solutions: PO_4^{-3}/HPO_4^{-2} buffer for pH 2.0 and 3.0; CH_3COO^{-1}/ CH_3COOH buffer for pH 4.0 to 6.0; HPO_4^{-2}/H2PO$_4^{-1}$ buffers for pH 7.0 and 7.5; NH_3/NH_4^+ buffers for pH 8.0 to 10.0. All aqueous standard solutions were prepared with quartz distilled deionised water, which was further purified using a Millipore Milli-Q water purification system. Standard stock solutions (2000 µg ml^{-1}) of U(VI), Th(IV), La(III) and Ce(III) were prepared separately by dissolving 0.42 gm UO2(NO3)2.6H2O; 0.49 gm Th(NO_3)4.5 H_2O; 0.63 gm La(NO_3)3.6H_2O and 0.62 gm Ce(NO_3)3.6H_2O in 2 mL concentrated HCl and dilute up to 100 mL with water in a volumetric flask.

Final concentration of individual metal ion was standardized spectrophotometrically [39]. UV-Vis Spectrophotometric Determination of U(VI), Th(IV), La(III) and Ce(III)

- U(VI) forms blue colored water soluble complex with Arsenazo-I reagent. pH = 8.5, λ_{max} = 596 nm, ε = 23000
- Th(IV) forms grey-green colored water soluble complex in 3M HCl with Arsenazo-III reagent.

$$\lambda\text{max} = 655\text{nm}, \varepsilon = 1150000$$

- La(III) forms pink-violet colored water soluble complex with Arsenazo-I reagent. pH = 8.0, λ_{max} = 580 nm, ε = 27000
- Ce(III) forms green colored water soluble complex with Arsenazo-III reagent. pH = 2.6, λ_{max} = 650 nm, ε = 56000

Working solutions were prepared by appropriate dilution of the stock solutions.

2.2. Methods

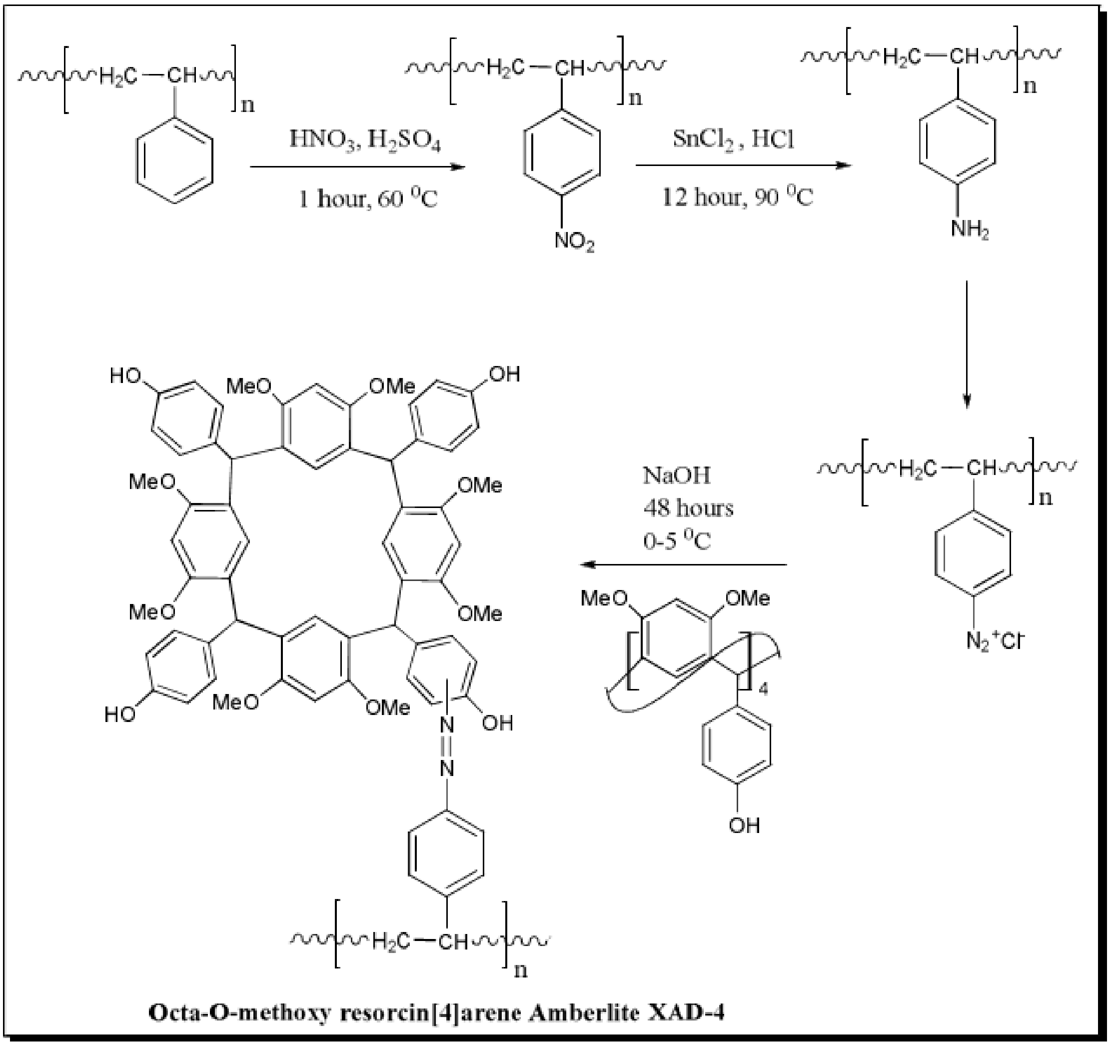
Inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) JY 2000-2 model with the plasma scan multitasking computer, and a peristaltic pump was used under optimum working conditions: concentric glass nebulizer, cyclonic glass spray chamber, three channels peristaltic pump, thermo-regulated, 0.64 meter focal length, 2400 g/mm grating used in the first order with optical resolution <19 pm for 160-800 nm (optional far UV for extended wavelength ranges 120-800nm), 12 L/min plasma gas, 0.2 L/min sheath gas. Spectral measurements were done using a JASCO 570 UV-vis spectrophotometer using 10 mm quartz cells. The flow of the liquid through the column was controlled by Miclins Peristaltic pump PP-10 EX. Elico digital pH-meter, model L1 614 equipped with a combined pH electrode was employed for measuring pH.

2.3. Synthesis

Basic platform of octa-*O*-methoxy resorcin[4]arene was synthesized by the acid catalyzed condensation reaction of 1,3 dimethoxy benzene and p-hydroxy benzaldehyde as reported earlier [40]. Immobilization of octa-*O*-methoxy resorcin[4]arene on the surface of Amberlite XAD-4 beads was performed through azo (-N=N-) linkage as per Scheme 1.

2.3.1. Synthesis of Amberlite XAD-4 -octa-*O*-methoxy resorcin[4]arene

The nitration of Amberlite XAD-4 beads, the reduction of the nitrated resin and the subsequent diazotization of the amino resin was carried out by the procedure reported earlier for Amberlite XAD-2 [41]. The resulting diazotized resin was allowed to react with octa-*O*-methoxy resorcin[4]arene (1.0 g dissolved in 50mL of 10% NaOH) at 0-5 ℃ for 48 h. The dark brown coloured beads were filtered, successively washed with double distilled water and finally dried for further studies.



Scheme 1. Synthesis of octa-*O*-methoxy resorcin[4]arene supported Amberlite XAD-4 polymeric chelating resin

2.4. General Column Method for Separation, Preconcentration and Determination of Metal Ions

Octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin (1.0 gm) was mixed with $CH_3OH:H_2O$ (1:1) to obtain a slurry and then poured onto a glass column (10 cm long, 1.0 cm inner diameter) equipped with a stopcock and a porous disk. The height of the column section containing resin (bed height) was 15 mm. The resin was washed with dilute acid, dilute base, deionized water and then conditioned with different buffer solutions for the samples containing U(VI), Th(IV), La(III) and Ce(III). After adjusting the appropriate pH, suitable aliquot of the solution containing U(VI), Th(IV), La(III) and Ce(III) was passed through the column at an optimum flow rate controlled by a peristaltic pump. The bound metal ions were stripped from the column with eluting agents like HCl or HNO_3. The preconcentrated metal ions in the eluants were collected in a 25 mL volumetric flask, made to volume by double distilled water and determined by spectrophotometry or ICP-AES.

2.5 General Batch Method for Preconcentration and Determination of Metal Ions

The known volume of sample solutions of U(VI), Th(IV), La(III) and Ce(III) were placed in glass stoppered bottles at an optimum pH and then octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin (0.5 g) was added to the solution. The bottles were shaken for about 1.0 hour at room temperature and later chelated resin was filtered. Filtrate and resin were treated separately for metal content determination. Metal content in chelated resin was determined by shaking it again with a suitable eluting agent (HCl/HNO_3) for 2-3 minutes. The resin was filtered, eluant was collected, and its volume was made up to mark in a 25 mL volumetric flask. Metal content in filtrate, and eluant was determined by spectrophotometry /ICP-AES.

3. Results and Discussion

3.1. Spectral interpretation of synthesized octa-*O*-methoxy resorcine[4]arene Amberlite XAD-4 polymeric chelating resin

The resulting resin was characterized by elemental analysis, FT-IR and mass difference. The nitrogen content in NH_2-XAD-4 was found to be 2.73% higher than NO_2-XAD-4, which confirms the successful reduction of NO_2-XAD-4 resin. The FT-IR spectra of nitrated Amberlite

XAD-4, intermediate NH_2-XAD-4 and octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 chelating resin, are given in Figure 1. Asymm (N-O) and symm (N-O) stretching bands of the nitrated Amberlite XAD-4 were observed at1540 and 1325 cm^{-1}, respectively. The N-H stretching vibrations of NH_2-XAD-4 were identified with the bands at 3400 and 1625. The conspicuous band of -N=N- at 1470 cm^{-1} confirms the formation of octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 chelating resin through –N=N- linkage. Furthermore, the loading of octa-*O*-methoxy resorcin[4]arene (0.61 mmole g^{-1}) on polymeric support was evaluated by mass difference of dried resin, which also confirms the successful nitration, reduction and coupling of diazotized Amberlite XAD-4 resin with octa-*O*-methoxy resorcin[4]arene.

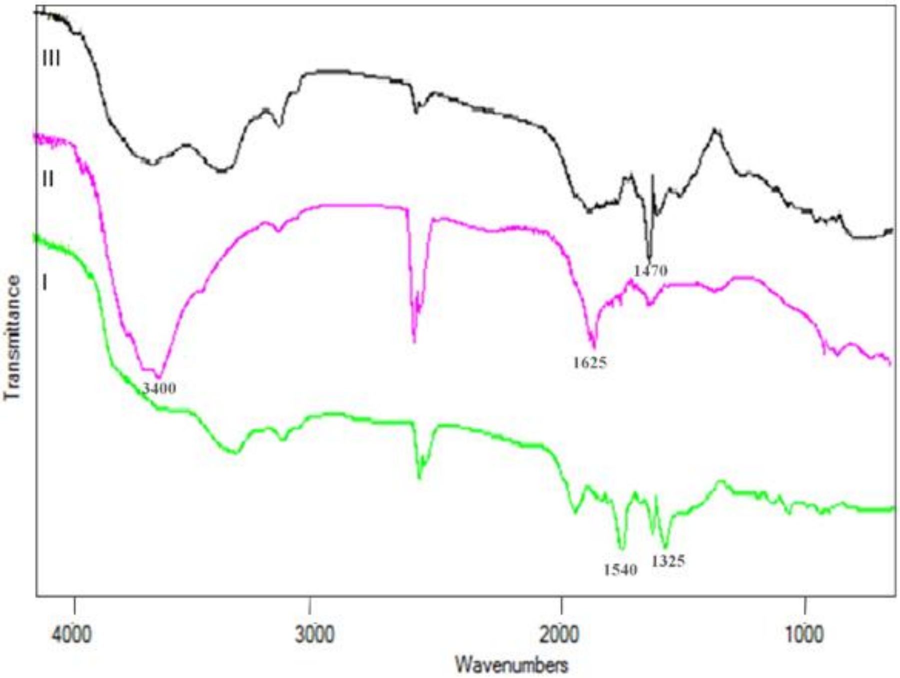


Figure 1. IR of I) NO_2-XAD-4 resin II) NH_2-XAD-4 resin III) octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 chelating resin

3.2 Parameters Optimized for Separation and preconcentration of U(VI), Th(IV), La(III) and Ce(III)

In order to accomplish quantitative recoveries of U(VI), Th(IV), La(III) and Ce(III) from the octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin, separation and preconcentration procedures were optimized with respect to various parameters such as pH of maximum extraction, flow rate, concentration and volume of the eluting agents, total sorption capacity, distribution coefficient (K_d), exchange kinetics, breakthrough studies, preconcentration factor, reusability of the resin and effect of electrolytes.

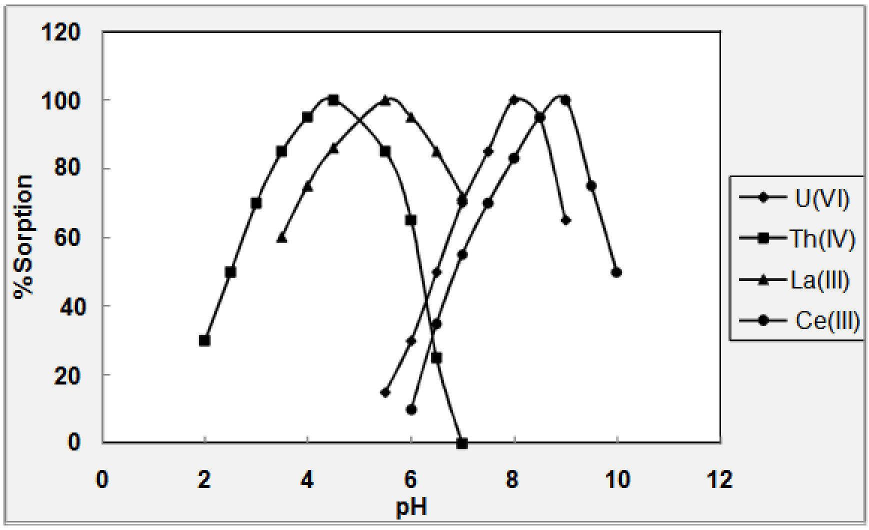


Figure 2. Effect of pH on the sorption of U(VI), Th(IV), La(III) and Ce(III) by octa-O-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin. **[Experimental conditions**: Amount of resin in column: 1.0 gm, concentration of metal ions: 10 µg mL^{-1}; U(VI): pH: 8.0; Th(IV): pH: 4.5; La(III): pH: 5.5; Ce(III): pH: 9.0]

3.2.1. Effect of pH on Extraction

As the pH of the aqueous sample solution is one of the important parameters for the quantitative retention of analytes, the influence of pH on aqueous solution containing 10 µg mL^{-1} of U(VI), Th(IV), La(III) and Ce(III) on the quantitative sorption of analytes on octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4, polymeric chelating resin (1.0 gm) was investigated in the pH range of 2.0-10.0 using batch method. 100 mL of each of aqueous solution of U(VI), Th(IV), La(III) and Ce(III) was placed in glass stoppered bottles at different pH and was stirred slowly for 1 h. The optimum pH for maximum extraction of U(VI), Th(IV), La(III) and Ce(III) was found to be 8.0, 4.5, 5.5 and 9.0 pH, respectively (Table 1, Figure 2). The studies revealed selective extraction of metal ions at particular pH and thereby suggesting the possibility of separation of metal ions in presence of each other.

3.2.2 Influence of Flow Rate of Feed Solution on Metal Ion Extraction

The amount of metal ions extracted on the resin was studied at various flow rates with 1.0 gm resin in the packed column at room temperature. Feed solutions containing 10 µg mL^{-1} U(VI) and Th(IV), La(III) and Ce(III) were passed at different flow rates (1.0-6.0 mL min^{-1}) maintained by a peristaltic pump at their optimum pH. The optimum flow rate was found to be 2.0 mL min^{-1}, 1.5 mL min^{-1}, 1.0 mL min^{-1} and 1.0 mL min^{-1} for U(VI), Th(IV), La(III) and Ce(III), respectively (Table 1, Figure 3).

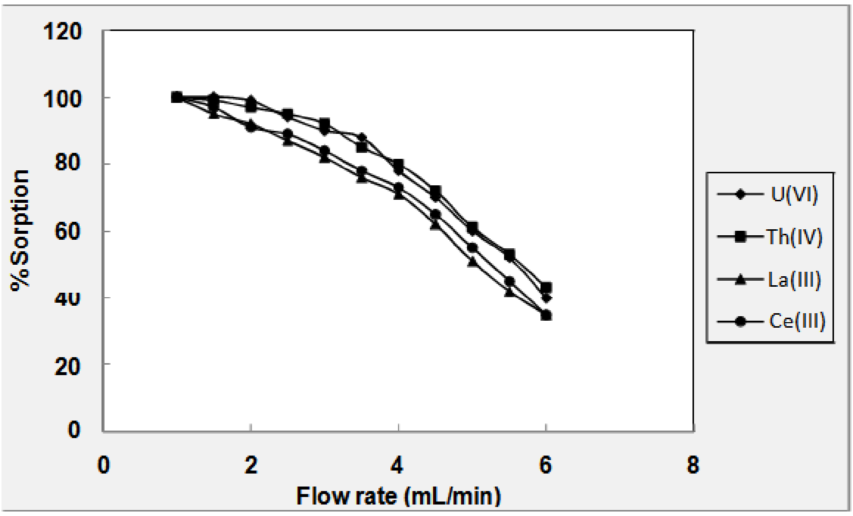


Figure 3. Effect of flow rate on the sorption of U(VI), Th(IV), La(III) and Ce(III) on octa-O-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin. **[Experimental conditions**: Amount of resin in column: 1.0 gm, Concentration of metal ions: 10 µg mL^{-1}; U(VI): pH: 8.0; Th(IV): pH: 4.5; La(III): pH: 5.5; Ce(III): pH: 9.0]

Table 1. Parameters optimized for sorption and desorption of U(VI), Th(IV), La(III) and Ce(III) on resin

No.	Parameters	Resin			
		U(VI)	**Th(IV)**	**La(III)**	**Ce(III)**
1	**pH range**	8.0	4.5	5.5	9.0
2	**Flow rate (mL Min-1)**	2.0	1.5	1.0	1.0
3	**Concentration of acid for desorption**	2.0 N HNO_3	2.0 N HCl	1.5 N HNO_3	1.0 N HCl
4	**Total sorption capacity (µg gm-1 of resin)**	1,74,460	1,53,450	84,680	86,400
5	**Distribution coefficient (Kd)**	29,064	25,573	14,225	14,400
6	**Preconcentration factor (PF)**	117	105	90	95
7	**Breakthrough capacity (µg gm-1 of resin)**	62,805	55,242	29,638	31,104
8	**Average recovery (%)**	98	97-98	99	98-99
9	**t1/2 for exchange (minutes)**	6.0	8.0	9.5	10.0
10	**Relative standard deviation (%)**	1.3	1.2	1.5	1.7

3.2.3. Effect of Concentration of Eluting Agents

To evaluate the influence of eluant type and its concentration on desorption of the analyte, 1.0 gm resin in the column was conditioned at pH of maximum extraction and then fed with 100 mL solution of each U(VI), Th(IV), La(III) and Ce(III) with concentration of 10 µg mL^{-1}. For quantitative desorption of metal ions different concentrations of HNO_3 and HCl solutions were used, and the metal contents were determined by ICP-AES (Table 1 and Table 2). It was observed that quantitative elution was possible with of 2.0 N HNO_3 for U(VI), 2.0 N HCl for Th(IV), 1.5 N HNO_3 for La(III) and 1.0 N HCl for Ce(III) for the synthesized chelating resin.

3.2.4. Sorption Capacity and Distribution Coefficients

In order to show the applicability of resin for extraction of metal ions, the total sorption capacity of resin for U(VI), Th(IV), La(III) and Ce(III) was determined using the batch technique. At optimum pH conditions, the chelating resin (0.5 gm) was equilibrated with the excess of metal ion solution (100 mL, 2000 µg.gm^{-1}) by shaking for 1 h. The amount of metal ions sorbed on the resin was calculated from the difference in the metal ion concentration in the solution before and after sorption by ICP-AES. The total sorption capacity of the resin was found to be 1,74,460 μg.gm^{-1}, 1,53,450 μg.gm^{-1}, 84,680 μg.gm^{-1} and 86,400 μg.gm^{-1} for U (VI), Th(IV), La(III) and Ce(III), respectively (Table 1).

Table 2. Effect of concentration of eluting agents for desorption of U(VI), Th(IV), La(III) and Ce(III) from resin. [Experimental conditions: Resin: 1.0 gm; Volume of solution passed: 100 mL; Metal Ions: 10 μg ml^{-1} U(VI):pH 8.0 ; Th(IV): pH 4.5; La(III): pH 5.5; Ce(III): pH 9.0}]

Resin								
Conc. (N)	**HCl**				**HNO$_3$**			
	U(VI) (%)	**Th(IV) (%)**	**La(III) (%)**	**Ce(III) (%)**	**U(VI) (%)**	**Th(IV) (%)**	**La(III) (%)**	**Ce(III) (%)**
0.01	2.5	20.4	10.2	25.7	22.2	5.0	3.2	15.2
0.05	7.5	25.4	10.5	45.8	45.7	15.5	21.3	35.1
0.1	10.2	45.4	15.7	75.5	72.3	21.7	34.8	64.1
0.5	12.0	62.1	35.6	85.4	82.5	40.5	50.2	82.5
0.7	14.8	73.5	42.3	90.2	85.5	65.0	65.3	90.5
1	15.9	80.1	75.2	99.4	90.2	75.5	80.2	95.7
1.5	28.0	89.2	96.7	99.4	95.2	97.5	99.7	96.3
2	45.3	99.8	97.8	99.5	99.7	97.6	99.7	98.5
2.5	60.9	99.9	98.1	99.6	99.8	98.1	99.7	98.5

Exchange equilibria are very often expressed in terms of the distribution coefficient K_d. This quantity is given by the ratio of the equilibrium concentrations of the same metal ion in the resin phase and in the solution.

$$V_d - \frac{\text{Amount of the metal ion taken up by the resin}}{\text{Amount of the metal ion remaining in the solution}}$$

$$\vee \frac{\text{Volume of the solution}}{\text{Amount of resin taken}}$$

The distribution coefficient K_d of the metal ions was determined by batch method. 0.5 gm resin was equilibrated with 100 mL solution containing not more than 872.3, 767.2, 423.4, 432 μg mL^{-1} of U(VI), Th(IV), La(III) and Ce(III) for 1 hour at room temperature. The solution was filtered, and the filtrate was subjected to ICP-AES for determination of the metal ion content (Table 1). K_d for U(VI), Th(IV), La(III) and Ce(III) of chelating resin was found to be 29064, 25573, 14225, 14400, respectively.

3.2.5. Exchange Kinetics

To determine the rate of loading of U(VI), Th(IV), La(III) and Ce(III) on resin, 1.0 gm resin was stirred with 100 mL of solution containing 1744.6, 1534.5, 846.0, 864.0 μg mL^{-1} of U(VI), Th(IV), La(III) and Ce(III) for resin at room temperature. Aliquots of 1.0 mL solution was withdrawn at predetermined intervals and analyzed by ICP-AES. The amount of metal ions loaded on the resin phase was calculated by difference in the concentration of aqueous solution. The time taken ($t_{1/2}$) for the sorption of 50% of the metal ions loaded on to the resin was found to be 6.0, 8.0, 9.5 and 10.0 minutes for U(VI), Th(IV), La(III) and Ce(III) (Table 1, Figure 4), indicates good accessibility of these metal ions towards chelating sites.

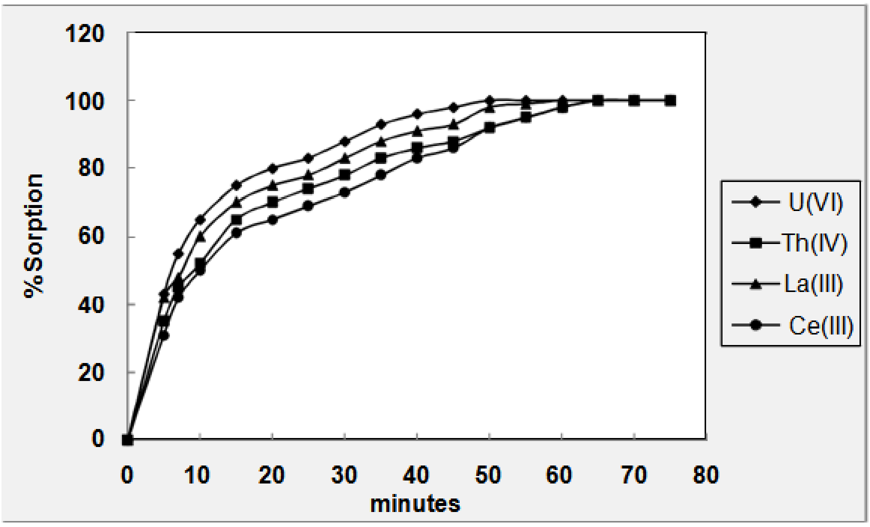


Figure 4. Exchange kinetics of U (VI), Th(IV), La(III) and Ce(III) on the resin. **[Experimental conditions**: Amount of the resin: 1.0 gm; volume of the feed solution: 100 mL; U(VI): 1774.5 μg mL^{-1}; pH: 8.0; Th(IV): 1534.5 μg mL^{-1}; pH: 4.5; La(III): 846.0 μg mL^{-1}; pH: 5.5 ; Ce(III): 864.0 μg mL^{-1}; pH: 9.0]

3.2.6. Breakthrough Capacities of Resin for Metal Ions

Breakthrough capacity is the capacity at the moment when the analyte to be extracted, starts appearing in the effluent. It is significant for chromatographic separation as well as preconcentration of elements and one of the most critical parameters when working under dynamic conditions.

Breakthrough studies were carried out by column method by taking 1.0 gm resin and passing 100 μg.gm^{-1} of metal ions [U(VI), Th(IV), La(III) and Ce(III)] at their optimum pH and flow rate. An aliquot of 25 mL eluant was collected each time and analyzed by ICP-AES for the metal ion content. Breakthrough capacity of resin for U(VI), Th(IV), La(III) and Ce(III) was found to be 62,805, 55242, 29638, 31104 μg.gm^{-1}, respectively (Table 1, Figure 5).

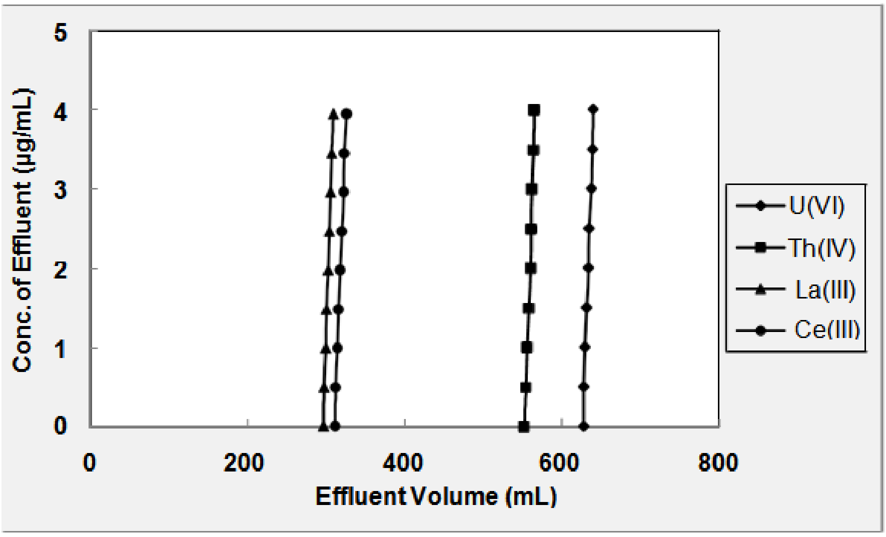


Figure 5. Breakthrough curve for U(VI), Th(IV), La(III) and Ce(III) on the resin. **[Experimental conditions**: Amount of the resin: 1.0 gm; concentration of the metal ion solution passed: 100 μg mL^{-1}; U(VI): 8.0pH ; Th(IV): 4.5pH, La(III): pH 5.5; Ce(III): pH 9.0]

3.2.7. Stability and Reusability of Resin

Accuracy and reproducibility in analytical data is a challenging task when reusing the same resin. To evaluate the resin's stability, repeated cycles of sorption and desorption of U(VI), Th(IV), La(III) and Ce(III) at their optimum conditions through a batch process were performed. 0.5 gm of resin was stirred with 100 mL solution containing 1000 μg.mL^{-1} metal ions at room temperature. Metal ions were then stripped off from resin with 25 mL of suitable eluant. The same experiment was repeated with same resin, and it was observed that resin showed very good stability up to 8-10 cycles of sorption and desorption, after which it showed 3-4% decrease in efficiency, which may be attributed due to the oxidation or breaking of chelating sites in the organic moiety when treated with mineral acids (Figure 6).

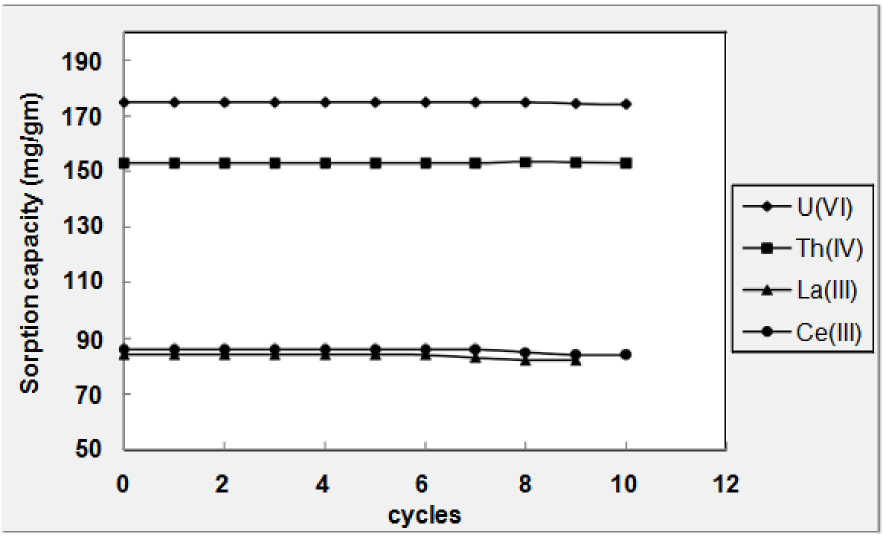


Figure 6. Stability of the resin for U(VI), Th(IV), La(III) and Ce(III) by Sorption and Elution. **[Experimental condition**: Amount of the resin in the column: 1.0 gm; volume of the feed solution: 100 mL; concentration of feed solution: 1000 μg mL^{-1}; U(VI): pH 8.0; elution by 2.0 N HNO_3; Th(IV): pH 4.5; elution by 2.0 N HCl ; La(III): pH 5.5; elution by 1.5 N HNO_3; Ce(III): pH 9.0; elution by 1.0 N HCl]

3.2.8. Preconcentration of U(VI), Th(IV), La(III) and Ce(III)

The preconcentration factor is one of the most important parameters to evaluate the performance of solid phase extraction methodologies.

$$PF = \frac{\text{Concentrat ion of metal in stripping solution}}{\text{Initial concentrat ion of metal in feed solution}}$$

To study preconcentration factor of U(VI), Th(IV), La(III) and Ce(III) for resin, 1000 mL solutions containing 10 μg L^{-1} U(VI), Th(IV), La(III) and Ce(III) at pH 8.0, 4.5, 5.5 and 9.0, respectively, were passed through the column containing 1.0 gm resin. Metal contents in the stripped solution were determined by ICP-AES. The preconcentration ability of the resin was assessed from the elution profile of the metals by plotting the amount of metal ions as a function of the volume of stripping solution. It was found that only 8.5 mL, 2.0 N HNO_3 for U(VI); 9.5 mL, 2.0 N HCl for Th(IV); 11.0 mL, 1.5 N HNO_3 for La(III); 10.5 mL, 1.0 N HCl for Ce(III) was required for quantitative recovery. The preconcentration factor or resin was found to be 117, 105, 90, and 95 for U(VI), Th(IV), La(III) and Ce(III) with 98-99 % recovery (Table 1, Table 3 and Figure 7).

Table 3. Preconcentration factors for the sorption of U(VI), Th(IV), La(III) and Ce(III) on resin. [Experimental conditions: Resin: 1.0 gm; U (VI): pH 8.0; Elution by 2.0 N HNO_3; Th(IV): pH 4.5; Elution by 2.0 N HCl; La(III): pH 5.5; Elution by 1.5 N HNO_3; Ce(III): pH 9.0; Elution by 1.0 N HCl

Metal ions	Volume of solution passed (mL)	Concentration of feed solution (µg L^{-1})	Volume of eluted solution (mL)	Recovery (%)	Preconcentration Factor (PF)
Resin					
U(VI)	1000	10	8.5	98	117
Th(IV)	1000	10	9.5	98-99	105
La(III)	1000	10	11.0	98-99	90
Ce(III)	1000	10	10.5	98	95

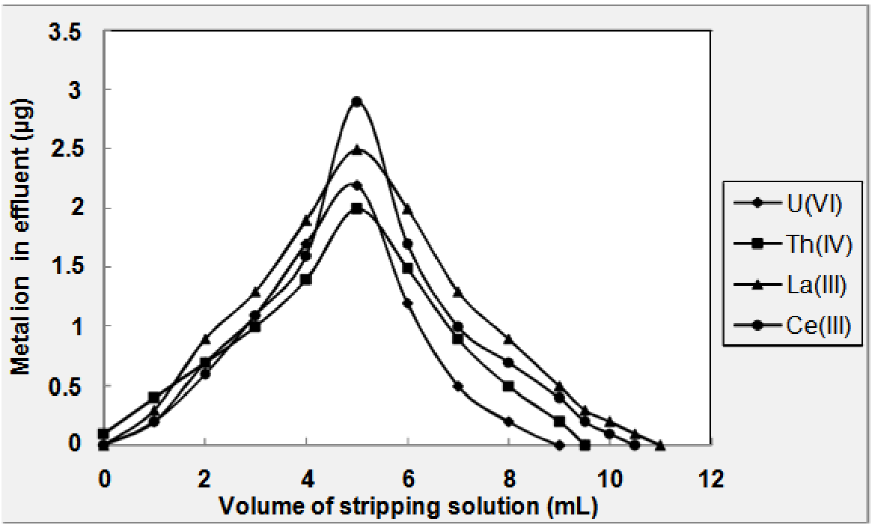


Figure 7. The elution profile of U(VI), Th(IV), La(III) and Ce(III) on the resin. **[Experimental conditions**: Amount of the resin 1.0 gm; concentration of the solution passed: 1000 mL: 10 µg L^{-1}; U(VI) pH 8.0: elution by 2.0 N HNO_3; Th(IV): pH 4.5; elution by 2.0 N HCl; La(III): pH 5.5; elution by 1.5 N HNO_3; Ce(III): pH 9.0; elution by 1.0 N HCl]

3.2.9. Effect of Electrolytes

The effect of several anions was studied for the sorption of U(VI), Th(IV), La(III) and Ce(III) by column experiments. The limit of tolerance of anions on the sorption of U(VI), Th(IV), La(III) and Ce(III), is defined as that concentration which causes an error of 2-3% in the recovery of these metal ions. The effect of different anions and their limit of tolerance on the sorption of U(VI), Th(IV), La(III) and Ce(III) by resin was studied by taking different concentrations of electrolytes like NaCl, NaF, NaBr, $NaNO_2$, Na_2SO_4, Na_3PO_4, and CH_3COONa (Table 4). It was concluded that except NaF and Na_3PO_4, other electrolytes did not interfere between 1.5-3.5 M concentration ranges, which further extend the possible application of resin for the analysis of real samples.

Table 4. Tolerance limits of electrolytes on the sorption of U(VI), Th(IV), La(III) and Ce(III) on resin. [Experimental conditions: Resin: 1.0 gm; Volume of solution passed: 100 ml; U(VI):pH 8.0; Th(IV): pH 4.5; La(III): pH 5.5; Ce(III): pH 9.0]

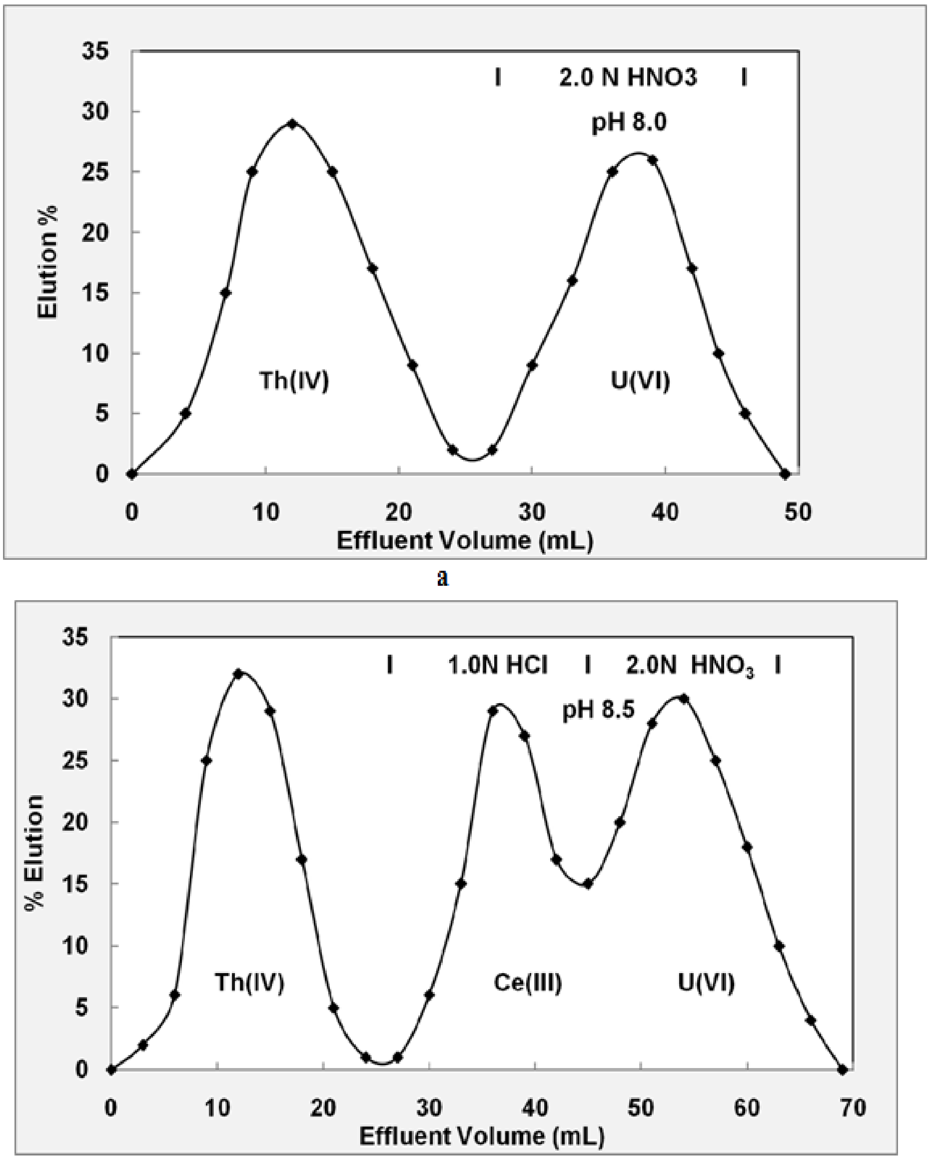
Metal ions	Concentrations of Electrolytes (mol L^{-1})						
(2.5 (µg mL^{-1})	NaF	NaCl	NaBr	$NaNO_2$	Na_2SO_4	Na_3PO_4	CH_3COONa
Resin							
U(VI)	1.0	1.5	2.0	2.5	1.7	1.0	1.5
Th(IV)	1.4	2.0	1.6	3.0	1.9	1.1	1.9
La(III)	1.2	1.6	1.9	2.1	2.0	1.3	2.2
Ce(III)	1.3	2.5	2.9	3.2	1.6	1.0	2.0

3.3. Chromatographic Separations

The binary and ternary mixtures of U(VI), Th(IV), La(III) and Ce(III) can be separated by selective adjustment of the pH and eluting agents. The following mixtures (100 µg in 25 mL buffer solution) were passed through the column at pH of maximum extraction and optimum flow rate. The amounts of metal ions in the column effluents were analyzed by spectrophotometry/ICP-AES.

3.3.1. Separation of a Binary Mixture

100 µg each of U(VI) and Th(IV) was passed through the column maintained at pH 8.0 and flow rate of 1.0 mL min^{-1}. At 8.0 pH, Th(IV) does not get sorbed on the resin, so it came out with the effluent while U(VI) was retained in the column which was eluted with 15 mL, 2.0 N HNO_3. Quantitative separation was achieved in the binary mixture as shown in their separation pattern in Figure 8(a).



a

b

Figure 8(a). Separation of U(VI) and Th(IV) on the resin. **[Experimental conditions**: Amount of resin: 1.0 gm; column maintained at pH 4.5; 100 µg in 25 mL buffer; Th(IV): 100 µg in 25 mL buffer ;U(VI); Total volume: 50 mL], **(b).** Separation of U(VI), Th(IV) and Ce(III) on the resin. **[Experimental conditions**: Amount of resin: 1.0 gm; column maintained at pH 8; Th(IV): 100 µg in 25 mL buffer; U(VI): 100 µg in 25 mL buffer; Ce(III): 100 µg in 25 mL buffer; total volume: 75 mL]

3.3.2. Separation of a Ternary Mixture

100 µg each of U(VI), Th(IV) and Ce(III) was passed through the column maintained at pH 8.5 with 1.0 mL min^{-1} of flow rate. At this pH, Th(IV) was not sorbed on resin, and it came out with the effluent while U(VI) and Ce(III) were retained in the column and then separated on the basis of selective eluting agents. Ce(III) was eluted first with 20mL, 1.0 N HCl followed by U(VI) with 15mL, 2.0 N HNO_3. Quantitative separation was achieved in the ternary mixture as shown in their separation pattern in Figure 8(b).

3.4. Application to Analysis of Monazite Sand and Geological Samples

In recent year many applications in the field of calix system. The applicability of the proposed method in the determination of U(VI), Th(IV), La(III) and Ce(III) by resin was subjected to monazite sand and standard geological samples. The standard geological materials USGS: BCR-1, USGR: GSP-1 [46] were decomposed in mixture of acids as described. 0.1 gm of monazite sand sample was digested with conc. H_2SO_4 at 250℃ for 4 h. Further, it was digested using 5 mL of HF followed by conc. HNO_3 to remove excess HF. Subsequently, the digested solution was evaporated to dryness, and the residue was redissolved in minimal volumes of diluted HCl and passed through the resin column [47]. The calix system has the ability to bind to metal ions and act as a fluorescence sensorThe results are tabulated in Table 5.

Table 5. Determination of U(VI), Th(IV), La(III) and Ce(III) in Monazite Sand and standard geological samples. [Experimental conditions: Resin: 1.0 gm; Sample volume: 1000 mL] Determination of U(VI), Th(IV), La(III) and Ce(III) in monazite sand and U.S. standard geological samples by chelating resin

Sample	**Metal ions**			
	U(VI)	**Th(IV)**	**La(III)**	**Ce(III)**
Monazite Sand Travancore, India (%)	0.019 0.001	8.40±0.07	23.96 ± 0.60	42.74 ± 0.43
USGS: BCR-1 (μg.g-1)	1.705 ±0.004	6.1 ±0.1	27.27 ±0.46	52.70 ±0.40
USGR:GSP-1 (μg.g-1)	2.10 ±0.02	104.0 ±1.5	180.5 ±2.3	397.0 ±2.8

Table 6. Comparable methods for preconcentration and determination of U(VI), Th(IV), La(III) and Ce(III)

SPE Materials	**Sorption Capacity (ug gm-1)**				**Preconcentration Factor**				**Reference**
	U(VI)	**Th(IV)**	**La(III)**	**Ce(III)**	**U(VI)**	**Th(IV)**	**La(III)**	**Ce(III)**	
XAD $_{4}$ - HA		34.8				99			[48]
Aliquat-336 - Amberlite XAD-4			4730						[12]
Amberlite XAD-4-OVSC	2890	3230	2300	2480	125	120	95	97	[34]
Merrifield polymer-DB2EHMA	62500	38200							[49]
ChloromethylatedMerrifield resin -DMDBMA	18780	15740							[50]
Amberlite XAD-2-Tiron	76169				150				[35]
Merrifield resin-calix[4]arene-ovanillinsemicarbazone	48734	41175	25190	28143	143	153	153	133	[4]
Polymer supported calix[4]arene- semicarbazone	3033	2831	1875.5	1443.03	97-98	98	125	130	[51]
Amberlite XAD-4 Succinic acid	12330				100				[52]
2-nitroso-1-naphthol - MCI GEL CHP20P					20				[53]
Amberlite XAD-16-ADHA	164700								[54]
Amberlite XAD-16-octa carboxy methyl-*c*-methyl			10418	11629			125	83	[36]
Calix [4] resorcinarene **octa-*O*-methoxy resorcin[4]arene Amberlite XAD-4 polymeric chelating resin**	**1,74,460**	**1,53,450**	**84,680**	**86,400**	**117**	**105**	**90**	**95**	

3.5. Comparison with Other Solid Phase Extraction Methods

The present method shows higher sorption capacity and preconcentration factor in comparison to various adsorbents (Table 6) showing that resin have high sorption capacity and good preconcentrating ability for U(VI), Th(IV), La(III) and Ce(III) metal ions.

4. Conclusion

Octa-*O*-methoxy resorcin[4]arene, third-generation supramolecule, is covalently linked with Amberlite XAD-4 resin through -N=N- group to yield a new polymeric resin which has been duly characterized. The resin was found to be highly selective in extracting the U(VI), Th(IV), La(III) and Ce(III) in the presence of various electrolytes at a particular pH. The resin was found to exhibit faster exchange kinetics, good breakthrough capacity, high sorption capacity, reusability and preconcentration factors, thereby it was successfully used in the separation of U(VI), Th(IV) and Ce(III) from their binary and ternary mixtures by control of pH or gradient elution. The reliability of the proposed method which is simple, sensitive and selective was checked by the determination of U(VI), Th(IV), La(III) and Ce(III) from monazite sand and standard geological samples.

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References

[1] R. Keim, Springer-Verlag, Berlin, 1983.

[2] S. Zhang, P. Liu, B. Zhang, World Nuclear Geoscience, 2 (2005).

[3] Y. Shen, S. Wang, L. Zhu, J. Wang, W. Wu, Industrial & Engineering Chemistry Research, 50 (2011) 13990.

[4] V.K. Jain, R.A. Pandya, S.G. Pillai, P.S. Shrivastav, Talanta, 70 (2006) 257.

[5] A. Dufresne, G. Krier, J.F. Muller, B. Case, G. Perrault, Science of the total environment, 151 (1994) 249.

[6] J.B. Ghasemi, E. Zolfonoun, Talanta, 80 (2010) 1191.

[7] A. Trovarelli, Catalysis by ceria and related materials, Imperial College Pr, 2002.

[8] E.P. Horwitz, M.L. Dietz, D.M. Nelson, J.J. LaRosa, W.D. Fairman, Analytica chimica acta, 238 (1990) 263.

[9] L. Spjuth, J.O. Liljenzin, M.J. Hudson, M.G.B. Drew, P.B. Iveson, C. Madic, Solvent Extraction and Ion Exchange, 18 (2000) 1.

[10] Y. Sasaki, S. Tachimori, Solvent Extraction and Ion Exchange, 20 (2002) 21.

[11] S. Lawroski, 1955.

[12] E.A. El-Sofany, Journal of hazardous materials, 153 (2008) 948.

[13] J. Korkisch, Handbook of ion exchange resins: their application to inorganic analytical chemistry, CRC, 1988.

[14] A. Mizuike, (1983).

[15] M. Merdivan, M.Z. Düz, C. Hamamci, Talanta, 55 (2001) 639.

[16] Z. Mester, R. Sturgeon, J. Pawliszyn, Spectrochimica Acta Part B: Atomic Spectroscopy, 56 (2001) 233.

[17] S. Caroli, A. Alimonti, F. Petrucci, Z. Horváth, Analytica chimica acta, 248 (1991) 241.

[18] E.M. Thurman, M.S. Mills, Solid-phase extraction: principles and practice, Wiley New York, 1998.

[19] F.A. Aydin, M. Soylak, Talanta, 73 (2007) 134.

[20] F. Shemirani, A.A. Mirroshandel, M. Salavati Niasari, R. Rahnama Kozani, Journal of Analytical Chemistry, 59 (2004) 228.

[21] Z. Fan, B. Hu, Z. Jiang, Spectrochimica Acta Part B: Atomic Spectroscopy, 60 (2005) 65.

[22] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta, 58 (2002) 831.

[23] J. Otero-Romaní, A. Moreda-Piñeiro, A. Bermejo-Barrera, P. Bermejo-Barrera, Analytica chimica acta, 536 (2005) 213.

[24] G. Absalan, M.A. Mehrdjardi, Separation and purification technology, 33 (2003) 95.

[25] M. Benamor, Z. Bouariche, T. Belaid, M.T. Draa, Separation and purification technology, 59 (2008) 74.

[26] S. Tokahoglu, V. Cetin, S. Kartal, Chemia analityczna, 53 (2008) 263.

[27] S. Boussetta, C. Branger, A. Margaillan, J.L. Boudenne, B. Coulomb, Reactive and Functional Polymers, 68 (2008) 775.

[28] N. Rajesh, R.K. Jalan, P. Hotwany, Journal of hazardous materials, 150 (2008) 723.

[29] J.M. Traviesa-Alvarez, J.M. Costa-Fernandez, R. Pereiro, A. Sanz-Medel, Analytica chimica acta, 589 (2007) 51.

[30] L. Elci, D. Sahan, A. Basaran, M. Soylak, Environmental monitoring and assessment, 132 (2007) 331.

[31] C.H. Lee, M.Y. Suh, K.S. Joe, T.Y. Eom, W. Lee, Analytica chimica acta, 351 (1997) 57.

[32] K. Dev, R. Pathak, G.N. Rao, Talanta, 48 (1999) 579.

[33] M. Kumar, D.P.S. Rathore, A.K. Singh, Microchimica Acta, 137 (2001) 127.

[34] V.K. Jain, A. Handa, S.S. Sait, P. Shrivastav, Y.K. Agrawal, Analytica chimica acta, 429 (2001) 237.

[35] M. Kumar, D.P.S. Rathore, A.K. Singh, Analyst, 125 (2000) 1221.

[36] C. Gok, S. Seyhan, M. Merdivan, M. Yurdakoc, Microchimica Acta, 157 (2007) 13.

[37] M. Soylak, N.D. Erdogan, L. Elci, journal of chinese chemical society, 51 (2004) 703.

[38] N. Demirel, M. Merdivan, N. Pirinccioglu, C. Hamamci, Analytica chimica acta, 485 (2003) 213.

[39] J.G. Crock, R.C. Severson, S. Geological, Four reference soil and rock samples for measuring element availability in the western energy regions, US Department of the Interior, Geological Survey, 1980.

[40] D. Moore, G.W. Watson, T. Gunnlaugsson, S.E. Matthews, New Journal of Chemistry, 32 (2008) 994.

[41] V.K. Jain, H.C. Mandalia, H.S. Gupte, D.J. Vyas, Talanta, 79 (2009) 1331.

[42] Bharat A. Makwana, Disha J. Vyas, Keyur D. Bhatt, Vinod K. Jain, Yadvendra K. Agrawal, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 134 (2015) 73

[43] Keyur D. Bhatt, Bharat A. Makwana, Disha J. Vyas, Divya R. Mishra, Vinod K. Jain, Journal of Luminescence146(2014)450-457.

[44] Keyur D. Bhatt, Disha J. Vyas, Bharat A. Makwana, Savan M. Darjee, Vinod K. Jain Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121 (2014) 94-100.

[45] Keyur D. Bhatt & Hrishikesh S. Gupte & Bharat A. Makwana & Disha J. Vyas & Debdeep Maity & Vinod K. Jain, J Fluoresc (2012) 22:1493-1500.

[46] S.J. Hill, Inductively Coupled Plasma Spectrometry and its Applications, Academic Press, Sheffield, 1999.

[47] S. Seyhan, M. Merdivan, N. Demirel, Journal of hazardous materials, 152 (2008) 79.

[48] S. Erdogan, M. Merdivan, C. Hamamci, O. Akba, A. Baysal, Analytical letters, 37 (2004) 2565.

[49] D. Prabhakaran, M.S. Subramanian, Talanta, 65 (2005) 179.

[50] S.A. Ansari, P.K. Mohapatra, V.K. Manchanda, Journal of hazardous materials, 161 (2009) 1323.

[51] V.K. Jain, A. Handa, R. Pandya, P. Shrivastav, Y.K. Agrawal, Reactive and Functional Polymers, 51 (2002) 101.

[52] P. Metilda, K. Sanghamitra, J. Mary Gladis, G.R.K. Naidu, T. Prasada Rao, Talanta, 65 (2005) 192.

[53] F.A. Aydin, M. Soylak, Journal of hazardous materials, 173 (2010) 669.

[54] M.A. Maheswari, M.S. Subramanian, Solvent Extraction and Ion Exchange, 23 (2005) 249.