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Recovery of plutonium from polymeric waste matrices using supercritical fluid extraction

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ABSTRACT

Polymers are widely used materials and are indispensable in handling radioactive materials in fumehoods, gloveboxes, etc. Supercritical fluid extraction (SFE) technique is widely employed for the removal of radioactive contaminants from various matrices using supercritical carbon dioxide (Sc-CO_2) modified with suitable ligands as an extraction medium. In the present study, recovery of plutonium from various polymeric matrices, such as neoprene, polyvinyl chloride (PVC) and surgical gloves has been demonstrated using Sc-CO_2 modified with n-octylphenyl N,N-diisobutyl carbamoylmethylphosphine oxide (ϕCMPO) in methanol. The matrix was initially subjected to neat Sc-CO_2 extraction to prevent co-extraction of organic compounds during SFE of plutonium; in the initial extraction with Sc-CO_2, organic compounds added as additives to the polymeric matrix were extracted. In the initial studies, SFE method was developed for the complete recovery of plutonium from simulated polymeric waste matrices. Subsequently, the actual waste, i.e. plutonium present in PVC matrix was processed from a 0.1 L extraction vessel for its recovery. The plutonium recovery was found to be ~97% from the actual PVC waste matrix. The technique was also demonstrated for the recovery of important actinides e.g. americium from simulated neoprene waste matrix. As the disposal of polymer waste is of major concern in nuclear waste management, the SFE technique developed in the present study offers a potential opportunity for the recovery of actinides with generation of minimum secondary waste.

Keywords: Supercritical CO_2; SFE; Plutonium; Polymeric waste matrix; CMPO

1. Introduction

Advanced separation techniques, such as solid phase extraction, supercritical fluid and ionic liquid extraction for the removal and recovery of radioactive contaminants from various solid waste matrices are essential for nuclear waste management. Disposal of polymer waste is of major concern in nuclear waste treatment. Supercritical fluid extraction (SFE) technique is an attractive to nuclear industry to recover actinides such as uranium and plutonium from such

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waste matrices, since it reduces the generation of secondary liquid waste volume significantly and minimize or eliminates the use of organic solvents.

Supercritical fluids exhibit unique properties of gas like diffusivity and viscosity, liquid-like density and low surface tension. These properties of supercritical fluids provide ideal conditions to extract the components of interest with a high degree of recovery in a short period of time. Supercritical fluids provide faster, cleaner and efficient extractions and CO_2 escapes as a gas after the extraction leaving the dissolved solute, resulting in little or no waste. Carbon dioxide is the most commonly used supercritical fluid. It has a low critical temperature of 304 K and a moderate critical pressure of 73 bar [1–3]. CO_2 being a non-polar molecule with a low dielectric constant limits its ability to dissolve the ionic species. Supercritical CO_2 modified with extractants has been employed for the extraction of various metal ions including the actinides [4–20].

Extraction of lanthanides and actinides from solid samples was extensively investigated by several research groups. Lin et al. reported the SFE of lanthanides and uranium from solid materials using modified CO_2 [6]. Wai reported extraction of di and tri valent metal ions from spiked cellulose based filter paper and sand [7]. Recovery of about 69% plutonium and 88% americium from surrogate soil using supercritical carbon dioxide (Sc-CO_2) modified with tributyl phosphate (TBP) and theonyl trifluoroacetone (TTA) was reported by Mincher et al. [8]. Sc-CO_2 modified with trifluoroacetylacetone (F_3acac), pyridine and water resulted in the extraction efficiency of about 97% of plutonium (IV) nitrate and 66% of plutonium (IV) oxide from stainless steel plate surface [9]. Uranium dioxide and its solid solutions with neptunium, plutonium and americium dioxides were dissolved using TBP saturated with nitric acid [10]. Sc-CO_2 modified with TBP was employed for the extraction of both uranium and plutonium from nitric acid medium [11]. Sc-CO_2 modified with HNO_3–TBP complex was employed for the dissolution of UO_2 and U_3O_8 [12,13]. The removal of uranium from solid waste matrices, e.g. tissue paper matrix was established using modified Sc-CO_2 [14,15]. An SFE procedure was developed earlier in our laboratory for the complete removal of plutonium from simulated waste matrices; e.g. plutonium from matrices such as tissue, glass, stainless steel and Teflon using Sc-CO_2 modified with octylphenyl N,N-diisobutyl carbamoylmethylphosphine oxide (ϕCMPO) in methanol [19]. Studies on various parameters and their influence on the extraction efficiency of the simulated waste suggested that the actual wastes encountered in the laboratory are found to have variation in the extraction efficiency depending upon their physical conditions, oxidation state of actinides, presence of moisture, drying time or storage durations from its production, etc.

The polymeric waste generated from radioactive laboratory typically includes radioactive contaminated gloves, polyvinyl chloride (PVC), neoprene, etc. An extensive investigation was carried out for the extraction and recovery of plutonium from these matrices using SFE. Synthesis of polymers involves addition of organic compounds, such as additives, plasticizers, etc. in order to achieve the desirable physical properties. The unreacted monomers, initiators, catalysts, low molecular oligomers, etc. can also co-extract along with actinides. The interaction of CO_2 with polymer can rapidly swell and plasticize the polymer resulting in faster diffusion rate followed by solubilization and extraction [21]. Initial studies were carried out on the extraction and recovery of simulated uranium and plutonium waste from polymeric matrices, such as neoprene, PVC and surgical gloves using modified Sc-CO_2. Subsequently, the recovery of plutonium from an actual polymeric matrix has been demonstrated using Sc-CO_2 modified with CMPO. In the initial studies, SFE experiments were carried out in a 1 mL extraction vessel and the methods were evolved for the complete removal of plutonium from actual polymeric matrix. The entire waste was then processed using a 0.1 litre capacity extraction vessel and recovery of plutonium was demonstrated from the polymeric PVC waste matrix.

2. Experimental

The SFE system used for the study consists of two reciprocating pumps, one for pumping carbon dioxide and another pump for the co-solvent (modifier), a constant temperature oven (±1˚C) and a backpressure regulator. Carbon dioxide gas used had a purity > 99.9%. All reagents used were of analytical grade. The ligand, CMPO used was synthesized in our laboratory [22]. Extraction vessels of 1, 10, 50 and 100 mL capacity were employed in the study.

The SFE system was set-up in a glove box incorporating certain modifications for handling high pressures and radioactive materials [23]. A secondary vessel accommodated the extraction vessel of higher capacity (e.g. 0.1 L) to contain any accidental pressure release during the extraction. In addition, methanol level was monitored using a gas detection system and controlled within the safety level in the glove box. The two pumps for pumping liquid carbon dioxide and the modifier were placed outside the glove box, whereas the backpressure regulator, heating oven required to maintain the temperature of the extraction vessel, was placed inside the glove box. The extracts were collected in a suitable medium inside a glove box and the aliquots were taken out for the assay of actinides. The schematic of SFE system used in the present study is shown in Fig. 1.

2.1. Preparation of simulated waste

The neat polymeric matrices (without actinides) were initially subjected to SFE using Sc-CO_2 or Sc-CO_2 + methanol for the removal of organic compounds (e.g. additives). The extraction was carried out typically at 250 bar and 40–60°C and the extracts were collected in isopropanol medium and assay was carried out by HPLC, IR and mass spectrometry. The matrix was initially subjected to neat Sc-CO_2 extraction to prevent co-extraction of organic compounds during SFE of plutonium. In the initial extraction with Sc-CO_2, organic compounds were added as additives to the polymeric matrices which were extracted.

An aliquot of plutonium solution, Pu(III)/Pu(IV) containing ~10–15 μg was loaded onto a polymeric matrices, such as PVC, neoprene and surgical gloves and dried at fumehood over a period of 10 days. Pu (III) solution was prepared from plutonium nitrate solutions with the addition of hydroxylamine hydrochloride. Plutonium in its Pu(IV) state was prepared with the addition of $NaNO_2$. These solutions were kept at ~1 N HNO_3 medium.

The polymeric matrices were initially washed with distilled water and isopropanol prior to preparation of simulated matrices. The matrix containing plutonium was cut into small pieces, typical dimension being 4 × 5 cm. The cut pieces were inserted into a 1 mL extraction vessel, 1 N HNO_3 (~50 μL) was sprinkled and extraction was carried out under typical conditions viz. pressure: 250 bar, temp: 50°C, Sc-CO_2 flow rate: 3 mL/min, modifier solution flow rate: 0.1 mL/min. The modifier solution was prepared by the addition of 3 g CMPO and 1.8 mL of conc. HNO_3 to 100 mL of methanol. The extraction was carried out for a period of 2 h. The plutonium present in extract was collected in 10 mL of 1:1 isopropanol and 0.1 N HNO_3 medium. The plutonium content of the extract after the SFE experiment was assayed by liquid scintillation counting technique. The un-extracted plutonium remains in polymeric waste matrix was estimated by leaching with 4 N HNO_3. The leaching efficiency using ultrasonication was found to be ~97–99%.

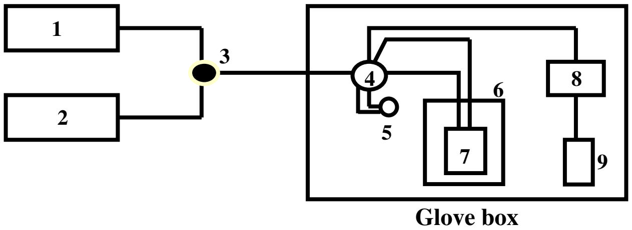

Fig. 1. Schematic of SFE system in a glove box for recovery of plutonium from polymeric matrix. 1. Sc-CO_2 pump; 2. Modifier/Co-solvent pump (ligand dissolved in a co-solvent); 3. CO_2–Co-solvent mixer; 4. Six way valve; 5. Vent lines; 6. Secondary vessel; 7. Primary extraction vessel with heater (for accommodating plutonium sample); 8. Back-pressure regulator; and 9. Plutonium sample collection vessel with a suitable solvent.

2.2. Recovery of plutonium from actual waste

The PVC matrix containing plutonium was cut into small pieces (5 × 5 cm) and was loaded in to a 1 mL capacity extraction vessel and SFE was carried out using Sc-CO_2 modified with CMPO/methanol under the typical experimental conditions viz. pressure 250 bar and temperature 50°C. An extraction period of about 1–2 h was used. The extract was collected in isopropanol–nitric acid medium for the assay of plutonium. Subsequently, the polymeric waste were loaded in a 0.1 L (11 cm height × 4 cm dia) capacity extraction vessel and SFE was carried out in several batches for the recovery of plutonium from polymeric matrix. In a typical batch, approximately 50 g of PVC waste was loaded in a 0.1 L scale extraction vessel for the recovery of plutonium. Long extraction periods were employed when samples were processed from a 0.1 L capacity vessel as Sc-CO_2, throughput was not adequate for its geometry i.e. number of CO_2 changes per unit time was less compared to the one observed with 1 mL vessel.

2.3. Preparation of U and Am simulated waste matrices

An aliquot of uranyl nitrate solution containing ~1,000 μg of uranium was loaded onto polymeric matrices, such as PVC, neoprene and surgical gloves (5 × 5 cm) and dried at fumehood for 10 days. Similarly, an aliquot of americium nitrate solution containing ~0.1 μg of americium was loaded onto a neoprene matrix and dried at fumehood for 10 days. The simulated matrices were inserted into a 1 mL extraction vessel for SFE experiments.

3. Results and discussion

The organic compounds added as additives in neoprene, surgical gloves and PVC were co-extracted during SFE of actinides from these matrices. Hence, SFE of these matrices without actinides were studied initially.

3.1. SFE of neat polymeric matrices

Extraction of neoprene glove sample using neat Sc-CO_2 produced blisters. Sc-CO_2 was readily absorbed into polymers at elevated pressures, which resulted in polymer swelling. Addition of small amounts of methanol resulted in enhanced swelling. HPLC analysis of the extract indicated the presence of four compounds in it. Analysis of the extract by IR suggested the presence of C=O group which was also found to be in the base polymer i.e. neoprene. Mass spectrometry of the extract showed the presence of peaks at 170, 212, 325, 368, 379 and 396. The extracts contain some of the additives like plasticizers e.g. dioctylphthalate, methacrylic acid, dioctyl sebatate, etc. Extraction after two hours resulted in the weight loss of 2.5% with Sc-CO_2 modified with methanol. However, the extraction of the species ceased after an hour.

SFE of PVC was carried out using Sc-CO_2 modified with methanol. HPLC results of the extract suggested the presence of at least one major component (Fig. 2). IR study indicated the presence of C=O in extract as in the case of neoprene matrix. A weight loss of about 10–12% was observed. The major part of extraction of the organic species was found to cease after a few hours.

Surgical gloves were also subjected to SFE using methanol modified Sc-CO_2 and the analysis of the extracts by HPLC indicates the presence of two components. Extraction for about 3 h showed a weight loss of about 2%.

3.2. SFE of plutonium from simulated waste

Initial results on the extraction and recovery of plutonium from simulated PVC matrix are shown in Fig. 3. A highest recovery of about 99.9% was observed using Sc-CO_2 modified with CMPO in methanol at 50°C. The extraction efficiency was found to vary from 97 to 99.9% (10 independent SFE experiments) during the course of these studies. The extraction profiles indicated that major portion of plutonium was removed and extracted in about 30–45 min itself. Similarly, near complete extraction and recovery of plutonium from simulated waste matrices, i.e. neoprene matrix (96 ± 3.5%, six independent experiments) and surgical glove matrix (95 ± 4.6%, six independent experiments) were demonstrated.

3.3. SFE of plutonium from actual polymeric waste

The polymeric PVC matrix containing plutonium was initially subjected to SFE from a 1 mL extraction vessel and near complete extraction (97–99%) was established. Recovery of plutonium was achieved using Sc-CO_2 modified with CMPO in methanol containing HNO_3. The extract as well as remains were analysed for determining the extraction efficiency. The matrix was initially subjected to Sc-CO_2 + methanol to prevent co-extraction of organic compounds during SFE of plutonium. Organic compounds added as additives to the PVC were extracted and weight loss of ~10% of PVC matrix was observed.

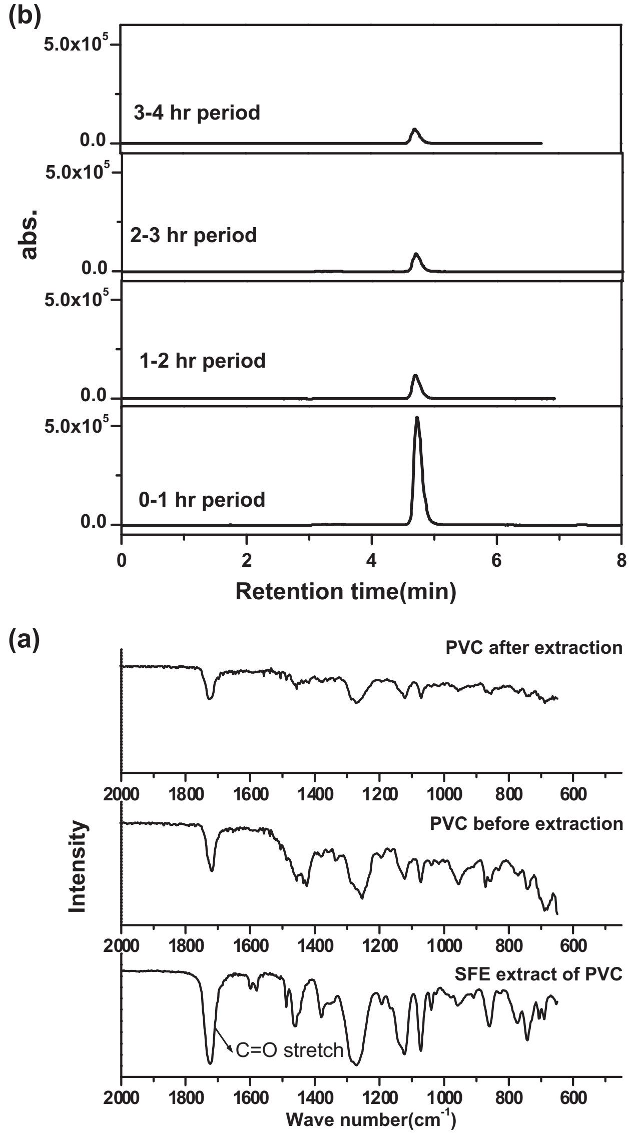

Fig. 2. IR (a) and HPLC (b) analysis of PVC extract during SFE. Exp. Sample PVC (~10 g) cut pieces in 50 mL extraction vessel. P: 250 bar; Temp.: 50°C; Sc-CO_2: 3 mL/min; methanol: 0.1 mL/min. HPLC carried out on a C_{18} column (25 cm length & 4.6 mm dia) using methanol as mobile phase and detection at 254 nm.

The plutonium containing polymeric matrix was subsequently processed from a 0.1 L capacity extraction vessel and samples were processed in many

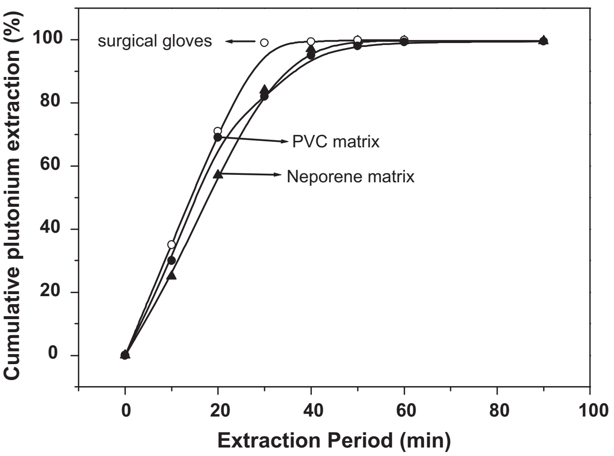

Fig. 3. Recovery of plutonium from simulated polymeric waste matrices. Sample: plutonium nitrate (~10 µg Pu equivalent) dried on neoprene/surgical glove/PVC in a fumehood for 10 days prior to SFE. Waste matrix was placed in a 1 mL extraction vessel. Exp: Sc-CO_2: 3 mL/min; modifier flow rate: 0.1 mL/min; P: 250 bar; Temp.: 50°C. Modifier composition: 3 g CMPO + 1.83 mL conc. HNO_3 made up to 100 mL in methanol.

batches for its recovery. A typical extraction profile for the recovery of plutonium from PVC matrix is shown in Fig. 4. About 500 µg of plutonium was extracted and recovered in a typical batch. The extraction was continued till the presence of plutonium in the extract.

For the recovery of plutonium from polymeric matrices, CMPO was chosen compared to ligands, such as TBP, TTA and acetyl acetone as it gave better extraction efficiency during recovery of plutonium from cellulose matrix. Nitric acid was sprinkled onto the polymeric matrices to convert plutonium into its soluble species for its complete extraction, especially from long term dried waste matrices. The extraction efficiency of plutonium during SFE decreased with the increased drying period of the simulated matrix, in the absence of addition of nitric acid [19]. The formation of unextractable plutonium species was mainly responsible for its lower recovery in the absence of HNO_3 addition. Hence, HNO_3 was added to modifier solvent to improve the extraction efficiency.

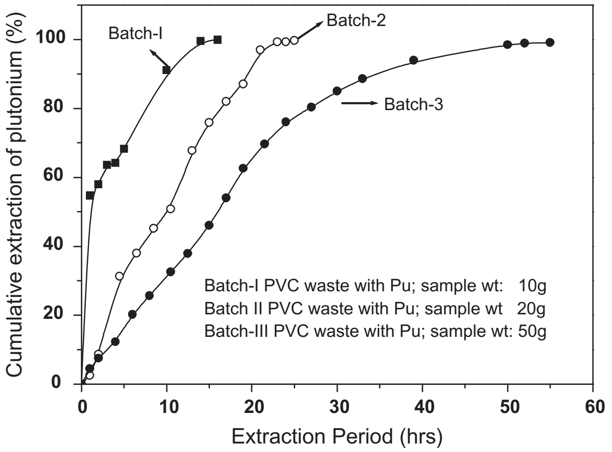

Fig. 4. SFE and recovery of plutonium from actual PVC waste matrix using a 0.1 L extraction vessel. Sample: Plutonium in PVC matrix; Exp: Sc-CO_2: 3 mL/min; modifier flow rate: CMPO/methanol (5 g CMPO + 1.83 mL conc. HNO_3 made up to 100 mL in methanol) 0.1 mL/min; P: 250 bar; Temp.: 50°C.

3.4. Recovery of americium and uranium from PVC waste matrix

Americium is also an important actinide encountered in nuclear fuel cycle and is chemically analogous to Pu(III). Hence, an investigation on its recovery from polymeric matrix, e.g. PVC matrix assumes significance from waste management point of view. The SFE studies of Am(III) demonstrated its near complete extraction (96–99.8%) using Sc-CO_2 modified with methanol containing 2 wt.% CMPO (Fig. 5). Similarly, complete extraction of uranyl nitrate (98–99.9%) was demonstrated from polymeric waste matrices, such as neoprene, PVC and surgical

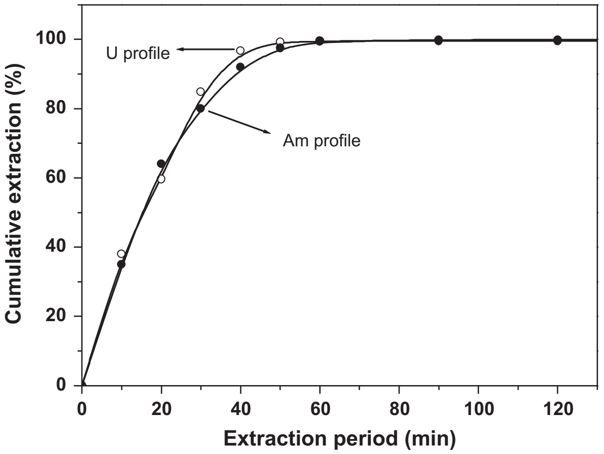

Fig. 5. Recovery of uranium and americium from simulated polymeric waste matrix. Samples of uranyl nitrate/americium nitrates were loaded and dried on a neoprene matrix for 10 days in fumehood prior to SFE. Exp. Sc-CO_2: 2.5 mL/min; P: 250 bar; Temp. 50°C; modifier flow rate: 0.1 mL/min. Modifier used for uranium recovery: 2 wt.% acetyl acetone in methanol; Modifier used for americium recovery: 2 g CMPO + 1 mL conc. HNO_3 in 100 mL methanol.

gloves using Sc-CO_2 modified with methanol containing 2 wt.% acetyl acetone (Fig. 5).

4. Conclusion

SFE technique was developed for the complete recovery of plutonium from various simulated polymeric waste matrices. The SFE technique was demonstrated for the complete recovery of plutonium from actual PVC based polymeric waste matrix. Sc-CO_2 modified with CMPO was employed for the recovery of plutonium from waste matrices. These studies have established that SFE is a potential technique for the efficient removal of actinides from waste matrices with minimum generation of secondary solvent waste. The actinides present in the polymeric waste matrices will be mainly sorbed on the surfaces of these matrices (e.g. PVC, neoprene) and decontamination of actinides from these matrices are different from the decontamination from cellulose/cloth/soil matrices, where the interactions between actinide ion and matrices are expected to be much higher.

These studies also demonstrated the feasibility of recovery of actinides from various waste matrices in a preparative scale facility which is an attractive feature for processing of large amount of radioactive waste.

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