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Selective Extraction of Actinides Using EEBEHBA Grafted Polymer: A Green Process for Nuclear Reprocessing Program

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ABSTRACT

A new amide grafted polymer has been developed using Merrifield chloromethylated resin (inert solid support) anchored with 4-ethoxy-4-ethyl-*N*,*N*-bis-2-ethylhexylbutanamide (EEBEHBA), for the selective extraction of actinides from lanthanides in acidic matrices. The polymer has been characterized using ^{13}C- CPMAS (cross-polarized magic angle spin) NMR spectroscopy, FT-NIR spectroscopy, and also by CHN elemental analysis. The fabricated polymeric sorbent shows greater selectivity in extracting U(VI) over Th(IV) and other lanthanides, even under high acidities (2–4 M HNO_3). The grafted polymer offers good distribution ratio (D) values for actinides of interest over a wide range of solution acidity, with the maximum metal sorption capacity being 0.629 mmol g^{-1} and 0.214 mmol g^{-1} for U(VI) and Th(IV),

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respectively, in 4 M HNO_3 medium. The functionalized resin matrix shows moderately fast metal ion phase exchange kinetics, with $t_{1/2}$ values < 3 min for both the analytes. The notable feature of the resin is the quantitative desorption of actinides using distilled water as eluant, a simple green process of recovery which has not yet been reported in the literature using polymeric sorbents. The practical utility has been tested using synthetic low-level nuclear reprocessing mixtures and also with real samples like monazite sand. The analytical data obtained from triplicate measurements are within 3.6% rsd reflecting the reproducibility and reliability of the developed method.

Key Words: Actinides; Amide grafted polymer; Preconcentration; Acidic matrices.

INTRODUCTION

The increasing public attention for radioactive waste disposals and potential public health hazard effects has gained substantial interest in preconcentrating trace level actinides from both environmental and biological samples, in the recent years.[1] In addition to this, the depletion of uranium and thorium resources, which are potential fuels for nuclear energy and power generation programs, paved the way for the separation scientists to search for an efficient technique to extract these metal ions from spent nuclear fuels. Recently, polymeric resins grafted with a variety of functional groups have gained rapid acceptance for a wide range of separation processes such as the extraction of heavy and toxic metals,[2–4] recovery of U(VI) from seawater,[4–9] etc. Moreover, these functionalized polymers have greater amenability to automation, an essential feature for routine analysis.[10]

Several research projects have evaluated the potential advantages of using neutral *N*,*N*,*N*,*N*-tetraalkylamides [11–14] and *N*,*N*-dialkylamides,[15,16] for the extraction and separation of lanthanides and actinides from high-level radioactive wastes, by solvent extraction technique. They have been considered as the better alternatives to TBP, due to their innocuous nature of the degradation products, complete incinerability, and low cost.[11–16] In general, it was inferred that amides serve as good extractants for the extraction of both lanthanides and actinides. But in recent years, it was observed that the use of branched alkyl chains on both the carbonyl and the N-side of the amide moiety can bring out high degree of selectivity and separation for both lanthanides and actinides.

The majority of the grafted polymers developed earlier were mainly focused on the extraction of various metal ions from both synthetic and environmental samples, which are mostly near-neutral or low-pH aqueous solutions. Only limited works have been done on the extraction of actinide ions from acidic environments using solid-phase extractants, which is of great significance in the reprocessing nuclear spent-fuel solutions.[17–20] But, very few attempts have been made so far to develop amide-grafted resins [20] for the efficient extraction of actinides from acidic matrices, which have been proved to be promising in solvent extraction technique. In the current research work, a new amide grafted polymer has been developed by anchoring EEBEHBA via an ether linkage to an inert polymeric support and its ability to selectively extract actinides (mainly uranium and thorium) was studied. Various physiochemical parameters such as effect of sample acidity, kinetics, effect of diverse ions, breakthrough volume and flow rates were studied and optimized by both static and dynamic methods. This newly developed resin matrix was found to be more selective in extracting actinides over lanthanides under acidic matrices, which was proved by testing with synthetic reprocessing fuel mixtures. The main advantage of the developed polymer is the noninvolvement of any organic solvents either during the process of extraction or at the elution steps. Moreover, the eluants used for analyte recovery are very cheap and totally incinerable, thereby avoiding the formation of secondary waste products. The synthesis, characterization, and the ion selective behavior of the newly grafted amide resin matrix have been studied and the obtained results are discussed in detail in this paper.

EXPERIMENTAL

Instrumentation

A Bruker-Avance 400 model ^{13}C-CPMAS (12 KHz, Magnetic field – 9.01 Tesla) NMR Spectrometer, a Perkin-Elmer Spectrum One model FT-IR spectrometer, and an Elementar Vario EL model CHNPS analyzer were employed for the characterization of the grafted polymer. A Bruker IFS 66V model Far IR Spectrometer was used for confirming the metal ion complexation to the polymeric matrix and a Perkin-Elmer TGA-7 model thermal analyzer was employed for water regain capacity studies. A Jasco V-530 model spectrophotometer was used for the estimation of U(VI), Th(IV), La(III), and Nd(III). A Hitachi F-4500 fluorescence spectrophotometer was utilized for determining ppb-level concentrations of uranium from synthetic spent-fuel samples. The analysis of transition metal ions and other diverse cations was performed using a Varian SpectrAA-20 model flame atomic absorption spectrometer. 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.

Chemicals and Reagents

The standard metal ion stock solutions were prepared by dissolving exact amounts of AnalaR (AR) grade $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$ (Fluka Chemicals) in slightly acidified double distilled water and were standardized by complexometric titrations using EDTA. Similarly, lanthanides and transition metal ion stock solutions were prepared from their corresponding oxides (Indian rare earths) and salts (Merck & Qualigens fine chemicals), respectively, and were subsequently standardized. 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.

Merrifield chloromethylated styrene-divinylbenzene resin (Capacity [C1]: $\sim$5.5 mmol g^{-1} resin, 16–50 mesh) obtained from Fluka chemicals was purified with 1 : 1 ethanol and water mixture followed by washing with absolute ethanol to remove the monomer impurities. Finally, the beads were filtered, dried, and vacuumized prior to usage.

Synthesis of EEBEHBA Grafted Polymer

The 4-hydroxy-4-ethyl-*N*,*N*-*bis*-2-ethylhexylbutanamide was synthesized by reacting γ-caprolactone (11.1 mL, 0.1 mol) and dihexylamine (36 mL, 0.12 mol) in dichloroethane (DCE), in the presence of anhydrous aluminium chloride-triethylamine ($AlCl_3$-Et_3N) couple at 20–25°C. The product was purified by vacuum distilling out the impurities after subjecting the crude solution to workup procedures. The resulting red-orange-colored hydroxyamide (96% yield) was characterized using FT-IR, ^1H, and ^{13}C NMR spectroscopic techniques.

The grafting of the amide moiety to the polymeric matrix was performed by reacting 5 g of the purified resin with the synthesized amide (10.7 mL, 0.03 mol), in the presence of sodium hydride (NaH) in dry dimethylformamide (DMF) at 70–80°C for 48 h. The resulting amide anchored resin matrix was filtered; washed subsequently with ethanol, water, and acetone; and finally vacuum dried. The synthetic scheme leading to the desired grafted polymer is shown in Fig. 1.

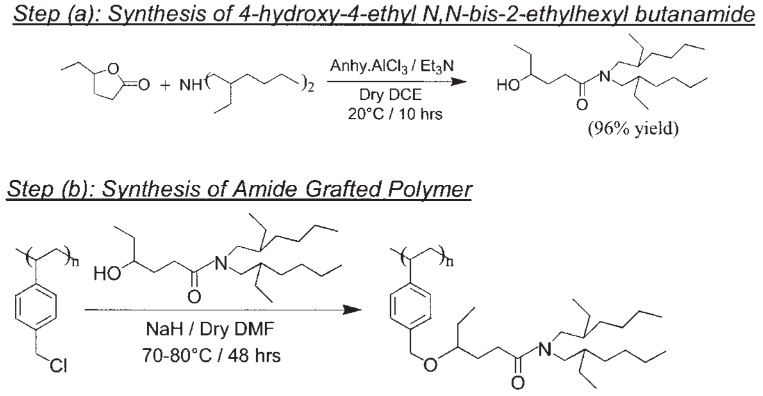

Figure 1. Synthesis scheme.

Methods Adopted in Optimizing the Physio-chemical Parameters for Quantitative Metal Ion Extraction

Static Method

In this method, most of the basic analytical properties of the grafted polymer were studied and optimized to ensure quantitative extraction of analytes. This was performed by equilibrating a known analyte concentration with a definite amount of grafted resin beads for limited time duration, using a mechanical shaker at 200 rpm. The D values were calculated using the following expression,

$$D\ (\mathrm{mL\,g^{-1}}) = \frac{(A_o - A_f)V}{A_f W}$$

where A_o and A_f are the amount of metal ions in the aqueous phase before and after equilibration, W is the weight of the dry resin (g), and V is the volume of the aqueous phase (mL). The metal ions like U(VI), La(III), and Nd(III) were estimated spectrophotometrically using Arsenazo-III and for Th(IV) using Thoron, as chromogen. The optimum experimental parameters for quantitative metal ion sorption and desorption are listed in Table 1.

Dynamic Method

For this study, an extraction chromatographic glass column (15 × 4 mm i.d) packed with 0.5 g of resin beads was used for optimizing all the column

Table 1. Optimum experimental parameters.

Experimental parameters	U(VI)	Th(IV)
$t_{1/2}$ (minutes)	2.5	2.8
Metal sorption capacity (mmol g^{-1})		
(i) 4M HNO_3	0.629	0.214
(ii) 4M HCl	0.610	0.196
Maximum sample flow rate (mL min^{-1})	14	12
Lower limit of detection (μg L^{-1})	20	20
Sample breakthrough volume (L)	6	4
Preconcentration factor (2M HNO_3)	400	267

parameters in order to perform an efficient dynamic operation. The efficiency and uniformity in column packing was ensured and the packed column was preconditioned with 2 M HNO_3. The influent metal ion solution was passed through the preconditioned column bed, and the extent of metal ion extraction under varying experimental conditions was studied. Finally, the conditions favoring quantitative sorption were optimized and the results were tabulated in Table 1.

Since the data obtained by both static and dynamic methods were encouraging, the grafted polymer was then employed for the extraction of metal ions from both synthetic spent-fuel mixtures and real monazite sand sample. The analytes enriched in the resin phase were eluted and analyzed spectrophotometrically. For the estimation of ppb-level uranium concentrations, a steady-state spectrofluorimetric procedure (21) using 1 M H_3PO_4 medium was adopted, with the excitation and emission wavelengths being 266 nm and 515 nm, respectively.

RESULTS AND DISCUSSION

Resin Characterization

The synthesis of the hydroxy amide and the chemical modification of the chloromethylated resin matrix were studied by FT-IR spectroscopy. The spectral data are itemized in Table 2. The disappearance of spectral band at 673.9 cm^{-1} and at 1264.5 cm^{-1} and the subsequent appearance of amide $C{=}O$ band at 1653.3 cm^{-1} along with the enhancement of the $-CH_2$ stretching vibrations at 2963.5 cm^{-1}, clearly confirms the chemical modification of the polymeric matrix as shown in Table 2. The involvement of the complexation

Table 2. Characterization of the various stages of functionalization.

Characterized compound/resin	FT-IR Spectral data (cm^{-1})	(%) C : H : N Elemental data
4-hydroxy-4-ethyl-*N*,*N*-di-bis-2-ethylhexylbutanamide	–OH (3390.0), $-CH_2$-aliphatic side chain (2956.2), –C═O (1649.1), –C–N (1466.2)	Theoretical: 74.37 : 12.68 : 3.94 Experimental: 74.35 : 12.72 : 3.96
Merrifield chloromethylated resin	$-CH_2Cl$ (673.9), $-CH_2$ wagging (1264.5)	Theoretical: 72.04 : 6.10 Experimental: 72.91 : 6.10
EEDBEHBA grafted polymer	$-CH_2$-aliphatic side chains (2963.5), –C═O (1653.3), –C–N (1469.8), –C–O–C– (1117.2)	Theoretical: 79.23 : 10.96 : 3.05 Experimental: 79.31 : 10.90 : 2.99

of the amide carbonyl to the metal ions of interest was confirmed by Far-IR studies in the spectral regions of 222–180 cm^{-1}.

The extent of amide grafted to the polymer matrix was monitored by performing CHN elemental analysis. The data obtained for the hydroxy amide ligand moiety, chloromethylated resin, and the amide grafted polymer are given in Table 2. The close agreement of the obtained data with the corresponding theoretical values shows that >98% ligand grafting has occurred to the polymeric matrix.

^{13}C CPMAS NMR spectral studies were performed before and after functionalization of the chloromethylated resin, which is shown in Fig. 2. A low-intensity resonance signal was observed at 198.10 ppm for the grafted polymer, which corresponds to the amide carbonyl group anchored to the polymeric matrix, which was absent for the nonfunctionalized chloromethylated resin. Also, the resonance signals observed at 39.21 ppm and 57.69 ppm corresponding to the aliphatic side chains attached to the nitrogen side of the amide moiety anchored to the polymer. The signal appearing at 122.38 ppm corresponds to the polymer aromatic moiety.

Thermo gravimetric analysis (TGA) data obtained for water regaining capacity studies showed a weight loss of 4.5% up to 110°C. Similarly studies performed for the non-grafted chloromethylated resin showed a

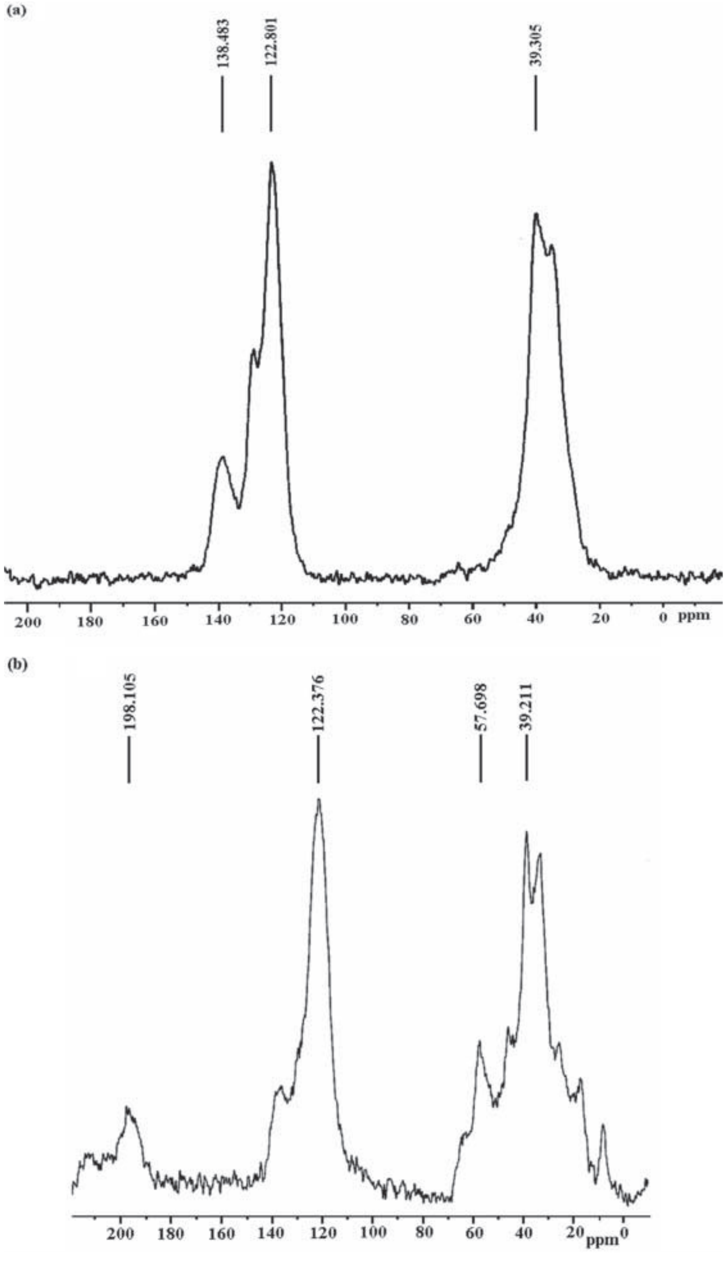

Figure 2. (a) ^{13}C-CPMAS NMR: Unfunctionalized Merrifield polymer. (b) ^{13}C-CPMAS NMR: Grafted polymer.

weight loss of only 2.5%. This difference is due to the presence of bulky amide moiety, which enhances the net weight of the grafted polymer, thereby providing better surface contact with the aqueous phase. Due to this, water percolation through the polymer pores is facilitated inspite of the increase in the hydrophobic character.

Static Equilibration Studies

Extraction Efficiency in Acidic Solutions

The influence of sample acidity on the extracting ability of the grafted polymer was studied by equilibrating 50 mg of the resin beads with (40 mL, 10 μg mL^{-1}) individual metal ion concentrations over a wide range of HCl and HNO_3 concentrations (0.1–10 M), on a mechanical shaker for 1 h. The metal ion concentrations in the aqueous solution were analyzed and results are shown in Fig. 3. It is evident from the plot that the resin shows greater

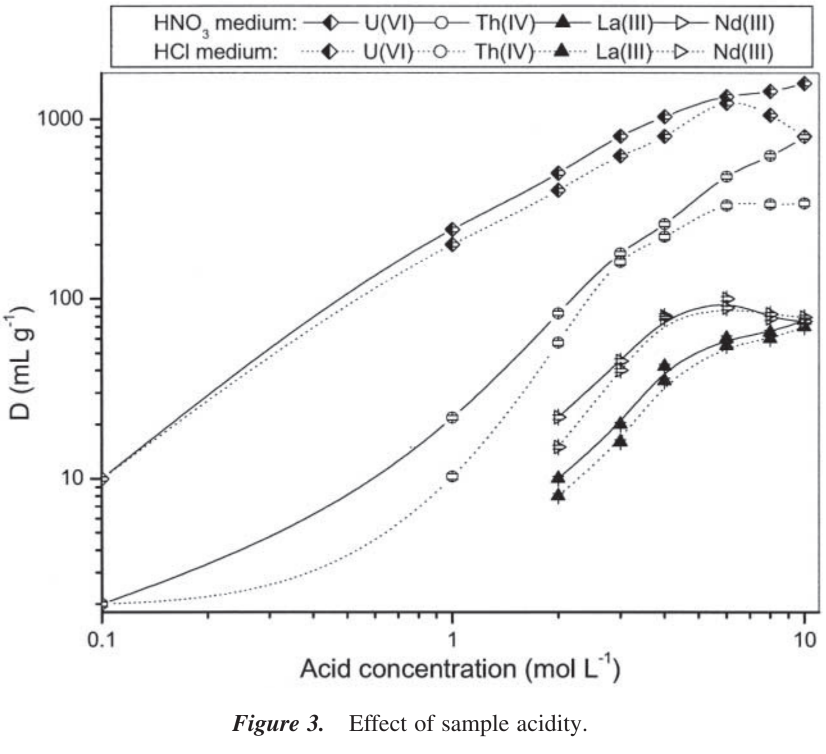

Figure 3. Effect of sample acidity.

affinity for U(VI), which is reflected from the higher D values observed in the order of 10^3 even at high acidities (4–10 M). In the case of Th(IV), appreciable D values (>500) were obtained in the acidity range (4–10 M), but for lanthanides like La(III) and Nd(III) poor extractability ($D < 100$) was observed. It can also be seen that for all the metal ions, the D values showed a positive trend with increasing acidity, which is due to the fact that amides are neutral extractants. In high acid media, the oxygen atoms of the amide carbonyl groups are known to undergo protonation. As a result, the increase in metal ion D values at high acidities may be due to the formation of ion-pair complex between the protonated amide moiety and the anionic metal complexes, by an acid-base mechanism. The high D values observed in the case of U(VI) could support this mechanism. The high selectivity for U(VI) ions can be attributed to the greater steric hindrance created by the bulky alkyl chain on the N-side of the amide moiety for the extraction of large size neutral $Th(NO_3)_4$ and $La(NO_3)_3$ species over $UO_2(NO_3)_2$ species. Also, under 2 M HNO_3 medium, the developed resin matrix was highly selective in preconcentrating actinides from lanthanides ($D < 20$) and therefore all the studies were performed under 2 M HNO_3 medium.

Elution Studies

For this study, 50 mg of the resin beads were equilibrated with metal ion solution (40 mL, 10 $\mu g\,mL^{-1}$) in 2 M HNO_3 medium for 2 h. In order to obtain quantitative recovery, the sorbed metal ions were desorbed using various eluting agents and the corresponding recovery values are shown in Table 3. An important aspect observed during elution studies was that even distilled water could serve as a good eluting agent for the quantitative recovery of U(VI) and Th(IV). As a result the process becomes simpler and green and this kind of elution behavior was never reported earlier using SPE technique.

Kinetic Studies

The kinetics of analyte extraction by the grafted polymer were studied by equilibrating 50 mg of the resin beads with a series of analyte solutions (40 mL, 10 $\mu g\,mL^{-1}$) in 2 M HNO_3 for varying time durations. The kinetic data were analyzed in terms of aqueous phase metal ion concentration $(1 - F)$ as function of time, as shown in Fig. 4. The term F is defined as the fractional attainment of metal ion equilibration, which is expressed as,

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

Table 3. Optimum eluting agents.

Eluants	Eluant volumes (mL) static (dynamic)[a]	% recovery	
		U(VI)[b]	Th(VI)[b]
Water	100 (50)	99.0 ± 3.98 (99.9 ± 3.47)	97.0 ± 3.82 (99.7 ± 3.87)
0.1M HNO_3	20 (15)	99.3 ± 4.01 (99.8 ± 3.52)	99.4 ± 3.96 (99.5 ± 4.06)
0.1M $(NH_4)_2CO_3$	20 (15)	99.8 ± 3.91 (99.9 ± 3.41)	99.5 ± 3.42 (99.4 ± 3.96)
0.1M EDTA (pH $\geq$ 5)	20 (15)	92.6 ± 3.82 (95.7 ± 3.79)	97.9 ± 3.41 (98.8 ± 3.53)
0.1M $(NH_4)_2$oxalate	20 (15)	74.6 ± 4.21 (70.3 ± 4.60)	99.9 ± 3.72 (99.9 ± 3.81)

[a] Values given in parenthesis represent % recovery in dynamic conditions.
[b] Data obtained from triplicate measurements.

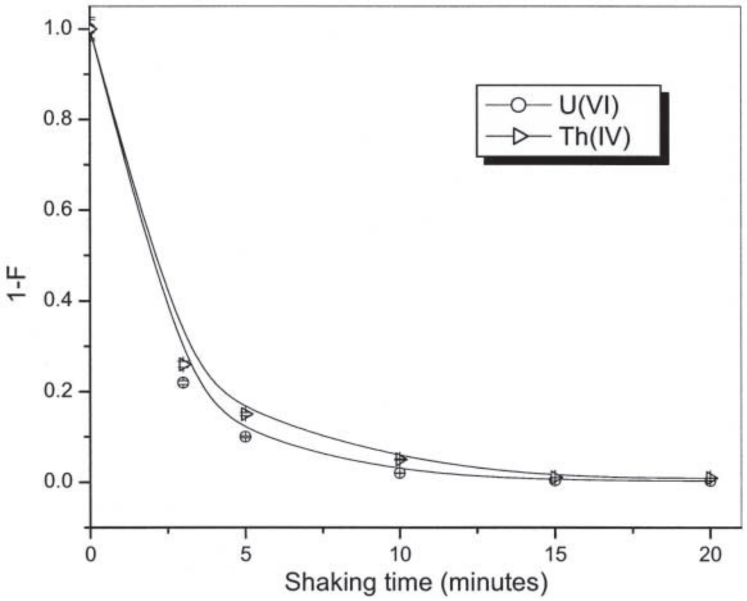

Figure 4. Rate of actinide extraction.

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.[22] Even though the resin was more of hydrophobic in nature, it is evident from the graph that near-complete extraction was achieved within 5 min, due to the macroporous structure of the resin matrix which favored the greater accessibility of the neutral metal complex toward the anchored hydrophobic amide moiety.

Maximum Metal Sorption Capacity

The maximum metal loading capacity of the grafted resin matrix was determined by equilibrating 50 mg of resin beads with higher concentrations of analyte solution (50 mL, 200 μg mL^{-1}) at 4 M HNO_3 and HCl medium respectively for time duration of 12 h. After desorption and subsequent analysis, it was found that the resin showed good sorption capacity values of 0.629 and 0.214 mmol g^{-1} at 4 M HNO_3 and 0.610 and 0.196 mmol g^{-1} at 4 M HCl for U(VI) and Th(IV), respectively. The high sorption values were accounted for the greater degree of ligand functionalization and also to the enhanced chelating site accessibility. From the experimental capacity values, it can be inferred that at least two amide moieties are involved for the coordination of a single metal ion, during the process of extraction to the resin phase.

Analyte Distribution Ratio in the Presence of Electrolytes

The influence of $NaNO_3$ and NaCl on the extraction behavior of the resin matrix was studied using varying salt concentrations, since they form the major matrix constituents in nuclear reprocessing streams. For this, 50 mg of the resin was equilibrated with metal ion solution (40 mL, 10 μg mL^{-1}) with increasing salt concentration in, 2 M corresponding acids for 1 h. A slight positive dependency on the D values with increasing salt content was observed for $NaNO_3$ due to the salting out effect (Fig. 5). However, in NaCl medium, a slight negative impact was seen for both the analytes, probably due to the formation of anionic actinide chloro complexes, which are comparatively more stable.

Tolerance Limits Toward Complexing Anions and More 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

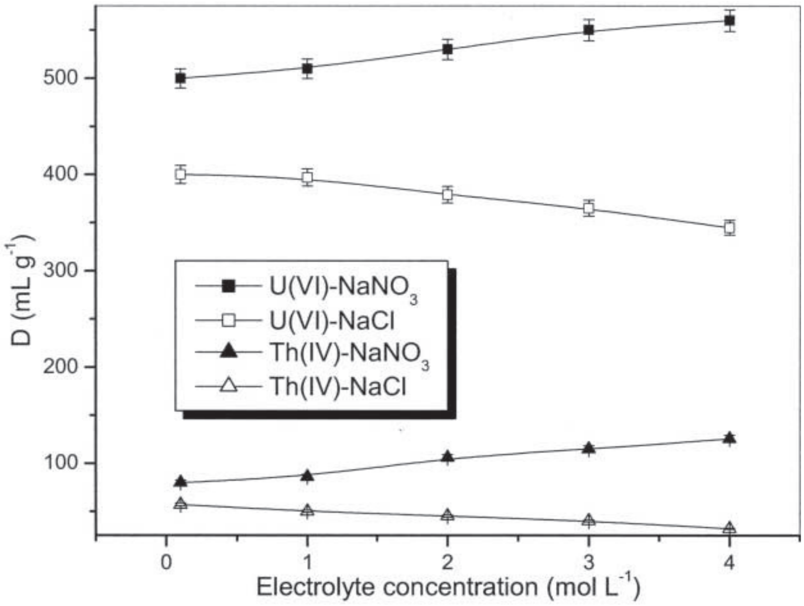

Figure 5. Influence of electrolyte concentration.

of individual matrix components. The tolerance limits for various electrolyte and diverse ion species are tabulated in Table 4. The resin showed complete nonextractive behavior (0% extraction) for the transition and post-transition metal ions. In the case of lanthanides, a poor D value of <20 were observed (shown in the case of Nd(III) and La(III) in Fig. 3 and so as the case for ZrO^{2+} and Bi(III). Thus, it is clear from all these observations that the amide grafted polymeric matrix is exhibiting exclusive selectivity for the extraction of actinide ions.

Table 4. Tolerance limits of electrolyte species.

Metal ions	Tolerance limits for electrolytes (mol L^{-1})				
	Na_2SO_4	Na_3PO_4	NaF	CH_3COO^-	$C_2O_4^{2-}$
U(VI)	0.73	0.15	0.21	0.15	0.10
Th(IV)	0.76	0.10	0.23	0.26	0.01

Dynamic Method

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 2 M HNO_3, through the extraction column under varying flow rates (4–20 mL min^{-1}) using a peristaltic pump. Maximum flow rate limits of 14 mL min^{-1} and 12 mL min^{-1}were achieved for the quantitative extraction of U(VI) and Th(IV), respectively (Table 1), thus revealing the greater accessibility and faster phase equilibration of the analytes to the anchored amide moiety. During metal ion desorption, an eluant flow rate of 1 mL min^{-1} was fixed to achieve quantitative analyte recovery.

Sample Breakthrough Volume

The ability of the functionalized resin matrix to extract trace levels of analytes from large sample volumes was tested in terms of sample breakthrough studies. For this study, 20 μg L^{-1} of influent concentration (C_0) in 2 M HNO_3

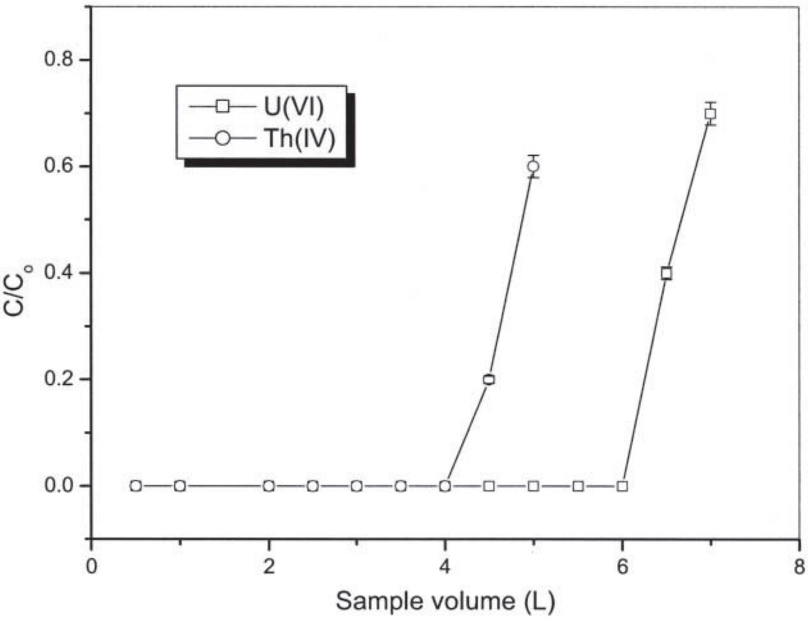

Figure 6. Dynamic sample breakthrough curve.

was passed through a preconditioned resin column, under varying volumes of sample solution (0.5–7 L) at a flow rate of $10\,\mathrm{mL\,min^{-1}}$. A good enrichment factor value of 400 and 267 was achieved for U(VI) and Th(IV), respectively, which is evident from Fig. 6.

Limit of Quantification

For this study, 1 L of 2 M HNO_3 solution spiked with 5–50 μg of individual analytes was passed through the preconditioned resin bed. The sorbed metal ions were desorbed and estimated. The lower limits of analyte extraction were found to be $20\,\mu\mathrm{g\,L^{-1}}$ for both the analytes as shown Table 1, which indicates the high sensitivity associated with the developed method in targeting ppb-level trace analytes even from large sample volumes.

Resin Bed Reusability

The reusability of the grafted resin was tested by passing metal ion solution (1 L, $500\,\mu\mathrm{g\,L^{-1}}$) in 2 M HNO_3 medium through the resin bed, and the sorbed metal ions were eluted and analyzed. Similar operations were performed on the same column, and it was found that the sorption capacity remained constant with reproducible D values even up to 20 cycles of repeated usage with rsd values of $<3.6\%$.

APPLICATIONS

Recovery of Actinides from Simulating Synthetic Nuclear Spent-Fuel Mixture

The selective extraction of U(VI) and Th(IV) from low-level nuclear spent fuels was tested using a synthetic nuclear spent-fuel mixture (21) containing more common metal ions and rare earths with $>10^3$ fold concentrations to that of the analyte ions. The resin matrix gave 99.9% recovery for actinides with an rsd of 3.4%, for triplicate trials, thereby proving its applicability in nuclear spent-fuel reprocessing.

Extraction of Thorium from Monazite Sand

A 0.1 g of monazite sand sample (Travancore, India) was digested initially at low temperature using concentrated H_2SO_4 followed by vigorous heat treatment up to 250°C and was evaporated to dryness. The resulting residue was redissolved in minimal volumes of HNO_3 and a known volume of the aliquot was passed through the resin bed under optimum experimental conditions. After desorption, the amount of thorium extracted was found to be $79.98\,mg\,g^{-1}$. The recovery data was further cross-checked by standard addition method and the rsd values were found to be within 3.5%, on triplicate analysis.

CONCLUSIONS

The newly developed amide grafted polymer sorbent proved to be a selective preconcentrator for actinides from large concentrations of lanthanides and transition metal ions under high acidities. This newly developed grafted polymer is found to be the most successful extractant for the recovery of actinides with high preconcentration factors and sorption capacities. It was found to be robust in various acidic conditions whose extractability was found to be more or less constant even up to 20 cycles of repeated usage. Moreover, the grafting process is simple and the process as a whole is green and economical.

REFERENCES

1. Demirel, N.; Merdivan, M.; Pirinccioglu, N.; Hamamci, C. Thorium(IV) and uranium(VI) sorption studies on octacarboxymethyl-*C*-methylcalix[4]resorcinarene impregnated on a polymeric support. Anal. Chim. Acta **2003**, *485*, 213–219.
2. Cekic, S.D.; Filik, H.; Apak, R. Use of an *o*-aminobenzoic acid-functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal(II) ions. Anal. Chim. Acta **2004**, *505* (1), 15–24.
3. Yalcin, S.; Apak, R. Chromium(III, VI) speciation analysis with preconcentration on a maleic acid-functionalized XAD sorbent. Anal. Chim. Acta **2004**, *505* (1), 25–35.
4. Myasoedova, G.V.; Savvin, S.B. Chelating sorbents in analytical chemistry. CRC Critical Reviews in Anal. Chem. **1987**, *17* (1), 1–63.
5. Pakalns, P. Separation of uranium from natural waters on chelex-100 resin. Anal. Chim. Acta **1980**, *120*, 289–296.
6. Kabay, N.; Egawa, H. Chelating polymers for the recovery of uranium from seawater. Sep. Sci. Tech. **1994**, *29* (1), 135–150.
7. Prabhakaran, D.; Subramanian, M.S. Synthesis, characterization and metal extractive behavior of functionalized AXAD-16 polymeric matrix using oxyacetone acetamide. Sep. Sci. Tech. **2004**, *39* (4), 941–957.

8. Maheswari, M.A.; Subramanian, M.S. Selective extraction of U(VI) and Th(IV) from high saline matrices using AXAD-I6-BHBPD as chelating polymeric matrix. Anal. Lett. **2003**, *36*, 2875–2892.
9. Prabhakaran, D.; Subramanian, M.S. Selective extraction and sequential separation of actinide and transition ions using AXAD-I6-BTBED polymeric sorbent. React. Func. Polym. **2003**, *57*, 147–155.
10. Garg, B.S.; Sharma, R.K.; Bist, J.S.; Bhojak, N.; Mittal, S. Separation and preconcentration of metal ions and their estimation in vitamin, steel and milk samples using *o*-vanillin-immobilized silica gel. Talanta **1999**, *48*, 49–55.
11. Meng, B.; Gue-Xin, S. Extraction of U(VI) with *N*,*N*,*N*′,*N*′- tetrabutylmalonamide and *N*,*N*,*N*′,*N*′-tetrahexylmalonamide. J. Radioanal. Nucl. Chem. **1998**, *231* (1,2), 203–205.
12. Mowafy, E.; Aly, H. Extraction behaviors of Nd(III), Eu(III), La(III), Am(III) and U(VI) with some substituted malonamides from nitrate medium. Sol. Extr. Ion Exch. **2002**, *20* (2), 177–194.
13. Sasaki, Y.; Tachimori, S. Extraction of actinides (III), (IV), (V), (VI) and lanthanides (III) by structurally tailored diamides. Sol. Extr. Ion Exch. **2002**, *20* (1), 21–34.
14. El-Reefy, S.A.; Mowafy, E.A.; Abdel-Badei, M.M.; Aly, H.F. Extraction of uranium and selected fission products from nitric acid medium by diamides. Radiochem. Acta **1997**, *77*, 177–194.
15. Condamines, N.; Musikas, C. The extraction by *N*,*N*-dialkylamides. II. Extraction of actinide cations. Sol. Extr. Ion Exch. **1992**, *10* (1), 69–100.
16. Mowafy, E.; Aly, H. Extraction of actinides and selected fission products from nitric acid medium using long chain monoamides. Sol. Extr. Ion Exch. **2001**, *19* (4), 629–641.
17. Horwitz, E.P.; Chiarizia, R.; Diamond, H.; Gatrone, R.C. Uptake of metal ions by a new chelating ion-exchange resin. Part 1: acid dependencies of actinide ions. Sol. Extr. Ion Exch. **1993**, *11* (5), 943–966.
18. Maheswari, M.A.; Subramanian, M.S. Selective enrichment of U(VI), Th(IV) and La(III) from high acidic streams using a new chelating ion-exchange polymeric matrix. Talanta **2004**, *64* (1), 202–209.
19. Prabhakaran, D.; Subramanian, M.S. 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. **2004**, *379*, 519–525.
20. Ismail, M.; Nogami, M.; Suzuki, K. The utilization of TMMA chelating resin for the adsorption of U(VI) and some lanthanide ions from acidic media. Sol. Extr. Ion Exch. **2003**, *21* (3), 465–481.

21. Maji, S.; Sundarajan, K.; Hemamalini, G.; Viswanathan, K.S. Fluorimetic Estimation of Uranium: Applications in Nuclear Technology, IGC 228; Indra Gandhi Centre for Atomic Research, India, 2001, 1–19.
22. Chiarizia, R.; Horwitz, E.P. Uptake of metal ions by a new chelating ion-exchange resin. Part. 4: kinetics. Sol. Extr. Ion Exch. **1994**, *12* (1), 211–237.

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