Experimental strategy for acid-free plutonium recovery from assorted matrices: Non-aqueous leaching followed by selective solid phase extraction

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Abstract−Methodologies comprising usage of innocuous reagents, lower overall chemical inventory and simplification of process scheme for plutonium recovery from assorted matrices, solid as well as liquid, are key to establishing sustainability of the nuclear fuel cycle. The present study demonstrates, for the first-time, plutonium leaching from different refractory matrices: oxide, mixed oxide as well as simulated cellulosic waste using the benign halide anion free choline citrate - urea (1 : 2 mole ratio) based eutectic solvent (referred to as CU). This mineral acid and hydrofluoric acid-free, non-aqueous route of plutonium recovery with controlled infra-red heating yielded ≥93% efficiency. CU was diluted with biodegradable, less viscous propylene glycol (referred to as PG), which was chosen as the non-aqueous polar phase for facile solid phase extraction (SPE), which is a green alternative to liquid-liquid extraction owing to process simplification and solvent inventory reduction. Exclusive stabilization of tetravalent plutonium in the novel media, confirmed by ultraviolet-visible spectrophotometry and electrochemical methods, led to process simplification, eliminating any pre-extraction requirement for oxidation state adjustment. Extractant, di-2-ethyl hexyl phosphoric acid encapsulated polyether sulfone beads, prepared by phase inversion method, were employed for efficient SPE of plutonium (Distribution co-efficient, k_D=950±6). Selectivity of non-aqueous SPE was found to be Pu(IV)$>>$UO$_2^{2+}>$Am(III) vis-à-vis aqueous acid medium.

Keywords: Plutonium Oxide, Eutectic Solvent, Propylene Glycol, Polyether Sulfone Beads, Solid Phase Extraction

INTRODUCTION

Nuclear power is considered to be a very important component in the future energy blend owing to associated carbon neutrality, being an energy dense source as well as its technological maturity [1]. However, management of radioactive waste has globally remained a key concern that calls for development of sustainable processes for the separation and purification of actinides. Hydrometallurgy and pyrometallurgy, involving corrosive acids or alkali based aqueous solutions and molten salts at high temperature (>573 K), respectively, are the explored routes for actinide processing.

During the course of nuclear fuel fabrication, quality control operations and reprocessing of irradiated fuel, different plutonium bearing matrices are encountered [2-4]. Due to its radiochemical toxicity, strategic and economical value, the recovery of plutonium from all such matrices, solid as well as liquid, is crucial. The refractory nature of Pu bearing solid matrices and co-existence of multiple oxidation states of Pu in aqueous solution make the recovery of plutonium complex and challenging. Hence, recovery of Pu from solid matrices mandates refluxing or continuous infra-red heating

with mineral acids: nitric acid, sulfuric acid promoted by corrosive hydrofluoric acid [4]. Efficient Pu extraction from aqueous medium is preceded by oxidation state and acid molarity adjustment to ensure control of redox speciation, i.e., solvent extraction in PUREX process for reprocessing of spent nuclear fuel [5] and anion exchange recovery of Pu from nuclear waste streams [6].

Solvometallurgy [7] is the area of research where non-aqueous routes are explored for separation of metals starting from ores to wastes. Presently, investigations on non-aqueous routes for metal recovery are being pursued fervently so as to establish a sustainable alternative to hydrometallurgical processes based on harsh mineral acids [8-12] and to complement established methodologies for low grade sources. Deep eutectic solvents (DES), as named by Abbott et al. [13], are solvents endowed with several advantageous features that are derived from non-toxic and biodegradable components by simple mixing followed by controlled heating. Acid-free recovery of metal ions in DES is reported [13-18]. Authors have also prepared eutectic solvent based on choline citrate and urea (1 : 2 mole ratio), referred to as CU and used for dissolution of U containing matrices [19]. Dissolution of (U,Pu)O$_2$ was carried out in halide-based DES as a part of study on U based matrices [20]. However, reports on exclusive Pu leaching using DES and redox speciation in non-aqueous media are lacking, seemingly due to complex matrix and handling difficulties.

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The aim of the present study is to investigate and develop understanding about various aspects of non-aqueous acid free leaching of plutonium from solid matrices as well as solid phase extraction (SPE) using a non-aqueous mineral acid-free phase as the polar phase. This will, in turn, aid in devising simplified process schemes aimed at minimization of overall chemical inventory and usage of 'green' solvents. For plutonium dissolution and leaching from solid matrices, halide anion free, green, hydrophilic eutectic solvent based on innocuous reagents, such as urea and citric acid, CU [19] has been used. This non-aqueous phase has been diluted with less viscous propylene glycol (propan-1,2-diol, PG), as the polar phase, for facile SPE. Solid phase extraction (SPE) of actinides is acknowledged to have several benefits, such as extractant inventory minimization and ease of operation. Propylene glycol based solvent systems have been enlisted in the preferred group of solvents to design sustainable separation processes [7]. It is biodegradable, non-toxic and a popular food additive [21]. Few studies on transition metal and rare earth extraction from non-aqueous polar phase have been reported [8-11]. The associated advantages of non-requirement of pH control and enhanced selectivity vis-a-vis aqueous acid medium are promising. Pu-Am extraction employing extractant encapsulated polyether sulfone beads (PES) has been studied by us [22]. To the best of our knowledge, the potential of SPE of metal ions from non-aqueous polar medium has, however, not been probed yet. Pu dissolved in non-aqueous media, CU and PG, represents novel systems. Hence, ultraviolet-visible (UV-Vis) spectrophotometry and electrometry were employed to probe the redox speciation of Pu in these media. This aided in devising an approach for Pu extraction. Also, di-2-ethyl hexyl phosphoric acid (DEHPA) encapsulated PES beads were prepared and characterized by scanning electron microscopy and thermogravimetry. Conditions were optimized for SPE of Pu from PG. Investigations were made to explore benefits of this non-aqueous system vis-à-vis aqueous acid-based system.

EXPERIMENTAL

1. Chemicals

Analytical reagent (AR) grade choline dihydrogen citrate and urea were used for preparation of eutectic solvent, referred to as CU and characterized for water content, viscosity, density and thermal stability as described elsewhere [19]. Poly ether sulfone, PES (average molecular weight of 30,000) and organic extractant, DEHPA (diester>95%) were obtained from Gharda Chemicals and Heavy Water Board, India, respectively, and were used as received. AR grade N-methyl pyrrolidone (NMP), polyvinyl alcohol (PVA) were used for PES bead preparation and AR grade propylene glycol (PG) was used for solid phase extraction.

2. Leaching

The solid matrices were weighed in a dry glove box, the samples were transferred to another glove box containing heating set-up. The heating set-up, housed inside a glove box, consisted of an IR lamp and hood with trap. Accurately weighed amounts of plutonium oxide and mixed oxide, corresponding to ~10-20 mg of plutonium, were taken with CU. Intermittent IR heating (not more than 15 min) followed by mixing was done for the required time.

For leaching study, simulated cellulosic waste matrix was prepared by smearing an accurately weighed amount of plutonium dioxide solid or plutonium nitrate solution on a rectangular adsorbent paper (3×1 cm^2 area). The paper with loaded plutonium nitrate solution was air dried for 24 hr and then dipped in ~3 g of CU followed by controlled IR heating for required time. The dissolution/leaching was ascertained visually, and after the homogenization of the systems by ultrasonication the Pu amount in DES was determined by biamperometry [23]. This method, referred to as the modified Drummond and Grant method, is based on the oxidation of Pu in 1 M sulfuric acid medium with the silver oxide, AgO to Pu(VI). This was followed by its reduction of Pu(VI) with known excess of ferrous, Fe(II) and determination of excess of Fe(II) with standard dichromate to a biamperometric end-point. The overall random error, quantified by standard deviation, was 0.5%, including weighing, aliquoting and determination.

$$\text{Standard deviation, } s = \sqrt{\frac{\Sigma(x-\mu)^2}{n-1}} \tag{1a}$$

$$\text{Percentage relative standard deviation, } \%RSD = s/\mu \times 100 \tag{1b}$$

where μ is the mean, x is the experimental result, and n is the number of repetitions.

3. Redox Speciation of Pu

Cyclic voltammetry (CV) was carried out on an electrochemical analyzer CHI 760E consisting of three-electrode systems of gold as working electrode, Ag-AgCl/sat. KCl as a reference and platinum wire as an auxiliary electrode. Prior to each experiment, the working electrode was polished with alumina powder (graded 5 μM), followed by rinsing with doubly distilled water and methanol. High purity N$_2$ gas was used to purge the solution for at least ten minutes before experiments. For recording UV-Visible spectra of Pu compounds dissolved in CU and PG, UV-VIS-NIR light source DH-2000-BAL Ocean Optics spectrophotometer with QE 65000 detector was used.

4. Solid Phase Extraction

Polyether sulfone beads were prepared by non-solvent phase inversion method under optimized conditions of 12% PES in NMP solution having polymer solution-to-extractant ratio of 5 : 1, as described elsewhere [24,25]. Subsequently, the polymer and extractant mixture (3 M DEHPA) was used to synthesize the PES beads with and without using PVA (1%). The beads were characterized by scanning electron microscope (SEM) and thermogravimetric analysis (TGA). Zeiss system, Model-evo-18 was used to record SEM images after the samples were sputter-coated with thin gold film. SETARAM Instruments, model Setsys Evolution was used for TGA experiment carried out in flowing nitrogen atmosphere, up 300-1,000 K at a heating rate of 10 K min^{-1}.

In-house ^{241}Am, ^{233}U tracer solutions were used for the extraction studies. 0.5 mL of Pu stock solution in PG was taken with accurately weighed amount of the extractant encapsulated polymer beads (~150-200 mg) in polypropylene tubes for batch sorption studies and equilibrated in water bath for given time period. After equilibration, Pu activity was assayed by liquid scintillation counting (LSC) with dioxane based scintillator cocktail. The result of extraction experiments was reported as the average of three repetitions and

associated random error as standard deviation (Eq. (1a)).

Radiation Hazard! Considering the radioactive hazard of Pu, weighing of powders and IR heating was carried out in leak-tight glove boxes under negative pressure. The diluted Pu stock used for SPE was handled in a fume hood with the necessary precautions.

RESULTS AND DISCUSSION

Pu ends up in different forms in the nuclear fuel cycle, and the methodology adopted for plutonium recovery is dependent on the type of matrix. The present investigation was directed to explore routes for Pu recovery with the aim to simplify overall process scheme, lower chemical inventory and promote usage of innocuous reagents.

1. Pu Leaching from Solid Matrices

The leaching of Pu from solid matrices is a challenging task owing to the refractory nature of oxides that has been traditionally carried out employing harsh mineral acids, such as nitric acid, sulfuric acid promoted by hydrofluoric acid under constant IR heating or reflux [4,26]. In a bid to avoid corrosive mineral acids, studies on dissolution of many metal ions using hydrophilic eutectic solvents were carried out [14], but any systematic report on Pu recovery is lacking. Though mineral acid usage was avoided for dissolution in these reported processes, sustainability was reduced by employing corrosive halide-based hydrogen bond acceptors for eutectic solvent system. We have reported the direct supercritical fluid CO_2 dissolution and uranium extraction [19] employing halide anion free eutectic solvent, CU based on innocuous reagents like urea and choline dihydrogen citrate. In the present study, we attempted Pu leaching from oxide matrices and simulated waste using CU.

Solid matrix containing ~10-20 mg of plutonium was was added to CU and controlled IR heating was carried for a required time. The plutonium leaching was described as:

$$\text{Plutonium Leaching (\%)} = \frac{\text{Plutonium leached in CU}}{\text{Plutonium taken as solid}} \times 100 \quad (2)$$

Pu amount leached in CU was determined as per procedure described in section 2.2. However, continuous heating for a higher duration led to generation of a dark brown color viscous liquid (Fig. 1). Thermal instability of eutectic solvents at ≥ 373 K had recently been reported [27]. Hence, one of the associated challenges was to carry out controlled IR heating (intermittently for 10 min).

To represent assorted solid waste matrix, porous cellulose based adsorbent paper loaded with plutonium oxide/nitrate was taken. The cellulose based adsorbent paper matrix was left effectively unchanged and clarification/filtration step to remove cellulosic material required after aqueous acid leaching was, thus, not required. Table 1 summarizes the findings of the leaching study. As is observ-
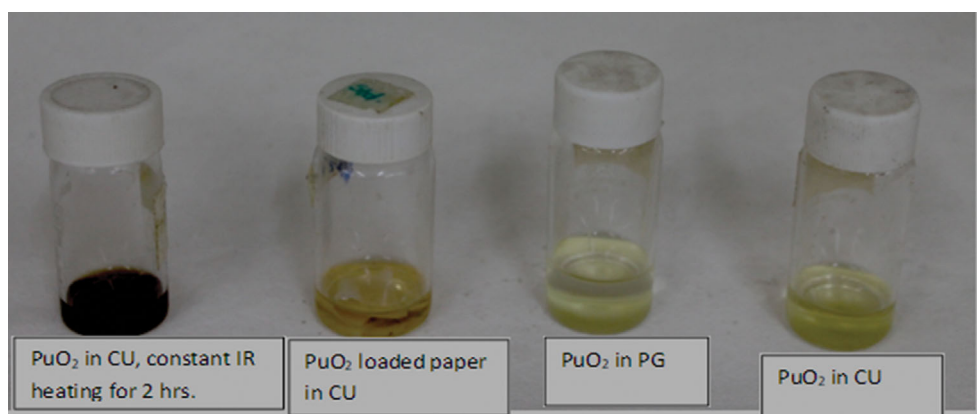

Fig. 1. Photographs of Pu in CU and PG medium.

Table 1. Leaching study of Pu bearing matrices in CU

Matrix	Pu weight (mg)	CU weight (g)	Leaching time (hr)[*]	Leaching efficiency[#] (%)
PuO₂	11.02	2.236	6	93
	10.8	2.055	6	
(U,Pu)O₂	11.1	2.074	6	95
	16.4	2.403	6	
Sim. waste (with PuO₂)	16	3.015	8	95
	16	3.140	8	
Sim. waste (with Pu nitrate)	14	3.053	8	97
	14	3.035	8	

*Refers to total time which comprises IR heating for 15 min followed by 15 min swirling & cooling; #Redox titrimetry, AgO oxidation method with biamperometric end-point determination, ±0.5% RSD

able, significant Pu leaching (≥93 %) is obtained for all matrices. Oxides require lesser treatment time (6 hr) for the same as compared to simulated waste (8 hr). Highest leaching of 97% was obtained with nitrate. Therefore, the study demonstrates the achievement of Pu leaching from refractory matrices at a mild temperature of 353 K (±10 K) without mineral acid usage. Once dissolved, a portion of the eutectic solvent was diluted with PG (1 : 10 v/v) by ultrasonication for further studies.

2. Probing Redox Speciation of Pu

Pu has a very complex aqueous chemistry with co-existence of multiple oxidation states, which is dependent on the type of medium (acid/alkali and its molarity), presence of other redox reagents and even isotopic composition of Pu [28]. This leads to the requirement of stringent condition control (aqueous phase composition, redox reagents) and pre-treatment during its separation in all stages of nuclear fuel cycle [28]. CU as well as PG represent novel media and this study represents the first investigation for Pu dissolved in these non-aqueous media. Hence, redox speciation of these Pu containing systems has not been studied earlier. To examine requirement of oxidation state adjustment for designing suitable separation scheme, redox speciation of Pu in CU and PG was investigated. Fig. 2 shows the UV-Vis spectra recorded for neat CU, PG and Pu containing solutions. Presence of peaks at 470, 663 and 811 leads to inference of presence of Pu(IV) [28], while absence of 601, 569 and 504 nm peaks indicates absence of Pu(III), Pu(V) and Pu(VI), respectively. This may be rationalized by the very high stability of citrate com-
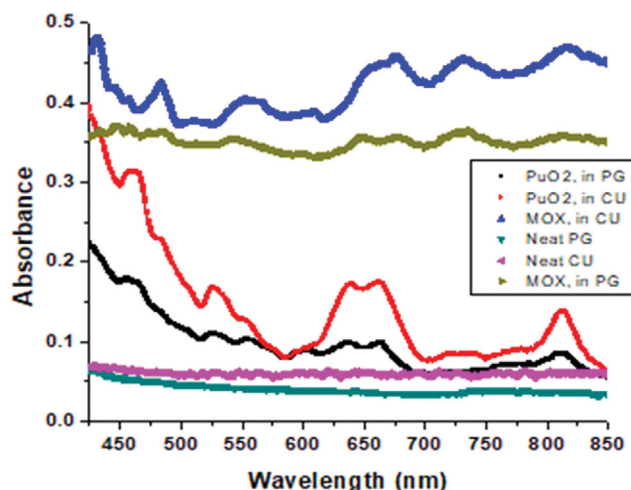

Fig. 2. UV-Visible spectra of Pu in CU and PG.

plex for Pu(IV) [29]. To further confirm the oxidation state of Pu in the non-aqueous media, electrometric studies were carried out. Cyclic voltammetry (CV) was carried out (Fig. 3) with Pu in PG solution, the medium for SPE, on gold as working electrode. However, due to non-conducting nature of PG, 0.1 M KCl in PG was used as medium for study. CV of uranium in PG was also recorded. For PuO$_2$ and (U,Pu)O$_2$, a single reductive peak at 0.315 V and 0.375 V, respectively, corresponds to quasi-reversible reduction of
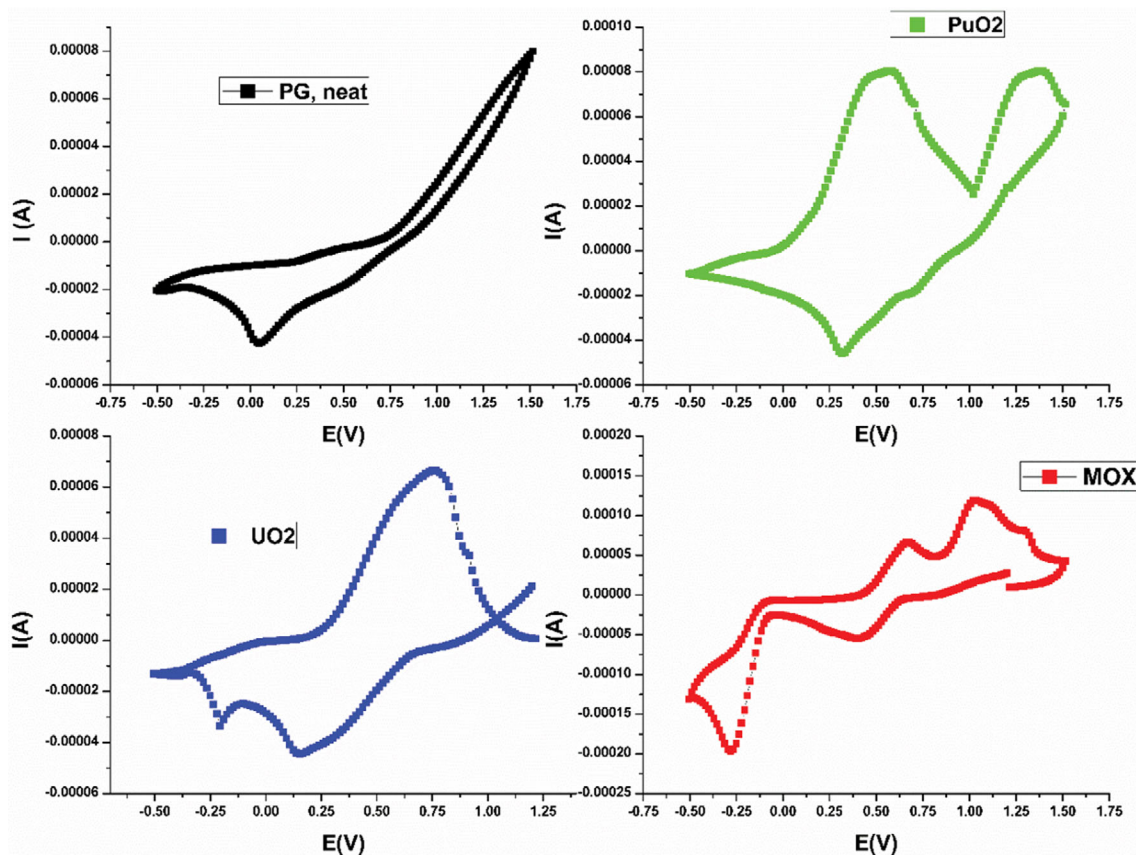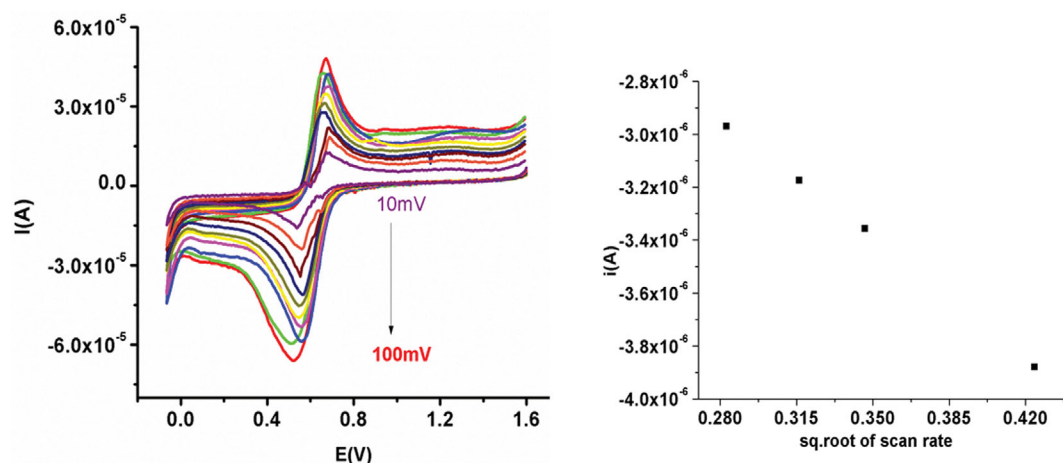

Fig. 3. Cyclic voltammetry of Pu in PG+0.1 M KCl.

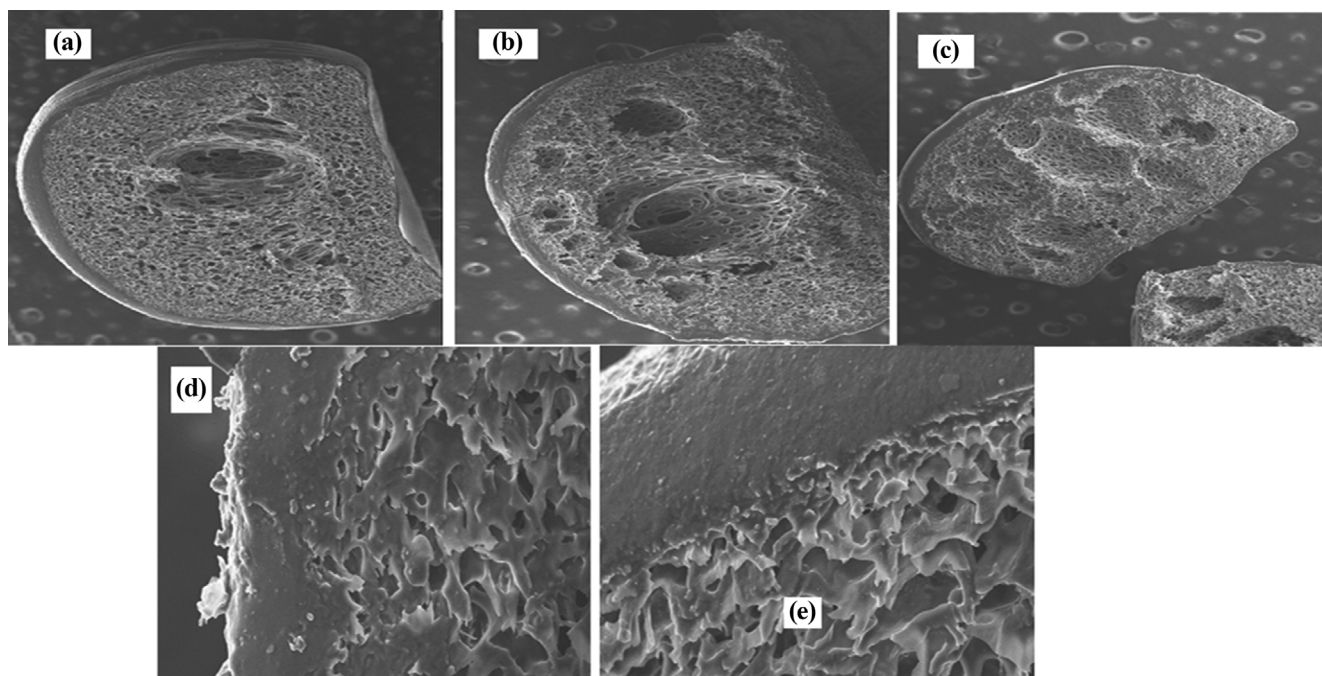**Fig. 4. Scan rate variation of Pu in PG+0.1 M KCl.**

Fig. 5. Scanning Electron Microscopic images of DEHPA encapsulated beads (a) With PVA, big (magnification 70 X); (b) Without PVA, big; (magnification 70 X); (c) With PVA, small (magnification 84 X); (d) With PVA, big (magnification 200 X); (e) Without PVA, big (magnification 200 X).

Pu species in PG and confirms absence of multiple oxidation states. The reduction peak for UO_2 and MOX at ~-0.25 V corresponds to U reduction [30]. The scan rate variation study (Fig. 4) revealed a linear plot for current vs. (scan rate)$^{1/2}$ depicting a diffusion-controlled mechanism. The exclusive stabilization of Pu(IV) in CU as well as PG (CU : PG = 1 : 10 v/v) is a boon eliminating any preconditioning requirement and offers promise towards a simplified Pu separation scheme in non-aqueous media.

3. Solid Phase Extraction

Liquid-liquid extraction, the workhorse for actinide separation in the nuclear industry, has several drawbacks: huge chemical inventory, cumbersome operation and emulsion formation. Solid phase extraction of metal ions with extractant encapsulated polymer

beads was pioneered by Warshawsky [31] and has been preferred due to requirement of less extractant inventory and operational simplicity. However, the success of the SPE of metal ion is dependent on bead preparatory parameters, choice of solvent as well as extractant.

4. Bead Preparation and Characterization

Simple phase inversion procedure, with water as anti-solvent, was employed for the present study using Gong's apparatus [32]. High chemical, thermal and mechanical stability make PES a popular choice as polymer support [24,25,31] for extractant encapsulated polymer beads and was used in present study. DEHPA was selected for the preparation of extractant encapsulated PES beads due to high extraction of Pu(IV) from various nuclear process streams
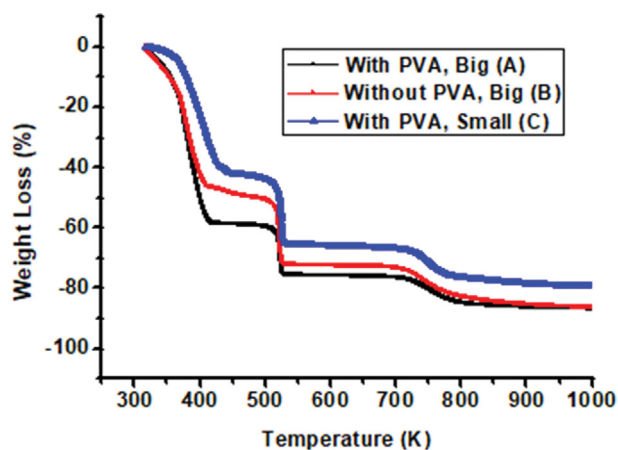
Fig. 6. Thermogram of thermal decomposition of polymeric beads in nitrogen atmosphere (Heating rate: 10 K min^{-1} in nitrogen atmosphere).

[33]. To investigate microstructural features, thermal stability and extent of extractant encapsulation, SEM and TGA of the prepared beads were carried out. Addition of PVA during bead preparation is known to enhance porosity and promote higher extraction. Effect of size of beads and presence of PVA additive on Pu extraction was investigated. Microstructural investigation of cross-section of beads by SEM (Fig. 5) revealed oval shaped beads (70 X magnification) with voids in the inner core indicating DEHPA encapsulation ((a), (b), (c)). The bigger beads had average outer diameter of 1,300 μm ((a), (b)) and smaller one had 900 μm (c). Also, at a magnification of X200 for beads without PVA (e) outer rim showed a thicker, less porous structure as compared to those with PVA (d). Hence, beads containing PVA are expected to be more amenable to extraction by promoting facile entry of liquid phase containing metal ion into the extractant encapsulated core of the beads.

Thermogravimetric analysis of the DEHPA encapsulated beads was carried out by gradual heating in nitrogen atmosphere at a heating rate of 10 K min^{-1} and thermal degradation patterns were recorded (Fig. 6). Independent of the bead size and usage/non-usage of PVA as additive, three regions for weight loss were observed in the experimental range of 310-1,000 K for all the three types of beads:

1. First region (350-400 K) corresponds to loss of retained water, which is ~60% for PVA containing big beads (A), ~50% for PVA containing smaller ones (C) and 40% for beads without PVA (B). Note that this water retention is due to its usage as anti-solvent during bead preparation and is least for beads without additive PVA.
2. Second region (500-550 K region) corresponds to DEHPA decomposition, which is 15% for A, 20% for C and 25% for B. Hence, extent of DEHPA encapsulation: B>C>A.
3. Third region (750-800 K) corresponds to polymer composite decomposition.

5. Batch Sorption Studies

Hydrophilic eutectic solvents have been touted as a green medium for non-aqueous liquid-liquid extraction [11-16]. Though micro-extraction for analytical use or pre-concentration can be achieved

Table 2. SPE of Pu(IV) from different non-aqueous media

PES beads	Medium	Equilibration time (hr)	$k_{D, Pu}$
C*	CU	4	30
C*	PG	4	950
C*	PG+0.5 M LiNO$_3$	4	1,010
	PG+1 M LiNO$_3$	4	1,030

* With PVA, small (Results are avg. of triplicate extractions; Standard deviation: ±6)

by ultracentrifugation, the higher viscosity of eutectic solvent obscures its potential application as the more polar phase in bulk extraction schemes involving mixer-settlers. In the present study as well, attempts to directly extract Pu(IV) from DES yielded very minimal extraction (Table 2), indicating the hindrance caused by medium viscosity as well as strong citrate complexation [28]. It is noteworthy that the viscosity of water, propylene glycol and CU [19] is 1 cP, 56 cP and 200 cP, respectively, at 298 K. Propylene glycol based solvent systems have been enlisted in the preferred group of solvents to design sustainable separation processes [7] and known to be biodegradable and non-toxic [21]. As mentioned, judicious choice of solvent and extractant plays a crucial role in successful process design. PG was hence selected over other polar non-aqueous solvents as the liquid phase for SPE of Pu. The hydrophilic eutectic solvent, CU was found to be miscible with polar organic solvent, PG in upto 1 : 5 v/v by mechanical shaking or ultrasonication for 10 min. Typically, dilution of a 1 : 10 volume ratios of CU : PG was used for present extraction experiments.

DEHPA, an acidic extractant for aqueous separation of Pu [33], was selected for our study. DEHPA is known to exist in dimeric form in apolar diluents during solvent extraction [24]. However, due to absence of any diluent in case of SPE, DEHPA exists in monomeric form and extracts metal ions by cation exchange mechanism subsequent to deprotonation (pK$_a$=5.2) [34]. Extraction of Pu from non-aqueous medium is expected to follow the given equation:

$$M^{n+}_{non-aq} + nDEHPA_{res} \rightarrow M(DEHPA)_{n, res} + nH^+_{non-aq} \qquad (3)$$

Kinetics of extraction (Fig. 7) was investigated by equilibrating a known amount of DEHPA encapsulated PES beads with Pu(IV), in PG medium, for different contact times (0.25 to 8 hours). The distribution coefficient (k$_D$) is given by the equation:

$$k_D = (C_0 - C_e)/C_e * V/m \qquad (4)$$

where C_0 and C_e stand for the initial and equilibrium metal ion concentrations (mg L^{-1}) in the solution, V represents the total volume of solution (mL); and m stands for the mass of adsorbent (g). The batch sorption studies revealed that smaller beads (C) require less contact time to attain equilibrium and have higher k$_D$ as compared to bigger beads. The DEHPA loading in resins is as obtained from TGA, which follows the order: B>C>A. The DEHPA content is expected to mirror the extent of metal ion extraction in case of solvent extraction [33]. However, the distribution coefficient follows the order of C>A>B. This indicates that bead size and presence of pore former additive PVA also play a decisive role in case of SPE. Lower bead size and higher porosity promote extraction
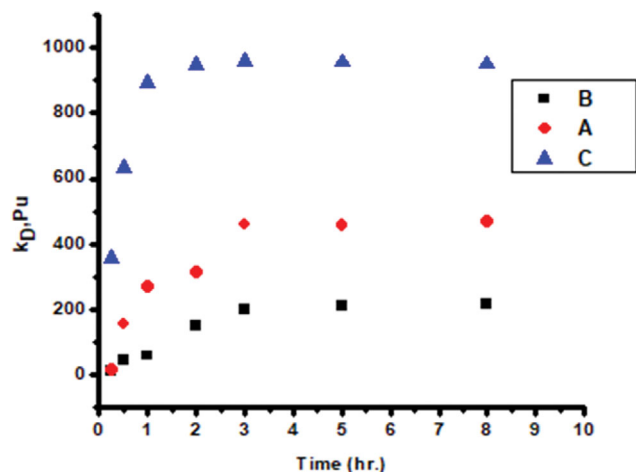
Fig. 7. Variation of distribution ratio, K_D of Pu(IV) with time (hrs) for DEHPA encapsulated PES beads; (A) With PVA, big; (B) Without PVA, big; (C) With PVA, small (Pu taken: 20 mM; More polar phase: propylene glycol; Results are avg. of triplicate extractions; Standard deviation: ±6).

Fig. 8. Comparison of distribution co-efficient of actinides in aqueous and non-aqueous medium (Results are avg. of triplicate extractions; Standard deviation: ±6).

by facilitating the entry of Pu containing liquid phase into the extractant encapsulated core. It is interesting to note that smaller beads with PVA, i.e. C, have intermediate water as well as extractant loading and highest extraction. Hence, the metal ion extraction mechanism by SPE can be visualized to be a combination of solvent extraction and chromatography. Interestingly, the maximum extent of extraction obtained with DEHPA encapsulated beads for non-aqueous medium was better (with PVA, small, k_D=950) than the extraction obtained for aqueous nitric acid medium (0.35 M, k_D= 656) [24].

Also, to understand the effect of the presence of salt, addition of $LiNO_3$ was studied. $LiNO_3$ was selected in the present study because of its reported high solubility in ethylene glycol [7]. Very small increase in distribution coefficient was observed with increasing with salt concentration (Table 2), which was presumably due to lack of salting out effect in non-aqueous medium. This indicated that de-solvation of metal ions in non-aqueous medium is not a dominating factor as against aqueous medium.

Fig. 8 gives the k_D values for different metal ions for PG (this study) and nitric acid medium [22]. k_D follows the order similar to that for solvent extraction from aqueous nitric acid [31] reflecting the complexing abilities of different metal ions towards acidic extractant DEHPA. However, extent of extraction for Pu(IV)$\gg$UO$_2^{2+}$> Am(III) in PG medium. This could be rationalized by the vastly different chemistry in PG medium vis-a-vis aqueous nitric acid medium. In PG, suppression of dissociation of DEHPA by aqueous acid medium is absent and ease of Pu(IV) de-solvation followed by complexation with DEHPA is very high. This very high selectivity for Pu(IV) extraction with respect to Am(III) brings out one of the key advantages of non-aqueous extraction. In case of aqueous SPE, two step Pu-Am separation was required [20]. As against solid phase extraction from aqueous phase where simultaneous extraction of Am(III) and Pu(IV) followed by two step stripping was prescribed [22], Pu(IV) separation is achieved in single step itself for non-aqueous SPE.
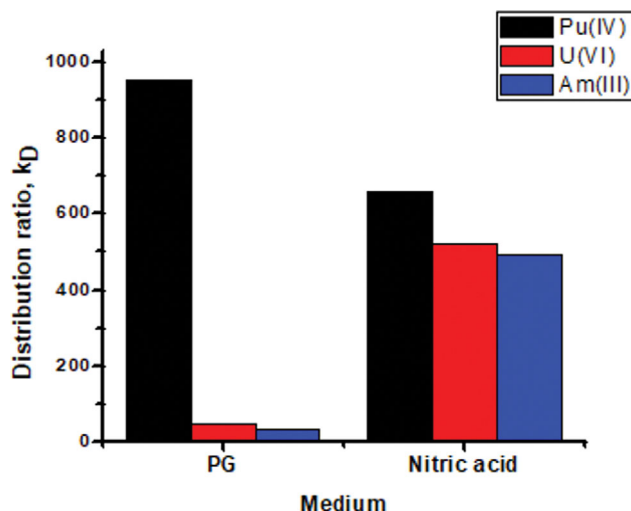
Pu stripping was attempted from DEHPA encapsulated PES beads with biodegradable organic acid methane sulphonic acid (MSA). With equilibration time of 2 hr, stripping agents MSA+PG (1 : 1) and neat MSA yielded 45% and 95% stripping (standard deviation= ±5 for triplicate experiments).

CONCLUSION

The present work demonstrates acid-free, non-aqueous Pu recovery from various matrices and reveals promising insights for actinide separation in the nuclear fuel cycle. Plutonium leaching from refractory oxide matrices and simulated cellulosic waste was successfully carried out with halide anion free eutectic solvent based on urea and choline dihydrogen citrate with >93% efficiency by controlled IR heating. The sustainable method of SPE was chosen over liquid-liquid extraction for Pu recovery, and for the same the Pu solution in CU was diluted in less viscous PG (1 : 10 v/v). Redox speciation investigation (UV-Vis spectrophotometry and electrometry) in these novel 'green' media, CU and PG, confirmed the exclusive presence of Pu(IV), thus eliminating the complication of pre-extraction oxidation state control. Extractant encapsulated smaller PES beads (average diameter 900 µm), with PVA additive having intermediate DEHPA and water content, were used for fast and efficient SPE of Pu (k_D=950±6). This demonstrates the impact of solvent extraction as well as chromatography on the mechanism of SPE. Another interesting advantageous feature is the highly selective extraction for Pu(IV) than Am(III) and U(VI) as compared to aqueous medium.

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CONFLICT OF INTEREST

Authors have no conflict of interest to declare.

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