First example of diglycolamide-grafted resins: synthesis, characterization, and actinide uptake studies

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Prasanta K. Mohapatra,^{*a} Seraj A. Ansari,^a Mudassir Iqbal,^b Jurriaan Huskens^b and Willem Verboom^b

Two diglycolamide (DGA)-functionalized chelating extraction resins were prepared for the first time by grafting onto a silica matrix and were evaluated for their actinide ion uptake behavior. The resins with one and two DGA moieties, termed as resin-I and resin-II, were quite efficient for the actinide ions, particularly the tri- and the tetravalent ions in a way similar to the diglycolamide extractants. The hexavalent UO_2^{2+} ion was poorly sorbed onto the resins. The resins were characterized by thermal analysis, while the surface area and surface morphology were analyzed by BET and SEM techniques. Resin-II showed a pre-concentration factor of >100 for Am(III) by elution with 0.01 M EDTA.

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1. Introduction

Detection of actinide ions in environmental samples is usually preceded by their pre-concentration and selective separations. Environmental samples such as soil are digested and feed adjusted¹ prior to any such separation steps using specific extractants to separate actinides in the bulk from the other metal ions. Since the digestion occurs in acids, these separation steps involve dilute acidic feeds. Moreover, recovery of actinides from dilute radioactive waste samples is also a stringent requirement from the radioactive waste management point of view.² Therefore the development of efficient and selective separation methods for actinide ion recovery from acidic feeds becomes mandatory. Especially, when such feeds include trivalent actinides such as Am^{3+} and Cm^{3+} this task is quite challenging. Though TBP (tri-*n*-butyl phosphate) and D2EHPA (di-2-ethylhexylphosphoric acid) have been extensively used for the extraction of actinide ions such as UO_2^{2+} and Pu^{4+} from moderate and dilute acid solutions, respectively, they are rather ineffective for the extraction of trivalent actinides.³ Out of the extractants used for the extraction of trivalent actinide ions from acidic feeds, CMPO (carbamoylmethyl phosphine oxide), TRPO (tri-*n*-alkyl phosphine oxide), malonamides such as DMBTMDMA (*N,N,N',N'*-dimethyldibutyltetradecyl malonamide) and DMDOHEMA (*N,N,N',N'*-dimethyldioctylhexylethoxy malonamide), and diglycolamides such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) have been found to be far more efficient than TBP and D2EHPA.^{4–11}

Though solvent extraction-based separation methods have been used for actinide ion extraction in many radioactive waste remediation related activities, concern for the environment makes one imperative to explore other separation techniques, which are based on low inventory of volatile organic compounds (VOCs). Out of such techniques, solid phase extraction (SPE) has emerged as an excellent separation technique in view of a variety of factors such as low solvent inventory, easy phase sorption and elution, low physical degradation, minimum release of toxic organic solvents, and recycling options.^{12,13}

Solid phase extractants can be of the type where the extractant in a suitable solvent is impregnated in the pores of a solid support. These SPEs have the advantages of both solvent extraction and ion-exchange based separation methods and can effect selective separations in column mode operations. However, though the solvent inventory is low as compared to solvent extraction-based separation methods, repeated use may give rise to a significant loss of the impregnated organic extractant from the pores by leaching. This can be limited by chemically grafting the resin with suitable ligating groups. Actinide ion sorption studies using grafted solid phase extraction resins have been reported by several groups. Though TODGA is generally known to be the most efficient extractant for trivalent actinides, its use as extraction chromatographic resin material is limited.^{14,15} There are several reports by Kumagai *et al.*^{16–18} who have prepared TODGA-based resins bound to polymer-immobilized silica particles. To our knowledge, the use of diglycolamide (DGA)-grafted solid phase extractants is unprecedented.

Herein, we report the first time synthesis and characterization of two DGA-grafted resin materials (Fig. 1), in addition to actinide ion uptake studies under acidic feed conditions. A comparative evaluation of these grafted resin materials is made

^aRadiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India. E-mail: mpatra@barc.gov.in; Fax: +91-22-25505151

^bLaboratory of Molecular Nanofabrication, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Fig. 1 Structures of the DGA-functionalized resins.

with the analogous TODGA-impregnated extraction chromatographic resin material.

2. Experimental

2.1. Materials

All reagents used in the present studies were of AR grade. Suprapur HNO_3 (Merck) was used for preparing the aqueous feed solutions using Milli-Q water. Freshly obtained 2-thenoyl-trifluoroacetone (TTA, Fluka) was used along with HPLC grade xylene for preparing the Pu(IV) extracts (*vide infra*).

2.1.1. Synthesis of DGA-functionalized resins

General. All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Compounds **1** (ref. 19) and **2** (ref. 20) were prepared according to literature procedures. Solvents were dried according to standard procedures and stored over molecular sieves. ^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER (400 MHz) spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. All NMR measurements are recorded in CDCl_3 . Electrospray ionization (positive mode) mass spectra and high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminium). Column chromatography was carried out with Merck silica gel 60 (230–400 mesh).

Synthesis of ethyl *p*-DGA-benzoate (3**).** A mixture of *N,N'*-diocetyl diglycolamic acid (**1**) (5.50 g, 15.4 mmol), and ethyl 4-aminopropoxybenzoate (**2**) (3.43 g, 15.4 mmol), triethylamine (1.81 g, 18.0 mmol), DCC (3.30 g, 16.0 mmol), and HOBT (2.16 g, 16.0 mmol) in chloroform (200 mL) was stirred for 2 days at room temperature. The solvent was evaporated and the resulting solid dissolved in *n*-hexane (150 mL). After filtration the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2 , CH_2Cl_2 –MeOH = 98 : 2) to afford **3** (6.84 g, 79%) as an oil. ^1H NMR: δ

0.84–0.95 (6H, m, CH_3), 1.19–1.34 (20H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.40 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.46–1.59 (4H, m, NCH_2CH_2), 2.09 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.09, 3.30 (2H, t, $J = 7.5$ Hz, NCH_2), 3.53 (2H, q, $J = 6.4$ Hz, NHCH_2), 4.12 (2H, t, $J = 6.4$ Hz, OCH_2), 4.10, 4.25 (2H, s, OCH_2), 4.36 (2H, q, $J = 7.2$ Hz, $\text{C}(\text{O})\text{OCH}_2$), 6.93, 7.99 (2H, d, $J = 8.8$ Hz, ArH), 8.05–8.15 (1H, m, NH). ^{13}C NMR: δ 14.2, 20.7, 22.6, 26.8, 27.5, 28.2, 28.8, 29.1, 31.8, 36.2, 46.3, 46.9, 60.4, 65.8, 69.5, 71.7, 113.7, 122.1, 132.1, 163.13, 168.5, 170.4, 175.6. HRMS: calculated 563.7889 for $\text{C}_{32}\text{H}_{55}\text{N}_2\text{O}_6$; found: 563.7823, $[\text{M} + \text{H}]^+$.

Synthesis of *p*-DGA-benzoic acid (4**).** To a solution of ester **3** (5.00 g, 8.9 mmol) in a mixture of THF–methanol = 6 : 1 (70 mL) was slowly added NaOH (0.42 g, 10.6 mmol) at 0 °C. The mixture was allowed to come to room temperature and was stirred overnight. The solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed successively with 20% HCl solution (5×50 mL). The organic layer was concentrated under reduced pressure to give the *p*-DGA-benzoic acid (**4**) in quantitative yield. ^1H NMR: δ 0.84–0.96 (6H, m, CH_3), 1.21–1.38 (20H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.45–1.62 (4H, m, NCH_2CH_2), 2.10 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.09, 3.31 (2H, t, $J = 7.5$ Hz, NCH_2), 3.54 (2H, q, $J = 6.4$ Hz, NHCH_2), 4.11 (2H, t, $J = 6.4$ Hz, OCH_2), 4.12, 4.27 (2H, s, OCH_2), 6.93, 8.01 (2H, d, $J = 8.8$ Hz, ArH), 8.11–8.19 (1H, m, NH). ^{13}C NMR: δ 14.2, 20.7, 22.6, 26.8, 27.5, 28.8, 29.1, 31.8, 36.2, 46.3, 46.9, 60.4, 65.8, 69.5, 71.7, 113.7, 122.1, 132.1, 163.13, 168.5, 170.4, 175.6. HRMS: calculated 535.3747 for $\text{C}_{30}\text{H}_{51}\text{N}_2\text{O}_6$; found: 535.3769, $[\text{M} + \text{H}]^+$.

Synthesis of *p*-DGA-benzoyl chloride (5**).** To a solution of *p*-DGA benzoic acid (**4**) (2.00 g, 3.7 mmol) in dichloromethane (50 mL) was added a solution of oxalyl chloride (0.51 g, 4.0 mmol) in dichloromethane (20 mL) and a few drops of DMF as a catalyst. The resulting solution was refluxed overnight. The solvent was evaporated under reduced pressure to give *p*-DGA-benzoyl chloride (**5**) as an oil, which was directly used in the next step. ^1H NMR: δ 0.81–0.96 (6H, m, CH_3), 1.16–1.39 (20H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.45–1.62 (4H, m, NCH_2CH_2), 2.13 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.09, 3.30 (2H, t, $J = 7.5$ Hz, NCH_2), 3.55 (2H, q, $J = 6.4$ Hz, NHCH_2), 4.17 (2H, t, $J = 6.4$ Hz, OCH_2), 4.17, 4.28 (2H, s, OCH_2), 7.00, 8.08 (2H, d, $J = 8.8$ Hz, ArH), 8.11–8.19 (1H, m, NH).

Synthesis of resin-I. To a suspension of amino-functionalized silica particles (**6**) (degree of functionalization = 0.07 mmol g^{-1}) (1.5 g) in dichloromethane (50 mL) containing triethylamine was added *p*-DGA-benzoyl chloride (**5**) (1.61 g) in dichloromethane (15 mL) at 0 °C. The reaction mixture was brought to room temperature and stirring was continued for 5 days. The reaction mixture was filtered, washed with dichloromethane, and the residue was dried under vacuum pump to get the DGA-functionalized silica particles (resin-I).

Synthesis of ethyl 3,5-bis(phthalimidopropoxy)benzoate (9**).** A mixture of commercially available ethyl 3,5-dihydroxybenzoate (**7**) (2.50 g, 13.7 mmol), *N*-(3-bromopropyl)phthalimide (**8**) (7.35 g, 27.4 mmol), K_2CO_3 (3.5 g, 25.3 mmol), and KI (2.00 g) in acetonitrile (100 mL) was refluxed overnight. The acetonitrile was evaporated and the residue was dissolved in dichloromethane (100 mL). The resulting solution was washed with dil.

HCl (3×50 mL) and water (2×100 mL). The organic layer was dried over anhydrous MgSO_4 and concentrated under reduced pressure and the residue was recrystallized with methanol to afford pure product (**9**) (4.65 g, 61%) as a white solid. M.p. 107–109 °C. Elem. anal. calculated: C, 66.90; H, 5.07; N, 5.03, found: C, 66.83; H, 5.22; N, 4.69%. ^1H NMR: δ 1.36 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 2.17 (4H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.90 (4H, t, $J = 6.4$ Hz, NCH_2), 4.00 (4H, t, $J = 6.4$ Hz, NCH_2), 4.32 (4H, q, $J = 7.2$ Hz, $\text{C}(\text{O})\text{OCH}_2$), 6.39 (1H, s, ArH), 7.05 (2H, s, ArH), 7.69–7.75 (4H, m, ArH, phthalimide), 7.80–7.95 (4H, m, ArH, phthalimide). ^{13}C NMR: δ 14.2, 28.2, 35.4, 60.9, 65.9, 106.0, 107.7, 123.3, 132.0, 133.9, 159.6, 166.2, 168.3.

Synthesis of ethyl 3,5-bis(aminopropoxy)benzoate (10). Hydrazine hydrate (10 mL, 200 mmol) was added to a suspension of ester **9** (2.00 g, 3.6 mmol) in a 6 : 3 mixture of ethanol–dichloromethane (90 mL). The mixture was refluxed for 12 h, cooled and then diluted with water (100 mL). The precipitate formed was filtered and subsequently extracted with dichloromethane (4×50 mL). The organic layer was then dried (MgSO_4) and the solvent evaporated to give **10** as an oil in quantitative yield. ^1H NMR: δ 1.40 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.95 (2H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 2.93 (2H, t, $J = 6.4$ Hz, NCH_2), 4.09 (2H, t, $J = 6.4$ Hz, NCH_2), 4.37 (2H, q, $J = 7.2$ Hz, $\text{C}(\text{O})\text{OCH}_2$), 6.66 (1H, s, ArH), 7.19 (2H, s, ArH). ^{13}C NMR: δ 14.2, 28.3, 35.4, 60.8, 65.9, 106.1, 107.7, 123.2, 159.6, 166.1. HRMS: calculated 297.1814 for $\text{C}_{15}\text{H}_{25}\text{N}_2\text{O}_4$; found: 297.1794, $[\text{M} + \text{H}]^+$.

Synthesis of ethyl 3,5-di-DGA-benzoate (11). It was prepared by a similar procedure as described for the synthesis of ester **3** starting from N,N' -dioctyldiglycolamic acid (**2**) (5.00 g, 13.9 mmol), diamine **10** (2.07 g, 7.0 mmol), triethylamine (1.51 g, 15.0 mmol), DCC (3.09 g, 15.0 mmol), and HOBT (2.02 g, 15.0 mmol) in chloroform (200 mL). The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2 –MeOH = 96 : 4) to get ester **11** (8.31 g, 61%) as an oil. ^1H NMR: δ 0.84–0.95 (12H, m, CH_3), 1.19–1.36 (40H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.40 (6H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.46–1.61 (8H, m, NCH_2CH_2), 2.07 (4H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.10, 3.30 (4H, t, $J = 7.5$ Hz, NCH_2), 3.52 (4H, q, $J = 6.4$ Hz, NHCH_2), 4.07 (4H, t, $J = 6.4$ Hz, OCH_2), 4.10, 4.27 (4H, s, OCH_2), 4.36 (4H, q, $J = 7.2$ Hz, $\text{C}(\text{O})\text{OCH}_2$), 6.67 (1H, s, ArH), 7.18 (2H, s, ArH), 8.00 (1H, br s, NH). ^{13}C NMR: δ 14.4, 22.7, 26.8, 27.5, 28.7, 29.3, 31.7, 36.4, 46.3, 46.9, 60.4, 66.0, 69.5, 71.7, 108.2, 131.7, 159.7, 168.4, 169.0, 170.0. HRMS: calculated 975.7361 for $\text{C}_{55}\text{H}_{99}\text{N}_4\text{O}_{10}$; found: 975.7415, $[\text{M} + \text{H}]^+$.

Synthesis of 3,5-di-DGA-benzoic acid (12). It was synthesized in a similar way as described for the synthesis of **4** in quantitative yield. ^1H NMR: δ 0.83–0.95 (12H, m, CH_3), 1.19–1.39 (40H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.44–1.63 (8H, m, NCH_2CH_2), 2.09 (4H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.10, 3.31 (2H, t, $J = 7.5$ Hz, NCH_2), 3.54 (2H, q, $J = 6.4$ Hz, NHCH_2), 4.04 (2H, t, $J = 6.4$ Hz, OCH_2), 4.12, 4.27 (4H, s, OCH_2), 6.65 (1H, s, ArH), 7.19 (2H, s, ArH), 8.05–8.14 (1H, m, NH). 14.4, 22.7, 26.8, 27.5, 28.2, 28.7, 29.3, 31.7, 36.4, 46.3, 46.9, 60.4, 66.0, 69.5, 71.7, 108.2, 131.7, 159.7, 168.4, 169.0, 170.0. HRMS: calculated 947.7048 for $\text{C}_{53}\text{H}_{95}\text{N}_4\text{O}_{10}$; found: 947.7125, $[\text{M} + \text{H}]^+$.

3,5-Di-DGA-benzoyl chloride (13). It was synthesized in the same way as described for the preparation of **5** in quantitative yield and was directly used. ^1H NMR: δ 0.83–0.95 (12H, m, CH_3),

1.19–1.38 (40H, m, $\text{CH}_3(\text{CH}_2)_5$), 1.46–1.61 (8H, m, NCH_2CH_2), 2.09 (4H, pentet, $J = 6.4$ Hz, OCH_2CH_2), 3.10, 3.31 (2H, t, $J = 7.5$ Hz, NCH_2), 3.54 (2H, q, $J = 6.4$ Hz, NHCH_2), 4.09 (2H, t, $J = 6.4$ Hz, OCH_2), 4.18, 4.30 (4H, s, OCH_2), 6.79 (1H, s, ArH), 7.23 (2H, s, ArH), 8.41–8.55 (1H, m, NH).

Synthesis of resin-II. Resin-II was prepared in an analogous way as described for resin-I starting from 3,5-di-DGA-benzoyl chloride (**13**) and amino-terminated silica particles (**6**).

2.1.2. Radiotracers. The actinide radiotracers were taken from laboratory stock solutions and were used after purification from the daughter products. On the other hand, $^{152,154}\text{Eu}$, ^{137}Cs , and $^{85,89}\text{Sr}$ were obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai. ^{241}Am was purified by the procedure given elsewhere.²¹ ^{233}U tracer was purified from its daughter products by an anion exchange method described elsewhere²² and its purity was confirmed by α -spectrometry. Pu (principally ^{239}Pu) was purified from ^{241}Am by an anion exchange method from 7 M HNO_3 feeds and its radiochemical purity was ascertained by gamma-ray spectrometry for the absence of ^{241}Am .²¹

The conversion of Pu to its +4 oxidation state was carried out using a standard procedure using drop wise addition of a sodium nitrite solution (0.05 M) into a solution of Pu in 1 M HNO_3 followed by the extraction of Pu^{4+} by 0.5 M TTA in xylene. The extracted Pu^{4+} was subsequently stripped with 8 M HNO_3 , which was then used as stock for Pu^{4+} . Further, during the studies, the plutonium valency in the aqueous phase was adjusted and maintained in the tetravalent state by the addition of 1×10^{-3} M NH_4VO_3 as the holding oxidant.

Assaying of ^{241}Am , ^{137}Cs , $^{85,89}\text{Sr}$, and $^{152,154}\text{Eu}$ was done by gamma counting using a NaI(Tl) scintillation counter (Para Electronics, India) interfaced to a multi-channel analyzer (ECIL, India), while nuclides such as ^{239}Pu and ^{233}U were assayed by a liquid scintillation counting system (Hidex, Finland) using an Ultima Gold scintillator cocktail (Sisco Research Laboratory, Mumbai).

2.2. Methods

2.2.1. Instrumental methods. The SEM pictures of the resin beads were obtained using a Stereoscan 100 Cambridge model operating at 15/25 kV with a magnification of $500\times$ at a working distance of 15 mm at a tilt angle of 45° . Since the resin materials are non-conducting, a 15 nm coating of gold was given to the samples using a Balzer's coating unit model CEA 30. Thermogravimetric analyses were performed using a Netzsch Thermobalance (Model: STA 409 PC Luxx), at a heating rate of $10^\circ\text{C min}^{-1}$, in air. Surface area analysis of the resins was carried out using equipment supplied by Thermo Scientific.

2.2.2. Distribution studies. The sorption of metal ions onto the resin materials was determined by equilibrating a known volume of an aqueous solution (usually, 1 mL) containing the required radiotracer at a given acidity with a known quantity of resin (~ 20 –50 mg) in leak tight Pyrex glass tubes. The tubes were agitated in a thermostated water bath maintained at $25 \pm 0.1^\circ\text{C}$ for 1 h, which was optimized from the sorption kinetics studies (*vide infra*). Subsequently, the tubes were centrifuged to

clearly settle the resin materials and suitable aliquots (usually 100 μL) of the aqueous phase were removed for the assaying of the metal ions as mentioned above. The distribution coefficients (K_d) were calculated from the counts in the aqueous phase prior to the uptake by the resin material (C_o) and those obtained after equilibration (C_{eq}) as per the following formula:

$$K_d = [(C_o - C_{eq})/C]V/W \text{ (mL g}^{-1}\text{)} \quad (1)$$

where V is the volume of the aqueous phase used (mL), and W is the weight of the resin material employed (g). All experiments were carried out in duplicate and the reproducibility of the results was within $\pm 5\%$.

3. Results and discussion

3.1. Synthesis of the resins

Resins-I and -II were prepared as summarized in Schemes 1 and 2, respectively. *N,N'*-Dioctyldiglycolamic acid (**1**) and ethyl 4-aminopropoxybenzoate (**2**) were reacted under peptide coupling conditions to give ethyl *p*-DGA-benzoate **3** in 79% yield. Subsequent hydrolysis of the ester moiety in **3** afforded the corresponding *p*-DGA-benzoic acid (**4**) in quantitative yield, which was reacted with oxalyl chloride to give *p*-DGA-benzoyl chloride (**5**). A suspension of amino-functionalized silica particles (**6**) in dichloromethane was reacted with acid chloride **5** to give resin-I.

Ethyl dihydroxybenzoate (**7**) was dialkylated with two equiv. of *N*-(3-bromopropyl)phthalimide (**8**) in the presence of potassium iodide and potassium carbonate as a base to give ethyl 3,5-bis(phthalimidopropoxy)benzoate (**9**) in 61% yield. Subsequent treatment with hydrazine afforded ethyl 3,5-bis(aminopropoxy)benzoate (**10**) in quantitative yield. In a similar way as described above resin-II was prepared.

3.2. Characterization of the resins

Some of the physical parameters of the resins are listed in Table 1. In the IR spectra the resins-I and -II showed broad absorption

bands at 1650–1600 cm^{-1} corresponding to the amide C=O groups. Solid state ^{13}C NMR spectroscopy showed peaks at 11.8, 23.0, 24.7, 29.3, 31.6, 34.1, and 44.9 ppm for resin-I and at 11.73, 23.1, 24.81, 29.4, 31.7, 34.0, 45.0, 49.5, and 99.9 for resin-II, clearly indicating the functionalization of the silica particles. The resins were characterized by various methods such as thermal analysis (TG-DTA), surface area by BET, and surface morphology by SEM. The thermal analysis data are presented in Fig. 2 which show about 34% and 58% weight loss with the resins-I and -II, respectively, which closely correspond to the DGA groups appended onto the silica particles. The average particle size of the grafted resins was determined by SEM as 80 and 70 microns for resins-I and -II, respectively. The SEM micrographs of the resins at 200 $\times$ and 1000 $\times$ magnifications are shown in Fig. 3. The resin particles were nearly spherical in most cases, which results in a very high surface area. BET analysis gave 180 and 429 $\text{m}^2 \text{g}^{-1}$ as the surface areas of the resins-I and -II, respectively. Further magnification to 10 000 $\times$ (Fig. 3) indicated a layered surface morphology of the resins, which was more prominent in case of resin-II.

3.3. Sorption of Am(III) from HNO_3 solutions

High level radioactive waste contains about 3 M HNO_3 apart from various actinides, fission product elements and structural elements. In view of this, the Am(III) uptake behavior of the resin materials was investigated from a 3 M HNO_3 solution. Distribution coefficients of 1850 and 3050 were obtained for resin-I and resin-II, respectively, from triplicate measurements. The metal ion sorption kinetics was monitored in terms of fractional attainment of the equilibrium expressed as follows:

$$F = [\text{M}^{\text{R}}]_t / [\text{M}^{\text{R}}]_{\text{eq}} \quad (2)$$

where $[\text{M}^{\text{R}}]_t$ and $[\text{M}^{\text{R}}]_{\text{eq}}$ are the metal ion concentrations in the solid phase at time ' t ' and at equilibrium, respectively. Fig. 4 shows the sorption kinetics data of Am(III) on the grafted resins. The sorption of Am(III) onto resin-I was slow and the plateau

Scheme 1 Synthesis of resin-I.

Scheme 2 Synthesis of resin-II.

values were approached after 20 minutes of equilibration, however, in case of resin-II, equilibrium was reached in 10 minutes.

The diglycolamide extractants TODGA and T2EHDGA are reported to extract metal ions by a solvation mechanism, commonly observed with neutral donor extractants.²³ It has a

Table 1 Resin parameters for pre-concentration of Am(III)

Parameter	Resin-I	Resin-II
Resin type	Silica particles appended with one DGA moiety	Silica particles appended with two DGA moieties
Particle size (μm)	70 ± 20	80 ± 20
Surface area ($\text{m}^2 \text{g}^{-1}$)	180	429
Density (g mL^{-1})	0.982	0.973
Color	Pale yellow	Pale yellow
Affinity for water or acid solution	Good	Good
Column characteristics		
Bed volume	—	0.82 cm^3
Bed density	—	0.49 g cm^{-3}
Flow rate	—	4 drops per min
Feed solution	—	3 M HNO_3
Eluent	—	0.01 M EDTA

Fig. 2 Thermogravimetric analysis of the DGA-grafted resins.

Fig. 3 SEM micrographs of the DGA-functionalized resins.

Fig. 4 Fractional sorption of Am(III) with time on the DGA-grafted resins; aqueous phase: 3 M HNO_3 ; temperature: 25 °C.

signature of increased metal ion extraction with increasing nitric acid concentration up to a certain acidity beyond which a plateau is observed.^{9,10} A similar trend was also seen in solid phase extraction studies involving extraction chromatographic resin materials containing diglycolamide extractants as the stationary phase.¹⁵ On the other hand, studies on the effect of the HNO_3 concentration on the sorption of Am(III) by the DGA-grafted resins-I and -II (Fig. 5) showed a rather unusual behavior of an increase in the uptake of the metal ion with increasing acidity up to 6 M HNO_3 . Horwitz *et al.*¹⁴ have observed a similar trend with both TODGA-as well as T2EHDGA-based extraction chromatographic resin materials. At any given acidity, the distribution coefficient of Am(III) by resin-II was higher than

Fig. 5 Distribution coefficients of Am(III) as a function of the HNO_3 concentration by the DGA-grafted resins; temperature: 25 °C.

that of resin-I. This feature can be ascribed to the higher diglycolamide density present at resin-II.

The batch uptake capacity of the resins was determined by equilibrating about 100 mg of the resin materials with a feed solution containing about 100 mg L^{-1} Eu(III) in 3 M HNO_3 at 25 ± 0.1 °C for 24 h to give values of 11 and 14 mg g^{-1} for resins-I and -II, respectively. Though TODGA-impregnated extraction chromatographic resin material has higher metal ion uptake efficiency in terms of larger K_d values (*vide infra*), the capacity was reported to be lower, namely 10 mg g^{-1} .¹⁵

3.4. Uptake of other actinide and fission product ions

Radioactive wastes usually contain a host of actinide and fission product ions the most important of those being Am(III), U(VI), Pu(IV), Sr(II), and Cs(I). In addition, some of the rare earth elements are also likely to be present.²⁻⁵ In the present study,

the uptake behavior of these metal ions along with Eu(III) (representative of the rare earth elements) was studied from 3 M HNO₃. The metal ion uptake data show the following trend for resin-I: Eu(III) > Pu(IV) ≥ Am(III) ≫ U(VI) > Cs(I) > Sr(II). The K_d values with resin-II are about 1.5–2 times larger, except for Cs(I), which is expected on the basis of their ligating group density. The K_d values for Eu(III) were compared with those reported in previous studies. Extraction chromatographic materials made by Anasari *et al.*¹⁵ and Horwitz *et al.*¹⁴ exhibited a significantly higher uptake of Eu(III) from 3 M HNO₃ with K_d values in the range of $\sim 10^4$ as compared to values of 2705 and 5650 obtained with resins-I and -II, respectively. This could be ascribed to several factors which include, higher ligand loading in the extraction chromatographic resins, reported earlier, favourable diffusion coefficient values with the extraction chromatographic resins due to the presence of a liquid phase rather than the entirely solid phase in the present resins which would have lower diffusion coefficients. Zhang *et al.* reported a K_d value for La(III) of ~ 1000 , while Nd(III) yielded K_d values in the excess of $>10^4$ using a feed consisting of 0.1 M HNO₃ and 3 M nitrate and 0.05 M DTPA, which, however, operates in an entirely different mechanism.²⁴

The selectivity coefficients, defined as the ratio of the K_d values of Am(III) and the metal ion of interest, were also calculated and are listed in Table 2. These data suggest that the separation of Am(III) with respect to Eu(III) and Pu(IV) is not very encouraging, while that with respect to U is reasonably high. The very large selectivity coefficients with respect to Sr(II) and Cs(I) indicate that ¹³⁷Cs and ⁹⁰Sr can be very easily decontaminated from the sorbed Am(III). We have previously prepared a malonamide-grafted resin, which showed about 30 and 5000 times lower selectivity coefficients with respect to Pu(IV) and

U(VI), respectively.²⁵ It is interesting to note that the resins do not hold U(VI), Sr(II), and Cs(I), while metal ions such as Am(III), Eu(III), and Pu(IV) are effectively sorbed, suggesting that separation of trivalent lanthanides and actinides from U, Pu, Sr, and Cs is possible by selectively oxidizing Pu to its hexavalent state.

3.5. Analytical application

One of the prerequisites of metal ion determination in dilute solutions is the pre-concentration of the trace metal ions in the feeds. In order to achieve pre-concentration of ²⁴¹Am present in dilute waste solutions, a column containing resin-II was used. The column parameters are summarized in Table 1. In an experiment carried out to evaluate the pre-concentration ability of this resin, a 1 L solution containing trace amounts of ²⁴¹Am (64.16 Bq mL⁻¹) at 3 M HNO₃ was passed through the column at a flow rate of 10 mL h⁻¹. During the loading step, no breakthrough was observed for ²⁴¹Am, which was monitored by counting the effluents intermittently using a NaI(Tl) detector. After passing the entire lot of the solution, the elution was performed with 0.01 M EDTA (at pH 2.0); the results of the pre-concentration are summarized in Table 3. Quantitative recovery of ²⁴¹Am was possible with about 10 mL of the eluting solution, giving a pre-concentration factor of >100. This is significantly better than the pre-concentration factor of about 40 obtained with the malonamide-grafted resin for the pre-concentration of U.²⁶

4. Conclusions

The newly prepared diglycolamide-grafted resins-I and -II showed an interesting sorption behavior of actinide ions from 3 M nitric acid solutions, the uptake and kinetics being dependent on the amount of DGA units present. The resins showed relatively lower extraction efficiency than the previously reported TODGA-based extraction chromatographic resins.^{14,15} However, the metal ion uptake capacities were comparable and in view of the possibility of longer reusability the grafted resins may find application. The resins showed a better analytical performance in terms of the pre-concentration factor compared to the analogous malonamide-grafted resins.²⁶

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Table 2 Distribution coefficients of metal ions by DGA-functionalized resins-I and -II obtained using 3 M HNO₃

Metal ions	K_d at 3 M HNO ₃		Selectivity coefficient ($K_{d,Am}/K_{d,M}$)	
	Resin-I	Resin-II	Resin-I	Resin-II
Am(III)	1850	3050	—	—
Eu(III)	2705	5650	0.68	0.54
Pu(IV)	2150	3150	0.86	0.97
Pu(VI)	15.0	23.0	123	133
U(VI)	5.7	11.1	324	276
Sr(II)	0.33	0.75	5606	4067
Cs(I)	0.67	0.68	2762	4485

Table 3 Pre-concentration of metal ions by resin-II column; feed: 1 L 3 M HNO₃ solution containing ²⁴¹Am; Eluent: 0.01 EDTA

Metal ions	Conc. in loading solution (Bq mL ⁻¹)	Amount eluted ^a (Bq)	Percentage Recovery	Pre-concentration factor
Am(III)	64.16	66615	103.83	>100

^a As determined from 10 mL of the eluted fraction.

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