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], ion-exchange [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
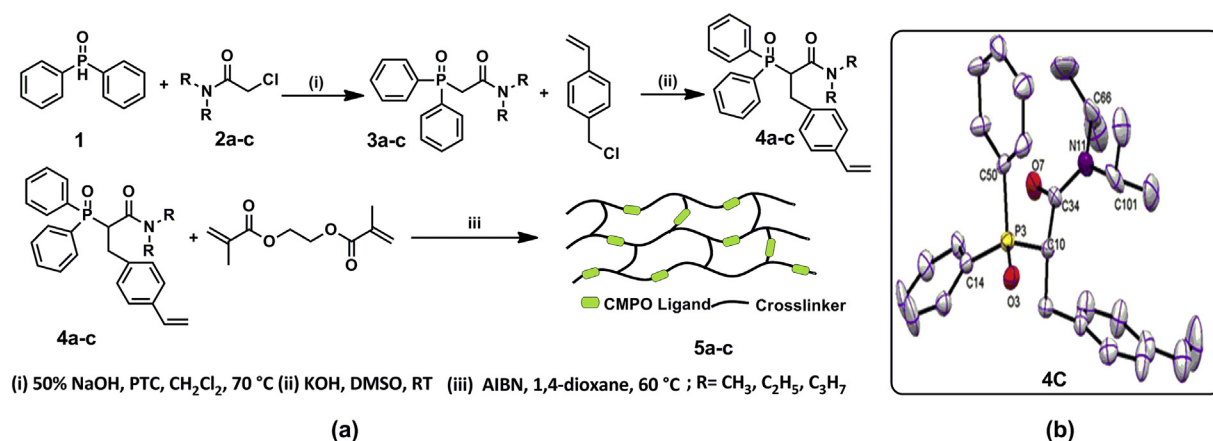
Scheme 1. (a) Synthesis of CMPO functionalized crosslinked polymers **5a-c**. (b) ORTEP plot of vinyl functionalized CMPO monomer **4c** (Thermal ellipsoids are drawn at the 30% probability level; For clarity H atoms are omitted).

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-dihexylsuccinic 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

Diphenyl phosphine oxide, chloroacetyl chloride, 4-vinyl benzyl chloride, ethylene glycol 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 ^{241}Am tracer were used for the measurement of distribution ratios.

2.2. Characterization methods

The ^{1}H, ^{13}C and ^{31}P 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 equipped with graphite-monochromated Cu Kα radiation (λ = 1.54184 Å). The N$_2$ 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 mL min^{-1} with a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed using TA DSC-Q2000 instrument between −90 °C and +200 °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 ^{241}Am 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 C$_{18}$ monolith column using 0.05 M 2-hydroxy 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 metal-loaded 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 ± 1 and 661 ± 1 nm for uranium and thorium respectively and Am(III) was estimated by γ-counting. 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.

$$D_M = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \tag{1}$$

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

$$\%uptake = \frac{C_o - C_e}{C_o} \times 100 \tag{3}$$

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 × 10 mm i.d)