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Two novel extraction chromatographic resins containing benzene-centered tripodal diglycolamide ligands: Actinide uptake, kinetic modeling and isotherm studies

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ABSTRACT

Two novel extraction chromatographic resins (EC), termed as RL-1 and RL-2, were prepared by impregnating two benzene-centered tripodal iglycolamide ligands (Bz-T-DGA) containing different spacer groups where the ligands are termed as L-1 and L-2, respectively. They were employed for the uptake of actinide and fission product ions, *viz.* Am^{3+}, Eu^{3+}, UO_2^{2+}, Np^{4+}, Pu^{4+}, Sr^{2+}, and Cs^{+}, from acidic feeds. Weight distribution coefficient (K_d) values were measured by the batch method and the loaded metal ions were back extracted using a 0.01 M EDTA solution at pH 4. Kinetic modeling of the sorption data of Am(III) on both resins suggested pseudo-second order rate kinetics with rate constants of 1.68×10^{-6} and 2.47×10^{-6} g/cpm.min for the resins containing L-1 and L-2, respectively. Sorption isotherm studies indicated the Langmuir monolayer chemisorption phenomenon with Eu(III) experimentally determined saturation uptake capacities of 6.02 ± 0.11 and 5.49 ± 0.14 mg per g of RL-1 and RL-2 resins, respectively. As the batch uptake study results appeared encouraging, column studies were also carried out using both resins. The resin reusability data indicated a marginal change in the K_d values for the RL-1 resin up to three repeat runs beyond which a steady decrease of the K_d value was seen. On the other hand, in the case of RL-2 a steady decrease in the K_d values was observed for three repeat runs beyond which there was marginal change.

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1. Introduction

Actinide ion separation from lean effluents emanating from various streams of the radioactive waste processing activities is required for the decontamination of the radioactive feeds [1]. This has been done by several methods such as precipitation, solvent extraction, ion exchange, etc. While the major actinide content comprising of U and Pu can be separated by TBP (tri-*n*-butyl phosphate) extraction [2] of the feeds, the minor components containing elements such as Am, Cm, etc., can be extracted by a strategy called 'Actinide Partitioning' [3–5] using extractants *viz.* CMPO (carbamoylmethylphosphine oxide) [6], TRPO (trialkylphosphine oxide) [7], malonamides [8], etc., designed for these metal ions. In recent years, diglycolamide-based extractants, which are similar to the malonamides with the difference that an etheric 'O' atom is positioned in between the two amide groups (Fig. 1), have been shown to be highly efficient in the extraction of actinides including the minor actinides [9]. This gives more flexibility to the diglycolamide ligands and results in better extractability of the metal ions. There have been numerous reports on the extraction of metal ions including the actinide ions using TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) which is one of the most studied diglycolamides [10–12].

The metal ion binding has been subjected to research efforts by several groups and different theories have emerged. It has also been reported that the binding of the metal ions by a diglycolamide is through the two amidic 'O' atoms as well as the etheric 'O' atom (Fig. 1). The figure shows the cartoon representation of TODGA (Fig. 2) with three 'O' donor atoms. There are also suggestions that the diglycolamides form a sort of cavity and metal ions of ionic radii close to 100 pm have been found to be selectively extracted irrespective of their oxidation states [13]. This has also led to an unusual trend of metal ion extraction of $M^{3+} > M^{4+} > MO_2^{2+}$, which is not in accordance to their ionic potentials. In a separate study, formation of reverse micellar aggregation has been proposed in non-polar diluents such as *n*-dodecane [14] resulting in a very high extraction of metal ions such as Eu^{3+} with K_d-values of >500 at 1 M HNO_3 while using only 0.1 M TODGA [10]. This study also suggested the participation of 3–4 units of TODGA in the complexation process.

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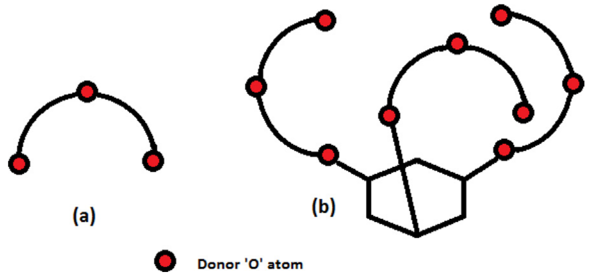
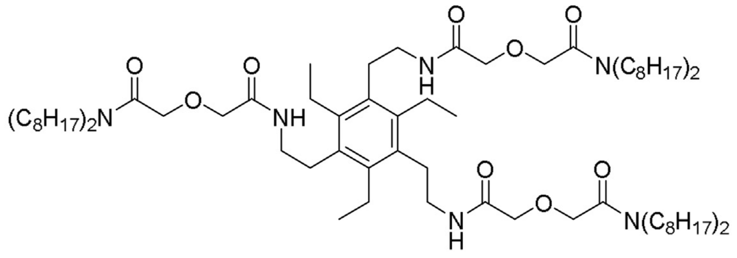


Fig. 1. Pictorial representation of (a) linear diglycolamide (TODGA) and (b) Bz-T-DGA.

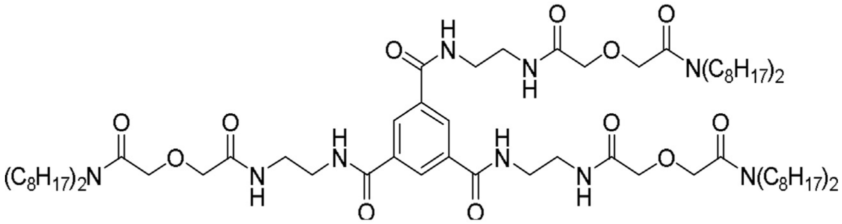
In view of these observations, studies involving multiple diglycolamide extractants will be of importance. Several tripodal diglycolamide extractants containing a carbon or a nitrogen atom at the center have been studied before and indicated an interesting separation behavior towards actinides [15–17]. Benzene-centered tripodal digycolamide ligands (abbreviated henceforth as Bz-T-DGA) have been recently studied by us for the extraction of actinide ions from acidic feeds using molecular diluents [18] as well as ionic liquids [19] with very interesting results in terms of both extraction as well as mutual separation behavior as there are three DGA arms available for complexation with a total of 9 'O' donor atoms (Fig. 1). However, as these extractants are rather exotic and may be far more expensive as compared to TODGA, there is a need for separation methods with minimal use of these extractants.

Solid phase extraction (SPE) is one of the 'green' separation methods which minimizes the use of VOC (volatile organic compound) such as the extractant as well as the diluent [20–24]. Also, the distribution coefficients can be much larger in view of the very high surface area of the resins, whose pores are filled with the extractant solution and hence, can be used efficiently in a column mode for the separation of different actinide ions. There are several reports available on the preparation of solid phase extractants, mainly by impregnation of the porous support material, using CMPO [25], malonamides [26,27] and diglycolamides [27–29]. Similar to the trend seen in the solvent extraction studies, the diglycolamide-based resins are reported to be superior to those prepared with other extractants. Van Hecke and Modolo [27] made a comparative evaluation of two extraction chromatographic (EC) resins prepared using DMDOHEMA (*N,N'*-dimethyl-*N,N'*-di-*n*-octylhexylethoxymalonamide) and TODGA for the uptake of actinide ions such as U(VI), Th(IV), Am(III), and Cm(III). Subsequently, Horwitz et al. used extraction chromatographic resins containing TODGA and its branched homolog TEHDGA (*N,N,N',N'*-di-2-ethylhexyl diglycolamide) for the extraction of actinide ions such as Th(IV), U(VI), Pu(IV) and Am(III), and other metal ions such as Ca(II), Sr(II), Ba(II), Ra(II), Pb(II), Y(II), Ce(II), Eu(III), Bi(III), Zr(IV), V(V), Nb(V), etc. [28]. In a separate study, Ansari et al. used TODGA impregnated resins with chromosorb-W, chromosorb-102, XAD-4 and XAD-7, etc., as the support material for the uptake of actinide ions from feed similar to that encountered in high level waste [29]. Though there are reports on polymeric SPE beads containing TODGA, prepared by the phase inversion method [30], extraction chromatographic materials appear more promising in view of their small particle sizes and large surface areas.

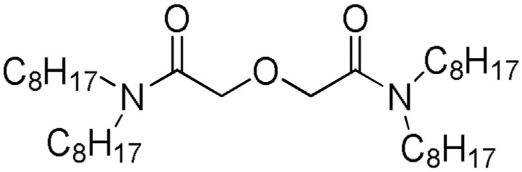
There are very limited reports on SPEs containing multiple diglycolamide extractants and absolutely no report on Bz-T-DGA ligands which are reported to be highly promising. The present paper



L-1



L-2



TODGA

Fig. 2. Structural formulae of the Bz-T-DGA extractants used in the present study and TODGA.

deals with the preparation of SPE materials (termed henceforth as extraction chromatographic (EC) resins) containing two Bz-T-DGA extractants shown in Fig. 2. The EC resins were prepared by the impregnation method and the extraction chromatographic resins were prepared using *n*-hexane solutions of the two ligands. For convenience, the resins containing ligands L-1 and L-2 are termed as RL-1 and RL-2, respectively. Apart from the batch extraction studies, kinetic modeling and isotherm analysis were carried out. Column studies were also carried out apart from the elution and reusability of the resins.

2. Experimental

2.1. Chemicals

The Bz-T-DGA extractants (Fig. 2) were synthesized as reported previously [18]. L-1 was prepared by the reaction of 1,3,5-tris(aminoethyl)-2,4,6-triethylbenzene with *p*-nitrophenyl-activated DGA in refluxing toluene in the presence of triethylamine. Similarly, L-2 was made by the reaction of 1,3,5-benzenecarbonyl trichloride with 2-(2-((2-aminoethyl)amino)-2-oxoethoxy)-*N*,*N*-dioctyl acetamide in the presence of NaOH. The extractants were characterized by standard techniques such as ^{1}H NMR, HPLC, and ESI-MS. Chromosorb-W (dimethyl dichlorosilane treated acid washed celite diatomaceous silica, mesh size 60–80) was procured from John Manville, USA and was cleaned properly prior to use by giving repeated washings with distilled water and ethanol followed by drying in an oven at 70 °C to remove the sorbed impurities. Spec pure Eu_2O_3 (>99.99%) obtained from Johnson &Mathey was used for preparing the Eu stock solution for the isotherm and column studies. Suprapur nitric acid (Merck) and MilliQ water were used for the preparation of the feed solutions. All other chemicals were of AR grade.

2.2. Radiotracers

^{241}Am, Pu (mainly ^{239}Pu), ^{237}Np, and ^{233}U were used from the laboratory stock solutions after checking their radiochemical purities. The gamma ray emitting radiotracers, ^{152,154}Eu, ^{137}Cs and ^{85,89}Sr were obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai. The oxidation states of Pu and Np were adjusted to the +4 state using a standard procedure which uses TTA (2-thenoyltrifluoroacetone) extraction [31]. While the oxidation state of Pu was adjusted using $NaNO_2$ based on a literature report [32] and that of Np was done using a mixture of ferrous sulphamate and hydroxylamine hydrochloride [33].

The gamma ray emitting radionuclides *viz.*^{241}Am, ^{152,154}Eu, ^{85,89}Sr, and ^{137}Cs were assayed radiometrically using a well type NaI(Tl) scintillation counter interphased with a multichannel analyzer. On the other hand, the alpha emitting radionuclides (^{233}U, ^{237}Np, and ^{239}Pu) were assayed by a liquid scintillation counter (Hidex, Finland) employing a toluene-based scintillator cocktail containing 20% (v/v) HD2EHP, (0.7% (w/v) 2,5-diphenyloxazole (PPO), and 0.03% (w/v) 1,4-di-[2-(5-phenyloxazoyl)]benzene (POPOP).

2.3. Preparation of EC resins

The EC resins containing L-1 and L-2 were prepared by a standard procedure in which a slurry containing a known quantity of the extractants (78 mg L-1 and 80 mg L-2) and Chromosorb-W (1.002 g and 1.005 g, respectively) in *n*-hexane was equilibrated using a vortexed mixer for overnight. Though the solubility of L-1 was very good in *n*-hexane, this was not the case for L-2 and prolonged sonication (using an ultrasonic bath) was necessary for solubilization. The solvent was removed carefully by flushing nitrogen gas with gentle stirring. The EC material with the major part of the solvent evaporated was subjected to vacuum to yield a free flowing resin of constant weight. The loading of the ligands on the solid support was estimated from the weight gain of the support after the impregnation being ca. 7% (w/w) for both the resins.

Table 1
Various parameters of the columns containing RL-1 and RL-2 used in the present study.

Parameter	Column with RL-1	Column with RL-2
Column dimension	0.4 cm × 20 cm	0.4 cm × 20 cm
Weight of resin used (g)	0.3011	0.3016
Height	10.2 cm	10 cm
Flow rate	3-4 drops/min	3-4 drops/min
Bed volume	1.28 m L	1.26 mL

2.4. Characterization of the EC resins

The EC resins, RL-1 and RL-2, prepared as per the method described above, were characterized by thermogravimetry using a Netzsch Thermobalance (Model: STA 409 PC Luxx), at a heating rate of 10 °C per minute in air atmosphere up to 800 °C and the changes seen in the graph were correlated to mass loss of the particular component. The surface morphology of the EC material was analyzed by recording scanning electron micrograph (SEM) pictures using a Stereoscan 100 Cambridge model operating at 15/25 kV with a magnification of 3000x at a working distance of 15 mm at a tilt angle of 45° after giving a 15 nm coating of gold using a Balzer's coating unit (model: CEA 30).

2.5. Batch uptake studies

Batch uptake studies were carried out by equilibrating a weighed quantity of the resin (ca. 10 mg) with 1 mL of dilute nitric acid solution containing the required radiotracer in leak tight stoppered Pyrex glass tubes in a thermostated water bath at 25 ± 0.1 °C for about 3 h (*vide infra*). The tubes were subsequently centrifuged and aliquots (100 μL) were taken out from the aqueous phases, which were assayed radiometrically for gamma ray or alpha particles as mentioned above. The weight distribution coefficient (K_d) values of metal ions sorbed onto the EC resins were calculated using the following equation:

$$K_d = \left[\frac{(C_o - C)}{C}\right] \cdot \frac{V}{W}\ (mL/g) \tag{1}$$

where C_o and C are the concentrations of metal ions expressed in terms of counts per unit time per unit volume before and after equilibration, respectively, while V represents the volume of the aqueous phase used (mL) and W the weight of the resin (g). All batch uptake experiments were carried out in triplicate and the accepted data were found to be within the relative standard deviation of 5%.

2.6. Column studies

The column studies were carried out using glass columns with dimensions of 20 cm x 0.4 cm fitted with frits and stop cocks. The columns were packed using slurries of solutions containing about 300 mg of resin, which resulted in bed volumes of ca. 1.5 mL. Utmost care was taken to eliminate any air bubble in the columns. Detailed column parameters are listed in Table 1. Before the loading / elution studies were carried out, the columns were conditioned by passing about 7–8 mL nitric acid solution of the same molarity as the feed. After conditioning, the feed solution, containing the carrier (Eu) metal ion and the radiotracer (^{152,154}Eu), was passed through the column for the breakthrough studies. All column operations were carried out at ambient temperature (24 ± 1 °C) and the col-

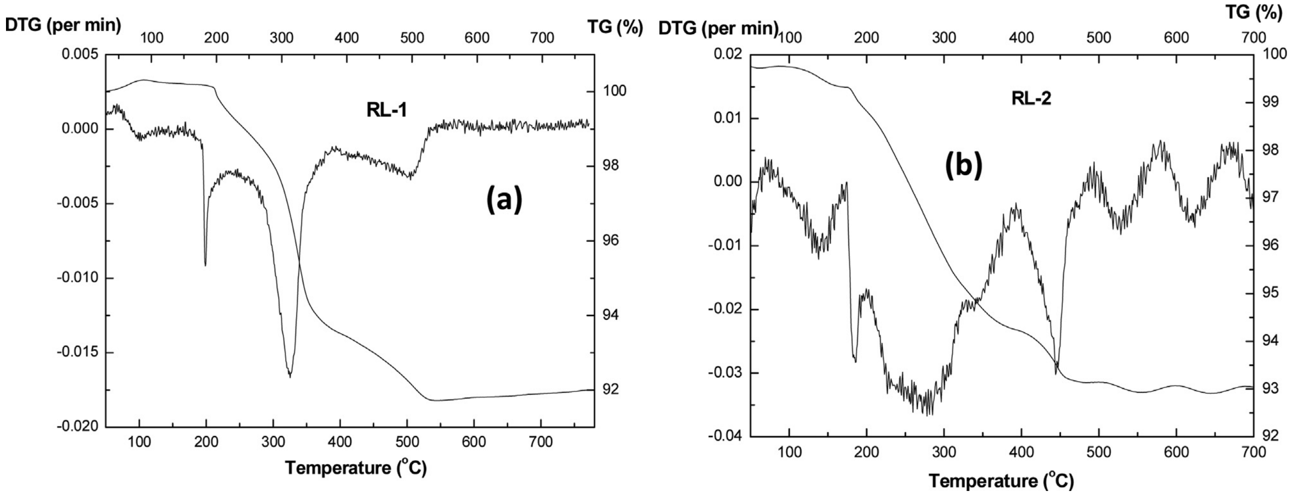


Fig. 3. Thermograms of (a) RL-1 and (b) RL-2 obtained in air. Heating rate: 10 °C/min.

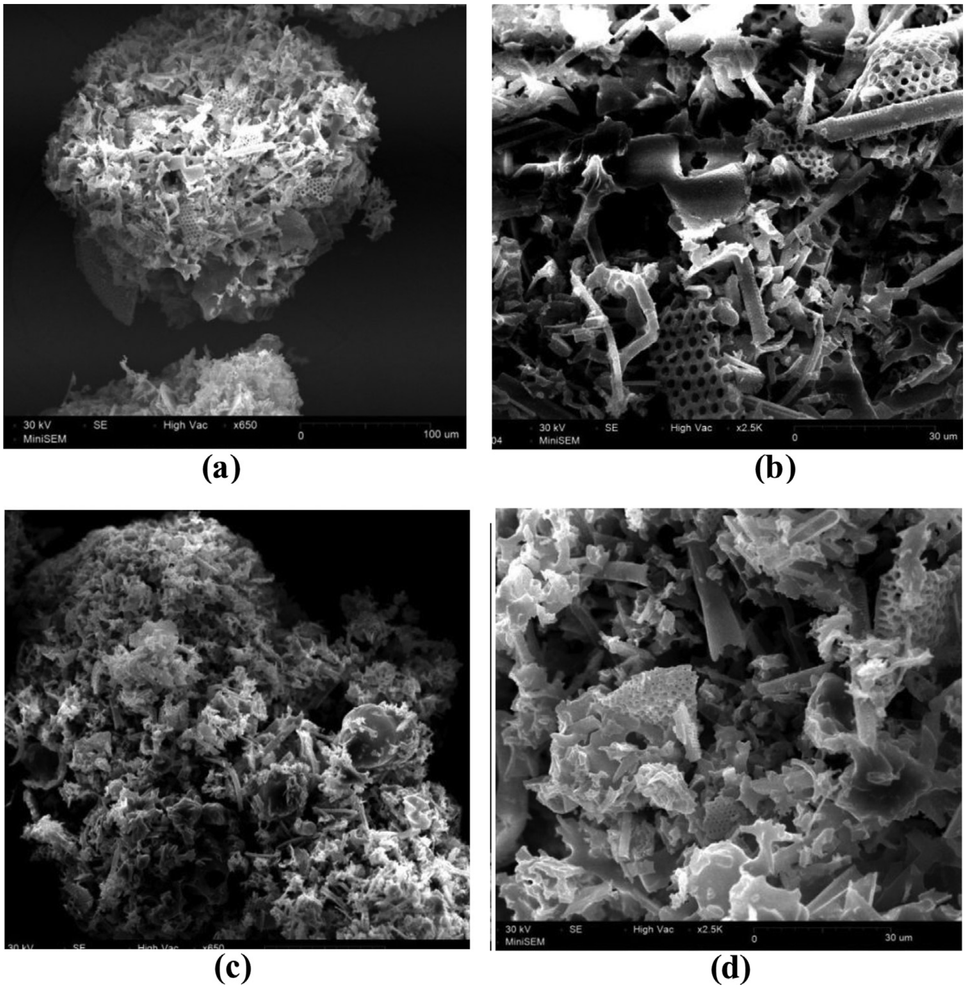


Fig. 4. SEM pictures of RL-1 with (a) 650X and (b) 2500X magnifications and those of RL-2 with (c) 650X and (d) 2500X magnifications.

umn operations were carried out at a flow rate of 4 drops/min (ca. 0.3 mL/h). The columns were closed using stop cocks after the column runs were completed. The solutions coming out of the columns were assayed radiometrically as mentioned above and the results were plotted as a function of volume of feed/eluent passed through the column to obtain the breakthrough / elution curves.

3. Results and discussion

The resins were found to be free flowing suggesting that no free extractant was sticking to the resin surface (the extractants were sticky viscous liquids). It was in the expected line as earlier literature report suggested that analogous resin prepared using TODGA

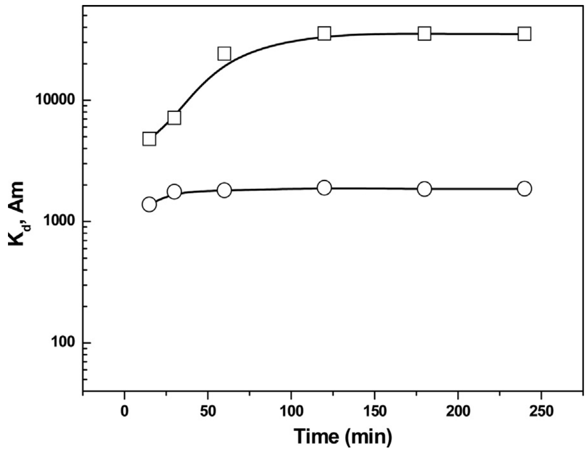


Fig. 5. Batch uptake kinetics of ^{241}Am using the EC resins RL-1 (square) and RL-2 (circle) from feed containing 3 M HNO_3.

with ca. 50% extractant loading was also free from any free extractant contamination [29]. The density of the resins was measured and was found to be 0.8316 g/L and 0.8500 g/L for RL-1 and RL-2, respectively.

3.1. Characterization of the EC resins

The EC resins were characterized by thermogravimetry for testing its thermal stability as well as obtaining information about any water uptake, decomposition of the extractant, etc. The weight losses from the thermogravimetric analysis carried out in air for both RL-1 and RL-2 are presented in Fig. 3. Weight loss in the temperature range of 100–120 °C is negligible (almost nil for RL-1 and <0.5% for RL-2) suggesting minimal moisture absorption by the resins. Fig. 3 also indicates that the resins were thermally stable up to 150 °C. On the other hand, subsequent weight losses were found to occur in two steps, one between 150–350 °C, while the other beyond that. A constant weight of 92% was seen for RL-1, while it was 93% for RL-2. Considering the minor amount of moisture for RL-2, it suggests about 7% loading of the ligands for both the resins. While the ligands are decomposed in the first step, the second step indicates complete removal of the oxide impurities.

The SEM pictures for both the resins with 650X and 2500X magnifications are presented in Fig. 4. The porous honeycomb like structure of the support material is clearly seen in the higher magnification pictures. The RL-2 resin pictures indicate a solid particle coating on the resins which is in line with the observation of the lower solubility of L-2. As will be seen below, the RL-2 resin displayed a relatively lower metal ion uptake than the RL-1 resin.

3.2. Metal ion uptake kinetics

The metal ion uptake studies were carried out using 3 M HNO_3 as the aqueous feed, which was spiked with ^{241}Am tracer. There was almost no uptake of the metal ion when pristine Chromosorb W (without any extractant) was used (K_d< 0.1). On the other hand, very large (>10^3) K_d values were obtained when RL-1 and RL-2 were used for ^{241}Am uptake from 3 M HNO_3. The large uptake of actinide ions such as Am(III) suggest that the resins can be effectively used for the extraction of actinide ions (as seen below, other actinide ions such as Pu(IV) and Np(IV) were also extracted effectively) from acidic feeds.

The batch uptake kinetics data with ^{241}Am as the radiotracer and 3 M HNO_3 as the feed were plotted and the results are presented in Fig. 5. Two broad observations can be made. Firstly, it took about 2 h to attain equilibrium K_d values for RL-1, which is much longer than the about 30 min required for the RL-2 resin. Secondly, the K_d value with RL-1 is about 20 times larger than that obtained with RL-2. As mentioned above, the poor solubility of L-2 in *n*-hexane possibly led to slight precipitation of the extractant in the pores of the solid support which might be the reason for the lower K_d value with RL-2.

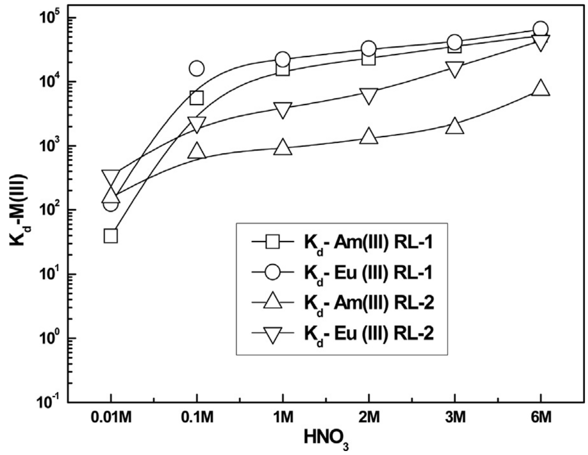


Fig. 6. Batch uptake profiles of Am^{3+} and Eu^{3+} using the EC resins RL-1 and RL-2 from feeds containing varying concentrations of HNO_3; Am-RL-1 (square); Am-RL-2 (triangle); Eu-RL-1 (circle); Eu-RL-2 (inverted triangle).

Table 2
Batch uptake data at 3 M HNO_3 along with the respective separation factor (SF) values for Eu^{3+} with respect to Am^{3+}.

DGA extractants in resin	$K_{d,Eu}$	$K_{d,Am}$	SF[a]	Reference
TODGA	9018	7212	1.25	[28]
TODGA	~10^4	~5×10^3	~2	[26]
DGA grafted resin	2705	1850	1.46	[34]
DGA-functionalized calix [4]arene	8330	6985	1.19	[33]
DGA-functionalized tripodal[b]	8335	9939	0.84	[33]
L-1	40845	35628	1.14	This work
L-2	16706	2424	6.89	This work

[a] $K_{d,Eu}/K_{d,Am}$.
[b] DGA groups are appended to a central '*C*' atom.

3.3. Effect of the aqueous feed acidity

An interesting separation behavior of the trivalent actinide (Am) and lanthanide (Eu) ions was reported in a previous paper with the two Benz-T-DGA extractants used in the present study [18]. In view of this, batch uptake studies were carried out for both Am(III) as well as Eu(III) as a function of the feed nitric acid concentration and the results are presented in Fig. 6. A monotonous increase in the K_d values with increasing HNO_3 concentration was seen for both metal ions with the resins (Fig. 6). This could be due to the extraction of the metal ions with these extractants which depend on the aqueous phase nitrate ion concentration as per the following equation in line with the extraction mechanism reported in the solvent extraction studies [18],

$$M^{3+}{}_{aq}+L_R+3NO_3{}^-{}_{aq}= M(NO_3)_3.L_R \tag{2}$$

where, M is either Am or Eu and the species with the subscript 'aq' and 'R' represent those in the aqueous and the resin phases, respectively. Though a partial contribution of 1:2 species has been reported in our previous solvent extraction study [18], such species have been excluded for simplicity.

The separation factor (SF) values were calculated as the ratio of the K_d values of the respective metal ions and are listed in Table 2 along with those reported in literature obtained with resins containing other diglycolamide-based extractants. In general, the

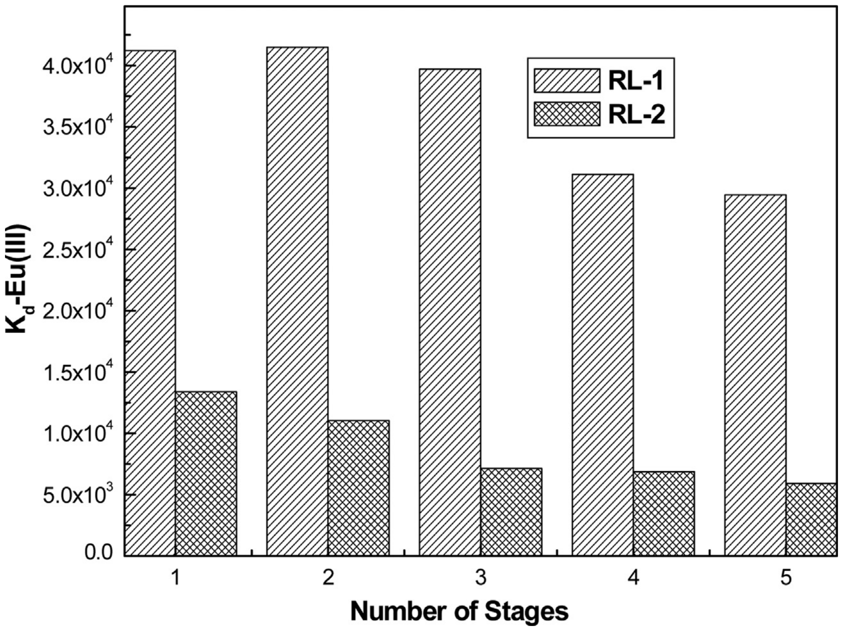


Fig. 7. Back extraction of the loaded Eu^{3+} ion from the resins using 0.01 M EDTA solution at pH 4.

uptakes of Eu^{3+} ion were distinctly larger as compared to those of Am^{3+} ion with all diglycolamide-based resins with the exception of a resin containing a 'C' pivot tripodal diglycolamide extractant [34]. The SF values are in general lower for RL-1 as compared to RL-2, though the metal ion uptake values are in the reverse order. Interestingly, RL-2 displays a relatively high SF value favoring Eu^{3+} ion uptake which was not the case with not only RL-1 nor with any other DGA-based extractants.

3.4. Uptake of other actinide and fission product elements

Radioactive wastes also contain other actinide ions such as UO_2^{2+}, Np^{4+}, Pu^{4+} and fission product ions such as Sr^{2+} and Cs^{+}, in addition to trivalent minor actinide ions such as Am^{3+} and rare earth ions such as Eu^{3+} mentioned above. In view of this, the batch uptake studies were extended to these metal ions and the K_d data are presented in Table 3. The uptake of the metal ions followed the trend: $Pu^{4+} > Eu^{3+} > Am^{3+} > Np^{4+} \gg UO_2^{2+} \sim Sr^{2+}$ and Cs^{+}. Furthermore, the very low uptake data of UO_2^{2+}, Sr^{2+}, and Cs^{+} ions indicate their negligible uptake and hence, the possibility of their easy decontamination. On the other hand, separation of other actinides from each other is not possible. Nevertheless, the uptake data shows that the resins hold promise for actinide ion uptake from acidic feeds such as nuclear wastes.

3.5. Back extraction and reusability

The back extraction of a metal ion is important from two counts, firstly, effective back extraction means effective recovery of the metal ion and, secondly, the resin can be applied for subsequent reuse. Therefore, experiments were carried out using ca. 40–50 mg of the resin and the batch back extraction was carried out using the sodium salt of EDTA (0.01 M solution) after careful removal of the aqueous phase after the batch extraction experiment. The resin after the extraction experiment was washed with a pH 4 solution (10^{-4} M HNO_3) several times to ensure complete washing of the nitric acid sticking to the resins. It was interesting to note that this washing step resulted in very little back extraction and the radiotracer loading of the resin was calculated taking this into consideration. The back extraction was, however, carried out using 0.01 M EDTA at pH 4 which resulted in quantitative stripping of the loaded activity. The reusability graph is presented in Fig. 7, which suggests deterioration of the resins. RL-1 remains quite stable up to three repeat runs, whereupon the K_d-values decrease. The behavior of RL-2 is the reverse with a steady decrease of the K_d-values for the first three runs followed by a marginal decrease in the following runs.

Table 3
Batch uptake data for actinide and fission product metal ions from 3 M HNO_3 using RL-1 and RL-2.

Metal ion	K_d values at 3 M HNO_3	
	RL-1	RL-2
UO_2^{2+}	10.3 ± 0.1	10.8 ± 0.1
Np^{4+}	(2.13 ± 0.02)×10^4	(6.42 ± 0.07)×10^3
Pu^{4+}	(8.20 ± 0.04)×10^4	(1.12 ± 0.01)×10^4
Am^{3+}	(3.56 ± 0.02)×10^4	(2.42 ± 0.05)×10^3
Eu^{3+}	(4.08 ± 0.07)×10^4	(1.67 ± 0.02)×10^4
Sr^{2+}	4.31 ± 0.02	4.40 ± 0.03
Cs^{+}	0.80 ± 0.01	0.92 ± 0.01

3.6. Kinetic modeling

Kinetic modeling of the metal ion uptake by the two extraction chromatographic resins was done by monitoring the time dependence of the Eu^{3+} ion uptake (feed contained 200 ppm Eu carrier in 3 M HNO_3 which was spiked with $^{152,154}Eu$ tracer) under continuous shaking (1 mL feed was equilibrated with 30 mg lots of the resins taken in leak tight Pyrex glass tubes) using a thermostated water bath. Samples from the tubes were removed at different time intervals and were assayed radiometrically and the results were fitted to the following equations.

Pseudo first-order kinetic model:

$$\mathrm{Ln}(q_e\text{-}q_t) = \mathrm{Ln}q_e - k_1 \cdot t \tag{3}$$

Pseudo second-order kinetic model:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{4}$$

where q_e and q_t are the mass of the metal ion retained per unit mass of the resin at equilibrium and at time 't', respectively, while k_1 and k_2 are constants.

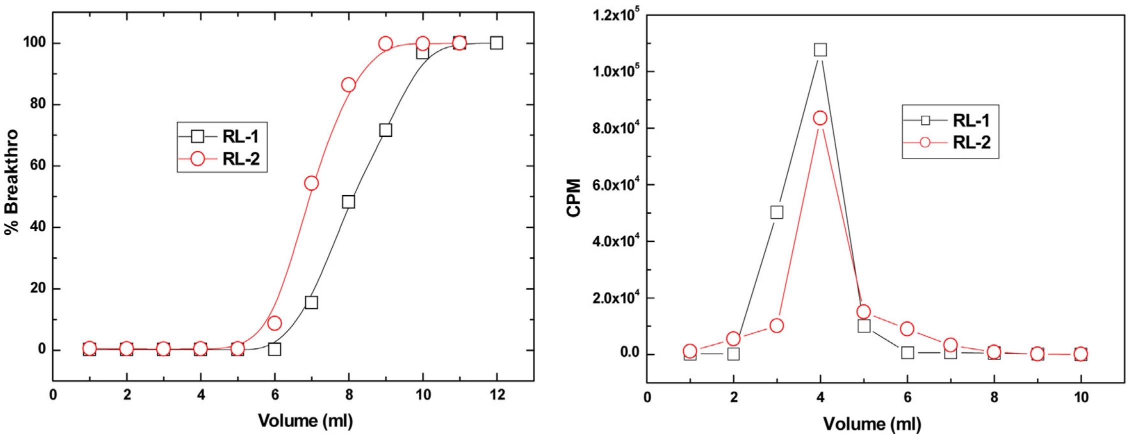


Fig. 8. (a) Breakthrough profiles of ^{152,154}Eu in a feed containing 200 ppm of Eu in 3 M HNO_3 and (b) elution profiles.

Table 4
The kinetic modeling fitted parameters for the uptake of Eu onto the Bz-T-DGA containing resins LR-1 and LR-2.

Resin	Pseudo first order		Pseudo second order	
	k_1 (min^{-1})	R^2	k_2 (g/cpm.min)	R^2
RL-1	1.06×10^{-2}	0.977	1.68×10^{-6}	0.999
RL-2	1.35×10^{-2}	0.944	2.47×10^{-6}	0.999

For the Lagergren's pseudo first-order kinetic model [35], Ln (q_e-q_t) vs t was plotted to result in straightline plots with negative slopes (Supporting Information). On the other hand, t/q_t vs t was plotted for fitting to the Ho's pseudo second-order model [36] (Supporting Information). Better fitting of the data to the pseudo second-order kinetic model suggested chemisorption as the rate-limiting step [37] i.e., a chemical reaction controls the uptake mechanism. This is only logical as the uptake reaction is mainly the extraction of the metal ion as per the reaction given by Eq. (2). The equilibrium uptake capacity (q_e) values obtained from the linear plots of the pseudo-second order kinetic model (Supporting Information) are very close to the experimentally obtained saturation uptake capacity (*vide infra*) proving the validity of the kinetic model.

The results of the kinetic modeling or the fitting parameters are listed in Table 4. As indicated from the square of the correlation coefficient (R^2) values, the pseudo second-order kinetics has a better fitting and hence, should be valid for the present case. Also, the pseudo second-order rate constants are nearly comparable that for RL-2 being marginally higher as compared to that obtained for RL-1.

3.7. Sorption isotherms

The initial metal ion concentration is very important for the selection of an optimal uptake condition for the metal ion of interest. Therefore, the equilibrium metal ion uptake capacity q_e is dependent on the initial metal ion concentration. Keeping this in mind, sorption or uptake isotherm studies were carried out where the equilibrium sorption capacity was determined at varying metal ion concentrations in the aqueous feed solution. The results were fitted to the following isotherm models viz. Langmuir [38], Freundlich [39], D–R [40] and Temkin [41,42].

Langmuir isotherm model:

$$\frac{C_{eq}}{q_t} = \frac{[1]}{b \cdot q_{\max}} + \frac{C_{eq}}{q_{\max}} \tag{5}$$

Freundlich isotherm model:

$$\log q_{eq} = \log K_f + \frac{1}{n} \log C_{eq} \tag{6}$$

D–R isotherm model

$$\ln q_t = \ln X_m - \beta \varepsilon^2 \tag{7}$$

Temkin isotherm model :

$$q_e = B\ln A_T + B\ln C_e \tag{8}$$

The straight line plots for the four isotherm models are given in the Supporting Information and, as can be seen, the Langmuir isotherm model fits with very little disagreement between the data points and the fitted lines suggesting that the monolayer uptake model may be operative. The coefficients obtained from the fittings are listed in Table 5. The maximum uptake capacity (q_{max}) values of

Table 5
Sorption isotherm constant for the uptake of Eu (III) on to the extraction chromatographic resins (RL-1 and RL-2) used in the present study.

Isotherm	Plot	Parameters	
		RL-1	RL-2
Langmuir	$\frac{C_e}{q_e}$ vs C_e	$q_{max} = 5.78 \pm 0.10$ (mg g–1) $b = 0.11 \pm 0.01$ (L/mg) $R^2 = 0.999$	$q_{max} = 5.15 \pm 0.20$ (mg g–1) $b = 0.55 \pm 0.01$ (L/mg) $R^2 = 0.998$
Freundlich	log q_e vs log C_e	log $K_f = 0.36 \pm 0.03$; n = 6.1 $R^2 = 0.951$	log $K_f = 0.31 \pm 0.06$; n = 5.3 $R^2 = 0.919$
D-R	ln $q_e$vs · ε^2	$q_{max} = 0.047 \pm 0.16$ (m mol/g) β = -1.23 × 10–3($mol^2 \cdot kJ^{-2}$) $E = 20.16 \pm 0.72$ (kJ/mole) $R^2 = 0.965$	$q_{max} = 0.057 \pm 0.14$ (m mol/g) β = -1.59 × 10–3($mol^2 \cdot kJ^{-2}$) $E = 17.73 \pm 0.57$ (kJ/mole) $R^2 = 0.943$
Temkin	q_e vs ln C_e	$B = 0.46 \pm 0.04$ $A_T = 0.28 \pm 0$ .01(L/g) $R^2 = 0.973$	$B = 0.560 \pm 0.05$ $A_T = 0.086 \pm 0.007$(L/g) $R^2 = 0.970$

Table 6
Results of the column studies using the RL-1 and RL-2 resins. Feed: 200 ppm Eu (spiked with ^{152,154}Eu tracer) in 3 M HNO_3.

Parameters	Column study results	
	RL-1	RL-2
Tracer activity in feeds[a]	25612 cpm/mL	35125 cpm/mL
Break through volume	6 ml	5 ml
Height	10.2 cm	10 cm
Peak elution volume	4 m L	4 m L
Total elution volume	4 m L	7 mL

[a] Though the feed contained 200 ppm Eu and 3 M HNO_3 for both the column experiments using RL-1 and RL-2 resins, the tracer concentrations were different.

5.78 ± 0.10 and 5.15 ± 0.20 mg per gram of the resin matched fairly well with the experimentally determined values of 6.02 ± 0.31 and 5.49 ± 0.24 mg per gram of the resin for RL-1 and RL-2, respectively. This validates the Langmuir model being the most suitable for the present study involving the two Bz-T-DGA based resins.

3.8. Column studies

The columns were prepared as mentioned above, the parameters of which are given in Table 1. The breakthrough profiles were obtained using the feed solution prepared with macro concentrations of Eu (200 ppm) and spiked with the ^{152,154}Eu radiotracer in 3 M HNO_3. As mentioned above, the columns were conditioned using 3 M HNO_3, which is the same acidic medium as the feed solution used subsequently. As seen from Fig. 8(a), the RL-1 based column has a higher breakthrough volume (6 mL) as compared to the column containing the RL-2 resin, which is commensurate with their batch uptake behavior. In view of the higher breakthrough volume obtained for the RL-1 resin-based column, a much larger amount of Eu was loaded as compared to the second column based on the RL-2 resin.

The elution of the loaded metal ion was carried out using 0.01 M EDTA at pH 4. The elution profiles are plotted in Fig. 8(b) and indicate sharp elution profiles for both the resins. However, a careful observation of the figure shows a slightly broader elution profile for the RL-2 as compared to the RL-1 resin based column. The column study results are summarized in Table 6.

4. Conclusions

It is clear from the solid phase extraction studies involving Eu(III) and Am(III) ions that the uptake of the metal ions is significantly large for the RL-1 resin, which is about 4–5 times larger than that of TODGA-based resins reported previously, though the ligand loading in the present resins is about 7 times lower. This is attributed to the pre-organized structure of the Bz-T-DGA ligands, which can coordinate with the three DGA arms with relative ease (Fig. 1). The kinetic modeling studies indicate pseudo second-order kinetics conforming to the Langmuir sorption isotherm. The column studies indicate facile loading and elution with both the resins, though the RL-1 resin-based column showed a significantly higher efficiency. From the present study it can be concluded that the Bz-T-DGA-based resin RL-1 can be used for the uptake of trivalent actinides / lanthanides from feeds similar to the high level liquid nuclear waste (HLLW) and hence, shows promise for application to radioactive waste remediation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2019.03.067.

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