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DAPPA grafted polymer: an efficient solid phase extractant for U(VI), Th(IV) and La(III) from acidic waste streams and environmental samples

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Abstract

A new class of polymeric resin has been synthesized by grafting Merrifield chloromethylated resin with (dimethyl amino-phosphonomethyl)-phosphonic acid (MCM–DAPPA), for the preconcentration of U(VI), Th(IV) and La(III) from both acidic wastes and environmental samples. The various chemical modification steps involved during grafting process are characterized by FT-IR spectroscopy, ^{31}P and ^{13}C-CPMAS (cross-polarized magic angle spin) NMR spectroscopy and CHNS/O elemental analysis. The water regain capacity data for the grafted polymer are obtained from thermo-gravimetric (TG) analysis. The influence of various physico-chemical parameters during the quantitative extraction of metal ions by the resin phase are studied and optimized by both static and dynamic methods. The significant feature of this grafted polymer is its ability to extract both actinides and lanthanides from high-level acidities as well as from near neutral conditions. The resin shows very high sorption capacity values of 2.02, 0.89 and 0.54 $\mathrm{mmol\,g^{-1}}$ for U(VI), 1.98, 0.63 and 0.42 $\mathrm{mmol\,g^{-1}}$ for Th(IV) and 1.22, 0.39 and 0.39 $\mathrm{mmol\,g^{-1}}$ for La(III) under optimum pH, HNO_3 and HCl concentration, respectively. The grafted polymer shows faster phase exchange kinetics (<5 min is sufficient for 50% extraction) and greater preconcentration ability, with reusability exceeding 20 cycles. During desorption process, all the analyte ions are quantitatively eluted from the resin phase with >99.5% recovery using 1 M $(NH_4)_2CO_3$, as eluent. The developed grafted resin has been successfully applied in extracting Th(IV) from high matrix monazite sand, U(VI) from sea water and also U(VI) and Th(IV) from simulated nuclear spent fuel mixtures. The analytical data obtained from triplicate measurements are within 3.9% R.S.D. reflecting the reproducibility and reliability of the developed method.

Keywords: Merrifield chloromethylated polymer; Preconcentration; Extraction; Actinides and lanthanides

1. Introduction

Nuclear spent fuels generally contain actinides like uranium, thorium and various fission products. It is a challenging task to quantitatively recover these trace metal ions from these systems due to high acidic matrix environment [1–3]. Extraction and preconcentration of these valuable metal ions from such solutions are extremely important not only from the point of view of their limited resource availability, but also to reduce their quantum for disposal as radioactive wastes [4,5].

Various organic extractants were employed in solvent extraction (SE) technique for the selective extraction of actinides from high acidic wastes [6–10]. Amongst them, phosphorus based ligands are known to be more selective for actinide ions [11–14]. But the main problems encountered in SE technique are: (a) the third phase formation; (b) disposal of large volumes of extractants and diluents; (c) multi-stage 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 [15–18]. Slow reaction kinetics results in the under utilization of resin capacity and premature ion breakthrough. Also, due to their low acidic properties, majority of

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the chelating resins are ineffective for metal ion extraction studies from high acidic solutions [19].

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. Horwitz and co-workers prepared diphonix resin (patented and commercialized by Eichrom industries) to extract actinides [20–22]. But, it also co-extracts alkaline-earth and transition metal ions.

With a view of overcoming this drawback, a new type of chelating ion exchange polymer termed as MCM–DAPPA has been synthesized. This resin is a polyfunctional polymer containing diphosphonic acid groups and dimethyl amino groups. The diphosphonic acid ligand moiety contributes for the resin's selectivity behavior towards actinides even from high acidities. The hydrophilic hydroxyl and dimethyl amino moieties enhance the metal ion accessibility into the polymer matrix, thereby significantly improving the kinetics. The present paper will discuss about the synthesis, characterization and the metal extraction studies performed for U(VI), Th(IV) and La(III). Also, the grafted polymer has been tested for its practical utility using various synthetic simulated samples, geological and seawater samples.

2. Experimental

2.1. Instrumentation

The grafted polymer was characterized using a Perkin-Elmer Spectrum One model FT-IR spectrometer, a Bruker-Avance 400 model CPMAS NMR Spectrometer, Perkin-Elmer 2400 model CHNS/O analyzer and a Perkin-Elmer TGA-7 model thermal analyzer (for water regain capacity studies). 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. Flow rates during column operations were adjusted with a Ravel Hi-Tech S-50 model peristaltic pump. Static equilibration studies were performed using an Orbitek DL model mechanical shaker with shaking rate of 200 rpm.

2.2. Chemicals and reagents

Standard individual metal ion solutions (1000 ppm) 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 2.10 and 2.46 g in 1 L of slightly acidified double distilled water. Similarly, 1000 ppm of La(III) and Nd(III) solutions were prepared from the corresponding oxides obtained from Indian Rare earths Ltd. (1.17 g, 1 L). The ligand tetraethyl (dimethyl amino methylene) diphosphonate was procured from Lancaster Chemicals and all other reagents and solvents were purchased from E-Merck chemicals, which are of AR grade.

Merrifield chloromethylated styrene-divinylbenzene resin (Capacity [Cl]: ∼5.5 mmol g^{-1} resin, 16–50 mesh) obtained from Fluka chemicals was purified by washing with distilled water, 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.

2.3. Synthesis of the resin

The vacuum dried Merrifield resin (5 g) was reacted with tetra ethyl (dimethyl amino methylene) diphosphonate (1.1 equiv.) for 30 h at 70 °C, which was initially treated with NaH in dry DMF medium [23]. The formed diphosphonate resin was converted to diphosphonic acid resin by refluxing in conc. HCl for 24 h. The grafted polymer was washed thoroughly with methanol, acetone followed by water to remove all the starting materials. The resultant polymer was filtered and vacuum dried. The synthetic scheme leading to the formation of the grafted polymer is shown in Fig. 1.

2.4. Methods adopted for metal ion extraction and preconcentration

2.4.1. 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 amounts of resin beads (50 mg) were equilibrated with known concentrations of individual metal ion solution (40 mL, 10 μg 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 1 M ammonium carbonate. The amount of metal ions extracted were estimated spectrophotometrically using arsenazo(III) as chromogen for U(VI) (7 M HNO_3) [24] and La(III) (pH 3) [25] and using thoron as chromogen for Th(IV) [25] at 655 and 545 nm, respectively.

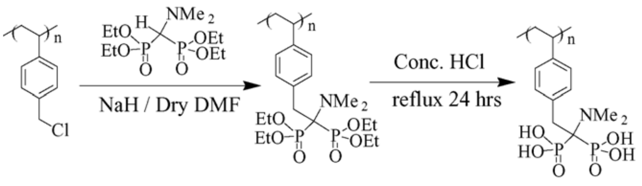

Fig. 1. Chemical modification of MCM polymer with DAPPA.

Table 1
Optimum experimental parameters for quantitative analyte extraction

Experimental parameters	U(VI)	Th(IV)	La(III)
pH range	6.0–6.5	4.0–5.0	4.0–5.0
$t_{1/2}$ (min)	3	5	8
Metal sorption capacity (mmol g^{-1})			
At optimum pH	2.02	1.98	1.22
At 4 M HNO_3	0.89	0.63	0.39
At 4 M HCl	0.54	0.42	0.39
Eluting agent	1 M $(NH_4)_2CO_3$	1 M $(NH_4)_2CO_3$	1 M $(NH_4)_2CO_3$
Maximum flow rate achieved (mL min^{-1})	20	15	15
Average % recovery	99.9	99.8	99.5
Lower limit of quantification (ng mL^{-1})	10	50	80
Sample breakthrough volume (mL)	5000	4000	4000
Enrichment factor (4 M HNO_3)	500	400	400

2.4.2. Column ‘dynamic’ method

A glass column (15 cm × 0.4 cm) was packed uniformly with 1 g of preconditioned resin beads by slurry method and the sample solution was passed at a constant flow rate using a peristaltic pump. All the column parameters such as break through volume, sample flow rate and lower limit of analyte quantification were optimized using this method. Based on the data obtained from dynamic method, the practical applicability of the resin matrix was tested for the preconcentration of U(VI) from synthetic mixture mimicking nuclear spent fuels in acid medium and seawater and also Th(IV) from monazite sand. The optimum parameters for both static and dynamic methods are listed in Table 1.

3. Results and discussion

3.1. Characterization of the resin matrix

3.1.1. NMR studies

The ^{13}C CPMAS solid-state NMR spectra of MCM and MCM–DAPPA polymer are shown in Fig. 2(a) and (b). The peak observed at 39.33 ppm for MCM polymer, which corresponds to the alkyl ($-CH_2-$) groups was shifted to 64.06 ppm in MCM–DAPPA due to the substitution of additional functional groups. The broad peak observed at 40.14 ppm for the grafted polymer is attributed to the dimethyl groups. The grafting process was also monitored using ^{31}P solid-state NMR spectra, where a sharp resonance signal at −9.21 ppm which is due to diphosphonic acid moiety, as shown in Fig. 2(c).

3.1.2. FT-IR studies

Each step of the grafting process was monitored using FT-IR spectra, as shown Fig. 3. From the spectra, it can be seen that the band at 672 cm^{-1} corresponding to C–Cl stretching frequency has completely disappeared in the MCM–DAPPA spectra and new set of bands are observed at 3412 cm^{-1} (–OH), 1477 cm^{-1} (–C–P), 1081 cm^{-1} (P=O), 1017 cm^{-1} (P–OH), thereby confirming the grafting process.

3.1.3. CHN elemental analysis and TG analysis

The resin was further characterized by CHN elemental analysis. The experimental (%) values were C 43.4, H 7.9, N 3.4 and P 16.5, which are in close agreement with the corresponding theoretical values of C 42.2, H 7.5, N 3.8 and P 17.3. This suggests the presence of one ligand moiety per polymer repeat unit and also confirms quantitative ligand grafting.

TG analysis was performed to study the water regain capacity, wherein the resin was equilibrated with water for 4 h, then after filtered and air dried prior to analysis. The results showed a weight loss of 25% up to 110 °C. The high weight loss could be attributed to the presence of four hydroxy groups, which increases the hydrophilic nature of the resin matrix by providing better surface contact with the aqueous phase, thereby improving the accessibility of the metal ions to the chelating sites.

3.2. Metal extraction studies by batch method

3.2.1. Influence of acidity for the 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 μg mL^{-1}) of different acid concentrations, for 90 min. The results were expressed in terms of the distribution ratio (D) using the following expression [26],

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

where A_o and A_f are the metal ion concentration before and after equilibration, V refers to the overall volume (mL) and W the dry weight of the resin matrix (g). The extraction of actinides even in high acid medium reflects the ability of the gem P=O groups, which resulted in high affinity towards

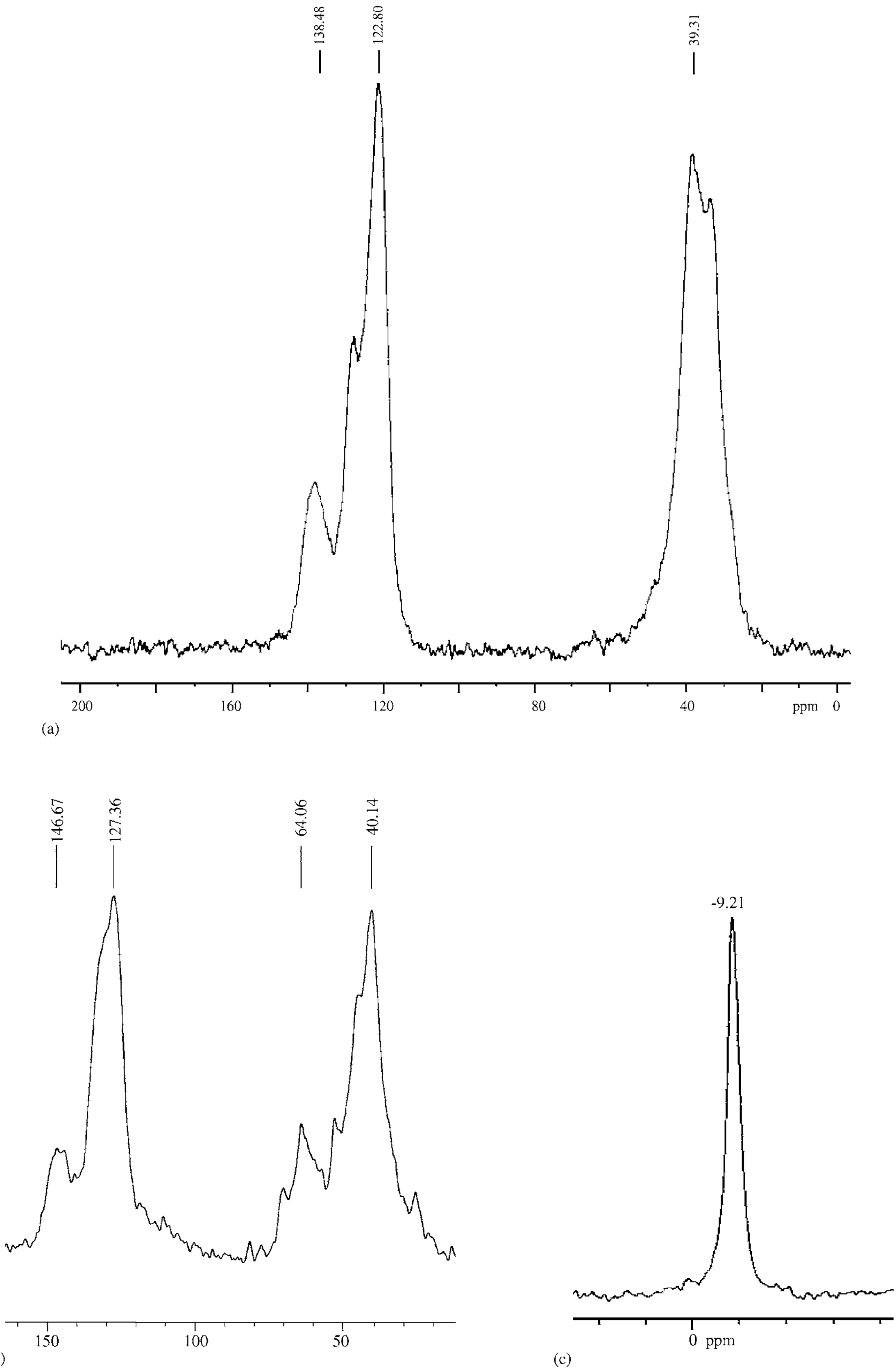

Fig. 2. (a) ^{13}C-CPMAS NMR spectra of MCM polymer; (b) ^{13}C-CPMAS NMR spectra of MCM–DAPPA; (c) ^{13}P solid state NMR spectra of MCM–DAPPA.

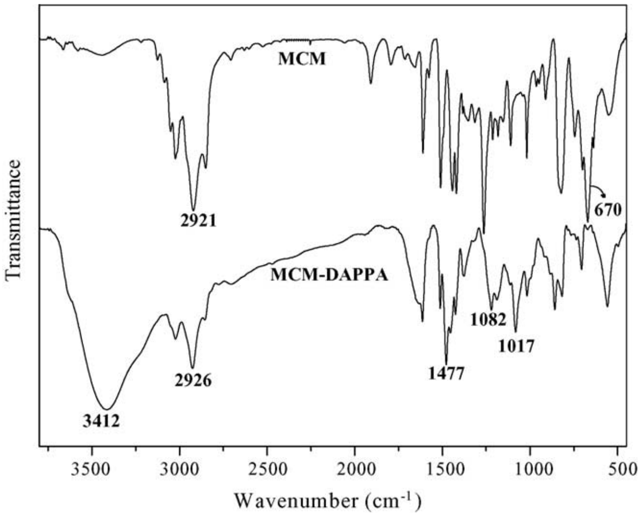

Fig. 3. FT-IR spectra of MCM and MCM–DAPPA.

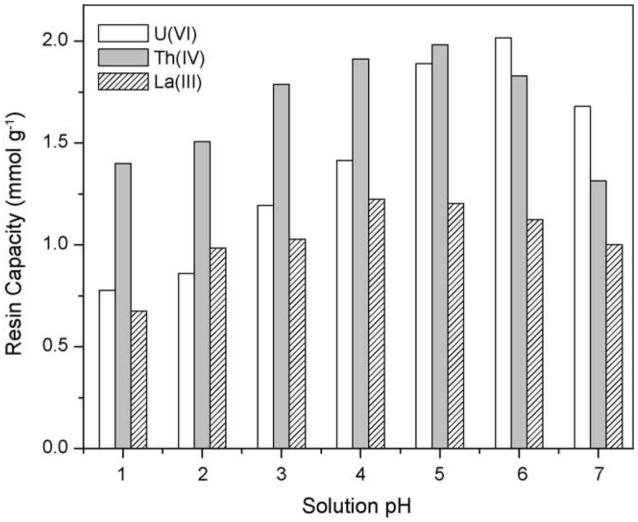

Fig. 5. Resin capacity as a function of pH.

neutral complexes of actinides (charge neutralized by the anions Cl^-, $NO_3{}^-$ which are present in the acidic solution) (Fig. 4). This behavior has been attributed to their capacity to chelate actinides with neutral diphosphonic ligands leading to high stable metal complexes. The slow decrease in *D* values at high acid concentrations may be due to the existing competition between nitric acid and metal ion species to the P═O active sites. This is because of the basic nature of the P═O group, which also can extract nitric acid. Also, the formation of more stable anionic metal complexes, which are non-extractable by the chelating gem P═O group can influence the decrease in the *D* values to a greater extent.

In HCl medium, both U(VI) and Th(IV) showed similar extractive behavior and their extraction decreases after 2 M HCl concentration, which is greater than in nitric acid medium due to their tendency to form more stable anionic metal chloro complexes. In the case of La(III), the observed *D* values in both HNO_3 and HCl medium shows a negative trend with increasing acidities, more than actinides. This behavior may be attributed to the ligand's selectivity in extracting actinides (size factors) and also due to fact of lanthanides tending to form more stable anionic complexes, which are non-extractable by the resin phase.

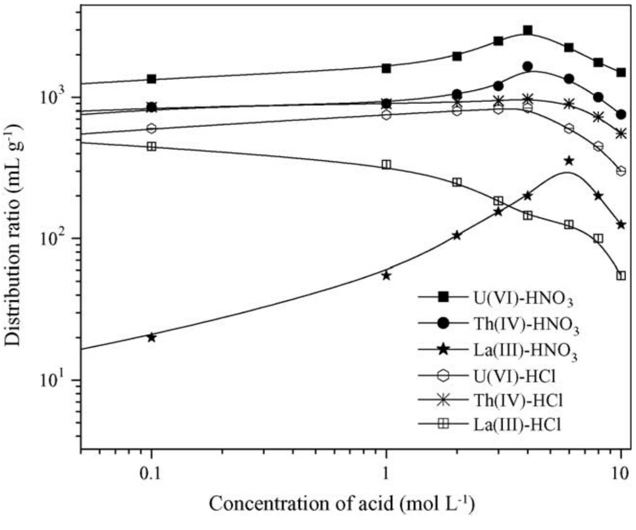

Fig. 4. Influence of acid concentration on analyte extraction.

3.2.2. Resin metal sorption capacity

The maximum metal sorption capacities of the developed resin matrix was studied by equilibrating 0.02 g of the grafted polymer with individual solutions of excess metal ion concentration (100 mL, 100 μg mL^{-1}) under wide pH range (1.0–7.0) and also at 4 M acidity for a time duration of 6 h. The analyte solutions were diluted accordingly in calibration range and estimated spectrophotometrically. The resin's metal sorption capacities as a function of solution pH are plotted in Fig. 5. 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 be at pH 6.0 (2.02 mmol g^{-1}), pH 5.0 (1.98 mmol g^{-1}) and at pH 4.0 (1.22 mmol g^{-1}), respectively. The resin also showed remarkable sorption capacities even under optimum (4 M) acid concentration, as shown in Table 1. The resin's high sorption capacities in near neutral conditions compared to acidic conditions may be due to the involvement of both chelating and ion exchange mechanism, which are playing a predominant role in the extraction by forming more stable metal chelates. Also, the aqueous phase contact by the resin matrix was improved by the presence of hydrophilic functional groups like, P–OH and dimethyl amino group, which ultimately increases site accessibility of the metal ions towards the active chelating sites. These features make this resin superior to earlier literature reported chelating polymers in this area [27–36], as shown in Table 2.

Table 2
Comparison of resin sorption capacity with other chemically modified polymers

Polymeric sorbent	Resin sorption capacity (mmol g^{-1})	
	U(VI)	Th(IV)
Merrifield polymer–DAPPA	*2.01*	*1.98*
Merrifield polymer–TTA [24]	0.13	0.11
Amberlite XAD-4-Bicene [25]	0.38	0.25
Amberlite XAD-2-Tiron [26]	0.03	–
Amberlite XAD-4-OVSC [27]	0.01	0.01
Amberlite XAD-4-octa carboxy methyl-c-methyl Calix [4] resorcinarene [28]	0.27	0.29
Amberlite XAD-16-AsP [29]	1.49	1.40
Amberlite XAD-16-BTBED [30]	1.43	1.19
Amberlite XAD-16-BTBPD [31]	0.66	0.66
Amberlite XAD-16-DBBT [32]	0.90	–
Amberlite XAD-16-CMPA [33]	1.42	1.22

3.2.3. Elution studies

Quantitative desorption of U(VI), Th(IV) and La(III) was performed with various eluting agents like 0.1–2 M EDTA, oxalate and ammonium carbonate, where in ammonium carbonate was found to be successful in quantitatively recovering the analytes. The desorption process involves the formation of strong anionic carbonato complex, which tends to be in the aqueous phase. Therefore, the elution studies were tried with various concentrations of ammonium carbonate (0.1–2 M) and quantitative recovery (>99.5%) was observed with 1 M ammonium carbonate. The high concentration of carbonate required during recovery process shows the strong retention behavior of analytes by the diphosphonic groups.

3.2.4. 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 $\mu g\,mL^{-1}$) in 4 M HNO_3. The kinetic data were plotted in terms of $(1-F)$ values as function of equilibration time where, F is the fractional attainment of equilibrium, which is expressed as [37],

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

where $[M^{R}]_{t}$, $[M^{R}]_{eq}$ are the metal ion concentration in the resin phase at time 't' to that at equilibrium. From the Fig. 6, it is evident that complete equilibrium is attained within 10 min of duration for all the analytes. The enhanced kinetics can be attributed to the presence of hydrophilic diphosphonic acid groups and dimethyl amino group, which provides greater surface contact thus increasing the accessibility of metal ions to the active sites, thereby enhancing the equilibration process.

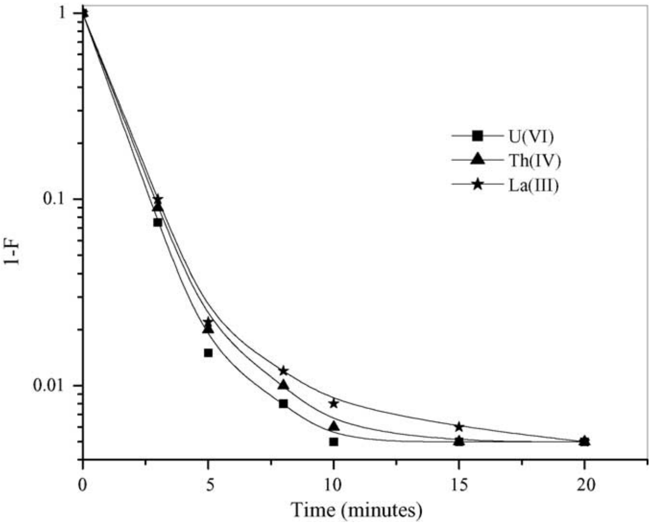

Fig. 6. Extraction kinetics in 4 M HNO_2.

3.2.5. Effect of $NaNO_3$ and NaCl on metal ion extraction

As $NaNO_3$ and NaCl are the main electrolytes present 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 exist a positive trend with increasing $NaNO_3$ concentration (up to 2 M) and thereafter it remained constant. This perhaps may be due to the reduction of the hydration sphere around the metal ions enabled by the salting out effect of $NaNO_3$. The negative trend on increasing NaCl concentration may be due to the formation of more stable metal anionic chloro complexes, which are non-extractable by the phosphoryl oxygen of the diphosphonic groups.

3.2.6. Tolerance limit towards interfering ions and common metal ions

The resin's tolerance limits towards various electrolytes and diverse metal ions was studied by equilibrating 0.05 g

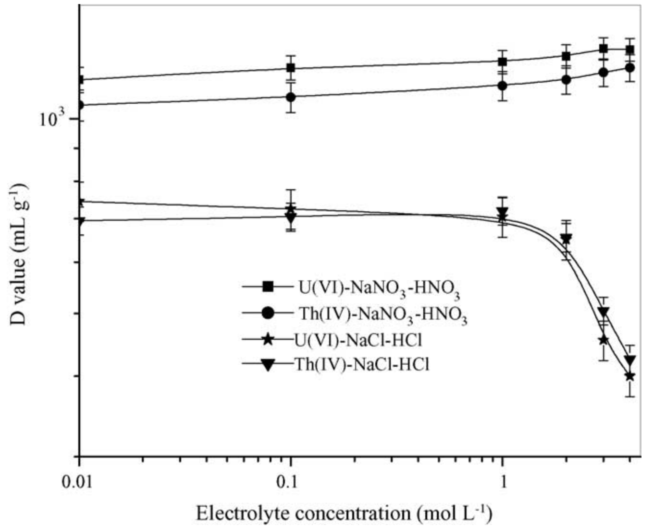

Fig. 7. Effect of salt concentration in corresponding 2 M acidity.

Table 3
Tolerance limits of various diverse metal ions and electrolytes

Metal ions	Tolerance limits of electrolytes (mol L^{-1})					
	Na_2SO_4	Na_3PO_4	NaF	CH_3COO^-	Ca^{2+}	Mg^{2+}
U(VI)	0.62	0.31	0.08	0.1	0.54	0.5
Th(IV)	0.63	0.32	0.13	0.06	0.55	0.5

Metal ions	Tolerance limits of interfering metal ions (mmol L^{-1})								
	Zr(IV)	Mo(VI)	Pb(II)	Cd(II)	Bi(III)	Ce(IV)	Nd(III)	Sm(III)	Gd(III)
U(VI)	2.5	1.8	0.8	3.8	5.4	6.0	8.5	5.5	5.1
Th(IV)	4.2	2.2	1.1	3.5	6.6	7.5	9.7	5.8	4.8

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 except for Fe(III) with a D value of 100 (tolerance limit-2.4 mmol L^{-1}). The degree of tolerance for some post-transition ions, rare earths and electrolyte species, are shown in Table 3. D values of these diverse ions were found to be in the range 20–80. From the tolerance data, it can be seen that the resin shows high selectivity towards the studied analytes when compared to other diverse ions.

3.3. *Metal extraction studies by dynamic method*

3.3.1. *Influence of sample flow rate on metal ion sorption*

The maximum flow rate at which the quantitative sorption could be achieved was studied using a packed resin bed column by varying the sample flow rates using a peristaltic pump. The metal ion solution (1000 mL, 0.5 μg mL^{-1}) was passed through the column (bed volume, 1.2 mL) with varying flow rates from 1 to 25 mL min^{-1}. The results showed that quantitative extraction of analytes was achieved even with high flow rates of 20, 15 and 15 mL min^{-1} for U(VI), Th(IV) and La(III), respectively.

3.3.2. *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 (500–6000 mL) containing 50 μg of each individual analytes were passed through the column bed. The sorbed metal ions were eluted with 10 mL of 1 M $(NH_4)_2CO_3$. A sample breakthrough volume of 5000 mL for U(VI) and 4000 mL for Th(IV) and La(III) (Fig. 8) was obtained.

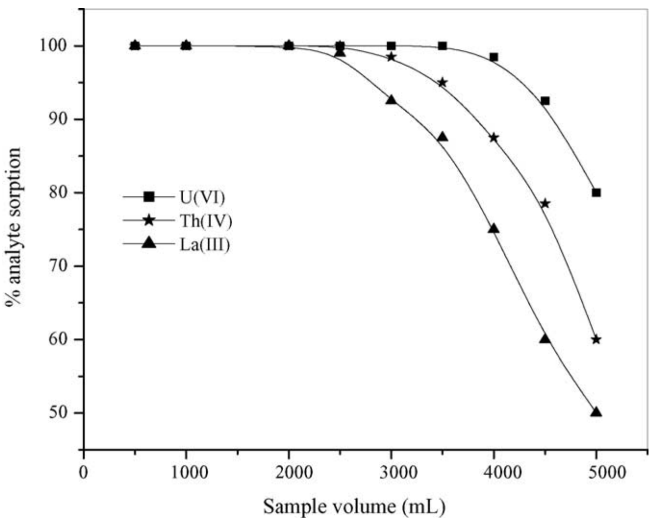

Fig. 8. Sample breakthrough volume.

3.3.3. *Lower limit of analyte quantification*

The ability of the resin to extract the lowest limit of trace analytes quantitatively is termed as lower limit of analyte quantification, which is a very important parameter to be optimized in order to test the resin's sensitivity. For this study, 1000 mL of sample solution was passed through the optimized column bed (analyte concentration range 10–100 ng mL^{-1}). The sorbed metal ions were eluted and estimated. The limits of quantification were found to be 10, 50 and 80 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.

4. Applications

4.1. *Synthetic mixture mimicking reprocessing streams*

The ability of the resin matrix to extract the analytes of interest from acidic wastes was tested with the synthetic mixture mimicking nuclear spent fuels [38]. A volume of 3 L of the synthetic mixture spiked with 100 μg of analyte was passed through the chromatographic column at 4 M HNO_3. The sorbed metal ions were eluted and estimated. It was found that the resin was successful in extracting the actinides of interest quantitatively even in the presence of various diverse ions. The analytical data were reproducible with an R.S.D. value of 3.6% for triplicate measurements.

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

Water sample	Source of the sample	Method	Conc. of U(VI) (ng mL^{-1})	R.S.D. (%)[a]
Seawater – 1	Chennai, India	Direct	5.05 ± 0.38	4.1
		SA	5.12 ± 0.46	3.8
Seawater – 2	Mahabalipuram, India	Direct	5.85 ± 0.48	3.5
		SA	5.88 ± 0.52	3.6
Well water – 1	Adyar, Chennai, India	Direct	3.85 ± 0.41	3.2
		SA	3.88 ± 0.46	3.5
Well water – 2	IIT Madras, Chennai, India	Direct	3.42 ± 0.38	3.8
		SA	3.65 ± 0.42	4.0

[a] 95% Confidence levels, $t = 3.18$ (for triplicate measurements).

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

The resin's applicability in extracting Th(IV) from monazite sand was studied. An amount of 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 79.5 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% R.S.D. for triplicate measurements.

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

Synthetic seawater was prepared using the literature reported procedure [39]. An amount of 100 μg of U(VI) was spiked to 3 L of synthetic sea water mixture solution and was passed through the extraction column at a flow rate of 10 mL min^{-1}. The sorbed metal ions were eluted and estimated. The values showed satisfactory recovery (>99.5%) with a R.S.D. value of 3.1% for U(VI), on triplicate measurements. Its applicability was tested by extending to real water samples (sea water and well water samples). These samples were filtered to remove the particulate matters using membrane filter (0.45 mm) and was passed through the preconditioned resin bed. The sorbed U(VI) was desorbed and analyzed using steady state spectrofluorimetric method [38]. The values are confirmed further using standard addition method and the results were shown in Table 4.

5. Conclusions

The developed grafted polymer showed high selectivity in extracting U(VI) and Th(IV) from both high level acidic streams and near neutral conditions, thus proving its wide range of practical applications. The significant features of the developed resin matrix are its superior metal sorption capacity with good enrichment factor values at high extraction rates. The grafted polymer showed good durability and reusability even up to 20 cycles. The polymer also showed good selectivity and sensitivity towards analytes down to ppb levels.

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References

[1] E.P. Horwitz, M.L. Dietz, D.M. Nelson, J.J. La Rosa, W.L. Fairman, Anal. Chim. Acta 238 (1990) 263.
[2] Y. Sasaki, S. Tachimori, Sol. Extr. Ion Exch. 20 (2002) 21.
[3] L. Spjuth, J.O. Liljenzin, M.J. Hudson, M.G. Drew, P.B. Iveson, C. Madic, Sol. Extr. Ion Exch. 18 (2000) 1.
[4] T. Sekine, Y. Hasegawa, Solvent Extraction Chemistry: Fundamentals and Applications, Marcel Decker, New York, 1977.
[5] K.K. Gupta, V.K. Manchanda, M.S. Subramanian, R.K. Singh, Sol. Extr. Ion Exch. 1 (2000) 273.
[6] G. Thiollet, C. Musikas, Sol. Extr. Ion Exch. 7 (1989) 813.
[7] E.A. Mowafy, H.F. Aly, J. Radioanal. Chem. 250 (2001) 199.
[8] T. Nakamara, C. Miyake, Sol. Extr. Ion Exch. 13 (1995) 253.
[9] N. Condamines, C. Musikas, Sol. Extr. Ion Exch. 6 (1988) 1007.
[10] P. Pakalns, Anal. Chim. Acta 120 (1980) 289.
[11] M.R. Yaftian, R. Taheri, A.A. Zamani, D. Matt, J. Radioanal. Chem. 262 (2004) 455.
[12] M.R. yaftian, M.E. Eshraghi, L. Hassanzadeh, Iran. J. Chem. Chem. Eng. 22 (2003) 71.
[13] C. Hill, C. Madic, P. Baron, M. Ozawa, Y. Tanaka, J. Alloys Compd. 271 (1998) 159.
[14] A.W. Herlinger, R. Chiarizia, J.R. Ferraro, P.G. Rickert, E.P. Horwitz, Sol. Extr. Ion Exch. 15 (1997) 401.
[15] M. Merdivan, M.Z. Duz, C. Hamamci, Talanta 55 (2001) 639.
[16] A. Suresh, C.V.S. Brahmananda Rao, R. Devanayaki, T.G. Srinivasan, P.R. Vasudeva Rao, Sol. Extr. Ion Exch. 21 (2003) 449.
[17] W. Lee, S.E. Lee, M. Kim, C. Lee, Y. Kim, Bull. Kor. Chem. Soc. 23 (2002) 1067.
[18] J.M. Suh, M.K. Kim, J.H. Lim, C.H. Lee, W. Lee, Anal. Sci. Tech. 8 (1995) 397.
[19] G. Myasaedova, S.B. Savvin, CRC Crit. Rev. Anal. Chem. 17 (1987) 1.
[20] R. Chiarizia, E.P. Horwitz, S.D. Alexandratos, Sep. Sci. Tech. 32 (1997) 1.
[21] R. Chiarizia, E.P. Horwitz, K.A. D'Arcy, S.D. Alexandratos, A.W. Trochimczuk, Sol. Extr. Ion Exch. 14 (1996) 1077.

[22] R. Chiarizia, E.P. Horwitz, K.A. D'Arcy, S.D. Alexandratos, A.W. Trochimczuk, Sol. Extr. Ion Exch. 14 (1996) 519.

[23] Q.D. Quan, S.X. Dong, C. RuZhen, L. Lunzu, Heteroatom Chem. 10 (1999) 271.

[24] P.R.V. Rao, S.K. Patil, J. Radioanal. Chem. 42 (1978) 399.

[25] F.D. Snell, Photometric and Fluorometric Methods of Analysis Metals, Wiley, New York, 1978.

[26] E.P. Horwitz, R. Chiarizia, H. Diamond, R.C. Gatrone, Sol. Extr. Ion Exch. 11 (1993) 943.

[27] D. Prabhakaran, M.S. Subramanian, Anal. Lett. 36 (2003) 2277.

[28] K. Dev, R. Pathak, G.N. Rao, Talanta 48 (1999) 579.

[29] M. Kumar, D.P.S. Rathore, A.K. Singh, Analyst 125 (2000) 1221.

[30] V.K. Jain, A. Handa, S.S. Sait, P. Shrivastav, Y.K. Agarval, Anal. Chim. Acta 429 (2001) 237.

[31] N. Damirel, M. Merdian, P. Necmettin, C. Hamamci, Anal. Chim. Acta 485 (2003) 213.

[32] D. Prabhakaran, M.S. Subramanian, Anal. Bioanal. Chem. 379 (2004) 519.

[33] D. Prabhakaran, M.S. Subramanian, React. Funct. Polym. 57 (2004) 147.

[34] D. Prabhakaran, M.S. Subramanian, Talanta 61 (2003) 423.

[35] M. Merdian, M.Z. Duz, C. Hamamci, Talanta 16 (2001) 639.

[36] M. Akhila Maheswari, M.S. Subramanian, Talanta 64 (2004) 204.

[37] R. Chiarizia, E.P. Horwitz, S.D. Alexandratos, Sol. Extr. Ion Exch. 12 (1994) 211.

[38] S. Maji, K. Sundarajan, G. Hemamalini, K.S. Viswanathan, Fluorimetic Estimation of Uranium: Applications in Nuclear Technology, IGC 228, Indira Gandhi Center for Atomic Research, India, 2001.

[39] H. Whitefield, D. Jagnee, Marine Electrochemistry: A Practical Introduction, Wiley-Interscience, North Ireland, 1956, pp. 35–36.