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Application of Hollow Fiber Contactor in Nondispersive Solvent Extraction of Pu(IV) by TBP

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Abstract: Data on dispersion-free solvent extraction (DFSX) of Pu(IV) from acidic nitrate media using microporous hydrophobic polypropylene hollow fiber membrane contactor with tri-n-butylphosphate (TBP) employing as an extractant are being presented. The DFSX operation was carried out with various concentration of TBP in n-dodecane by passing acidic feed containing Pu (IV) through the tube side at the flow rate of 5.83 $cm^3\ s^{-1}$ and organic extractant through the shell side at the flow rate of 1.53 $cm^3 s^{-1}$. Extraction studies were performed under different hydrodynamic conditions and the overall mass-transfer coefficient was evaluated with countercurrent flow condition. It was possible to extract and concentrate Pu(IV) from aqueous phase by employing this technique. For back extracting the Pu, uranous nitrate and hydroxylamine hydrochloride solution as strippants were examined, which flowed through the tube side (flow rate: 6.11 $cm^3\ s^{-1}$) and the loaded organic was passed through the shell side with the flow rate of 1.66 $cm^3 s^{-1}$.

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Results revealed that ~80% of Pu(IV) from oxalate supernatant waste could be extracted by utilizing this technique.

Keywords: Hollow fiber contactor, dispersion free solvent extraction, tri-*n*-butyl phosphate, plutonium, mass transfer coefficient, oxalate supernatant

INTRODUCTION

In the current scenario, separation/recovery of actinides from different sources is of paramount importance with respect to strategic importance and radiotoxicity. Several methodologies, such as solvent extraction (SX), ion exchange (IX) and precipitation are being tried on plant scale. There are inherent drawbacks and practical difficulties with these techniques. In view of this, search of a new technique is always continued. Among recently developed technologies, membrane extraction processes using microporous hollow fibers are of particular interest because of their versatility and the fact that they overcome problems encountered in conventional liquid-liquid extraction (1, 2). In recent review, Alguacil et al. have studied the liquid membrane system in detail (3). Dispersion-free solvent extraction (DFSX) is simply a liquid-liquid extraction in hollow fiber contactor, which involves the use of a standard commercial hollow fiber module to contact aqueous and organic phase without dispersion, which minimizes the possibility of forming emulsion/third phase or crud formation with extractant. A second module would be used to strip the solute from the loaded organic phase.

DFSX techniques have been extensively deployed in separation science applications, such as metal recovery from leaching waste waters, extraction of precious and strategic metals from neutral waters, and treatment of large volumes of the effluents including toxic and hazardous waste generated by industries. Kathios et al. (4) have demonstrated the utility of the membrane-based extraction modules for the extraction of actinides. The performance of this technique was stated to be promising.

Recently, studies were conducted on extraction of Pu(IV) employing DFSX technique using hollow fiber contactors. In the previous studies, the hollow fiber supported liquid membrane configuration was checked with TBP-Pu(IV) from acidic nitrate media. Although the results were consistent with respect to the operating conditions and stability of the system (5), high flow rates (to obtain high mass-transfer) could not be used in the impregnation mode, which could force out the organic extractant from the pores. Therefore, to obtain a high mass-transfer coefficient with stable membrane process, the dispersion-free hollow fiber liquid-liquid extraction mode was selected. The aim of this work is to evaluate the effect of various chemical and hydrodynamic parameters in order to optimize performance of DFSX technique for the extraction of Pu(IV) from acidic nitrate media. The overall mass-transfer coefficients ($\boldsymbol{K}^{E}_{Pu}$) for extraction and stripping ($\boldsymbol{K}^{S}_{Pu}$) of Pu(IV) were calculated. The extraction of Pu(IV) and preconcentration studies were performed under same experimental conditions. Dodecane was employed as a diluent due to its proven performance in PUREX process. The recovery of plutonium from oxalate supernatant was also attempted under different experimental conditions.

EXPERIMENTAL

Reagents

All the chemicals were of A. R. grade. The ^{239}Pu tracer was purified by the usual ion-exchange method (6). Reagent-grade dodecane (Fluka) was used as received. The organic solution was prepared by dissolving a required volume of TBP (A.R. grade) in dodecane to get carrier concentration of varying percentage.

Fabrication and Characteristics of Hollow Fiber Contactor

The module is fabricated using a bundle of hollow fibers and the details of contactor are given in Table 1. Provision was made for recirculating the aqueous solution from inside lumens without mixing the organic solution of shell side. Prior to experiment, leak test was carried out using distilled water by circulating inside the lumens.

Table 1. Specifications of hollow fiber contactor

Material	Polypropylene membrane equivalent to Accurel-PPS $_{6/2.}$
Number of lumens	20
Effective length	27 cm
I.D. of lumen	1800 μm
I.D. of glass tube	1.6 cm
Inner surface area of lumens	305.21 cm^2
Volume occupied by lumens	13.73 cm^3
Length of module	30 cm
Wall thickness	450 μm
Pore size	0.64 μm
Outer surface area of lumens	381.5 cm^2
Total volume of glass tube	54.26 cm^3
Surface area to volume ratio	22.23

The Non Dispersive Membrane Set-up

A schematic view of the membrane-based extraction process of Pu(IV) using a hollow fiber contactor in recirculation mode (using peristaltic pump) is shown in Fig. 1. Both aqueous and organic phases were contacted in a hollow fiber module in a countercurrent flow for extraction or stripping run under recirculating mode. In the extraction module, the feed aqueous phase flowed through the lumen of the fibers at the flow rate of $5.83\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, whereas the organic phase flowed through the shell side at the flow rate of $1.53\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ as shown in Fig. 2, wetting the wall of the hydrophobic fibers. The aqueous phase pressure was maintained higher than the pressure of organic phase. In the stripping run, as shown in Fig. 2, loaded organic TBP-Pu(IV) complex flowed through the shell side at the flow rate of $1.66\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ whereas uranous nitrate solution/hydroxylamine hydrochloride solution flowed through the tube side with the flow rate of $6.11\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ in countercurrent recirculation mode.

The organic phase was taken $\sim 200\,\mathrm{cm}^3$ of TBP diluted in n-dodecane solution with varying concentration of TBP. Also, $200\,\mathrm{cm}^3$ of aqueous feed solution of the desired concentration of Pu(IV) was taken which was prepared by taking a suitable aliquot from tracer stock solution with varying acidity of nitric acid. Uranous nitrate solution (stabilized with N_2H_4)/hydroxylamine hydrochloride solution was used as the stripping phase when back extraction of Pu(IV) was carried out in hollow fiber module.

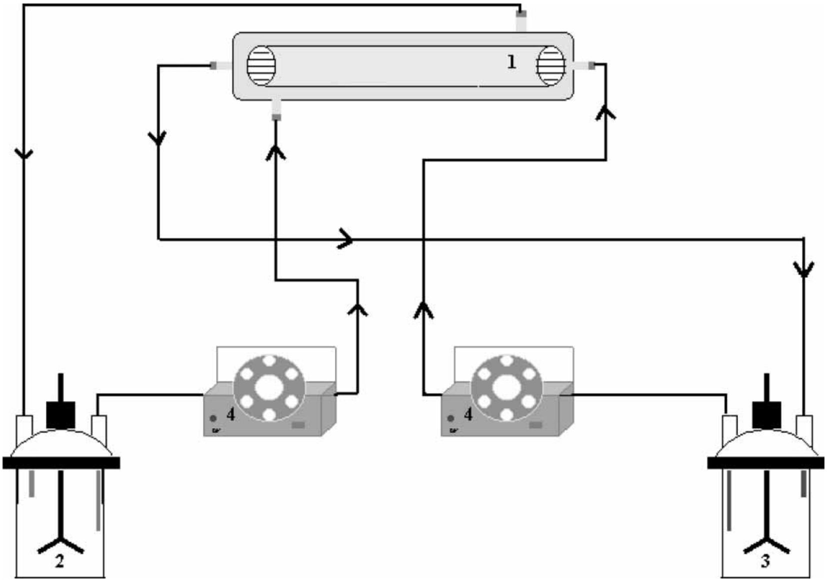

Figure 1. Schematic diagram of dispersion-free solvent extraction (DFSX) through hollow Fiber contactor in countercurrent recirculation mode for recovery of Pu(IV): 1: hollow fiber contactor; 2,3: extractant and feed/strip reservoir, 4: peristaltic pumps.

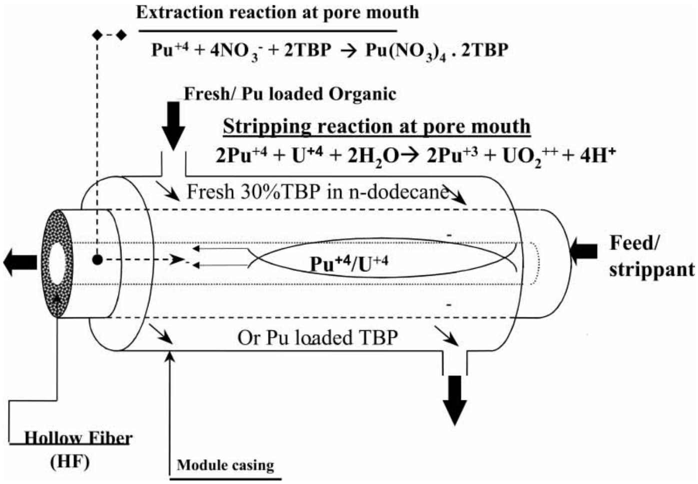

Figure 2. Extraction and stripping mechanism of Pu(IV) through hollow fiber contactor. Details of hollow fiber module is given in Table 1.

The feed and organic solutions were recirculated by means of calibrated peristaltic pumps. The measurement of transport of radionuclides through the hollow fiber membrane contactor was followed by periodically sampling the feed/strip solution. Samples were analyzed for α using PLA make ZnS silver activated detector and for γ using NaI(Tl) detector in scintillation counter.

THEORETICAL BACKGROUND

Extraction Equilibrium

The extraction of Pu(IV) in TBP is well established (7). The solvated type of complexes predominated in the nitric acid media ranging from 1–5 M HNO_3. The equilibrium constant can be represented as follows:

$$Pu^{4+}_{aq} + 4\mathrm{NO}^-_{3\mathrm{aq}} + 2\mathrm{TBP}_{\mathrm{org}} \Leftrightarrow \mathrm{Pu(NO_3)_4} \cdot 2\mathrm{TBP}_{org} \tag{1}$$

$$Kex = \frac{[Pu(NO_3)_4 \cdot 2TBP]_{org}}{[Pu^{4+}][NO_3^-]^4[TBP]^2} \tag{2}$$

$$\text{since, } D = \frac{[Pu(NO_3)_4 \cdot 2TBP]_{org}}{[Pu^{4+}]_{aq}}$$

$$Kex = \frac{D}{[NO_3^-]^4_{aq}[TBP]^2} \tag{3}$$

$$\log D = \log\,[Kex] + 4\,\log\,[NO_3^-] + 2\,log\,[TBP] \tag{4}$$

Evaluation of Mass-Transfer Coefficient

The mechanism of mass transfer in hollow fiber contactor (HFC) can be explained as the diffusion of metal ions through the pores of the fibers from one phase to another without dispersion of the two contacting phases in one another. The steps in the extraction process were assumed to be as follows (8):

Step 1: The metal ion/metal species in the aqueous phase diffused from the bulk to the aqueous-organic interface (inside wall of fiber) through the boundary layer.

Step 2: At the aqueous-organic interface, metal ion/metal species reacted with the extractant in the organic phase in the membrane pores to form the metal-organic complexes.

Step 3: Metal-organic complex diffused from the aqueous-organic interface to the outside wall of fiber through the organic-filled membrane pore; free extractant diffused in the opposite direction from the organic phase/shell side into the pore.

Step 4: Metal-organic complex diffused from the outside fiber wall to the organic phase bulk (or shell-side, which was flowing countercurrent to the aqueous phase).

This theory enables us to calculate the mass-transfer coefficient. The rate at which a component is transferred between two different phases depends on the mass-transfer coefficient, the interfacial area, and the degree of departure of the component from its partition equilibrium. Evaluation of mass-transfer coefficients is of importance because this determines the rate at which equilibrium is approached and controls the time required for a given separation, and therefore the size and the cost of equipment to be used. As derived by D'Elia, Cusslar et al. (9–11), the key equation for the calculation of $\boldsymbol{K}_{Pu}^{E}$ or $\boldsymbol{K}_{Pu}^{S}$ for countercurrent flow is,

$$\ln\left[\frac{(C_{e/s}^{0}/D - C_{f}^{0})}{(C_{e/s}^{0}/D - C_{f}^{0}) + (V_f/DV_{e/s})(C_{f}^{0} - C_f)}\right] = t\,\frac{[1 - \exp(-4K_{pu}^{E}V_m/d(1/Q_f - 1/Q_{e/s}D))][1/V_f + 1/V_{e/s}D]}{(1/Q_f) - (1/Q_{e/s})\exp[-(4K_{pu}^{E}V_m)/d\ (1/Q_f) - (1/Q_{e/s}D)]} \tag{5}$$

where Q_f and $Q_{e/s}$ are the feed and extract/strip flows; V_f and $V_{e/s}$ are the feed and extract/strip volumes; $\boldsymbol{K}_{Pu}^{E}$ and $\boldsymbol{K}_{Pu}^{S}$ are overall membrane mass-transfer coefficient for extraction and stripping respectively; C_f^0 and $C_{e/s}^0$ are the concentrations of the solute in the feed and in the extract/strip solutions at time zero; C_f is the concentration of the solute in the feed at time t; V_m is the volume of all the hollow fibers; D is the distribution ratio of the metal; and d is the diameter of one fiber.

In NDSX systems, overall mass-transfer coefficient is a weighted average of the individual mass-transfer coefficients in the aqueous feed phase, across the membrane, and in the organic phase. The reciprocal of the overall mass-transfer coefficient (the total resistance to mass transfer), can be described as the sum of mass-transfer resistances inside the fiber (feed phase), across the fiber wall (membrane resistance), and outside the fiber (organic phase). Recent work assumes that the main resistance to the solute transport lies in the membrane (12, 13a). Among those who deal with ionic species in the extraction step, it is also widely assumed that chemical reactions are fast enough to be considered to be instantaneous; then the reacting species are present in equilibrium concentration at the interface everywhere (13b).

The overall mass-transfer coefficient for the module, which was used throughout the present study, was calculated by slope analysis technique using Eq. 5.

RESULTS AND DISCUSSION

Influence of Aqueous Feed Acidity

The concentration of NO_3^- ion was increased, by increasing the nitric acid molarity in the aqueous feed solution. Table 2 shows that, percent of extraction increased up to 3 M with nitric acid solution and thereafter remained constant (maximum 83% extraction was obtained in 105 min.). This may be due to initially the salting out effect of NO_3^- ion as obvious from Eq. 3 and

Table 2. Influence of aqueous feed acidity on % Pu(IV) extraction

Time (min.)	Percentage extraction of Pu(IV) with varying feed acidity (HNO_3) M					
	0.5	1	2	3	4	5
5	25.7	29	58.3	60.2	52.6	34.6
10	39.2	49.7	67.1	69.9	58.2	42.8
15	43.7	62.8	73.8	76.3	59.7	53.8
20	50.2	67.4	76.8	79	64.9	64
25	51.5	70.5	78.2	79.8	67.8	74.4
30	56.5	71.5	79.1	80.6	70.6	75.7
45	62.5	74.6	80.3	82.2	81.4	76.1
60	69.4	75.7	82	82.8	82.1	76.5
75	72.8	78.3	83.1	83.5	82.9	79.3
105	74.1	80.4	83.1	83.9	83.3	82.2

Feed (aqueous medium): Pu(IV) in HNO_3; Extractant: 20% TBP/n-dodcane; Feed concentration: 1×10^{-5} mol dm^{-3}; A/O ratio: 1 ($200\,cm^3$); Hollow fiber module used: Specification given in Table 1.

Table 3. Mass-transfer coefficients for extraction of Pu(IV)

Sl. no.	Feed acidity HNO_3 (M)	$\boldsymbol{K}^{E}_{Pu}$ for Pu(IV) at 20% TBP ($\times 10^5$)
1.	0.5	1.7
2.	1.0	1.8
3.	2.0	1.8
4.	3.0	1.9
5.	4.0	1.9

Extractant: TBP/n-dodecane (v/v); Aqueous feed medium: HNO_3; Hollow fiber module used: Specification given in Table 1.

later at high molarity of HNO_3, it started competing with metal ion to form complex with TBP in 1:1 ratio as

$$\mathrm{TBP} + \mathrm{HNO_3} \Leftrightarrow \mathrm{TBP} \cdot \mathrm{HNO_3}$$

The mass-transfer coefficients were evaluated at different nitric acid molarities. The data from Table 3 show that the mass-transfer coefficient ($\boldsymbol{K}^{E}_{Pu}$) was found between $1.7 \times 10^{-5} - 1.9 \times 10^{-5}$ cm/s for the range of 0.5–5.0 M HNO_3. Equation (5) was utilized for determining the mass-transfer coefficient.

Effect of TBP Concentration on Transport

The overall mass-transfer coefficient ($\boldsymbol{K}^{E}_{Pu}$) at 20% TBP has been determined from the slope of the straight line of data which is plotted between Y [LHS of Eq. (5)] and time, t. The mass-transfer coefficient values at different TBP concentrations are listed in Table 4, which also reveals that the $\boldsymbol{K}^{\mathrm{E}}_{Pu}$ was found of the order of 10^{-5} cm/s for 10–50% extractant concentration. There is a marginal dependency of the total carrier concentration on the values of ($\boldsymbol{K}^{\mathrm{E}}_{Pu}$) with an increase with TBP concentration.

Equation 4 predicts that the extraction of Pu(IV) should vary linearly with total concentration of TBP. This relationship has been observed in solvent extraction studies ((14a)). To verify this relationship using hollow fiber in DFSX, 1×10^{-5} mol dm^{-3} of $Pu(NO_3)_4$ solution was tested with the TBP concentration at 10–50% in the dodecane. Figure 3 shows that the %E of Pu(IV) increases with increase in extractant concentration. Since we are not dealing with concentrated stream of Purex process, therefore we do not require higher concentration of TBP. Also adhering to PUREX process conditions for purification of Pu or recovery of plutonium from oxalate waste, 20% TBP was chosen. If we keep higher percentage of extractant, the space available for other than actinides will be more, in that case the fission products, e.g., ^{95}Zr, ^{95}Nb for which the TBP has got sufficient distribution coefficient may get extracted in the organic phase and product will get

Table 4. Mass-transfer coefficients for extraction of Pu(IV)

Sl. no.	Extractant (%)	K^E_{Pu} for Pu(IV) at 3.0 M HNO_3($\times 10^5$)
1.	10	1.7
2.	20	1.8
3.	30	1.8
4.	40	1.9
5.	50	1.9

Extractant: TBP/n-dodecane (v/v); Aqueous feed medium: HNO_3; Hollow fiber module used: Specification given in Table 1.

contaminated, resulting in low decontamination factor. Once the sufficient extraction value is achieved in 20% TBP then in the view of reagent economy and product purity, it is not advisable to carry out extraction at higher percentage of TBP.

Effect of Different Strippants

In any practical chemical separation, which is carried out utilizing solvent extraction, it is necessary to be able to back-extract or strip the metal from the organic phase after it has been initially extracted. Two different strippants were checked to determine their ability to strip Pu(IV) from loaded dodecane solutions of TBP. Since the value of D_{Pu} with TBP is significant in dilute HNO_3 solution, therefore, at low nitric acid molarities the complete stripping of Pu(IV) from organic phase is not possible. Therefore, stripping of Pu(IV) by

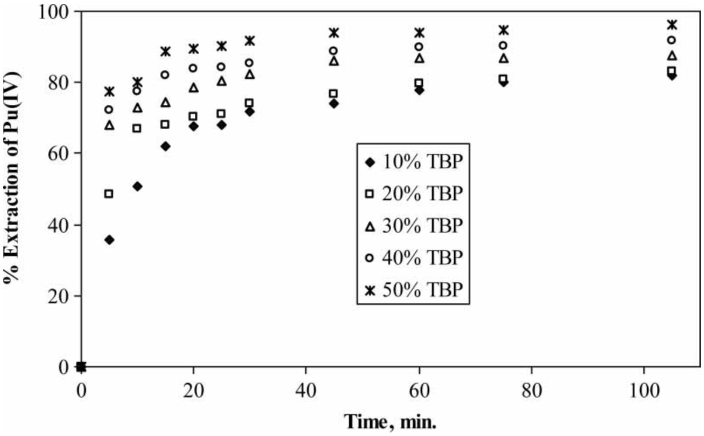

Figure 3. Effect of extraction concentration on Pu(IV) extraction, Feed acidity: 3.0 M HNO_3; extractant: TBP/n-dodcane; A/O ratio: 1 (200 cm^3 of each).

Table 5. Effect of strippants on % Pu(IV) stripping

Time (min.)	Percentage stripping with different strippants	
	0.5 M hydroxylamine hydro chloride in 0.3 M HNO_3	6.6 gmdm^{-3} uranous nitrate in 1.0 M $HNO_3 + 0.4$ M hydrazine
15	2.9	11.3
30	4	14.3
45	5.5	21.6
75	6	28.8
105	10.9	32.5
135	12.2	34.9
165	16.5	37.4
195	19.8	39.3
225	22.2	42.0
255	26.4	46.9
285	29.9	49.3
315	32.2	53.4
345	37.4	57.7
375	39.8	62.0
435	45.1	64.4

Feed: Pu(IV) loaded 20% TBP/n-dodecane; Pu(IV) concentration in organic: 3×10^{-5} mol dm^{-3}; A/O ratio: 1 (200 cm^3 of each); Hollow fiber module used: Specification given in Table 1.

changing the valency is preferred. The stripping experiments were performed in a single module using strippants such as 0.1 M NH_2OH. HCl in 0.3 M HNO_3 and uranous nitrate [$U(NO_3)_4$] solution stabilized with N_2H_4 by flowing loaded organic solution (20% TBP/n-dodecane loaded with Pu) on the shell side and strippant solutions from tube side. Table 5 shows that, among these, uranous nitrate solution gave more than 64% back extraction, therefore, uranous nitrate solution stabilized with N_2H_4 has been selected for further recovery of Pu(IV) in aqueous phase as it is more feasible and the product solution directly can be recycled to main process stream. The K_{Pu}^{S} was evaluated and found to be 1.2×10^{-6} cm/s. Further, stripping could be enhanced by increasing the surface area of the membrane or using hydrophilic membrane in the module, as suggested by Cussler et al. (15a).

Effect of Pu(IV) Concentration

Effect of Pu concentration (1×10^{-5} to 5×10^{-5} mol.dm^{-3}) on extraction of Pu(IV) was studied; different experiments were carried out for 135 min. The

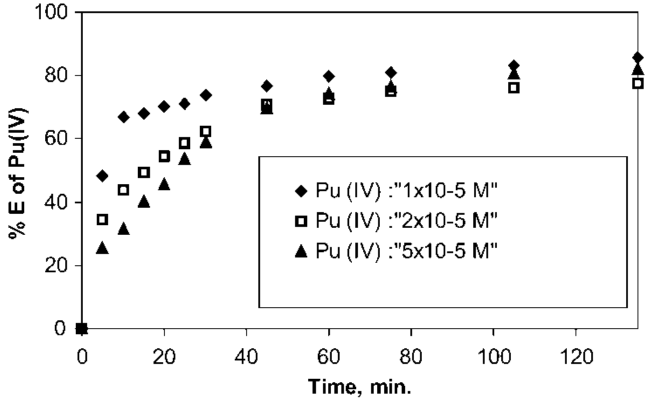

Figure 4. Effect of initial Pu(IV) concentration on % Pu(IV) extraction: Feed acidity: 3.0 M HNO_3; extractant: 20% TBP/n-dodcane; A/O ratio: 1 (200 cm^3 of each).

results from Fig. 4 show that the rate of extraction is faster for concentration of 1×10^{-5} mol/dm^{-3}. As the metal ion concentration increases, initially (at 5 min.) the percentage extraction of Pu(IV) decreases from 48 to 25%. The reason behind this behavior may be the limitation of membrane surface area, due to which the rate of extraction is comparatively slower for higher concentration of metal ions in the feed solution; however, for an experimental time of 135 min., there was no marked effect on final Pu(IV) extraction values (85–82%). But on the other hand, we should not forget the other possibility which is more common in non dispersive equilibrium-based membrane process. In this case, organic phase within the membrane pores get saturated with metal complex on increasing the metal concentration and further, this organic complex diffuse slowly into bulk of organic phase, which in a nutshell decreased the mass transfer in organic phase. Our earlier experience with gold and silver extraction demonstrated similar behavior (15b), (15c).

Influence of Flow Rate

In HFC, aqueous pressure was kept slightly higher than the organic pressure to avoid intermixing of the phases. By keeping higher aqueous flow rate, effective diffusion path length at pore mouth can be decreased, which results in effective diffusion of the metal ions through microporous hollow fiber membrane. The percentage extraction of Pu(IV) in the system with the flow rates of 5.8, 7.8, and 9.7 cm^3 s^{-1} were compared. Table 6 shows even after the increase of the aqueous flow rate significant increase in %E of Pu(IV) was not observed. On the other hand, Table 6 shows that the %E of Pu(IV) increases with increase in organic flow rates. In the first 30 min of the experiment, extraction was increased from 52 to 66% by increasing flow rates from

Table 6. Effect of extractant (organic) flow rate on %Pu(IV) extraction

Time (min.)	% Extraction			
	Extractant (organic) flow rate ($cm^3\ sec^{-1}$)			
	1.5	1.9	2.8	4.2
5	35.8	35.3	37.8	44.1
10	39.6	39.7	44.9	48.3
15	46.7	46.3	50.11	53.5
20	48.8	49.9	52.6	60
25	49.9	52.3	62.6	62.3
30	52.1	60.9	66.9	65.6
45	61.2	68.1	72.6	71.7
60	67.1	72.7	75.2	75.3
75	70.9	77.6	80.3	81.5
105	77.6	80.5	83.1	83.9

Feed acidity: 3.0 M HNO_3; Extractant: 20% TBP/n-dodcane; A/O ratio: 1 (200 cm^3 of each); Feed (aqueous) flow rate: 9.72 cm sec^{-1}; Feed concentration: 2×10^{-5} mol dm^{-3} of Pu(IV); Hollow fiber module used: Specification given in Table 1.

1.5 to 4.2 $cm^3\ s^{-1}$. This may be probably due to insufficient aqueous flow rate and hydrophobicity of the membrane which is not reducing the thickness of unstirred boundary layer, whereas in the case of higher organic flow rate the higher percent extraction of Pu(IV) was observed. Although we have not calculated the Re values (Reynolds number) but manufacturer (Enka Accurel) ensures that with this inner diameter of hollow fiber Re will be in the range of $0<Re>500$. This indicates that flow in tube side will be laminar (13b).

If flow rate is less, there could be a problem of concentration polarization. Hence, this could result in reduction of mass transfer. Similarly, aqueous boundary layer thickness at the aqueous-organic interface will be influenced by flow rate. When the flow rate is increased, the thickness of aqueous boundary layer is reduced which in turn increases the mass transfer. As such, there is no direct relation between hydrophobicity and thickness of aqueous boundary layer but more hydrophobic membrane will try to repel the water droplets and hence wetability of membrane will be less.

Variation in A/O Volume Ratio

Studies were performed to asses if large A/O (aqueous-to-organic) ratios could be tolerated for the successful extraction of Pu(IV) by the TBP under

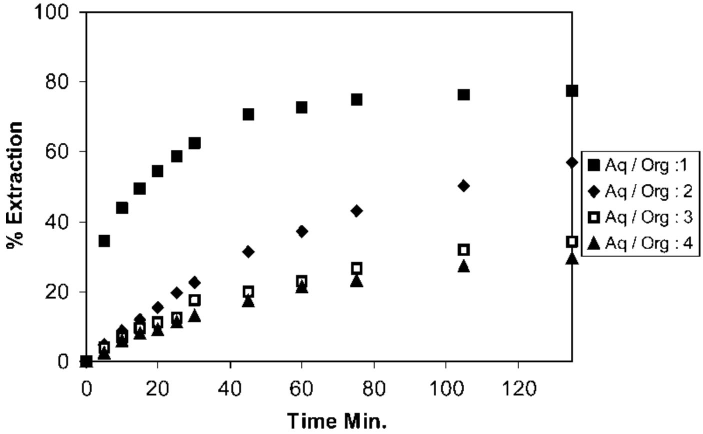

Figure 5. Effect of different A/O ratio on Pu(IV) extraction. Feed acidity: 3.0 M HNO_3; extractant: 20% TBP/n-dodcane; volume of aqueous/organic: 200 cm^3; feed concentration: 2×10^{-5} mol dm^{-3} of Pu(IV).

the optimum conditions. The results (Fig. 5) indicated that the %E was 77% at A/O: 1, which was further decreased to 33% at the A/O ratio of 4. This may be due to a fixed area coming in contact with the varied volume, which may take longer time to pre-concentrate the metal ions from large volume. This could be overcome by increasing the surface area of the module.

Stability of the Module

The same hollow fiber module was repeatedly used for all the experiments after washing with the solvent and distilled water. The flow rate of aqueous and organic phase was increased up to 9.7 cm^3 s^{-1} and 4.7 cm^3 s^{-1}, respectively. The operation was continued for more than 7 h at a time, but no mixing of phases was observed which confirms its physical stability toward the rupture of the polypropylene membrane. The radiation stability of polypropylene hollow fiber lumens has already been examined (5). The scanning electron micrograph shows that up to 1 M rad, the morphology of the lumens was not affected.

Applicability of DFSX Using HFC for Separation of Pu(IV) from Oxalate Waste

The typical composition of oxalate supernatant waste is as follows: Pu: 25 mg dm^{-3}, U: 5 gm dm^{-3}, Ru^{106}: 0.0032 mci dm^{-3}, Cs^{137}: 0.003 mci dm^{-3} HNO_3: 3M, $H_2C_2O_4$: 0.1M

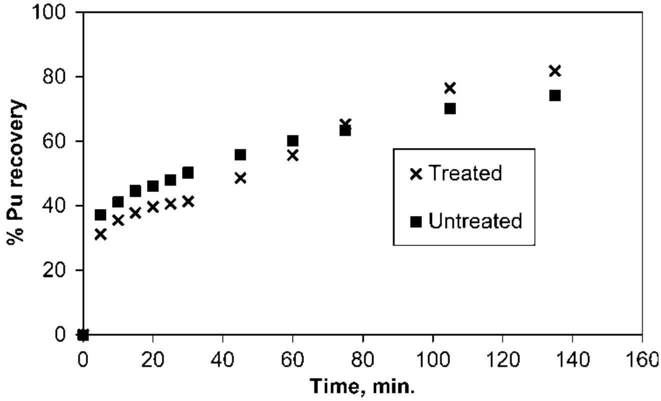

Figure 6. Recovery of Pu from oxalate supernatant waste: Treated: Waste free from $C_2O_4^-$ ions; untreated: waste containing $C_2O_4^-$ ions.

In this study the percentage recovery of Pu(IV) from oxalate supernatant (actual solution) without addition of nitric acid using 30% TBP/n-dodecane as extractant was studied. Experiments were performed in countercurrent recirculation mode with A/O ratio at 1 using treated ($C_2O_4^-$ ions destroyed by $KMnO_4$ and H_2O_2) and untreated (in presence of $C_2O_4^-$ ions) wastes separately. Results (Fig. 6) clearly indicate that the recovery of Pu(IV) from untreated waste was well above 70% and from treated waste, it was more than 80%. The extraction of Pu(IV) in presence of fission products like ^{137}Cs, ^{106}Ru, and ^{154}Eu was not affected as there was no transport of Cs, Ru and Eu under similar conditions. This may be due to insignificant D values at this particular condition in TBP/n-dodecane system for such fission products (5).

CONCLUSIONS

The experimental results revealed that, using feed solution in 3 M nitric acid, 20% TBP and higher flow rate of feed and organic in hollow fiber contactor results in efficient transport of plutonium across the membrane utilizing DFSX technique. The overall mass transfer coefficient (K_{Pu}^{E}) for extraction was found to be of the order of 10^{-5}. The stripping of Pu(IV) from loaded organic phase, using uranous nitrate solution as a strippant, took longer time, which could be reduced by using hydrophilic membrane. The feasibility of this technique for separation of Pu(IV) from dilute solution even in presence of oxalate ions and fission products from waste streams has been clearly established as an alternative tool than other conventional methods for treating process effluents.

NOMENCLATURE

C	metal concentration (M)
V_M	volume of all the hollow fiber (cm^3)
A	effective surface area of the membrane (cm^2)
$\boldsymbol{K}_{ex}$	extraction consant
$\boldsymbol{K}_{Pu}^{E}$	overall membrane mass-transfer coefficient for extraction (cm/s)
$\boldsymbol{K}_{Pu}^{S}$	overall membrane mass-transfer coefficient for stripping (cm/s)
D	distribution ratio
A/O	aqueous/organic ratio
t	time (second)

Subscripts

f and s	refer to feed and stripping solution respectively
e	extractant
s	strippant
M	metal ion
aq	aqueous
org	organic
0	refer to concentration at time zero

Superscript

n	number

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