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Extraction of plutonium (IV) from aqueous nitrate solutions into ligand modified micellar phase (LMMP) of Tergitol 15-S-9 with tri-octylphosphine oxide and separation by ultrafiltration

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ABSTRACT

Pressure-driven membrane-based ultrafiltration (UF) techniques have definite use in the effluent treatment process. One of the promising applications of UF is the extraction of solute into a surfactant micellar pseudo-phase and its removal by filtering through suitable semi-permeable membrane. Extraction of Plutonium (IV) from nitric acid solutions using nonionic polyethylene glycol ether, Tergitol 15-S-9 (Tergitol) surfactant with trioctylphosphine oxide (TOPO) was investigated under different experimental conditions. For the separation of surfactant micelles, polyethersulfone membranes with nominal molecular weight cut-offs (NMWCO), 3, 5, and 10 kDa were used in the batch and stirred cell UF unit. The effects of NMWCO of the membrane and feed solution conditions, such as the concentration of surfactant, organic ligand TOPO, and ionic concentrations on the efficiency of the removal of Pu (IV) were studied. More than 90% recovery of Pu(IV) could be achieved using membrane of NMWCO 3 kDa from aqueous solution contained 0.42 mM Pu with 1–3 M HNO_3, 85.6 mM Tergitol, and 3.8 mM TOPO. The selectivity for the separation of plutonium was investigated by observing rejection of some commonly associated metal ions from nitric acid solutions of three different concentrations. The rejection of Cs(I) was negligible, whereas maximum 54% of Zr, 10% Ce(III) and Eu(III) and 7% of Ru(III) were rejected along with 90% of plutonium from the aqueous solution.

Keywords: Extraction; Micellar enhanced ultrafiltration; Plutonium; Tri-octylphosphine oxide; Tergitol 15-S-9

1. Introduction

Nuclear energy appears to be a vital option to meet the constant growing demand of electricity under the constraints, to limit the emission of carbon to the atmosphere [1]. But, this option inherits problems arising from the radioactive waste generation, which is to be kept isolated from normal civilian life. Transuranium elements are very long-lived radiotoxic elements and gives out high ionizing alpha radiation. Presence of long-lived radio nuclides of intense radio-

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toxic nature makes waste storage more risky and expensive. Hence, removal of these transuranium elements from nuclear waste is essential, which can shorten long-term hazard of such waste solutions. The risk and expenditure in the storage are directly proportional to the volume of waste solution. Selective removal and concentration of low level actinides from these wastes appear to be the most practical remedy [2,3]. The most commonly used solvent extraction process is not economical under such conditions, as it requires multi-stage operations in a series of mixer and settler units to achieve desired recovery of extractable metal components [4]. It also requires a quantity of extractant, which is unacceptably high from environmental and safety considerations. After utilization, the material used in the processing of radioactive waste solutions generates secondary radioactive waste. Hence, to minimize recurring waste generation, it is more practical to choose a process, which gives very little secondary waste or process with multi-cycle applicability which can effectively reduce volume of waste generated in long term operations. Filtration through semi-permeable membrane with the potential of selective retention is a well-established commercial technique, which also has great applicability in the treatment of radioactive waste [5,6].

The UF-based separation is a solute fractionation using appropriate pore size membrane as a sieve. The advantage of working with UF is that a high throughput can be achieved as compared to reverse osmosis, while using low driving pressure and temperature [7,8]. One of the promising applications of UF is the extraction of solute in the surfactant micellar pseudophase and its removal by ultrafiltration (UF) [9–15]. The micellar extraction of metal ions can be achieved in two different ways: (i) complexation of metal ions with the monovalent counter ions of anionic micelles and (ii) complexation of metal ions by lipophilic complexing agents solubilized in the hydrophobic core of the micelles. In the first case, the extent of binding of the metal ions is controlled by the equilibrium relations governing the process of ion exchange. In the second case, it depends on the stability constant of the metal–extractant complex which is very similar to classical solvent extraction [16]. The high level radioactive waste solution, which needs treatment for safe disposal, contains very low concentration of targeted metal species for removal or recovery. This prompted us to develop a UF technique for the selective removal of Pu from such solutions.

The objective of this study, is to determine an applicability of the UF technique for the removal/recovery of Pu(IV) from low concentration nitrate solutions using its extraction in the ligand modified micellar phase (LMMP) containing non-ionic surfactant, Tergitol 15-S-9 and a small quantity of ligand, trioctylphospine oxide (TOPO). Experiments are carried out to characterize the filtration of metal solutions containing surfactant and organic ligand in terms of the retention of the metal ions. Polyethersulfone membranes are selected in this work due to their hydrophobic nature and very good stability in the acidic nitrate solutions. The effect of various process parameters such as nominal molecular weight cut-offs (NMWCO) of the membrane filters, concentrations of metal ions, nitric acid, complexing ligand, and surfactant on efficiency of Pu(IV) rejection is investigated.

2. Experimental

2.1. Materials

Tergitol, type 15-S-9 (Sigma, USA, Batch #093K0002), and TOPO from Fluka Switzerland (AR grade), were used as received. Specific details of these chemicals are given in Table 1. All other chemicals and reagents used were of analytical reagent grade.

Plutonium-239, being the major constituent in the Pu solution, was used to study its retention characteristics in UF experiments. Plutonium was purified by Dowex 1×4 anion-exchange resin [17]. The Pu solution as a feed with acidity of 7.2 M HNO_3 was loaded on this resin followed by washings with 7.2 M HNO_3. The purified Pu product was eluted with 0.5 M HNO_3. The tetravalency of Pu in the stock solutions was adjusted by the addition of solid sodium nitrite (ca. 0.03 M) [18]. Further, the tetravalency of plutonium is confirmed by its quantitative extraction in 1-(2-thenoyl)-3,3,3-trifluoroacetone[19].

A mixture of fission product solutions containing ^{144}Ce, ^{137}Cs, $^{152–154}Eu$, $^{103,106}Ru$, and ^{95}Zr was used to study rejection of these elements under given experimental conditions.

The UF membranes used in this study were polyethersulfone (PES) membranes with 3, 5, and 10 kDa NMWCO. These circular flat sheets membranes of diameter of 47 mm were obtained from Pall-Filtron OMEGA. Prior to UF experiment, the membranes were soaked in water for 24 h.

2.2. Experimental procedures

The aqueous ligand-modified micellar solutions were prepared by dissolving required quantity of surfactant (10–100 mM of Tergitol) and TOPO (0–4.5 mM), in solutions of desired concentration of nitric acid (0.5–4 M). Required quantity of Pu(IV) nitrate was added to these solutions from its stock solution.

Table 1
Characterizations data of surfactant and extractant employed

Name	Type	Formula	M.W. (g/mol)
Polyethylene glycol ether (Tergitol 15-S-9)	Non-ionic surfactant	$CH_3(CH_2)_{12–14}(OC_2H_4)_9OH$	584
Tri-octylphosphine oxide (TOPO)	Neutral metal extactant	$(CH_3\ (CH_2)_7)_3P=O$	386.65

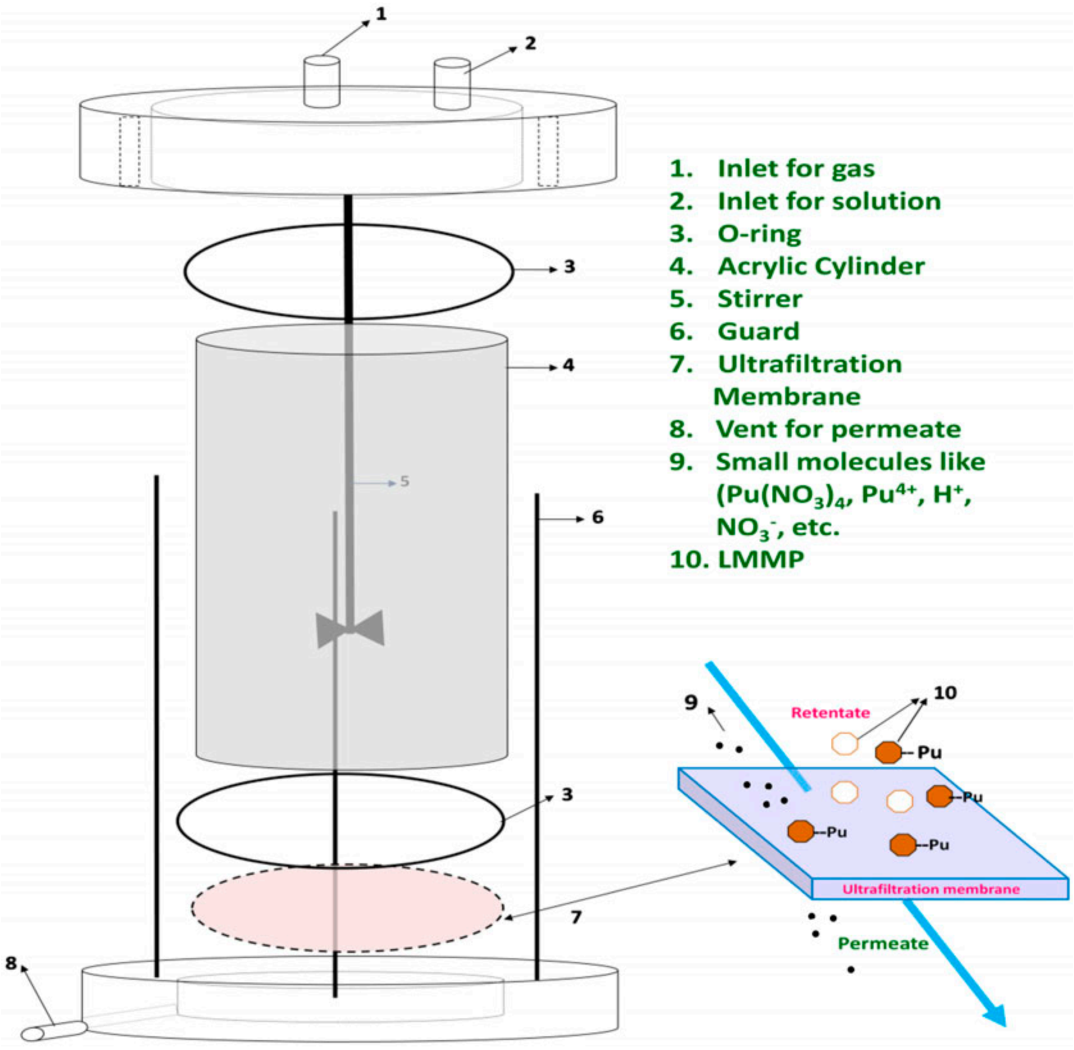

Fig. 1. Schematic diagram of UF cell and the conceptual process of ligand modified micellar enhance rejection of Pu(IV).

UF experiments were carried out at room temperature (controlled at 25 ± 2°C by air conditioner) in a 70 mL batch-stirred cell unit (fabricated indigenously). The test cell consists of three detachable parts; the lower part is an SS flange with grooved chamber for the placement of the membrane. The grooved chamber is open ended. The membrane disc was placed on the base of the grooved chamber, through which permeate was collected. A magnetic stirring bar was fitted in the upper part, which is placed just above the membrane after acrylic hollow cylinder is mounted. Lower part, acrylic chamber, and upper part of the unit were clamped tightly using O-rings. The schematic diagram of cell is depicted in Fig. 1. The cell was initially filled with 20 mL water and connected to nitrogen gas cylinder that was used to maintain the pressure gradient across the membrane at 200 kPa. The UF test cell was placed on a magnetic stirrer with adjustable speed and feed solution near the solution–membrane interface and was stirred at a speed of 220 ± 20 rpm. Permeate solutions were collected in 10 mL graduated plastic vials. In case of experimental solutions, the cell was filled with 20 mL feed solution and filtered through different pore-size membrane under desired pressure of N_2. Each experiment was terminated when 70% (14 mL) of the feed was filtered, before the stirred-induced vortex reached the membrane. After each UF experiment, the used membrane was immediately flushed with deionized water, and then rinsed with 0.1 M NaOH, 100 ppm NaOCl, 0.01 M HNO_3, and DD water. Used membrane was discarded when its permeate flux for water reduced by < 95% of its original value. The percentage recovery of Pu(IV) denoted by Pu(IV)_R was calculated as [7].

$$\%\text{Pu(IV)}_R = 100 \times (1 - [\text{Pu(IV)}]_{\text{permeate}}/[\text{Pu(IV)}]_{\text{feed}}) \quad (1)$$

The concentrations of Pu in permeate phase for each experiment was determined periodically for every 2 mL of permeate collected. At least, three similar experiments were carried out to observe the statistical reproducibility of the results.

2.3. Analysis of plutonium

Suitable aliquots of permeate phase were analyzed for plutonium by radiometry. This was performed by pipetting a known volume of plutonium solution on SS disc; after drying the solution on hot plate, the disc was further heated to red hot on Bunsen flame. Then this disc was counted for alpha activity on ZnS scintillation alpha probe-type counter made by PLA Electro Appliances Pvt. Ltd., Mumbai, India.

2.4. Analysis of fission products

HPGe detector (Princeton Gamma Tech, Inc., Germany) of 62cm^3 coupled to a 4 K multi-channel analyzer was used for the gamma spectrometric determination of activities due to ^{144}Ce, ^{137}Cs, ^{152,154}Eu, ^{103,106}Ru, and ^{95}Zr.

3. Results and discussion

Preliminary experiments of MEUF rejection of Pu (IV) were carried out using aqueous solutions containing 0.42 mM of plutonium, 2 M nitric acid, and different concentrations (10–100 mM) of Tergitol. A 5 kDa NMWCO UF membrane was used in these experiments. Practically negligible rejection of Pu(IV) was observed in all these experiments. This suggests the rejection of Pu(IV) in presence of TOPO which is incorporated in the micelle core of the surfactant molecules through complexing of Pu(IV) with TOPO. The chemical equilibrium involved in the MEUF rejection of plutonium can be written as:

$$\text{Pu}^{4+} + 4\text{NO}_3^- + 2\overline{\text{TOPO}} \overset{K_E}{\longleftrightarrow} \overline{\text{Pu(NO}_3)_4 \cdot 2\text{TOPO}} \quad (2)$$

The above reaction suggests dependency of Pu(IV) rejection on the concentration of nitrate ions and TOPO in the micellar phase. The conceptual process of LMMP rejection of Pu(IV) by UF is illustrated in Fig. 1.

3.1. Effect of the concentration of nitric acid and sodium nitrate

Fig. 2 describes rejection of Pu(IV) in the micellar phase at different concentrations of nitric acid and sodium nitrate in the aqueous phase. Rejection of Pu (IV) is comparatively less when nitric acid content is below 0.75 M and above this, more than 90% of Pu(IV) could be retained in the micellar phase. As described by Eq. (2), the increasing concentration of nitrate ions promotes formation of Pu-TOPO complex and hence, more Pu(IV) is retained in the micellar phase. The rejection of Pu(IV) further decreases sharply beyond 3 M concentration of nitric acid in the micellar solution. This is due to the competition for the complexing of nitric acid with TOPO. The interaction of TOPO with nitric acid can be given as:

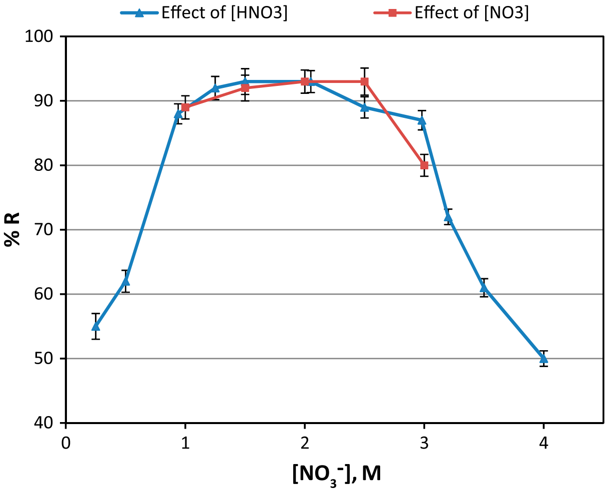

Fig. 2. Rejection of Pu(IV) as a function of the concentration of nitric acid and sodium nitrate in the aqueous solution. Aqueous solutions contained 85.6 mM Tergitol + 3.8 mM TOPO, UF memebrane—3 kDa NMWCO, Transmembrane pressure = 200 kPa.

$$\mathrm{H}^+ + \mathrm{NO}_3^- + \mathrm{TOPO} \xleftrightarrow{K_\mathrm{H}} \mathrm{HNO}_3 \cdot \mathrm{TOPO} \qquad (3)$$

where $K_\mathrm{H} = 8.9$

At 4 M HNO_3 in the micellar solution, the rejection of Pu(IV) is only 50%. To investigate the effect of nitrate ions on the rejection of plutonium, different quantity of sodium nitrate is added to the micellar solution containing 0.5 M nitric acid and 0.42 mM of Pu(IV). The rejection of Pu(IV) increases up to 2.5 M of nitrate concentration and beyond this decreases. The reduction in the retention of plutonium at higher concentrations of sodium nitrate solution is probably due to the changes that occur in the micellar phase composition of Tergitol molecules.

3.2. Effect of the concentration of TOPO

The 3 kDa NMWCO membranes were used in the experiments carried out to investigate the effect of the concentration of TOPO on the rejection of Pu(IV). Maximum about 5 mM of TOPO could be solubelized in 85.6 mM of Tergitol solution. The flux of permeate across the membrane decreases with increasing concentration of surfactant in the aqueous phase, hence the concentration of Tergitol is restricted to 85.6 mM. As seen in Fig. 3, the rejection of Pu(IV) increases with increasing concentration of TOPO in the micellar solution. 95% of Pu could be removed when micellar solution contained 4.0 mM of TOPO. The higher concentration of TOPO reduces permeate flux (Fig. 3). Beyond 3 mM of TOPO, there is no appreciable improvement in the rejection of Pu(IV), hence 3.8 mM of TOPO concentration is chosen for all other experiments.

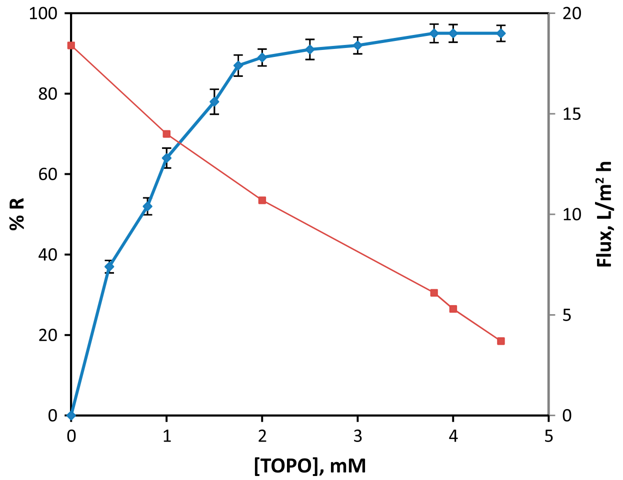

Fig. 3. Rejection of Pu(IV) as a function of the concentration of TOPO in the micellar phase. Aqueous solutions contained 85.6 mM Tergitol + 2 M HNO_3, UF memebrane—3 kDa NMWCO, Transmembrane pressure = 200 kPa.

3.3. Effect of the NMWCO of membrane

Table 2 illustrates effect of the NMWCO size of the membrane. The maximum 95% rejection of plutonium is obtained with 3 kDa NMWCO membrane whereas with 10 and 5 kDa MWCO membranes, the rejection of plutonium is 66 and 83%, respectively. The lesser rejection of plutonium with membranes of higher NMWCO is related with the size of micelles of Tergitol molecules formed in presence of TOPO. The permeate flux reduces considerably with membranes of lower NMWCO.

Table 2
Effect of membrane pore size on the rejection of Pu(IV) and permeate flux

NMWCO, kDa	% *R*	Flux, L/m^2 h
3	95 ± 3	17.4 ± 0.7
5	83 ± 4	22.2 ± 0.9
10	66 ± 4	29.5 ± 1.2

Aqueous solution: 85.6 mM Tergitol + 3.8 mM TOPO + 2 M HNO_3 + tracer quantity of Pu(IV). UF memebrane—3 kDa NMWCO, Transmembrane pressure = 200 kPa.

Table 3
Rejection of fission product elements

Element	[HNO_3], M	% *R*
Ce(III)	0.5	4 ± 0.5
	1.0	8 ± 0.5
	2.0	10 ± 0.5
Cs(I)	0.5	Nil
	2.0	Nil
Eu(III)	0.5	2 ± 0.4
	1.0	4 ± 0.5
	2.0	9 ± 0.5
Ru(III)	0.5	6 ± 0.5
	1.0	7 ± 0.4
	2.0	7 ± 0.5
Zr(IV)	0.5	15 ± 0.7
	1.0	41 ± 2
	2.0	54 ± 3

Aqueous solution: 85.6 mM Tergitol + 3.8 mM TOPO + tracer quantity of metal ions. UF memebrane—3 kDa NMWCO, Transmembrane pressure = 200 kPa.

3.4. Rejection of fission product elements

Initially, the rejection of usually accompanied fission product elements, Ce(III), Cs(I), Eu(III), Ru(III), and Zr(IV) is studied in the absence of surfactant and TOPO from three different concentrations of HNO_3 (0.5, 1, and 3). Under this range of acidity in the aqueous phase, there is no rejection of selected fission product elements. Similar experiments are repeated with 85.6 mM of Tergitol in the aqueous phase and in this case also, practically negligible rejection of above fission product elements is noted. The rejection of fission products in presence of Tergitol and TOPO in the aqueous solutions under specified conditions is summarized in Table 3. The rejection of Cs(I) is negligible under all experimental conditions where as among fission products, Zr(IV) is retained maximum (54%) in the micellar phase containing 2 M HNO_3, 3.8 mM TOPO, and 85.6 mM Tergitol in the aqueous phase. The rejection of rare earth elements such as Ce(III) and Eu(III) is about 10% where as 7% of Ru(III) is rejected under similar conditions.

4. Conclusion

An efficient removal of plutonium from its low concentrate solutions by UF is achieved using ligand-modified micellar solution of Tergitol. As such, micelles of Tergitol are inefficient to retain metal ions and removal of plutonium is achieved through its complexing with TOPO solvated in the hydrophobic core of non-ionic Tergitol micelles. More than 90% removal of plutonium could be achieved from aqueous solution containing 85.6 mM Tergitol with 3.8 mM TOPO by UF through the membrane of 3 kDa NMWCO. Maximum 10% Ce(III) and Eu(III), 54% Zr(IV), and 7% of Ru(III) rejected from aqueous solution of 2 M nitric acid in the given MEUF system. In all experiments, almost 100% of Cs(I) is passed through the UF membrane in the permeate solution.

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