



Highly efficient plutonium scavenging by an extraction chromatography resin containing a tetraaza-12-crown-4 ligand tethered with four diglycolamide pendent arms

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ABSTRACT

An efficient extraction chromatography resin, containing tetraaza-12-crown-4 functionalized with four diglycolamide moieties, was evaluated for the separation of plutonium. This chromatography resin yielded very large distribution coefficients for Pu⁴⁺ (>10⁵) in 0.5 – 6 M HNO₃ feed solutions. Various physico-chemical properties such as sorption kinetics, Pu⁴⁺ sorption mechanism, and its sorption capacity were investigated. The sorption kinetics, following a pseudo-second-order model, showed that about 10 minutes of equilibration was sufficient for >99.9% sorption of Pu⁴⁺. The sorption of Pu⁴⁺ on the resin followed the Langmuir monolayer model, which was confirmed by a theoretical calculation based on the kinetic model. The Pu⁴⁺ sorption on the resin was driven by a large exothermic enthalpy change ($\Delta H = -31.4 \pm 2.2$ kJ/mol) and a positive entropy change ($\Delta S = 224 \pm 15$ J/mol/L). The resin could sorb a maximum of 12.1 ± 0.8 mg of Pu per gram of resin, which is equivalent to 1:2 metal/ligand complex on the resin. The Pu⁴⁺ from the resin phase was completely stripped with 0.5 M oxalic acid. A possible application of this resin for the separation / pre-concentration of Pu⁴⁺ was successfully demonstrated in the column mode.

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1. Introduction

Radioactive waste management is one of the most challenging tasks in the nuclear fuel cycle. Innovations in the processing of acidic wastes such as the high level liquid waste (HLLW) has attracted maximum interest of researchers in recent times [1]. Though TBP (tri-*n*-butyl phosphate) can extract U and Pu from the spent nuclear fuel dissolver solution as in the PUREX (Plutonium Uranium Redox Extraction) process, extraction of the trivalent actinide ions such as Am³⁺ and Cm³⁺ is not possible [2]. Subsequent R&D efforts have led to the synthesis of several extractants, viz. CMPO (carbamoylmethyl phosphine oxide) [3], DIDPA (diisodecyl phosphoric acid) [4] and malonamides [5], which can extract the

minor actinides from the PUREX raffinate concentrate, also known as the HLLW (high-level liquid waste), leading to the genesis of the strategy termed as 'Actinide Partitioning' [6–8]. Out of these, the malonamides are considered 'green' in view of their complete incinerability. Subsequently, diglycolamides (DGA), a modified version of the tetra-alkyl malonamides, have been found to be the most efficient version of all such extractants used for actinide partitioning [9].

Multiple DGA extractants containing calix[4]arene [10] or pillar[5]arene [11] scaffolds have been found to be much more efficient extractants than the commonly used DGA extractants such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) or T2EHDGA (*N,N,N',N'*-tetra-2-ethylhexyl diglycolamide) [12–15]. Subsequently, a host of other multiple DGA ligands were evaluated with tripodal configurations with a carbon centre [16], a nitrogen centre [17], and a benzene centre [18] with varying degrees of extraction efficiencies and selectivities. Recently, a tetraaza-macrocycle based multiple DGA ligand with four DGA moieties was found to be the

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most efficient extractant out of all classes of multiple DGA ligands [19]. This ligand, with a tetraaza-macrocycle at the core and four DGA moieties linked to the N-atoms, termed as TAM-4-DGA, was found to be quite effective for Pu⁴⁺ extraction [20].

The above mentioned multiple DGA ligands are considered exotic in nature and would cost much more than simple DGA ligands such as TODGA. In such cases, extraction chromatography can be used as the separation method where a porous solid support is coated with the ligand. It can act as a hybrid technique where the selectivity of the solvent extraction and the column mode operation of the chromatography can be made use of in a manner similar to that in many solid phase extraction methods [21–24]. We have recently developed an extraction chromatography method using TAM-4-DGA and evaluated the uptake possibility of Eu³⁺ from acidic feed solutions [25]. The results were highly encouraging and hence, it was thought of interest to use this resin for the uptake of Pu⁴⁺ from acidic feed solutions. It is quite logical to separate Pu from acidic feeds such as analytical laboratory waste operating in the nuclear industries, in which there are significant amount of Pu are accumulated. Pu, due to its strategic nature and possible use in fast breeder reactors and also as a power source, is one of the most important actinide elements and its recovery using novel separation methods is attracting a great deal of R&D attention.

In the present work, Pu⁴⁺ uptake studies were taken up from dilute HNO₃ solutions using the TAM-4-DGA-based extraction chromatography resin. Apart from batch uptake studies, column studies were carried out using a feed containing 128 μg/mL Pu. The uptake data were fitted to various kinetic and sorption isotherm models. As will be seen below, the results are highly promising and, to our best knowledge, the best reported for Pu⁴⁺ uptake onto an extraction chromatography resin.

2. Experimental details

2.1. Materials

Diglycolamide-functionalized tetraaza-12-crown-4 ligand (TAM-4-DGA, Fig. 1), having 4 DGA units with terminal octyl groups, was prepared by following the earlier described procedure [19]. Other chemicals such as *n*-dodecane (Lancaster, UK), *iso*-decanol (>99%) and Suprapur nitric acid (Merck, Germany) were used as received. The solid support, Chromosorb-W (Johns Manville, USA, particle size: 175 – 250 μm), was thoroughly washed with acetone / water and dried in a vacuum oven at 60 °C before its use. A stock solution of Pu (0.2 mg/mL) was used from the laboratory stock after confirming its radiochemical purity. During the entire study, the oxidation state of Pu was adjusted to the +4 state by adding 0.05 M NaNO₂ (as a reducing agent) and 0.005 M NH₄VO₃ as the holding oxidant for Pu.

2.2. Preparation of impregnated resin

The TAM-4-DGA impregnated extraction chromatography resin was prepared by following a method described earlier [26]. In a

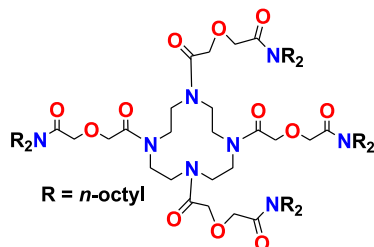


Fig. 1. Chemical structure of TAM-4-DGA

100 mL stoppered conical flask, TAM-4-DGA ligand (0.7 g) was first dissolved in 5% *iso*-decanol / *n*-dodecane (1.5 g) and 5 mL acetone. To this clear solution, 2.52 g Chromosorb-W was added. Due to excellent radiation stability and large porosity, Chromosorb-W was the choice of as an inert solid support in this work. Finally, enough acetone (about 20 mL) was added to the flask to make a slurry. This slurry was then agitated in a mechanical shaker for 24 h. On the following day, the acetone from the slurry was flushed out carefully with the help of nitrogen gas. The impregnated resin was finally dried at 60 – 80°C under vacuum to get a free-flowing product. The loading of TAM-4-DGA onto the Chromosorb-W was 96.9 μmoles per g of resin. Detail characterization of the impregnated resin was done by thermal gravimetry, FT-IR spectroscopy, SEM and EDX techniques and the results have been given in our earlier publication [25].

2.3. Measurement of distribution coefficient

The distribution coefficient (K_d) of Pu⁴⁺ on the resin was obtained by shaking 1 mL of aqueous solution containing Pu tracer at a given acidity with about 10 mg of resin. The shaking was done in an equilibration tube rotated vertically in a thermostated water bath maintained at 25.0±0.1°C. Kinetics studies suggested that the shaking of aqueous phase with the resin for about 30 minutes was enough for obtaining the equilibrium K_d values (*vide infra*). After shaking, the equilibration tubes were centrifuged and then suitable aliquots (200 μL) of aqueous phases were removed centrifuged again. After second time centrifuge, 50 μL clear particle free aqueous samples were transferred in liquid scintillation vials for gross alpha counting after adding Ultima Gold (Perkin Elmer) scintillation cocktail. For counting, a Hidex liquid scintillation counter (Hidex 300 SL) was used. The K_d values of Pu⁴⁺ was finally calculated as:

$$K_d = \frac{(C_0 - C_e) V}{C_e W}, \text{ mL/g} \quad (1)$$

where C_0 and C_e are the gross alpha counts per unit time per unit volume of the aqueous phase before and after mixing of the resin, respectively, V (mL) is initial aqueous phase volume, and W (g) is the amount of resin used. For each experimental point, triplicate K_d values were obtained, and the relative standard deviations (RSD) on the triplicate measurements were less than 5% for the K_d values between 1 – 5000. However, about 10% RSD were accepted for the K_d values >5000.

2.4. Sorption kinetic measurements

The Pu⁴⁺ sorption kinetic data were obtained at 0.5 M HNO₃. The mixing time of aqueous and resin phases was varied. The amount of Pu⁴⁺ retained on the resin was obtained between 2 – 60 minutes of shaking. Subsequently, the data were treated in different kinetic equations [27,28] such as pseudo-first order (Eq. (2)) and pseudo-second order (Eq. (3)).

$$\ln(q_e - q_t) = \ln q_{\max} - k_1 \cdot t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_{\max}^2} + \frac{t}{q_{\max}} \quad (3)$$

where k_1 and k_2 are the rate constants for pseudo-first order and pseudo-second order rate equations. The amount of Pu⁴⁺ loaded onto the resin at equilibrium and at time t is represented as q_e and q_t , respectively. The kinetic data were also treated with the Elovich model (Eq. (4)) given below [29,30].

$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

Where α and β are the initial sorption rate, and desorption constant, respectively.

2.5. Sorption isotherm studies

The sorption experiments were carried out using Pu^{4+} solutions in the concentration range 0.01 – 0.2 mg/mL at 1 M HNO_3 . (*Caution: Plutonium is a highly radiotoxic element. Extreme care must be taken while handling Pu solutions. It must be handled in a glove box designed for Pu handling*). The percentage Pu^{4+} ion retention ratio (R) by the resin was calculated as [27]:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (5)$$

where C_0 and C_e represent the initial and equilibrium concentrations of Pu^{4+} in solution, respectively. The Pu^{4+} sorption isotherm data were fitted in the following linearized Langmuir isotherm model (Eq. (6)) [27,31] and the Freundlich isotherm model (Eq. (7)) [32,33].

$$\frac{C_e}{q_e} = \frac{[1]}{b \cdot q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

2.6. Column studies

A small glass column (0.4 cm diameter \times 6.9 cm bed height) was prepared by packing 0.2 g of resin, which yielded a bed volume of 0.87 cm^3 and a bed density of 0.23 g/cm^3 . The stock loading solution of Pu was 0.128 mg/mL at 1 M HNO_3 . A constant flow rate of about 4 – 5 drops/min was maintained, and 1 mL feed was passed through the column in about 5 minutes. Preconditioning of the column was necessary and was carried out by passing 2 mL of 1 M HNO_3 . Loading and elution profile was obtained by plotting the amount of metal ions in the effluent versus the volume of solution passed.

3. Results and discussion

3.1. Distribution behavior of Pu^{4+}

To determine the minimum time of equilibration required for equilibrium sorption values, the K_d value of Pu^{4+} was measured at 0.5 M HNO_3 as a function of time. As shown in Fig. 2a, the extraction kinetics for Pu^{4+} was fast and the equilibrium K_d values were

reached within 10 minutes with a maximum K_d value of 9.2×10^5 mL/g. Similar fast extraction kinetics for Eu^{3+} was also reported with this resin, where the K_d values reached equilibrium condition within 15 minutes [25]. The kinetics with TAM-4-DGA was relatively faster as compared to that of multiple DGA-containing ligands impregnated resins such as T-DGA and C4DGA, where about 45 minutes were necessary for reaching the equilibrium K_d values [34]. In this work, a plateau region after 10 minutes of mixing indicated a minimum shaking time that must be given for getting equilibrium K_d values. Accordingly, a minimum of 30 minutes of equilibration time was given for all the subsequent K_d value measurements.

The K_d values of Pu^{4+} by the TAM-4-DGA resin were measured from a wide range of aqueous phase acidities and are shown in Fig. 2b. The K_d values increased with increasing feed acidity from 0.5 – 6 M HNO_3 , the values being very large ($>10^5$) in the entire range. The distribution pattern of Pu^{4+} on the resin is a clear indication of “solvation extraction” mechanism, which is common with neutral DGA ligands like TODGA [21]. Nonetheless, it is evident from the distribution data that Pu^{4+} can be held onto the present resin efficiently from a wide range of aqueous feed compositions without adjusting the feed acidity. However, it may not be possible to back extract the loaded Pu^{4+} from the resin phase with dilute acid of 0.5 M HNO_3 due to the very large K_d values. It was unavoidable, therefore, for using a suitable complexing ligand for the back-extraction of the loaded Pu^{4+} . Looking at the efficient complexation ability of oxalic acid with Pu^{4+} , we used 0.5 M oxalic acid dissolved in 0.5 M HNO_3 as a strippant for Pu^{4+} . The K_d value of Pu^{4+} was <10 with this complexing solution, and therefore, it was used as the eluent for Pu in the column studies (*vide infra*).

3.2. Sorption kinetics for Pu^{4+}

To get an insight into the type of kinetics followed for the uptake of Pu^{4+} on the resin, the kinetic data were treated in various kinetic models described in Eqs. (2)–(4). At first instant, we tried to fit the data with Eq. (2), which yielded a poor fitting (Fig. 3a), indicating the absence of the pseudo first-order rate kinetics. Subsequent fitting of the data in Eq. (3) gave a straight line (Fig. 3b) confirming that pseudo second-order kinetics prevailed in the present case. The value of k_2 was calculated from the slope and the intercept of the linear fit, and was found to be 2.6×10^{-6} g/cpm/min. The value of k_2 for Pu^{4+} is an order of magnitude higher than that observed for Eu^{3+} on the same resin ($k_2 = 6.33 \times 10^{-7}$ g/cpm.min) [25]. This feature is well reflected in the time needed for getting the equilibrium K_d values for Pu^{4+} and Eu^{3+} , where about 10 and 15 minutes were needed, respectively, for reaching the K_d values in the plateau region (*vide supra*).

Fitting of the kinetic data in the second-order kinetic rate model is the sign of chemical interaction between the Pu^{4+} ion in the aqueous phase and the ligand present on the solid support is indeed controlling the sorption process. In other words, Pu^{4+} will form a monolayer on the resin surface where it will be held by chemical bonding with the ligands present on the surface. To understand more into this feature, the kinetic data were fitted in the Elovich model given in Eq. (4), which is a good test for the multilayer sorption process [29,30]. As obvious from Fig. 3c, an irregular pattern of data in the plot obtained from the Elovich model equation manifest that the multilayer sorption phenomenon may be absent in the present case. This was later confirmed by the sorption isotherm studies described later (*vide infra*).

3.3. Sorption isotherm of Pu^{4+} on resin

The sorption isotherm for Pu^{4+} on the resin was secured in the initial Pu concentration range (C_0) of 0.01 – 0.2 mg/mL. As evident

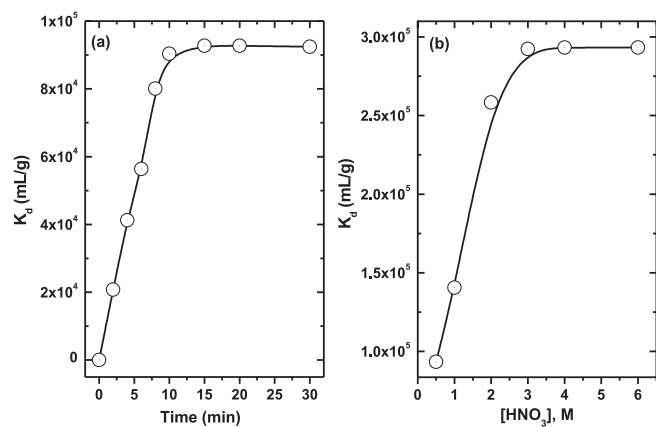


Fig. 2. (a) Variation of the distribution coefficient of Pu^{4+} as a function of time on the TAM-4-DGA resin at 0.5 M HNO_3 . (b) Distribution coefficient of Pu^{4+} as a function of nitric acid concentration by the TAM-4-DGA resin.

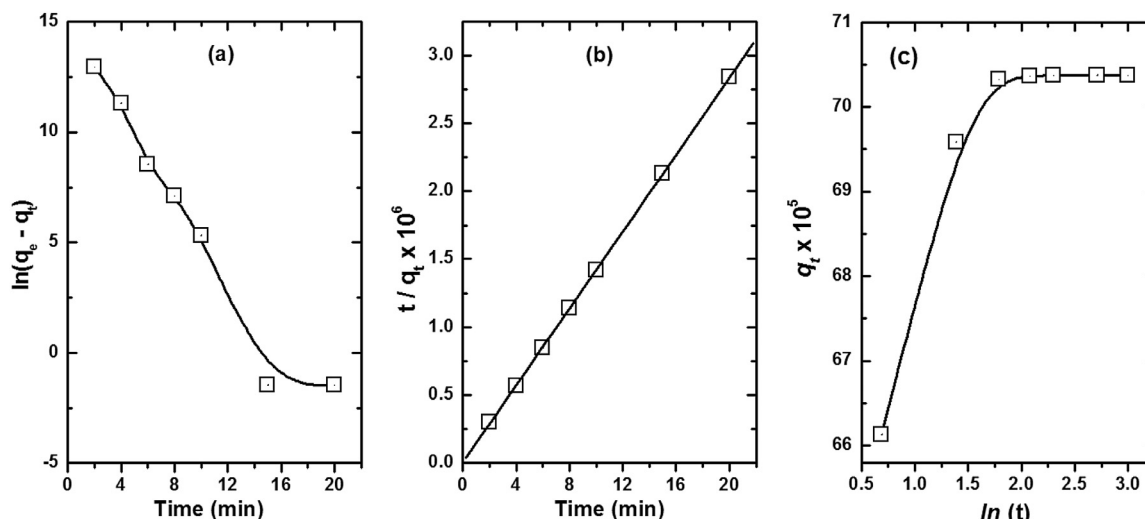


Fig. 3. Plots of (a) first order kinetic model, (b) second order kinetic model, and (c) Elovich kinetic model equations for the sorption of Pu⁴⁺ on TAM-4-DGA resin. Aqueous phase: 0.5 M HNO₃.

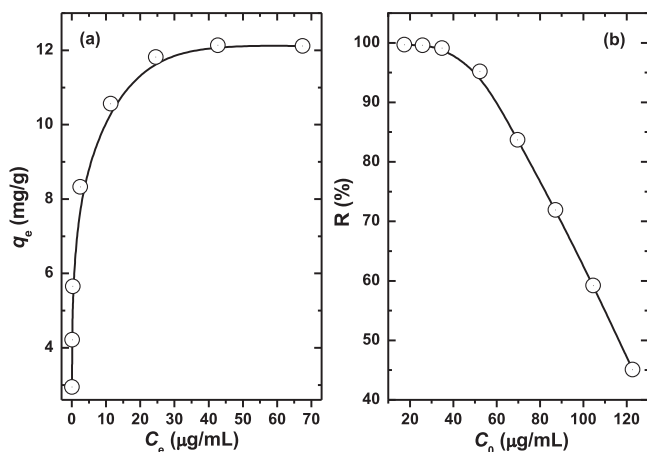
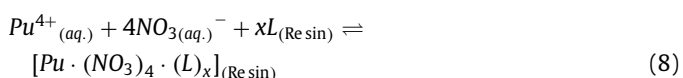


Fig. 4. (a) Sorption isotherm of Pu(IV) on the TAM-4-DGA resin. (b) Influence of initial Pu concentration on its sorption ratio (R).

from Fig. 4a, the maximum sorption capacity of Pu⁴⁺ is 12.1±0.8 mg/g of resin. The variation of the retention ratio R vs. C₀ is depicted in Fig. 4b, which shows that for lower C₀ values, the R value is close to 100%, indicating complete retention of Pu⁴⁺ from the aqueous solution. On the other hand, decrease in the R value with increasing C₀ is an indication that the complexation site on the resin is getting saturated. As the impregnated resin has finite number of ligand complexation sites, once all these sites are occupied the additional Pu⁴⁺ ions will not be retained. The existence of a plateau for R ≈ 45% indicates the final saturation of the resin.

As obtained from the isotherm data, the maximum loading capacity (q_{max}) of Pu⁴⁺ on the resin was 12.1 mg/g of resin, which is equivalent to 50.6 µmoles of Pu/g resin. Since the TAM-4-DGA loading on the impregnated resin was 96.9 µmoles per g of resin, a maximum loading of 50.6 µmoles of Pu indicates the formation of a limiting 1:2 (Pu⁴⁺/ligand) complex on the resin. To confirm this stoichiometry, a detailed investigation was carried out based on the following equilibrium reaction:



Eq. (8) represents a solvation type extraction mechanism, which is very common for the extraction of metal ions from nitric acid medium by neutral ligands like DGAs [9]. Here, the term L represents the ligand TAM-4-DGA, and x is the number of ligand molecules directly bonded with the metal ion. The equilibrium constant (K_{ex}) for the above equilibrium reaction can be written as:

$$K_{ex} = \frac{[Pu \times (NO_3)_4 \times (L)_x]_{(Resin)}}{[Pu^{4+}]_{(aq)} \cdot [NO_3^-]_{(aq)}^4 \cdot [L]^x_{(Resin)}} \quad (9)$$

Introducing the K_d term in the above equation, one gets:

$$K_{ex} = \frac{K_d}{[NO_3^-]_{(aq)}^4 \cdot [L]^x_{(Resin)}} \quad (10)$$

On converting into logarithmic form and on rearrangement, gives:

$$\log K_d = \log K_{ex} + 4 \log [NO_3^-]_{(aq)} + x \log [L]_{(Resin)} \quad (11)$$

In order to get the value of x in Eq. (11) by slope analysis, the K_d value of Pu⁴⁺ was measured by a series of resins containing a varying amount of TAM-4-DGA ligand (0.194 – 0.97 µmol/g) at a fixed nitrate ion concentration of 1 M HNO₃. As shown in Fig. 5, a slope of ~2 confirmed that the composition of the metal/ligand complex on the resin was [Pu·(NO₃)₄·(L)₂].

The sorption isotherm data of Pu⁴⁺ were analysed with two most widely used isotherm models, viz. (i) the Langmuir isotherm, which assumes a monolayer sorption phenomenon, and (ii) the Freundlich isotherm, which points to a multilayer sorption process. The Langmuir model [30] is based on the assumptions that (i) only one layer of adsorbing species occupies the surface, and (ii) all sites of the sorbent are equivalent, and the ability of a species to sorb at a given site is independent to the nature of the neighboring sites. The linearized form of the Langmuir isotherm model is represented by Eq. (6). As conveyed in Fig. 6a, the plot of C_e/q_e vs. C_e resulted in a straight line with excellent fitting correlation coefficient confirming the Langmuir monolayer sorption phenomenon. The graphically calculated value of q_{max} was found to be 12.2±0.2 mg of Pu/g resin. The confidence of the q_{max} value obtained graphically was excellent, as this value was in close agreement with those generated in batch experiments (12.1±0.8 mg/g).

If the sorption of Pu⁴⁺ on the present resin was proceeding via a chemical reaction with the ligand present on the resin surface and it formed a single layer on the resin surface, then the sorption

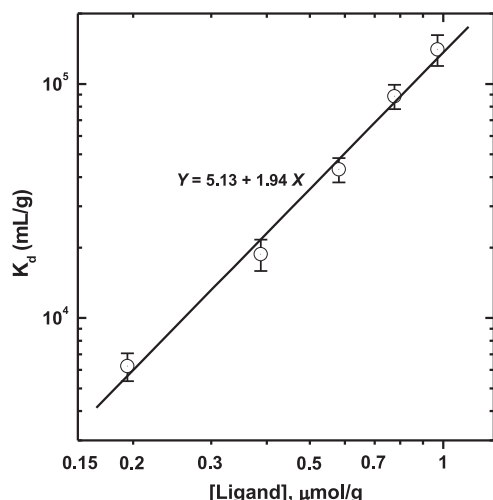


Fig. 5. Effect of ligand concentration on the resin on the distribution coefficient of Pu⁴⁺. Aqueous phase: 1 M HNO₃.

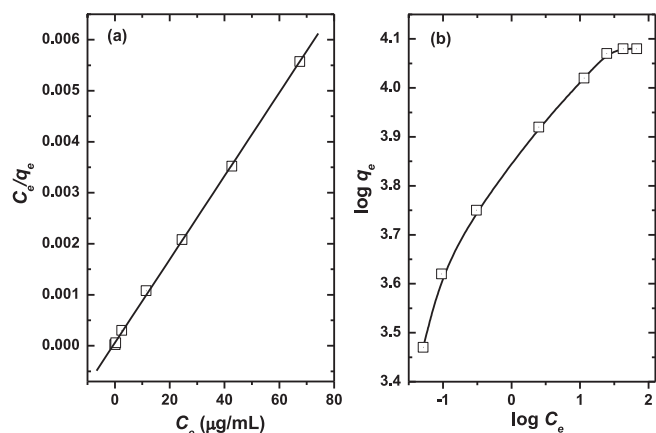


Fig. 6. (a) Langmuir plot and (b) Freundlich plot for the sorption of Pu⁴⁺ onto the TAM-4-DGA resin. Aqueous phase: 1 M HNO₃.

data should deviate from the multilayer Freundlich isotherm model [32,33]. The linearized form of the Freundlich isotherm model is given by Eq. (7). As evident from Fig. 6b, the Freundlich model gave poor fitting, reflecting the absence of the multilayer sorption mechanism. The monolayer sorption mechanism was further evident from a theoretical calculation given below.

3.4. Sorption mechanism of Pu⁴⁺

To further understand the sorption mechanism, a reported theoretical model on sorption kinetics was analyzed [35]. According to this model, if the sorption of Pu⁴⁺ on the resin is a mono-layer process, then its sorption rate on the resin should increase with its concentration available near the resin surface ($q_e - q_t$). In such a case, the rate of sorption should be independent of the contact time, and the sorption equation can be expressed as:

$$\frac{\partial C_t}{\partial t} = K(q_e - q_t) \tag{12}$$

Eq. (12) can be solved as:

$$-\ln \left[\frac{q_e - q_t}{q_e} \right] = K \cdot t \tag{13}$$

where q_e and q_t are the amount of Pu⁴⁺ sorbed at equilibrium and at time t , respectively, and K is the monolayer sorption constant. If

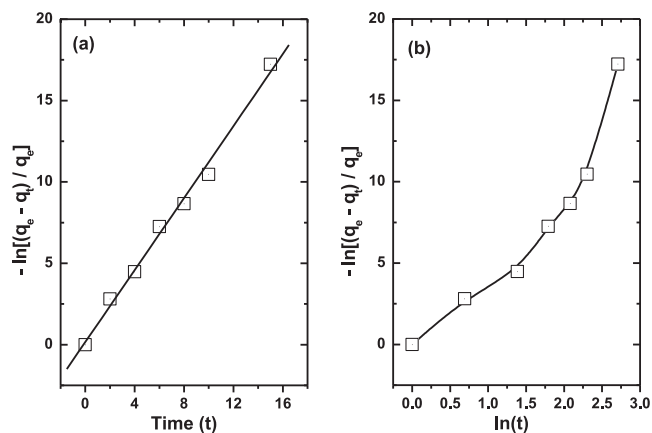


Fig. 7. (a) Relationship between $-\ln[(q_e - q_t)/q_e]$ vs time, and (b) relationship between $-\ln[(q_e - q_t)/q_e]$ vs $\ln t$ for evaluation of the sorption mechanism.

the Pu⁴⁺ sorption on the resin is a monolayer phenomenon, then the plot of $-\ln[(q_e - q_t)/q_e]$ vs. t should be a straight line. As shown in Fig. 7a, the linearity of this plot is evidence that the sorption of Pu⁴⁺ on the resin follows the monolayer mechanism. This observation further corroborates the Langmuir monolayer sorption isotherm. On the other hand, assuming that the sorption of Pu⁴⁺ on the resin was a multilayer phenomenon, then the rate of its sorption should increase with its available concentration ($q_e - q_t$). In such a case, the rate of sorption should decrease with the contact time, and the sorption equation can be expressed as:

$$\frac{\partial C_t}{\partial t} = K_m \left[\frac{(q_e - q_t)}{t} \right] \tag{14}$$

Eq. (14) can be solved as:

$$-\ln \left[\frac{q_e - q_t}{q_e} \right] = K_m \cdot \ln t \tag{15}$$

where K_m is the multilayer sorption constant. If the Pu⁴⁺ sorption on the resin is a multilayer phenomenon, then the plot of $-\ln[(q_e - q_t)/q_e]$ vs. $\ln(t)$ should be a straight line. However, poor fitting of the kinetic data in Eq. (15) (Fig. 7b) indicates that the assumption for multilayer sorption of Pu⁴⁺ onto the resin is incorrect. A similar observation was also exhibited by the Freundlich isotherm model, where nonlinearity of the plot suggested the absence of a multilayer sorption mechanism.

3.5. Thermodynamics of Pu⁴⁺ sorption

The effect of temperature on the distribution coefficient of Pu⁴⁺ on the resin was investigated at 1 M HNO₃. Since the K_d value of Pu⁴⁺ with the resin containing 96.9 μmoles of ligand was very large ($>10^5$), obtaining any significant change in the K_d value by varying the temperature was difficult. It was a judicious choice, therefore, to generate the temperature dependent K_d data with a resin having lower amount of ligand (0.194 μmoles/g). As evident from Fig. 8a, a decrease in the K_d value with increasing temperature is an indication of an exothermic sorption process. For the calculation of the free energy change (ΔG) of the reaction, the equilibrium constant (K_{ex}) as given in Eq. (9) is essential. It was calculated from the measured K_d value and using a value of $x = 2$ in Eq. (10). However, since the activity of the ligand on the resin is unknown, its molar concentration was used for the calculation. Therefore, the calculated K_{ex} value in this work was taken as the 'conditional equilibrium constant'. From the value of K_{ex} the Gibb's free energy change ($\Delta G = -RT \ln K_{ex}$) was calculated to be -98.2 ± 3.8 kJ/mol.

Table 1
Comparative performance of different extraction chromatography resins for Pu⁴⁺ uptake and recovery.

Ligand (% loading) ^a	K _d , Pu ⁴⁺ at 3 M HNO ₃	Highlights	Ref.
TBP (50%)	33.6	88% Pu loaded on column, >99% elution with 0.01 M hydroxylamine	[37]
TOA (50%)	7505	5.4 mg Pu loaded on column, >99% elution with 0.2 M ascorbic acid.	[38]
Aliquat 336 (15%)	1234	Pu loading was negligible when used under reducing condition	[39]
DEHPPr ^b (45%)	167	The Pu uptake was much higher than Np ⁴⁺ and UO ₂ ²⁺	[26]
DMDBTDMAC ^c	~4000	Pu ⁴⁺ uptake was about 2 orders of magnitude higher than that of Am ³⁺	[40]
CMPO (50%)	~3 × 10 ⁵	About 0.6 mg Pu loaded on column, >99% elution with 0.01M oxalic acid	[41]
TODGA (47%)	4969	Pu ⁴⁺ uptake was reported to be much higher than UO ₂ ²⁺ and Am ³⁺ under loading conditions using SHLW ^d	[42]
TAM-4-DGA (15%)	~3 × 10 ⁵	Highest K _d value of Pu ⁴⁺ reported with this resin	This work

Note: ^aPercent extractant loading in the resin

^b Di-2-ethylhexyl-propanamide

^c N,N'-dimethyl-N,N'-dibutyl tetra-decyl malonamide

^d Simulated high level waste

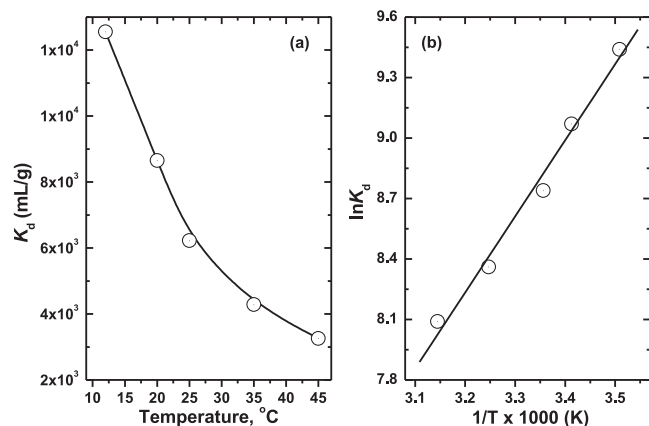


Fig. 8. (a) Relationship between the K_d value of Pu⁴⁺ with the temperature, and (b) Van't Hoff plot for the sorption of Pu⁴⁺ on the resin for the calculation of ΔH .

For the calculation of the enthalpy of the reaction, the following form of the Van't Hoff equation was employed [36]:

$$\ln K_d = - \left[\frac{\Delta H}{RT} \right] + C \quad (16)$$

Where R = the gas constant and C = constant. The value of ΔH was obtained from the slope of the plot of $\ln K_d$ vs. $1/T$ (Fig. 8b), and was calculated to be -31.4 ± 2.2 kJ/mol. The value of the entropy change (ΔS), calculated from the relation $\Delta G = \Delta H - T\Delta S$, was found to be 224 ± 15 J/mol/K. Both the exothermic enthalpy and positive entropy changes are an indication that the sorption of Pu⁴⁺ on the resin was both enthalpy as well as entropy driven.

3.6. Column studies

A column study was performed to examine the possible use of the present resin for the recovery / pre-concentration of Pu from an acidic feed. Fig. 9 shows the loading profile and elution profile of Pu⁴⁺ from the column. A total of 17 mL of the loading solution could be passed without any breakthrough of Pu⁴⁺ from the column. After adjusting the column dead volume (about 1 mL), 2.048 mg Pu could be loaded on the column without any breakthrough. This value corresponds to 10.24 mg Pu/g of the resin in the column. As the resin maximum sorption capacity for Pu was 12.1 mg/g (obtained in the batch experiment), the results indicate that the column dynamic loading capacity was about 85% of the static equilibrium loading capacity of the resin. After loading the column with Pu⁴⁺, the column was washed with 1 M HNO₃ to clear it from any un-complexed Pu⁴⁺. Finally, the loaded Pu⁴⁺ from the column

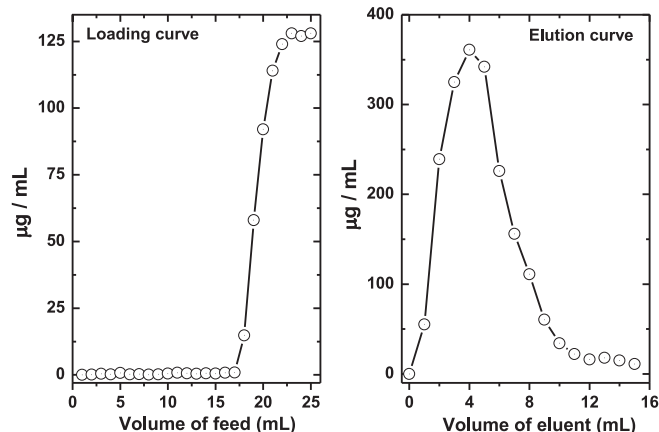


Fig. 9. Loading and elution curves for Pu⁴⁺ on the TAM-4-DGA resin column. Feed solution: 0.128 mg/mL Pu⁴⁺ at 1 M HNO₃; Eluent: 0.5 M oxalic acid in 0.5 M HNO₃. Column dead volume: 1.0 mL.

was successfully eluted within 15 mL of the eluent consisting of 0.5 M oxalic acid in 0.5 M HNO₃. The recovery of Pu was 97.2% indicating a good performance of the column. Use of oxalic acid was rationalized due to its excellent complexing ability for Pu⁴⁺, and a saturated solution of oxalic acid was used for the final precipitation of Pu⁴⁺ and its conversion into PuO₂ solid.

3.7. Comparison with literature reports

The Pu⁴⁺ uptake has also been reported in various other extraction chromatography resins as summarized in Table 1. Though there are many reports where various commercial extraction chromatography columns have been used for analytical applications, we have included results obtained with resins containing a variety of extractants. As seen from the Table, the present extraction chromatography resin contains much lower extractant loading as compared to those used in the literature but yielded the highest K_d value for Pu⁴⁺ reported so far. Though the CMPO based resin was reported to yield comparable K_d values, the extractant loading is more than 3 times larger for the resin and also the elution volumes are reported to be very high [43]. Combined with the very good column performance (*vide supra*), the TAM-4-DGA resin promises to be very useful for separation of Pu from acidic feeds. However, this resin cannot differentiate between the lanthanides, trivalent and tetravalent actinides as evident from the distribution data [25]. That means, this resin cannot be used for the preferential separation of Pu over trivalent actinides (Am, Cm) and lanthanides as such. However, selectivity of Pu⁴⁺ over UO₂²⁺ is very large, so the

resin can be used for preferential separation of Pu over U. Accordingly, in case one can oxidize Am to its +6 oxidation state, as in the SESAME (Selective Extraction and Separation of Americium by Means of Electrolysis) process [44], the separation is feasible.

Credit author statement

P. Banerjee: Experiment
 S.A. Ansari: Planning and data analysis
 P.K. Mohapatra: Conceptualization of problem and manuscript preparation
 R.J.M. Egberink: Synthesis
 T.P. Valsala: Supervision
 D.B. Sathe: Supervision
 R.B. Bhatt: Supervision; Project administration
 J. Huskens: Synthesis
 W. Verboom: Manuscript preparation

4. Conclusions

An efficient chromatographic resin, containing tetraaza-12-crown-4 functionalized with four diglycolamide moieties (TAM-4-DGA), was evaluated for the separation of plutonium from acid solution. The distribution coefficient of Pu⁴⁺ was very high (>1 × 10⁵) in a wide range of acidity (0.5 – 6 M HNO₃). The sorption kinetics was fast, following a pseudo second order kinetic model, and the equilibrium condition was reached within 10 minutes of equilibration. The Pu⁴⁺ sorption on the resin followed a chemisorption phenomenon occupying a single layer on the surface of the resin. The monolayer sorption hypothesis was confirmed by theoretical calculations derived from the kinetic sorption data. The sorption of Pu⁴⁺ was an exothermic process and proceeded with a large positive entropy change. The stoichiometry of the complex sorbed on the resin was identified as 1:2 (metal/ligand), which was in conformity with the Pu loading capacity of the resin. Efficient column separation and pre-concentration of Pu were demonstrated, and the loaded Pu was successfully eluted with dilute oxalic acid solution. In view of the superior performance of the TAM-4-DGA resin, with very large K_d values and promising column performance, it is proposed to be quite useful for the studies involving Pu recovery from nitric acid feed solutions.

Declaration of Competing Interest

Authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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