



## A novel malonamide grafted polystyrene-divinyl benzene resin for extraction, pre-concentration and separation of actinides

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### ABSTRACT

A new chelating polymeric extraction chromatographic resin was prepared by chemical anchoring of *N,N'*-dimethyl-*N,N'*-dibutyl malonamide (DMDBMA) with chloromethylated Merrifield resin<sup>®</sup>. The grafted resin exhibited stronger binding for hexavalent and tetravalent actinides such as U(VI), Th(IV) and Pu(IV) over trivalent actinides, viz. Am(III) and Pu(III). Batch studies on solid phase extraction performed over a wide range of acid solution (0.01–6 M HNO<sub>3</sub>) revealed that ternary mixer of uranium, americium and plutonium or thorium, americium and plutonium could be separated from each other at 1 M HNO<sub>3</sub>. Desorption of U(VI), Pu(IV) and Am(III) from the loaded resin was efficiently carried out using 0.1 M  $\alpha$ -HIBA, 0.25 M oxalic acid and 0.01 M EDTA, respectively. Quantitative pre-concentration of actinide ions such as Th(IV) and U(VI) was possible from 3 M HNO<sub>3</sub> solution. The practical utility of the grafted resin was evaluated by uranium sorption measurements in several successive cycles. The sorption efficiency of the resin with respect to uranyl ion remained unchanged even after 30 days of continuous use. The surface morphology of the resin was monitored with the help of scanning electron microscopy (SEM) technique.

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### 1. Introduction

To restrict the impact of industrialization on our planet, the industrial effluents containing hazardous elements need to be processed prior to their release to the environment. At the same time, precise estimation of the hazardous elements in the industrial effluent is necessary and need to be separated prior to their final disposal. With increasing concern for the environment, it is imperative to explore the separation techniques other than “solvent extraction” which is based on large inventory of hazardous volatile organics (VOCs). The solid phase extraction (SPE) has emerged as an excellent separation technique in the recent years in view of immiscibility of resins with aqueous phase, low rate of physical degradation, minimum release of toxic organic solvents and recycling options [1,2]. In SPE, the organic extractants are either sorbed or anchored to an inert polymeric support and it has the advantages of both solvent extraction and ion-exchange methods [3,4]. However, slow leaching of the sorbed extractant from the pores of the support material poses a serious limitation to the reusability and hence the economic viability of the extraction chromatographic material for analytical application. In this context, grafted resins with suitably appended functional groups have been found to be

free from this drawback. They have been used for the separation of hazardous metal ions such as Cd(II), Pb(II), Hg(II), Ag(I), etc. from industrial effluents [5,6] and also pre-concentration of various metal ions from their dilute solutions [7–12].

Safe management of nuclear waste with minimum impact to the environment is emerging as one of the major challenges to the separation scientists. Selective extraction and/or pre-concentration of long-lived alpha emitters such as <sup>241</sup>Am, <sup>243</sup>Am, <sup>244</sup>Cm, <sup>239</sup>Pu, <sup>233</sup>U, <sup>235</sup>U, etc. from waste stream may reduce the burden on the environment thereby increasing the acceptability of closed nuclear fuel cycle. Recovery of these elements from nitric acid solutions require functionalized resins with >P=O, >C=O or other functional groups of desired basicity and stereochemistry. Amide based resins are particularly interesting because of their innocuous degradation products, high radiolytic stability and complete incinerability [13–15]. Raju and Subramanian, carried out SPE of actinides and lanthanides with grafted resins using malonamide ligands such as tetrahexyl malonamide [9] and a Merrifield resin derivatized with *N,N*-dihexyl succinic acid [10]. Grafting of various chelating ligands has been attempted by many researchers using polymeric foam, silica, Merrifield resin and other inert polymers as the solid support [6–12].

Authors have reported a detail study on the preparation and the sorption behaviour of U(VI) and Th(IV) ions on Merrifield chloromethylated resin grafted with *N,N*-dimethyl-*N,N'*-dibutyl-malonamide (DMDBMA) [16]. The present work describes the

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analytical application of the malonamide grafted resin for pre-concentration and separation of actinide ions, viz. Am(III), Th(IV), Pu(III), Pu(IV) and U(VI) at micromolar concentration.

## 2. Experimental

### 2.1. Reagents and radionuclides

Chloromethylated Merrifield resin (chloromethylated polystyrene-divinyl benzene resin containing ~5.5 mmol of Cl per gram of resin, 16–50 mesh) obtained from Fluka Chemicals was washed thoroughly with water and methanol followed by vacuum drying before use. Dimethyl formamide was vacuum distilled at 50 °C after refluxing with calcium hydride at 60 °C. All the other reagents used were of analytical reagent grade and were used without further purification.

$^{233}\text{U}$  tracer was purified by anion exchange in HCl medium and its purity was confirmed by  $\alpha$ -spectrometry [17]. Pu (principally  $^{239}\text{Pu}$ ) was purified from  $^{241}\text{Am}$  in  $\text{HNO}_3$  medium and its radiochemical purity was ascertained by gamma spectrometry for the absence of  $^{241}\text{Am}$  [18]. Oxidation state of Pu was adjusted to Pu(IV) with sodium nitrite and was subsequently extracted by 0.5 M HTTA (2-thenoyl trifluoro acetone) in xylene at 1 M  $\text{HNO}_3$  followed by its stripping with 8 M  $\text{HNO}_3$ . The resulting plutonium solution was used as stock for Pu(IV) [19]. Further, during the studies, plutonium valency in the aqueous phase was adjusted and maintained in tetravalent state by the addition of 0.05 M  $\text{NaNO}_2 + 0.005\text{ M NH}_4\text{VO}_3$  (holding oxidant).  $^{241}\text{Am}$  was purified by the procedure given elsewhere [20].  $^{234}\text{Th}$  is a daughter product of  $^{238}\text{U}$  and, therefore, it is separated from the natural uranium [21]. Uranium solution at 8 M HCl was loaded in 30% aliquat 336 (tricapryl methyl ammonium chloride) dissolved in chloroform. The organic

phase was then stored for about 6 months to allow the growth of  $^{234}\text{Th}$  activity ( $t_{1/2} = 24.1\text{ d}$ ) when a secular equilibrium with  $^{238}\text{U}$  ( $t_{1/2} = 4.47 \times 10^9\text{ y}$ ) was attained.  $^{234}\text{Th}$  thus produced was stripped in the aqueous phase by contacting the uranium loaded organic phase with 8 M HCl. At this stage the stripped thorium is contaminated with the parent uranium. Therefore, the tracer  $^{234}\text{Th}$  was further purified by preferential extraction with 0.01 M HPBI (3-phenyl-4-benzoyl-5-isooxazolone) in xylene at 0.5 M  $\text{HNO}_3$ . Finally, the pure  $^{234}\text{Th}$  tracer was stripped with 8 M  $\text{HNO}_3$  and used as the stock solution after confirming the purity by gamma spectrometry.

### 2.2. Synthesis and characterization of DMDBMA grafted resin

The chemical anchoring of the resin was carried out by reacting *N,N'*-dimethyl-*N,N'*-dibutyl malonamide with the chloromethylated resin as detailed earlier [16]. Five grams of vacuum dried chloromethylated polystyrene-divinyl benzene resin was reacted with 30 mmol of *N,N'*-dimethyl-*N,N'*-dibutyl malonamide and 30 mmol of NaH in 50 mL of dried dimethyl formamide (DMF). The reaction mixture was refluxed on an oil bath at 60 °C for 16 h. The final product was purified from the excess reactants by repeated washing with methanol and water. The resultant grafted resin was vacuum dried and characterized by C, H, N elemental analysis, NMR and IR spectroscopy. The synthesis scheme for chemical grafting of the resin is represented in Fig. 1.  $^{13}\text{C}$  solid-state NMR spectra of the Merrifield resin showed resonance signal at 40.1 ppm, which corresponds to alkyl ( $-\text{CH}_2-\text{Cl}$ ) group, was shifted to 48.4 ppm in the grafted resin due to the substitution of malonamide moiety. The presence of lateral methyl group ( $-\text{CH}_3$ ) of the malonamide was confirmed by the resonance signal at 14.2 ppm. In addition to this, a broad resonance signal of carbonyl carbon ( $>\text{C}=\text{O}$ ) of malonamide in the grafted resin was observed at 169.5 ppm, which was absent in

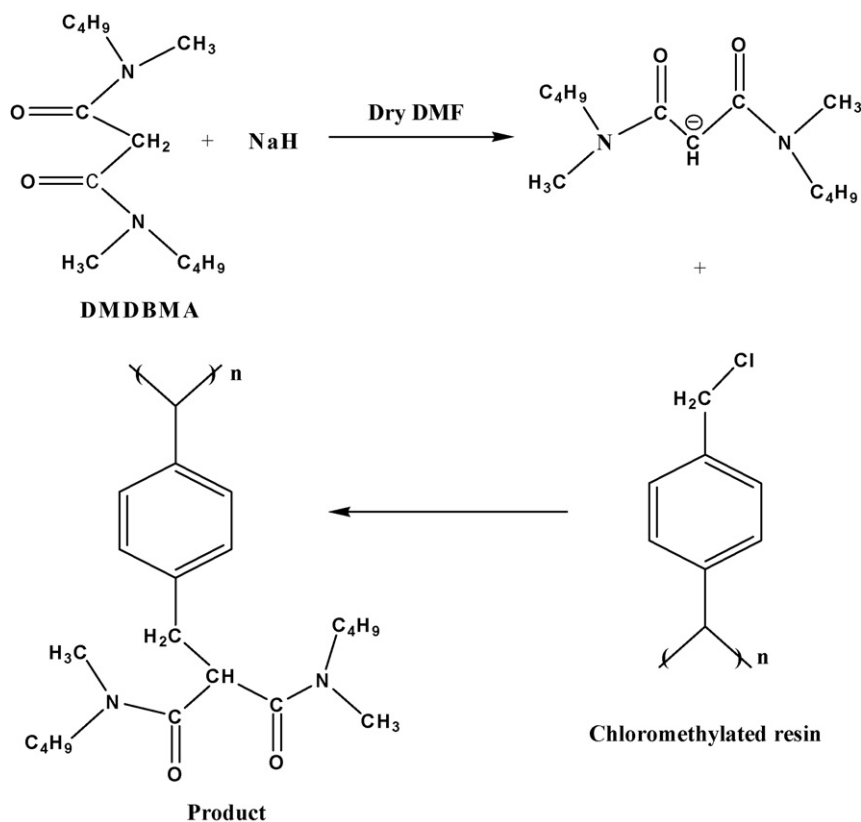


Fig. 1. Scheme for the synthesis of malonamide grafted resin.

the non-functionalized resin, suggesting the successful anchoring of the resin. FT-IR spectra of the modified resin showed enhanced stretching vibrations between 3000 and 2800  $\text{cm}^{-1}$  corresponding to  $-\text{CH}$ ,  $-\text{CH}_2$  and  $-\text{CH}_3$  groups of malonamide. Appearance of characteristic band of carbonyl group ( $>\text{C}=\text{O}$ ) at 1645  $\text{cm}^{-1}$ , in addition to a band at 1390  $\text{cm}^{-1}$  due to C–N stretching vibration, suggested the presence of amide moiety on the grafted resin. Similarly, disappearance of vibrational band at 670  $\text{cm}^{-1}$ , which corresponded to  $-\text{CH}_2\text{Cl}$  group in non-functionalized resin, confirmed the chemical modification of the Merrifield resin. The CHN elemental analysis of the grafted resin yielded 6.58% of nitrogen as compared to 7.23 of the theoretical yield, suggesting  $\sim 91\%$  anchoring of the malonamide moiety on the polymeric support. This nitrogen content corresponded to 60% (w/w) loading of the malonamide ligand on the polymeric support.

### 2.3. Distribution studies

The sorption of metal ions was determined by equilibrating a known volume of aqueous solution (1 mL) containing radiotracer at given acidity with a known quantity of resin ( $\sim 25$  mg) in glass stoppered test tubes. Agitation of the two phases was carried out in a thermostated water bath maintained at  $25 \pm 0.1$  °C for 45 min. Subsequently, the tubes were centrifuged and suitable aliquots of the aqueous phase were removed before and after equilibration for assaying radiometrically.  $^{241}\text{Am}$  and  $^{234}\text{Th}$  were assayed by gamma counting in a well type NaI(Tl) scintillation counter connected to a PC based multi channel analyzer. Alpha counting for  $^{233}\text{U}$  and  $^{239}\text{Pu}$  was performed employing a liquid scintillation counter in a toluene-based scintillator containing 10% (v/v) di(2-ethylhexyl) phosphoric acid (HD2EHP), 0.7% (w/v) 2,5-diphenyloxazole (PPO), 0.03% (w/v) 1,4-di-[2-(5-phenyloxazolyl)]-benzene (POPOP). The distribution coefficient ( $K_d$ ) was calculated by employing the following formula,

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

where  $C_0$  and  $C$  are the concentrations of metal ions (in counts per unit time per unit volume) before and after equilibration, respectively,  $V$  is the volume of aqueous phase used (mL), and  $W$  is the weight of the resin material employed (g). All the experiments were carried out at least in duplicate and certainty in all the measurements were within the standard deviation of 5%.

## 3. Results and discussion

### 3.1. Kinetics of sorption of the actinide ions

The rate of transfer of actinides ions, viz. Th(IV), U(VI) and Am(III) from aqueous phase to the solid phase was investigated at 3 M  $\text{HNO}_3$  by measuring the distribution coefficient of the metal ions as a function of equilibration time. It is evident from the Fig. 2 that the equilibrium conditions reached within 20 min for all the actinide ions investigated. On the other hand, neither degradation of the resin nor desorption of the sorbed metal ions was observed even after 2 h of the equilibration. Our sorption kinetics data were in good agreement with the sorption kinetics of actinides and lanthanides by 4-ethoxy-*N,N*-dixethyl butanamide grafted resin [22]. Though Pu(IV) sorption kinetics was not studied, however, its sorption behaviour could be predicted from the Th(IV) sorption data because of their similar oxidation state. In the present work, an equilibration time of 45 min was employed.

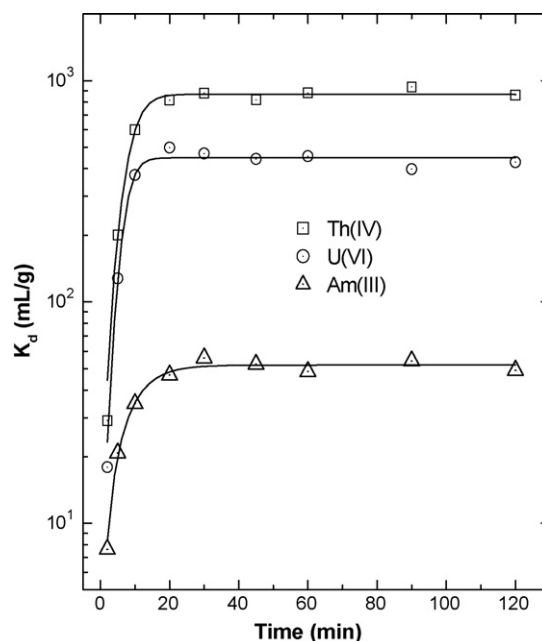


Fig. 2. Kinetics for the sorption of actinide ions by DMDBMA-grafted resin; aqueous phase: 3 M  $\text{HNO}_3$ ; temperature: 25 °C.

### 3.2. Sorption behaviour of actinide ions from $\text{HNO}_3$ solution

The distribution behaviour of actinide ions, viz. Am(III), Pu(III), Th(IV), Pu(IV) and U(VI) onto DMDBMA grafted resin was investigated from varying concentration of  $\text{HNO}_3$ . The valency of Pu was adjusted to Pu(IV) as given in the experimental section. On the other hand, Pu was reduced to Pu(III) by addition of a mixture of 0.2 M hydroxyl ammonium nitrate (HAN) and 0.2 M hydrazinium nitrate (HN) as reported earlier [23]. The sorption of metal ions on the

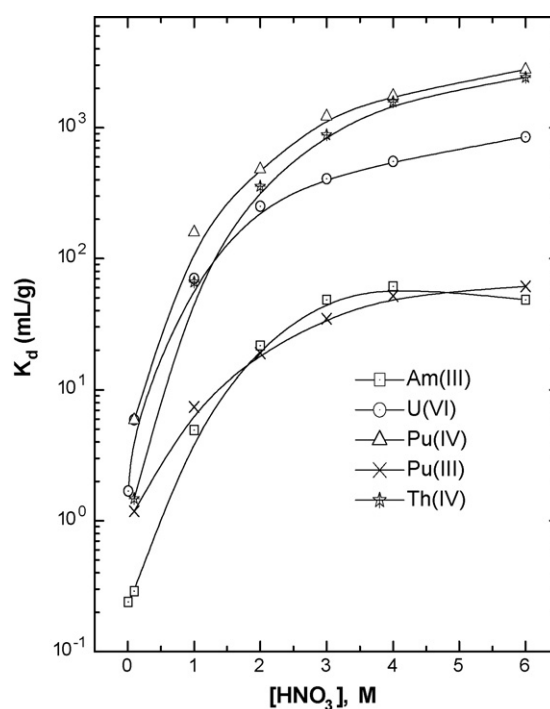
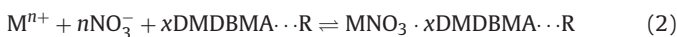


Fig. 3. Distribution coefficient of actinide ions by malonamide grafted resin from varying concentration  $\text{HNO}_3$ ; temperature: 25 °C.

**Table 1**  
Selectivity factor for actinide ions by DMDBMA grafted resin; aqueous phase: 1 M HNO<sub>3</sub>

Meta1 ions	K <sub>d</sub> (mL/g)	Selectivity factor	
Am(III)	4.9	Pu <sup>4+</sup> /Am <sup>3+</sup>	32.2
Pu(III)	7.4	UO <sub>2</sub> <sup>2+</sup> /Am <sup>3+</sup>	15.3
Pu(IV)	158	UO <sub>2</sub> <sup>2+</sup> /Pu <sup>3+</sup>	10.1
Th(IV)	66	Th <sup>4+</sup> /Am <sup>3+</sup>	13.5
U(VI)	75	Th <sup>4+</sup> /Pu <sup>3+</sup>	8.9

malonamide grafted resin from nitric acid medium can be expressed by the following equilibrium reaction,



where, *x* is the number of malonamide molecules taking part in the complexation with the metal ions. The sorption profile of actinide ions on the DMDBMA grafted resin is given in Fig. 3. The distribution coefficient (*K<sub>d</sub>*) of all the metal ions increased gradually with nitric acid concentration up to 4 M HNO<sub>3</sub>. Increase in the distribution value with acidity can be explained by the law of mass action (equilibrium reaction (2)) due to increased nitrate concentration. However, at higher acidities, there was a decrease in the free ligand concentration due to the formation of malonamide–HNO<sub>3</sub> adduct, thereby giving a near constant *K<sub>d</sub>* values at higher acidity. Higher distribution coefficient for tetravalent metal ions, viz. Th(IV) and Pu(IV) was attributed to their stronger complexation with the bidentate malonamide molecule due to higher charge density on the metal ions. On the other hand, trivalent Am and Pu show significant distribution coefficient only above 3 M HNO<sub>3</sub> (Fig. 3). However, at 1 M HNO<sub>3</sub> the *K<sub>d</sub>* values for Am(III) and Pu(III) were 4.9 and 7.4 mL/g, respectively, suggesting insignificant sorption of these metal ions at low acidity. The critical analysis of Fig. 3 suggested the possible analytical application of the malonamide grafted resin for the separation of Am, Pu and U or Am, Th and Pu from each other at lower acidic region. The analysis of *K<sub>d</sub>* values and the selectivity factors of these metal ions at 1 M HNO<sub>3</sub> are listed in Table 1. Relatively good selectivity factor for Am(III)/Pu(IV), Am(III)/U(VI) and Pu(III)/U(VI) facilitate the analytical separation of these metal ions. These observations reflected that U(VI) along with Pu(IV) or Th(IV) along with Pu(IV) can be selectively sorbed on the DMDBMA column leaving behind Am(III) in the aqueous stream. Afterwards, the loaded Pu(IV) could be selectively eluted from the column after reducing to Pu(III) using a reducing mixture of 0.2 M HAN and 0.2 M HN in 1 M HNO<sub>3</sub>. After eluting plutonium as Pu(III), the remaining fraction of uranium can be eluted separately.

### 3.3. Desorption studies

Desorption studies on uranium, plutonium and americium from the loaded malonamide grafted resin were conducted employing various equilibrating solutions such as 0.01 M HNO<sub>3</sub>, 0.01 M EDTA, 0.25 M Na<sub>2</sub>CO<sub>3</sub>, 0.25 M oxalic acid and 0.1 M alpha-hydroxy isobutyric acid (α-HIBA). Additionally, a reducing mixture, viz. 0.2 M HAN + 0.2 M HN was also studied for the desorption of plutonium as Pu(III) [23]. As reported in Table 2, the maximum desorption of uranium was observed in first stage with Na<sub>2</sub>CO<sub>3</sub> due to strong complexation of carbonate ions with uranyl ions. However, comparable desorption yields were obtained using α-HIBA as well. Similarly, plutonium was effectively desorbed with 0.25 M oxalic acid which was generally used for its elution from other solid phase extractants [4,24]. Comparable desorption data were obtained when Pu was reduced to the +3 state using the reducing mixture of HAN and HN at 1 M HNO<sub>3</sub>. On the other hand, though americium was only partially sorbed on the grafted resin, it could be quantitatively desorbed with 0.01 M EDTA solution in

**Table 2**  
Desorption data of actinide ions from DMDBTMA grafted resin; each activity was loaded from 1 mL of 3 M HNO<sub>3</sub> on 100 mg of resin

Elements	Eluting solution	%Desorption		
		I stage	II stage <sup>b</sup>	III stage <sup>b</sup>
Am (III)	0.01 M HNO <sub>3</sub>	84.47	96.93	99.04
	0.01 M EDTA <sup>a</sup>	85.51	99.63	99.87
Pu (IV)	0.01 M HNO <sub>3</sub>	29.49	62.27	83.07
	0.25 M Oxalic acid	86.02	99.62	101.21
	0.2 M HN + 0.2 M HAN (at 1 M HNO <sub>3</sub> )	88.93	99.17	99.89
	0.01 M HNO <sub>3</sub>	33.27	78.12	89.92
U (VI)	0.25 M Na <sub>2</sub> CO <sub>3</sub>	89.62	96.02	99.28
	0.1 M α-HIBA <sup>a</sup>	83.21	97.11	99.15

<sup>a</sup> pH of the solution was not adjusted.

<sup>b</sup> Cumulative value.

three stages. Alternatively, Am(III) could be eluted by 1 M HNO<sub>3</sub> (*vide supra*).

### 3.4. Metal loading capacity

The loading capacities of uranium and thorium by DMDBMA grafted resin were evaluated at 4 M HNO<sub>3</sub> and the results were compared with different amide grafted resins reported in the literature. The metal loading capacity was determined by equilibrating 100 mg of the resin material with 5 mL of individual solution of U and Th (1 mg/mL for each metal ions) for 24 h. Suitable aliquots of the aqueous phases were removed before and after equilibration for the estimation of uranium and thorium. The analyte solutions were diluted suitably for spectrophotometric estimation using arsenazo-III as the chromophoric agent. The metal sorption capacities were found to be 18.78 ± 1.53 and 15.74 ± 1.59 mg/g resin for U and Th, respectively. Higher loading capacity for U(VI) was attributed to the greater metal ligand complex stability and also to the lesser steric hindrance involved for U(VI) complexation over Th(IV) as later requires four nitrate ions for metal charge neutralization. Similar observation was also reported for 2-ethylhexyl malonamide grafted resin for the sorption of uranium and thorium from 5 M HNO<sub>3</sub> at 25 °C [25]. Table 3 lists the sorption capacities of uranium and thorium by various amide grafted resins obtained from the literatures. It is worth mentioning that there are many literature on the grafted resin for pre-concentration of actinides, however, their sorption studies have been reported at lower acidities (pH range), and therefore, are not listed in the table. If one calculates the amount of malonamide moiety grafted on the resin, it comes out to be ~0.002 mol/g of resin. Considering the equilibrium reaction (2), the number of DMDBMA molecules involves in the complexation of U(VI) is reported to 2 [16]. From the amount of malonamide loaded on the resin, the maximum theoretical loading of U(VI) comes about 24 mg/g of resin. Loading of about 18 mg of U(VI) per gram of resin suggested about 80% malonamide molecules are

**Table 3**  
Comparison of resin sorption capacity for uranium and thorium by several chemically grafted resins

Grafted resin	Aqueous phase	Resin capacity (mg/g)	
		U(VI)	Th(IV)
Merrifield polymer-DMDBMA [P.W.] <sup>a</sup>	4 M HNO <sub>3</sub>	18.78	15.74
Merrifield polymer-EDHBA [22]	6 M HNO <sub>3</sub>	84.97	157.78
Merrifield polymer-DB2EHMA [25]	5 M HNO <sub>3</sub>	62.50	38.20
Merrifield polymer-DAPPA [28]	4 M HNO <sub>3</sub>	211.82	143.64
Amberlite XAD-16-ADHA [29]	4 M HNO <sub>3</sub>	164.70	–

<sup>a</sup> Present work.



**Table 4**

Tolerance of foreign cations on the sorption of uranium by DMDBMA grafted resin; Feed: 3 M HNO<sub>3</sub>

Metal ions	K <sub>d</sub> of U (mL/g)			R.S.D. (%)
	100 ppm	500 ppm	1000 ppm	
Fe	419	407	417	1.55
Al	431	404	392	4.88
Sr	417	398	414	2.49
Cs	426	436	430	1.17
V	415	433	415	2.47

**Table 5**

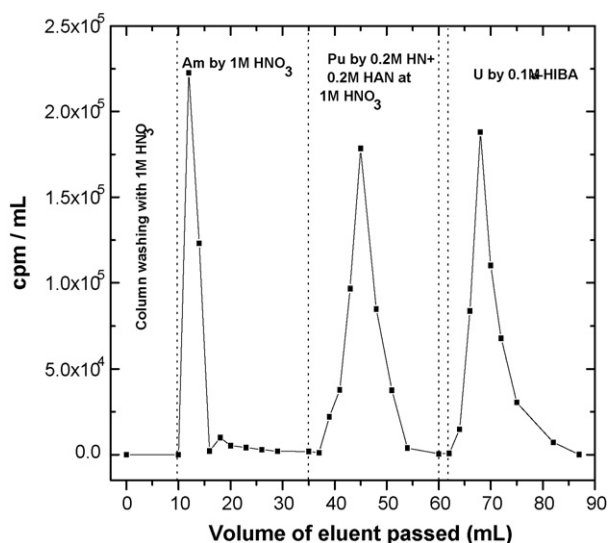
Optimized experimental parameters for the separation of Am, Pu and U by DMDBMA grafted resin column

Stationary phase	DMDBMA
Support material	Merrifield resin <sup>®</sup>
Mesh size	16–50
Bed volume	0.69 cm <sup>3</sup>
Bed density	0.43 g/cm <sup>3</sup>
Flow rate	3 drops/min
Eluent for Am	1 M HNO <sub>3</sub>
Eluent for Pu	0.2 M HAN + 0.2 M HN at 1 M HNO <sub>3</sub>
Eluent for U	0.1 M α-HIBA

complexed with the metal ions. Though DMDBMA grafted resin reflected lower metal loading capacity as compared to other amide grafted resins, the present resin appears to be highly suitable for the pre-concentration of actinide ions from their dilute solutions of moderate acidity (3–4 M HNO<sub>3</sub>).

### 3.5. Tolerance of metal ions on sorption of uranium

It was of interest to investigate the role of some of the common interfering elements present in radioactive waste as well as environmental samples, viz. Fe, Al, V, Sr and Cs on the sorption behaviour of U. Therefore, the ability of the malonamide grafted resin matrix for the quantitative extraction of trace level uranium in the presence of large concentrations of various interfering metal ions was investigated by batch method. As shown in Table 4, the distribution coefficient values of uranium was found to be practically unchanged in the presence of 100–1000 ppm of various interfering metal ions, viz. Fe(III), Al(III), Sr(II), Cs(I) and V(V). The result clearly depicts the ion selectivity behaviour of the DMDBMA grafted resin towards actinide ions.



**Fig. 4.** Elution profile of Am, Pu and U from the malonamide grafted resin column; temperature: 25 °C.

**Table 6**

Pre-concentration of metal ions by DMDBMA resin column; feed: 1 L aqueous solution containing metal ions at 3 M HNO<sub>3</sub>; eluent: 0.1 M α-HIBA

Metal ions	Concentration in loading solution (mg/L)	Amount eluted <sup>a</sup> (mg)	Percentage recovery	Pre-concentration factor
Th (IV)	4.10	4.23	103.17	40
U (VI)	0.124	0.118	95.16	40

<sup>a</sup> As estimated from 25 mL of the eluted fraction.

### 3.6. Column separation of Am, Pu and U

After demonstrating the possible separation of Am, Pu and U in batch studies, an attempt was made to separate these metal ions from a synthetic solution employing the malonamide grafted resin column. A glass column (dimension 5.5 cm × 0.4 cm) was packed with 0.3 g of grafted resin beads. The bed volume and the bed density were calculated from the column dimensions and the weight of the packed chromatographic resin material. The column was pre-conditioned by passing excess of 1 M nitric acid solution, prior to the introduction of the sample solution. The column operations were carried out at ambient temperature (25.0 ± 1 °C) at a flow rate of 3 drops/min (~9 mL/h). The elution curve was obtained by plotting the concentration of metal ions in the effluent (in terms of counts per unit time per unit volume) as a function of volume of eluent passed through the column. The optimized experimental column parameters are listed in Table 5.

A synthetic mixture of known quantity of <sup>241</sup>Am, <sup>233</sup>U and <sup>239</sup>Pu at 1 M HNO<sub>3</sub> was prepared and the valency of Pu was adjusted to Pu(IV) with 0.05 M NaNO<sub>2</sub>. The resulting solution was subsequently loaded on the column at a flow rate of 3 drops/min. The first fraction of Am was eluted with 1 M HNO<sub>3</sub> where all the activity could be recovered with in 25 mL of the eluent. As shown in the batch distribution data, low complexation of the trivalent metal ions with DMDBMA resulted in the elution of trivalent Am at 1 M HNO<sub>3</sub>, where tetravalent Pu and hexavalent U were satisfactorily complexed with the malonamide on the column. The next fraction of Pu was quantitatively eluted with 30 mL of a reducing mixture of 0.2 M HAN and 0.2 M HN at 1 M HNO<sub>3</sub> when Pu(III) formed could be eluted from the column due to its low affinity to the malonamide ligand. Sufficiently low flow rate used in the present study (~9 mL/h) could provide sufficient time for the reduction of Pu due to the fast reduction kinetics of the system as reported earlier [23]. Finally, the remaining fraction of the U was quantitatively eluted with 0.1 M alpha hydroxyl isobutyric acid. The chromatogram resulting from the elution is presented in Fig. 4. As presented in the figure, first 10 mL of 1 M HNO<sub>3</sub> solution was passed for pre-conditioning of the column. Subsequently, the column was loaded with the mixture of three metal ions followed by elution of different metal ions using different eluents. The purity of the eluted fraction was determined by alpha spectrometry and found that the Am fraction was fairly pure with <0.01% contamination of U and Pu. However, it was noticed that the Pu fraction was contaminated with 6% of Am and

**Table 7**

Performance of the malonamide grafted resin in several successive cycles

No. of cycles performed	K <sub>d</sub> , U at 1 M HNO <sub>3</sub>	% of N on the resin
1	68.97	6.76
2	63.04	6.58
3	65.21	6.53
4	62.60	6.61
5	63.11	6.43
Mean	64.59	6.50
S.D.	2.65	0.07
R.S.D.	4.11	1.12

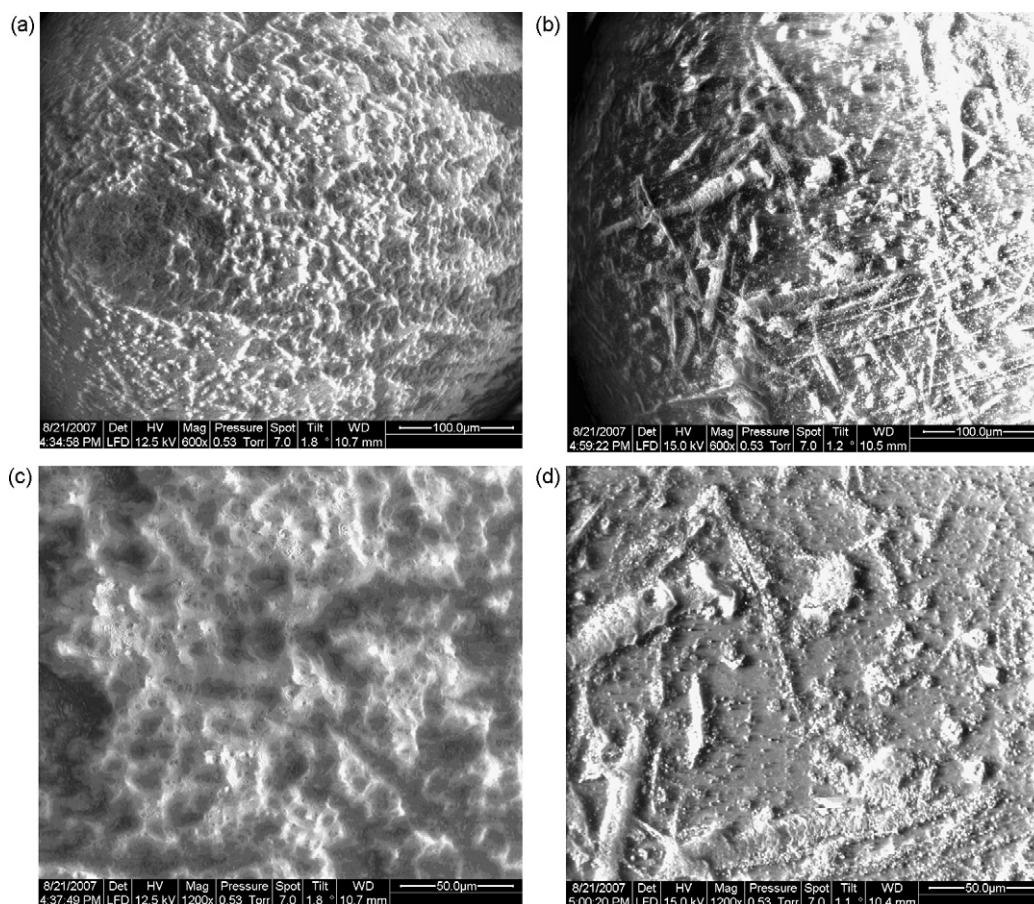


Fig. 5. SEM images of the fresh grafted resin (a and c) and the resin after continuous use for 30 days (b and d). Magnification: 600 $\times$  (a and b); 1200 $\times$  (c and d).

<0.1% of U. Similarly, U fraction was contaminated with 4% of Am as well as 2% of Pu. It seems that though cross contamination of actinides was observed, nevertheless, the column performance can be improved by increasing the column length [26,27].

### 3.7. Pre-concentration of uranium and thorium

Pre-concentration of the trace metal ions such as uranium and thorium was carried out from 3 M HNO<sub>3</sub> using DMDBMA grafted resin column. The column parameters were identical as described in Table 5. In independent experiments, 1 L solution containing trace amount of either uranium or thorium at 3 M HNO<sub>3</sub> was passed through the column at flow rate of 9 mL/h. During the loading step, no breakthrough was observed for both the metal ions. After passing the complete solution, the elution was performed with 0.1 M  $\alpha$ -HIBA and the results of pre-concentration are shown in Table 6. It was observed that the quantitative recovery of both the metal ions was possible in 25 mL eluting solution. It is evident from the table that about 4.10 mg of Th and 0.124 mg of U were loaded on the column which could be recovered quantitatively with in the error limits of  $\pm 5\%$ .

### 3.8. Stability and reusability of the resin

Finally, to ensure the stability and reusability of DMDBMA grafted resin, uranium was sorbed and desorbed on the resin in five successive cycles. The resin was loaded with a solution containing 1 g/L U at 3 M HNO<sub>3</sub>. After loading, the resin was washed thoroughly with excess of 0.5 M  $\alpha$ -HIBA and water followed by

vacuum drying to the constant weight. The resulting resin was then used for elemental analysis as well as for the distribution coefficient measurement of U(VI) at 1 M HNO<sub>3</sub>. It was observed that the nitrogen content of the recycled resin and distribution coefficient of U(VI) were within the relative standard deviation of 1 and 4%, respectively in five successive cycles (Table 7), suggesting good stability of the grafted resin. In another study, the resin was continuously equilibrated with 3 M HNO<sub>3</sub> for 30 days followed by distribution measurement. A constant value of U(VI) suggested no significant change in the sorption behaviour, demonstrating appreciable hydrolytic stability of the resin. The surface morphology of the recycled resin was monitored with the help of scanning electron microscopy (SEM). The SEM images indicated minor erosion on the surface of the resin which was smooth in the case of unused resin (Fig. 5). However, practically unchanged sorption behaviour of uranium revealed that the erosion may have taken place to the support without affecting the grafted malonamide molecules (active site) which are present on the surface.

## 4. Conclusions

The extraction chromatographic resin prepared by chemical anchoring of *N,N*-dimethyl-*N,N'*-dibutyl malonamide with chloromethylated Merrifield resin appears promising for the separation of Am, Pu and U from their mixture. The grafted resin showed superior binding for hexavalent and tetravalent metal ions such as U(VI) and Pu(IV) over trivalent metal ions, viz. Am(III) and Pu(III). The metal sorption capacity of the resin was found to be  $18.78 \pm 1.53$  mg and  $15.74 \pm 1.59$  mg/g resin for U and Th,

respectively. Various metal ions interference depicted the ion selectivity behaviour of the DMDBMA grafted resin towards actinide ions. The resin could be used for pre-concentration of U and Pu (possibly Th also) from environmental/waste effluents and could continuously be used for a long period of time without any appreciable change in the sorption properties towards the heavy metals.

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