Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Amberlite XAD-2 Impregnated with Cyanex302 for Separation of Traces of Thorium(IV)

Manjusha Karve[a]; Reeta V. Rajgor[a]
[a] Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai, India

To cite this Article Karve, Manjusha and Rajgor, Reeta V.(2007) 'Amberlite XAD-2 Impregnated with Cyanex302 for Separation of Traces of Thorium(IV)', Separation Science and Technology, 42: 10, 2255 — 2273
To link to this Article: DOI: 10.1080/01496390701310439
URL: http://dx.doi.org/10.1080/01496390701310439

Separation Science and Technology, 42: 2255–2273, 2007
Copyright © Taylor & Francis Group, LLC
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701310439

Amberlite XAD-2 Impregnated with Cyanex302 for Separation of Traces of Thorium(IV)

Manjusha Karve and Reeta V. Rajgor
Department of Chemistry, University of Mumbai, Vidyanagari,
Mumbai, India

Abstract: Amberlite XAD-2 resin impregnated with Cyanex302 has been used to separate and preconcentrate thorium(IV) from associated elements prior to its spectrophotometric determination. The impregnated resin (HL-XAD-2) was characterized by IR spectra. A column packed with HL-XAD-2 was used to understand sorption and desorption behaviour of thorium(IV). The effect of various parameters such as acidity of aqueous phase, nature and concentration of eluting agents, eluent volume and its flow rate were evaluated to optimize conditions for isolation of thorium(IV). Adsorption characteristics of thorium(IV) on HL-XAD-2 in batch studies indicated that the data fit well in Langmuir and Freundlich adsorption isotherm models. The maximum sorption capacity of the modified resin for thorium(IV) was 8.48 mmol g^{-1} while the limit of detection ($3\sigma_B$) was 0.75 $\mu g\ dm^{-3}$. A preconcentration factor greater than 100 was achieved. The influence of diverse ions on extraction of thorium(IV) was examined and the method developed was applied for the separation of thorium(IV) from synthetic mixtures and monazite sand. The method is reproducible with a relative standard deviation (R.S.D.) of 0.6%.

Keywords: Solid phase extraction, thorium, Cyanex302, Amberlite XAD-2

INTRODUCTION

Thorium has a wide range of applications due to its characteristic physical and chemical properties. It is used in the manufacture of mantles, ceramics,

Received 18 August 2006, Accepted 26 January 2007

Address correspondence to Manjusha Karve, Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai-400 098, India. Fax: +91 22 26528547; E-mail: mkarve@yahoo.com or manjusha@chem.mu.ac.in

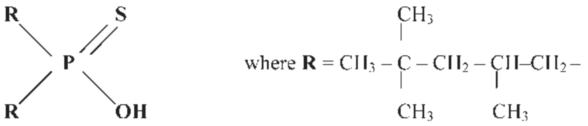
alloys, high quality glasses, electronics, scientific instruments, and finds use in the aerospace industry. It is also used as an important source for nuclear energy.

Several methods exist for the separation and isolation of thorium due to its industrial importance and toxic effects. Monazite sand is a major source of thorium, while some silicate rocks (1) like cheralite, yttrocrasite, iraquite etc. contain traces of it. The accurate and sensitive determination of thorium in such complex matrices necessitates a separation step prior to its detection (2). An analysis of geological and environmental samples for thorium using liquid-liquid extraction, ion exchange, flotation, solid phase extraction, cloud point extraction, co-precipitation, and ion imprinted polymers was recently reviewed (3).

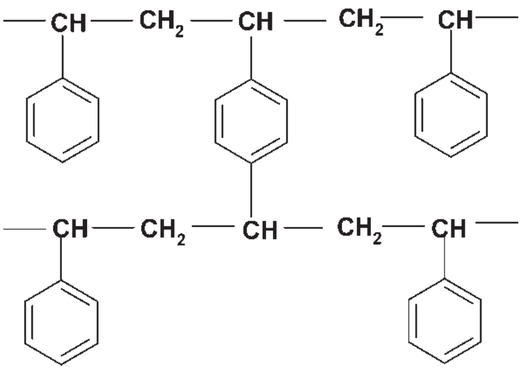
The inherent limitations of the methods based upon solvent extraction are the high costs of solvents and the environmental concerns regarding their disposal. Hence, solid phase extraction methods based upon the binding of chelating groups to solid supports were proposed as an alternative to overcome these drawbacks of liquid-liquid extraction. The separation, preconcentration, and determination of metal ions at trace levels has been successfully accomplished using polymeric resins modified with selective ligands (4, 5). A simple and interesting approach involving the physical rather than the chemical interactions for the preparation of the solid phase is based upon the impregnation of a suitable extractant onto a polymer resin. The high distribution coefficients amenable with well-established extractants and multistage process operative in column chromatography can thus be advantageously used for selective separation. Amberlite XAD series resins containing various liquid cation exchangers were studied to understand the kinetics and mechanism of the sorption process (6–10). Cyanex272 (bis(2,4,4-trimethylpentyl)phosphinic acid) and Cyanex302 (bis(2,4,4-trimethylpentyl)monothiophosphinic acid) impregnated on Amberlite XAD series resins were reported for the extraction separation of iron(III), nickel(II), cadmium(II), and copper(II) (11, 12). So far, no reports have appeared on the use of solid phase extraction using Amberlite XAD-2 impregnated with Cyanex302 for the separation and the recovery of thorium. The chemical structure of Cyanex302 and Amberlite XAD-2 resin is as follows (Scheme 1):

Amberlite XAD-2 has structural rigidity, good mechanical stability and zero or minimal expansion in organic solvents (13). Cyanex302 has low aqueous solubility and high resistance to hydrolysis (14) hence less chances for extractant losses to the aqueous phase during successive cycles.

The present report focuses on systematic investigations for sorption and desorption of thorium(IV) on a column packed with Amberlite XAD-2 impregnated with Cyanex302 (HL-XAD-2). The impregnation of Cyanex302 on Amberlite XAD-2 was characterized by FT-IR spectroscopy and investigated systematically to devise the optimum conditions for recovery of thorium(IV).



Cyanex302



Scheme 1. Amberlite XAD-2: A styrene divinyl benzene co polymer.

The reusability and reproducibility of the column packed with HL-XAD-2 for thorium(IV) determination was also checked. The practical applicability of the method developed was checked for the determination of thorium in some synthetic mixtures and monazite sand.

EXPERIMENTAL

Instrumentation

A Digispec 110-D visible spectrophotometer, Feedback India Ltd., and a Perkin Elmer atomic absorption spectrophotometer, AAnalyst200 were employed for determining metal ion concentration. An Elico LI-120 digital pH meter, Elico India Ltd., was used for pH adjustments. A Perkin Elmer Spectrum one FT-IR spectrometer and an inductively coupled plasma atomic emission spectrophotometer, ICP-AES GBC 8440 plasma lab were also used.

Chemicals and Reagents

A stock solution of thorium(IV) 2.5 mg cm^{-3} was prepared by dissolving appropriate quantity of thorium sulphate (Loba Chemie) in slightly acidified distilled water. The solution was standardized volumetrically (15), and a working solution containing 20 μg cm^{-3} thorium(IV) was prepared by appropriate dilution. Arsenazo(III) (S.D. Fine chemicals) was prepared as a 0.100% (w/v) solution. Amberlite XAD-2 (20–60 mesh size, 330 m^2 g^{-1} average surface area) obtained from Supelco, Sigma Aldrich Co. was pretreated by washing with 2 M HNO_3, 2 M HCl, distilled water, and acetone to remove impurities and air dried prior to use (9). Cyanex302 obtained from Cytec Canada as a gift sample was used without purification. All chemicals and reagents used were of A.R. grade.

A 0.100 g sample of monazite sand was digested at 250°C with concentrated sulphuric acid followed by extraction with 1:10 H_2SO_4 (16), and then diluted to a suitable volume.

Preparation of Amberlite XAD-2 Impregnated with Cyanex302 and its Characterization by FT-IR

Cyanex302 (HL) was impregnated on Amberlite XAD-2(XAD-2) using the following procedure. 0.100 g of Cyanex302 in methanol and 0.100 g of Amberlite XAD-2 were mixed together until the solvent was almost evaporated and then kept overnight at ambient temperature.

The modified resin thus obtained (hence forth will be mentioned as HL-XAD-2) was characterized by IR spectroscopy. The IR spectra of Amberlite XAD-2 resin and HL-XAD-2 (Fig. 1) indicated only physical linkage between the extractant and the resin. This is evident from the existence of a characteristic band at 601.29 cm^{-1} due to P = S of Cyanex302 and very small shift in the frequency of the normal modes of methyl groups of Cyanex302 and the methyl, the methylene groups, and the benzene rings of Amberlite XAD-2. The spectra of HL-XAD-2 also showed the emergence of a new band near 1365.02 cm^{-1} due to the deformation of -C-H in the alkyl chain of Cyanex302 and bands in the region 1100 cm^{-1} − 1200 cm^{-1} and at 913.06 cm^{-1} arising from the stretching vibrations of P-O in the P-OH group and at 820.64 cm^{-1} due to $-P\text{-}CH_2$ bending. The sorption of thorium(IV) [Fig. 1(C)] on HL-XAD-2 was evident from the disappearance of the bands due to -P-OH in the region 1100cm^{-1} − 1200 cm^{-1} and P=S band at 601.29 cm^{-1}. These changes in the IR spectra of thorium(IV) sorbed on HL-XAD-2 are indications of involvement of P = S and P-OH bonds with thorium(IV).

Procedure for Column Method for Preconcentration and Determination of Thorium(IV)

HL-XAD-2 was uniformly packed in the glass column (150 mm length × 10 mm i.d.) having glass wool as supports. The general procedure for extraction of thorium(IV) was as follows: The column was preconditioned with 10–12 bed lengths of appropriate mineral acid before use. A 10 cm^3 solution containing

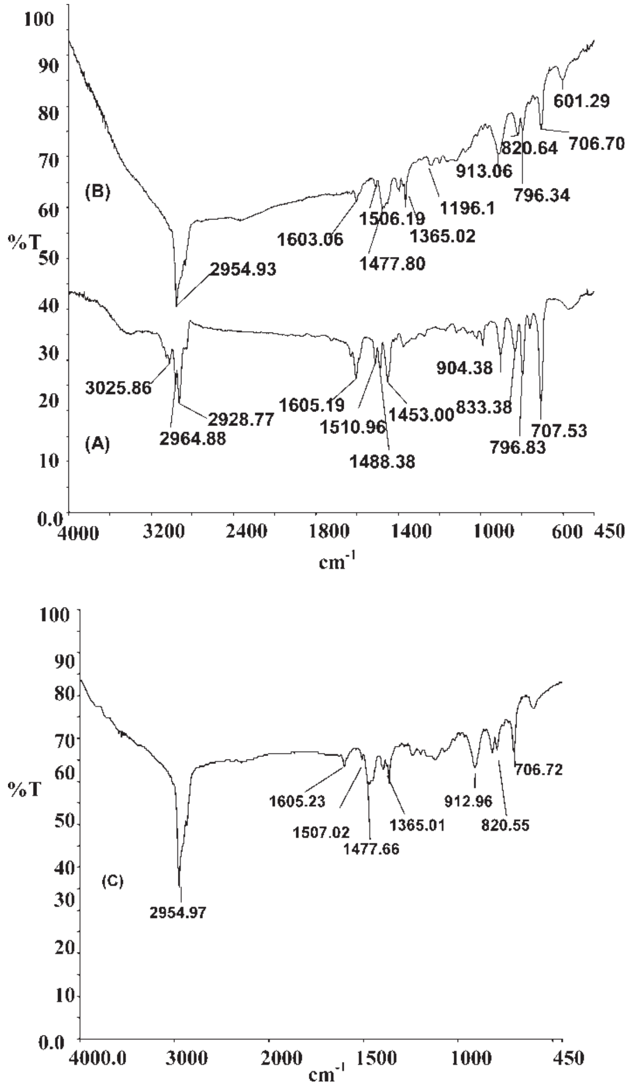


Figure 1. IR spectra of (A) Amberlite XAD-2 resin beads and (B) HL-XAD-2. (C) IR spectra of thorium(IV) sorbed on HL-XAD-2.

2 μg cm^{-3} thorium(IV) in 1×10^{-3} M HCl was passed through the column at the optimum flow rate of 1.0 cm^3 min^{-1}. Desorption of thorium(IV) from resin bed was carried out with 10 cm^3 of 4 M HCl at 0.4 cm^3 min^{-1} flow rate and the amount of thorium(IV) recovered was determined spectrophotometrically with Arsenazo(III) at 660 nm (17). The optimum conditions for quantitative sorption and desorption of thorium(IV) are presented in Table 1.

Table 1. Parameters optimized for sorption and desorption of thorium(IV)

Sr. no.	Parameters	Optimum condition
1.	Aqueous phase acidity	1×10^{-3} M HCl
2	Flow rate for sorption (cm^3 min^{-1})	1.0
3	Concentration of acid for desorption	4.0 M HCl
4	Flow rate for desorption (cm^3 min^{-1})	0.4
5	Total sorption capacity (mmol g^{-1})	8.48
6	Preconcentration factor	>100
7	Breakthrough volume (cm^3)	>1000
8	R.S.D. (%)	0.6
9	Average recovery (%)	99.1

RESULTS AND DISCUSSION

Optimization of Parameters for Sorption and Desorption of Thorium(IV)

1. Effect of amount of Cyanex302 impregnated on Amberlite XAD-2: Amberlite XAD-2 is hydrophobic in nature and an inadequate filling of its pores with an extractant has been reported to result in a lower distribution coefficient of metal on account of the hydrophilic nature of metal complexes (9). The amount of Cyanex302 necessary for quantitative sorption of thorium(IV) was optimized using 0.100 g of Amberlite XAD-2 resin loaded with different quantities of Cyanex302 (Fig. 2). It was observed that 0.100 g Amberlite XAD-2 impregnated with 0.100 g Cyanex302 was adequate for complete sorption (99.1 ± 0.6) of thorium(IV). Hence 0.100 g Amberlite XAD-2 impregnated with 0.100 g Cyanex302 (HL-XAD-2) packed in a column was used for further studies.
2. Effect of aqueous phase acidity: A solution containing 20 μg of thorium(IV) in different mineral acids was passed through a column packed with HL-XAD-2 at an optimum flow rate and desorbed using a suitable eluent (Table 1). Subsequent determination of thorium(IV) was done spectrophotometrically. The sorption of thorium(IV) was quantitative (99.1 ± 0.6%) with 1×10^{-3} M HCl as the aqueous phase (Fig. 3).
3. Effect of sample flow rate: The influence of the aqueous phase flow rate on the degree of sorption of thorium(IV) on HL-XAD-2 packed column was studied by passing 20 μg thorium(IV) in 1×10^{-3} M HCl at different flow rates (0.4–10.0 cm^3 min^{-1}). The sorption of thorium(IV) was 99.1 ± 0.6% using a sample flow rate 0.4–1.0 cm^3 min^{-1}. At a flow rate of 1.0 cm^3 min^{-1}, the column effluent did not contain more than 0.018 ± 0.012 μg cm^{-3} of thorium(IV). While the sorption of thorium(IV) on the column decreased with the sample flow rates greater

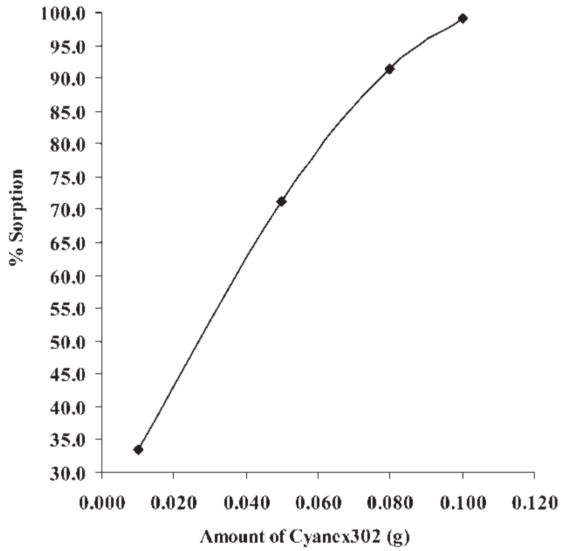


Figure 2. Effect of amount of Cyanex302 on thorium(IV) sorption. Experimental condition: Column packed with HL-XAD-2. Aqueous phase condition = 20 μg thorium(IV) in 10 cm^3 of 1×10^{-3} M HCl, at 1.0 cm^3 min^{-1} flow rate, Elution condition = 10 cm^3 of 4 M HCl, at 0.4 cm^3 min^{-1} flow rate.

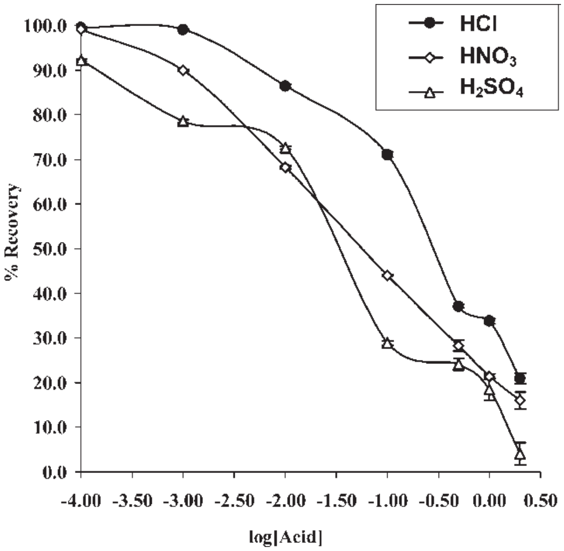


Figure 3. Effect of aqueous phase acidity on thorium(IV) sorption. Experimental condition: Column packed with HL-XAD-2, Aqueous phase condition = 20 μg thorium(IV) in 10 cm^3, at 1.0 cm^3 min^{-1} flow rate, elution condition = 10 cm^3 of 4 M HCl, at 0.4 cm^3 min^{-1} flow rate.

than 1.0 cm^3 min^{-1} due to its insufficient contact with HL-XAD-2. Hence an optimum flow rate of 1.0 cm^3 min^{-1} was selected for all studies.

4. Effect of concentration, volume, and flow rate of eluting agents: Various eluting agents were studied to optimize the conditions for desorption of thorium(IV) from the column (Table 2). A 10 cm^3 solution containing 2 μg cm^{-3} thorium(IV) was passed through a column under its optimum extraction condition (Table 1). Thorium(IV) was desorbed using different eluting agents and determined spectrophotometrically. The effect of the flow rate and volume of 4 M HCl for the recovery of thorium(IV) was also studied. It was observed that the recovery of thorium(IV) was incomplete with eluent volumes lower than 10 cm^3 and flow rates higher than 0.4 $cm^3 min^{-1}$. Thus the elution condition for quantitative desorption of thorium(IV) was 10 cm^3 of 4 M HCl at a flow rate of 0.4 cm^3 min^{-1}.
5. Breakthrough volume: The maximum volume of the sample solution which is just sufficient for quantitative sorption of thorium(IV) without any leakage is the breakthrough volume. A 10 cm^3 – 1000 cm^3 sample solution containing 20 μg thorium(IV) was passed through a column packed with HL-XAD-2 under the optimum conditions. The effluent from the column did not contain more than 0.018 ± 0.012 μg cm^{-3} thorium(IV), indicating that the breakthrough volume of HL-XAD-2 for thorium(IV) was greater than 1000 cm^3.
6. Preconcentration factor of thorium(IV): A 1000 cm^3 sample solution containing 20 μg thorium(IV) was passed through a column containing HL-XAD-2 at an optimum flow rate. Desorption with 10 cm^3 of 4 M HCl resulted in $99.1 \pm 0.6\%$ recovery of thorium(IV) (Table 1). Hence the enrichment of thorium(IV) was 100 times. Thus the method developed can be used for the determination of very low concentrations of thorium(IV).
7. Stability test of column: The stability and potential reusability of the HL-XAD-2 column was assessed by monitoring the recovery of thorium(IV) through several sorption – desorption cycles using the same column. A 10 cm^3 solution containing 20 μg thorium(IV) solution was passed through the column packed with HL-XAD-2 and desorbed with 10 cm^3 of 4 M HCl. It was observed that column was stable up to 50 cycles with a $99.1 \pm 0.6\%$ recovery of thorium(IV) (Fig. 4). This indicates a very high reusability and reliability of the modified resin for continuous usage.
8. Effect of diverse ions: The tolerance limits of various cations and anions for sorption of thorium(IV) was defined as the maximum amount of foreign ion required to cause ± 2% error in the recovery of thorium(IV). The sorption of thorium(IV) in the presence of other ions was carried out under the optimum conditions (Table 1). Thorium(IV) was preferentially sorbed in the presence of other commonly associated ions and very high tolerance limits were obtained. Cations like K^+, Ca^{2+} and Co^{2+} were tolerated in 1:175, 1:190, and 1:150 ratios respectively while $Mn^{2+}$was tolerated in 1:30 ratio. Na^+, Cu^{2+}, and Pb^{2+} were tolerated in 1:5 ratio, whereas Cd^{2+}, Nd^{3+}, and Y^{3+} were tolerated in

Table 2. Effect of eluents on recovery of thorium(IV)

Conc.[M] →	Recovery of thorium(IV) (%)$^{\pm a}$						
Eluents ↓	0.01	0.1	0.5	1.0	2.0	3.0	4.0
HNO_3	42.2 ± 0.1	71.1 ± 0.2	94.6 ± 0.4	96.3 ± 0.1	96.8 ± 0.3	—	—
HCl	41.3 ± 0.5	72.3 ± 0.2	94.8 ± 0.6	96.1 ± 0.1	96.9 ± 0.1	98.4 ± 0.3	99.1 ± 0.6
H_2SO_4	72.1 ± 0.2	76.6 ± 0.4	81.9 ± 0.3	84.9 ± 0.5	88.2 ± 0.6	96.3 ± 0.1	98.8 ± 0.2
$HClO_4$	5.0 ± 0.6	42.8 ± 0.2	65.7 ± 0.2	71.6 ± 0.2	81.7 ± 0.4	73.6 ± 0.4	69.9 ± 0.1
CH_3COOH	10.3 ± 0.3	10.9 ± 0.5	17.3 ± 0.3	30.3 ± 0.3	43.6 ± 0.1	50.7 ± 0.4	58.2 ± 0.4
$H_2C_2O_4$	91.9 ± 0.6	93.9 ± 0.5	95.7 ± 0.5	98.6 ± 0.1	97.1 ± 0.3	—	—
NaOH	10.8 ± 0.2	14.0 ± 0.2	25.1 ± 0.2	64.7 ± 0.2	67.8 ± 0.1	78.1 ± 0.3	81.3 ± 0.3
$(NH_4)_2CO_3$	21.4 ± 0.5	27.6 ± 0.2	61.1 ± 0.6	50.5 ± 0.2	40.0 ± 0.4	—	—

$^{\pm a}$ = %R.S.D. of six determinations.

Experimental condition: Column packed with HL-XAD-2.

Aqueous phase condition = 20 μg thorium(IV) in 10 cm^3 of 1×10^{-3} M HCl, at 1.0 cm^3 min^{-1} flow rate.

Eluent = 10 cm^3, at 0.4 cm^3 min^{-1} flow rate.

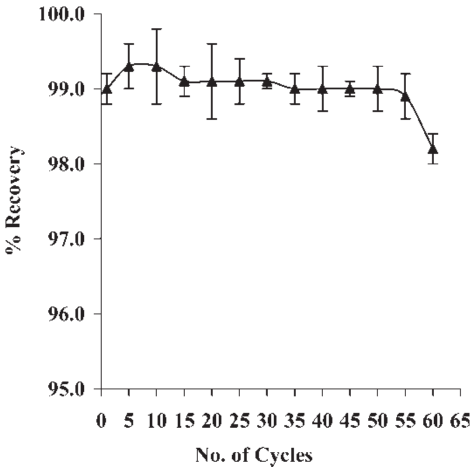


Figure 4. Column bed reusability. Experimental condition: Column packed with HL-XAD-2. Aqueous phase condition = 20 μg thorium(IV) in 10 cm^3 of 1×10^{-3} M HCl, at 1.0 cm^3 min^{-1} flow rate, elution condition = 10 cm^3 of 4 M HCl, at 0.4 cm^3 min^{-1} flow rate.

1:2 ratio. Ce^{4+}, Ni^{2+}, La^{3+}, and Zn^{2+} were tolerated in 1:3.5, 1:2.5, 1:1.5, and 1:1.25 ratio respectively but Mg^{2+}. Cr^{6+}, Dy^{3+}, Gd^{3+}, Pr^{3+}, Yb^{3+}, and U^{6+} were tolerated in 1:1 ratio. Anions like Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} were tolerated in 1:50 ratio.

9. Total sorption capacity of Amberlite XAD-2 impregnated with Cyanex302: The sorption capacity of HL-XAD-2 for thorium(IV) was determined by the following method. A 20 cm^3 solution containing 1–90 mg thorium(IV) in 1×10^{-3} M HCl was shaken for 20 minutes in a batch process. Thorium(IV) was then determined in the aqueous phase spectrophotometrically (Fig. 5). The maximum sorption capacity of the modified solid support for thorium(IV) was 8.48 mmol g^{-1} which was much higher than that reported with other modified solid supports (18–38).

Adsorption Isotherms for Thorium(IV) on Impregnated Resin

HL-XAD-2 and 20 cm^3 of 1×10^{-3} M HCl solutions containing 50–2,000 mg dm^{-3} of thorium(IV) were shaken in a stoppered bottle on a mechanical shaker for a predetermined equilibrium time of 20 minutes. The resin beads were filtered and the residual solution was analyzed for the determination of thorium(IV) concentration spectrophotometrically.

The experimental data for the adsorption isotherm was treated for the Langmuir model and the Freundlich model. The rearranged Langmuir

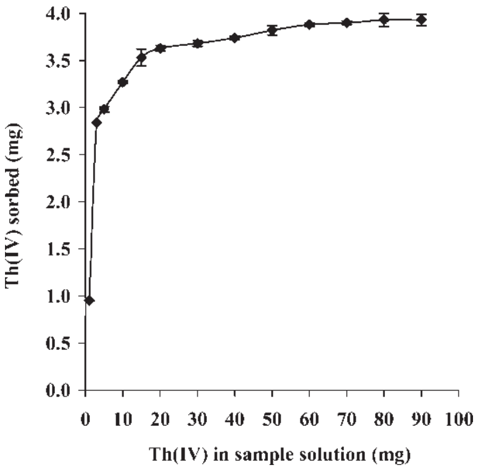


Figure 5. Sorption capacity of HL-XAD-2. Experimental condition: HL-XAD-2, aqueous phase condition = 1–90 mg thorium(IV) in 20 cm^3 of 1×10^{-3} M HCl shaking time = 20 min.

equation (39) is as shown below:

$$\frac{C_e}{q_e} = \frac{1}{q_{0^b}} + \frac{C_e}{q_0}$$

Where C_e is the equilibrium concentration (mg dm^{-3}), q_e is the amount adsorbed at equilibrium and q_0 and b are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively.
While the Freundlich equation (39) is represented as follows:

$$\log\left(\frac{x}{m}\right) = \log K_f + \left(\frac{1}{n}\right)\log C_e$$

Where x/m is the amount of metal adsorbed per 0.1 g HL-XAD-2, Freundlich constants K_f is the measure of the adsorption capacity and 1/n is the adsorption intensity. The plots of C_e/q_e versus C_e and log(x/m) versus log C_e indicated that the adsorption of thorium(IV) on Cyanex302 impregnated on Amberlite XAD-2 resin obeyed Langmuir as well as Freundlich adsorption models (Fig. 6 and Fig. 7). The correlation coefficient (R^2) for the linear regression fit of the Langmuir plot and Freundlich plot were 0.999 and 0.994 respectively while the values for q_0, b, K_f, and n were 3.85, 0.030, 1.78, and 9.36 respectively.

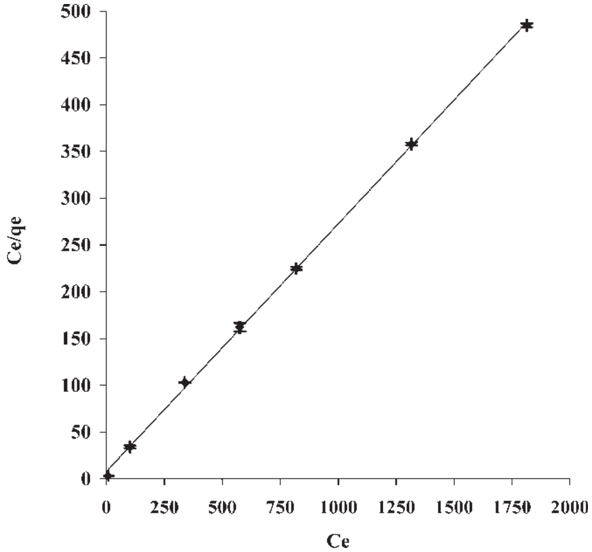


Figure 6. Langmuir adsorption isotherm. Experimental condition: HL-XAD-2. Aqueous phase condition = 1–50 mg thorium(IV) in 20 cm^3 of 1×10^{-3} M HCl Shaking time = 20 min.

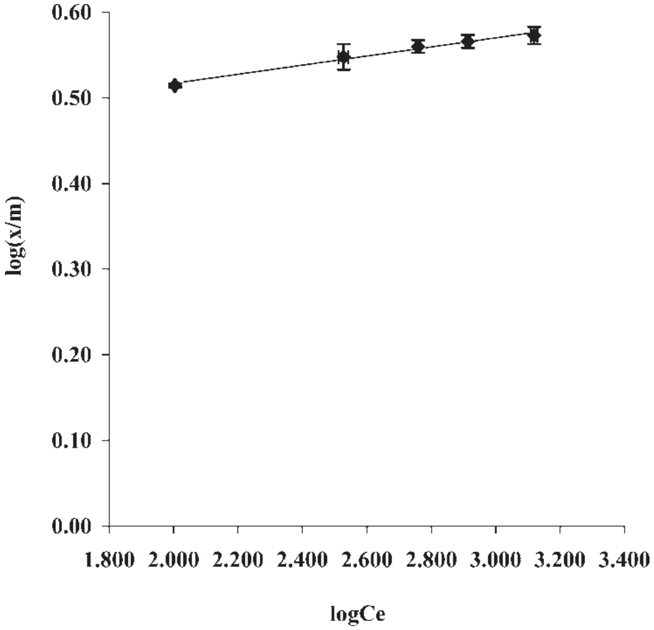


Figure 7. Freundlich adsorption isotherm. Experimental condition: HL-XAD-2. aqueous phase condition = 1–50 mg thorium(IV) in 20 cm^3 of 1×10^{-3} M HCl. Shaking time = 20 min.

Analytical Performance (Precision and Detection Limit)

The precision of the method developed was investigated using optimum conditions for sorption and desorption of thorium(IV) (Table 1) on the column and expressed in terms of the relative standard deviation (R.S.D.). Thorium(IV) determination in six replicate experiments had a R.S.D. of 0.6 %.

The limit of detection (LOD) defined as that analyte concentration giving a signal equal to three times the standard deviation of blank signal (4) was 0.75 μg dm^{-3}.

Analytical Application

1. Separation of thorium(IV) from other elements in binary mixtures: Thorium(IV) was separated from certain commonly associated elements like alkali, alkaline earths, transition metals, and rare earths in binary mixtures. The distribution ratio was calculated from the ratio of concentration of metal in an organic phase to its concentration in the aqueous phase ($D = [M]_{Org.}:[M]_{Aq.}$). These results indicated that thorium(IV) was almost completely retained by the column, while the sorption of the diverse ions was negligible under the optimum conditions (Table 1) engendering very high separation factors ($\beta = D_{Th}:D_M$) (Table 3).
2. Separation of thorium(IV) in synthetic mixtures: The applicability of the method for isolation and determination of thorium(IV) at trace levels from complex mixtures was checked. Some synthetic mixtures were analyzed for recovery of thorium(IV) (Table 4). The other elements in these synthetic mixtures were not sorbed by HL-XAD-2 under the optimum sorption conditions for thorium(IV) (Table 1). They were thus quantitatively determined in the aqueous phase using AAS/ICP-AES. These results indicated that thorium(IV) could be quantitatively separated from complex matrices with a relative standard deviation (R.S.D.) not more than 0.6%.
3. Analysis of Monazite sand: The accuracy of the method was assessed for analysis of a real sample. The sample solution of monazite sand was prepared as described in the experimental section. A known aliquot of the sample solution was passed through the column as per the general procedure for the isolation of thorium. The amount of thorium recovered by the present method on three replicate analyses was 90.80 ± 0.2 mg g^{-1} as against 91.68 mg g^{-1} found by ICP-AES analysis. The results of the sample solution were crosschecked using ICP-AES indicated a recovery of $99.0 \pm 0.2\%$ for thorium(IV) with a R.S.D. within 0.6%.

Table 3. Separation of thorium(IV) from binary mixtures

Metal ion	Amount of metal added (μg)	Metal unextracted (%)$^{\pm a}$	Recovery of thorium(IV) (%)$^{\pm a}$	Separation factor (β) $\beta = D_{Th}:D_M$
Na(I)	100	99.1 ± 0.2	99.0 ± 0.2	11.0×10^3
K(I)	3500	99.1 ± 0.2	99.0 ± 0.2	11.0×10^3
Ca(II)	3800	99.3 ± 0.1	98.9 ± 0.2	12.8×10^3
Cd(II)	40	99.1 ± 0.1	99.0 ± 0.2	11.0×10^3
Co(II)	3000	99.4 ± 0.1	99.1 ± 0.2	18.3×10^3
Mn(II)	600	99.3 ± 0.1	99.0 ± 0.1	14.1×10^3
Ni(II)	20	98.8 ± 0.1	98.9 ± 0.2	74.9×10^2
Pb(II)	100	98.8 ± 0.1	99.1 ± 0.1	91.7×10^2
Zn(II)	25	99.0 ± 0.1	99.0 ± 0.1	99.0×10^2
Dy(III)	20	99.0 ± 0.2	99.0 ± 0.2	99.0×10^2
Gd(III)	20	98.8 ± 0.1	98.8 ± 0.1	68.6×10^2
La(III)	30	99.0 ± 0.1	98.9 ± 0.1	82.5×10^2
Nd(III)	40	98.8 ± 0.1	99.0 ± 0.1	89.9×10^2
Pr(III)	20	98.8 ± 0.1	99.1 ± 0.1	91.7×10^2
Y(III)	40	98.9 ± 0.2	99.0 ± 0.2	90.0×10^2
Yb(III)	20	98.9 ± 0.1	99.0 ± 0.2	90.0×10^2
Ce(IV)	60	98.9 ± 0.2	98.9 ± 0.2	95.6×10^2

$^{\pm a}$ = %R.S.D. of six determinations.

Experimental condition: Column packed with HL-XAD-2.

Aqueous phase condition = 20 μg thorium(IV) in 10 cm^3 of 1×10^{-3} M HCl, at 1.0 $cm^3\ min^{-1}$ flow rate.

Elution condition = 10 cm^3 of 4 M HCl, at 0.4 $cm^3\ min^{-1}$ flow rate.

Table 4. Separation of thorium(IV) from synthetic mixtures

Composition of mixture	Recovery of thorium(IV) (%)$^{\pm a}$
Ni(II);20 μg, Co(II);20 μg, Th(IV);20 μg	99.1 ± 0.1
Ca(II);100 μg, Y(III);40 μg, Th(IV);20 μg	99.2 ± 0.3
Mn(II);20 μg, Co(II);20 μg, Th(IV);20 μg	98.9 ± 0.2
Mn(II);500 μg, Cd(II);40 μg, Th(IV);20 μg	98.9 ± 0.2
Ce(IV);10 μg, La(III);20 μg, Ca(II);100 μg, K(I);100 μg, Th(IV);20 μg	98.8 ± 0.2
Fe(III);10 μg, Cu(II);10 μg, Zn(II);15 μg, Pb(II);25 μg, Th(IV);20 μg	99.0 ± 0.3
Nd(III);10 μg, Ce(IV);12 μg, La(III);15 μg, Pr(III);15 μg, Th(IV);20 μg	98.8 ± 0.1

$^{\pm a}$ = %R.S.D. of three determinations.

Experimental condition: Column packed with HL-XAD-2.

Aqueous phase condition = 10 cm^3 mixture in 1×10^{-3} M HCl, at 1.0 $cm^3\ min^{-1}$ flow rate.

Elution condition = 10 $cm^3$of 4 M HCl, at 0.4 $cm^3\ min^{-1}$flow rate.

Table 5. Summary of solid phase extraction methods reported for thorium(IV)

Solid support	Ligand	Method for modification of solid support	Reusability of modified solid support (No. of cycles)	Sorption capacity (mmol g^{-1})	Ref.
XAD-16	(4,4-Bis-[bis-(2-ethyl-hexyl)-carbamoyl]-2-oxo-butyl)-phosphonic acid	(C)	15	1.41	(18)
XAD-16	[2-(1-Methyl-3-oxo-2-phenyl-2,3 dihydro-1H-pyrazol-4-ylcarbamoyl)-ethyl]-phoshonic acid	(C)	25	1.39	(19)
XAD-16	3,4-Dihydroxybenzoyl methyl phosphonic acid	(C)	30	1.51	(20)
XAD-16	4-ethoxy-N,N-dihexyl butanamide	(C)	20	0.69	(21)
XAD-16	Oxyacetone acetamide	(C)	30	0.797	(22)
XAD-16	N,N-dihexylcarbamoylmethyl phosphonic acid	(C)	30	1.228	(23)
XAD-16	(3-Hydroxy phosphinoyl-2-oxo-propyl) phosphonic acid dibenzyl ester	(C)	30	1.33	(24)
XAD-16	[(2-Dihydroxyarsinoylphenylamino) methyl]phosphonic acid	(C)	30	1.40	(25)
XAD-16	(Bis-2-hydroxy benzyl)p-phenylene diamine	(C)	30	1.62	(26)
XAD-16	(Bis-3,4-dihydroxy benzyl)p-phenylene diamine	(C)	35	0.664	(27)
XAD-16	(Bis-2,3,4-trihydroxy benzyl) ethylene diamine	(C)	30	1.19	(28)
XAD-4	Octacarboxymethyl-C-methyl calix[4]resorcinarene	(I)	10–12	0.29	(29)
XAD-4	o-Vanillin semicarbazone	(C)	10–12	3.230[a]	(30)
Merrifield Chloromethylated resin	Calix [4]arene-o-vanillinsemicarbazone	(C)	20	41.175[a]	(31)

(*continued*)

Table 5. Continued

Solid support	Ligand	Method for modification of solid support	Reusability of modified solid support (No. of cycles)	Sorption capacity (mmol g^{-1})	Ref.
Merrifield Chloromethylated resin	(Dimethyl-amino-phosphono-methyl)-phosphonic acid	(C)	20	1.98	(32)
Merrifield Chloromethylated resin	Di-bis(2-ethylhexyl)malonamide	(C)	15	38.2[a]	(33)
Merrifield Chloromethylated resin	Thenoyl trifluoro acetone	(C)	30	0.1172	(34)
Merrifield Chloromethylated resin	4-Ethoxy-4-ethyl-N,N-bis-2 ethylhexylbutanamide	(C)	20	0.214	(35)
Merrifield Chloromethylated resin	11,23-Disemicarbazono-26,28-n-dipropoxy-25,27-dihydroxy calix[4]arene	(C)	10–12	0.0122	(36)
Cellulose	Quinoline-8-ol	(C)	—	20[a]	(37)
Poly(styrene-β-hydroxylamine)	37,38,39,40,41,42-Hexahydroxy,1,8,13,19,25,31-hexacarboxy calix[6]arene	(C)	—	0.463	(38)
XAD-2	Cyanex302	(I)	50	8.48	This Work

(C) = Chemical reactions involved for modification of solid support.

(I) = Impregnation or physical linkage of ligand on to the solid support.

[a] Sorption capacity in mg g^{-1}.

CONCLUSION

The solid phase extraction method developed using Amberlite XAD-2 resin impregnated with Cyanex302 (HL-XAD-2) is simple and selective for the isolation of thorium(IV). The solid phase prepared without involving chemical reactions exhibited better reusability and sorption capacity for thorium(IV) (Table 5). The LOD obtained is superior and a preconcentration factor achieved is >100. Thorium(IV) can be separated from alkali, alkaline earths, and rare earths. The practical applicability of the method was checked for recovery of thorium(IV) from monazite sand and some complex mixtures.

REFERENCES

1. http://webmineral.com/Alphabetical_Listing.shtml
2. Hicsonmez, U. and Eral, M. (1998) Investigation of thorium(IV) separation from cerium(IV) on a silica gel column coated with tri-octylphosphine oxide. *J. Alloys Compd.*, 271: 620.
3. Rao, T.P., Metilda, P., and Gladis, J.M. (2006) Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination-an overview. *Talanta*, 68 (4): 1047.
4. Jain, V.K., Pandya, R.A., Pillai, S.G., et al. (2006) Merrifield resin supported chelate forming calix[4]arene-*o*-vanillinthiosemicarbazone resin employed for the separation, preconcentration and trace determination of Cr(VI), As(III) and Tl(I) in water samples. *Sep. Sci. Technol.*, 41 (1): 123.
5. Lemos, V.A., Santos, J.S., and Baliza, P.X. (2004) Synthesis of α-nitroso-β-naphthol modified Amberlite XAD-2 resin and its application in on-line solid phase extraction system for cobalt preconcentration. *Sep. Sci. Technol.*, 39 (14): 3317.
6. Juang, R.S. (1999) Preparation, properties and sorption behavior of impregnated resins containing acidic organophosphorus extractants, *Proc. Natl. Sci. Counc. ROC(A)*; 23 (3) 353.
7. Chen, Jyh-Herng, Kao, Ying-Yun, and Lin Chia-Hung (2003) Selective separation of vanadium from molybdenum using D_2EHPA-immobilized amberlite XAD-4 resin. *Sep. Sci. Technol.*, 38 (15): 3827.
8. Draa, M.T., Belaid, T., and Benamor, M. (2004) Extraction of Pb(II) by XAD7 impregnated resins with organophosphorus extractants (DEHPA, IONQUEST 801, CYANEX 272). *Sep. Purif. Technol.*, 40 (1): 77.
9. Matsunaga, H., Ismail, A.A., Wakui, Y., and Yokoyama, T. (2001) Extraction of rare earth elements with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate impregnated resins having different morphology and reagent content. *React. Funct. Polym.*, 49 (3): 189.
10. Kabay, N., Gizli, N., Demircioglu, M., et al. (2003) Removal of cadmium from phosphoric acid solution by solvent-impregnated resins (SIRs) - sorption kinetics and equilibria studies. *Chem. Eng. Comm.*, 190 (5–8): 936.
11. Gonzalez, M.P., Saucedo, I., Navarro, R., Avila, M., and Guibal, E. (2001) Selective separation of Fe(III), Cd(II), and Ni(II) from dilute solutions using solvent-impregnated resins. *Ind. Eng. Chem. Res.*, 40 (25): 6004.

12. Kabay, N., Demircioglu, M., Ekinci, H., et al. (1998) Extraction of Cd(II) and Cu(II) from phosphoric acid solutions by solvent-impregnated resins (SIR) containing Cyanex 302. *React. Funct. Polym.*, 38 (2–3): 219.
13. Warshawsky, A. (1984) *Ion Exchange and Solvent Extraction*; Marinsky, J.A. and Marcus, Y. (eds.), Vol. 8. Marcel Dekker: New York.
14. Rickelton, W.A. and Boyle, R.J. (1990) The selective recovery of zinc with new thiophosphinic acids. *Sol. Extr. Ion. Exch.*, 8 (6): 783.
15. Welcher, F.J. (1978) *The Analytical uses of Ethylenediamine tetraacetic acid*; D. Van Nostrand Co. Inc.: New Jersey.
16. Scott, W.W. (1939) *Standard Methods of Chemical Analysis 5th edn.*; Furman, N.H. (ed.), Vol. 1. D. Van Nostrand Co. Inc.: New Jersey.
17. Snell, F.D. (1978) *Photometric and Fluorometric Methods of Analysis of Metals*; John Wiely and Sons: New York.
18. Maheswari, M.A. and Subramanian, M.S. (2006) Polymer based ion-sensor for the selective recognition of UO_2^{2+} and Th^{4+} ions. *React. Funct. Polym.*, 66 (12): 1452.
19. Raju, Ch. S. K., Srinivasan, S., and Subramanian, M.S. (2005) New multi-dentate ion-selective AXAD-16-MOPPA polymer for the preconcentration and sequential separation of U(VI), Th(IV) from rare earth matrix. *Sep. Sci. Technol.*, 40 (11): 2213.
20. Maheswari, M.A. and Subramanian, M.S. (2005) AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid: a selective preconcentrator for U and Th from acidic waste streams and environmental samples. *React. Funct. Polym.*, 62 (1): 105.
21. Maheswari, M.A. and Subramanian, M.S. (2005) Extraction chromatographic method for the separation of actinides and lanthanides using EDHBA grafted AXAD-16 polymer. *Talanta*, 65 (3): 735.
22. Prabhakaran, D. and Subramanian, M.S. (2004) Synthesis, characterization, and metal extractive behavior of functionalized AXAD-16 polymeric matrix using oxyacetone acetamide. *Sep. Sci. Technol.*, 39 (4): 941.
23. Maheswari, M.A. and Subramanian, M.S. (2004) Selective enrichment of U(VI), Th(IV) and La(III) from high acidic streams using a new chelating ion-exchange polymeric matrix. *Talanta*, 64 (1): 202.
24. Prabhakaran, D. and Subramanian, M.S. (2004) Extraction of U(VI), Th(IV), and La(III) from acidic streams and geological samples using AXAD-16–POPDE polymer. *Anal. Bioanal. Chem.*, 380 (3): 578.
25. Prabhakaran, D. and Subramanian, M.S. (2004) Selective extraction of U(VI), Th(IV), and La(III) from acidic matrix solutions and environmental samples using chemically modified Amberlite XAD-16 resin. *Anal. Bioanal. Chem.*, 379 (3): 519.
26. Maheswari, M.A. and Subramanian, M.S. (2003) Selective extraction of U(VI) and Th(IV) from high saline matrices using AXAD-16-BHBPD as chelating polymeric matrix. *Anal. Lett.*, 36 (13): 2875.
27. Prabhakaran, D. and Subramanian, M.S. (2003) A column system for the selective extraction of U(VI) and Th(IV) using a new chelating sorbent. *Talanta*, 61 (4): 423.
28. Prabhakaran, D. and Subramanian, M.S. (2003) Selective extraction and sequential separation of actinide and transition ions using AXAD-16-BTBED polymeric sorbent. *React. Funct. Polym.*, 57 (2–3): 147.
29. Demirel, N., Merdivan, M., Pirinccioglu, N., and Himamci, C. (2003) Thorium(IV) and uranium(VI) sorption studies on octacarboxymethyl-C-methylcalix[4]resorcinarene impregnated on polymeric support. *Anal. Chim. Acta*, 485 (2): 213.

30. Jain, V.K., Handa, A., Sait, S.S., Shrivastav, P., and Agrawal, Y.K. (2001) Preconcentration, separation and trace determination of lanthanum(III), cerium(III), thorium(IV) and uranium(VI) on polymer supported *o*- vanillinsemicarbazone. *Anal. Chim. Acta*, 429 (2): 237.
31. Jain, V.K., Pandya, R.A., Pillai, S.G., and Shrivastav, P.S. (2006) Simultaneous preconcentration of uranium(VI) and thorium(IV) from aqueous solutions using a chelating calix[4]arene anchored chloromethylated polystyrene solid phase. *Talanta*, 70 (2): 257.
32. Raju, Ch. S. K. and Subramanian, M.S. (2005) DAPPA grafted polymer: An efficient solid phase extractant for U(VI), Th(IV) and La(III) from acidic waste streams and environmental samples. *Talanta*, 67 (1): 81.
33. Prabhakaran, D. and Subramanian, M.S. (2005) Selective extraction of U(VI) over Th(IV) from acidic streams using di-bis(2-ethylhexyl) malonamide anchored chloromethylated polymeric matrix. *Talanta*, 65 (1): 179.
34. Prabhakaran, D. and Subramanian, M.S. (2003) Chemically modified chloromethylated resin as an effective metal chelator in the extraction of U(VI) and Th(IV). *Anal. Lett.*, 36 (10): 2277.
35. Maheswari, M.A. and Subramanian, M.S. (2004) Selective extraction of actinides using EEBEHBA grafted polymer: A green process for nuclear reprocessing Program. *Sep. Sci. Technol.*, 39 (15): 3621.
36. Jain, V.K., Handa, A., Pandya, R., et al. (2002) Polymer supported calix[4]arene-semicarbazone derivative for separation and preconcentration of La(III), Ce(III), Th(IV) and U(VI). *React. Funct. Polym.*, 51 (2–3): 101.
37. Metilda, P., Gladis, J.M., and Rao, T.P. (2003) Quinoline-8-ol modified cellulose as solid phase extractant (SPE) for preconcentrative separation and determination of thorium(IV). *Radiochim. Acta*, 91 (12): 737.
38. Trivedi, U.V., Menon, S.K., and Agrawal, Y.K. (2002) Polymer supported calix[6]arene hydroxamic acid, a novel chelating resin. *React. Funct. Polym.*, 50 (3): 205.
39. Metilda, P., Sanghamitra, K., Gladis, J.M., et al. (2005) Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium(VI). *Talanta*, 65 (1): 192.