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Selective extraction of U(VI) over Th(IV) from acidic streams using di-bis(2-ethylhexyl) malonamide anchored chloromethylated polymeric matrix

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Abstract

A new chelating polymeric sorbent has been developed using Merrifield chloromethylated resin anchored with di-bis (2-ethylhexyl) malonamide (DB2EHM). The modified resin was characterized by ^{13}C CPMAS NMR spectroscopy, FT–NIR–FIR spectroscopy, CHN elemental analysis and also by thermo gravimetric analysis. The fabricated sorbent showed superior binding affinity for U(VI) over Th(IV) and other diverse ions, even under high acidities. Various physio-chemical parameters, like solution acidity, phase exchange kinetics, metal sorption capacity, electrolyte tolerance studies, etc., influencing the resin's metal extractive behavior were studied by both static and dynamic method. Batch extraction studies performed over a wide range of solution acidity (0.01–10 M) revealed that selective extraction of U(VI) could be achieved even up to 4 M acidity with distribution ratios (D) in the order of $\sim 10^3$. The phase exchange kinetics studies performed for U(VI) and Th(IV) revealed that time duration of <15 min was sufficient for $>99.5\%$ extraction. But similar studies when preformed for trivalent lanthanides gave very low D values (<50), with the extraction time extending up to 60 min. The metal sorption studies performed for U(VI) and Th(IV) at 5 M HNO_3 was found to be 62.5 and 38.2 mg g^{-1},respectively. Extraction efficiency in the presence of inferring electrolyte species and inorganic cations were also examined. Metal ion desorption was effective using 10-15 mL of 1 M $(NH_4)_2CO_3$ or 0.5 M α-hydroxy isobutyric acid (HIBA). Extraction studies performed on a chromatographic column at 5 M acidity were found to give enrichment factor values of 310 and 250 for U(VI) and Th(IV), respectively. The practical utility of the fabricated chelating sorbent and its efficiency to extract actinides from acidic waste streams was tested using a synthetic nuclear spent fuel solution. The R.S.D. values obtained on triplicate measurements ($n = 3$) were within 5.2%.

Keywords: Chelating sorbent; Acidic streams; Actinides; Metal enrichment and malonamide

1. Introduction

Trace analysis of metal ions pose unique problems to analysts, as it involves rigorous requirements of versatility, specificity, sensitivity and accuracy during chemical analysis [1–6]. These factors are crucial mainly in nuclear spent fuel reprocessing units, where quantification of fertile and fissile products at trace and macro quantities is of immense value. With the growing depletion of uranium resources, one needs to look for methods that are both efficient and economical for effective spent fuel reprocessing. Solvent extraction (SE) technique using organo phosphorous extractants like tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO), and carbamoyl methyl phosphine oxide (CMPO) were considered for this purpose [7–10]. But owing to their tendency to undergo faster radiolytic degradation, formation of large secondary waste volumes, a better alternative to these extractants was explored which resulted in the use of high molecular weight N,N'-dialkyl aliphatic amides since these compounds showed good metal extractive behavior, high radiolysis stability and complete incinerability [11–14]. Based on this, a number of research papers have been published using various N,N'-dialkyl aliphatic amides, for actinide extraction [11–20]. It was also found that branched substituted diamides could bring out selectivity amongst actinides and

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lanthanides, which is an important task in nuclear reprocessing and decontamination processes. However, despite these positive features they do possess inherent limitations, such as finite aqueous phase solubility and third phase formation [21–23]. In order to over shade these problems, the current paper will focus on the development of a new solid phase extraction method using Merrifield chloromethylated polymeric resin anchored with DB2EHM, for the selective extraction of actinides from acidic waste streams. The positive features of this solid support diamide matrix were examined and their extractive behaviors under varying experimental conditions were studied. In order to examine its practical applicability, a synthetic nuclear spent fuel mixture was passed through the extraction chromatographic column and its metal extractive capabilities were analysed.

2. Experimental

2.1. Instrumentation

A Bruker Avance-400 model ^{13}C CPMAS (12 kHz) solid state NMR spectrometer and a Bruker IFS 66V model FT–NIR–FIR Spectrometer, were employed for structural characterization of the anchored polymer. An Elementar Vario EL model CHNPS analyzer was used to study the extent of ligand functionalization. A Jasco V-530 model spectrophotometer and a Hitachi F-4500 model fluorescence spectrophotometer were used for the determination of metal ion concentrations. A Varian SpectrAA-20 model flame atomic absorption spectrometer was employed during interference studies. A Perkin-Elmer TGA-7 model thermal analyzer was used to study the water regaining capacity of the modified polymeric matrix. An Orbitex DS model mechanical stirrer with 200 rpm was used for batch equilibration experiments. An extractive chromatographic column (15 cm × 0.4 cm i.d.) interfaced with a Ravel Hi-Tech S-50 model peristaltic pump were employed for column studies.

2.2. Chemicals and reagents

Standard individual metal ion stock solutions were prepared by dissolving exact amounts of $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$, in acidified double distilled water. All chemicals, reagents and standard individual metal ion stock solutions, used in the process of resin synthesis and subsequent metal extractive studies were of analytical grade.

Merrifield chloromethylated styrene–divinylbenzene resin (capacity [Cl]: ∼5.5 mmol g^{-1} resin, 16–50 mesh) obtained from Fluka chemicals was purified with methanol followed by successive water washings. The resin beads were filtered, dried and vacuumized prior to usage.

2.3. Synthesis of DB2EHM anchored polymeric support

Five gram of dry chloromethylated resin matrix was functionalized with DB2EHM (28 mmol) using sodium hydride (30 mmol) in 50 mL dry dimethylformamide (DMF). The reaction mixture was refluxed at 60 °C for 12 h. The modified resin beads were purified from excess reactants by washing with methanol, water and acetone. The resin beads were filtered and vacuum dried. The synthesis scheme leading to the formation of the desired chelating polymeric matrix is depicted in Fig. 1.

2.4. Methods adopted for metal ion equilibration and preconcentration studies

2.4.1. Batch ‘static’ method

Fifty milligram of the resin beads were equilibrated with metal ion solution of known concentration, using a mechanical shaker at 200 rpm, in well-stopped reagent bottles for 60 min. Metal ions were desorbed using 10–15 mL of 1 M $(NH_4)_2CO_3$ or 0.5 M HIBA and their concentrations were estimated spectrophotometrically using Arsenazo-III at 655 nm and Thoron at 545 nm, as chromogens for U(VI) and Th(IV), respectively. Similar batch studies performed using non-functionalized resin beads showed non-extractive behavior.

2.4.2. Column ‘dynamic’ method

A glass column of dimension (16 cm × 0.4 cm) was slurry packed with 1 g of resin beads, preconditioned at 5 M HNO_3 for Th(IV) and 3 M HNO_3 for U(VI), prior to sample passage under optimum flow rate conditions. The sorbed metal ions were eluted using 10 mL of 1 M $(NH_4)_2CO_3$ and were estimated. Trace concentrations of U(VI) ions from synthetic samples were estimated by steady state spectrofluorimetric method, using 1 M phosphoric acid medium, wherein the UO_2^{2+} fluorescence emission was recorded at 515 nm with

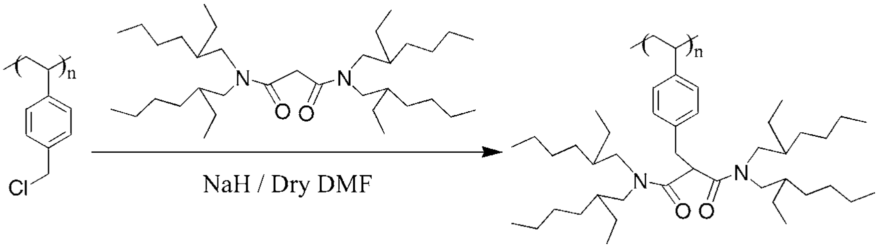

Fig. 1. Synthesis scheme.

an excitation wavelength of 266 nm [24]. The optimum experimental parameters for the quantitative sorption and desorption of analytes, by both static and dynamic method are listed in Table 1.

3. Results and discussion

3.1. Characterization

^{13}C CPMAS NMR spectra showed resonance signals between 39.2 and 33.8 ppm corresponding to the aliphatic ($-CH_2$) regions attached to the nitrogen side of the ligand moiety. Similarly the presence of aliphatic moiety on the carbonyl side was confirmed by the NMR signal peak at 58.2 ppm. The resonance signal for lateral $-CH_3$ was also observed at 17.5 ppm. The ^{13}C CPMAS NMR spectra for both unmodified resin and grafted polymer are shown in Fig. 2.

FT–NIR spectra of the modified polymer showed, showed characteristic $-CH$, $-CH_2$ and $-CH_3$ stretching vibrations in the spectral range 3000–2800 cm^{-1}. The presence of C=O groups in the final stage was confirmed by spectral bands at 1650 cm^{-1} (*b*), in addition to the band at 1363 cm^{-1} (*s*) corresponding to C–N stretching vibration. The existence of metal–ligand moiety complexation was confirmed by Far-IR in the spectral regions of 290–120 cm^{-1} corresponding to $\nu_{O-M}{}^{n+}$ stretching vibrations. The FT-IR spectra for both unmodified resin and grafted polymer are shown in Fig. 3.

CHN analysis, with an experimental data of (%) C 78.89 H 11.63 N 4.10; compared with the theoretical data of (%): C 79.16 H 11.63 N 4.29, confirms quantitative anchoring of the amide moiety to the polymeric support. TGA studies carried out for water regaining capacity measurements of the air dried resin, which was water equilibration for 2 h, showed a weight loss of 10.3% up to 110 °C. This 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 its hydrophobic nature.

Table 1
Optimized experimental parameters for metal ion sorption and desorption

Experimental parameters	U(VI)	Th(IV)
$t_{1/2}$ (min)	2.5	4.1
Metal sorption capacity (mg g^{-1})		
At 5 M HNO_3	62.5	38.2
At 5 M HCl	60.7	33.1
Eluting agent $(NH_4)_2CO_3$/HIBA (mol L^{-1})	1.0/0.5	1.0/0.5
Flow rate (mL min^{-1})	13	11
Average percent recovery	99.7	99.3
Lower limit of detection (ng mL^{-1})	20	23
Sample breakthrough volume (mL)	4500	3750
Preconcentration factor (5 M HNO_3)	310	250

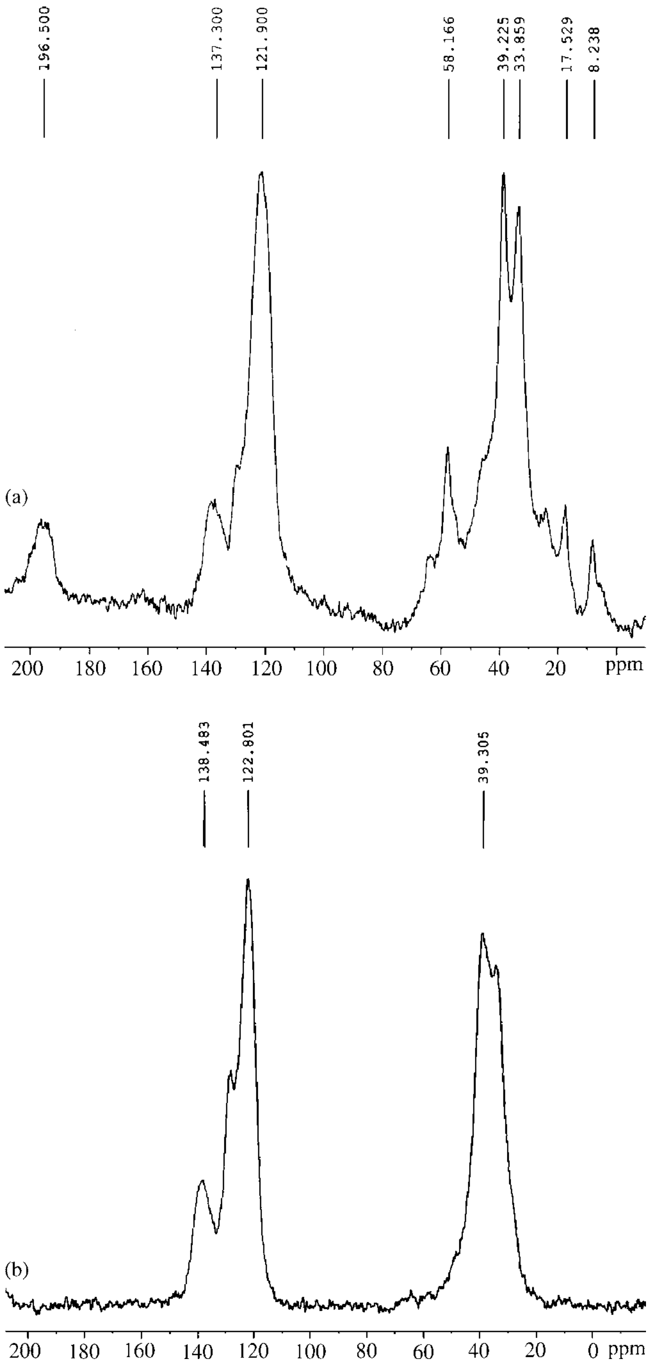

Fig. 2. ^{13}C CPMAS NMR for (a) grafted polymer; (b) merrifield chloromethylated resin.

3.2. Batch 'static' studies

3.2.1. Metal ion phase distribution in the presence of HCl and HNO_3

The influence of solution acidity on metal ion extraction was studied using varying concentrations of nitric and hydrochloric acid. Studies were performed using 50 mg of resin beads equilibrated with (40 mL, 10 μg mL^{-1}) metal ion concentration for the time duration of 60 min, under static

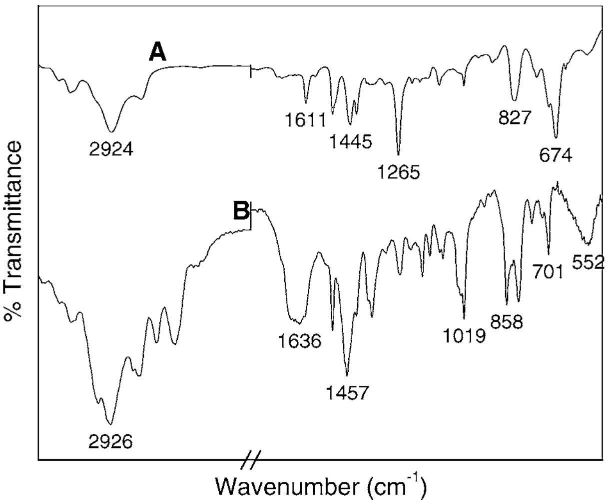

Fig. 3. FT-IR spectra for chloromethylated resin (A) and grafted polymer (B).

conditions. The extraction efficiency of the grafted polymer towards actinide ions has been plotted in terms of distribution ratios [25] (*D* values) as shown in Fig. 4. It is evident from the plot that both U(VI) and Th(IV) showed positive dependency with increasing acidity. However, the resin matrix showed greater affinity towards U(VI) over Th(IV) (<4 M acidity) due to greater steric hindrance created by the bulky alkyl chain on the N-side of the amide moiety for the extraction of neutral $Th(NO_3)_4$ species. However, with increasing acidity, Th(IV) showed a positive trend due to its extraction as an ion-pair complex with the protonated amide moiety.

3.2.2. Kinetics of U(VI), Th(IV) extraction

Extraction rate studies were performed in 5 M HNO_3 using 50 mg resin beads contacted with metal ion solution (40 mL, 10 μg mL^{-1}) for different time periods. The phase exchange kinetics was monitored in terms of fractional attainment of equilibrium [26], which is expressed as

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

where $[M^{\mathrm{R}}]_t/[M^{\mathrm{R}}]_{\mathrm{eq}}$ are the ratios of metal ion concentration in the resin phase at time '*t*' to that at equilibrium. From Fig. 5, it is visible that complete extraction for metal ions could be achieved within 15 min of time period, along with a half time ($t_{1/2}$) of <5 min (data obtained by plotting percent extraction as a function of time) due to greater surface contact of the resin matrix with the aqueous phase.

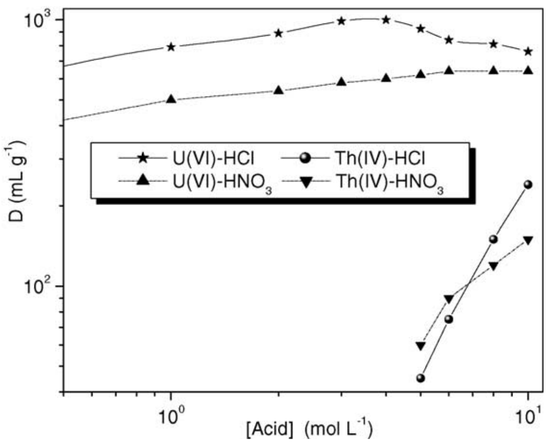

Fig. 4. Acid dependency on metal ion extraction.

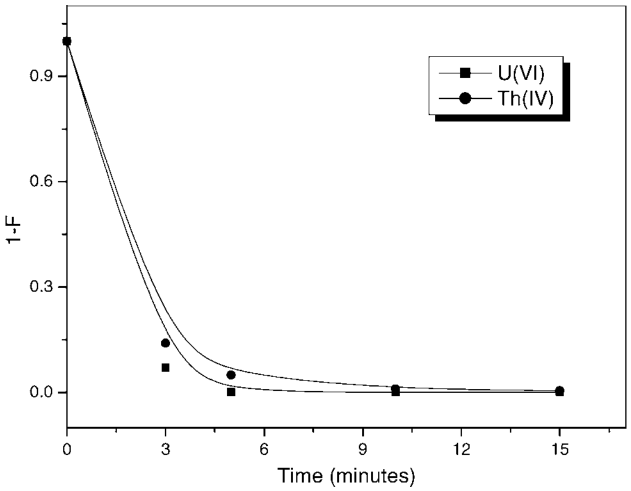

Fig. 5. Rate metal ion phase equilibration.

3.2.3. Extraction efficiency from highly salted conditions

It is well known that $NaNO_3$ and NaCl are the major constituents in nuclear waste streams and therefore their influence on U(VI) extraction efficiency was studied using varying salt concentrations. From Fig. 6, it is evident that the extraction efficiency for U(VI) showed a positive trend with increasing nitrate content. However in chloride medium,

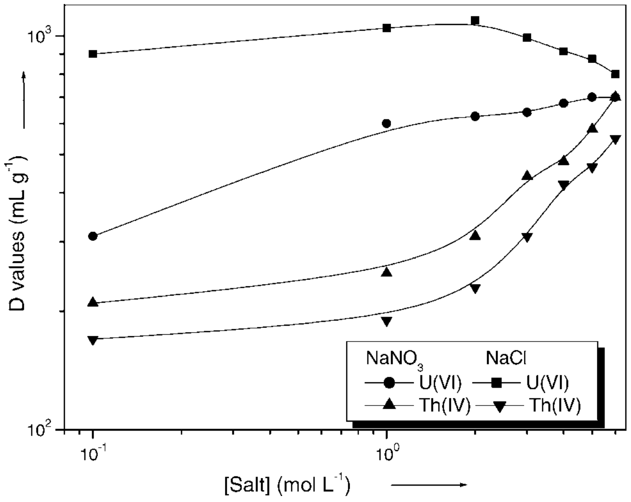

Fig. 6. Influence of salt content during analyte extraction.

Table 2
Diverse ions/electrolyte species tolerance limits

Metal ions[a]	Tolerance limits for electrolytes ($mol\,L^{-1}$)									
	Na_2SO_4	Na_3PO_4	NaF	CH_3COO^-	$C_2O_4{}^{2-}$					
U(VI)	0.87	0.21	0.40	0.51	0.10					
Th(IV)	0.82	0.19	0.51	0.55	0.07					
	Tolerance limits for interfering metal ions ($mmol\,L^{-1}$)									
	Zr(IV)	Mo(VI)	Pb(II)	Cd(II)	La(III)	Bi(III)	Ce(IV)	Nd(III)	Sm(III)	Gd(III)
U(VI)	12.1	6.3	15.1	16.8	5.3	12.1	5.2	4.9	4.8	4.5
Th(IV)	6.4	4.2	15.2	16.0	3.9	11.8	3.3	3.2	3.2	3.0

[a] Amount of U(VI) and Th(IV): 100 μg.

a positive dependency was up to 2 M [salt] but at >2 M a decrease in the *D* value was observed. The decreasing trend beyond 2 M [salt] was due to formation of more stable metal anionic complexes. However, in the case of Th(IV), even at higher salt concentrations the formation of neutral $Th(NO_3)_4$ and $ThCl_4$ species is more prevalent thereby resulting to an increase in the extraction efficiency. But, it can be observed that due to steric factors, the observed *D* value at a particular salt concentration was always lower for Th than that of U.

3.2.4. Resin metal loading capacity

The maximum metal loading capacity for U(VI) and Th(IV) at 5 M HNO_3 and 5 M HCl acidity was examined individually using 100 mg of resin beads, equilibrated with excess amounts of metal ion solution (100 mL, 75 $\mu g\,mL^{-1}$) at 200 rpm for time duration of 12 h. The metal sorption capacity values in HNO_3 medium were found to be 62.5 and 38.2 $mg\,g^{-1}$ for U(VI) and Th(IV), respectively. Similarly, in HCl medium it was found to be 60.7 and 33.1 $mg\,g^{-1}$ for U(VI) and Th(IV), respectively. The superior capacity for U(VI) was attributed to greater metal ligand stability and also to the lesser steric hindrance involved for U(VI) complexation over Th(IV).

3.2.5. Resin tolerance limits towards interfering electrolytes and common metal ions

The ability of the resin matrix to quantitatively extract trace level analytes in the presence of large concentrations of electrolyte species, transition and post-transition metal ions were studied by batch 'static' method. The resin showed non-extractive behavior towards first row transition ions but showed relatively poor distribution ratios (<10 at 5 M HNO_3) for post-transition metal ions. However in the case of lanthanides, *D* values <100 was observed and their degree of tolerance towards 100% analyte recovery is shown in Table 2, which clearly depicts the ion-selectivity behavior of the developed resin matrix towards actinide ions. Similarly, interference studies performed with various complexing species gave high tolerance limit values, which show the resin's greater chelating ability for the studied actinide ions, even under high saline conditions.

3.3. Column 'dynamic' method

3.3.1. Sample flow rate studies

The rate at which quantitative extraction could be achieved was examined in terms of sample flow rate studies. In this, metal ion solution (1 L, 1000 $\mu g\,L^{-1}$) in 5 M HNO_3 was passed through the resin bed under varying sample flow rates using a peristaltic pump. From Table 1, it is clear that even at a high flow rate of 10–13 $mL\,min^{-1}$ quantitative extraction could be achieved. The values obtained are well supported by the data obtained from kinetic studies.

3.3.2. Sample breakthrough volume studies

The analyte preconcentrating ability of the polymeric matrix from large sample volumes was studied by passing a series of sample volumes (0.5–6.0 L), spiked with 1000 μg of individual metal ions, through the preconditioned packed resin column. An enrichment factor of 310 and 250 was achieved for U(VI) and Th(IV), respectively, as shown in Table 1.

3.3.3. Column bed reusability

The reusability of the resin matrix was studied by passing metal ion solution (1 L, 1000 $\mu g\,L^{-1}$) through the precondition resin bed, along with other matrix components. The reproducibility of analyte recovery was checked using the same resin bed column up to 15 cycles and the values obtained were within 4.6% relative standard deviation (R.S.D.), which reflects the reusability character of the chemically modified polymer.

4. Applications

4.1. Recovery of U(VI) and Th(IV) from synthetic nuclear spent fuel mixture

The main purpose of fabrication of this chelating polymer was to study its capability to extract actinide ions from nuclear spent fuel systems. The extractive behavior was tested using a synthetic nuclear acidic waste mixture of fission products [24] and more common metal ions with $>10^3$-fold

Table 3
Analyte recovery from synthetic mixture mimicking a reprocessing solution

Ions[a]	Percent of resin phase extraction	
	U(VI)[b]	Th(IV)[b]
Cd(II)	100 ± 1.5	100 ± 2.5
Sr(I)	100 ± 2.3	100 ± 3.6
Zr(IV)	100 ± 3.3	99.2 ± 5.1
Mo(VI)	99.7 ± 4.7	99.8 ± 6.2
Cs(I)	100 ± 2.0	100 ± 2.1
Ba(II)	100 ± 2.8	100 ± 2.4
Ce(IV)	99.8 ± 4.9	99.8 ± 7.6
Nd(III)	99.7 ± 6.5	99.4 ± 8.6
Fe(III)	100 ± 2.7	100 ± 3.5
Cr(VI)	100 ± 3.1	100 ± 4.7
Sm(III)	99.3 ± 7.1	99.6 ± 9.5
Gd(III)	99.2 ± 8.3	99.4 ± 10.1
Ni(II)	100 ± 1.8	100 ± 2.0
Na(I)	100 ± 1.0	100 ± 1.2
Ru(IV)	100 ± 1.9	100 ± 2.6

[a] Amount of diverse ions: 0.1–0.5 g L^{-1}.
[b] Amount of U(VI) and Th(IV): 1000 μg L^{-1}.

concentrations to that of the analyte ions. Table 3 clearly reflects the affinity of the diamide anchored polymer towards U(VI) and Th(IV) over other diverse ions, thereby proving its application in nuclear reprocessing units.

4.2. Recovery of thorium from monazite sand (Travancore, India)

Monazite sand sample (0.1 g) was digested initially at low temperature using concentrated H_2SO_4 followed by vigorous heat treatment up to 250 °C, in the presence of 30% H_2O_2, for 4 h to dryness. The resulting residue was redissolved in minimal volumes of HNO_3 and a known volume of aliquot was passed through the resin bed under optimum experimental conditions. After desorption, the amount of thorium extracted was found to be 78.99 mg g^{-1}. The recovery data was cross-checked by standard addition method and the R.S.D. values were within 5.2%.

5. Conclusions

Selective extraction of U(VI) and Th(IV) from other diverse ions could be achieved using the developed chelating sorbent. The malonamide anchored polymer matrix brought out sequential separation of analytes, by varying the solution acidity. Also, the sorbent was successful in overcoming problems faced in conventional extraction methods with its notable features like ion-selectivity, better metal sorption capacity, rapid attainment of phase equilibration and good enrichment factor values. The analytical data confirms the resin's ability to extract both macro and micro level analytes without any loss in analytical signal even in the presence of large concentrations of matrix components. The data accuracy with relatively low (%) R.S.D. values highlights the better reliability and reproducibility of the resin matrix even up to 15 cycles of continuous usage. The fabricated resin proves to be a novel, economical and eco-friendly and also it provides a new dimension for actinide extraction from acidic waste streams.

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