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Synthesis and radiometric evaluation of diglycolamide functionalized mesoporous silica for the chromatographic separation of actinides Th, Pa and U

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Abstract

The separation of Th, Pa, and U is of high importance in many applications including nuclear power, nuclear waste, environmental and geochemistry, nuclear forensics and nuclear medicine. Diglycolamide (DGA)-based resins have shown the ability to separate many elements, however, these resins consist of non-covalent impregnation of the DGA molecules on the resin backbone resulting in co-elution of the extraction molecule during separation cycles; therefore, limiting their long-term and repeated use. Covalently binding the DGA molecules onto silica is one way to overcome this issue. Herein, measured equilibrium distribution coefficients of normal extraction chromatographic DGA resin and a covalently bound form (KIT-6-N-DGA sorbent) are reported. Several differences are observed between the two systems, the most significant being observed for uranium, which demonstrated significantly lower sorption behavior on KIT-6-N-DGA. These results indicate that U can effectively be separated from Th and Pa using KIT-6-N-DGA; a task that could not be completed with the use of normal DGA alone.

Introduction

The primordial actinides (Th, U) and their associated decay products (Ac, Pa) have a wide variety of practical applications associated with the dating of environmental and geochemical processes,[1] their ubiquitous application in the nuclear power industry,[2, 3] use as tracers in the field of nuclear forensics[4, 5] and use as target materials and therapeutic agents in nuclear medicine.[6] A common theme among these applications is the need to separate, isolate and purify these elements from a variety of matrices. Methods such as cation- exchange, anion-exchange, and liquid-liquid solvent extraction[7-12] have been investigated for separation, however, with the advent of highly sensitive detection methods and potential applications in medicine, highly efficient, simple and fast separation methodologies are desired. Age dating applications in particular demand high radiochemical yields in the analysis of more complex matrices[13] in order to avoid Pa detection limit increase. Many reported Pa separation methods[14, 15] either rely on a larger acid matrix amounts and a sequence of sorption columns or on the use of organic solvent matrices. Multiple column steps and larger matrix volumes decrease the separation yield of the analyte under investigation. Moreover, larger acid/ organic solvent quantities lead to the generation of larger quantities of problematic mixed wastes. Thus, methods are sought that minimize the separation steps and the volume of the analyte solution. With respect to the production of short-lived radionuclides, fast and efficient separation methods are sought that employ solid state sorption matrices with high radiation resistance. Since short-lived, high specific activity radionuclides often only represent a very small mass of a particular element, procedures for their separation, recovery and purification often borrow from analytical chemistry methodologies.

The uranium isotope ^{230}U ($t_{1/2}$=20.8 d) is of interest to the medical community for the treatment of cancer and various diseases through targeted alpha therapy (TAT).[16-18] TAT utilizes the high linear energy transfer (LET) and short range of alpha particles emitted from radionuclides attached to specified biological molecules that selectively bind to and destroy cancer cells while leaving surrounding tissue unperturbed. Uranium-230 is also the parent of the much short-lived radionuclide of ^{226}Th ($t_{1/2}$=30.6 m), which has potential as a therapy isotope for TAT as well.[17]

Uranium-230 can be formed directly through the reactions ^{231}Pa (p,2n)^{230}U[18], ^{232}Th(α, 6n)^{230}U, and ^{232}Th(^{3}He,5n)^{230}U[19] or through the partial decay (7.8%) of its parent radionuclide ^{230}Pa ($t_{1/2}$=17.4 days). Protactinium-230, in turn, is available via particle induced reactions ^{232}Th(p,3n)^{230}Pa[16, 17] and ^{232}Th(d,4n)^{230}Pa[20]. Other potential reaction pathways for the production of ^{230}Pa include bremsstrahlung irradiation (^{231}Pa(γ,n)^{230}Pa)[21] and the fast neutron induced reaction^{231}Pa(n,2n)^{230}Pa.[22] Regardless of the production path, a robust separation is required to obtain either a pure Pa or U product.

Apart from the recovery of irradiation products Pa or U, there is further demand for rapid and efficient Pa/U or U/Th separation methods with respect to decay products: Figure 1 depicts the decay chain of ^{230}Pa with emphasis on the potential therapeutic dose from ^{230}U and ^{226}Th. This entire decay series produces a combined 33.5 MeV alpha dose from ^{230}U (through five alpha decays), or a combined 27.7 MeV alpha dose from ^{226}Th (through four alpha decays). If ^{226}Th is used for medical applications, a radionuclide generator is required that enables the rapid chemical recovery of ^{226}Th as a decay product from the ^{230}U parent stock activity on the basis of solid-phase sorption of the parent and mobilization of the daughter isotope. Similarly, if ^{230}U is obtained from the decay of ^{230}Pa and is to be used as a direct TAT treatment agent, a ^{230}Pa/^{230}U generator needs to be available that relies on an efficient Pa/U separation procedure.

Novel extraction chromatographic resins greatly improved the ability to separate actinides. Particular focus has been on diglycolyl amide (DGA, also as diglycolamide) extraction chromatographic resin (N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide,[23] or TODGA) from Eichrom Industries. Unlike ion-exchange chromatography that makes use of electrostatic interactions between ions and the functional group of the solid phase, extraction chromatographic resins use the interactions between metallic ions as Lewis acids and the extractant molecule (TODGA in this case) as a Lewis base with different metal ions having different affinities to the extractant. This allows for the separation of a mixture of actinides.

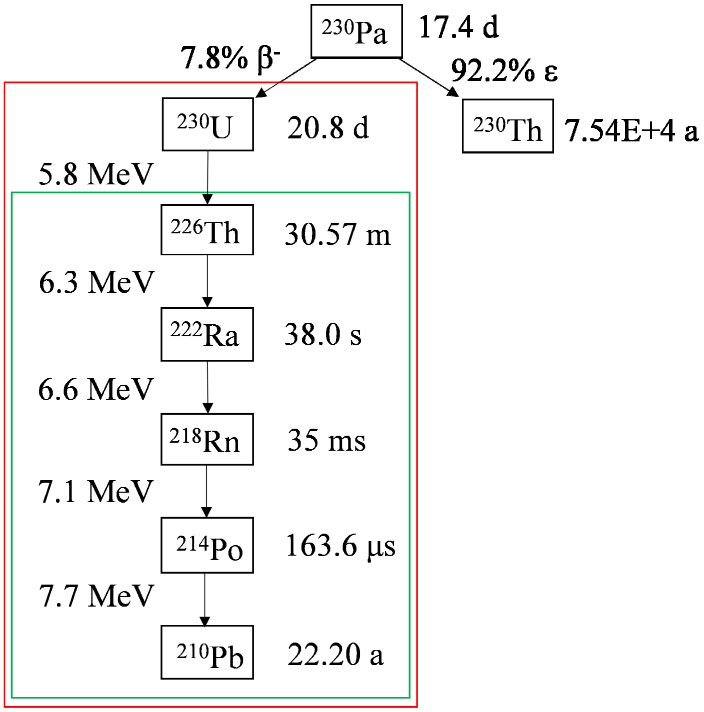

Figure 1: Decay scheme of ^{230}Pa, ^{230}U, and ^{226}Th.

The extractant in an extraction chromatographic resin is present in the form of an organic solution which is impregnated in a porous support (e. g., polymer resin, silica, carbon). The solution of the extractant molecule remains in the pores due to surface tension interactions between the extractant solution and the solid support. This leads to one major drawback of using such an extraction chromatography resin, in that the resin will break down as the extractant washes off the solid support over time. Recent research performed by Kleitz et al. has demonstrated the utility of covalently binding DGA to porous silica materials and has shown its suitability for the recovery of rare-earth elements.[24-26] In addition to the benefit of fixing the DGA molecule to the resin, the use of silica is advantageous due to its ability to withstand highly radioactive environments.[27] Compared to 2-D hexagonal pore systems like SBA-15 or MCM-41, the choice of the 3-D cubic KIT-6 silica is motivated by the highly interconnected nature of the pore network of this material, which could reduce the risks of pore blocking and enhance the diffusion of liquids through the system.[28-31]

Little work has been done to investigate the sorption affinity of actinide elements uranium, thorium and protactinium towards covalently bound DGA as compared to DGA solution in the conventional extraction chromatographic form. Herein we report the measurement of equilibrium distribution coefficients (K_d) for both the normal-impregnated (extraction chromatography) resin (referred to as DGA throughout manuscript) and the covalently bound DGA-solid phase (referred to as KIT-6-N-DGA throughout manuscript), using varying concentrations of hydrochloric and nitric acids, which are typically used in the context of actinide separation techniques.

To the best of our knowledge, a systematic sorption behavior of light actinide elements on DGA functionalized silica over a wide matrix concentration range has not been reported as yet. Our work further demonstrates the utility of the short-lived, high specific activity uranium tracer ^{230}U for analytical studies.

Experimental Section

Materials and Methods

Trace metal grade nitric acid (HNO_3) and hydrochloric acid (HCl) were obtained from Fisher Scientific, and all dilutions were performed using 18 MΩ milli-Q water. Extraction chromatographic resin (DGA, normal) was obtained from Eichrom Industries. All chemicals were used without further purification. Radionuclides used in this work were obtained from Oak Ridge National Laboratory and were available as by-products from the proton irradiation of thorium targets for the production of ^{225}Ac.[16, 32]

Synthesis of KIT-6 Silica

High quality KIT-6 silica was obtained following the procedure reported by Kleitz et al.[33] Briefly, 8.00 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Sigma-Aldrich) was dissolved in 290 g of distilled water and 14.75 g HCl (37%) was added under vigorous stirring. After complete dissolution, 8.00 g of n-butanol (BuOH, Aldrich, 99%) was added. The mixture was left under stirring at 35 °C for 1 h, after which 20.63 g of tetraethoxysilane (TEOS, Acros, 99%) was added at once to the homogenous clear solution. The molar composition of the starting reaction mixture was TEOS/P123/HCl/H_2O/BuOH = 1.0/0.014/1.54/165.6/1.11. This mixture was left under stirring at 35 °C for 24 h, followed by an aging step at 100 °C for 24 h under static conditions. The resulting solid product was then filtered and dried for 24 h at 100 °C. For template removal, the as-synthesized silica powder was first shortly slurried in ethanol-HCl mixture and the resulting material was subsequently calcined in air at 550 °C.

Synthesis of the Diglycol-2,4-diamido-propyltriethoxysilane (DGA-N) Ligand DGA-Functionalization of Silica

The KIT-6-N-DGA material was prepared following a modified procedure as reported by Florek et al.[24,22] First, the DGA derivative of the aminosilane (DGA-N) was prepared as follows: 600 mg (3.51 mmol) of diglycol chloride (Sigma Aldrich, 95%) was dissolved in 15 mL of anhydrous toluene and cooled to 0 °C (ice bath). Then, a mixture of 1.72 mL (1.63 g, 7.36 mmol) of (3-aminopropyl)-triethoxysilane (APTS, Sigma Aldrich, 99%) and 4.89 mL (3.55 g, 35.1 mmol) of triethylamine (Alfa Aesar, 99%) in 15 mL of anhydrous toluene was slowly added to the solution. The reaction was allowed to warm up to room temperature overnight. The reaction mixture was filtered, and the filtrate was evaporated and dried under vacuum. The structure of the modified silane was confirmed by liquid ^{1}H NMR analysis: ($CDCl_3$) $\delta = 0.63$ (Si–CH_2, 4H, t); 1.21 (CH_3–CH_2, 18H, t); 1.64 (CH_2–CH_2–CH_2, 4H, m); 3.29 (CH_2–NH, 4H, q); 3.80 (CH_3–CH_2,12H, q); 3.99 (CO=CH_2–O, 4H, s); 6.79 (NH, br.) ppm.

Prior to the addition of the modified silane (500 mg), 1 g of activated mesoporous silica (treated overnight at 150 °C under vacuum) was dispersed in 100 mL of anhydrous toluene. The mixture was refluxed at 100 °C for 3 h under stirring and nitrogen flow. Then, the modified silane and triethylamine were added and the resulting mixture was left at 100 °C for 24 h under stirring and inert atmosphere. After cooling down to room temperature, the solid product was filtered, washed thoroughly with toluene and ethanol three times and dried at 70 °C overnight in air. Un-reacted silane molecules were removed by Soxhlet extraction in dichloromethane for 6 h. The final product was dried at 70 °C overnight in air.

Materials Characterization

N_2 adsorption-desorption isotherms were measured at -196 °C (77 K) using an Autosorb-iQ2 sorption analyzer (Quantachrome Instruments, USA). Prior to the analysis, the samples were outgassed for 10 h at 200 °C (unmodified silica support) or at 80 °C for 12 h (functionalized sorbents). The specific surface area (S_{BET}) was determined using the Brunauer-Emmett-Teller (BET) equation in the range $0.05 \leq P/P_0 \leq 0.20$ and the total pore volume (V_{pore}) was measured at $P/P_0 = 0.95$. The pore size distribution for all materials were calculated by using the nonlocal density functional theory (NLDFT) method (Autosorb ASiQWin software) considering the sorption of nitrogen at -196 °C in silica with cylindrical pores.[34] The pore widths were determined by applying the NLDFT kernel of equilibrium isotherms (desorption branch). Simultaneous thermogravimetric analysis-differential scanning calorimetry analysis (TGA-DTA/DSC) was performed using a Netzsch STA 449C thermogravimetric analyzer, under air flow of 20 mL min^{-1} and with temperature-programmed heating rate of 10 °C min^{-1}. Carbon-13 cross-polarization magic-angle-spinning (CP/MAS) nuclear magnetic resonance (NMR) analyses were carried out on a Bruker Avance 300 MHz spectrometer (Bruker Biospin Ltd, Milton, Canada) at 75.4 MHz for ^{13}C. The ^{13}C CP/MAS NMR spectrum was recorded with a 4 mm MAS probe with a spinning rate of 8 kHz and contact time of 1 ms. Chemical shifts were referenced to adamantane for ^{13}C.

HPGe Spectrometry

Gamma-ray spectrometry for the distribution coefficients and dynamic column separation studies was conducted using an EG & G Ortec Model GMX-35200-S HPGe detector system in combination with a Canberra Model 35-Plus multichannel analyzer. Detector diameter was 50.0

mm; detector length 53.5 mm; Be window thickness 0.5 mm; outer dead-layer thickness 0.3 µm. Detector response function determination and evaluation were performed using standards of radionuclide mixtures containing ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{88}Y, ^{60}Co, traceable to the National Institute of Standards and Technology (NIST) and supplied by Eckert & Ziegler, Atlanta, GA, USA. The detector was a p-type Al-windowed HPGe detector with a measured FWHM at 1333 keV of approximately 2.2 keV and a relative efficiency of about 10%. Relative total source activity uncertainties ranged from 2.6% to 3.3%. Counting dead time was kept below 10%.

Equilibrium Distribution Coefficients

Equilibrium distribution coefficients (K_d) were determined for uranium, protactinium, and thorium using the batch extraction mode. Each condition was run in duplicate. Approximately 50 mg of extraction chromatographic diglycolamide resin (DGA) or approximately 20 mg of covalently bound KIT-6-N-DGA were added to pre-weighed and tared 2 mL centrifuge tubes. One mL of liquid phase (HCl or HNO_3 of variable concentrations ranging from 0.1-12 M) along with a 10 µL aliquot containing 4 kBq ^{230}U, 7 kBq ^{227}Th, or 5 kBq ^{233}Pa in 0.1 M HCl were added to each tube and weighed. The mixtures were allowed to equilibrate for 24 h on a rocker at ambient temperature. The mixtures were filtered with 4 mm nonsterile hydrophilic polytetrafluoroethylene (PTFE) syringe filters (EMD Millipore, Billerica, MA) and the characteristic gamma-ray lines of ^{230}U, ^{227}Th, and ^{233}Pa in the filtrate were measured with a high purity germanium (HPGe) detector. Determination of ^{230}U was performed by waiting 5 h to allow secular equilibrium to form between ^{230}U and ^{226}Th, and measuring characteristic ^{226}Th gamma-ray lines due to the very low intensity of ^{230}U decay gamma-ray lines. The total activity in the aqueous phase was calculated from this aliquot; the activity adsorbed on the resin was determined by subtraction of total aqueous activity from the total original activity added. Distribution coefficients were calculated using Equation 1, where A_i is the initial activity, A_{eq} is the equilibrium activity in the aqueous phase, V is the volume of the equilibrium phase (mL) and m is the mass of the resin (g).

$$K_d = \frac{C_{resin}}{C_{solution}} = \frac{A_i - A_{eq}}{A_{eq}} \cdot \frac{V_{solution}}{m_{resin}} \quad \text{(Equation 1)}$$

Results and Discussion

After grafting the DGA-disilane on KIT-6 silica, the resulting hybrid material demonstrates a typical type IV isotherm with a steep capillary condensation step and a hysteresis loop (type H1) in the relative pressure range P/P_o of 0.6–0.8, which is characteristic of mesoporous solids with large cylindrical mesopores[35] (> 4 nm) (Figure 2). The physicochemical characteristics of the hybrid sorbent are compiled in Table 1. The KIT-6-N-DGA sample exhibits relatively high BET[36] specific surface area, 443 $m^2\,g^{-1}$, and high pore volume, 0.69 $cm^3\,g^{-1}$. Upon surface modification, the pore width of the synthesized sorbent became smaller (7.1 nm vs 8.1 nm for the pristine KIT-6 silica), while the pore size distribution remained fairly narrow (see Figure 2 inset), in line with our previous reports.[24, 25] This suggests a rather uniform grafting of the ligand over the pore surface of the materials, with no pore blocking/obstruction effects. The integrity of the chemically grafted DGA ligand was verified by solid state ^{13}C CP/MAS NMR spectroscopy (Figure 3) and the data agree well with the covalent anchoring of the ligand on the surface of silica, as reported previously.[24, 25]

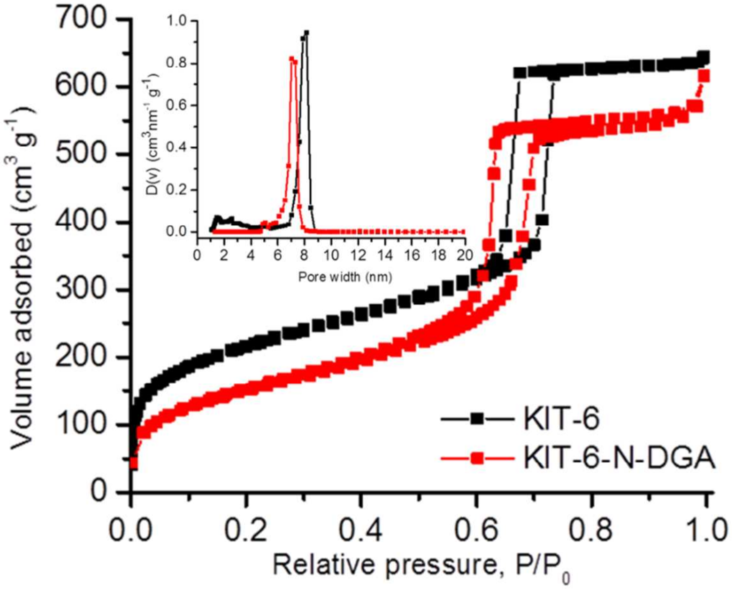

Figure 2: N_2 adsorption-desorption isotherms measured at -196 °C for the pristine KIT-6 silica and DGA-modified KIT-6-DGA sorbent, as indicated. Inset shows the respective pore size distributions calculated from the desorption branch using the NLDFT method (silica with cylindrical pore model).

Table 1: Physicochemical parameters derived from N_2 physisorption measurements at low temperature (-196°C) and organic content from thermogravimetric analysis (TGA).

Sample	Surface area S_{BET}^{a} (m^2 g^{-1})	Pore size NLDFT$_{des}$^{a} (nm)	Total pore volume^a(cm^3 g^{-1})	Organic content^b (%)
KIT-6	781	8.1	0.98	-
KIT-6-N-DGA	443	7.1	0.69	25

[a] – Based on the N_2 physisorption analysis.

[b] – Calculated from the thermogravimetric analysis in the 150-650 °C temperature range.

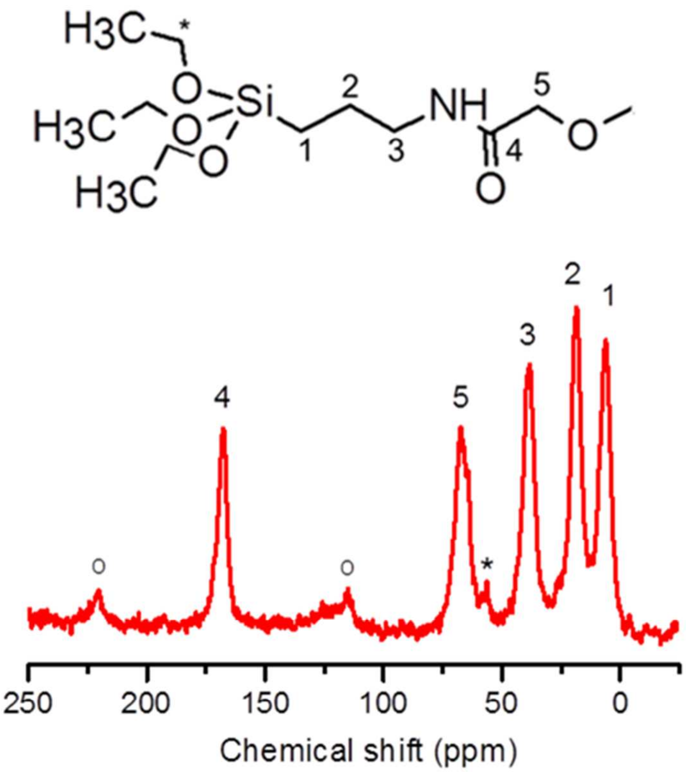

Figure 3: Solid state ^{13}C CP/MAS NMR spectrum for the DGA-modified mesoporous sorbent. The two additional small bands visible on the ^{13}C NMR spectrum are spinning side-bands of the carbonyl peak.

Equilibrium distribution coefficients (K_d) for Th, Pa, and U in hydrochloric and nitric acid media on extraction chromatography DGA resin and on the covalently bound DGA equivalent, i.e., KIT-6-N-DGA, were measured and are shown in Figure 4. Measured equilibrium K_d's for Th, Pa, and U on extraction chromatography DGA resin are in agreement with previously published data.[37, 38] With respect to KIT-6-N-DGA, protactinium showed high sorption capacity at all of the measured HCl and HNO_3 concentrations, while high sorption was not observed at low acid concentrations with the DGA resin. The thorium sorption behavior was similar for both resins for all concentrations of HCl tested, however, the measured equilibrium K_d's were significantly lower for HNO_3 concentrations ≥ 2 M with KIT-6-N-DGA as compared to DGA resin. Uranium, on the other hand, demonstrated a significantly lower sorption behavior with KIT-6-N-DGA for HCl and HNO_3 concentrations $\geq$ 2 M than for DGA. Souka et al. measured the sorption behavior of actinides on silica and showed that Pa had high affinity for non-functionalized silica itself.[39] Therefore, as a control, equilibrium distribution coefficients for Pa and Th were measured on non-functionalized "plain" KIT-6 powder to determine if the high sorption observed was due to silica support itself. In this case, no sorption affinity was observed for Th on pure silica for all HCl and HNO_3 concentrations measured. Protactinium demonstrated some sorption on pure silica, which can account for the higher binding to KIT-6-N-DGA observed at low acid concentrations. In HNO_3, Pa sorption behavior does not significantly differ between pure silica and KIT-6-N-DGA, however, in HCl Pa sorption is significantly higher for KIT-6-N-DGA than for silica at concentrations $\geq$ 3 M. Previous work by Lebed et al. demonstrated minimal affinity of uranium for the KIT-6 silica support. Therefore another control experiment was not performed for uranium.[28]

The most striking difference between the DGA resin and KIT-6-N-DGA is the sorption behavior of uranium. The equilibrium K_d's for U with DGA indicate substantial binding affinity in both HCl and HNO_3 with concentrations > 2 M. However, little to no binding affinity was observed at lower concentrations. This trend is also seen with Pa; rendering extraction chromatography DGA resin ineffective for the separation of Pa and U under these conditions. However, KIT-6-N-DGA shows minimal binding of uranium, especially at HCl concentrations between 0.1 and 2M. Uranium is present as the sterically demanding uranyl dioxocation $(O=U=O)^{2+}$ in aqueous solution at all concentrations of both hydrochloric and nitric acids studied. Considering that Th and Pa bind rather well to KIT-6-N-DGA over the entire acid concentration range investigated, this offers a promising way for the separation of U from Pa and Th using a single column, which constitutes a novelty in terms of simplicity and mild matrix conditions.

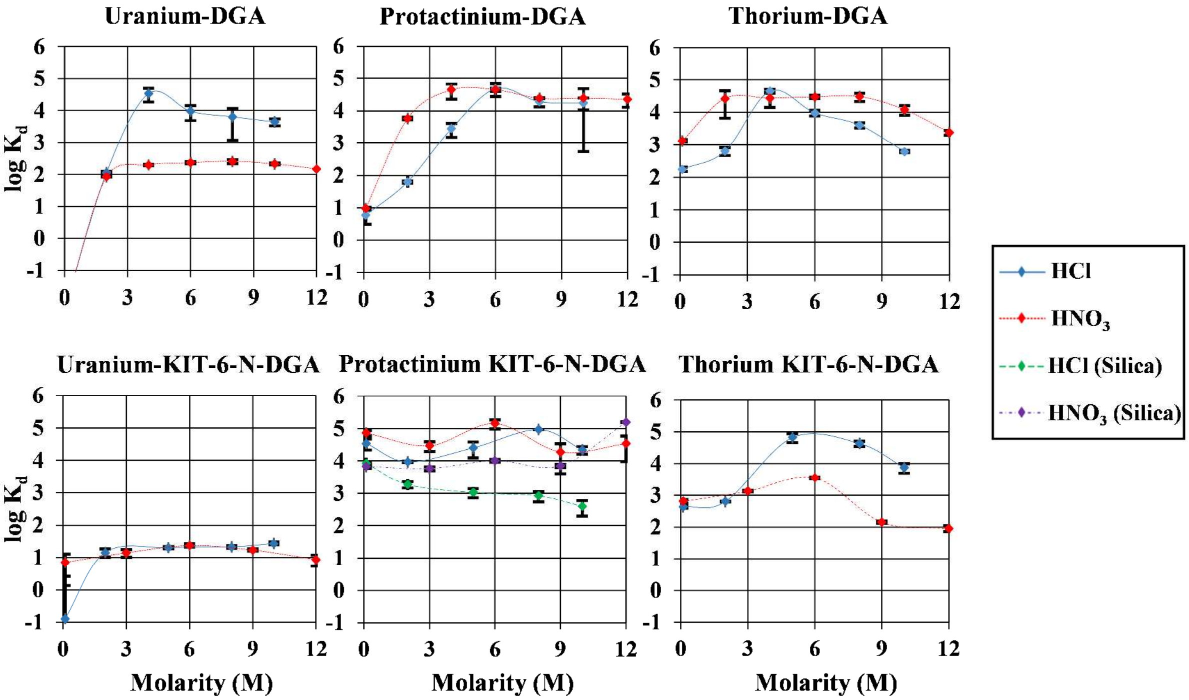

Figure 4: Equilibrium distribution coefficients for U, Pa, and Th on DGA resin (extraction chromatographic) and KIT-6-N-DGA sorbent (covalent). For the Pa KIT-6-N-DGA K_d graph, the KIT-6 silica control is also plotted as significant adsorption of Pa occurs.

The lower sorption behavior of KIT-6-N-DGA observed with U could be owing to steric hindrances related to chelation to the (more rigid) covalently bound DGA moiety as opposed to DGA chelation in solution (impregnated on the resin). The U(VI) uranyl dioxocation, $(O=U=O)^{2+}$ is significantly larger than Th^{4+}. Protactinium, on the other hand, which is predominantly pentavalent in aqueous solutions, exhibits aqueous speciation behavior that corresponds to its location between Th and U on the periodic table: the stability of oxo-hydroxides relative to oxide hydrates decreases in the order Th(IV) > Pa(V) > U(V) > Np(V) >Pu(V) resulting in increasing covalency and species size upon proceeding from Th to Pu

Consequently, steric hindrance is more prominent with UO_2 than with $PaO(OH)_2$, and, in turn, $PaO(OH)_2$ is sterically more hindered than Th^{4+}. Pa(V) is rapidly hydrolyzed in water, however, it can be stabilized in the presence of complexing agents so that a Pa(V)-DGA chelate may be formed without steric hindrance.[40, 41] Regarding UO_2^{2+} sorption behavior on KIT-6-N-DGA, it would be of interest to study whether adding a polyethylene glycol (PEG) linker between the silica and diglycolamide molecule could lead to an increase of the affinity, since an increase in distance between the DGA moieties allows for more stable complexation of larger acceptor groups. Moreover, the PEG chain would provide additional donor sites for a Lewis acid cation.

The KIT-6-N-DGA sorbent offers additional advantages in radiochemical separations over the classical DGA resin. Silica has been shown to be resistant to radiolysis; potentially allowing higher activities to be processed and repeated use of a KIT-6-N-DGA in an automated chemical processing setting.[27, 42, 43] Furthermore, covalently binding the extraction molecule to the resin reduces the breakdown associated with the coelution of extractant solution and cross-contamination that may occur with repeated use of the noncovalent DGA form.

Conclusions

In this work, we showed that the covalent grafting of the DGA ligand on mesoporous KIT-6 silica affords a porous sorbent which has the potential to separate U from Pa and Th. This has promise for use in targeted alpha therapy applications in the $^{230}Pa/^{230}U$ radionuclide generator, especially as high $^{230}Pa/^{230}U$ loading activities (several GBq) are concerned. KIT-6-DGA, in which the ligand is being covalently bound to a silica backbone, should be able to withstand higher quantities of radionuclide activities than the conventional DGA extraction chromatography resin as silica appears more resistant to radiolysis. Future work includes dynamic column and loading capacity studies with KIT-6-N-DGA-type resins, and determining the ability of these mesoporous hybrid resins to withstand higher activity loads without sustaining radiolysis. In a future efforts we will also pursue radiation resistance studies of the KIT-6-N-DGA-type resin utilizing column loads of higher actinide radionuclide activities.

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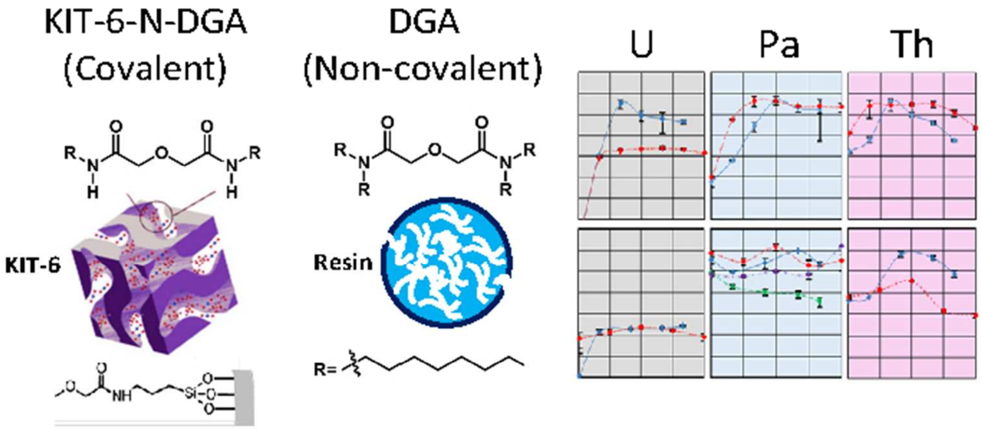

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