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Selective enrichment of U(VI), Th(IV) and La(III) from high acidic streams using a new chelating ion-exchange polymeric matrix

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Abstract

An off-line extraction chromatographic technique has been developed using Amberlite XAD-16 (AXAD-16)-*N*,*N*-dihexylcarbamoylmethyl phosphonic acid, as the stationary phase for the extraction of uranium, thorium and lanthanum from nuclear spent fuels as well as from geological and natural water resources. The chemical modifications of the polymeric matrix were monitored using FT-IR spectroscopy, CHNPS elemental analysis and also by thermo gravimetric analysis for water regain measurements. Various physio-chemical parameters influencing the quantitative metal ion extraction by the resin phase were optimized by both static and dynamic methods. The developed resin matrix showed good distribution ratio values under wide concentrations of acidity and pH conditions. Moreover, the sequential separation of analytes is also possible at sample pH 6.5. Also, the polymeric matrix showed superior metal sorption capacities and rapid metal exchange kinetics with a high sample flow rate value of 26 $\mathrm{cm^3\,min^{-1}}$ for all the three analytes. Thus, reducing the time of analyte extraction from large number of samples anticipated in nuclear waste management programs. The quantitative metal ion recovery of >99.8% was effected with 0.5 M $(NH_4)_2CO_3$ solution. The method was highly sensitive with lower limits of detections to be 10, 20 and 15 $\mathrm{ng\,cm^{-3}}$ for U(VI), Th(IV) and La(III), respectively, with a better pre-concentration values of 333 for U(VI) and Th(IV) and 400 for La(III), respectively paving way for its applicability in pre-concentrating trace analytes from large sample volumes. The analytical data were within 4.2% R.S.D. reflecting the reproducibility and reliability of the developed method.

Keywords: Chelating ion-exchange resins; Pre-concentration; Extraction chromatographic column; AXAD-16; Actinide extraction

1. Introduction

Uranium and Thorium are very essential elements in nuclear and atomic energy program. Their recovery is essential to minimize their discharge into the environment from the point of view of safety and economy. So their extraction and separation from geological samples and nuclear spent fuels which are very complex systems becomes a very significant task. Solvent extraction (SE) technique has been serving this purpose for many decades. The most effective extractants are long chain substituted mono and diamides, and various organophosphorous extractants like trioctyl phosphine oxide, di-2-ethyl phosphoric acid, etc., for the selective extraction of lanthanides and actinides from high level wastes in nuclear reprocessing units [1–3]. Bidentate organophosphorus reagents like carbamoylmethyl phosphine oxide (CMPO) are very good extractants especially for trivalent actinides and lanthanides from spent fuels [4,5]. But these organic extractants are cost and labor intensive involving multi-stage extraction procedures. Moreover, the technical problems associated in terms of third-phase formation leading to explosive hazards and non eco-friendliness due to the problems associated in organic waste disposals makes this technique a less preferred one [6].

Solid phase extraction (SPE) technique is thus recognized as the fast and reliable approach for quantitative metal ion extraction and pre-concentration [7–10]. The impregnated resins which are designed by physically loading the successful organic extractants on a solid inert support material also found effective for this process [11,12]. They had high distribution ratios but owing to their ligand bleeding tendency the number of reusable cycles decreases thus making them non-economical. The use of ion-exchange resins offered faster extraction kinetics but lacked in metal

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ion selectivity leading to the development of ion-selective chemically modified chelating sorbents [13–22]. But owing to their weak acidic properties of the ligand moiety, these sorbents were ineffective in extracting actinides from high acid medium. In addition, premature ion breakthrough and under utilization of available chelating sites were observed due to their slow exchange kinetics, low metal sorption capacities and co-extractive ability for transition metal ions [23].

To over shadow the drawbacks associated in ion-exchange and chelating resins, a novel chelating ion-exchange resin has been developed using Amberlite XAD-16 (AXAD-16) as the inert polymeric support chemically modified with *N*,*N*-dihexylcarbamoylmethyl phosphonic acid. The synthesized resin serves as a quantitative extracting media for uranium, thorium and lanthanum from various acidic solutions (acts as a neutral metal chelator) as well as from wide pH conditions (acts as a chelating-cation exchanger). The developed system exhibited faster kinetics due to the introduction of hydrophilic (–OH) group which in turn increased the chelating site accessibility of metal ions, by providing better surface contact with the aqueous phase. In addition to these, the resin possesses significant features like good ion-selectivity, sensitivity and greater pre-concentration factor values. The studies on metal extractive behavior using an off-line extraction chromatographic column method for the recovery of actinides from synthetic mixtures mimicking a nuclear reprocessing solution as well as from monazite sand and real water samples are discussed in this paper.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer spectrum one model FT-IR spectrometer was used for functional group identification. An Elementar Vario EL model CHNPS analyzer was employed to ensure the quantitative functionalization of the resin matrix. A Bruker IFS 66 V model Far IR spectrometer was used for confirming the metal ion complexation to the polymeric matrix. A Bruker-400 NMR spectrometer was used for the characterization of the chloro amide. A Jasco V-530 model spectrophotometer was used in the estimation of U(VI), Th(IV) and La(III). A Hitachi F-4500 fluorescence spectrophotometer was utilized for determining trace level uranium from synthetic and real samples. The analysis of transition metal ions and other diverse cations were performed using a Varian SpectrAA-20 model flame atomic absorption spectrometer. The water regaining capacity studies were performed using a Perkin-Elmer TGA-7 model thermal analyzer. A Ravel Hi-Tech S-50 model peristaltic pump was used for adjusting the flow rates during column operation. An Orbitek DL model mechanical shaker with 200 rpm was used for static equilibration studies. A Digisun DI-707 model pH-meter was employed for solution pH adjustments.

2.2. Chemicals and reagents

All the standard metal ion stock solutions were prepared by dissolving exact amounts of the corresponding AR grade salts (Fluka Chemicals) in slightly acidified double distilled water. The chemicals and reagents required for the chemical modification of the polymeric matrix were of AR grade which were purchased from Lancaster and E-Merck Chemicals.

AXAD-16 resin beads (surface area 825 $m^2 g^{-1}$, pore diameter of 20–50 mesh and bead size of 0.3–1.2 mm) purchased from Fluka Chemicals were used as the polymer backbone for the synthesis of the desired chelating ion-exchange resin.

2.3. Synthesis of AXAD-16-*N*,*N*-dihexylcarbamoylmethyl phosphonic acid

AXAD-16 resin beads were purified prior to usage using 2 M HCl followed by 2 M NaOH in order to remove both basic and acidic impurities. The resin beads were water washed until the washings showed neutral pH. The resin was again subjected to ethanol wash filtered and vacuum dried prior to usage. Five grams of purified AXAD-16 resin matrix was refluxed with 20 cm^3 of phosphorus trichloride in the presence of anhydrous aluminium chloride for 3 h, followed by hydrolysis to the corresponding phosphonic acid resin. The hydroxyl group of the phosphonic acid resin was protected with chlorotrimethylsilane in dry DCE medium for 1 h at 50 °C prior to further reaction. The protected resin was reacted with 2-chloro-*N*,*N*-dihexylacetamide (synthesized by reacting chloroacetyl chloride with dihexylamine in the presence of dry diethyl ether and triethylamine which was characterized by FT-IR, ^{13}C and ^{1}H NMR spectroscopy) in the presence of triethylamine. The resulting modified resin beads were deprotected and further washed with water and acetone, filtered and vacuum dried. The synthetic scheme used in designing the chelating ion-exchange resin is given below.

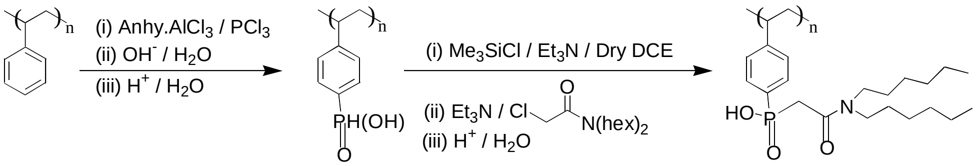

Table 1
Optimum experimental parameters for quantitative sorption and desorption of analytes

Experimental parameters	U(VI)	Th(IV)	La(III)
pH range	6.5	4.0	4.0–5.0
$t_{1/2}$ (min)	2.6	2.3	2.1
Metal sorption capacity (mmol g^{-1})			
(i) At optimum pH	1.429	1.228	1.356
(ii) At 2 M HNO_3	0.423	0.586	1.735
(iii) At 2 M HCl	0.442	0.573	1.728
Eluting agent $(NH_4)_2CO_3$ (M)	0.1	0.1	0.5
Maximum flow rate (cm^3 min^{-1})	26	26	26
Average percentage recovery	99.8	99.8	99.9
Lower limit of detection (ng cm^{-3})	10	20	15
Sample breakthrough volume (cm^3)	5000	5000	6000
Pre-concentration factor (2 M HNO_3)	333	333	400

2.4. *Extractive methods adopted during the process of metal ion extraction*

2.4.1. *Batch 'static' method*

This method is used for optimizing all the basic experimental parameters like the influence of sample acidity/pH, extraction kinetics, diverse ion interference, etc., on quantitative analyte extraction. For this, a known amount of the resin was equilibrated with a known analyte concentration for a definite time duration using a mechanical shaker at 200 rpm. The sorbed metal ions were desorbed using 15 cm^3 of the suitable eluant and analyzed. The metal ions were estimated spectrophotometrically using Arsenazo-III as chromogen for U(VI) and La(III) and Thoron as chromogen for Th(IV), respectively. The optimum experimental parameters for quantitative metal ion sorption and desorption are listed in Table 1.

2.4.2. *Column 'dynamic' method*

An extraction chromatographic glass column (15 cm × 4 cm) was packed with 1 g of pre-conditioned resin beads uniformly by slurry method. The resin bed (5 cm) was initially washed with distilled water followed by the passage of sample solution under optimized flow rates, using a peristaltic pump. The sorbed metal ions were eluted and estimated by spectrophotometric method. Trace concentrations of U(VI) ions from synthetic and real samples were estimated by steady state spectrofluorimetric method, in 1 M phosphoric acid medium, wherein the ${UO_2}^{2+}$ fluorescence emission was recorded at 515 nm with 266 nm as excitation wavelength [25]. The resin bed was washed with plenty of distilled water until neutral pH and subsequently reused.

3. Results and discussion

3.1. *Characterization of the chelating ion-exchange resin*

The quantitative conversion of the desired functionality in the resin matrix was followed by FT-IR spectra. The phosphonic acid resin showed spectral bands at 2314.1, 1044.5, 1157.5, and 3435.5 cm^{-1}, respectively, corresponding P–H, P–OH, P=O and O–H groups, respectively. The subsequent disappearance of P–H band followed by the appearance of spectral band at 1653.5 cm^{-1} was ascertained to amide C=O and the enhancement of the $–CH_2$ stretching vibrations at 2992.4 cm^{-1} confirms the chemical modification of the polymeric matrix. The chelation of the metal ion with phosphoryl and carbamoyl oxygens was confirmed by Far-IR studies which showed stretching vibrations in the spectral region 220–190 cm^{-1} and also from the red shift studies in the corresponding P=O and C=O stretching vibrations.

The extent of ligand functionalization was also monitored by performing CHNPS analysis during each stage of functionalization which corroborates with the corresponding theoretical value. The experimental data for the desired final polymer was found to be C, 68.3; H, 9.05; N, 3.49; and P, 7.57%, respectively. Assuming each of the repeat unit to be derivatized, the calculated theoretical values are: C, 67.34; H, 9.15; N, 3.54; and P, 7.84%, respectively. Thus, the elemental analysis reflects the incorporation of at least one ligand moiety per repeat unit giving a ligand capacity of 3.18 mmol g^{-1} of the resin.

The water regaining capacity studies showed a weight loss of 4.5% up to 110 °C from TGA studies which was assigned to the percolated water molecules in the pores of the chemically modified resin while for the unfunctionalized AXAD-16 matrix a value of only 1.1% was obtained. The results show the enhanced hydrophilic character of the resin after chemical modification thus increasing the accessibility of the chelating sites by the metal ions.

3.2. *Static equilibration studies*

3.2.1. *Influence of acid concentrations on metal ion retention*

The extracting ability of the resin in acidic media was studied using varying concentrations of nitric and hydrochloric acid. For this study 50 mg of resin beads were equilibrated individually with (40 cm^3, 10 μg cm^{-3}) metal ion concentration for 1 h. The aqueous phase metal ion concentration were analyzed and the corresponding distribution ratios were calculated using the following expression

$$D\,(\mathrm{cm^3\,g^{-1}}) = (A_0 - A_\mathrm{f})\frac{V}{A_\mathrm{f}W}$$

A_0 and A_f are the concentrations of metal ions before and after equilibration, V refers to the overall volume ($\mathrm{cm^3}$) and W is the dry weight of the resin matrix (g).

From Fig. 1a and b, it is evident that the extraction is very effective for La(III) with D values in the range of 10^4–10^5 when compared to U(VI) and Th(IV) which is in the order of 10^3. In acidic conditions, the chelation mechanism involving phosphoryl and carbonyl oxygens is predominant which can effectively extract neutral metal complexes. The charges on the metal ions are balanced by the nitrate and chloride ions supplied by the corresponding acid. However, with increasing acidity a slight negative dependency was observed due to the formation of metal anionic complexes. But under very low acidities, both chelation and cation exchange mechanism prevails thus increasing the metal ion extraction.

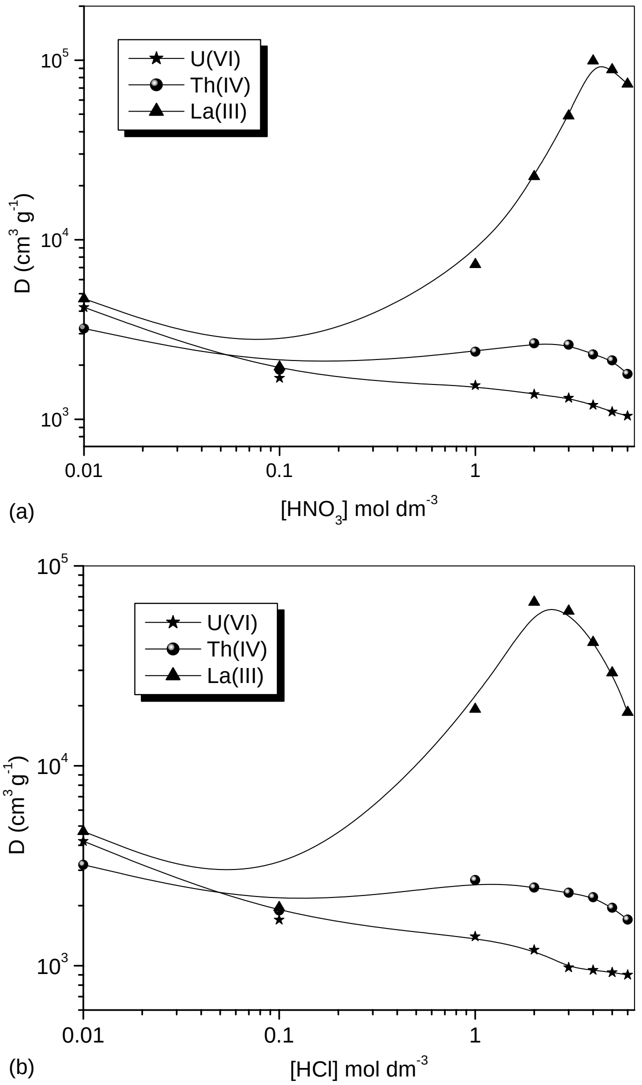

Fig. 1. (a) Effect of [HNO_3] on metal ion extraction. (b) [HCl] dependency on metal ion uptake.

3.2.2. Effect of solution pH on metal ion-extraction

The pH at which the resin functions at its maximum extracting capacity was investigated by equilibrating 50 mg of the resin with metal ion solutions (40 $\mathrm{cm^3}$, 10 $\mu\mathrm{g\,cm^{-3}}$) in the pH range (1–6.5) for 1 h. The uptake of the metal ions has been plotted in terms of distribution ratios. From Fig. 2, it can be seen that the extraction efficiency increases with increasing pH for U(VI). But the D values decreases after pH 4 for Th(IV) and pH 5 for La(III). Thus, the separation of U(VI) from La(III) and Th(IV) is also envisaged at pH 6.5.

3.2.3. Elution studies

The optimum eluant for quantitative metal ion recovery were studied by equilibrating 50 mg of resin matrix with metal ion solution (40 $\mathrm{cm^3}$, 10 $\mu\mathrm{g\,cm^{-3}}$) in both acid (2 M HNO_3) and optimum pH medium. Quantitative desorption of the sorbed metal ions was tested using various eluting agents as shown in Fig. 3. A recovery value of 99.8% was obtained using 0.1 M and 0.5 M $(NH_4)_2CO_3$ for U(VI), Th(IV) and La(III), respectively.

3.2.4. Kinetics of extraction in terms of fractional attainment equilibration (F) studies

The rate of metal ion-extraction by the resin matrix was studied by equilibrating 50 mg of resin beads in a series of metal ion solutions (40 $\mathrm{cm^3}$, 10 $\mu\mathrm{g\,cm^{-3}}$) in 2 M HNO_3 acidity for various time durations at 200 rpm. The kinetic data were plotted in terms of 1-F versus shaking time as shown in Fig. 4. The fractional attainment of equilibrium is

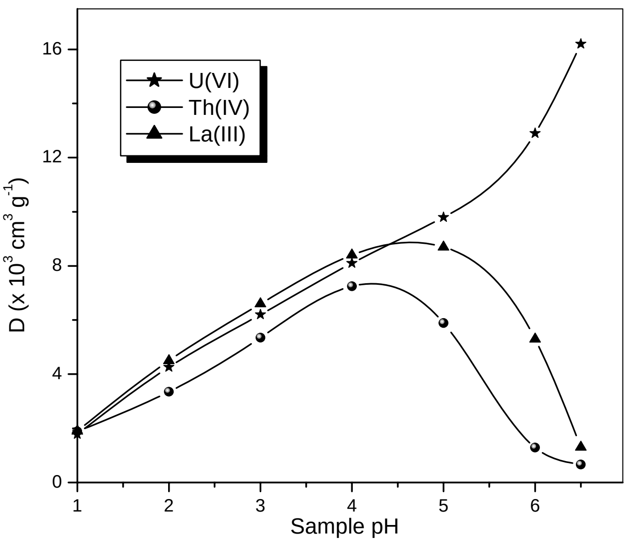

Fig. 2. Effect of solution pH for efficient extraction by the resin.

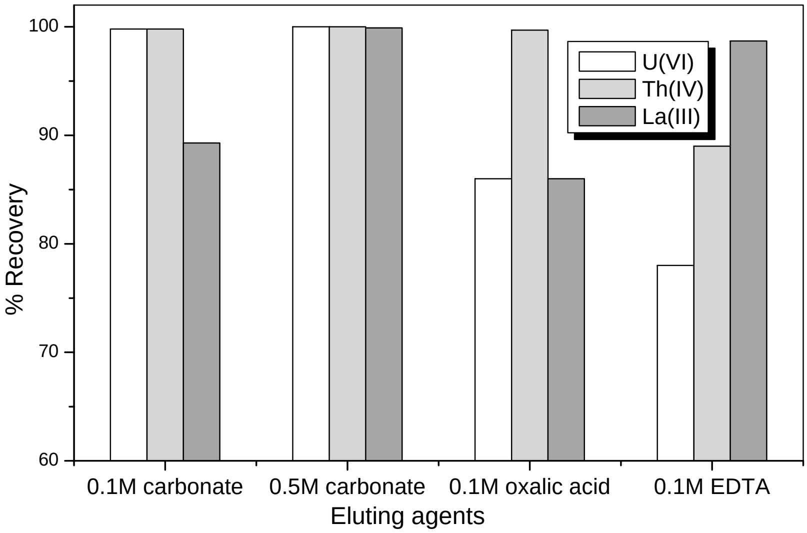

Fig. 3. Optimum eluants for quantitative recovery.

defined as

$$F = \frac{[M^R]_t}{[M^R]_{eq}}$$

where $[M^R]_t/[M^R]_{eq}$ are the ratios of metal ion concentration in the resin phase at time t to that at equilibrium [24]. It is evident from the graph that the equilibrium was attained much faster within 7.5 min, due to the enhanced hydrophilic character of the resin phase by the incorporated –OH group.

3.2.5. *Metal sorption capacity of the resin matrix*

The maximum metal sorption capacities of the resin matrix was studied by shaking 20 mg of the resin with an excess concentration of metal ion solution (100 cm^3, 100 $\mu g\,cm^{-3}$) under pH optimum conditions as well as at 2 M HNO_3 medium for 6 h and the results obtained are given in Table 1. Assuming a 1:1 complex formation with the resin matrix, the theoretical resin capacity based on elemental analysis was calculated to be 3.18 $mmol\,g^{-1}$. The decrease in actual sorption capacity for these ions may be attributed mainly to the non-accessibility of some of the chelating sites. The superiority in the metal ion sorption capacities of the developed chelating resin was compared with other chelating resins reported earlier [13–24].

3.2.6. *Effect of electrolytes on metal ion extraction*

As $NaNO_3$ and NaCl are the major components in nuclear spent fuels, a study to ensure a good tolerance for these electrolytes for quantitative metal extraction becomes essential. For this study, 50 mg of the resin was shaken with metal ion solution (40 cm^3, 10 $\mu g\,cm^{-3}$) with increasing salt concentration in 2 M corresponding acids for 1 h. It is evident from Fig. 5, that there is a negative impact on increasing NaCl concentration for all the analytes because

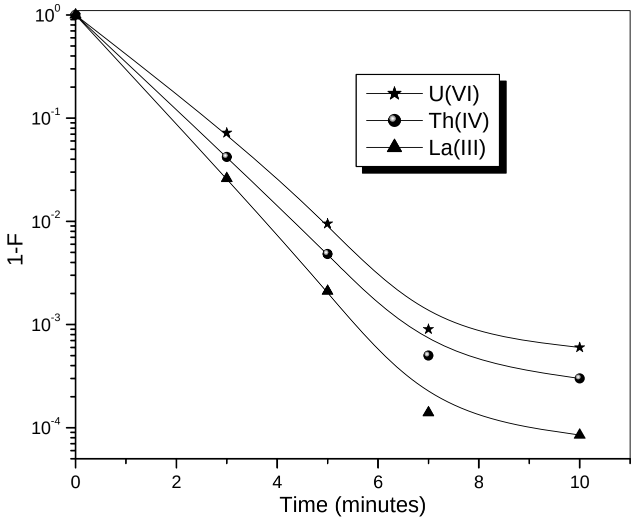

Fig. 4. Extraction kinetics.

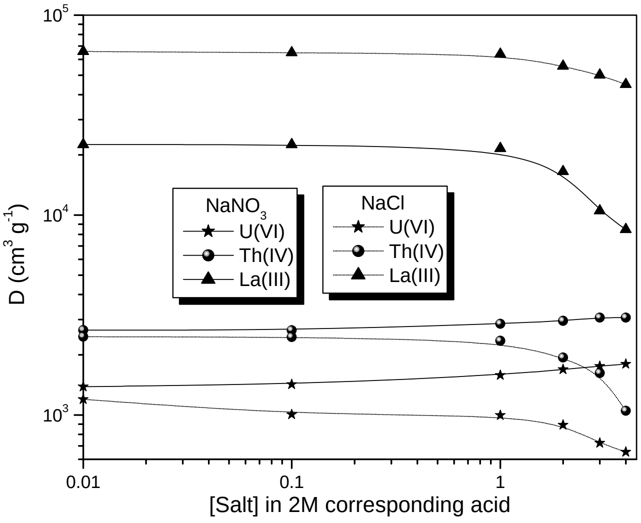

Fig. 5. Effect of electrolyte concentration.

Table 2
Tolerance limits of diverse ions and electrolytes in optimum pH conditions

Metal ions[a]	Tolerance limits for electrolytes (mg/50 mg resin)									
	NaCl	KNO_3	Na_2SO_4	Na_3PO_4	NaF	CH_3COO^-	Ca^{2+}	Mg^{2+}		
U(VI)	2010	2050	560	130	260	150	1200	1690		
Th(IV)	2140	1950	525	140	310	250	1020	1450		
La(III)	1920	1800	485	95	390	410	1950	1590		
	Mn(II)	Co(II)	Cu(II)	Fe(III)	Ni(II)	Zn(II)	Pb(II)	Cd(II)	Zr(IV)	Bi(III)
U(VI)	4.2	4.9	4.9	2.6	4.8	5.9	5.6	6.3	1.4	9.0
Th(IV)	4.9	4.5	4.7	2.5	5.6	5.2	6.3	4.6	1.5	8.2
La(III)	3.9	5.3	6.9	3.9	7.5	9.6	8.6	9.4	0.9	10.6

[a] Amount of U(VI), Th(IV), La(III) = 50 μg.

of the competition for more stable anionic chloro complex formation. But in the case of $NaNO_3$, a slight positive trend was observed for both U(VI) and Th(IV).

3.2.7. Effect of various diverse ion species

The efficiency of the resin matrix to quantitatively extract the analytes of interest in the presence of large concentrations of electrolyte and common metal ion species was studied by equilibrating 50 mg of the resin with analyte concentration (40 cm^3, 1.25 $\mu g\,cm^{-3}$) along with varying concentrations of individual diverse ions under optimum pH as well as in 2 M HNO_3 conditions. In acidic media the resin was very selective for analytes of interest showing 0% extraction for transition and more common metal ions. But when the resin is subjected for extraction under pH conditions they found to compete for the active sites whose tolerance limits i.e. diverse ion concentration up to which 100% analyte extraction is observed are given in Table 2. It shows that the resin matrix is highly ion-selective in nature even in the presence of 10^2–10^6-fold concentrations of diverse ions and electrolyte species, paving way for its applicability in quantitative trace level analyte extraction also from high saline conditions.

3.3. Dynamic studies—–extraction chromatographic column

3.3.1. Effect of sample flow rate on metal ion sorption

The effect of sample flow rate was examined by passing metal ion solutions (2000 cm^3, 0.5 $\mu g\,cm^{-3}$) in 2 M HNO_3 under varying flow rates from 10 to 30 $cm^3\,min^{-1}$ through the extraction column using a peristaltic pump. It was found that even at a flow rate 26 $cm^3\,min^{-1}$ quantitative metal ion sorption was observed (Table 1), reflecting the greater chelating site accessibility by the analytes. The most significant fact to be noted is that such high sample flow rates were never reported in the literature using other chelating sorbents thereby making it the most suitable sorbent in routine nuclear reprocessing units.

3.3.2. Sample and eluant breakthrough volume

The pre-concentrating ability of the polymeric matrix was studied in terms of sample breakthrough volume by passing varying volumes ranging from 0.5 to 8 dm^3 of 30 $\mu g\,cm^{-3}$ as influent concentration (C_0) in 2 M HNO_3 at a flow rate of 20 $cm^3\,min^{-1}$. The sorbed metal ions were desorbed using 15 cm^3 of optimum eluant at a flow rate of 1 $cm^3\,min^{-1}$ and were estimated. The effluent concentration (C) is obtained by the difference in the influent and eluant concentration and the metal ions are analyzed using Arsenazo III and Thoron as post-column reagents. It is evident from Fig. 6, that a good enrichment factor value of 330 in the case of U(VI) and Th(IV) and 400 for La(III) was achieved, reflecting the resin's capability of pre-concentrating trace metal ions from large sample volumes. The C/C_0 ratio started to increase once the dynamic capacity for the metal ions has reached. The enrichment factor values can increase if the influent concentration is still lesser.

3.3.3. Sensitivity studies-lower limit of analyte extraction

The lower limit of quantitative analyte extraction was performed by passing 1 dm^3 of analyte solutions spiked

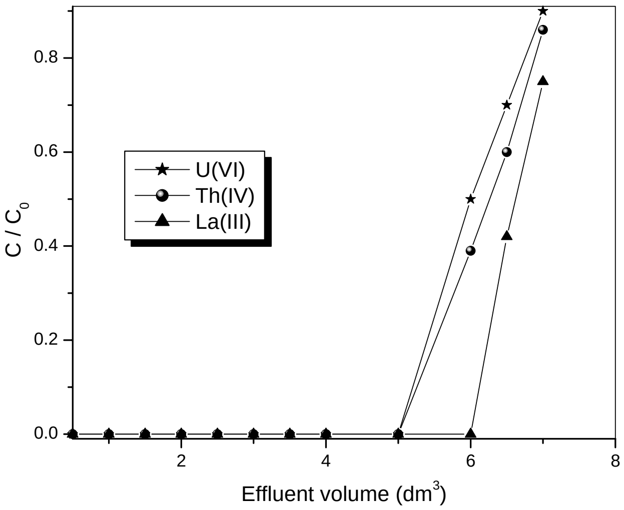

Fig. 6. Sample breakthrough volume curve.

Table 3
Recovery of targeted analytes from synthetic mixture mimicking a reprocessing solution (4 M HNO_3)

Metal ions[a]	Percentage extraction
U(VI)	100
Th(IV)	100
La(III)	100
Sr(I)	–
Cd(II)	–
Ba(II)	–
Zr(IV)	0.02
Mo(VI)	0.01
Cs(I)	–
Ce(IV)	0.08
Cr(III)	0.03
Na(I)	–
Nd(III)	1.2
Pr(III)	1.1
Gd(III)	1.6
Fe(III)	0.01
Ni(II)	–

Amount of U(VI), Th(IV) and La(III) = 1000 μg dm^{-3}.
Amount of diverse ions −0.1 to 0.5 g dm^{-3}.

with 5–50 μg of individual analytes in 2 M HNO_3 medium through the pre-conditioned resin bed. The sorbed metal ions were desorbed and estimated. The lower extraction limits were very low as shown in Table 1 indicating the resin's ability in targeting ppb level trace analytes for their quantitative extraction.

3.3.4. Stationary phase reusability test

The reusability of the stationary phase was tested by passing metal ion solution (1 dm^3, 500 μg dm^{-3}), in 4 M HNO_3 medium and the sorbed metal ions were eluted and analyzed. Similar operations were performed on the same column and it was found that the extraction capacity remained constant with reproducible *D* values even up to 30 cycles of repeated usage whose R.S.D. values were within 4.2%. Thus, the stationary phase is found to be durable even under high acidity which is of great significance.

4. Applications

4.1. Synthetic mixtures of nuclear reprocessing streams

To ascertain the practical applicability of the resin matrix in reprocessing units, 5 dm^3 of the synthetic mixtures mimicking typically nuclear spent fuel composition [25] was passed through the chromatographic column. The sorbed metal ions were eluted and estimated. It is evident from Table 3 that the practical breakthrough volume is not affected even in the presence of various diverse ions showing the resin's greater selectivity towards the analytes of interest. The analytical data were reproducible with an R.S.D. value of 3.9% for triplicate measurements.

4.2. Synthetic seawater

A 5 dm^3 synthetic seawater sample spiked with 50 μg U(VI) was prepared as per standard literature procedures [26]. The synthetic mixture was passed through the pre-conditioned resin bed at a flow rate of 20 cm^3 min^{-1} and the sorbed metal ions were recovered and estimated spectrofluorimetrically which showed a satisfactory recovery with an R.S.D. value of 3.1% for U(VI), for triplicate measurements.

4.3. Extraction of U(VI) from seawater and well water samples

A 5 dm^3 of the seawater and well water samples were filtered to get rid of the particulate matters using membrane filter (0.45 mm) and was passed through the pre-conditioned resin bed. The sorbed U(VI) was desorbed and analyzed using spectrofluorimetric procedure. The reliability of analysis was cross-checked by performing standard addition technique wherein 20 μg of U(VI) was spiked to the sample solution and the results obtained are shown in Table 4.

4.4. Thorium extraction from monazite sand (Travancore, India)

A 0.1 g of monazite sand sample was digested with concentrated H_2SO_4 at 250 °C for 4 h. The precipitate was

Table 4
Extraction of U(VI) from natural water samples

Water sample	Source of the sample/year of sampling	Method	Concentration of U(VI) (ng cm^{-3})	R.S.D. (%)[a]
Seawater-1	Chennai, India/August 2003	Direct	5.52 ± 0.54	4.0
		SA	5.47 ± 0.52	3.8
Seawater-2	Mahabalipuram, India/August 2003	Direct	5.93 ± 0.53	3.6
		SA	5.95 ± 0.55	3.7
Well water-1	Adyar, Chennai, India/September 2003	Direct	5.55 ± 0.54	3.9
		SA	5.60 ± 0.47	3.4
Well water-2	Guindy, Chennai, India/September 2003	Direct	4.51 ± 0.44	3.9
		SA	4.56 ± 0.46	4.1

[a] Data obtained on triplicate measurements; SA: standard addition.

filtered and redissolved in minimal volumes of dilute HCl and passed through the resin bed for pre-concentration. After desorption, the amount of thorium extracted was estimated spectrophotometrically, which was found to be 79.9 mg g^{-1}. The data were further confirmed by standard addition method, the values were within 4.1% R.S.D., for triplicate measurements.

5. Conclusions

The developed chelating ion-exchange resin matrix was successful as a good stationary phase for the extraction chromatographic column in extracting U(VI), Th(IV) and La(III) from highly acidic waste streams and as well as from various environmental samples, thus showing its wide range of practical applicability. From the extraction studies of La(III), a good extractive behavior for Am(III), a very essential radioactive element present in nuclear spent fuels is also anticipated which is a very significant task in nuclear waste management program. The most highlighting features of the resin matrix are its superior metal sorption capacity with good enrichment factor values and enhanced extraction rate due to the good hydrophilic character which were never reported in the literature. Also the developed bi-functional polymer is highly selective towards analyte extraction even in the presence of various diverse ions and electrolyte species. Moreover, the resin was highly sensitive in trapping trace analytes down to ppb levels ensuring its good practical applicability. Also, the developed polymer is highly durable under acidic conditions which is reflected from its greater reusability nature even up to 30 cycles of continuous usage.

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