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New Multi-Dentate Ion-Selective AXAD-16-MOPPA Polymer for the Preconcentration and Sequential Separation of U(VI), Th(IV) from Rare Earth Matrix

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Abstract: A new class of multi-dentate ligand anchored polymeric resin has been synthesized by grafting Amberlite XAD-16 with [2-(1-Methyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazol-4-ylcarbamoyl)-ethyl]-phosphinic acid (AXAD-16-MOPPA). The modification steps involved during the grafting process are characterized by FT-IR spectroscopy, ^{31}P and ^{13}C-CPMAS (cross-polarized magic angle spin) NMR spectroscopy, CHNPS elemental analysis and thermogravimetric analysis. The influence of various physio-chemical parameters on the quantitative extraction of metal ions by the resin phase are studied and optimized by both static and dynamic methods. The developed grafted polymer shows greater selectivity for actinide ions like U(VI) and Th(IV) when compared to the lanthanides with greater distribution ratio values in highly acidic matrices. However, the lanthanides compete for the active sites in near neutral conditions. But the sorbed actinide ions and lanthanide elements can be separated by the sequential elution methodology. Moreover, the polymer exhibits faster metal ion phase exchange kinetics, where with a high sample flow rate of 25 mL min^{-1} quantitative analyte sorption is achievable during the extraction chromatographic column operation for all the analytes. It also offers good ion-selectivity and greater preconcentration factor values of 400 for U(VI) and 333 for Th(IV) in 4M HNO_3 conditions. The resin shows very high sorption capacity values of 1.45 mmol g^{-1} for U(VI), 1.39 mmol g^{-1} for Th(IV), and 1.31 mmol g^{-1} for La(III) at near neutral conditions. Finally, the developed grafted resin has been successfully applied in extracting Th(IV) from matrix monazite sand which comprises large rare earth matrix, U(VI) from seawater and

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also U(VI) and Th(IV) from simulated nuclear spent fuel mixtures. The analytical data obtained from triplicate measurements are within 3.5% rsd, reflecting the reproducibility and reliability of the developed method.

Keywords: AXAD-16, preconcentration, sequential separation, grafted polymer, nuclear spent fuels

INTRODUCTION

The separation of actinide elements from various waste materials is a significant problem facing developed countries. The issue arises not only because of the potential long-term hazard of many of the actinides, but also due to the regulatory requirements associated with actinide waste disposal, which are different from those associated with other radioactive wastes. Similar problems exist for waste produced in the past as a result of nuclear weapons production programs and wastes likely to be produced in the future emerging from operations required for waste disposal. It is a challenging task to quantitatively recover these trace actinide metal ions from these wastes which are in high acidic matrix environment (1–4).

Various methods were adopted for separation of actinides, such as precipitation (5) and co-precipitation (6) and ion-exchange chromatography (7). Solvent extraction has been proved to be promising in this aspect, and using this technique several extractants have been developed with various organic ligands like phosphonic acid based ligands (8–11), *N,N*-dialkyl amides (12–14), crown ethers (15, 16), β-diketones (17), picolamides (18), calixarenes (19). Among them, phosphorus-based ligands are known to be more selective for actinide ions and are used extensively in the actinide separations like TBP in PUREX (20), CMPO in TRUEX (21), tri alkyl phosphineoxide in TRPO (22), di(2-ethyl hexyl) phosphonic acid in TALSPEAK (23). Solvent extraction, in spite of its versatility, suffers from problems like (a) third-phase formation, (b) disposal of large volumes of extractants and diluents, and (c) multistage extraction procedures. To solve this, more recently polymer-based chelating sorbents are being employed in these extraction studies, but they are associated with two distinct drawbacks: (a) slow metal uptake kinetics and (b) limited operating pH range. Slow reaction kinetics results in the under utilization of resin's capacity and premature ion breakthrough. Also, due to their low acidic properties, a majority of the chelating resins are ineffective for metal ion extraction studies from high acidic solutions (24, 25).

These drawbacks of chelating resins have been overcome by using a new class of chelating ion-exchange resins called dual mechanism bifunctional polymers (DMBPs). DMBPs use hydrophilic ion-exchange ligands like conventional ion-exchange resins that provide rapid exchange kinetics and also chelating ligands like chelating resins, to achieve ion-selectivity (26–29).

In view of the above, a new type of chelating ion-exchange polymer termed as AXAD-16-MOPPA has been synthesized. The aim of this grafted polymer is to introduce phosphonic acid group and amide-based ketone groups. Since 4-amino antipyrine derivatives are known to form coordination complexes with lanthanides (30, 31), 4-acrylamido antipyrine ligand was synthesized from 4-amino antipyrine and was then successfully anchored onto phosphinic acid polymer. This functionalized resin is a multi-dentate ion-selective polymer containing phosphinic acid group, amide, and cyclic amide groups. The phosphinic acid, amide carbonyl ligand moieties contribute to the resin's selectivity behavior toward actinides even at high acidities. The hydrophilic hydroxyl and antipyrine moieties enhance the metal ion accessibility into the polymer matrix, thereby significantly improving the kinetics. In low acidic conditions the antipyrine ring also significantly participates in the extraction process, thereby, exhibiting extraction for lanthanides also. The present paper will discuss the synthesis, characterization, and the metal extraction studies performed for U(VI), Th(IV), and La(III) in high acidic matrices and also in near neutrality. Also, the grafted polymer has been tested for its practical utility using various synthetic simulated nuclear reprocessing samples and also real geological and seawater samples.

EXPERIMENTAL

Instrumentation

A Bruker Avance-400 model CPMAS ^{13}C (12 KHz) solid-state NMR spectrometer and a Perkin-Elmer Spectrum One model FT-IR spectrometer, Perkin-Elmer 2400 model CHNS/O analyzer, and a Perkin-Elmer TGA-7 model thermal analyzer (for water regain capacity studies) were employed for structural characterization of the anchored polymer. A Jasco V-530 model UV-Visible spectrophotometer was used for the estimation of U(VI) and Th(IV) and trace amounts of U(VI) from real and synthetic samples were determined using Hitachi F-4500 model fluorescence spectrophotometer. A Varian SpectrAA-20 model flame atomic absorption spectrometer was used for the estimation of transition metal ions during interference studies. For batch static method, studies were performed using an Orbitex DS model mechanical stirrer with 200 rpm. For column dynamic studies, an extractive chromatographic column (15 cm × 0.4 cm i.d.) equipped with a Ravel Hi-Tech S-50 model peristaltic pump was employed. Solution pH adjustments were made using a Digisun DL-707 model digital pH meter.

Chemicals and Reagents

Standard individual metal ion solutions for U(VI) and Th(IV) were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$ (AR grade, Fluka chemicals) by dissolving appropriate amounts in slightly acidified double distilled water. La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), and Dy(III) solutions were prepared from the corresponding oxides obtained from Indian rare earths limited and were dissolved in concentrated nitric acid. All chemicals and reagents used were of analytical reagent grade purity and used without further purification. AXAD-16 resin (20–50 mesh, surface area 825 $m^2 g^{-1}$, bead size 0.3–1.2 mm) was obtained from Fluka chemicals.

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.

Synthesis of the Resin

The ligand 4-acrylamido antipyrine (AAP) was prepared by drop-wise addition of acryloyl chloride to the 4-amino antipyrine (10 g, 0.05 moles) and triethyl amine (8 mL, 0.06 moles) which were dissolved in dry dichloroethane (DCE) at 0°C. The pure product was separated and characterized with FT-IR, NMR spectroscopy.

AXAD-16 resin beads were purified by washing with 2M HCl followed by 2M NaOH in order to remove both basic and acidic impurities and finally with distilled water until the washings showed neutral pH. The resin beads were further washed with ethanol, filtered and vacuum dried. Five grams of vacuum dried AXAD-16 resin beads were refluxed with 20 mL of phosphorus trichloride in the presence of anhydrous aluminum chloride for 3h, followed by hydrolysis to the corresponding phosphinic acid resin. The hydroxyl group of the phosphinic acid resin was protected with chlorotrimethylsilane and was further reacted with AAP (10.3 g, 0.04 moles) in the presence of triethylamine (8 mL, 0.06 moles). The resulting modified resin beads were deprotected with dil. HCl, washed with water, acetone and finally vacuum dried. The synthetic scheme involved in the designing of the chelating ion-exchange resin is shown in Fig. 1.

Methods Adopted for Metal Ion Extraction and Preconcentration

Batch Static Method

Batch method was performed to optimize the basic experimental conditions for quantitative analyte extraction such as acid/pH dependence, kinetic studies, and diverse ion tolerance. For this study, known amount of resin beads (50 mg) was equilibrated with known concentrations of metal ion solution (40 mL, 10 $\mu g\, mL^{-1}$) in 125 mL reagent bottles for 90 min using a mechanical shaker at 200 rpm under different acid/pH conditions. The extracted metal ions were desorbed using 15 mL of the optimum eluting

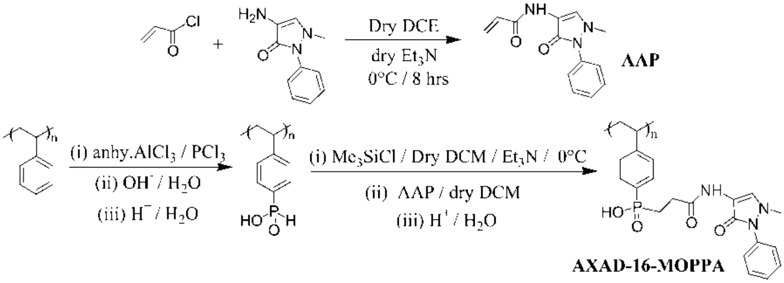

Figure 1. Grafting procedure.

agents. The amount of metal ions extracted were estimated spectrophotometrically using Arsenazo (III) as chromogen for U(VI) (7M HNO_3) (32) and La(III) (pH-3) (33) at 655 nm and using Thoron as chromogen for Th(IV) (0.5M HCl) (33) at 545 nm, respectively.

Column Dynamic Method

For this study, an extraction chromatographic glass column (15 × 0.4 cm) was packed uniformly with 1 g of preconditioned resin beads by slurry method. The sample solution was passed through the column at a constant flow rate using a peristaltic pump, which is interfaced between the sample reservoir and the column. All column parameters such as breakthrough volume, sample flow rate, stationary phase reusability tests, and lower limit of analyte quantification were optimized using this method. The trapped metal ions in the column bed were desorbed and estimated. Trace concentrations of U(VI) from synthetic and real samples were also estimated by steady-state fluorimetric method using 1 M phosphoric acid at 515 nm as emission wavelength and 266 nm as excitation wavelength (34). The column was washed with water and reused for further studies. The optimum experimental parameters for column operation to ensure quantitative metal ion retention and elution are listed in Table 1.

RESULTS AND DISCUSSION

Characterization of the Resin Matrix

The ^{13}C-CPMAS NMR spectra showed resonance signals at 197.3 ppm, and 212.9 ppm corresponds to the two carbonyl groups present in the ligand moiety of the grafted polymer, as shown in Fig. 2b. Also, it could be seen that the resonance signals for the aliphatic side chains were enhanced and shifted from 34.4 ppm to 40.7 ppm when the polymer backbone is chemically

Table 1. Optimum experimental parameters for quantitative analyte extraction

Experimental parameters	U(VI)	Th(IV)	La(III)
pH range	1.0–6.5	2.0–6.5	3.0–5.0
$t_{(1/2)}$ (minutes)	3	4	6
Metal sorption capacity (mmol g^{-1})			
(i) At optimum pH	1.45	1.39	1.31
(ii) At 4 M HNO_3	0.777	0.646	—
(iii) At 1M HCl	0.425	0.625	—
Eluting agent	0.5M $(NH_4)_2CO_3$	0.5M $(NH_4)_2CO_3$	4M HNO_3, 2M HCl
Maximum sample flow rate (mL min^{-1})	25	25	20
Average % recovery	99.9	99.8	99.5
Lower limit of detection (ng mL^{-1})	4	15	20
Sample breakthrough volume (mL)	6000	5000	—
Enrichment factor (4M HNO_3)	400	333	—

modified by the ligand. The corresponding spectra for the nonfunctionalized AXAD-16 polymer is shown in Fig. 2a. Also, the resonance signals for aromatic ring and substitution were also observed at 127.8 ppm and 145.5 ppm in Fig. 2b. for the functionalized resin. The presence of $P = O$ moiety in the grafted polymer was inferred from ^{31}P solid state NMR spectra, whose resonance signals were observed at 15.0 ppm along with side bands at 7.8 ppm and 28.6 ppm.

Each stage of the grafting process is confirmed by FT-IR spectra. In the final grafted polymer, bands due to –C=C–(Acryloyl) (1543.2) present in the ligand moiety and P–H (2314.1) appearing in the phosphinic acid stage of the polymer disappear and new bands were originated at 1650 cm^{-1} and 1687 cm^{-1} corresponding to the amide and the lactum carbonyls, respectively. FT-IR spectral data for all the grafting steps were given in Table 2.

CHNPS elemental analysis was performed during each stage of the grafting process and the data obtained are given in Table 2. From the table it is observed that the experimental (%) values are in close agreement with the corresponding theoretical values, which suggests the presence of one ligand moiety per polymer repeat unit and also confirms quantitative ligand grafting.

For resin hydrophilicity studies, water regaining capacity measurement was performed by equilibrating 0.1 g of the grafted resin beads with distilled water for 2 h. The equilibrated resin beads were filtered, air-dried, and subjected to TGA measurements. A weight loss of 18.5% was observed

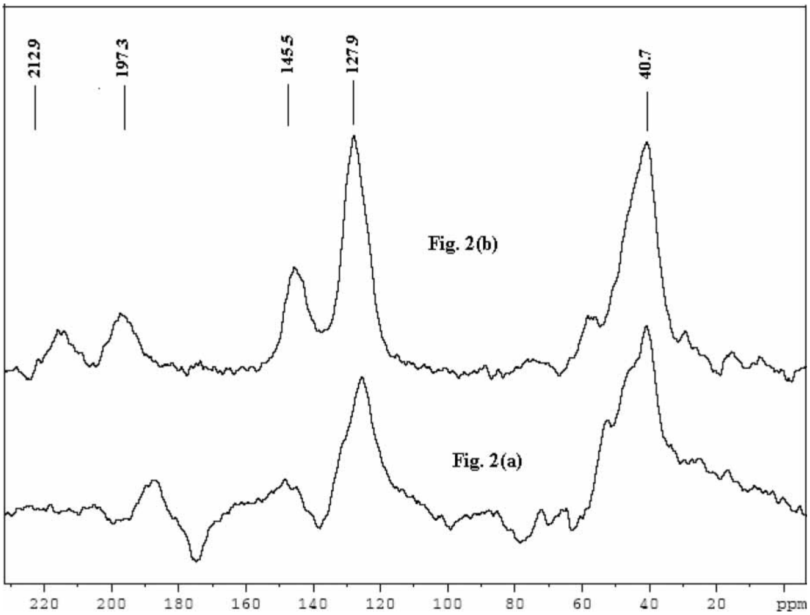

Figure 2. 13C-CPMAS NMR spectra of AXAD-16 and AXAD-16 and AXAD-16-MOPPA polymer.

up to 110°C, which was ascertained to the percolated water molecules into the polymer pores. Similar studies performed for the corresponding nonfunctionalized AXAD-16 resin matrix resulted in the weight loss of only 1.6%. This enhancement in the weight loss in the grafted polymer could be attributed to the better hydrophilic character upon incorporating hydrophilic groups

Table 2. Characterization of the various stages of functionalization

Grafting stage	FT-NIR Spectral data (cm^{-1})	CHNPS elemental data
AAP	–C=C–(Acryloyl)-(1543.3), C=O (1688.2, 1650)	C 65.25 (65.30): H 5.75 (5.83): N 15.95 (16.32)
AXAD-16	–C=C–(1610.2)	C 91.74 (92.31): H 7.86 (7.69)
AXAD-16-PHOH	P–H (2314.1), P–OH (1044.5), P=O (1157.5), O–H (3435.5)	C 57.41 (57.45): H 5.21 (5.42): P 18.31 (18.27)
AXAD-16-MOPPA	O–H (3440.6), P–OH (1042.9), C=O (1686.3, 1649.3)	C 62.16 (61.68): H 6.89 (6.55): N 11.25 (11.92): P 7.15 (7.47)

The values given in parentheses under CHNP elemental data are the corresponding theoretical values.

like phosphinic acid and antipyrine groups to the polymer back bone. As a result, the accessibility of the chelating sites by the analytes will be improved by providing better surface contact with the aqueous phase.

Metal Extraction Studies by Batch Method

Influence of Sample Acidity for Metal Extraction

The metal ion extracting ability of the grafted polymer in varying acid concentrations of HNO_3 was studied, as it forms the major constituent in nuclear spent fuels. The effect of HCl concentration was also studied because most of the analytical procedures for metal ion separation and preconcentration from environmental, biological, and geological samples are performed in this medium.

For this study, 0.05 g of the resin beads were batch equilibrated with metal ion solutions (40 mL, $10\,\mu g\,mL^{-1}$) of different acid concentrations, for 90 min. The results were expressed in terms of the distribution ratio (D) using the following expression,

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

where A_o and A_f are the metal ion concentration before and after equilibration, V refers to the overall volume (mL) and W is the dry weight of the resin matrix (g). From Fig. 3, it can be seen that the resin shows good selectivity toward actinides (U(VI) and Th(IV)) when compared to lanthanides in both media in high acid concentrations. The extraction of uranium and thorium at low acid medium ($D > 1000$) was attributed to the simultaneous role played by both cation exchange mechanism (phosphonic acid group) and chelation mechanism (P═O and C═O groups). Even at higher acid concentrations (4 M–6 M) the grafted polymer showed good extractability for U(VI) and Th(IV) ($D > 500$) because of strong multi-dentate chelation mechanism. However, with increasing acidity, a negative trend was observed due to the formation of anionic metal complexes like $[UO_2(NO_3)_3]^-$ and $[UO_2Cl_3]^-$, which disfavors extraction.

In HCl medium, both U(VI) and Th(IV) showed similar extractive behavior, and their extraction decreases as HCl concentration increases. This behavior may be attributed to their tendency to form more stable anionic metal chloro complexes. Significant extraction profile was observed in the case of La(III), where there is no uptake in both nitric acid and hydrochloric acid media. From this observation, we infer that our grafted polymer will be successful in separating actinides from lanthanides in acidic medium. The metal sorption capacities of the polymer for the U(VI) and Th(IV) were studied at 4 M nitric acid and 1 M hydrochloric acid

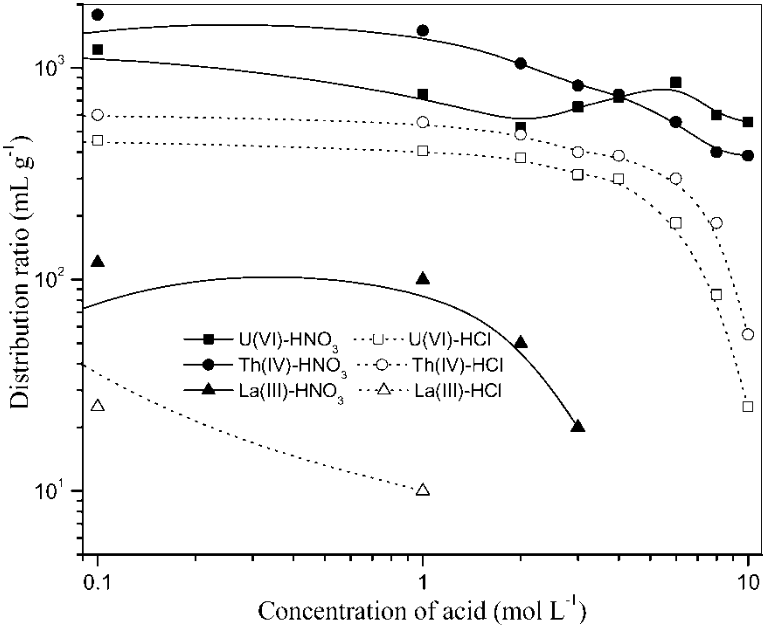

Figure 3. Influence of acid concentration on analyte extraction.

concentrations by shaking 0.02 g of the resin matrix with an excess concentration of the metal ions (100 mL, 100 μg mL^{-1}) for a time duration of 6 h. The polymer showed excellent sorption capacity values as shown in Table 1.

Extractability in Near Neutral Conditions and Maximum Metal Sorption Capacity

The maximum metal sorption capacities of the developed resin matrix were studied by equilibrating 0.02 g of the grafted polymer with a solution of excess metal ion concentration (100 mL, 100 μg mL^{-1}) under wide pH range (1.0–7.0) for a time duration of 6 h. The resin's metal sorption capacities as a function of solution pH are plotted in Fig. 4. From the figure, it could be noted that the resin showed good extractability for lanthanides also despite its selectivity toward actinide ions in acidic conditions. This is due to the fact that the incorporated antipyrine ring plays an active part in the metal ion extraction in low acidic and near neutral conditions. Along with this ligand, the P-OH group also acts as a chelating ion-exchange site for the metal ion extraction in near neutrality. Thus the resin showed a good extractive behavior for all the analyte ions under wide pH range, where the maximum capacity for U(VI), Th(IV), and La(III) were found to

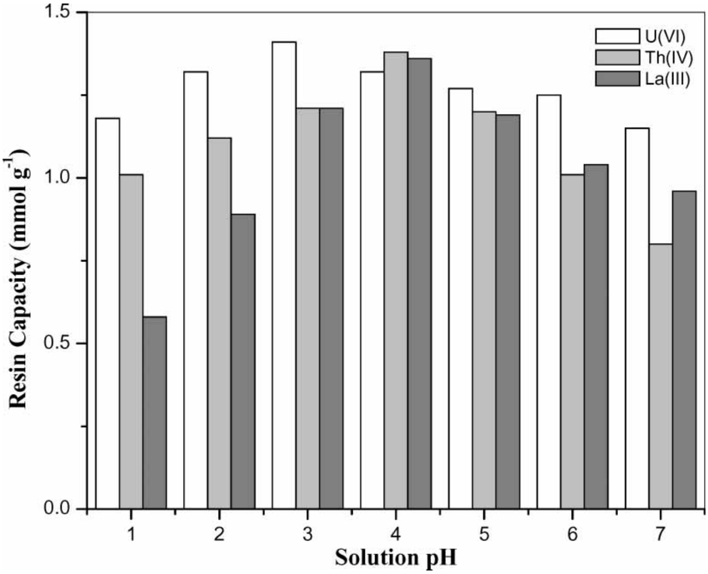

Figure 4. Resin capacity as a function of pH.

be at pH 3.0 (1.45 mmol g^{-1}), pH 4.0 (1.39 mmol g^{-1}), and at pH 4.0 (1.31 mmol g^{-1}), respectively.

Elution Studies

The resin matrix was subjected to quantitatively and sequentially elute the sorbed metal ions from the resin phase. For this study, various eluting agents were tried for the recovery studies as shown in Fig. 5. It was found that 4 M nitric acid/2 M hydrochloric acid was sufficient to bring out complete elution of all the co-extracted lanthanides as it could not show any extraction under the same conditions (Fig. 3). Since the extraction profiles and the stability constants for U(VI), Th(IV) are very similar. Only 0.5 M ammonium carbonate was found successful in their quantitative recovery. The desorption process involves the formation of strong anionic carbonato complex, which tends to be in the aqueous phase.

Kinetic Studies

The rate of transfer of metal ions from the aqueous to solid phase was studied at various time durations by equilibrating 0.05 g of resin beads with a series of metal ion solutions (40 mL, 10 μg mL^{-1}) in 4 M HNO_3. The kinetic data were plotted in terms of (1 − F) values as function of equilibration time where

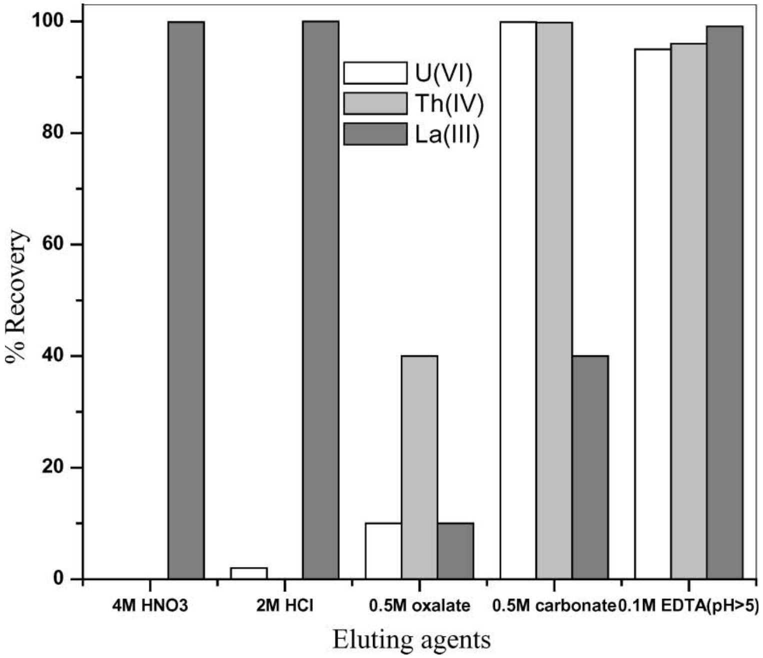

Figure 5. Optimum eluting agents.

F is the fractional attainment of equilibrium, which is expressed as (35)

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

where $[M^R]_t$, $[M^R]_{eq}$ are the metal ion concentration in the resin phase at time 't' to that at equilibrium. From Fig. 6, it is evident that complete equilibrium is attained within 12 min for all the analytes. The enhanced kinetics can be attributed to the presence of hydrophilic antipyrine and phosphinic acid groups, which provide greater surface contact thus increasing the accessibility of metal ions to the active sites thereby enhancing the equilibration process.

Effect of $NaNO_3$ and NaCl on Metal Ion Extraction

As $NaNO_3$ and NaCl are the main electrolytes present in nuclear spent fuels and environmental samples, respectively, their influence on the quantitative extraction of U(VI) and Th(IV) was studied at varying concentrations (0.01–4 M) of $NaNO_3$ and NaCl in 2 M HNO_3 and 2 M HCl, respectively. From Fig. 7, it can be observed that there exists a slight positive trend with increasing $NaNO_3$ concentration. This perhaps may be due to the reduction of hydration sphere around the metal ions through salting out effect. The negative trend on increasing NaCl concentration may be due to the

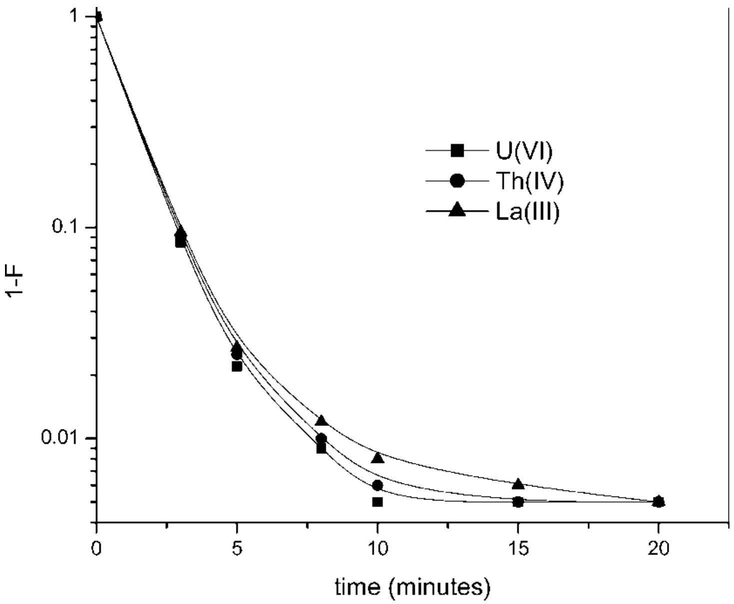

Figure 6. Extraction kinetics.

formation of more stable metal anionic chloro complexes, which are non-extractable by the multi-dentate chelating groups.

Tolerance Limit Towards Interfering Ions and Common Metal Ions

The resin's tolerance limits toward various electrolytes and diverse metal ions was studied by equilibrating 0.05 g of the resin beads with analyte concentration (40 mL, 1.25 μg mL^{-1}) along with increasing concentrations of individual diverse ions under 4 M HNO_3 conditions until some decrease in the analyte signal was observed. The resin showed very less uptake with a $D < 20$, for common transition metal ions. The degree of tolerance for some post-transition ions, rare earths, and electrolyte species at near neutral conditions are shown in Table 3. D values of these diverse ions were found to be in the range 20–50. From the tolerance data, it can be seen that the resin shows high selectivity toward the studied analytes when compared to other diverse ions.

Metal Extraction Studies by Dynamic Method

Influence of Sample Flow Rate on Metal Ion Sorption

The maximum sample flow rate which can provide the quantitative sorption that was possible was studied using a packed resin bed column by varying

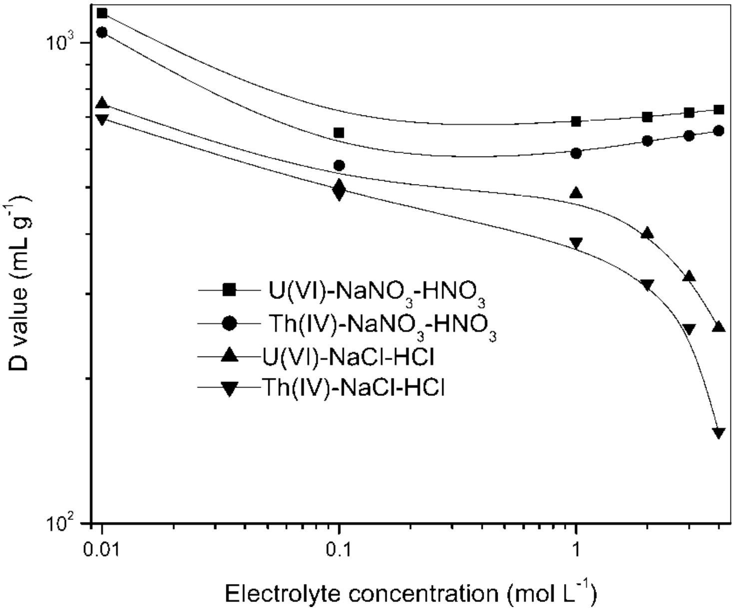

Figure 7. Effect of salt concentration in corresponding 2 M acidity.

the sample flow rate using a peristaltic pump. The metal ion solution (1000 mL, 0.5 μg mL^{-1}, bed volume −1.2 mL) was passed through the column with varying flow rates from 1–30 mL min^{-1}. The grafted polymer was highly efficient in extracting metal ions of interest with very high flow (25 mL min^{-1}, 25 mL min^{-1}, and 20 mL min^{-1} for U(VI), Th(IV), and La(III)).

Sample Breakthrough Volume Studies

The ability of resin matrix to extract quantitatively the trace amounts of metal analytes of interest from large sample volumes was studied in terms of sample breakthrough volume. For this study, various sample volumes (500–8000 mL) containing 50 μg of each individual analytes in both acidic (U(VI) and Th(IV)) and near neutral conditions (La(III), U(VI), and Th(IV)) were passed through the column bed. The sorbed metal ions were eluted with 15 mL of 4 M HNO_3 in the case of La(III) and 0.5 M $(NH_4)_2CO_3$ for U(VI) and Th(IV). A sample breakthrough volume of 6000 mL for U(VI), 5000 mL for Th(IV), and 4500 mL La(III) were observed with high enrichment factors of 400, 333, 300 as shown in Fig. 8. This high sample breakthrough volume along with greater flow rates make this extraction chromatographic system powerful in extracting analytes from bulk volumes within less span of time.

Table 3. Tolerance limits of various diverse metal ions and electrolytes

	Metal ions	
	U(VI)	Th(IV)
Tolerance limits of electrolytes (mol L^{-1})		
Na_2SO_4	0.528	0.654
Na_3PO_4	0.373	0.325
NaF	0.098	0.122
CH_3COO^-	0.102	0.098
Ca^{2+}	0.555	0.585
Mg^{2+}	0.503	0.519
Tolerance limits of interfering metal ions (mmol L^{-1})		
Zr(IV)	4.6	4.5
Mo(VI)	4.2	4.0
Pb(II)	3.5	3.8
Cd(II)	5.4	4.2
Bi(III)	6.2	6.6
Ce(IV)	4.9	3.5
Nd(III)	6.8	5.5
Sm(III)	5.2	4.3
Gd(III)	5.7	4.4

Concentrations of U(VI) and Th(IV) are 0.210 mmol L^{-1} and 0.215 mmol L^{-1}, respectively.

Lower Limit of Analyte Quantification

To test the resin's capability to preconcentrate trace metal ions, studies were performed by passing 1000 mL of sample solution through the optimized column bed (analyte concentration range 1–50 ng mL^{-1}). The sorbed metal ions were eluted and estimated. The limits of quantification were found to be 4 ng mL^{-1}, 15 ng mL^{-1}, and 25 ng mL^{-1} for U(VI), Th(IV), and La(III), respectively, thereby indicating the resin's sensitivity to extract the trace metal ions of interest even at ppb level.

APPLICATIONS

Synthetic Mixture Mimicking Reprocessing Streams

The ability of the resin matrix to extract the analytes of interest from acidic wastes was tested with 5 L of the synthetic mixture mimicking nuclear spent fuel composition (34) spiked with 100 μg of analyte (4 M HNO_3) using the chromatographic column. The sorbed metal ions were eluted and

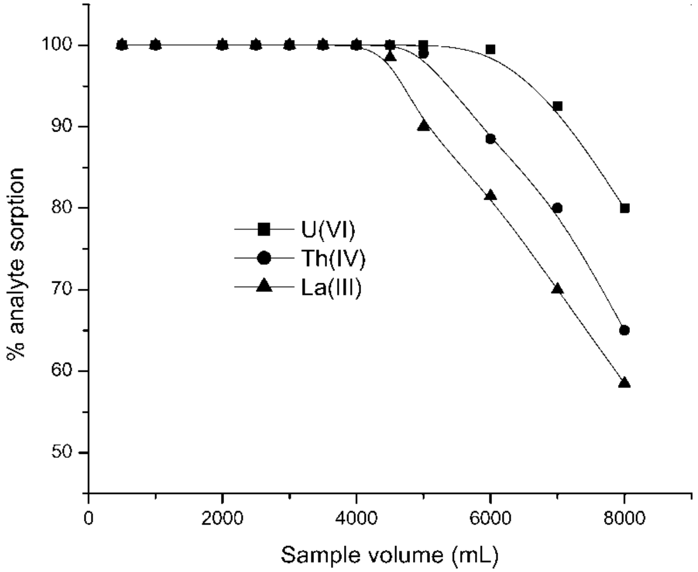

Figure 8. Sample breakthrough volume.

estimated. It was found that the resin was successful in extracting the actinides of interest quantitatively even in the presence of large amount of lanthanides and various diverse ions. The analytical data were reproducible with an rsd value of 3.6% for triplicate measurements.

Extraction of Thorium from Monazite Sand (Travancore, India)

The resin's applicability in extracting Th(IV) from monazite sand was studied. 0.1 g of monazite sand sample was digested with conc. H_2SO_4 at 250°C for 4 h. Further, it was digested using 5 mL of HF followed by conc.HNO_3 to remove excess HF. Subsequently, the digested solution was evaporated to dryness and the residue was redissolved in minimal volumes of dil. HCl and passed through the resin column. The amount of Th(IV) extracted was found to be $79.8\,mg\,g^{-1}$, which was comparable with the certified value of $81\,mg\,g^{-1}$. The data was further confirmed by standard addition method, and the values were within 4.0% rsd for triplicate measurements.

Extraction of U(VI) from Synthetic Seawater, Seawater, and Well Water Samples

Synthetic seawater was prepared using the literature reported procedure (36). A total of 100 μg of U(VI) was spiked to 5 L of synthetic sea water mixture

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

Water sample	Source of the sample	Method	Con. of U(VI) (ng mL^{-1})	RSD (%)[a]
Seawater—1	Chennai, India	Direct	4.85 ± 0.33	3.9
		SA	5.03 ± 0.38	3.1
Seawater—2	Mahabalipuram, India	Direct	5.48 ± 0.45	3.8
		SA	5.88 ± 0.49	3.2
Well water—1	Adyar, Chennai, India	Direct	3.42 ± 0.45	3.5
		SA	3.65 ± 0.42	3.1
Well water—2	IIT Madras, Chennai, India	Direct	2.98 ± 0.41	3.8
		SA	3.02 ± 0.37	3.5

[a] 95% confidence levels, $t = 3.22$ (for triplicate measurements).

solution and was passed through the extraction column at a flow rate of 20 mL min^{-1}. The sorbed metal ions were eluted and estimated. The values showed satisfactory recovery (>99.5%) with an rsd value of 3.1% for U(VI), on triplicate measurements.

Therefore, tests were extended to real seawater and well water samples collected from coastal regions of Tamil Nadu (India). These samples were filtered to remove the particulate matters using membrane filter (0.45 mm) and were passed through the preconditioned resin bed. The sorbed U(VI) was desorbed and analyzed using steady-state spectrofluorimetric method. The values are confirmed further using standard addition method and the results were shown in Table 4.

CONCLUSIONS

The developed grafted polymer showed high selectivity in extracting U(VI) and Th(IV) from both high-level acidic streams even in the presence of large lanthanide matrix. It is also highly applicable in extracting the analytes from near neutral conditions, thus proving its wide range of practical applications. The sequential separation of actinides and lanthanides was achieved in acidic medium during the sequential elution step. The grafted polymer showed superior metal sorption capacities with faster extraction rates when compared to other reported resins in literature. The other significant features of the developed resin matrix are its greater enrichment factor values with high flow rates. This resin is highly durable and reusable even up to 25 extraction cycles.

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