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Carbamoylmethylphosphine oxide functionalised porous crosslinked polymers towards sequential separation of uranium (VI) and thorium (IV)

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ABSTRACT

A new class of highly crosslinked porous polymeric materials with an ethylene glycol dimethacrylate (EGDMA) backbone appended with carbamoylmethylphosphineoxide (CMPO) ligands has been synthesized via precipitation polymerization. The polymers were characterized by CP-MAS NMR, FT-IR, DSC-TGA, SEM and elemental analysis. The polymers prepared in various porogens were evaluated by nitrogen adsorption/desorption experiments, which revealed the existence of large pore volume and surface areas. The ability of polymers to extract actinides (U, Th, Am) utilizing solid phase extraction (SPE) strategy by batch sorption methods as a function of nitric acid concentration are studied. The crosslinked polymers show - a good sorption ability towards U(VI), Th(IV) and Am(III); – selective extraction of U(VI) over Th(IV); and -high radiolytic stability towards gamma radiation. The effect of porogen on pore structure, sorption kinetics, metal loading, release behavior and recycling studies were also discussed. Sequential and selective separation of U(VI) and Th(IV) was demonstrated by extraction chromatography.

1. Introduction

Over the past five decades, a great deal of both scientific and engineering insight has been gained into the application of selective separation/recovery of valuable actinides (Ac) and lanthanides (Ln) from various sources, including mining, spent nuclear fuel reprocessing, waste streams etc. [1, 2]. The reprocessing operations produce both low and high level liquid wastes (LLW and HLLW) containing numerous long-lived radionuclides [3, 4]. Due to its great value, together with health and environmental concerns, there is great need to separate different radioactive components for further processing and safe disposal [5–8]. So far a variety of conventional separation techniques such as liquid-liquid extraction [9, 10], chemical precipitation [11, 12], ionexchange [13, 14] and solid phase extraction (SPE) [15, 16] have been explored for the separation and preconcentration of actinide elements from the different matrices. Among these, solid phase extraction (SPE) has emerging as potential a separation method due to its operational simplicity, high efficiency, absence of emulsion and easy recycling options [17]. It is noteworthy to mention that the selective separation of actinides by SPE method is relies on the properties of adsorbent material, for this reason, designing of effective sorbent materials with

chelating ligand receives the great emphasis.

Among various chelating ligands phosphorus based extractants are of particular interest due to their selectivity and complexing ability towards heavy metal ions under acidic conditions [18-20]. Carbamoylmethylphosphine oxide (CMPO) [21-23], a bidentate organophosphorus ligand is a well-known and most widely used chelating agent for the extraction of actinide and fission products. These CMPOs show very good chemical stability in highly acidic conditions [24]. In the recent years, CMPO and modified CMPO derivatives impregnated on porous polymeric (XAD-4, XAD-7) or silica supports have been studied for the extraction actinide elements [25-29]. Development of sorbent materials still depend on the physical sorption of chelating agentson the surface of solid supports, which could lead to ligand leaching and limited reusability [30, 31]. From the perspective of physical properties of solid supports, an adsorbent material with chelating ligands are covalently bound to the polymer support could provide efficient adsorbents for the separation of actinide ions.

Recent advances in polymer chemistry, a great deal of attention is devoted to the application of cross-linked polymer network as adsorbents for effective removal of actinide elements, because of the pore structure, high internal surface area and introduction of different

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(a)



chelating groups into the polymeric networks [32-35]. Numerous recent studies have focused on the preparation polymers networks are covalently functionalized with phosphoramidates [36], amidoximes [37] and hydroxamic acids [38] etc. were used for the removal of actinide ions from waste solutions. Subramanian et al., have reported the separation of actinides and lanthanides with malonamide and chloromethylated polystyrene grafted resin functionalized with N,N-dihexvlsuccinic acid [39, 40]. Mohapatra et al. reported the sorption affinities of N,N-dimethyl-N,N-dibutylmalonamide grafted polymeric resin towards actinides [41]. In view of this, we have prepared a new class of mesoporous cross-linked polymers bearing carbamoylmethyl-phosphine oxide (CMPO) pendant groups to an ethylene glycol dimethacrylate (EGDMA) backbone via. precipitation polymerization (Scheme 1). The synthesized porous cross-linked polymers were assessed for the extraction of actinide elements such as uranium, thorium and americium from nitric acid media ranging from 0.01-6 M by batch sorption methods and column dynamic method.

2. Experimental section

2.1. Chemical reagents

Diphenvl phosphine oxide, chloroacetvl chloride, 4-vinvl benzvl glycol chloride, ethylene dimethacrylate (EGDMA), Azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich India. Dimethylamine, diethylamine, diisopropylamine and Arsenazo-III were purchased from TCI chemicals. Br-PADAP (2-(5-Bromo-2-pyridylazo)-5-(diethylamino)-phenol) and Thoron (1-(2-Arsonophenylazo)-2-naphthol-3,6-disulfonic acid disodium salt) were purchased from Merck India. All other reagents were of analytical grade used without any further purification. Laboratory stock solutions of standard uranium nitrate, thorium nitrate and ²⁴¹Am tracer were used for the measurement of distribution ratios.

2.2. Characterization methods

The ¹H, ¹³C and ³¹P NMR spectra of precursor molecules were recorded using Bruker DMX-400 spectrophotometer. Mass spectral analyses were carried out on a Perkin-Elmer Clarus 680 GC coupled to a Clarus 600 mass analyzer. Single-crystal X-ray diffraction measurements were performed on Oxford Xcalibur CCD diffractometer Cu equipped with graphite-monochromated Κα radiation $(\lambda = 1.54184 \text{ Å})$. The N₂ adsorption-desorption isotherms were measured using a micromeritics NOVA 1000 accelerated surface area and porosity analyzer. Thermogravimetric analysis (TG) was performed using TA-Q500 thermogravimetric analyzer under a nitrogen flow of

 40 mLmin^{-1} with a heating rate of $10 \degree \text{Cmin}^{-1}$. Differential scanning calorimetry (DSC) was performed using TA DSC-Q2000 instrument between -90° C and $+200^{\circ}$ C with a heating rate of 10° C min⁻¹. Solid-state MAS-NMR spectra were obtained on a Jeol ECX-400 MHz NMR spectrometer. CHN elemental analysis was carried out by Vario-EL III elemental analyzer. Surface morphology was investigated using SEM-EDAX analysis (S4800 Hitachi). Irradiation of crosslinked polymers were performed using Co-60 gamma source with a dose rate of 2 kGy/h and the doses of 50, 100 and kGy were used. Radiometric assay of ²⁴¹Am was assayed by a well-type Na(Tl) scintillation counter coupled to a multi-channel analyzer (ECIL, India), U(VI) and Th(IV) were estimated by UV-Vis absorption spectra, recorded on SHIMADZU UV-3600 double-beam spectrophotometer. The HPLC analysis were carried out on a JASCO LC-4000 with C18 monolith column using 0.05 M 2hydroxy isobutric acid as a mobile phase with pH-4.

2.3. Batch sorption experiments

Distribution ratios (D) of U(VI), Th(IV) and Am(III) with polymeric resins 5a-c were measured as a function of equilibrium aqueous phase nitric acid concentration ranging from 0.01-6 M. The procedure involves the equilibration of about 100 mg of dried polymer material with 3 mL of the feed metal ion solution in an appropriate nitric acid medium at 303 K. Subsequently, the aqueous solution containing the metalloaded polymer was centrifuged and the metal concentration in the aqueous phase was estimated by spectrophotometry using Arsenazo-III as the chromogenic agent [42] at 655 \pm 1 and 661 \pm 1 nm for uranium and thorium respectively and Am(III) was estimated by ycounting. All the experiments were carried out in triplicate. The distribution ratios of metal ions (D_M), sorption capacity(Q) and % of uptake was calculated according to the following equations.

$$D_{\rm M} = \frac{C_{\rm o} - C_{\rm e}}{C_{\rm e}} \times \frac{\rm V}{\rm W} \tag{1}$$

$$Q = \frac{C_o - C_e}{C_o} \times \frac{V}{W}$$
(2)

$$\text{%uptake} = \frac{C_{o} - C_{e}}{C_{o}} \times 100$$
(3)

Where C_o and C_e represent the initial and equilibrium concentrations respectively, W is the amount of polymer (g) and V is the volume of metal solution (mL).

2.4. Extraction chromatographic method

A chromatographic glass column (dimension 200 mm \times 10 mm i.d)

was packed with 6 g of CMPO functionalised crosslinked polymer resin and preconditioned with 6 M nitric acid solution A synthetic mixture of thorium (100 mg L⁻¹) and (200 mg L⁻¹) uranium solution was prepared in 6 M nitric acid solution for the column studies and the loading studies were carried out with a flow rate of ~10 mL/h at room temperature (30 °C). The concentration of metal ions in the effluent samples during loading of U(VI) and Th(IV) was estimated by spectrophotometry using thorin [43] and Br-PADAP [44] as chromogenic agents at 545 ± 1 nm and 578 ± 1 nm for thorium and uranium respectively. The purity of the eluted samples were analysed by HPLC using 0.05 M 2-hydroxy isobutric acid as a mobile phase with pH -4.

3. Results and discussion

3.1. Synthesis and characterization of CMPO functionalised crosslinked polymers

2-Chloro N,N-dialkyl acetamides **2a-c** [45] were synthesized by reacting secondary amines with chloroacetyl chloride at lower temperatures, which further reacted with diphenyl phosphine oxide in the presence of aliquat-336 to give corresponding diphenyl-N, N-dialkyl carbamoylmethylphosphine oxide **3a-c**. [46] As depicted in the Scheme 1a, treatment of CMPO **3a-c** with 4-vinyl benzyl chloride under basic conditions yields corresponding vinyl anchored CMPO monomers **4a-c** in good yields. [47] The compounds thus synthesized (**2a-c**, **3a-c** and **4a-c**) were characterized by NMR and GC–MS (for spectral data see ESI, Fig. S1- S33).

Unequivocal confirmation of the structure of 4c is provided by X-ray analysis (CCDC no. 1499017, Scheme 1b). Complete crystal data and structure refinement details for monomer 4c are given in the Table S1, ESI. Furthermore, the synthesis of CMPO functionalized crosslinked polymers 5a-c was achieved using precipitation polymerization technique [48]. For instance, the polymer 5a was prepared by reacting CMPO monomer 4a (65 wt%) with crosslinker EGDMA (35 wt%) in the presence of radical initiator AIBN (1 wt% to the monomer) (For detailed experimental procedures see ESI).

The structural integrity, the presence of functional groups in the polymer matrix and thermal stability of the polymers were confirmed by the CP-MAS NMR, FT-IR and elemental analysis. Fig.1a shows the 13 C CP-MAS NMR spectra of cross-linked polymer materials

functionalised with CMPO derivatives. The resonance signals at 183 ppm and 175 ppm belongs to the amide and ester carbonyl groups present in CMPO ligand and crosslinker respectively. Likewise, multiple signals in the range of 40–70 ppm and 135 ppm correspond to the alkyl groups and phenyl groups of CMPO. The existence of phosphoryl (P=O) moiety in the polymer matrix was confirmed by ³¹P CP-MAS NMR spectra (Fig. 1b). The resonance signals were observed at 28.1 ppm for P=O, along with sidebands at 114 and – 58 ppm, these results clearly confirm the presence of CMPO derivatives covalently bonded to the crosslinker.

FT-IR spectra of the polymers **5a-c** (Fig. S34, ESI) shows the typical adsorption bands at 1114 cm^{-1} (P=O), 1438 cm^{-1} (C–N str.), 1627 cm^{-1} (C=O (amide)), 1722 cm^{-1} (C=O (ester)). Fig. 2 shows the thermal properties of crosslinked polymers **5a-c**. From the TG curves (Fig. 2a), the degradation of polymers involves two main processes. The first stage of decomposition at around 100 °C can be accounted for the volatilization of physisorbed water. The second stage at around 300 °C, corresponds to the decomposition of ligand moieties tethered to the crosslinker. Fig. 2b shows the DSC profile of the three crosslinked polymers **5a-c**. No obvious T_g was detected for the polymers **5a-c**, due to the high degree of cross-linking (35%). From the DSC-TGA curves, it is clearly evident that the CMPO-functionalised crosslinked polymers showed good thermal stability.

3.2. Screening of porogen in polymer synthesis

In polymer synthesis, porous properties of polymers fairly depend on the type and concentration of porogens. Owing to the importance of porogens on pore volume and pore size of the polymers, different solvents viz., chloroform, toluene, *N*, *N*-dimethyl formamide and 1,4-dioxane were employed. The resulted polymers were subjected to nitrogen gas adsorption-desorption studies and was found to be mesoporous (2–50 nm), isotherms were shown Fig. 3 and the physical properties are listed in Table S2 (ESI). Among the synthesized polymers the usage of 1,4-dioxane resulted in large volume and ordered pore. The surface morphology of the polymers prepared in different porogens was evaluated by SEM analysis. As shown in (Fig. S35, ESI), a polymer prepared in chloroform resulted as agglomerated spherical beads, whereas the sheet-like morphology was observed in DMF, toluene and 1,4-dioxane.



Fig. 1. Overlay (a) ¹³C CP-MAS; (b) ³¹P CP-MAS NMR spectra of CMPO functionalised crosslinked polymers 5a-c.



Fig. 2. (a) TGA (b) DSC curves for CMPO grafted crosslinked polymers 5a-c.

Porosity in the polymers increases the ability to interact with metal ions not only at their surfaces but throughout the bulk of the material thereby provides more accessible metal coordination sites which results in high distribution values. The adsorption ability of the polymers was investigated by batch sorption methods towards uranyl ion. From the data in Fig. 4, it is evident that high distribution values are obtained for the polymer with large pores resulted in the porogens of the order 1,4-dioxane > N, N-dimethyl formamide > toluene > chloroform. From these results, polymers were synthesized using 1,4-dioxane as porogen for further studies.

3.3. Effect of contact time

The variation in extraction capacity of U(VI) and Th(IV) by the CMPO crosslinked polymer (**5c**) is examined at different time intervals in 6 M HNO₃ and the results are depicted in Fig. S36 (ESI). From the results, the extraction of U(VI) and Th(IV) is rapid within 60 min and equilibrium is attained within 120 min and no more significant extraction of U(VI) and Th(IV) was observed on prolonged contact time. Therefore, the contact time of 120 min is sufficient to attain the equilibrium for CMPO functionalised polymers in the extraction of U(VI) and Th(IV) ions, which was selected in the further experiments.



Fig. 3. (a) N2 Adsorption-desorption Isotherms; (b) Pore-size distribution of polymers prepared in different porogens.



Fig. 4. Effect of porogens on the extraction of $D_{U(VI)}$ for polymer 5c in equilibrium aqueous phase nitric acid at 303 K.

3.4. Actinide adsorption behavior of functionalized crosslinked polymers

The adsorption ability of the CMPO functionalised polymers (**5a-c**) towards U(VI), Th(IV) and Am(IIII) in broad range of nitric acid concentrations i.e. 0.01-6 M was investigated by batch operation are shown in Fig. 5. Results depict that, increase in nitric acid concentration is accompanied by an increase in the distribution ratios of U(VI), Th(IV) and Am(III). The distribution values increased with acidity, this can be explained by the law of mass action due to increased nitrate concentration [49]. From the data, it is evident that alkyl substituents on the nitrogen atom in CMPO molecule have no notable change in the distribution ratios of polymers towards the U(VI), Th(IV) and Am(III). However, the polymers show significantly higher distribution values for U(VI) than that of Th(IV) and Am(III).

It is well known that bifunctional neutral CMPO in HNO_3 forms a disolvated complex with U(VI) and trisolvated complex with Th(IV) and Am(III) [50]. The selectivity in extraction U(VI) by the polymers **5a-c** can be rationalized by the formation of disolvated complexes of U(VI) with CMPO groups present in the polymer matrix, which results in the high distribution values of U(VI) over the other actinide elements. Due to high degree of crosslinking, it is uncertain that the complexation bonding is occurring between CMPO groups on the same polymer chain or by groups on adjacent chains. Overall the pore structure of the



Fig. 6. Extraction behaviour of irradiated crosslinked polymers 5c towards U (VI) and Th(IV) in 6 M HNO₃.

polymers, the arrangement of chelating groups, coordination geometry are the factors responsible for the difference in the selectivity of the crosslinked polymers for U(VI) over the other actinide ions. From the batch sorption studies, it is evident that the CMPO functionalised porous polymers (**5a-c**) have a high potency to separate uranium from the high nitric acid concentrations and considered as an industrial option in reprocessing of spent nuclear fuel solutions.

3.5. Radiation stability studies

In the reprocessing of radioactive waste solution, adsorbent materials undergo continuous exposure to high energy gamma radiations which lead to the chemical decomposition of the sorbent and affect their physicochemical properties. In view of this, the functionalised crosslinked polymer **5c** is irradiated with different amount of gamma energy (50, 100 and 150 kGy) and the distribution ratios for uranyl and thorium ions were calculated and the results are presented in Fig. 6. Even after150 kGy 60 Co γ irradiation, there was no notable change in the distribution values of U(VI) and Th(IV), indicative of excellent resistance to radiation.

3.6. Maximum sorption studies

In order to find the maximum actinide sorption capacity of CMPO functionalised crosslinked polymers, 1 g of polymer 5c equilibrated with individual solutions of U(VI) and Th(IV) (250 mg/50 mL) at 6 M



Fig. 5. Effect of nitric acid concentration in the aqueous phase on the extraction of (a) D_{U(VI)}, (b) D_{Th(IV)} and (c) D_{Am(III)} for crosslinked polymers 5a-c at 303 K.

Table 1

Comparison of sorption capacities with other functionalised polymeric resins.

Polymeric adsorbent	[HNO ₃]	Polymer sorption capacity (mmol/g)	
		U(VI)	Th(IV)
Merrifield polymer-DB2EHMA [51]	5 M	0.262	0.164
Merrifield polymer-EDHBA [52]	6 M	0.356	0.679
Merrifield polymer-DMDBMA [49]	4 M	0.0789	0.067
Merrifield polymer-DAPPA [53]	4 M	0.889	0.619
CMPO-crosslinked polymer[PW] ^a	6 M	0.609	0.112

^a Present Work[PW].

HNO₃. After estimation process, it is noteworthy to mention that CMPO functionalised polymer showed excellent sorption capacity values of 0.609 and 0.112 mmol g⁻¹ for U(VI) and Th(IV) respectively and the resulted maximum sorption values are compared with various functionalised polymers obtained from the literature (Table 1). From the results, it is reasonable that the CMPO functionalised porous cross-linked polymer **5c** has strong selective adsorption ability to U(VI) i.e. around fivefold selectivity over the Th(IV). The maximum sorption capacity values by the crosslinked polymer (**5c**) can be attributed to the greater degree of ligand functionalization on polymer backbone.

3.7. Desorption and recyclability studies

From practical perspective, recovery and reuse is a significant feature of advanced adsorbent materials. In this connection, quantitative desorption of adsorbed uranium and thorium from the functionalised polymer (**5c**) was performed with various eluting agents viz., distilled water, 0.01 M nitric acid, 5% sodium carbonate, 5% ammonium carbonate and potassium oxalate, among which potassium oxalate was found to be best and their profile is shown in Fig. 7.

In order to evaluate the recyclability of crosslinked polymers, multiple desorption- adsorption studies were performed upto five consecutive runs using 5% potassium oxalate as the eluent. From the Fig. 8, it is clearly evident that there is no significant change in the efficiency of uptake of U(VI) and Th(IV) with even after five cycles. These results demonstrated that CMPO functionalized porous polymers can be efficiently regenerated and reused even at high nitric acid concentration.



Fig. 7. Metal release behavior of crosslinked polymer **5c** with various stripping agents.



Fig. 8. Reusability of the crosslinked polymer 5c towards U(VI) and Th(IV) in 6 M HNO_3

3.8. Extraction chromatographic method

After demonstrating the extraction behaviour as a function of nitric acid concentration and maximum sorption capacities of U(VI) and Th (IV) by batch sorption methods, we intended to separate these metal ions by extraction chromatography. The ability of the functionalised polymer matrix for the preconcentration of U(VI) and Th(IV) was tested by passing a synthetic mixture of 200 mg L^{-1} uranium and 100 mg L^{-1} of thorium in 6 M HNO₃ through the polymer (5c) packed column. The column breakthrough capacities were depicted in Fig. S37 (ESI), after estimating the metal ion concentrations in effluent samples after column loading, it was found that 53 mg of thorium and 253 mg of uranium was adsorbed on the column. Subsequently, the column was eluted with 1 mM sodium carbonate and selectively separated the thorium and uranium respectively and recovered within 30 mL of the eluent. The purity of the collected fractions was determined by HPLC (Fig. 9), the initial fraction (10 mL) contains fairly pure thorium (>99%), it was noticed that next fraction uranium (95%) contaminated with 5% of thorium and the final fraction contains pure uranium (> 99%). These chromatographic studies demonstrated that



Fig. 9. HPLC purity chromatograms of uranium and thorium samples eluted during extraction chromatography.

thorium and uranium can be effectively separated from highly acidic solutions with thermally and radiolytically stable CMPO functionalised crosslinked polymers (**5a-c**).

4. Conclusions

In conclusion, a new class of mesoporous adsorbent with EGDMA polymer backbone appended with dense bidentate CMPO ligating groups. These CMPO-functionalised polymers (5a-c) exhibited an excellent adsorption selectivity and affinity towards U(VI) over the Th(IV) and Am(III). From the extraction chromatographic studies selective separation of U(VI) and Th(IV) are achieved with 1 mM sodium carbonate as column eluent. Moreover the CMPO functionalised porous polymers were found to be stable in strong acidic conditions, and showed a high thermal and radiation stability. The extraction ability of functionalised porous polymers is almost identical up to 5 cycles of repeated usage. These studies demonstrated the better scope by introducing various multi-functionality into a polymer backbone for the separation, recovery and removal of actinides ions from the spent nuclear fuel. Further studies are taken to the large-scale separation of americium from high-level liquid waste (HLW) by extraction chromatographic method.

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Data availability statement

Synthetic procedure for the functionalized monomers, resin and their spectra data are provided in the supporting information section.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2018.07.026.

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