

Highly Efficient Extraction Chromatography Resin Containing Hexa-*n*-Octyl Nitrilotriacetamide (HONTA) for Selective Recovery of Plutonium from Acidic Feeds

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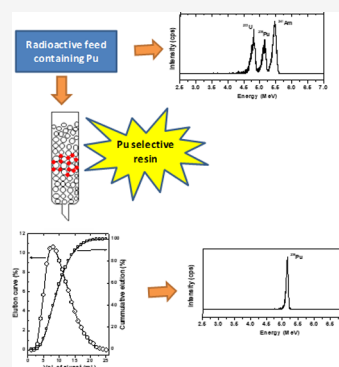
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ABSTRACT: An extraction chromatography resin was prepared by impregnating hexa-*n*-octyl nitrilotriacetamide (HONTA) on chromosorb-W. This resin shows very efficient performance for selective separation of Pu⁴⁺ over other actinides like uranium and americium. The distribution coefficient for Pu⁴⁺ (at 3 M HNO₃) was on the order of 10⁴ mL/g, with separation factors of >10³ for other actinides. The extraction kinetics for Pu⁴⁺ was slow and took 20 min of shaking for reaching the equilibrium conditions and followed both the film diffusion and the intraparticle diffusion kinetic models. The Pu⁴⁺ sorption on the resin followed the Langmuir monolayer model with a sorption energy of 11.2 kJ/mol. The maximum Pu⁴⁺ loading capacity on the resin was 58.2 mg/g resin, which corresponds to 1:1 Pu/ligand complex formation. Excellent column performance was observed for selective separation of Pu⁴⁺ from a mixture of Pu, Am, and U in a 3 M HNO₃ solution.



1. INTRODUCTION

Development and evaluation of suitable ligands for selective separation of plutonium from a mixture of actinides and lanthanides is the focus of many analytical scientists working in the area of the nuclear fuel cycle.^{1–3} To date, the selective separation of plutonium from a mixture of actinides and from a host of other elements in nuclear analytical laboratories has been realized by 2-thenoyltrifluoroacetone (HTTA), a β -diketone extractant.⁴ Here, the valency of Pu is adjusted as Pu⁴⁺ at 1 M HNO₃, followed by its selective extraction in a HTTA phase leaving behind all other tetravalent and hexavalent actinides in the aqueous phase. The main drawback of the HTTA extraction system is the stringent maintenance of the aqueous phase acidity, as the ligand loses its selectivity for Pu⁴⁺ at acidities lower than 1 M HNO₃. In addition, the HTTA loses its extraction power for Pu⁴⁺ at acidities higher than 1 M HNO₃. Therefore, maintaining the aqueous phase acidity is very important for the analytical separation of Pu⁴⁺ by HTTA. To overcome this issue, any ligand which can selectively extract Pu⁴⁺ from a wide range of acidities will be much desired. In this connection, a series of nitrilotriacetamide ligands were studied for selective separation of tetravalent actinides over lanthanides and actinides in other oxidation states.⁵ Nitrilotriacetamides, having three amide moieties attached to a tripodal N atom, show very good selectivity for tetravalent actinides.^{6,7} It was found that a nitrilotriacetamide ligand with *n*-octyl groups on the amidic nitrogens (HONTA, Figure 1) exhibits a very high extraction ability and selectivity for Th⁴⁺ in a wide range of

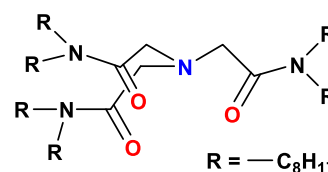


Figure 1. Structure of HONTA.

aqueous phase acidities (0.10–10.0 M HNO₃).⁸ The separation factor for Th⁴⁺ with respect to trivalent lanthanides was as high as 1000. Further studies confirmed that HONTA also has a very good extraction ability for Pu⁴⁺ but a very poor one for UO₂²⁺ and Am³⁺ at 3 M HNO₃.⁹ Therefore, several studies were performed to understand its complexation behavior with trivalent actinides and lanthanides.^{10,11} Solvent extraction studies were also reported with HONTA for separation of tetravalent actinides (Th and Pu) over trivalent actinides and lanthanides with reasonably good results.^{12,13}

Though solvent extraction-based separation methods are extensively used by the nuclear industry, it is desirable to use other alternative separation techniques where the organic

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solvent inventory is low. One such alternative technique is extraction chromatography, which is particularly interesting for pre-concentration of tiny amounts of any species of interest present in very large solution volumes.^{14,15} In such cases, extraction chromatography in column mode would be a better choice looking at its ease of operation and the extremely low inventory of ligands. In view of the good selectivity for tetravalent actinides over other actinides and lanthanides, HONTA has been studied in solvent extraction with very encouraging results.^{12,13}

In this work, an extraction chromatography resin was prepared by impregnating HONTA/*n*-dodecane solution on chromosorb-W. Detailed studies were taken up to evaluate the separation of Pu⁴⁺ from acidic solutions. Batch distribution data for Pu⁴⁺ ions were analyzed in various kinetic and isotherm models to understand the interaction of metal ions with the ligand present on the solid support. The radiation stability and recycling performance of the resin were investigated in detail. Apart from batch studies, column studies were performed using a feed solution containing 100 μg/mL Pu. The column separation of Pu from a mixture of Pu, Am, and U was successfully demonstrated.

2. EXPERIMENTAL SECTION

2.1. Materials. Hexa-*n*-octyl nitrilotriacetamide (HONTA, Figure 1) was synthesized as described in our earlier publication.¹⁶ The solid support, chromosorb-W (dimethyl dichlorosilane-treated acid-washed celite diatomaceous silica), was purchased from John Manville. The particle size of the solid support was 100–120 μm (60–80 mesh size). This solid support was thoroughly washed with distilled water, ethanol, and acetone, followed by air-drying before its use. Actinide tracers, ²³³U, ²³⁹Pu, and ²⁴¹Am, were used from the laboratory stock after their purity check by α-spectrometry. All of the other reagents used were of analytical reagent grade and were used without further purification.

2.2. Preparation of Impregnated Resins. The extraction chromatographic resins were prepared by impregnating HONTA on chromosorb-W. In a 100 mL glass stoppered conical flask, 1.0 g of HONTA and 1.0 g of 5% iso-decanol/*n*-dodecane were weighed. To this flask, about 50 mL of acetone was added to dissolve the ligand. Subsequently, 3.0 g of washed and dried chromosorb-W was added to the flask. The resultant slurry was equilibrated for 24 h in a mechanical shaker, followed by solvent removal by flushing nitrogen gas with gentle stirring. The final impregnated resins were dried at 120 °C to constant weight. The weight percentage of the ligand loaded on the resins was calculated from the difference in the weight of the resin before and after equilibration and was found to be 21.2% w/w (Table 1). The loading percentage of the extractant was also confirmed by thermal analysis.

2.3. Distribution Studies. Measurement of the distribution coefficient (K_d) of actinides was done by shaking 10 mg of resin with 1 mL of aqueous phase in a glass stoppered tube. The aqueous phase of desired acidity was prespiked with the radiotracers. The mixing was realized by vertical rotation of the tube submerged in a thermostated water bath maintained at 25 ± 0.1 °C. After mixing, the aqueous phase was separated after centrifuging the tube. The separated aqueous phase was centrifuged a second time to remove any traces of resin particles. For assaying the radiotracers in the aqueous phase, a suitable volume of the aqueous phase was collected initially and after mixing with the resin. An assay of ²³³U and ²³⁹Pu

Table 1. Properties of the HONTA Chromatography Resin Column

Resin Material	
Stationary phase	HONTA
Support material	chromosorb-W
Particle size	100–150 μm
Ligand loading on resin	250 μmol/g
Liquid loading on resin	40% (w/w)
Average density of resin	0.850 g/mL
Packed Column	
Resin weight	0.40 g
Bed height	10.6 cm
Bed volume	1.33 mL
Bed density	0.30 g/mL

radiotracers was performed by using a liquid scintillation counter using a DIN (di-isopropyl naphthalene) based scintillator (Gold Star Cocktail from Triskem, France). The K_d value of actinide ions on the resin was calculated as

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

where C_0 and C are the concentrations of actinide ions (in terms of dpm per unit volume) before and after equilibration, respectively. The terms V and W represent the volume of the aqueous phase used (mL) and the weight of the resin material employed (g), respectively. The entire K_d measurements were performed in triplicate, and the accepted data were within the limit of 5% relative standard deviation.

2.4. Kinetic Studies. Time-dependent K_d values of Pu⁴⁺ were determined by keeping the shaking time between 2 and 60 min. The activity of ²³⁹Pu sorbed per g of resin was then calculated, and the data were treated with different kinetic models such as pseudo-first order, pseudo-second order, the Elovich model, and the pore diffusion model given in eqs. 2–5, respectively.

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

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

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

$$q_t = k_{id} \cdot t^{0.5} + C \quad (5)$$

Here q_e is the amount of Pu⁴⁺ ions on the resin at equilibrium, q_t is the amount of Pu⁴⁺ ions on the resin at time t , and q_{\max} is the maximum Pu⁴⁺ ion on the resin at equilibrium, k_1 is the pseudo-first-order rate constant, and k_2 is the pseudo-second-order rate constant. The terms α is the initial sorption rate, and β is the desorption constant in the Elovich model. k_{id} is the inter-particle constant in the pore diffusion model, and C is a constant that gives information about the aqueous film thickness around the resin.

2.5. Sorption Isotherm Studies. The Pu⁴⁺ sorption isotherm on the HONTA resin was investigated by measuring the equilibrium K_d values at varying initial Pu⁴⁺ concentrations ranging from 25 to 500 μg/mL at 3 M HNO₃. Subsequently, Pu⁴⁺ sorption data were fitted in several sorption isotherm

models like the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models given in eqs. 6–9, respectively.

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

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

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (8)$$

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (9)$$

Here C_e is the amount of Pu^{4+} in the aqueous phase at equilibrium and K_f is the maximum sorbed mass of Pu^{4+} predicted by the Freundlich model.

2.6. Column Studies. A HONTA resin column was made by packing 0.4 g of resin in a 4 mm (diameter) \times 250 mm (height) glass column. The resin bed height in the column was 10.6 cm, with a dead volume of 1.5 mL. Detailed column parameters are summarized in Table 1. The feed solution was 1 mg/mL Pu^{4+} at 3 M HNO_3 , and the loaded Pu^{4+} from the column was eluted with 0.5 M oxalic acid dissolved in 0.5 M HNO_3 . The entire column operation (loading, washing, and elution) was done at a consistent flow rate of 0.3 mL/min.

3. RESULTS AND DISCUSSION

3.1. Characterization of Resin. The surface characteristics of the HONTA-impregnated resin are shown in the SEM pictures (Figure 2). As clearly seen at different resolutions, the

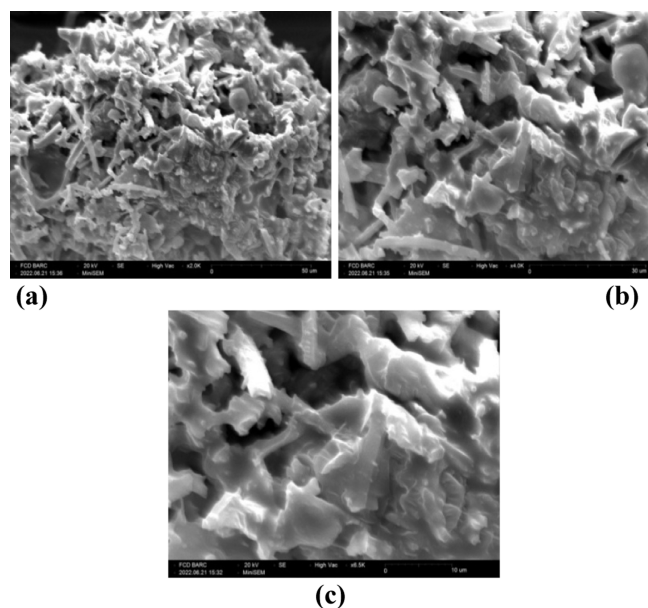


Figure 2. SEM pictures of the HONTA resin at different magnifications: (a) 2k, (b) 4k, and (c) 6.5k.

pores of the resin are open giving a large surface area for interaction with a metal ion. The glassy surface of the resin also confirms that it is indeed impregnated with HONTA ligand solution. Thermogravimetric curves for the impregnated resin and the blank chromosorb-W support were recorded at a heating rate of 10 °C/min in an O_2 atmosphere. Figure 3 shows a sharp weight loss between 200 and 310 °C in the impregnated resin, which was assigned to the volatilization of

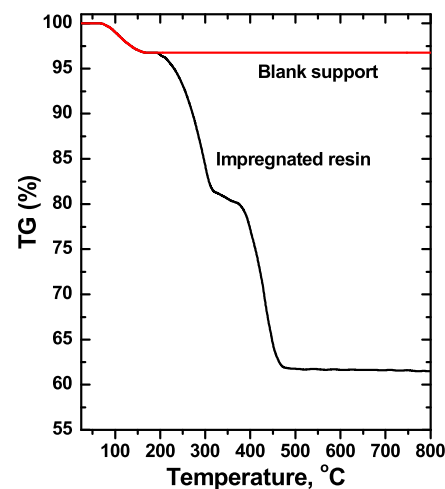


Figure 3. Thermogravimetric curve of the HONTA resin.

n-dodecane having a boiling point of about 215–220 °C.¹⁷ The exact weight loss was 19.5%, which was in accordance with the 20.8% loading of the solvent on the resin. The next step loss (20.1%) between 380 and 470 °C in the impregnated resin was ascribed to the pyrolysis of the HONTA ligand, which was matching with the loading of the ligand on the resin (21.2%). The minor difference in the expected data could be due to statistical variation. The net overall 40% loss in the mass of the impregnated resin is very well matching with the weight of the impregnated ligand solution on the resin (40% ligand loading on each resin, see Table 1). A further increase of the temperature between 470 and 800 °C practically did not show any loss of material, indicating the elimination of the entire ligand solution from the solid support before. The initial weight loss of about 3.5% up to 150 °C in both blank resin and impregnated resin is due to the loss of moisture content of the resin. Practically no loss in weight after 470 °C demonstrates the excellent stability of the chromosorb-W silica support.

3.2. Sorption Kinetics. To establish the minimum shaking time desired for getting equilibrium K_d values, time-dependent K_d values of Pu^{4+} were measured, and the data are shown in Figure 4. From the data, it is clear that equilibrium could be reached only after 20 min of shaking. The sorption kinetics for

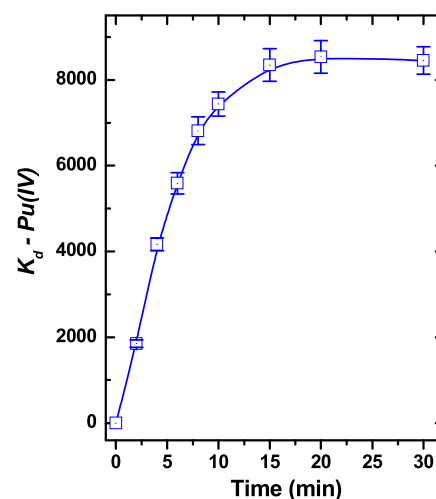


Figure 4. Time-dependent K_d value of Pu^{4+} ions by the HONTA resin; Aq. phase: 3 M HNO_3 .

Pu^{4+} in the present work is relatively slow as compared to other amide-based extraction chromatography resins, where the equilibrium K_d values could be reached within 10 min of shaking.¹⁸ Nonetheless, the plateau region after reaching equilibrium did not come down even after prolonged shaking (K_d values were measured up to 2 h of shaking, but the data in Figure 4 are given up to 30 min for better clarity), which confirms that the sorbed Pu^{4+} ions were not desorbed. Therefore, a shaking time of 60 min was used for all of the subsequent equilibrium K_d value measurements. It is important to mention here that the sorption kinetics for Am^{3+} and UO_2^{2+} ions were also measured giving equilibrium K_d values after 10 min (see Figure S1). However, due to their very low K_d values (<5 mL/g), the data are not presented in Figure 4.

In order to understand the mass transfer of Pu^{4+} from the aqueous phase to the resin phase, the kinetic data were treated with several known models described in eqs. 2–5. The obvious and first choice of the data fitting was the pseudo-first-order and pseudo-second-order rate kinetic models described by the linear eqs. 2 and 3, respectively.^{19,20} As shown in Figure 5a, the

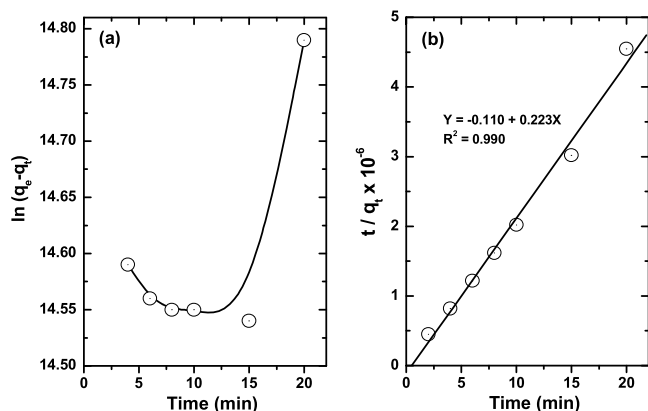


Figure 5. (a) Plot of pseudo-first-order rate kinetics and (b) pseudo-second-order rate kinetics for the sorption of Pu^{4+} on the HONTA resin; Aq. phase: 3 M HNO_3 .

plot $\ln(q_e - q_t)$ vs t yielded a nonlinear curve, which indicates the absence of a first-order sorption process. Subsequently, the kinetic data were fitted in the pseudo-second-order model. Figure 5b shows that the plot of t/q_t vs t is a straight line with a very good correlation coefficient of the regression fitting ($R^2 = 0.990$), indicating that the Pu^{4+} ion sorption on the resins indeed follows pseudo-second-order rate kinetics. The value of k_2 obtained from the fitted data is 4.5×10^{-7} g/cpm-min.

As the kinetic data are nicely fitting in the pseudo-second-order model, it indicates that the sorption process is controlled by interactions taking place between the metal ion and the ligand present in the resin. In other words, a monolayer of the metal ion may be formed on the resin surface by direct interaction with the donor sites of the ligands (vide infra). To test this postulate, the data were also fitted in the Elovich model^{21,22} described by eq 4. According to this model, if a species (say Pu^{4+} ion in this case) is sorbed on a surface by a multilayer phenomenon, the rate of sorption will decrease with time due to an increasing surface coverage. However, from the nonlinear plot of the Elovich equation (q_t vs $\ln t$) in Figure 6a, it is evident that there is no multilayer sorption in the present case.

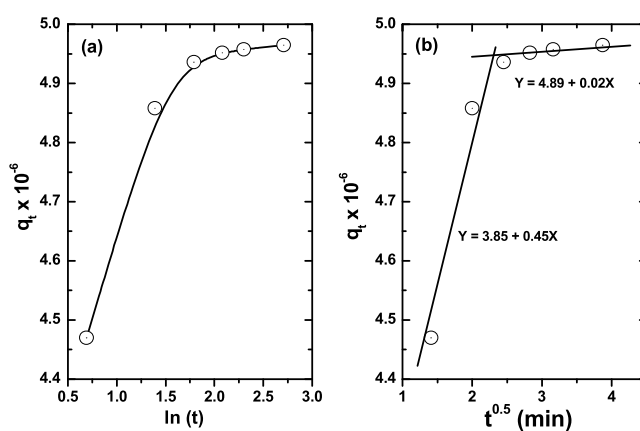


Figure 6. (a) Elovich kinetic model and (b) diffusion kinetic model for the sorption of Pu^{4+} on the HONTA resin; Aq. phase: 3 M HNO_3 .

Therefore, we extended our data treatment with the pore diffusion model^{23,24} given in eq 5. This model, proposed by Weber and Morris, helps in understanding the type of interaction that occurs between a metal ion and the ligand on the resin surface. It assumes that the sorption of the metal ion on the resin is controlled by a two-step diffusion process: (i) diffusion of the metal ions from the bulk of the solution to the boundary layer on the resin surface (film diffusion) and (ii) diffusion of the metal/ligand complex from the surface into the pore of the solid matrix (intraparticle diffusion). One or both diffusion processes may control the overall sorption kinetics. A plot of the linear equation of the pore diffusion model (eq 5) interestingly yielded two linear lines (Figure 6b), indicating that the sorption process is a two-step process indeed. The initial part of the plot indicates that the boundary-layer diffusion (film diffusion) probably controls the overall Pu^{4+} ion sorption on the resin. On the other hand, the second part of the curve shows that the sorption is probably controlled by intraparticle diffusion. This feature confirms that in this work, both the film diffusion and the intraparticle diffusion are concurrently operating in the Pu^{4+} ion sorption.

3.3. Effect of Feed Acidity on Sorption of Metal Ions.

Figure 7 shows the HNO_3 concentration-dependent K_d values of Pu^{4+} ions on the HONTA resin. The distribution data for

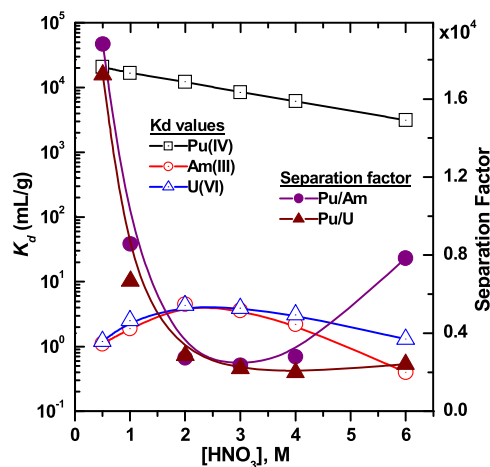


Figure 7. Influence of aqueous feed acidity on the distribution coefficient (K_d) and separation factor of actinides on the HONTA resin; temperature: 25 °C.

Am^{3+} and UO_2^{2+} ions are also included for comparison purposes. The K_d value for Pu^{4+} is in the range of a few thousands in the entire acidity range investigated (0.5–6 M HNO_3). In comparison to Pu^{4+} , the K_d values of the actinides Am^{3+} and UO_2^{2+} are extremely low and never exceed 5 mL/g in the entire acidity range. This feature demonstrates the excellent selectivity of the HONTA resin for tetravalent over tri- and hexavalent actinides.

The equilibrium describing the Pu^{4+} distribution on the resin is represented as



where x represents the number of HONTA ligands associated with the Pu^{4+} extracted complex and L is the HONTA ligand on the resin. The liquid–liquid extraction studies indicated the formation of a $[\text{Pu}(\text{NO}_3)_4(\text{L})_2]$ complex,^{12,13} which may be assumed to be the same in this case as well. As follows from equilibrium reaction 10, an increase in feed acidity will favor the equilibrium due to an increased nitrate ion concentration. Consequently, the K_d value of Pu^{4+} should increase upon increasing feed acidity. However, as shown in Figure 7, the K_d value has a decreasing trend with increasing feed acidity. This distribution pattern may be explained by the following two facts. First, HONTA also forms a complex with nitric acid, which should be increasing with increasing feed acidity. This will reduce the free ligand concentration on the resin and consequently will eventually reduce the K_d value. Second, Pu^{4+} is known to form an anionic complex in nitric acid medium, which is dominating at higher acidity (>6 M HNO_3).²⁵ This may also cause a reduction of the K_d value, especially at higher nitric acid concentrations. The separation factors of Pu^{4+} over Am^{3+} and UO_2^{2+} are very large, namely, in the range of a few thousands. The highest separation factor is at the lowest feed acidity (0.5 M HNO_3) primarily due to the maximum K_d value of Pu^{4+} at this feed acidity. The K_d values Am^{3+} and UO_2^{2+} did not affect the separation factor much as their K_d values were between 0.5 and 5 mL/g in the entire acidity range.

The separation of Pu^{4+} has been attempted with different ligand-impregnated extraction chromatography resins given in Table 2. The Pu^{4+} separation was classically attempted with a TPB-impregnated resin where Pu^{4+} was selectively loaded on the resin column over trivalent actinides and lanthanides.

Table 2. Extraction of Pu^{4+} by Different Extraction Chromatography Resins

Ligand loading (% w/w)	K_d at 3 M HNO_3	Comments	ref
TBP (50%)	33.6	Pu^{4+} loaded on column and eluted with 0.01 M hydroxylamine by reducing it to Pu^{3+}	26
DEHPRA ^a (45%)	167	The Pu^{4+} uptake was higher than Np^{4+} and UO_2^{2+} ions	27
DMDBDTMA ^b (50%)	4×10^3	Pu^{4+} extraction was 2 orders of magnitude higher than Am^{3+}	28
TODGA ^c (47%)	5×10^3	Preferential extraction of Pu^{4+} over UO_2^{2+}	29
TAM-4-DGA ^d (15%)	3×10^5	Highest K_d value of Pu^{4+} reported with this resin	18
HONTA (21%)	8.5×10^3	Clean separation of Pu^{4+} from a mixture of U, Pu, and Am	This work

^aDi-2-ethylhexyl-propanamide. ^b*N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide. ^cTetra-*n*-octyl diglycolamide. ^dDiglycolamide-functionalized tetraaza-12-crown-4.

Though a recently studied diglycolamide-based ligand resin (TAM-4-DGA) gave the highest K_d value for Pu^{4+} , the resin was not selective for Pu^{4+} over Am^{3+} ions. On the other hand, the present HONTA resin yielded excellent selectivity for Pu^{4+} over Am^{3+} and UO_2^{2+} , though the K_d value of Pu^{4+} was lower as compared to the TAM-4-DGA resin.

3.4. Sorption Isotherm. To understand the interaction of Pu^{4+} cations with the HONTA ligands present on the resin, its sorption isotherm was investigated at 3 M HNO_3 with initial Pu^{4+} concentrations ranging from 25 to 500 mg/L. The maximum Pu^{4+} sorption capacity obtained was 58.2 ± 0.5 mg/g resin. This value is consistent even when the measurement was done with 5 g/L initial Pu^{4+} solution, confirming that the entire ligand loading on the resin was complexed with the metal ion. A solvent extraction study on the distribution of Pu^{4+} ions with HONTA has shown the formation of a 1:2 metal/ligand complex.^{12,13} However, considering this stoichiometry, then only 29.8 mg of Pu^{4+} (0.125 mmol) should be sorbed per g of resin since the ligand loading on the resin is limited to 0.25 mmol/g. However, the loading of 58.2 mg of Pu^{4+} (0.24 mmol) per g of resin indicates that the stoichiometry must be 1:1 metal/ligand. This may be true as the solvent extraction distribution data were obtained at a tracer concentration of Pu^{4+} (10^{-6} M), but the present loading studies were performed at a macro concentration of $\text{Pu}(\text{NO}_3)_4$.

The sorption data were critically analyzed to understand the sorption mechanism by fitting the data in popular isotherm models, namely, Langmuir, Freundlich, Dubinin–Radushkovich (D–R), and Temkin. The linear forms of these isotherm equations are given in eqs. 6–9, respectively. Figure 8 shows

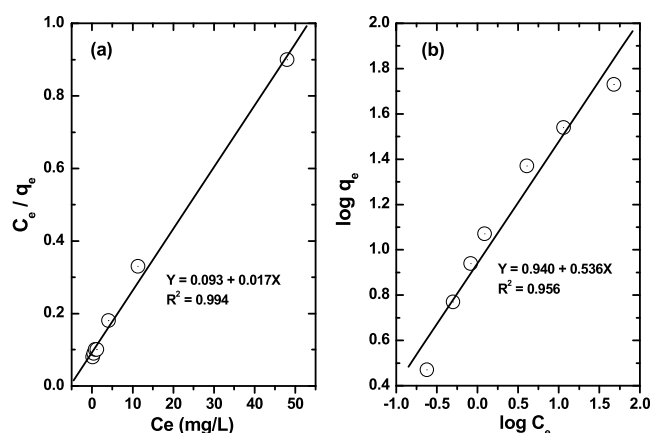


Figure 8. (a) Langmuir plot and (b) Freundlich plot for the sorption of Pu^{4+} on the HONTA resin; aqueous phase: 3 M HNO_3 ; temperature: 25 °C.

the data fitting in the Langmuir^{30,31} and Freundlich^{32,33} isotherm models. Though both plots yielded straight lines, the fitting is better in the Langmuir model with a better correlation coefficient as compared to the Freundlich plot (Table 3). Additionally, the maximum sorption capacity of Pu^{4+} obtained from the Langmuir plot (q_{max}) is 58.8 mg/g, which is an excellent match with that obtained independently in the batch experiment (58.2 mg/g). On the other hand, the maximum sorption capacity (K_f) obtained from the Freundlich plot is 8.71 mg/g, which is far away from the real value. This data analysis clearly proves that the sorption of Pu^{4+} follows the Langmuir monolayer isotherm model.

Table 3. Parameters Calculated from Langmuir, Freundlich, D–R, and Temkin Isotherm Models for the Sorption of Pu⁴⁺ on the HONTA Resin

Isotherms	Parameters	Values
Langmuir	R ²	0.994
	<i>b</i> (mL/mg)	0.183 ± 0.022
	<i>q</i> _{max} (mg/g)	58.8 ± 1.76
Freundlich	R ²	0.956
	<i>K</i> _F (mg/g)	8.71 ± 0.39
	1/ <i>n</i>	0.556 ± 0.051

To confirm the absence of the multilayer Freundlich isotherm model, we tried to fit the sorption data in the Temkin isotherm model in eq 8. This isotherm takes into account the presence of indirect sorbate/sorbate interactions and suggests that because of these interactions, the heat of sorption of all of the molecules in the layer will decrease linearly with coverage.²⁴ Fitting of the sorption data in the Temkin isotherm model would be predicting the presence of a multilayer sorption phenomenon. However, the nonlinear behavior of the Temkin isotherm (Figure 9a) indicates the

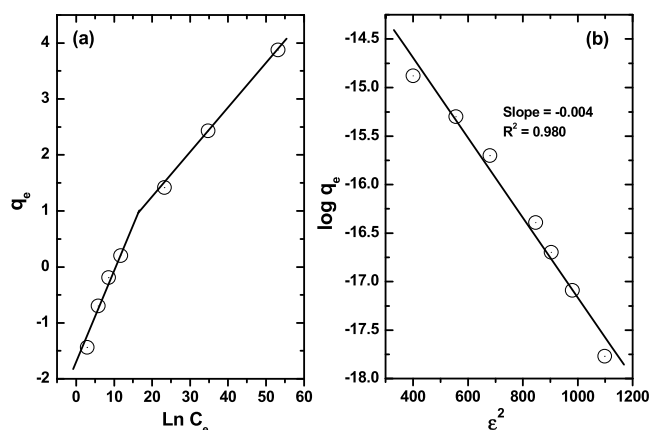


Figure 9. (a) Temkin and (b) D–R plots for the sorption of Pu⁴⁺ on the HONTA resin; aqueous phase: 3 M HNO₃; temperature: 25 °C.

absence of multilayer sorption in the present work, confirming the absence of the Freundlich model. The experimental sorption data were further fitted to the D–R isotherm model to distinguish between the physical and chemical sorption of Pu⁴⁺ on the HONTA resin.³⁴ The D–R constant β , which is related to the mean sorption energy, was obtained from the linear plot of eq 9 shown in Figure 9b. The D–R isotherm is based on the postulate that if the surface is heterogeneous and the Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equivalent, then the D–R constant β can be correlated to the mean sorption (*E*) energy as³⁵

$$E = 1/\sqrt{-2\beta} \quad (11)$$

Here, *E* is the free energy that is needed to transfer 1 mole of metal ions from infinity to the surface of the resin. The mean sorption energy gives information about the type of sorption mechanism, chemisorption, or physisorption.³⁶ A value of *E* > 8 kJ/mol signifies a chemisorption process, whereas a value < 8 kJ/mol points to a physical sorption process. The value of *E* in the present work was calculated to be 11.2 ± 0.7 kJ/mol, indicating that the sorption takes place via a chemical interaction.

3.5. Column Studies. After detailed batch studies, column experiments were performed to evaluate the feasibility of the possible application of these resins. The column was prepared by wet packing 0.4 g of resin in a 4 mm diameter glass column. The various column parameters are given in Table 1. The feed solution (loading solution) was 1 mg/mL Pu(NO₃)₄ nitrate at 3 M HNO₃. Before passing the loading solution, the columns were preconditioned by passing five bed volumes of 3 M HNO₃.

Figure 10 (left) shows the loading of Pu⁴⁺ as a function of the volume of the passed feed solution. The breakthrough of

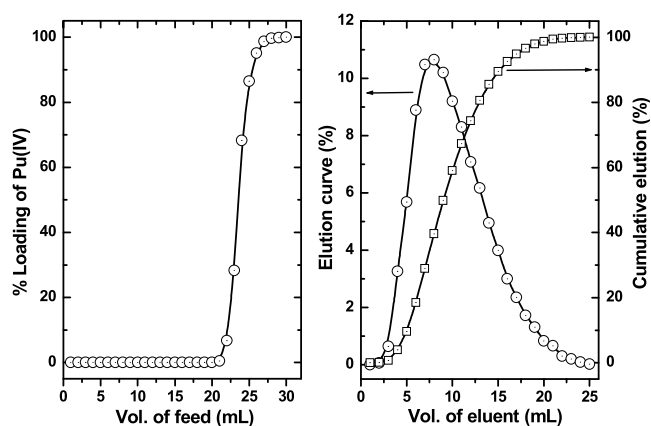


Figure 10. Loading curve (left) and elution curve (right) for Pu⁴⁺ on the HONTA resin column. Feed solution: 1.0 mg/mL Pu(NO₃)₄ at 3 M HNO₃; eluent: 0.5 M oxalic acid + 0.5 M HNO₃; flow rate: 0.4 mL/min.

Pu⁴⁺ started after passing 23 mL of feed solution. If we omit the dead volume of the column, being 1.5 mL, then 21.5 mL of feed solution could be passed without any leakage of Pu activity. In other words, 21.5 mg of Pu could be loaded on the column before the breakthrough since the feed solution was 1 mg/mL of Pu. Since the column contained 0.40 g of resin, the Pu column loading value came out to be 53.75 mg/g of resin. This column capacity of Pu corresponds to 92.4% of resin saturation in the column as the maximum loading capacity of the resin at static equilibrium was 58.2 mg/g. The somewhat lower Pu loading in the column can be understood due to nonequilibrium conditions in the column. Elution was performed with 0.5 M oxalic acid + 0.5 M HNO₃, which gave efficient elution of the loaded Pu, and all Pu could be eluted in about 25 mL (Figure 10). The mass balance of the loaded and eluted Pu⁴⁺ was within ±3%.

3.6. Analytical Separation of U, Pu, and Am. To evaluate the possible application of the HONTA resin column, an attempt was made for the analytical separation of Pu from a mixture of actinides. For this purpose, a synthetic mixture was prepared by mixing known activities of ²³³U, ²³⁹Pu, and ²⁴¹Am in 3 M HNO₃. To this solution, 0.05 M NaNO₂ was added to adjust the Pu valency as Pu⁴⁺. This solution was passed through the HONTA resin column where Pu⁴⁺ was selectively held on the column, and the entire Am and U activities were washed out with 3 M HNO₃. Finally, the loaded Pu from the column was eluted with 0.5 M oxalic acid + 0.5 M HNO₃. As shown in Figure 11, the α spectrum of the separated Pu is clearly free from any contamination from either ²⁴¹Am or ²³⁸U, the mass balance in the loaded and recovered Pu product being 95.7%.

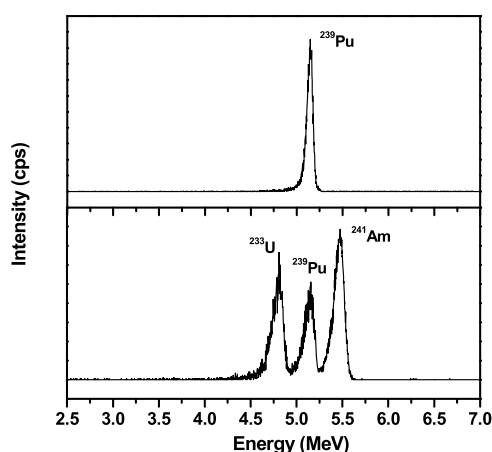


Figure 11. α spectra of the mixture of Am, Pu, and U from the feed and pure separated Pu. Feed solution: a mixture of actinide tracers at 3 M HNO_3 ; eluent: 0.5 M oxalic acid + 0.5 M HNO_3 ; flow rate: 0.4 mL/min.

3.7. Stability of the Resin. The stability of the HONTA resin was assessed in detail. Since the resin is proposed for the separation of radioactive elements, it is important to determine its radiolytic stability. To establish that, the resin was irradiated by γ radiation in a ^{60}Co source chamber at a 300 kGy absorbed dose. As shown in Figure 12a, there was no change in the FT-

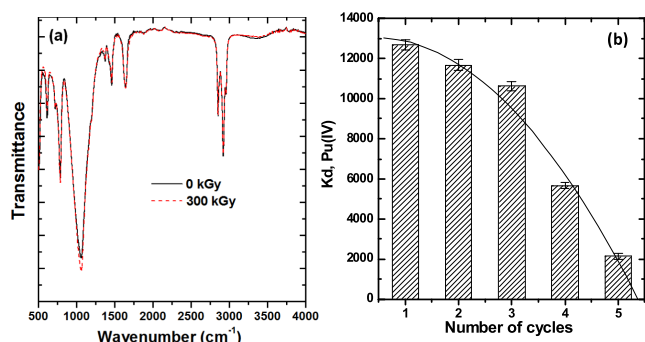


Figure 12. (a) FT-IR spectra of the pristine resin and 300 kGy γ irradiated resin. (b) K_d value of Pu^{4+} at 2 M HNO_3 in multiple cycles.

IR spectrum of the resin after the 300 kGy dose, confirming good radiation stability. To further assess the reusability of this resin, a reusability test was performed by measuring the K_d value of Pu^{4+} at 2 M HNO_3 in multiple cycles. Figure 12b shows that the performance of the resin dropped slowly up to the third cycle and then sharply. In the fifth cycle, the K_d value decreased 6 times the original value, indicating that the ligand was probably not held strongly inside the pores of the solid support.

4. CONCLUSIONS

An extraction chromatography resin, prepared by impregnating hexa-*n*-octyl nitrilotriacetamide (HONTA) on chromosorb-W, shows a very efficient performance for the selective separation of Pu^{4+} over other actinides like uranium and americium. The resin yields a separation factor of >1000 for Pu^{4+} with respect to either UO_2^{2+} or Am^{3+} ions, with distribution coefficients for Pu^{4+} in the range of 10^4 mL/g. The resin capacity for plutonium was 58.2 mg/g of resin, corresponding to 1:1 metal/ligand complex formation on the resin. With a volume of the

resin column of 1.33 mL (400 mg resin), the column capacity was 21.5 mg of Pu, and the loaded Pu could be efficiently eluted with a mixture of 0.5 M oxalic acid + 0.5 M HNO_3 . Analytical separation of Pu from a mixture of Am, Pu, and U was successfully demonstrated, indicating the possible analytical application of the resin column in nuclear analytical laboratories. Though HTTA has been used for analytical separations of actinides, the poor photostability and slow kinetics of HTTA make a strong case for HONTA as a suitable alternative.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c04516>.

(PDF)

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Notes

The authors declare no competing financial interest.

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