



AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid: a selective preconcentrator for U and Th from acidic waste streams and environmental samples

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Abstract

A novel chelating ion-exchange extraction chromatographic technique has been developed using AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid, as the stationary phase, for the selective extraction of uranium and thorium. The polymeric stationary phase was characterized by FT-IR spectroscopy, CHNPS elemental analysis and also by thermo gravimetric analysis. Various physio-chemical parameters influencing the quantitative metal ion extraction were optimized by both static and dynamic methods. The most notable feature of the developed resin matrix was its high distribution ratio values both under high acidities and pH conditions. The matrix showed superior metal sorption capacity values of 1.66 and 1.51 mmol g⁻¹ for U(VI) and Th(IV), respectively. Kinetics studies revealed that time duration of <5 min was sufficient for complete resin phase metal ion saturation. A good enrichment factor of 333 was achieved, with the lower limits of analyte extraction being 10 ng cm⁻³ for both U(VI) and Th(IV). Sequential separation of Th(IV) and U(VI) was possible using 6 M HCl as eluant. In order to check the practical utility of the developed system, extraction studies were performed using simulated nuclear reprocessing mixture, synthetic seawater, real water and monazite sand samples. All the data obtained were within 3.9% rsd, reflecting the reliability and data reproducibility using the developed method.

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1. Introduction

Fabrications of ion-selective solid phase extractants are of major concern in trace metal analysis. These extractants serve mainly two purposes namely, toxicity estimation and recovery of

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valuable metal ions. However, it is well known that the use of organic liquid extractants (solvent extraction) remains the preferred technique in chemical analysis, especially when it comes to recovering radioactive nuclides from acidic nuclear spent fuel systems [1–6]. In spite of its extensive usage, the major limitations of this technique are its labor intensiveness, cost effectiveness and potential explosive hazards due to third phase formation. In addition, severe environmental pollution is encountered due to finite solubility of the extractants, solvents and modifiers in the aqueous phase. Therefore, to overcome these limitations and also to encourage solvent-free extraction procedures, chelating polymers have grown significantly [7–9].

Chelating polymers comprise of two components, (a) inert solid support and (b) chelating ligand moiety. The incorporation of ligand moiety can be carried out either by physical adsorption (impregnation) to the solid support or by chemical modification (anchoring). But in the case of impregnated resins, in spite of their high phase distribution ratios, their tendency to undergo ligand bleeding on subsequent usage makes them the less preferred ones [10–13]. In the recent years, several types of chelating matrices anchored with a variety of ligand moieties have been developed for the selective extraction of trace metal ions prior to their analysis [14–21]. However, most of the developed sorbents were successful only under near neutral conditions and were ineffective for metal ion extraction from acidic matrices. In addition to this, slow phase exchange kinetics was also exhibited due to poor surface contact with the aqueous phase (hydrophobicity), thereby resulting in the underutilization of the available chelating sites. But despite these drawbacks, the use of chelating sorbent can be considered as a better alternative to the existing conventional methods.

The current research paper focuses on the development of a new kind of solid phase extractants termed as chelating ion-exchange resins using Amberlite XAD-16 (a styrene–divinyl benzene copolymer) functionalized with 3,4-dihydroxy benzoyl methyl phosphonic acid. This resin is incorporated with *hydrophilic groups* to ensure better surface contact of the resin with the aqueous

phase, and also with *chelate forming functionality* for the selective extraction of actinides [22–24]. Quite a few phosphorous based ion-exchangers as well as ligand loaded resins are being used for metal ion extraction [12,23–38]. But these resins are associated with problems like poor ion-selectivity, moderate kinetics, insufficient metal sorption capacity, low enrichment factor, ligand bleeding, etc. Moreover, their extraction behaviors are confined either to pH conditions or to acidic media. But the newly developed resin can be used for a variety of applications, as the phosphoryl and carbonyl oxygens function effectively act as neutral metal extractors at high acidic media and the two phenolic hydroxyl groups act as cation exchangers. Apart from this, the hydroxyl groups also serve as hydrophilicity enhancers. The resin showed excellent selectivity and good distribution ratios for U(VI) and Th(IV) even under high acidities which are of great significance in nuclear spent fuel reprocessing. The synthesis of the polymeric matrix and its extractive behavior towards U(VI) and Th(IV) from synthetic mixtures mimicking nuclear spent fuel systems and also from monazite sand and real water samples will be discussed in detail.

2. Experimental

2.1. Instrumentation

A Perkin–Elmer Spectrum One model FT-IR spectrometer was used for functional group identification. An Elementar Vario EL model CHNPS analyzer was employed to ensure the quantitative functionalization of the resin matrix. A Bruker IFS 66V model Far IR Spectrometer was used for metal–polymer complexation studies. A Perkin–Elmer TGA-7 model thermal analyzer was used to measure the resin's water regaining capacity (hydrophilicity studies). A Jasco V-530 model spectrophotometer was used for the estimation of U(VI) and Th(IV) and a Hitachi F-4500 model fluorescence spectrophotometer was employed for determining trace level U(VI) from synthetic and real samples. A Varian SpectrAA-20 model flame atomic absorption spectrometer was used for the

estimation of diverse metal ions for carrying out interference studies. Column studies were performed using an extraction chromatographic glass column (15 cm × 4 mm i.d) interfaced with a Ravel Hi-Tech S-50 model peristaltic pump. All static equilibration studies were carried using an Orbitek DL model mechanical shaker with 200 rpm. A Digisun DI-707 model pH-meter was employed for solution pH adjustments.

2.2. Chemicals and reagents

AXAD-16 resin beads (20–50 mesh, surface area $825 \text{ m}^2 \text{ g}^{-1}$, bead size 0.3–1.2 mm) were procured from Fluka Chemicals. Standard metal ion stock solutions were prepared by dissolving exact amounts of AR grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Fluka Chemicals) in slightly acidified double distilled water. All the chemicals and reagents used during the process of chemical modification of the polymeric matrix and subsequent extraction studies were of AR grade purchased from Lancaster and E-Merck Chemicals.

2.3. Synthesis of AXAD-16-3,4-dihydroxy benzoyl methyl phosphonic acid

AXAD-16 resin beads were purified by washing with 2 M HCl followed by 2 M 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 prior to usage. From this, 5 g of AXAD-16 resin beads were refluxed with 20 cm^3 of phosphorus trichloride in the presence of anhydrous aluminium chloride for 3 h, followed by hydrolysis to the corresponding phosphonic acid resin. The hydroxyl

group of the phosphonic acid resin was protected with chlorotrimethylsilane and was further reacted with 3,4-dihydroxy phenacylchloride in the presence of triethylamine. The resulting modified resin beads were deprotected, 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.

2.4. Adopted metal extractive methods

2.4.1. Batch 'static' method

The static experiments are performed to optimize the conditions for the experimental parameters like the influence of sample acidity/pH, extraction kinetics, diverse ion tolerance, etc., for quantitative analyte extraction. For this study, a known amount of the resin was equilibrated with a known analyte concentration for definite time duration, using a mechanical shaker at 200 rpm. The sorbed metal ions were desorbed using 15 cm^3 of suitable eluant as shown in Table 1 and the desorbed metal ions were estimated spectrophotometrically using Arsenazo-III and Thoron as chromogen for U(VI) and Th(IV), respectively.

2.5. Column 'dynamic' method

In this method, an extraction chromatographic glass column was packed uniformly with 1 g of preconditioned resin beads by slurry method and was connected to the sample reservoir by means of a peristaltic pump to ensure uniform flow rates. The resin bed was washed with water prior to passage of sample solution. 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

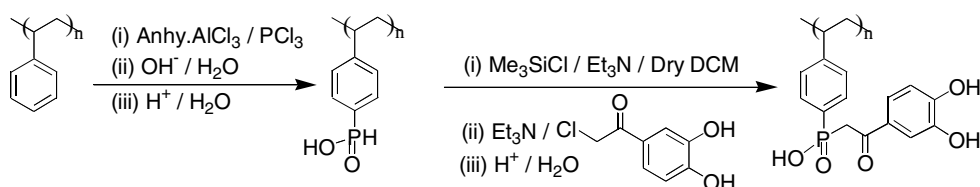


Fig. 1. Synthetic scheme.

Table 1
Optimum experimental parameters for quantitative extraction and desorption

Experimental parameters	U(VI)	Th(IV)
pH range	6.0–6.5	3.0–4.0
$t_{1/2}$ (min)	2.1	2.0
Metal sorption capacity (mmol g ⁻¹)		
(i) At optimum pH	1.660	1.509
(ii) At 2 M HNO ₃	0.630	0.690
(iii) At 2 M HCl	0.546	0.431
Eluting agent	1 M (NH ₄) ₂ CO ₃	1 M (NH ₄) ₂ CO ₃ and 6 M HCl
Maximum flow rate achieved (cm ³ min ⁻¹)	24	24
Average % recovery	99.9	99.8
Lower limit of detection (ng cm ⁻³)	10	10
Sample breakthrough volume (cm ³)	5000	5000
Enrichment factor (2 M HNO ₃)	333	333

state fluorimetric method using 1 M phosphoric acid at 515 nm as emission wavelength and 266 nm as excitation wavelength [39]. The optimum experimental parameters for column operation to ensure quantitative metal ion retention and elution are listed in Table 1.

3. Results and discussion

3.1. Characterization of the chelating ion-exchange resin

The *FT-IR spectroscopic technique* was used to confirm the presence of desired functionality in the resin matrix during each stage of chemical modification. The phosphonic acid resin showed spectral bands at 2317.3, 1044.5, 1157.5 and 3435.5 cm⁻¹ corresponding P–H, P–OH, P=O and O–H groups, respectively. The subsequent disappearance of P–H band followed by the appearance of spectral band at 1690.5 cm⁻¹ was assigned to the C=O group thus confirming the desired functionalization of the polymeric matrix. The involvement of metal ion chelation to the active site for both the analytes was confirmed by the red shift (15–20 cm⁻¹) observed for the P=O and C=O stretching frequencies and also by Far-IR studies which showed spectral bands in the region of 220–190 cm⁻¹.

CHNPS elemental analysis was performed during each stage of functionalization to check the extent of ligand functionalization. The experimental

data for the final stage was found to be C 60.51%, H 4.56%, P 9.59% which was in close agreement with the corresponding theoretical values C 60.41%, H 4.78%, P 9.71%. Thus, the elemental analysis reflects the incorporation of at least one ligand moiety per repeat unit giving a ligand capacity of 4.75 mmol g⁻¹ of the resin.

For the water regaining capacity studies, a known amount of the derivatized polymer was equilibrated with water and was filtered, air dried and subjected to *TGA analysis*. A weight loss of 8.2% up to 110 °C was observed, which was ascertained to the percolated water molecules in the polymer pores. Similar studies performed with non-functionalized AXAD-16 matrix gave a value of only 1.1% showing the enhanced hydrophilic character of the resin matrix after chemical modification.

3.2. Static equilibration studies

3.2.1. Influence of sample acidity on metal ion extraction

The metal extracting ability of the resin matrix in acidic samples was studied using varying concentrations of nitric and hydrochloric acid. For this study, 50 mg of the resin beads were equilibrated individually with metal ion solution (40 cm³, 10 µg cm⁻³) for 1 h. The aqueous phase metal ion concentration was analyzed and the corresponding distribution ratios were calculated using the following expression,

$$D(\text{cm}^3 \text{g}^{-1}) = (A_o - A_f)V/A_fW,$$

where A_o and A_f are the metal ion concentration before and after equilibration, V refers to the overall volume (cm^3) and W is the dry weight of the resin matrix (g). From Fig. 2, it is evident that good distribution ratio (D) in the order of 10^3 could be achieved for both U(VI) and Th(IV) in nitric acid medium. It was found that under very low acidities, both chelation and cation exchange mechanism operates, which is confirmed by the enhanced metal ion extraction. But with increasing acidity, a slight negative dependency was observed due to the passiveness of ion-exchange mechanism and also by the formation of metal anionic complexes. In the case of HCl medium, the extraction efficiency for all the analytes showed largely a negative dependency due to stable metal anionic chloro complexes formed in the aqueous phase.

3.2.2. Maximum metal sorption capacity under sample acidity/pH

The maximum metal sorption capacities of the developed resin matrix was studied by equilibrating 20 mg of the resin with a solution of excess metal ion concentration (100 cm^3 , $100 \mu\text{g cm}^{-3}$) under wide pH range (1–6.5) and also at 2 M acidity for 6 h. The resin showed a good extracting ability under wide pH conditions, where the maximum capacity for U(VI) and Th(IV) were found to be at pH 6.5 and

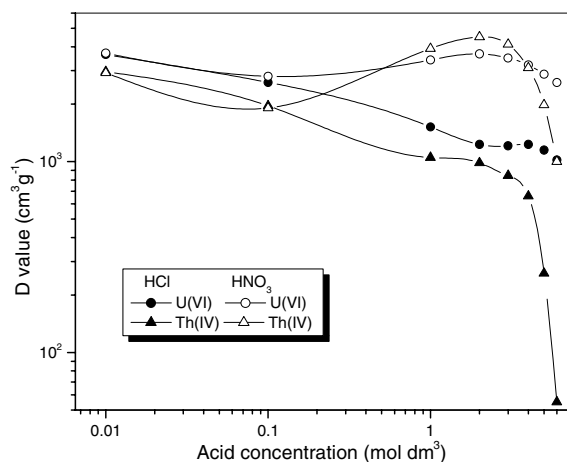


Fig. 2. Effect of sample acidity on metal ion extraction.

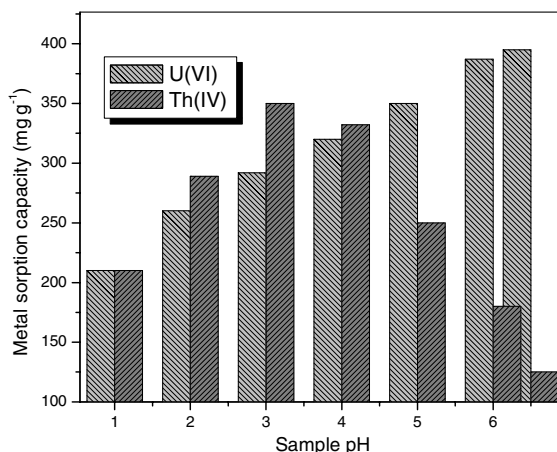


Fig. 3. Resin capacity as a function of sample pH.

3, respectively, as shown in Fig. 3. The resin also showed superior sorption capacities even under 2 M acid conditions (as shown in Table 1) when compared with other chelating resins reported earlier [16–21].

3.2.3. Elution studies

The optimum eluant for quantitative metal ion recovery were studied by equilibrating 50 mg of the resin beads with metal ion solution (40 cm^3 , $10 \mu\text{g cm}^{-3}$) in both 2 M HNO_3 and optimum solution pH. Quantitative desorption of the sorbed metal ions was tested using various eluting agents

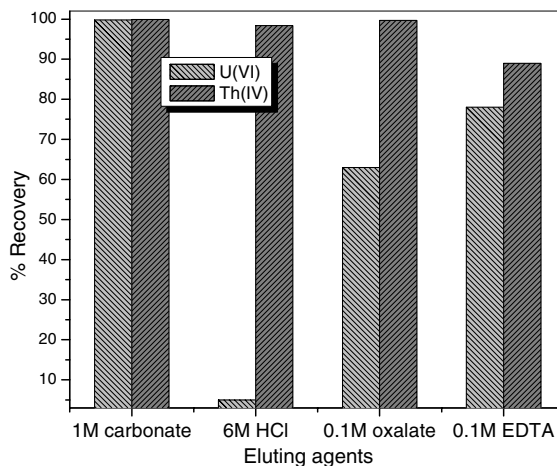


Fig. 4. Optimum eluants for quantitative recovery.

as shown in Fig. 4. A recovery value of >99.8% was obtained using 1 M $(\text{NH}_4)_2\text{CO}_3$ for both the analytes, but with 15 cm^3 of 6 M HCl, 99% elution was obtained only for Th(IV) which was concordant with its smaller D value at 6 M HCl, as shown in Fig. 2, resulting in the sequential separation of Th(IV) and U(VI).

3.2.4. Extraction kinetics

The rate of metal ion extraction by the resin matrix was studied by equilibrating 50 mg of resin beads using a series of metal ion solutions (40 cm^3 , $10 \mu\text{g cm}^{-3}$) in 2 M HNO_3 for varying time durations. The kinetic data were plotted in terms of $(1-F)$ versus shaking time as shown in Fig. 5. The fractional attainment of equilibrium (F) is defined as

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

where $[M^R]_t / [M^R]_{\text{eq}}$ are the ratios of metal ion concentration in the resin phase at time ' t ' to that at equilibrium [40]. It is evident from the graph that near complete extraction was attained within 5 min, due to the enhanced hydrophilic character of the resin phase by the incorporated $-\text{OH}$ groups, which favors better phase equilibration.

3.2.5. Effect of electrolytes on metal ion extraction

As NaNO_3 and NaCl are the major components in nuclear spent fuels, a study to ensure a good tol-

erance for these electrolytes for quantitative metal extraction becomes essential. For this study, 50 mg of the resin was shaken with metal ion solution (40 cm^3 , $10 \mu\text{g cm}^{-3}$) with increasing salt concentration in 2 M corresponding acids for 1 h. From Fig. 6, it is evident that a slight negative trend on increasing NaCl concentration was observed for both the analytes. But in the case of NaNO_3 , a slight positive trend was observed for both U(VI) and Th(IV).

3.2.6. Effect of various diverse ion species

The tolerance limit of the developed resin matrix towards matrix components and its ability to quantitatively extract analytes of interest in their presence was studied by equilibrating 50 mg of the resin with (40 cm^3 , $1.25 \mu\text{g cm}^{-3}$) analyte solution in the presence of varying quantities of individual matrix components. In acidic media, the resin showed exclusive selectivity for analytes of interest, exhibiting 0% extraction for transition and more common metal ions. However, lanthanides were found to compete for the active sites whose limits of tolerance (diverse ion concentration up to which 100% analyte extraction is observed) are shown in Table 2. Similar studies were also performed under pH conditions, for interfering electrolyte species and more common metal ions, and the obtained results are depicted

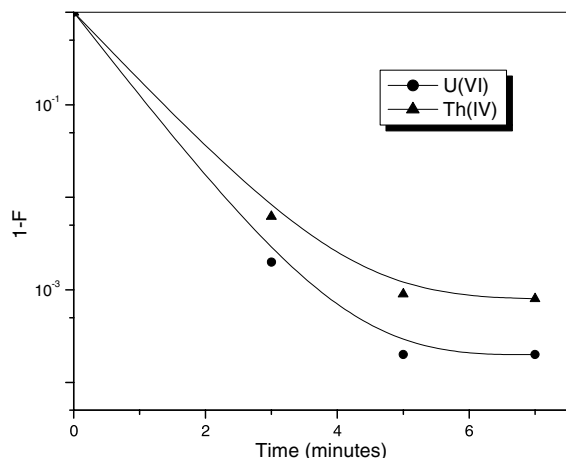


Fig. 5. Extraction kinetics in 2 M HNO_3 .

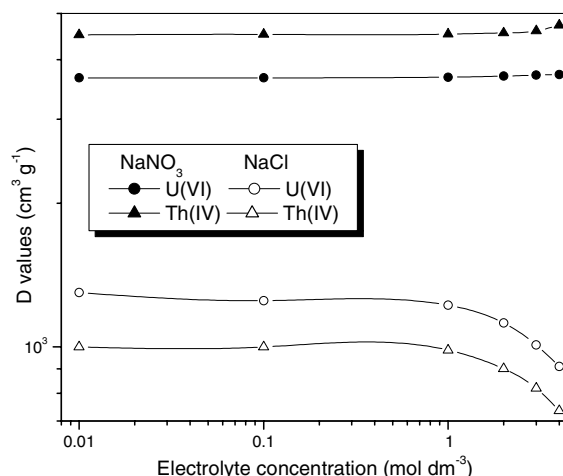


Fig. 6. Effect of salt concentration in corresponding 2 M acidity.

Table 2

Tolerance limits of metal ions present in reprocessing spent fuel sample (2 M HNO₃)

Metal ions ^a	Tolerance limits for interfering metal ions (g)							
	Zr(IV)	Fe(III)	La(III)	Ce(IV)	Nd(III)	Gd(III)	Mo(VI)	Eu(III)
U(VI)	0.035	0.045	0.006	0.031	0.022	0.017	0.026	0.019
Th(IV)	0.031	0.048	0.006	0.029	0.024	0.018	0.023	0.019

Resin quantity – 50 mg, sample volume – 40 cm³.^a Amount of U(VI), Th(IV) – 50 µg (rsd <3.8% for triplicate measurements).

in Table 3. From the data obtained from Tables 2 and 3, it is possible to infer the resin's applicability towards trace metal analysis from both high saline matrices as well as acidic low level reprocessing samples.

3.3. Dynamic studies using extraction chromatographic column

3.3.1. Effect of sample and eluant flow rate

The effect of sample flow rate was studied by passing metal ion solutions (2000 cm³, 0.5 µg cm⁻³) in 2 M HNO₃ under varying flow rates from 10–30 cm³ min⁻¹ through the extraction column, using a peristaltic pump. It was found that even at a flow rate of 24 cm³ min⁻¹ quantitative metal ion sorption was observed (Table 1), reflecting the greater chelating site accessibility and faster phase equilibration by the analytes. The sorbed metal ions were desorbed using 15 cm³ of optimum eluant at a flow rate of 1 cm³ min⁻¹. The most significant fact to be noted is that such

high sample flow rates were never reported in the literature [13–21] using other chelating sorbents.

3.3.2. Sample breakthrough volume

The preconcentrating ability of the polymeric matrix was studied in terms of sample breakthrough volume by passing varying volumes ranging from 0.5 to 6 dm³ of 30 µg dm⁻³ as influent concentration (C₀) in 2 M HNO₃ at a flow rate of 20 cm³ min⁻¹. The sorbed metal ions were desorbed and estimated. The effluent concentration (C) is C₀–C_E where, C_E is eluant concentration. The eluted metal ions are analyzed using Arsenazo III and Thoron, as post-column reagents. It is evident from Fig. 7, that a good enrichment factor value of 333 was achieved for both the analytes.

3.3.3. Limit of quantification

The lower limit of quantitative analyte extraction was performed by passing 1 dm³ of analyte solutions spiked with 5–50 µg of individual analytes in 2 M HNO₃ medium through the

Table 3

Tolerance limits of diverse ions and electrolytes in optimum pH conditions

Metal ions ^a	Tolerance limits for electrolytes (g)									
	NaCl	KNO ₃	Na ₂ SO ₄	Na ₃ PO ₄	NaF	CH ₃ COO ⁻	Ca ²⁺	Mg ²⁺		
U(VI)	2.00	1.95	0.56	0.15	0.29	0.09	1.51	1.75		
Th(IV)	2.15	2.15	0.61	0.16	0.23	0.20	1.02	1.52		
Metal ions ^a	Tolerance limits for interfering metal ions (mg)									
	Mn(II)	Co(II)	Cu(II)	Fe(III)	Ni(II)	Zn(II)	Pb(II)	Cd(II)	Zr(IV)	Bi(III)
U(VI)	3.8	3.2	3.6	2.6	3.4	4.6	5.9	5.6	0.8	10.1
Th(IV)	3.1	3.1	3.0	2.5	3.1	5.2	3.1	4.3	0.2	11.6

Resin quantity – 50 mg, sample volume – 40 cm³.^a Amount of U(VI), Th(IV) – 50 µg (rsd <3.5% for triplicate measurements).

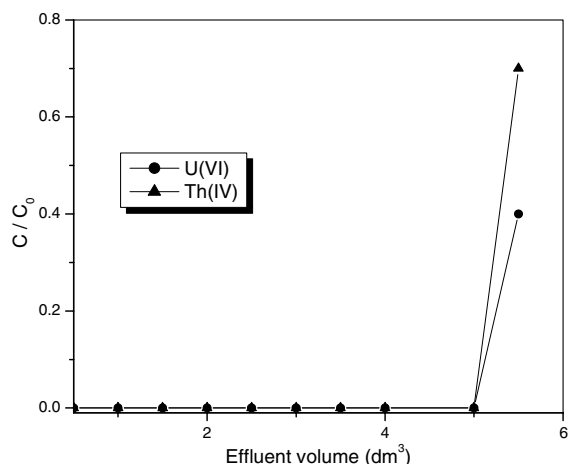


Fig. 7. Sample breakthrough volume curve.

preconditioned resin bed. The sorbed metal ions were desorbed and estimated. The lower limits of extraction are shown in Table 1 which indicates the resin's sensitivity in targeting even ppb level trace analytes.

4. Applications

4.1. Synthetic mixtures of nuclear reprocessing streams

To ascertain the practical applicability of the resin matrix in reprocessing units, 5 dm³ of the synthetic mixtures mimicking typically nuclear spent fuel composition [39] spiked with 1000 µg of both U(VI) and Th(IV) was passed through the chromatographic column. The sorbed analytes were sequentially eluted with optimum eluants and ana-

lyzed. A quantitative preconcentration of the studied analytes was observed with an rsd value of <3.9% for triplicate measurements.

4.2. Synthetic seawater

5 dm³ synthetic seawater sample spiked with 50 µg U(VI) was prepared as per standard literature procedure [41]. The synthetic mixture was passed through the preconditioned resin bed at a flow rate of 20 cm³ min⁻¹ and the sorbed metal ions were eluted and estimated spectrofluorimetrically which showed a satisfactory recovery with an rsd value of 3.1% for U(VI), on triplicate measurements.

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

5 dm³ of the seawater and well water samples were filtered to remove the particulate matters using membrane filter (0.45 µm) and was passed through the preconditioned resin bed. The sorbed U(VI) was desorbed and analyzed using spectrofluorimetric procedure. The reliability of analysis was cross-checked by performing standard addition technique using 20 µg of U(VI) which was spiked to the sample solution and the results obtained are shown in Table 4.

4.4. Thorium extraction from monazite sand

0.1 g of monazite sand sample (Travancore, India) was digested with conc. H₂SO₄ at 250 °C for 4 h. The precipitate was filtered and redissolved in minimal volumes of dil. HNO₃ and passed through the resin bed for preconcentra-

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

Water sample	Source of the sample/year of sampling	Method	Conc. of U(VI) (ng cm ⁻³)	rsd (%) ^a
Seawater – 1	Chennai, India/August 2003	Direct	5.53 ± 0.43	3.2
		SA	5.51 ± 0.48	3.5
Seawater – 2	Mahabalipuram, India/August 2003	Direct	5.87 ± 0.47	3.2
		SA	5.91 ± 0.55	3.8
Well water – 1	Adyar, Chennai, India/September 2003	Direct	5.59 ± 0.49	3.5
		SA	5.60 ± 0.47	3.4
Well water – 2	Guindy, Chennai, India/September 2003	Direct	4.58 ± 0.44	3.9
		SA	4.61 ± 0.43	3.8

tion. After desorption, the amount of thorium extracted was estimated spectrophotometrically, which was found to be 80.02 mg g^{-1} . The data were further confirmed by standard addition method, the values were within 3.8% *rsd*, for triplicate measurements.

5. Conclusions

The developed chelating ion-exchange resin matrix showed exclusive selectivity in extracting U(VI) and Th(IV) from highly acidic waste streams and various environmental samples, thus proving its wide range of practical applications. The important features of the developed resin matrix are its superior metal sorption capacity with good enrichment factor values and enhanced extraction rates which are never reported in the literature. Moreover, the developed chelating ion-exchange resin is highly sensitive in trapping trace analytes down to *ppb* levels. The stationary phase is highly durable even in high acid concentrations with greater reusability and data reproducibility up to 30 cycles of continuous usage.

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