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Surface Engineering of PAMAM-SDB Chelating Resin with Diglycolamic Acid (DGA) Functional Group for Efficient Sorption of U(VI) and Th(IV) from Aqueous Medium

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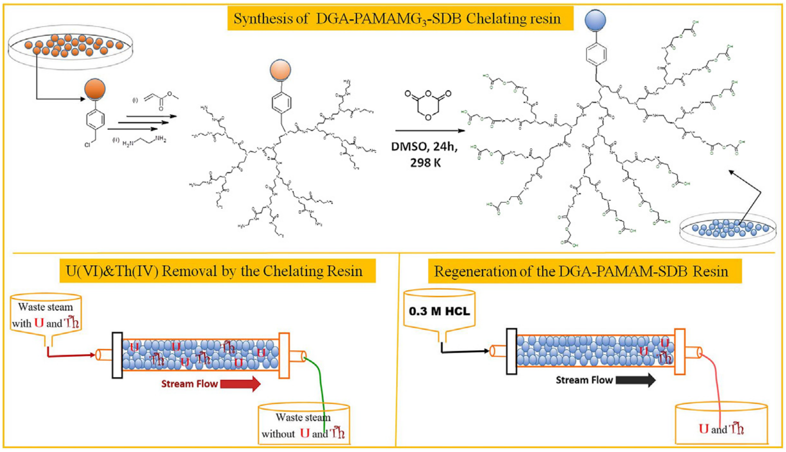
HIGHLIGHTS

- A new DGA-PAMAM-SDB chelating resin has been synthesized for actinide sorption.
- Maximum sorption capacities of resin are 682 and 544.2 mg g^{-1} for U(VI) and Th(IV).
- DGA-PAMAM-SDB chelating resin could be regenerated and reused.
- DFT calculation of actinides interaction with resin corroborates the experimental.
- Resin is effective for sorption of actinides from both aqueous and HNO_3 medium.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel chelating resin obtained *via* growth of PAMAM dendron on surface of styrene divinyl benzene resin beads, followed by diglycolamic acid functionalization of the dendrimer terminal. Batch experiments were conducted to study the effects of pH, nitric acid concentration, amount of adsorbent, shaking time, initial metal ion concentration and temperature on U(VI) and Th(IV) adsorption efficiency. Diglycolamic acid terminated PAMAM dendrimer functionalized styrene divinylbenzene chelating resin (DGA-PAMAM-SDB) is found to be an efficient candidate for the removal of U(VI) and Th(IV) ions from aqueous ($pH > 4$) and nitric acid media (> 3 M). The sorption equilibrium could be reached within 60 min, and the experimental data fits with pseudo-second-order model. Langmuir sorption isotherm model correlates well with sorption equilibrium data. The maximum U(VI) and Th(IV) sorption capacity onto DGA-PAMAMG$_5$-SDB was estimated to be about 682 and 544.2 mg g^{-1} respectively at 25 °C. The interaction of actinides and chelating resin is reversible and hence, the resin can be regenerated and reused. DFT calculation on the interaction of U(VI) and Th(IV) ions with chelating resin validates the experimental findings.

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Nomenclature

CSDB	Chloro-methylated styrene divinylbenzene
PAMAM	Poly(amido)amine
DGA	Diglycolamic acid
C_o	initial metal ion concentration ($mg\,L^{-1}$)
C_t	concentration of metal ion at time ‘t’ ($mg\,L^{-1}$)
C_e	concentration of metal ion at equilibrium ($mg\,L^{-1}$)
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$)
k_i	intraparticle diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$)
α	Elovich adsorption rate constant ($mg\,g^{-1}\,min^{-1}$)
β	Elovich desorption constant ($g\,mg^{-1}$)
c	intraparticle diffusion constant related to adsorption capacity ($mg\,g^{-1}$)
q_o	Langmuir saturated monolayer adsorption capacity ($mg\,g^{-1}$)
q_t	adsorption amount of metal ion at time ‘t’ ($mg\,g^{-1}$)
q_e	adsorption amount of metal ion at equilibrium ($mg\,g^{-1}$)
b	Langmuir constant related to the free energy of adsorption ($L\,g^{-1}$)
K_F	Freundlich constant raleted to adsorption capacity ($mg^{1-n}\,L^n\,g^{-1}$)
K_{DR}	activity coefficient related to the mean adsorption energy
ε	Polanyi potential
B_T	Heat of adsorption ($mg\,g^{-1}$)
A_T	Maximum binding energy between adsorbent and adsorbate ($L\,g^{-1}$)
n	Freundlich constant inductive of the intensity of the adsorption
R_L	Langmuir dimensionless parameter (or) Separation factor
ΔH^0	standard enthalpy change (kJ $mole^{-1}$)
ΔS^0	standard entropy change (kJ $mole^{-1}\,K^{-1}$)
ΔG^0	standard free energy change (kJ $mole^{-1}$)
K_d	distribution coefficient ($L\,g^{-1}$)
E_a	activation energy of adsorption ($kJ\,mol^{-1}$)
A	Arrhenius factor
m	mass of the adsorbent (g)
V	volume of the solution (L)
R	universal gas constant ($J\,K^{-1}\,mol^{-1}$)
R^2	Correlation coefficient
SD	Standard Deviation
T	temperature (K)
t	adsorption time (min)

1. INTRODUCTION

Radioactive wastes generated during various stages of nuclear fuel cycle generally contain actinides and various fission products in aqueous and nitric acid media. Accumulation of large volume of radioactive waste makes storage more risky and expensive. Therefore, these waste streams are treated to reduce their activity to a dischargeable level permitted as per national regulations. Conventional and recent methods for treating radioactive waste include solvent extraction, precipitation, ion exchange, sorption, membrane separation, electrodeposition, steam/solar evaporation and phyto remediation [1,2].

Radioactive waste separation based on solid phase extraction (SPE) has gained a considerable importance over the last few decades due to its simplicity, rapidity and cost effectiveness. SPE is carried out by metal ions transfer from aqueous phase to the adjacent active solid sites through adsorption, ion exchange, chelation, ion-pair formation, etc. subject to nature of sorbent and metal ions. The metal ions sorbed on the solid phase are recovered by changing the conditions or by using a suitable eluant. Various types of sorbents such as organic [3,4], inorganic [5,6], bio-sorbent [7,8], composites [9], foams [10], metal organic framework [11], nanocrystal [12] and carbon based material [13,14] have been developed for recovery of radionuclides. Among the solid sorbents, chelating resins are being increasingly used due to their high adsorption capacity and selectivity. These chelating resins are prepared either by coating/impregnating or chemically bonding/grafting the chelating agents on a solid substrate [15–21]. The choice of appropriate chelating agent is a critical factor to obtain maximum recovery.

The major aim of radioactive waste management is to separate long-life alpha emitting radionuclides of actinides. Being “hard” Lewis acids, actinide ions in aqueous solution show strong tendency to form complexes with “hard” donor-ligands (‘O’ or ‘F’ as donor atoms) rather than “soft” donor-ligands (‘N’, ‘S’ or ‘P’ as donor atoms) [22]. Actinides recovery from aqueous waste using chelating agents containing $>P=O$, $>C=O$ or other functional groups of desired basicity and stereochemistry have been extensively studied in recent years [23]. In strong acidic medium, various chelating resins containing phosphate and amide chelating groups were employed for the recovery of actinides [24–33]. Particularly amide based chelating agents are interesting due to their innocuous degradation products, high radiolytic stability and easy stripping of actinides from amide ligands. Amide ligands can be totally incinerated thereby significantly reducing the secondary wastes generated in the nuclear waste [23,32,33]. Among the various amide based resins reported, tridentate diglycolamides [34] and diglycolamic acid(DGA) [35,36] exhibit high distribution coefficient for actinide and lanthanide ions in high acidic condition.

Advances in macromolecular chemistry such as invention of highly branched dendritic polymers are providing unprecedented opportunities in developing effective separation processes for the treatment of waste water. Dendrimer functional groups can be formulated to provide the required properties of water solubility, selectivity and high loading capacity, etc. Poly(amido)amine (PAMAM) and poly(propylene)imine (PPI) dendrimers and their derivatives have shown potential applications in removal of metal ions such as Cu(II), Ni(II), Co(II), Pd(II), Pt(II), Zn(II), Fe(III), Ag(I), Au(I), Eu(III), U(VI), and Th (IV) from dilute aqueous solutions [37–40]. Our previous reports showed that the PAMAM dendron-SDB resin was effective in removal of uranium and thorium from aqueous solution rather than acidic medium [41]. However, a quantitative recovery of actinides present in traces from highly acidic medium is the most challenging task.

In the present work, terminal primary amine groups of PAMAM dendron-SDB chelating resin were modified with DGA functional groups (DGA-PAMAM-SDB). Batch experiments were performed to study the adsorption of U(VI) and Th(IV) metal ions onto DGA-PAMAMG$_3$-SDB chelating resin. The influence of pH, nitric acid concentration, initial metal ion concentration, adsorbent dosage, ionic strength and dendrimer generation on sorption was investigated. Effect of temperature on uptake of U(VI) and Th(IV) by DGA-PAMAMG$_3$-SDB chelating resin was studied. Selective removal of U(VI) and Th(IV) from simulated nuclear liquid waste (SNLW) was carried out and reusability of the resin was tested by conducting desorption experiments. Insights of nature of interaction between UO_2^{2+} and Th^{4+} with the resin, structure and bonding was revealed by performing DFT calculation.