

Extraction chromatographic method for the separation of actinides and lanthanides using EDHBA grafted AXAD-16 polymer

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Abstract

A new extraction chromatographic method has been developed by grafting chloromethylated polymer support with 4-ethoxy-*N,N*-dihexylbutanamide (EDHBA), for the selective extraction of U(VI), Th(IV), La(III) and Nd(III) from highly acidic matrices. The developed grafted polymer has been characterized using ^{13}C -CPMAS NMR spectroscopy, FT-NIR spectroscopy and also by CHN elemental analysis. The water regaining capacity of the grafted polymer is studied by TGA measurements and the active participation of the amide moiety towards metal ion complexation has been confirmed by Far IR spectroscopy. For the quantitative extraction of metal ions to the resin phase, various physio-chemical parameters are optimized by both static and dynamic methods. The developed amide grafted polymeric matrix shows good distribution ratio values even at high acidities, with the maximum metal sorption capacity values being 0.36, 0.69, 0.32 and 0.42 mmol g $^{-1}$ for U(VI), Th(IV), La(III) and Nd(III), respectively, at 6 M HNO $_3$ medium. The kinetics of metal ion phase equilibration is found to be moderately fast, with $t_{1/2}$ values of <6 min, for all the analytes of interest. The limits of analyte quantification (LOQ) using the developed method are in the range of 15–30 $\mu\text{g L}^{-1}$. Moreover, the sequential separation of the sorbed actinides and lanthanides could be achieved by first eluting with 100 mL of distilled water (for actinides) followed by elution with 20 mL of 0.1 M EDTA (for lanthanides). The selectivity behavior and the practical applicability of the developed resin are tested using synthetic low level nuclear reprocessing mixtures and also with monazite sand. The analytical data are within 3.8% relative standard deviation, reflecting the reproducibility and reliability of the developed method.

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1. Introduction

It is well known that metal ions play a major role in various industrial projects ranging from catalysis to nuclear power generation programs. But with the growing industrial revolution, the quantity of effluents discharged to the environment is also increasing day-by-day [1]. As a result of these waste discharge activities, it becomes a necessity to monitor their discharge levels, in order to estimate and also to prevent the level of toxicity imposed to the eco-system. Apart from environmental pollution, the continuous utilization of metal

ions in various activities can lead to depletion of mineral resources, in near future. Hence, there is a substantial awareness in preserving these valuable and toxic metal ions, by means of various reprocessing methods for effective recycling. One such area that necessitates for waste management programme is the recovery of actinides, and their separation from fission products in nuclear spent fuels. Solvent extraction technique using tri-*n*-butyl phosphate (TBP) based on PUREX process has remained to be the preferred method for this process. But the non-incinerable nature of the spent extractant, leading to the formation of secondary radioactive wastes, provoked chemists to the search for better alternatives [2–4].

From various research activities, it has been observed that the use of *N,N'*-dialkyl amides for the selective extraction

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of actinides from high acid streams proves to be fruitful, by solvent extraction. The advantageous features of these extractants include high radiolytic stability, the innocuous nature of the degradation products and complete incinerability [2–7]. But the main drawback associated with these extractants is the use of large volumes of *n*-dodecane as the process diluents, which has a tendency to form third phase formation with nitric acid [8]. In addition to this, problems are also encountered during disposal of organic solvents. As a result, extensive researches are being carried out world wide, to develop solvent free extraction procedures for nuclear reprocessing [9]. More recently, it was visualized that the use solid phase extractants (SPE) [10–21] for both recycling and decontamination process prove to be more advantageous over conventional extraction methods. In this, the organic extractants are anchored to an inert polymeric support and they serve effectively for metal ion extraction in an eco-friendly manner. In the recent years, several SPE methods have been proposed for actinide extraction [19–31] but majority of the sorbents had marginal extraction properties at high acidities due to various reasons like, the inappropriate choice of ligand moiety, solid support materials, etc. The current paper deals with a new grafted polymeric matrix in which *N,N*-dihexylbutanamide is anchored to the chloromethylated polymeric backbone via an ether spacer arm. The grafted polymer possesses all the characteristic features of an amide extractant and also can overcome the problems faced, using conventional methods. The ion-selectivity and the superior extractive behavior of the amide grafted polymer towards U(VI), Th(IV), La(III) and Nd(III), from high level acidic streams has been extensively studied.

2. Experimental

2.1. Instrumentation

For the structural characterization of the grafted polymer, a Bruker-Avance 400 model ^{13}C -CPMAS NMR (12 kHz, magnetic field: 9.01 T) spectrometer, a Perkin-Elmer Spectrum One model FT-IR spectrometer and an Elementar Vario EL model CHNPS analyzer were employed. A Bruker IFS 66 V model Far IR spectrometer was used for confirming the metal ion complexation to the polymeric matrix and a Perkin-Elmer TGA-7 model TG analyzer was employed for water regain capacity studies. A Jasco V-530 model spectrophotometer was used in the estimation of U(VI), Th(IV), La(III) and Nd(III). A Hitachi F-4500 fluorescence spectrophotometer was utilized for determining trace concentrations of uranium from synthetic reprocessing solution. A Varian SpectraAA-20 model flame atomic absorption spectrometer was used for the analysis of transition metal ions and other diverse cations. A Ravel Hi-Tech S-50 model peristaltic pump was used for maintaining a constant flow rate during column studies. An Orbitek DL model mechanical shaker with 200 rpm was used for static equilibration studies.

2.2. Chemicals and reagents

Standard metal ion stock solutions of U, Th and La were prepared by dissolving exact amounts of (AR grade) corresponding nitrate salts (Fluka Chemicals) in slightly acidified double distilled water and Nd stock solution was prepared from their corresponding oxide (Indian Rare Earths). All the stock solutions were standardized by complexometric titrations using EDTA. All the chemicals and reagents used during the process of chemical modification were purchased from Lancaster and E-Merck Chemicals and are of AR grade.

Chloromethylated resin beads (surface area: $825\text{ m}^2\text{ g}^{-1}$; pore diameter: 20–50 mesh; bead size: 0.3–1.2 mm; 5.4 mmol g^{-1} of Cl) were received as compliment from Thermax India Ltd.

2.3. Synthesis of EDHBA-grafted polymer

The desired 4-hydroxy-*N,N*-dihexylbutanamide was first synthesized by reacting γ -butyrolactone (7.6 mL, 0.1 mol) and dihexylamine (28.34 mL, 0.12 mol) in 100 mL of dichloroethane (DCE), in the presence of 16 g of anhydrous AlCl_3 and 12.5 mL of Et_3N , at 20–25 °C. The crude solution was then subjected to work up procedures followed by purification by vacuum distillation to give the desired viscous orange yellow colored hydroxyamide (92% yield). The amide was characterized using FT-IR, ^1H and ^{13}C NMR spectroscopic techniques and also by CHN analysis.

The chloromethylated resin beads were purified using 1:1 ethanol–water mixture followed by treatment with absolute ethanol, to remove the monomer impurities. The purified resin beads were filtered and vacuum dried prior to usage. 5 g of the purified resin beads were reacted with the synthesized amide (7.34 mL, 0.03 mol) using NaH in 50 mL of dry dimethylformamide (DMF), at 70–80 °C for 48 h. The resulting amide anchored resin beads were filtered, successively washed with ethanol, water and acetone and finally vacuum dried. The synthetic scheme leading to the desired grafted polymer is shown in Fig. 1.

2.4. Methods adopted for optimizing physio-chemical parameters

2.4.1. Static method

In this method, basic experimental parameters like kinetics, sorption capacity, solution acidity, matrix tolerance, etc., were optimized by equilibrating a known analyte concentration with a definite amount of grafted resin beads for definite time duration, using a mechanical shaker at 200 rpm. The resin's phase distribution ratios (*D*) were calculated using the following expression

$$D = \frac{(A_0 - A_f)V}{A_f W}$$

where A_0 and A_f are the amount of metal ions in the aqueous phase before and after equilibration, *W* the weight of the dry

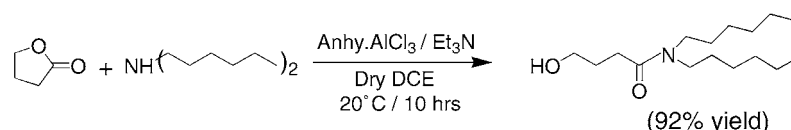
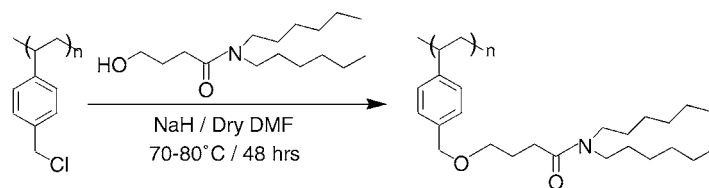
Step (a): Synthesis of 4-hydroxy *N,N*-dihexyl butanamide**Step (b): Synthesis of Amide Grafted Polymer**

Fig. 1. Synthesis scheme step.

resin (g) and *V* the volume of the aqueous phase (mL). The metal ions like U(VI) (7 M HNO₃ medium, 655 nm), La(III) and Nd(III) (pH: 3, 655 nm) were estimated spectrophotometrically using Arsenazo-III and for Th(IV) (0.2–0.5 M HCl medium, 545 nm) using Thoron, as chromogen. The optimum experimental parameters for quantitative metal ion sorption and desorption are listed in Table 1.

2.4.2. Dynamic method

For this method, an extraction chromatographic glass column (150 mm × 4 mm i.d.) packed with 0.5 g of resin beads was employed. The efficiency and uniformity in column packing was ensured using an activating solvent like ethanol, which was removed after packing. The packed column was preconditioned with 4 M HNO₃. The influent metal ion solution was passed through the preconditioned column bed using a peristaltic pump, which was interfaced between the sample reservoir and the column inlet. The extent of metal ion extraction under varying experimental conditions was studied. Finally, the conditions favoring quantitative sorption were optimized.

From the data obtained by both static and dynamic method, the grafted polymer was employed for the extraction of metal

ions from both synthetic mixtures and real sample. The analytes enriched in the resin phase were eluted and analyzed spectrophotometrically. For the estimation of trace uranium concentrations, a steady state spectrofluorimetric procedure [32] using 1 M H₃PO₄ medium was adopted, where 266 and 515 nm are the excitation and emission wavelengths, respectively.

3. Results and discussion**3.1. Resin characterization**

¹³C-CPMAS NMR spectra for the grafted polymer showed resonance signals at 39.2 and 25.6 ppm, which corresponds to the aliphatic groups attached to the carbonyl and N-side of the amide moiety. The presence of lateral CH₃ groups was confirmed by resonance signal at 10 ppm. The resonance signal for the amide carbonyl was observed as a low intensity signal at 198.3 ppm, which were absent for the spectra obtained for the non-functionalized chloromethylated resin.

The grafting of the amide moiety to the chloromethylated polymeric platform was also followed using FT-IR spectra. The appearance of spectral band at 1656.2 cm⁻¹ corresponds to the amide carbonyl (C=O) group and the enhancement of the –CH₂ stretching vibrations at 2963.5 cm⁻¹ shows the incorporation of the amide moiety. Also, the disappearance of the corresponding vibrations for the –CH₂Cl stretching and wagging vibrations at 673.9 and 1264.5 cm⁻¹ that appear in the non-functionalized resin, also confirms the chemical modification of the polymeric matrix, which is shown in Fig. 2.

The existence of metal complexation through the amide carbonyl group was confirmed by Far-IR studies, which showed bands in the spectral regions of 210–190 cm⁻¹, which corresponds to the ν_{O–[M]} stretching vibrations.

CHN elemental analysis was performed for the grafted polymer in order to monitor the extent of ligand functional-

Table 1
Optimum experimental parameters for quantitative analyte extraction

Experimental parameters	U(VI)	Th(IV)	La(III)	Nd(III)
<i>t</i> _{1/2} (min)	3.3	3.0	3.7	3.5
Metal sorption capacity (mmol g ⁻¹)				
(i) 6 M HNO ₃	0.357	0.690	0.324	0.416
(ii) 6 M HCl	0.336	0.647	0.263	0.381
Maximum sample flow rate (mL min ⁻¹)	12	12	10	11
LOQ (μg L ⁻¹)	30	20	15	15
Sample breakthrough volume (L)	5	6.5	4.5	5
Preconcentration factor (2 M HNO ₃)	250	325	225	250

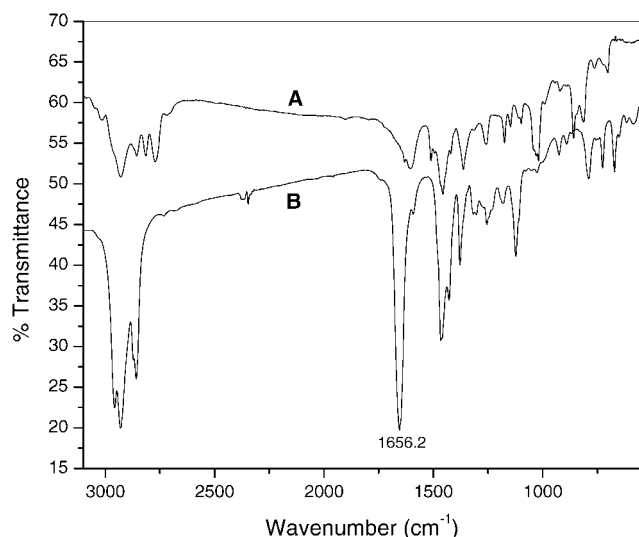


Fig. 2. FT-IR spectra of chloromethylated resin (A) and EDBHA-grafted polymer (B).

ization. The obtained experimental data (shown in Table 2) are in close agreement with the theoretical values, which confirms the effective functionalization of the resin matrix with the amide moiety.

The water regaining capacity studies were performed by equilibrating 100 mg of the grafted resin with 50 mL of water, for 2 h. The resin beads were filtered, air-dried and subjected to TGA measurements, which showed a weight loss of 3.5% up to 110 °C. Similarly studies performed for the non-grafted chloromethylated resin showed a weight loss of only 2.5%. This difference is due to presence of bulky amide moiety, which enhances the net weight of the grafted polymer thereby providing greater surface contact with the aqueous phase. Due to this, water percolation through the polymer pores is facilitated in spite of the increase in the hydrophobic character.

3.2. Static equilibration studies

3.2.1. Extraction efficiency in acidic solutions

The metal extracting ability of the grafted amide polymer from acidic solutions was studied by equilibrating 50 mg of the resin beads with (40 mL, 10 $\mu\text{g mL}^{-1}$) individual metal

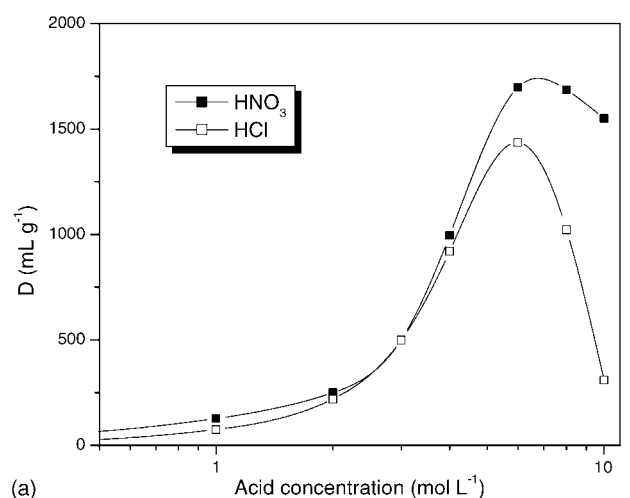
ion concentrations over a wide range of solution acidity (0.1–10 M), for 1 h at 200 rpm. The extent of metal ion resin phase sorption was studied in terms of D values after analyzing the aqueous phase metal ion concentrations. On comparing the data obtained (Fig. 3a–c), it is evident that the resin shows greater affinity for Th(IV), which is reflected from the high D values ($>10^3$), observed at 4–10 M acidity. However, for U, La and Nd, the D values were of the order of 10^2 , which is an unusual behavior to expect from amides. In general, for all the analytes the D values showed a positive trend with increasing acidity, which can be attributed to the extracting behavior of the amides as neutral metal species, using anions like $\text{NO}_3^-/\text{Cl}^-$, present in the sample solution for charge neutralization. However, with increasing acidity a slight negative dependency was observed due to the formation of metal anionic complexes and also due to the competition for the active sites by HNO_3/HCl . From the obtained data, it is possible to comment that the developed resin matrix is highly suitable for extracting actinides and lanthanides from low level reprocessing nuclear spent fuels.

3.2.2. Elution studies

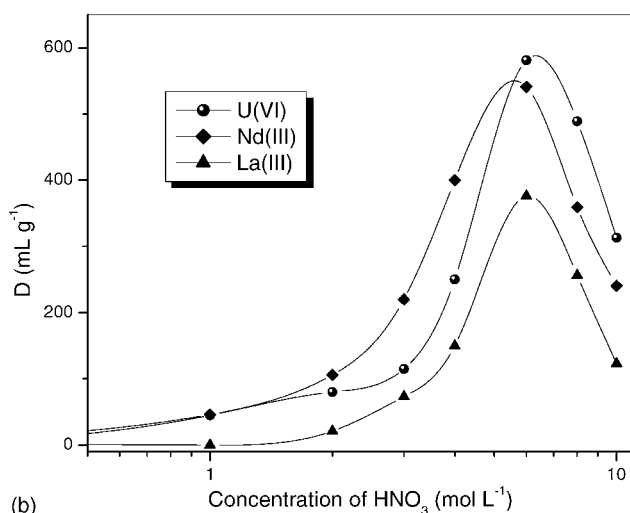
For this study, 50 mg of the resin beads were equilibrated with (40 mL, 10 $\mu\text{g mL}^{-1}$) metal ion solution, in 4 M HNO_3 for 2 h. The sorbed metal ions were desorbed from the resin phase using various eluting agents. The experimental results of their % recovery, are tabulated in Table 3. It was observed that on using 0.1 M EDTA ($\text{pH} \geq 5$, adjusted with dil. NH_3) as eluant, a quantitative recovery value of $>99.8\%$ was achieved for all the analytes except in the case of U(VI), where it was 96%. Similarly, quantitative recovery of U(VI) and Th(IV) were achieved using 0.1 M $(\text{NH}_4)_2\text{CO}_3$, where U(VI) and Th(IV) were eluted as anionic metal carbanato species ($[\text{UO}_2(\text{CO}_3)_3]^{4-}$, $[\text{Th}(\text{CO}_3)_5]^{6-}$). Also, complete recovery of Th(IV) was observed with 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, wherein Th(IV) gets eluted from the resin phase as more stable anionic $[\text{Th}(\text{C}_2\text{O}_4)_4]^{4-}$. It was also observed that distilled water could be used as an eluant, during extraction chromatographic column operation, where $>98\%$ recovery was achieved for both U(VI) and Th(IV). But in the case of lanthanides, a recovery value of $<5\%$ only was possible using distilled water, thus enabling the possibility for sequential separation of actinides from lanthanides. Also, the important feature to be considered is that the eluants used for recover-

Table 2
Characterization of the various stages of functionalization

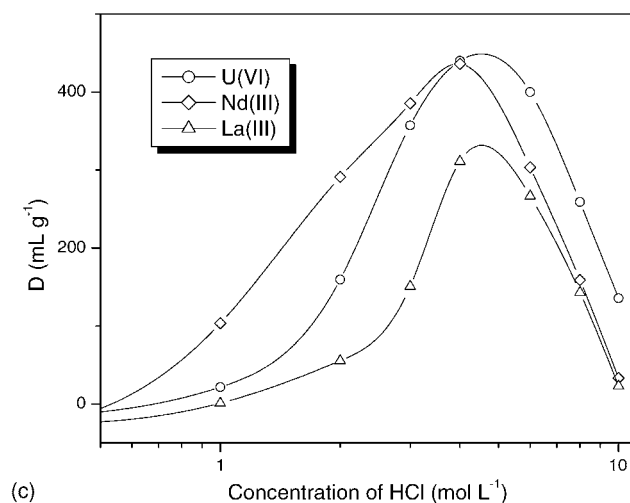
Item characterized	FT-IR spectral data (cm^{-1})	(%) C:H:N elemental data
4-Hydroxy- <i>N,N</i> -dihexylbutanamide	—OH (3412.6), —CH ₂ — aliphatic side chain (2928.8), —C=O (1645.1), —C—N (1466.2)	Theoretical – 70.85:12.18:5.20
Merrifield chloromethylated resin	—CH ₂ Cl (673.9), —CH ₂ wagging (1264.5)	Experimental – 70.65:12.02:5.01 Theoretical – 72.04:6.10
EDBHA-grafted polymer	—CH ₂ — aliphatic side chains (2963.5), —C=O (1656.2), —C—N (1462.8), —C—O—C— (1117.9)	Experimental – 72.91:6.10 Theoretical – 77.89:10.53:3.53
		Experimental – 77.93:10.6:3.42



(a)



(b)



(c)

Fig. 3. (a) Distribution ratios for Th(IV) in acidic matrices (analyte concentration: 40 mL, $10 \mu\text{g mL}^{-1}$; amount of resin: 50 mg; equilibration time: 1 h, 200 rpm). (b) Extraction profile in HNO_3 medium (analyte concentration: 40 mL, $10 \mu\text{g mL}^{-1}$; amount of resin: 50 mg; equilibration time: 1 h, 200 rpm). (c) Extraction profile in HCl medium (analyte concentration: 40 mL, $10 \mu\text{g mL}^{-1}$; amount of resin: 50 mg; equilibration time: 1 h, 200 rpm).

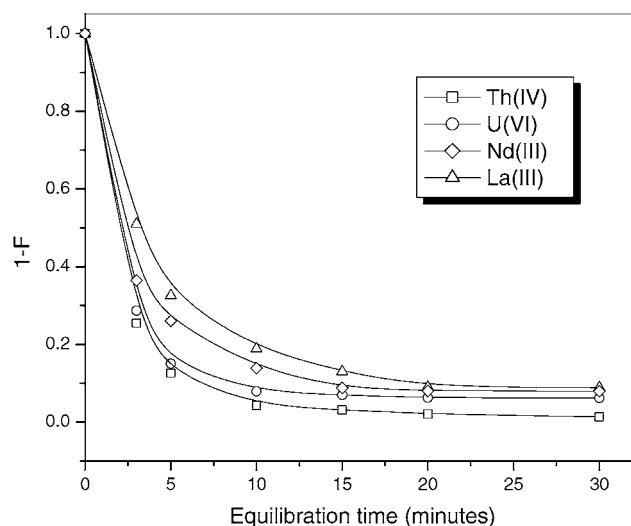


Fig. 4. Rate of analyte extraction (analyte concentration: 40 mL, $10 \mu\text{g mL}^{-1}$; medium: 4 M HNO_3 ; amount of resin: 50 mg; shaking speed: 200 rpm).

ing the analytes of interest were very cheap, eco-friendly and totally incinerable with no toxicity.

3.2.3. Kinetics studies

The rate at which metal ions under phase equilibration was studied by equilibrating 50 mg of the resin beads with a series of analyte solutions (40 mL, $10 \mu\text{g mL}^{-1}$) in 4 M HNO_3 , for varying time durations. The non-extracted metal ions in the aqueous phase were analyzed and the kinetic data were plotted in terms of $(1 - F)$, as shown in Fig. 4. The fractional attainment of equilibrium (F) is expressed as

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

where $[M^R]_t/[M^R]_{\text{eq}}$ are the ratios of metal ion concentration in the resin phase at time ' t ' to that at equilibrium [31]. Even though the resin was more of hydrophobic in nature, it is evident from the graph that near complete extraction was attained within 10 min, due to the macroporous structure of the resin matrix, which favored to the greater accessibility of the neutral metal complex towards the anchored hydrophobic amide moiety. The faster exchange kinetics can also be explained in terms of moderate water regaining nature of the grafted polymers, which facilitates greater transport of metal ion from the aqueous phase to the resin phase.

3.2.4. Maximum metal sorption capacity

The metal sorption capacity of the grafted resin matrix for the analytes of interest was determined individually by equilibrating 50 mg of resin beads with excess concentrations of analyte solution (50 mL, $200 \mu\text{g mL}^{-1}$) at 6 M HNO_3 and 6 M HCl mediums, for 12 h. After desorption and estimation process, it was observed that the grafted polymer showed good sorption capacity values of 0.357, 0.690, 0.416 and

Table 3
Analyte recovery with various eluants

Eluants	Eluant volumes (mL), static (dynamic)	% Recovery			
		U(VI)	Th(IV)	Nd(III)	La(III)
Water	100 (100)	89.2 (99.8)	759 (98.0)	7.2 (4.9)	8.3 (3.0)
0.1 M (NH ₄) ₂ CO ₃	15 (20)	99.9 (99.8)	99.8 (99.9)	42.3 (40.5)	89.7 (85.1)
0.1 M EDTA (pH ≥ 5)	15 (20)	96 (99.2)	99.9 (99.8)	99.9 (100.0)	100.0 (99.8)
0.1 M HCl	15 (20)	85 (82.1)	70.5 (72.9)	99.9 (100.0)	86.9 (87.4)
0.1 M (NH ₄) ₂ C ₂ O ₄	15 (20)	65.0 (68.9)	99.9 (99.9)	54.1 (46.3)	80.2 (79.5)

Values given in parenthesis represent % recovery in dynamic conditions.

0.324 mmol g⁻¹ at 6 M HNO₃ and 0.336, 0.647, 0.381 and 0.263 mmol g⁻¹ at 6 M HCl for U(VI), Th(IV), Nd(III) and La(III), respectively. The high sorption capacity values were accounted for the greater degree of ligand functionalization and also to the enhanced chelating site accessibility.

3.2.5. Analyte phase distribution ratio in the presence of electrolytes

As the developed resin showed good metal extractive behavior even at high acidities, it was decided to test its extraction efficiency in the presence of NaNO₃ and NaCl medium, which are the major matrix components in nuclear reprocessing solutions. For this study, 50 mg of the resin was equilibrated with (40 mL, 10 µg mL⁻¹) metal ion solution in the presence of increasing salt concentrations. The equilibrating studies were performed for 1 h at 200 rpm, in 2 M corresponding acid solutions. It was observed that NaNO₃ showed a salting out effect thereby showing a positive dependency on the *D* values with increasing salt content (Fig. 5). However, with increasing NaCl content, a negative trend was seen for all the analytes, which is probably due to the formation of more stable anionic metal chloro complexes.

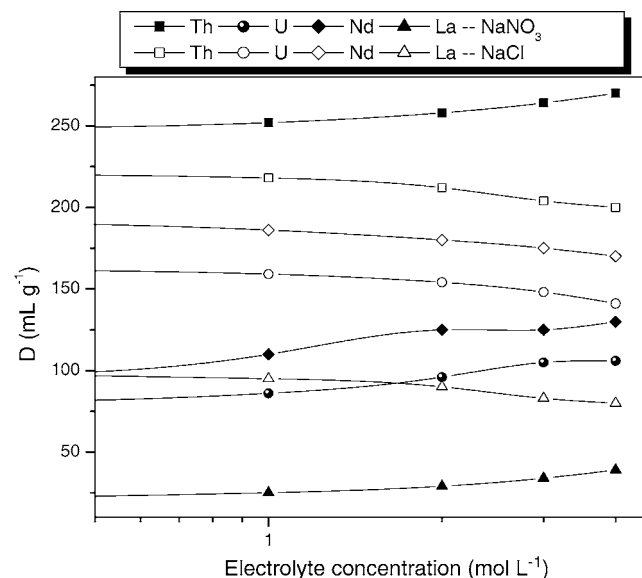


Fig. 5. Extraction efficiency in the presence of electrolytes (analyte concentration: 40 mL, 10 µg mL⁻¹; medium: 2 M corresponding acids; amount of resin: 50 mg; equilibration time: 1 h, 200 rpm).

3.2.6. Resin's tolerance towards complexing anions and common metal ions

The ability of the resin matrix to quantitatively extract trace level analytes even in the presence of large concentrations of complexing anion species and competing diverse ions, were studied by equilibrating 50 mg of the resin with (40 mL, 1.25 µg mL⁻¹) analyte solution in the presence of varying quantities of individual matrix components. The resin showed complete non-extractive behavior (0% extraction) for the first row transition metal series but for post-transition metal ions, it showed a very poor extracting ability with *D* values <50 at 4 M HNO₃. However in the case of lanthanides, *D* values <400 were observed and their degrees of tolerance towards 100% analyte recovery are shown in Table 4. The data also shows that the resin showed good selectivity in extracting analytes of interest even in the presence of large concentrations of anionic complexing agents and common electrolyte species.

3.3. Dynamic studies – extraction chromatographic method

3.3.1. Sample flow rate studies

The effect of sample flow rate was studied by passing (2000 mL, 0.5 µg mL⁻¹) metal ion solutions in 4 M HNO₃, through a preconditioned extraction chromatographic column, under varying flow rates (2–20 mL min⁻¹) controlled by means of a peristaltic pump. It was observed that the functionalized resin shows quantitative sorption for all the analytes, even up to a flow rate of 10–12 mL min⁻¹ (as shown in Table 1), which reflects the greater active site accessibility and faster metal ion phase equilibration exhibited by the amide grafted polymer. During metal ion desorption, eluant flow rates of 1 mL min⁻¹ was used to achieve quantitative recovery of analytes. Due to faster equilibration and rapid desorption, the time involved during metal ion preconcentration and their subsequent analysis, are reduced substantially.

3.3.2. Sample breakthrough volume

The ability of the grafted resin matrix to preconcentrate trace analytes from large sample volumes was tested in terms of sample breakthrough studies, by passing 10 µg L⁻¹ of influent analyte concentration (*C*₀) in 6 M HNO₃ through the resin packed column, under varying sample volumes

Table 4
Diverse ions/electrolyte species tolerance limits

Metal ions	Tolerance limits for electrolytes (mol L ⁻¹)							
	Na ₂ SO ₄	Na ₃ PO ₄	NaF	CH ₃ COO ⁻	C ₂ O ₄ ²⁻			
U(VI)	0.77	0.15	0.46	0.31	0.10			
Th(IV)	0.82	0.10	0.43	0.45	0.01			
Nd(III)	0.74	0.09	0.36	0.42	0.08			
La(III)	0.52	0.09	0.33	0.40	0.02			
	Tolerance limits for interfering metal ions (mmol L ⁻¹)							
	Zr(IV)	Mo(VI)	Pb(II)	Cd(II)	Bi(III)	Ce(IV)	Sm(III)	Gd(III)
U(VI)	9.1	6.2	12.1	12.8	10.9	3.2	1.8	1.0
Th(IV)	3.4	4.2	12.6	12.0	11.8	2.8	2.9	3.2
Nd(III)	2.1	3.6	11.6	12.9	13.6	2.9	0.9	0.6
La(III)	5.1	5.2	11.9	13.0	14.5	2.6	0.4	0.2

(0.5–8 L) at a flow rate of 10 mL min⁻¹. The sorbed metal ions were desorbed using 20 mL of 0.1 M (NH₄)₂CO₃ for U(VI) and 20 mL of 0.1 M EDTA for other analytes. It is evident from Fig. 6, that a good enrichment factor value of 250, 325, 225 and 250 were achieved for U(VI), Th(IV), La(III) and Nd(III), respectively.

3.3.3. Limit of quantification

The limit up to which quantitative extraction of analytes can be achieved using the developed resin matrix was studied by passing 1 L of 2 M HNO₃ solutions spiked with 5–50 µg of individual analytes, through the preconditioned resin bed under optimum experimental conditions. The preconcentrated metal ions were desorbed and estimated spectrophotometrically, except in the case of U(VI), the spectrofluorimetry procedure was adopted. The limits of analyte extraction are shown in Table 1, which indicates the high sensitivity associated with the developed grafted polymer in preconcentrating even ppb level trace analytes even from large sample volumes.

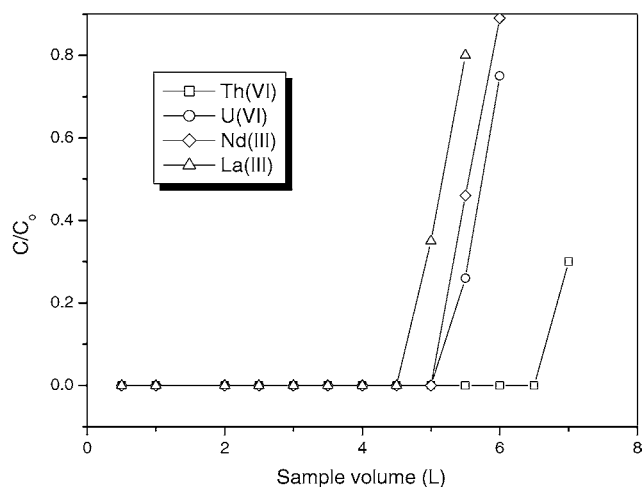


Fig. 6. Dynamic sample breakthrough curve (analyte concentration: 10 µg L⁻¹; medium: 6 M HNO₃; flow rate: –10 mL min⁻¹).

3.3.4. Reusability of the stationary phase

The reusability of the packed resin bed was tested by passing metal ion solution (1 L, 500 µg L⁻¹), in 4 M HNO₃ medium, through the mini-extraction column 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 more or less constant even up to 20 cycles of repeated usage, with rsd values <3.6%. It was also observed that the stationary phase showed good chemical durability even under high acidity (>6 M), thus paving way for its application to reprocessing solutions.

4. Applications

4.1. Separation of actinides and lanthanides from simulating synthetic nuclear spent fuel mixture

The practical utility of the grafted polymer for the selective extraction and sequential separation of actinides and lanthanides then was tested using a synthetic nuclear acidic waste mixture [32] of fission products and more common metal ions of >10³-fold concentrations to that of the analyte ions. The analytes extracted in the stationary phase were separated by applying sequential elution mode where, the actinides were first eluted using 100 mL of water followed by the recovery of the lanthanide ions with 20 mL of 0.1 M EDTA. The recovered U(VI) was estimated by U(VI) specific (even in the presence of Th(IV)) spectrofluorimetry method and then Th(IV) by thoron-spectrophotometry method. The resin matrix gave recovery of 99.8% for actinides, with an rsd value of <3.7%, on triplicate measurements.

4.2. Separation of Th from monazite sand (Travancore, India)

Monazite sand sample (0.1 g) was digested initially at low temperature using concentrated H₂SO₄ followed by vigorous heat treatment up to 250 °C, in the presence of 30% H₂O₂, for 4 h to dryness. The resulting residue was redissolved in min-

imal volumes of HNO_3 and a known volume of aliquot was passed through the extraction column under optimum experimental conditions. After desorption with 100 mL of distilled water, the amount of thorium extracted was estimated and was found to be 79.8 mg g^{-1} (certified value -81 mg g^{-1}). The data reliability and reproducibility was crosschecked by standard addition method and the values were within 3.5% *rsd*.

5. Conclusions

The grafted polymer proves to be an efficient solid phase extractant for the sequential separation of actinides from lanthanides present in high acidic wastes, during nuclear fuel reprocessing operation. Moreover, a considerable extractive behavior for Nd(III) was observed using the developed grafted polymer, which leads to the anticipation of extracting Am(III) ions (a long-lived radioactive isotope) from the reprocessing streams, for transmutation process. The grafted polymer was found to be robust in various acidic conditions whose extractability was found to be a more or less constant even up to 20 cycles of repeated usage. The developed grafted polymer thus proves to be simple, effective, eco-friendly and economical.

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