



# Highly efficient uptake of tetravalent actinide ions from nitric acid feeds using an extraction chromatography material containing tetra-*n*-butyl diglycolamide and a room temperature ionic liquid

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## ABSTRACT

An extraction chromatography (XC) material containing *N,N,N',N'*-tetra-*n*-butyl diglycolamide (TBDGA) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide ( $C_4mim\bullet NTf_2$ ), a room temperature ionic liquid, was used for the uptake of the tetravalent actinide ions Th(IV), Np(IV), and Pu(IV) from nitric acid feed solutions. The uptake of the metal ions followed the trend: Th(IV) < Np(IV) < Pu(IV), which is the same as that of their ionic potential values. While a decrease in the Np(IV) and Pu(IV) uptake was seen with increasing HNO<sub>3</sub> concentration at lower acidities, an opposite trend was observed at higher acidities. Th(IV) uptake was not affected with the acid concentration. In view of the very high uptake and its importance in the nuclear fuel cycle, the major part of the studies was carried out with Pu(IV) ion. The loaded Pu(IV) was back extracted from the XC material using a mixture of 0.5 M oxalic acid and 0.5 M nitric acid. The Pu(IV) uptake by the XC material was fitted into different kinetic and isotherm models. The results conformed to the pseudo-second order kinetic model and the Langmuir monolayer sorption model. Column studies were carried out using a feed having 1.6 mg/L Pu solution in 3 M HNO<sub>3</sub>. While the breakthrough was obtained after passing ca. nine bed volumes, a sharp elution peak was obtained with >99% recovery in about seven bed volumes.

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## 1. Introduction

Plutonium, one of the most important actinide elements, is produced in nuclear reactors in large quantities and is proposed to be the fuel element in fast breeder reactors (FBRs) [1]. During the operations in the nuclear fuel cycle, there are many lean waste streams which contain minor to significant quantities of Pu and hence, need to be recovered in view of its strategic importance. Pu is also found in the environment from nuclear weapon testing and accidents and has a very intriguing environmental chemistry making it one of the most researched topics [2]. In view of the very low concentration of Pu in the environmental samples, its estimation rather than recovery is of importance and it requires suitable methods for its pre-concentration prior to its estimation.

Out of the separation methods for Pu from lean effluents or environmental samples, techniques viz. solvent extraction and precipitation are not suitable. On the other hand, ion-exchange based methods lack selectivity, especially if cation exchange resins are used. However, solid phase extraction-based methods, especially those based on extraction chromatography (XC) with very low solvent inventory, appear to be highly promising in view of the unique advantages of both solvent extraction and chromatography [3-7].

Diglycolamides (DGAs), are known to have very high affinity for the tri- and tetravalent actinide ions and a relatively lower affinity for the hexavalent uranyl ion [8], are proposed for 'actinide partitioning' in radioactive waste management [9-11]. DGA-based XC materials are reported to be highly promising [12-15]. We have reported that when a room temperature ionic liquid (RTIL) was impregnated into the pores of DGA-based XC materials, the uptake of the metal ions increased manifold [16,17]. Furthermore, XC materials containing ionic liquids have shown a better stability and hence, can be reused for a longer length of operation [18].

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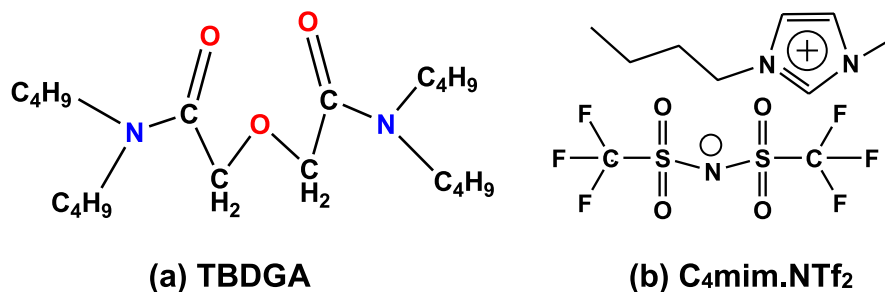


Fig. 1. Structural formulae of (a) TBDGA and (b) C<sub>4</sub>mim.NTf<sub>2</sub>.

Most of the extraction chromatography materials reported in the literature contained TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) or T2EHDGA (*N,N,N',N'*-tetra-2-ethylhexyl diglycolamide) as the DGA ligand [12–15]. Kazi et al. reported the separation of Am and Pu using TODGA-based XC material [19]. Though most of the work reported on DGA-based extractants is with TODGA and T2EHDGA, lower homologs, i.e., those containing shorter alkyl chains are reported to be better extractants in their solvent extraction studies [20].

The preparation of an XC material containing TBDGA (*N,N,N',N'*-tetra-*n*-butyl diglycolamide; Fig. 1a) in an RTIL which showed much better uptake and reusability characteristics towards trivalent *f*-cations viz. Am(III) and Eu(III) as compared to an analogous sorbent material containing *n*-dodecane, a molecular diluent, as the solvent was recently reported [18]. However, there are no data reported on the uptake of tetra valent actinide ions from acidic feeds with this resin. This is the novelty of this work which can find application in analytical separations involving tetra valent actinides in nuclear fuel cycle.

In view of the above reasons, it was thought of interest to evaluate the above-mentioned XC material containing TBDGA in C<sub>4</sub>mim.NTf<sub>2</sub> (Fig. 1b) for the uptake of tetravalent actinide cations such as Th(IV), Np(IV), and Pu(IV) from nitric acid feed solutions. Apart from uptake, stripping and reusability studies, column studies were carried out. The Pu uptake data are also fitted to various kinetic and thermodynamic models. We believe that this is the first ever report on Pu uptake studies using any DGA-based XC material containing an RTIL and as will be seen, it has superior efficiency in comparison to other analogous materials.

## 2. Experimental

### 2.1. Reagents

The synthesis of TBDGA was reported in an earlier publication [17] and was used after checking its purity by NMR and HRMS. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C<sub>4</sub>mim•NTf<sub>2</sub>), was purchased from IoliTech, Germany and was used as received. Both AR grade oxalic acid and Suprapur nitric acid were procured from Merck, Germany, and were used as such. The nitric acid solutions used for the uptake studies were prepared after making suitable dilutions of the Suprapur acid with Milli-Q water (Millipore, USA) and the strength estimation was performed by titrations against a standard NaOH solution (Merck). All the other chemicals used in the present study were of AR grade.

Chromosorb-W (dimethyl dichlorosilane treated acid washed celite diatomaceous silica, particle size: 180–250 micron) was obtained from Johns Manville, USA, and was cleaned as per the reported method prior to use [21]. The solid support material was washed with distilled water, methanol, and acetone, in the same sequence and was air-dried in an oven at 70 °C prior to its use.

### 2.2. Radiotracers

#### 2.2.1. Plutonium

Plutonium (mainly <sup>239</sup>Pu) from laboratory stock was freshly purified from <sup>241</sup>Am prior to use by a solvent extraction method using TTA (2-thenoyltrifluoroacetone) solution in xylene [22]. The oxidation state of Pu was adjusted to the +4 state by the addition of NaNO<sub>2</sub> prior to the extraction step which exclusively extracted Pu(IV). The TTA extract was subsequently stripped into an aqueous phase containing 8 M nitric acid and was used for subsequent studies after checking its radiochemical purity by alpha-spectrometry using a Si surface barrier detector and gamma ray spectrometry using an HPGe detector.

#### 2.2.2. <sup>239</sup>Neptunium

The <sup>239</sup>Np radiotracer was produced as per a reported method [23]. The method involved irradiation of natural U in a nuclear reactor at a neutron flux of  $5 \times 10^{13}$  n/cm<sup>2</sup>/s followed by separation of the thus produced <sup>239</sup>Np from bulk U and fission products by TTA extraction in a manner similar to that for Pu as described above. The oxidation state of Np was adjusted to the +4 state by the addition of a few drops of hydroxylamine hydrochloride (0.05 M) and ferrous sulphamate (0.01 M) solutions. The extracted Np(IV) was stripped into 8 M HNO<sub>3</sub> and was then used as the Np(IV) stock for all subsequent experiments.

#### 2.2.3. <sup>234</sup>Thorium

The <sup>234</sup>Th radiotracer was 'milked' from a natural U solution in 6 M HCl by extracting the anionic UO<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> complex by a solution of 30% Aliquat 336 in chloroform. The aqueous phase containing the radiotracer was contacted with barren chloroform several times to remove tracers of the dissolved extractant and was subsequently evaporated to dryness and the residual organic content was destroyed by adding a mixture of concentrated nitric acid and a few drops of perchloric acid followed by complete evaporation to dryness. Dilute nitric acid was added to the dried activity and the solution was used as the <sup>234</sup>Th tracer stock for subsequent experiments.

### 2.3. Radiometric assay

The assaying of Pu was done radiometrically using the Hidex (Finland) liquid scintillation counting system with alpha-beta discrimination facility. The Ultima Gold scintillator cocktail (Perkin Elmer) was used for the radiometric assay of Pu samples. About 5 mL of the scintillator cocktail was taken in a glass vial into which the Pu sample (usually 100 μL) was added and sonicated in an ultrasonic bath before the vials were counted.

<sup>234</sup>Th and <sup>239</sup>Np radiotracers were assayed by gamma ray counting using a NaI(Tl) scintillation detector (Para Electronics) coupled to a multi-channel analyzer (ECIL, India). While the 63

keV and 93 keV peaks were counted for  $^{234}\text{Th}$ , in view of multiple peaks for  $^{239}\text{Np}$  (106 keV: 25.34%; 228 keV: 10.73%; 278 keV: 14.5%; 334 keV: 2%), the integral counting mode was opted for. All counting data were background corrected, and decay correction was done for  $^{239}\text{Np}$  due to its short half life.

#### 2.4. Preparation and characterization of the extraction chromatography sorbent material

The XC material was prepared as per the procedure reported in a paper published recently [18]. To accurately weighed quantities of TBDGA (0.361 g),  $\text{C}_4\text{mim.NTf}_2$  (0.203 g) and Chromosorb-W (1.01 g), taken in a stoppered conical flask, 20 mL of acetone was added and vortexed for 24 h. As reported in previous publications, Chromosorb W was better than some of the other solid support materials [13,24]. Nitrogen gas was carefully purged into the slurry to remove almost the entire amount of the solvent. Subsequently, the product was kept under vacuum overnight to yield free flowing XC material. The overall ligand loading was 22.9% and the ionic liquid loading was 12.9%.

The XC material was characterized by different techniques viz. thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) and the results are in line with those available in an earlier report [18]. The size of the sorbent particles was measured using a microscope and was found to be  $240 \pm 60$  micron, while the  $\text{N}_2$ -BET surface area of the particles was found to be  $4.21 \text{ m}^2/\text{g}$ . FTIR spectra of the samples containing pristine and loaded XC materials were recorded on a Bruker Alpha II ATR-FTIR spectrometer which indicated presence of the extractant in the sorbent pores as reported before [18].

#### 2.5. Batch uptake studies

##### 2.5.1. Uptake from nitric acid feeds

The uptake of the metal ions viz.  $\text{Th(IV)}$ ,  $\text{Np(IV)}$ , and  $\text{Pu(IV)}$  was carried out from tracer spiked nitric acid feeds using a known quantity of the XC material. Usually, 10–12 mg of the sorbent material was weighed into leak tight Pyrex glass tubes (capacity 10 mL) containing 1 mL of the aqueous feed solution spiked with the radiotracers. The tubes were equilibrated in a thermostated water bath at  $25 \pm 0.1$  °C for a period of 1 h. The time required to attain equilibrium was decided by a separate experiment (vide infra). The tubes were kept aside after equilibration to settle the sorbent particles. The supernatant was transferred to another tube, which was subsequently centrifuged for about 2 min before the sample was taken out for radiometric assay as described above. Assuming some fine particles were still floating (not visible to naked eye), the solution was passed through a syringe fitted with a 0.45-micron filter and the sampling was redone. A very good match (within  $\pm 2\%$ ) was seen for the obtained results by the two methods suggesting the near complete removal of the fine floating particles and the assaying of the radionuclides in the remaining experiments were done without any filtration. The weight distribution coefficient ( $K_d$ ) was calculated using Eq. (1):

$$K_d = \left[ \frac{(C_0 - C)}{C} \right] \cdot \frac{V}{W} \quad (1)$$

where  $C_0$  and  $C$ , respectively are the final and initial concentrations (in terms of radioactivity) of the cation in the aqueous phase while the solution phase volume is 'V' and weight of the XC material is 'W' gram. The concentrations of the radiotracers used in the uptake studies were  $10^{-13}$  M,  $10^{-12}$  M and  $10^{-6}$  M for Np, Th, and Pu, respectively.

##### 2.5.2. Back extraction studies

For the back extraction of the loaded radiotracer, the XC material containing the radiotracer, as mentioned above, was carefully

**Table 1**  
Linearized forms of different sorption isotherm model equations.<sup>a</sup>

Model	Linearized form model equation	Plot	References
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Bq_{\max}} + \frac{C_e}{q_{\max}}$	$\frac{C_e}{q_e}$ vs $C_e$	[25]
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	[26]
D-R	$\ln q_e = \ln q_{\max} - \beta \varepsilon^2$	$\ln q_e$ vs $\varepsilon^2$	[27]
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	$q_e$ vs $\ln C_e$	[28]

<sup>a</sup>  $q_e$  is the concentration of the metal ion (Pu(IV)) sorbed per gram of the solid at equilibrium;  $C_e$  is the equilibrium concentration of metal ions in the aqueous phase;  $q_{\max}$  and  $K_f$  are the maximum sorbed mass of Eu(III) at saturation and Freundlich constant, respectively.

separated from the aqueous phase avoiding any loss of particles and was equilibrated with solutions suitable for back extracting the loaded metal ions. The equilibration and assaying methods were the same as those mentioned above. The percent back extraction (%BE) is given by the following equation:

$$\%BE = (C_R - C_S) \times 100/C_R \quad (2)$$

where  $C_R$  and  $C_S$  are the concentrations (in Bq) in the sorbent before the back extraction and the final concentration (in Bq) in the aqueous phase. While assessing the long-term reusability of the sorbent, the loaded XC material (quantity: ca. 20 mg) was stripped of the sorbed radiotracer and fresh contact was given with the feed. This process of loading and back extraction was repeated for four cycles.

##### 2.5.3. Kinetic modeling of the uptake data

Batch uptake studies were carried out for Pu alone by taking a nearly constant amount of the XC material in several tubes, which contained a known amounts of Pu (0.05 g/L and 0.2 g/L) and the tubes were equilibrated for different time intervals. The amounts of Pu in the supernatant were estimated by radiometry and plotted as a function of time to fit to a pseudo-first order kinetic model as given by the following equation:

$$\ln(q_e - q_t) = \ln q_{\max} - k_1 t \quad (3)$$

or to a pseudo-second order kinetic model as given by the following equation.

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_{\max}^2} + \frac{t}{q_{\max}} \quad (4)$$

##### 2.5.4. Isotherm modeling

The sorption isotherm modeling was done by obtaining the batch uptake data for Pu using nearly the same amount of the XC material taken in each tube, which contained varying amounts of Pu at a constant feed nitric acid concentration (3 M). The data obtained from the uptake studies were fitted to the Langmuir, Freundlich, Temkin, and D-R isotherm models as per the equations given in Table 1.

The radiotracer uptake studies were carried out in triplicate and the results were reproducible within an overall error limit of 5%.

#### 2.6. Column studies

The Pu loading onto a glass column was done for a possible application of the extraction chromatography material. Though the sorbent can be used for both environmental as well as radioactive waste samples, a feed containing a relatively larger amount of Pu (16 g/L) was used for a better capacity utilization point of view. A 4 mm diameter glass column (25 cm length) was used for the column studies including breakthrough and elution profile generation. The column dimensions are given in Table 2.

The glass column was carefully loaded with the XC material after making a slurry with water. Any void in the column bed was

**Table 2**  
Specifications of the column used in this study.

Parameter	TBDGA-ionic liquid XC material
XC material in the column	300.2 mg
Column dimensions	0.4 cm × 24.5 cm
Bed height	8.8 cm
Bed volume	1.106 cm <sup>3</sup>
Bed density	271.43 mg/cm <sup>3</sup>
Flow rate (mL/min)	0.05

**Table 3**  
Batch uptake of the tetravalent actinide ions by the TBDGA XC material from 3 M HNO<sub>3</sub>.

Metal ion	K <sub>d</sub> at 3 M HNO <sub>3</sub>	Ionic potential <sup>b</sup>
Th(IV)	1,219	3.81
Np(IV)	2,315	4.08
Pu(IV)	4,042	4.17
U(VI)	404	– <sup>c</sup>
Am(III)	29,785 <sup>a</sup>	2.75

<sup>a</sup> Data taken from ref. [18].<sup>b</sup> Obtained from the ratio of the charge to ionic radii [30].<sup>c</sup> The ionic potential of uranyl ion is not given here in view of its non-spherical geometry.

removed carefully. The column was conditioned with 3 M HNO<sub>3</sub> by passing about 10 bed volumes of the acid solution. After conditioning, the feed solution was passed through the column at a pre-decided flow rate of 0.05 mL per minute to obtain the breakthrough profiles of the loaded radiotracer with the XC material. The feed solution contained 1.6 g/L Pu in 3 M HNO<sub>3</sub> and about 10 mL of the loaded Pu solution was eluted using a mixture of 0.5 M oxalic acid and 0.5 M nitric acid.

### 3. Results and discussion

The uptake of the metal ions, Th(IV), Np(IV), and Pu(IV), was investigated with the pristine support material (Chromosorb W) and also with the XC material containing only the ionic liquid, but no TBDGA. Almost no uptake could be detected at 3 M HNO<sub>3</sub> (K<sub>d</sub> < 0.01) suggesting that the presence of the ligand in the sorbent was critical for the metal ion uptake.

#### 3.1. Batch uptake studies

The XC material was used for evaluating its batch uptake efficiency towards the tetravalent actinide ions Th(IV), Np(IV), and Pu(IV) from nitric acid medium. As compared to almost no uptake of the metal ions by the pristine support material or the XC material containing only the ionic liquid, the sorbent containing TBDGA resulted in a very large uptake of the metal ions. The K<sub>d</sub> values obtained at 3 M HNO<sub>3</sub> were 1219, 2315, and 4042 for Th(IV), Np(IV), and Pu(IV), respectively, which follow roughly their ionic potential values (Table 3). The comparative uptake of the metal ions by the sorbent was evaluated in more detail by generating the uptake profiles as a function of nitric acid concentration as given below. However, as the Pu(IV) uptake was the most efficient and in view of its strategic importance, most of the subsequent batch and column studies were carried out with Pu only. Table 3 also lists the K<sub>d</sub> values for U(IV) and Am(III) at 3 M HNO<sub>3</sub>. It is clear from the uptake data that, though the tetravalent actinide ions have much higher ionic potential values than the trivalent actinide ion Am(III), the uptake of the latter is much larger. Similarly, while UO<sub>2</sub><sup>2+</sup> ion has a larger effective charge (ca. 3.3 [29]) as compared to that of Am(III) ion, the uptake of the former is about two orders of magnitude lower. This suggests that apart from the electrostatic interaction other factors such as steric factors may be involved. Such

unusual uptake trend of higher uptake of Am(III) vis-à-vis Pu(III) was also reported before [13], though the reason is not understood clearly.

#### 3.2.1. Time taken for the attainment of equilibrium

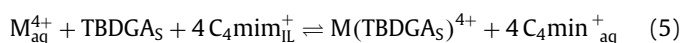
It is known that when ionic liquids are used as the diluent, metal ion extraction takes longer time to attain equilibrium *D* values (in solvent extraction studies) than using molecular diluents [31]. In some cases, containing ionic liquid-based solvents, the attainment of equilibrium *D* values took several hours [32]. It is expected that a similar trend may be prevailing when an ionic liquid-based XC material is used for the metal ion uptake studies. In our previous study, however, using the same XC material, Eu(III) uptake took only ca. 20 minutes to give equilibrium K<sub>d</sub> values.

The K<sub>d</sub> vs equilibration time data for Th(IV), Np(IV), and Pu(IV) are presented in Fig. 2. The results suggest that ca. 30 minutes are needed to obtain steady (or equilibrium) K<sub>d</sub> values for all the three metal ions. This is in sharp contrast to the results presented in case of solvent extraction studies involving ionic liquids as the diluent, which in general have higher viscosity values than molecular diluents [33]. However, for the sake of convenience, the time of equilibration in all subsequent studies was kept constant at 60 minutes.

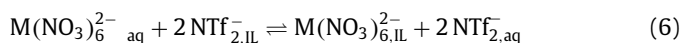
#### 3.2.2. Effect of feed acid concentration

Most of the radioactive feeds, including the high-level liquid waste, involve nitric acid solutions. Therefore, it was thought appropriate to determine the uptake profiles of the metal ions (in terms of the K<sub>d</sub>) as a function of the aqueous phase nitric acid concentration in the range of 0.5 M to 6 M (Fig. 3). In view of the ease of hydrolysis of the tetravalent actinide ions, the uptake studies were not carried out at an acid concentration range <0.5 M [34]. From Fig. 3, several key observations can be made. Firstly, the uptake of the metal ions follows the order: Pu(IV) > Np(IV) > Th(IV), which is observed in the entire range of nitric acid concentrations investigated. Secondly, Th(IV) uptake (as follows from the K<sub>d</sub> values) is almost invariant with the nitric acid concentration. On the other hand, both Np(IV) as well as Pu(IV) show a decreasing trend in the K<sub>d</sub> values from 0.5 M to 2 M HNO<sub>3</sub> while an increase is seen thereafter up to 6 M HNO<sub>3</sub>. This is in sharp contrast to our results on the trivalent *f*-cations such as Eu(III) and Am(III) reported before with the same XC material, where the K<sub>d</sub> values showed a continuous increasing trend in the nitric acid concentration range of 0.01 M to 6 M [18]. While the mechanism of uptake with the trivalent *f*-cations could be considered as purely 'solvation' type, a cation exchange mechanism may be operative in case of these tetravalent actinide ions [31,35]. Billard et al. have shown a similar cation exchange mechanism in case of the extraction of uranyl ion by a solvent system containing TBP (tributyl phosphate) in different ionic liquids [36]. They proposed a cation exchange mechanism at the lower nitric acid concentrations and an anion exchange mechanism at higher nitric acid concentrations (the increase in uranyl ion extraction after reaching a bottom value at 3 M HNO<sub>3</sub>). As TBDGA is also a neutral extractant, like TBP, one may suggest similar extraction mechanisms as per the following extraction equilibria, where the subscripts 'aq', 'S' and 'IL' refer to 'aqueous', 'sorbent' and 'ionic liquid' phases, respectively.

*Cation exchange mechanism:*



*Anion exchange mechanism:*



It is quite clear from Eq. (6) that the extractant in the XC resin plays a minimal role in metal ion uptake at higher nitric acid concentrations and it is the anionic hexanitrate complex of the tetravalent metal ions that will be exchanged with the NTF<sub>2</sub><sup>-</sup> ion

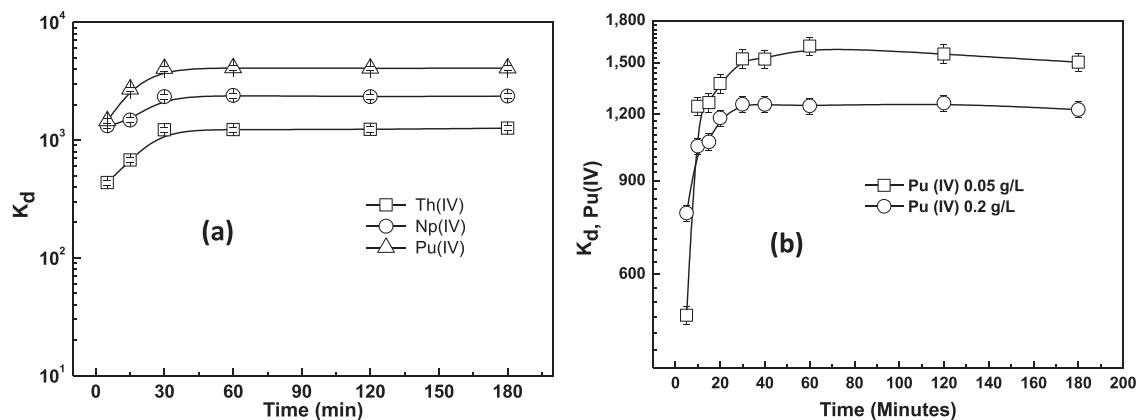


Fig. 2. Uptake of (a) Th(IV), Np(IV) and Pu(IV) in their tracer concentrations and (b) Pu(IV) at higher concentrations from 3 M HNO<sub>3</sub> as a function of equilibration time using the TBDGA + ionic liquid resin.

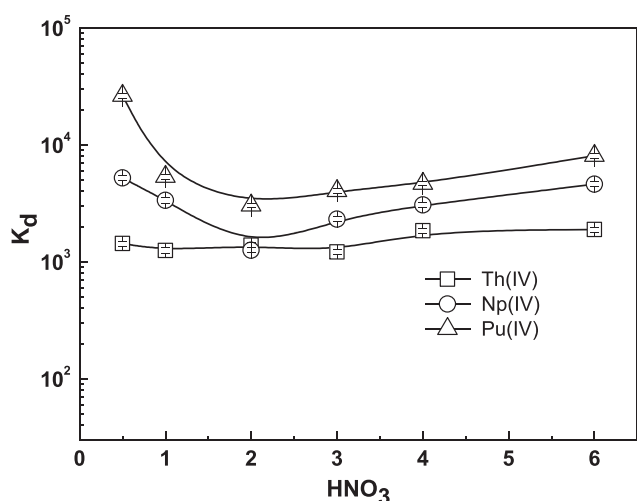


Fig. 3. Uptake profiles of Th(IV), Np(IV) and Pu(IV) as a function of aqueous feed nitric acid concentration using the TBDGA-ionic liquid resin.

Table 4

Solvent extraction of metal ions by the ionic liquid alone (C<sub>4</sub>mim•NTf<sub>2</sub>) from 3 M and 6 M HNO<sub>3</sub>.

Metal ion	D at 3 M HNO <sub>3</sub>	D at 6 M HNO <sub>3</sub>
Th(IV)	<0.01	0.17 ± 0.01
Np(IV)	0.18 ± 0.01	4.16 ± 0.21
Pu(IV)	0.32 ± 0.01	9.96 ± 0.45

present in the ionic liquid. Solvent extraction studies carried out with the metal ions from both 3 M as well as 6 M HNO<sub>3</sub> using only the ionic liquid, resulted in metal ion extraction values (Table 4) which could explain the trend of increasing  $K_d$  values at higher nitric acid concentrations as observed in Fig. 3. As there was a very low extraction of Th(IV) at 6 M HNO<sub>3</sub>, the  $K_d$  vs [HNO<sub>3</sub>] graph indicated a flat profile. On the other hand, the extraction of Np(IV) as well as Pu(IV) was quite significant at 6 M HNO<sub>3</sub>, the latter being much higher, which is also reflected in their uptake profiles by the XC material. Therefore, there could be a significant amount of anionic species present for Pu(IV), somewhat lesser for Np(IV), which may be getting extracted by the sorbent at higher nitric acid concentrations on the basis of the anion exchange mechanism given by Eq. (6).

Table 5

Back extraction (%BE) of the tetravalent actinide ions by some of the commonly used stripping agents.

Stripping agent	%BE
0.5 M oxalic acid	78.1
0.5 M oxalic acid + 0.5 M nitric acid	81.9
0.1 M hydroxylamine + 1 M nitric acid	1
0.1 M HEDTA + 0.25 M nitric acid	0.35

### 3.2.3. Back extraction and reusability

After the uptake studies, it was pertinent to recover the loaded metal ions by back extraction. However, as mentioned above, the back extraction studies were carried out using only Pu(IV). Several stripping agents viz. i) oxalic acid, ii) a mixture of oxalic acid and nitric acid, iii) a mixture of hydroxylamine and nitric acid and iv) a mixture of HEDTA (*N*-(2-hydroxyethyl)ethylenediamine triacetic acid) and nitric acid were used for the back extraction of Pu(IV) and the results are presented in Table 5.

It is well known that Pu(IV) can be reduced to Pu(III) as e.g. performed by Kazi et al. using TiCl<sub>3</sub> as a reducing agent [19]. However, as the trivalent actinide ion also has a much larger uptake as demonstrated previously [18], it was not considered appropriate to use a reducing agent. However, for completion sake, a more commonly employed reducing agent for Pu, i.e., hydroxylamine was used. As clear from the data presented in Table 5, it was not at all effective as a stripping agent. HEDTA, a complexing agent reported to be quite effective for the stripping of actinide ions including Pu(IV) [37], was also used for the back extraction of Pu. However, the results are not encouraging as only 0.35% of the loaded Pu(IV) was back extracted. On the other hand, a complexing agent such as oxalic acid and its mixture with nitric acid was much more effective. In view of the significantly high stripping of the loaded Pu(IV) onto the TBDGA-based XC material, this was used for all subsequent studies including the column studies.

In a subsequent related study to assess the long-term reuse of the XC material, the uptake and stripping cycle was repeated four times; the data are presented in Fig. 4. As seen from the figure, the % extraction is still >80% after four cycles of operations, suggesting that the sorbent can be effectively used for multiple times for Pu(IV) separation from nitric acid feed conditions. As the data presented here are batch uptake data, even an uptake >80% can be translated to ca. 100% when operated in a column mode considering the presence of many theoretical plates in a column [38].

The radiolytic stability of the XC material was also studied by irradiation with a <sup>60</sup>Co gamma irradiator (dose rate: 4 kGy/h) to

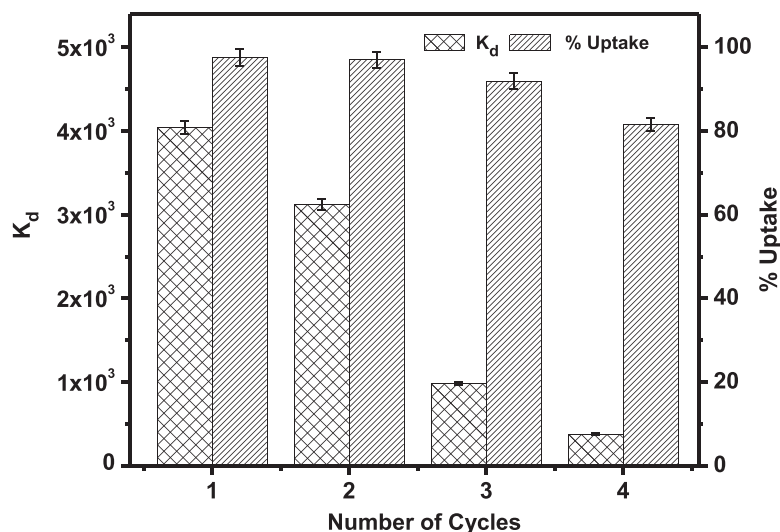


Fig. 4. Reusability of the resin: four cycles of extraction and back extraction.

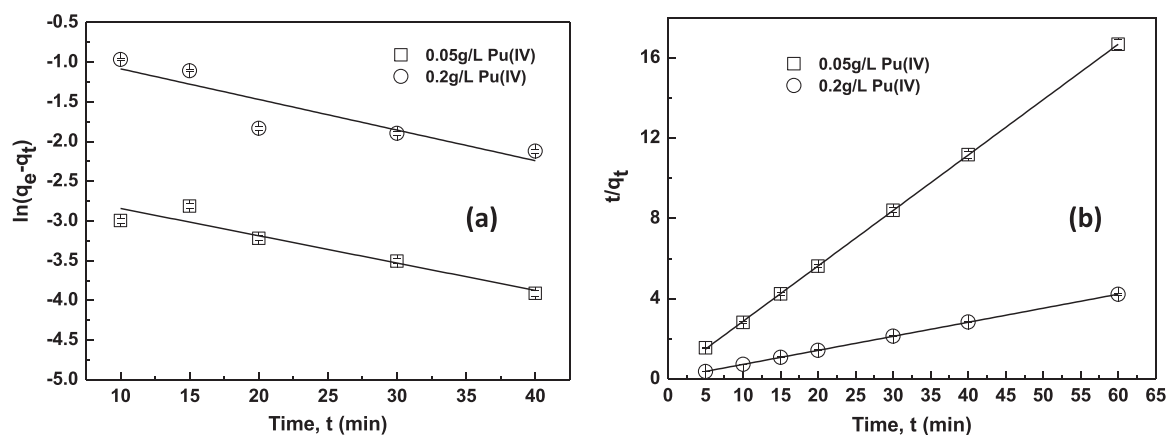


Fig. 5. Kinetic modeling of the Pu(IV) uptake data as a function of equilibration time. The data points are fitted to straight line plots for the (a) pseudo-first order and (b) pseudo-second order equations.

Table 6

Radiolytic stability of the XC material as observed by the decrease in the  $K_d$  values at 3 M  $\text{HNO}_3$ .

Metal ion	$K_d$ values	
	0 kGy	300 kGy
Np(IV)	$2315 \pm 115$	$882 \pm 44$
Pu(IV)	$4042 \pm 181$	$2118 \pm 102$
Th(IV)	$1219 \pm 61$	$562 \pm 28$

an absorbed dose value of 300 kGy. The results are presented in Table 6 showing a significant decrease (ca. 40–50%) in the  $K_d$  values for the metal ions. However, the  $K_d$  values are still quite high for obtaining very good separations, as  $K_d$  values as low as 30–50 have been used for metal ion recovery from feeds [24,39].

### 3.2.4. Kinetic modeling of the Pu(IV) uptake data

The effect of contact time on the Pu(IV) ion uptake was studied by carrying out the studies at three different initial Pu(IV) concentrations, viz. tracer concentration ( $\sim 10^{-6}$  M), 0.05 g/L, and 0.2 g/L. The uptake profiles as represented by the  $K_d$  values are presented in Figure 2b. As seen from the figure, initially fast uptake ( $q_t$ ) was seen which attained a constant value after 30 minutes.

The kinetic modelings of these data were carried out and are presented in Fig. 5.

The correlation coefficient ( $R^2$ ) values are very poor (0.881 for 0.05 g/L Pu and 0.760 for 0.2 g/L Pu) in the case of the pseudo-first order kinetic model fitting. On the other hand, the pseudo-second order kinetic model appears to be valid for the present case with much improved correlation coefficient values (0.999 for both 0.05 g/L and 0.2 g/L Pu). This suggests that there is chemical interaction between the sorbent (the XC material) and the sorbate (Pu(IV)), which is the mainstay of the uptake process. A similar applicability of the Ho's kinetic model was reported in the literature for other analogous systems [40–42].

### 3.2.5. Sorption isotherms

The data of the Pu(IV) uptake studies carried out at different amounts of Pu in the aqueous phase were subjected to fitting to different isotherm models viz. Langmuir, Freundlich, Dubinin-Radushkevich (D–R), and Temkin as per the linear equations given in Table 2. The saturation uptake of Pu(IV) was found out to be  $69.1 \pm 1.2$  mg/g of sorbent by carrying out batch uptake studies using 25 mg of the XC material in a stoppered tube with 1 mL of feed solution containing 1.6 g Pu/L in 3 M  $\text{HNO}_3$ .

The uptake data when fitted to the Langmuir adsorption isotherm model, i.e., plotted as  $C_e/q_e$  vs.  $C_e$ , resulted in straight line plots as shown in Fig. 6a. The very good linear fitting with  $R^2$  value

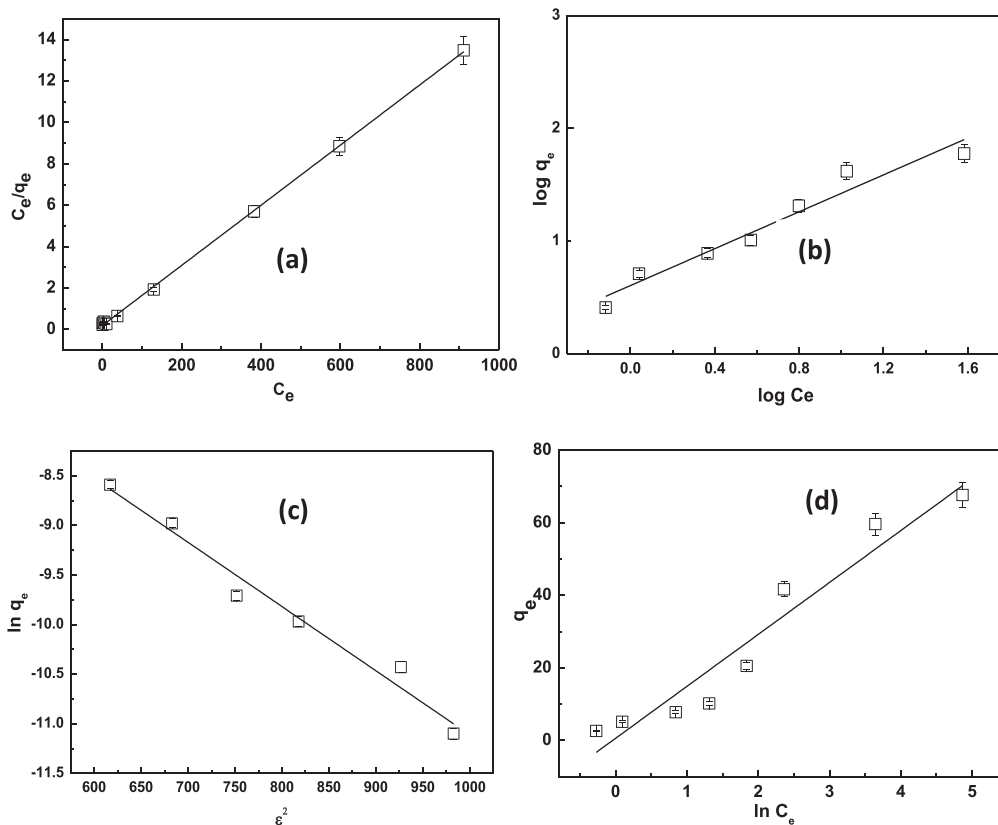


Fig. 6. Pu(IV) uptake data fitted to the linearized forms of (a) Langmuir, (b) Freundlich, (c) D-R, and (d) Temkin sorption isotherms.

Table 7

Summary of results obtained from the Pu(IV) uptake isotherm data fitted to various models.

Isotherms	Parameters	Values at 25°C
Langmuir	$b$ (mL/mg)	$0.08 \pm 0.01$
	$q_{\max}$ (mg/g)	$68.8 \pm 1.1^a$
	$R^2$	0.999
Freundlich	$K_f$ (mg/g)	$4.02 \pm 0.06$
	$n$	$1.22 \pm 0.08$
	$R^2$	0.943
D-R	$X_m$ (mmol/g)	$(9.6 \pm 0.3) \times 10^{-3}$
	$E$ (kJ/mole)	$8.8 \pm 0.4$
	$R^2$	0.969
Temkin	$A_T$	$1.04 \pm 0.02$
	$B_T$	$14.3 \pm 1.5$
	$R^2$	0.925

<sup>a</sup> Experimentally obtained  $q_{\max}$ :  $69.1 \pm 1.2$ .

of 0.999 suggests that the metal ion sorption conforms to the Langmuir sorption monolayer model. The  $q_{\max}$  value from the slope of the straight-line plot in Fig. 6a was calculated as  $68.8 \pm 1.2$  mg/g of XC material, which matches very well with the data obtained by the batch method (vide supra). The parameter 'b' is related to the dimensionless equilibrium constant  $R_L$ , which is used to evaluate the favourability of the Langmuir isotherm model [25].

$$R_L = 1/(1 + bC_0) \quad (7)$$

For reversible reactions,  $R_L > 1$  indicates an unfavourable reaction, while a favourable reaction is assumed by  $0 < R_L < 1$ . On the other hand,  $R_L = 0$  suggests an irreversible reaction. From a b value of  $0.08 \pm 0.01$  (Table 7), and from the  $C_0$  value (Pu concentration in the feed: 1.6 mg/mL), an  $R_L$  value of 0.887 is calculated, suggesting a favourable reaction.

The uptake data were also fitted to the other three isotherm models, viz. Freundlich, D-R, and Temkin and the results are presented in Fig. 6b-d, respectively. It is clear from the plots that the fittings are much inferior to that obtained for the Langmuir isotherm modelling. The  $R^2$  values are 0.944, 0.969, and 0.926 for the Freundlich, D-R, and Temkin isotherm models, respectively, and hence, no further data analysis was done.

### 3.4. Column studies

Even though the batch uptake data are highly promising, an actual application of the XC material can be certified only after a suitable column study. For this purpose, a glass column of the dimensions mentioned in Table 2 was used. A feed solution containing 1.6 g/L Pu in 3 M  $\text{HNO}_3$  was passed through the column.

The breakthrough profile of Pu loading onto the column is presented in Fig. 7a. About nine bed volumes are needed to get the breakthrough of Pu from the column. This can be easily calculated that about 53 mg of Pu is loaded per g of the XC material. This is somewhat lower than the capacity obtained from the Langmuir isotherm (Table 7). One reason to attribute this discrepancy is the competition from nitric acid to bind with the DGA molecule. From the feed concentration of Pu, it can be calculated that ca.  $5.5 \times 10^7$  cpm of the Pu activity was loaded onto the column. Subsequently, the loaded activity was eluted using a mixture of 0.5 M oxalic acid and 0.5 M nitric acid. Fig. 7b shows a sharp elution peak and 99.9% of the loaded Pu could be recovered from the column in about seven bed volumes (ca. 8 mL). The results are quite promising and suggest that the TBDGA sorbent-based column can be efficiently used for the separation of Pu from acidic radioactive feeds.

The column performance is compared with other such separation studies reported before and the results are presented in Table 8. From these reported methods, the Pu recovery is much

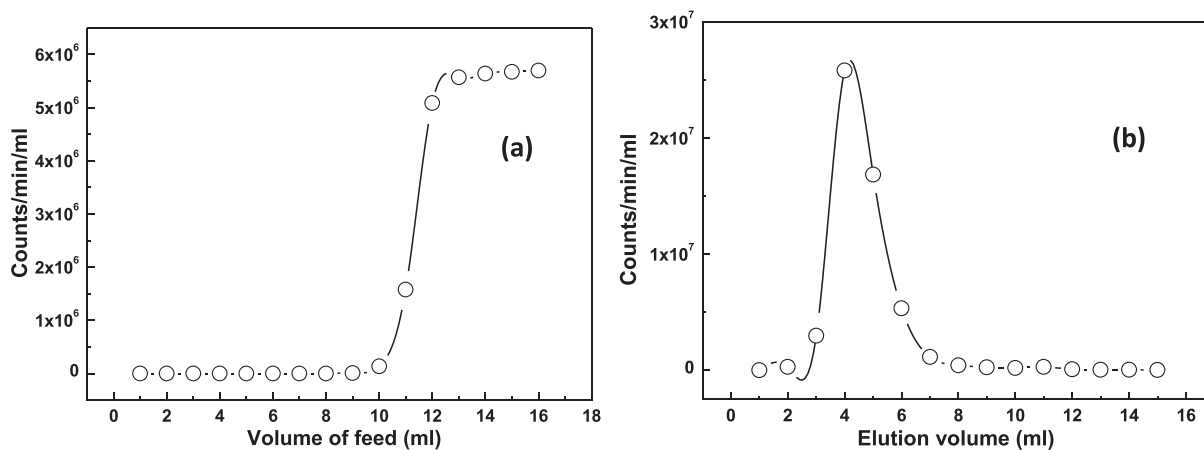


Fig. 7. Column study results (a) breakthrough and (b) elution profiles using 1.6 g/L Pu in 3 M HNO<sub>3</sub> as the feed and a mixture of 0.5 M oxalic acid and 0.5 M nitric acid as the eluent.

Table 8

Comparison of the performance of the TBDGA-based XC material used in the present study with those reported in the literature for the recovery of Pu.

Extraction chromatography resin	Eluent	Comment	Ref
TRU resin	0.4 M HCl + 0.1 M hydroquinone	Slow elution. 70–80% Recovery.	[43]
UTEVA resin	0.02 M ascorbic acid + 0.02 M NH <sub>4</sub> OH•HCl	95% Recovery.	[44]
CMPO resin	0.5 M acetic acid or 0.05 M ascorbic acid + 0.05 M HNO <sub>3</sub>	99.9% Elution. The elution volume is very high (ca. 20 mL) (column volume about 0.4 mL)	[45]
UTEVA resin	2 × 10 <sup>-3</sup> M ascorbic acid + 2 × 10 <sup>-3</sup> M NH <sub>4</sub> OH + 2 M HNO <sub>3</sub>	>90% Pu recovery. Fast elution.	[46]
DGA resin	0.02 M TiCl <sub>3</sub> in 0.1 M HCl	95.5% to 99.1% recovery depending on sample. Large elution volume (ca. 15 mL was needed).	[19]
TBDGA-RTIL resin	0.5 M oxalic acid + 0.5 M nitric acid	99.9% Elution. Relatively low elution volume needed.	This work

lower in case of the commercial TRU and UTEVA resins. On the other hand, while the CMPO (carbamoylmethyl phosphine oxide) resin resulted in a very good recovery, the elution volume is quite large affecting the efficiency of the method. Similarly, the commercially available DGA resin (which contains the analogous TODGA as the extractant) also gives 99.9% recovery but needs large elution volumes. Surprisingly, the authors have used a reducing agent to convert Pu(IV) to Pu(III) and reported elution, while Am(III), which is analogous to Pu(III), could be loaded onto the column. In comparison, the present XC material gave rise to a very high recovery rate (99%), as well as a much lower elution volume as indicated by the sharp elution peak (vide supra). This suggests that the TBDGA-RTIL resin, used in the present study, is quite effective for the Pu separation from acidic feeds, as it shows 99.9% recovery as well as fast elution.

#### 4. Conclusions

A TBDGA-based XC sorbent, containing an ionic liquid (C<sub>4</sub>mim•NTf<sub>2</sub>), was evaluated for Pu(IV) ion uptake from acidic feeds and the batch uptake data were compared with those obtained for Th(IV) and Np(IV) ions. The XC material showed preference for Pu(IV) ion uptake in accordance with the extraction mechanisms common for ionic liquid-based extraction systems. The loaded metal ion can be very easily back extracted using a mixture of 0.5 M oxalic acid and 0.5 M nitric acid. Based on these results, a column was set up and tested for the uptake and elution of the Pu(IV) ion. The recovery was ca. 99.9% using only seven bed volumes suggesting a very good efficiency of the extraction chromatography material. The reusability and radiolytic stability data indicate that the sorbent can be used for processing radioactive wastes. The results reported in this paper are superior to those re-

ported in the literature and it can be claimed that the column can be effectively used for the recovery of Pu from acidic radioactive feeds.

The Pu(IV) uptake data were modeled using pseudo-first and pseudo-second order kinetic models. It was found that the latter was operative conforming to a chemisorption model. The Pu(IV) uptake data were also fitted to various sorption isotherm models out of which the Langmuir monolayer sorption model was found to be operating with chemisorption as the mechanism for metal ion uptake by the XC material.

#### Credit author statement

- 1 Akalesh G. Yadav: Experiments
- 2 Rajesh B. Gujar: Data analysis
- 3 P.K. Mohapatra: Plan of experiments, Paper writing
- 4 T.P. Valsala: Facilitator
- 5 D.B. Sathe: Facilitator
- 6 R.B. Bhatt: Facilitator
- 7 W. Verboom: Manuscript preparation

#### Declaration of Competing Interest

The authors declare no conflict of interest.

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