



Two novel extraction chromatography resins containing multiple diglycolamide-functionalized ligands: Preparation, characterization and actinide uptake properties



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ABSTRACT

Two extraction chromatography resins were prepared for the first time by impregnating multiple diglycolamide-functionalized ligands such as diglycolamide-calix[4]arene (C4DGA) and tripodal diglycolamide (T-DGA) on Chromosorb-W, an inert solid support, for the removal of hazardous actinides like Am(III) from radioactive waste solutions at 3 M nitric acid. The resins were characterized by SEM, thermal and surface area (BET) analyses. The sorption of Am(III) on the two resins followed pseudo-second order sorption rate kinetics and was exothermic in nature. The sorption of trivalent *f*-elements proceeded through a chemisorption monolayer phenomenon as analyzed by using several isotherm models. The negative free energy change (ΔG) values of -34.46 and -28.45 kJ/mol for T-DGA and C4DGA, respectively, indicate a chemical interaction between the metal ions and the ligands on the surface of the resins. Distribution coefficient measurements of various metal ions showed a selective sorption of trivalent *f*-elements over hexavalent uranyl ions and other fission product elements. Column studies on breakthrough indicated 0.76 and 0.37 mg/g as the breakthrough capacities of the T-DGA and the C4DGA resins, respectively. It was possible to quantitatively elute the loaded metal ion using EDTA solutions.

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1. Introduction

Radioactive waste remediation is one of the most challenging research areas for separation scientists. The main objective in this area is to bring down the radiotoxicity of various waste effluents containing radioactive elements to acceptable levels. Out of the radioactive elements of concern, alpha emitting actinides with very long half-lives are of paramount importance and a great deal of efforts are directed toward their removal. Major techniques being used for this are solvent extraction, ion exchange, precipitation, and membrane separations [1]. While precipitation and solvent extraction techniques involve large volumes of chemicals, those involving ion-exchange- and membrane-based separations lack specificity. Ideally, one would opt for a technique which has the specificity of solvent extraction and easy operation as in ion-exchange. Extraction chromatography (XC) is a technique which combines these two techniques wherein the organic extractant is impregnated into the

pores of the solid support material which helps in the extraction of the metal ion when the aqueous stream is in contact with the resin material [2–4]. Subsequently, the extracted metal ions are eluted out by contacting with the strippant solution in a manner similar to that involved in ion-exchange-based separation methods. The major advantage of the XC based resins or solid phase extraction (SPE) materials is the very low inventory of the organic solvent. Furthermore, the property of the organic extractant can be tuned depending on the nature of the metal ion and selectivity requirement with respect to other metal ions.

Several XC resin materials have been used by different research groups for actinide ion uptake from various feeds. XC resin materials containing TBP (tri-*n*-butyl phosphate) have been extensively used and are found to be quite efficient for the recovery of tetra- and hexavalent actinide ions [5,6]. On the other hand, trivalent actinide ions have been recovered efficiently from acidic feed solutions using SPEs containing CMP (carbamoylmethyl phosphonate) [7] or CMPO (carbamoylmethylphosphine oxide) based [8] resin materials. We have reported [9] the uptake of actinide ions using a XC resin material containing DMBTDMA, a tetraalkyl malonamide extractant, which has been used in the early development of the DIAMEX

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process for actinide ions [10]. There have been reports on the use of XC resin materials containing basic [11] or acidic extractants as well, which are quite specific for the actinide ions [12]. These resin materials are being applied for the pre-concentration of actinides from various samples [13–16].

Recently, diglycolamide-based extractants such as TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide, Fig. 1(a)) have been found to be significantly more efficient as compared to the previously known extractants such as CMPO and malonamides for minor actinide partitioning [17]. This has led to the subsequent development of TODGA-containing XC resin materials, which have been found to be very promising for actinide ion uptake from acidic feed solutions [18,19]. Our subsequent studies on the extraction of actinides using multiple diglycolamide-functionalized extractants such as tripodal diglycolamide [T-DGA, Fig. 1(b)] [20,21] and diglycolamide-functionalized calix[4]arenes containing four diglycolamide pendent arms [C4DGA, Fig. 1(c)] [22–24] have shown a manifold increase in the extraction efficiency vis-à-vis TODGA. This makes them very promising to be included in XC resin materials.

The present study involves the preparation and characterization of two XC resin materials made from T-DGA and C4DGA and subsequent studies on their actinide ion uptake behavior from acidic feed solutions. They involve batch uptake studies including sorption kinetics and sorption isotherm studies. The batch loading studies were carried out for obtaining the capacities of these resins, which were compared with that of the TODGA-based XC resin material. Column studies were also carried out and the breakthrough and elution profiles were determined, which are prerequisite to evaluate the potential of the resins.

2. Experimental

2.1. Materials

Diglycolamide-functionalized calix[4]arene (C4DGA, Fig. 1(c)) [23] and tripodal diglycolamide (T-DGA, Fig. 1(b)) were prepared as described previously [20]. The ligands were characterized by NMR, HPLC, and ESI-MS. Chromosorb-W (dimethyl dichlorosilane treated acid washed celite diatomaceous silica, mesh size 60–80), obtained from John Manville, was washed with distilled water, ethanol, and acetone, followed by air-drying before use. ^{241}Am , Pu (mainly ^{239}Pu), and ^{233}U tracers were purified following standard procedures reported elsewhere [25] and the radiochemical purity of the tracers was checked by alpha-spectrometry. $^{152,154}\text{Eu}$, ^{137}Cs , and $^{85,89}\text{Sr}$ tracers, purchased from BRIT (Board of Radiation and Isotope Technology), Mumbai, were used after ascertaining their radiochemical purity by gamma ray spectrometry using a HPGe detector. Spec pure Eu_2O_3 (>99.99%) was used to prepare stock solutions for isotherm and column studies. All other chemicals were AR grade and were used as received.

2.2. Methods

All aqueous solutions were prepared using MilliQ water. The standard acid solutions were prepared from Suprapur acids obtained from Merck (Germany), followed by titration using a standard NaOH solution (titrated against potassium hydrogen phthalate) using phenolphthalein indicator (Fluka). Details of the resin preparation, characterization, and distribution studies are given below.

2.2.1. Preparation of XC resin materials

The extraction chromatographic resins were prepared by a standard procedure reported previously [9]. The method involves equilibration of a slurry containing 1.0 g of the DGA ligands (C4DGA or T-DGA), 1.0 g of *n*-dodecane, 0.25 g of *iso*-decanol, and 7.75 g of

solid support (Chromosorb-W) in a sufficient quantity of methanol for 24 h in a mechanical shaker, followed by solvent removal by flushing nitrogen gas with gentle stirring. The resulting material was vacuum dried to constant weight.

2.2.2. Characterization of the resin materials

The resin materials were characterized by SEM (Scanning Electron Microscopy) for the surface morphology, thermal analysis (for understanding the ligand loading), and surface area measurements by BET. The SEM pictures of the XC resin materials were obtained using a Stereoscan 100 Cambridge model operating at 15/25 kV with a magnification of 500 \times at a working distance of 15 mm at a tilt angle of 45 $^\circ$. As the resins were found to be non-conducting, a 15 nm coating of gold was given to all samples using a Balzer's coating unit model CEA 30 apparatus. Thermogravimetric analyses were performed using a Netzsch Thermo balance (Model: STA 409 PC Luxx) operating at a heating rate of 10 $^\circ\text{C}/\text{min}$ in air. The surface area analysis was done by BET measurements using a Surface Area analyzer (Thermo Scientific, Model: Surfer Analyzer).

2.2.3. Batch uptake studies

The sorption studies of metal ions were performed by equilibrating a known volume of aqueous phase (1 mL) containing the selected metal ion with a known amount of resin material (~10–20 mg) in a thermostated water bath. After equilibration, the tubes were centrifuged, the aqueous layer separated and centrifuged a second time. Suitable aliquots of the aqueous phase were taken before and after equilibration to assay the metal ions. The determination of ^{241}Am , $^{152,154}\text{Eu}$, ^{137}Cs , and $^{85,89}\text{Sr}$ was performed by gamma counting using a NaI(Tl) scintillation counter, while nuclides such as ^{239}Pu and ^{233}U were assayed by liquid scintillation counting. The distribution coefficient (K_d) of the metal ions on the resin was calculated by employing the following formula:

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

where C_0 and C are the metal ion concentrations (in counts per unit time per unit volume) before and after equilibration, V is the volume of the aqueous phase used (mL), and W is the weight of the resin material employed (g). The sorption isotherm experiments were carried out using Eu(III) solutions (30–300 mg L $^{-1}$ Eu) at 3 M HNO_3 spiked with $^{152,154}\text{Eu}$ tracer. All experiments were performed at 25 $^\circ\text{C}$, unless specified otherwise. All experiments were carried out in duplicate and the error limit was within the relative standard deviation of $\pm 5\%$.

2.2.4. Column studies

The column studies were carried out using a glass column (4 mm diameter \times 115 mm height) fitted with a stop cock to control the flow rate. The column used for the chromatographic experiments contained about 0.3 g of the resin material with a bed volume of 1.0 cm 3 and the flow rate was controlled to about 0.2 mL per minute using the stop cock. The column studies were carried out with a solution containing 1 g/L Eu in 3 M HNO_3 and spiked with $^{152,154}\text{Eu}$ radiotracer. The elution profiles were obtained after the column loaded with Eu was treated with a 0.01 M EDTA solution (pH 2.0). All runs were carried out at ambient temperature (24 \pm 0.5 $^\circ\text{C}$) and the results were reproducible within an error limit of $\pm 5\%$.

3. Results and discussion

3.1. Characterization of the materials

Using the N_2 -BET method, the specific surface area of the impregnated resins was calculated to be 3.84 \pm 0.19 and 4.71 \pm 0.13 m $^2/\text{g}$ m for the T-DGA and C4DGA resins, respectively,

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