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Pseudo-Emulsion Based Hollow Fiber Strip Dispersion Technique (PEHFSD): Optimization, Modelling and Application of PEHFSD for Recovery of U(VI) from Process Effluent

S. C. Roy,[1] J. V. Sonawane,[1] N. S. Rathore,[1] Anil Kumar Pabby,[1] P. Janardan,[1] R. D. Changrani,[1] P. K. Dey,[1] and S. R. Bharadwaj[2]
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Abstract: Pseudo emulsion based hollow fiber strip dispersion technique (PEHFSD) is the first of its kind ever explored in radioactive environment for the extraction of uranium from acidic process streams. Permeation of U(VI) was investigated as a function of various experimental variables such as hydrodynamic conditions (flow rates of pseudo-emulsion and feed phase), concentration of U(VI) in the feed phase, concentration of tri-n-butylphosphate (TBP), HNO_3 concentration in feed phase, O/A ratio and 0.01 M HNO_3 as stripping agent in pseudo-emulsion phase. The mass transfer coefficient was calculated from the experimental results and a model has been presented for determining mass transfer characteristics. PEHFSD has been demonstrated for separation/recovery of uranium from oxalate supernatant waste generated during plutonium precipitation by oxalic acid. PEHFSD and HFSLM (hollow fiber supported liquid membrane) performance has been compared in order to analyze the efficiency of the technique.

Keywords: Hollow fiber strip dispersion (PEHFSD), pseudo-emulsion, supported liquid membrane (SLM), uranium

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INTRODUCTION

In view of the process recycling concern for safe disposal of nuclear wastes, particularly process wastes, adequate reduction of radiotoxicity is of great importance. The major problematic contaminants in such effluents are long-lived fission products and actinides like uranium, plutonium and americium. If the alpha activity of radioactive streams is reduced to a level of less than 10 nCi gm^{-1}, it is treated as a non-alpha waste (1). To achieve this objective, the most commonly encountered actinide (ie. Uranium) present in the process waste must be partitioned from acidic wastes. Currently, these wastes are recycled. However, this poses operational problems such as an increase in the volume of waste reduction in the efficiency of the process, additional chemical requirement, and more manpower.

Liquid–liquid extraction is a proven separation technique (2–3), due to its simplicity, speed, and wide applicability. Diverse extraction processes have recently been studied to remove radiotoxic cations from high/medium level nuclear acidic wastes (4–6). When the concentration level of metal ions falls below the trace and the ultra trace level, solvent extraction has its inherent limitation for substantial take up of metal ions into the organic phase due to equilibrium limitation and fixed partition ratio.

Supported liquid membranes (SLMs) (7) are very effective in removing and recovering metals from waste waters and process streams, since they combine extraction and stripping in one step. The one-step membrane process provides the maximum driving force for separation of a targeted metal, leading to the best possible clean-up and recovery rates. Despite these advantages, stability problems and long-term performance of SLM and HFSLM (hollow fiber supported liquid membrane) are the subject of continued debate (8). As a result, it has been difficult to scale up the application of this technique for industrial use. Emulsion liquid membrane (ELM) has received significant attention for metal ion recovery due to the large surface area of the carrier. However, it poses certain problems in emulsion formation and breaking of emulsion. Since emulsion formation needs high speed stirring, it generates air born activity thereby making this process unfeasible in the field of radioactive waste decontamination. Taking all these factors into consideration, a novel technique, namely, pseudo emulsion based hollow fiber strip dispersion (PEHFSD) system was developed for extraction/separation of radionuclides from nitric acid media, (9,10). The PEHFSD technique overcomes the stability problems associated with SLM (by continuous flow of organic to the membrane) and adopts the merits of ELM (high surface area). Therefore, operational stability of PEHFSD is far superior than HFSLM. Microporous hollow fiber (MHF) membrane modules provide an inexpensive, low-maintenance, and dispersion-free approach to continuous-flow liquid-liquid extraction processes (11–21). This work involves analyzing the potential of these modules for process-scale metal separations such as radioactive waste stream cleanup and environmental remediation. In this work, laboratory fabricated MHF membrane module was used to remove uranium from nitric acid media using TBP (tri-n-butylphosphate) as extractant in nph (n-paraffin hydrocarbon). The performance of this technology is discussed after evaluating different operating parameters such as feed acidity, concentration of TBP in pseudo-emulsion, U(VI) concentration in feed, variation in volume of the strippant [organic to aqueous (O/A) ratio] etc. On the basis of previously published work (22–23), TBP (Tri-butyl phosphate) dissolved in nph was selected as the extractant for developing the PEHFSD technique for U(VI) extraction. The separation/recovery of uranium was carried out from the oxalate supernatant (generated from nuclear chemical facilities) by applying the PEHFSD technique. PEHFSD and HFSLM performance has been compared in order to analyze the efficiency of the technique.

EXPERIMENTAL

Details of Preparation of Solutions and Analytical Methods

The organic solution was prepared by dissolving a measured quantity of A.R. grade TBP in nph (n-paraffin hydrocarbon) v/v to get a carrier solution of varying concentrations.

Uranyl nitrate stock solution (0.5 M) was prepared by dissolving U_3O_8 powder in 1:1 nitric acid and standardized by modified Davies and Gray method using potentiometric end point detection (24). From this stock solution, standard uranyl nitrate solutions of various acidities were prepared as follows. An aliquot of uranyl nitrate stock solution was pipetted in a glass vial and evaporated to dryness under an infra-red lamp in a fume hood. The residue was dissolved subsequently in the required volume to obtain desired concentration.

At the nuclear chemical facility, different acidic waste streams are produced. During precipitation of Pu(IV) oxalate, large volumes of oxalate supernatant containing significant amounts of U and Pu are generated. Typical composition of the waste is given below:

Uranium(U): 5 gm dm^{-3}, Plutonium(Pu): 25 mg dm^{-3}, Ruthenium(^{106}Ru): 0.0032 mCi dm^{-3}, Ceasium(^{137}Cs): 0.003 mCi dm^{-3}, Nitric acid: 3 M, $H_2C_2O_4$: 0.1 M.

The measurement of transport of radionuclides through the hollow fiber membrane contactor was followed by periodically sampling the feed/strip solutions. Samples were analyzed for plutonium using PLA make ZnS silver activated detector and ^{137}Cs was estimated using NaI(Tl) detector in scintillation counter. More details about radioassay and calculations are already published by Rathore et al. (13).

Schematic and Details of PEHFSD Setup

The hollow-fiber device used for the present study was fabricated in the laboratory. The module fabrication details are published in our earlier publication (13). The details of the hollow-fiber membrane module and membrane characteristics are listed in Table 1. After the proven performance with fabricated modules is established, the commercial module from Celgard can be used for large scale applications. These modules are already applied for gold recovery from alkaline cyanide media using LIX79/*n*-heptane (25,26).

As shown in Fig. 1, an aqueous strip solution is dispersed in an organic membrane solution containing an extractant or extractants in a mixer. The pseudo emulsion is then pumped into a membrane module to contact with one side of a microporous support (which can be passed through the shell side of a microporous polypropylene hollow-fiber module). The aqueous feed solution containing the target species to be extracted is on the other side of the support (which is passed through the other side of the fibers, i.e. the tube side) (27). The continuous organic phase of the dispersion readily wets the pores of a hydrophobic microporous support (e.g., microporous polypropylene hollow fibers in the module), and a stable liquid membrane (the organic phase) supported in the pores of the microporous support is formed.

The pseudo-emulsion phase consist of 100 ml of 20% TBP/nph + 200 ml of 0.01 M HNO_3. 300 ml of aqueous feed solution of the desired U(VI) concentration was prepared by taking a suitable aliquot from the stock solution. Dilute nitric acid (0.01 M HNO_3) was used as a stripping agent for U(VI). During the experimental run, small aliquots from the feed stream and pseudo-emulsion reservoir were taken at fixed time intervals and analysed for U(VI) concentration by redox titrimetry /spectrophotometry.

An enlarged view of the PEHFSD with strip dispersion is shown in Fig. 2. A low pressure differential (0.2 bar) between the aqueous feed solution side (*Pa*) and the strip dispersion side (*Po*) is applied to prevent the leakage of organic solution of the strip dispersion to the aqueous side through the pores. The dispersed droplets have a typical size of 80–800 µm and the size of the pores of microporous polypropylene support is 0.2 micrometer . Thus, these droplets are retained on the strip

Table 1. Hollow fiber module and hollow fiber membrane specifications

Material:	Polypropylene membrane equivalent to Accurel-PPS		
Structure of Module:	Shell and Tube	Inner volume of lumens:	$14.2\,cm^3$
Number of lumens:	90	Length of module:	28 cm
Wall thickness:	0.02 cm	Volume occupied by lumens:	$39.6\,cm^3$
I.D. of lumen:	0.06 cm	Pore size:	2×10^{-5} cm
O.D. of lumen:	0.1 cm	I.D. of glass tube:	1.6 cm
Outer surface area of lumens:	$791 cm^2$	Inner surface area of lumens:	$475\,cm^2$
Total volume of glass tube:	$55\,cm^3$	Surface area to volume ratio:	$66.6\,cm^{-1}$
Feed linear flow velocity:	$13.09\,cm\ s^{-1}$	Porosity:	40%
Strip linear flow velocity:	$5.4\,cm\ s^{-1}$		

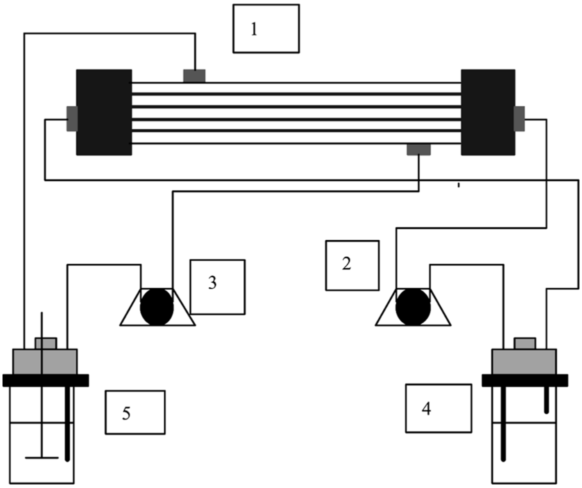

Figure 1. Schematic view of hollow fiber strip dispersion system operated in recycling mode for recovery of U(VI) from nitric acid media. (1) Hollow fiber contactor, (2) feed pump, (3) pseudo-emulsion of TBP/nph and 0.01 M HNO_3 strippant pump (4) feed reservoir (5) pseudo-emulsion + strip reservoir with mixing arrangement; volume of feed: 300 cm^3 and pseudo-emulsion of TBP/nph and 0.01 M HNO_3 reservoir: 300 cm^3.

dispersion side and cannot pass through the pores and penetrate into the feed solution side (28).

A typical PEHFSD system consists of a hollow-fiber module (or a series of SLM modules), a feed solution vessel, a feed pump, a strip

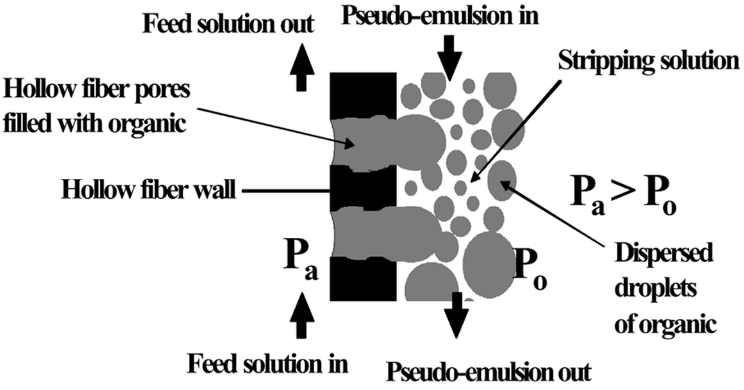

Figure 2. Enlarged view of PEHFSD.

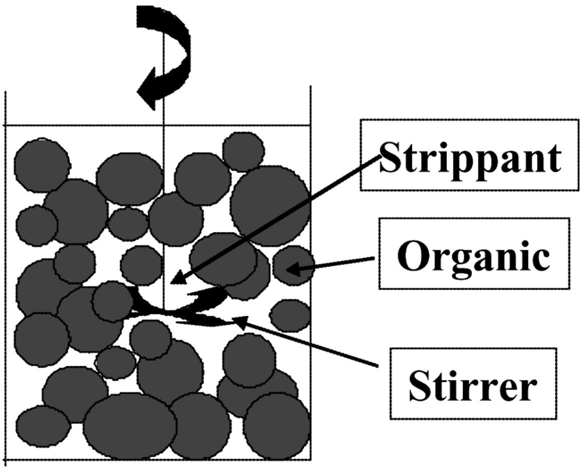

Figure 3. Preparation of pseudo-emulsion phase.

dispersion vessel, a mixer for the strip dispersion vessel (for dispersing an aqueous strip solution in an organic solution at 550–600 rpm) (Figs. 2 and 3), and a strip dispersion pump. The feed solution can also be operated in a single-pass mode. The strip dispersion is typically in the recycle mode. The configuration of the this module is similar to that of a shell-and-tube heat exchanger.

Upon the completion of the removal of the target species, the mixer for the strip dispersion is turned off, and the dispersion separates into two phases, the organic solution and the concentrated strip solution. Phase separation is very fast (less than about one minute), and there is no formation of any permanent emulsion. The concentrated strip solution is the product of this process.

THEORETICAL BACKGROUND

Extraction Equilibria for Uranium

UO_2^{2+} ion in nitrate medium (HNO_3) form $UO_2(NO_3)_2$ .2TBP complex with the extractant, expressed as

$$UO_2^{2+}aq + 2NO_3^{-}aq + 2TBP \Leftrightarrow UO_2(NO_3)_2 \cdot 2TBP_{org} \tag{1}$$

and stripping of U(VI) from loaded TBP with dilute HNO_3 is as below:

$$UO_2(NO_3)_2 \cdot 2TBP_{org} \Leftrightarrow UO_2^{2+}{}_{aq} + 2TBP_{org} \tag{2}$$

the extraction equilibrium can be described by the following equation and extraction constants for U:

From Eq. (1,2)

$$K_{ex} = [UO_2(NO_3)_2 \cdot 2TBP]_{org}/[UO_2^{2+}]_{aq}[NO_3^-]_{aq}^2[TBP]_{org}^2 \qquad (3)$$

or

$$D_U = [UO_2(NO_3)_2 \cdot 2TBP]_{org}/[UO_2^{2+}]_{aq}$$
$$K_{ex} = D_U/[NO_3^-]_{aq}^2[TBP]_{org}^2$$

where $K_{ex} =$ extraction coefficient and $D_U =$ distribution ratio
The values of K_{ex} for U(VI) with TBP in nph were calculated from the D_U values. The partition coefficient could be presented as

$$\log D_U = \log K_{ex} + 2\log[NO_3^-] + 2\log[TBP]_{org} \qquad (4)$$

PEHFSD Model Development

In case of PEHFSDs, the calculation of the overall permeability coefficients of the experimental system is based on a first-order mass transfer model with instantaneous chemical reaction on the stripping side, when a recycling mode is employed (16). The study of the liquid composition leads to the evaluation of the mass-transfer parameters.

For the recycling mode, both feed solution and stripping solution are recycled, as shown in Fig. 1 W.S. Ho et al. (28) suggested that operation of PEHFSD is similar to HFSLM. Hence, data obtained under PEHFSD technique should fit the typical liquid membrane equation. Hence the model used for HFSLM (16) was applied for the calculation of P_U (permeability coefficient of uranium) values and other different parameters from mass transfer modelling. The model for the transport of U(VI) in a hollow fiber supported liquid membrane system (16,28) operating in a recycling mode consists of four equations describing:

1. the change of U(VI) concentration in the feed and stripping streams when circulating through the membrane module and
2. the change of U(VI) concentration in the feed and stripping tanks, where the aqueous solutions are continuously recirculated, based on the complete mixing hypothesis.

Assuming linear concentration gradients and the lack of back-mixing, these equations are formulated as follows:

For the feed solution:

1. module mass balance

$$\frac{\partial C_f^m}{\partial t} = -\upsilon_f \frac{\partial C_f^m}{\partial z} - \left(\frac{A}{V_m}\right)_{in} P_U (C_f^m - C_s^m) \tag{5}$$

2. tank mass balance

$$\frac{dC_f^T}{dt} = \frac{Q_f}{V_f}(C_{f,z=L}^m - C_{f,z=0}^m) \tag{6}$$

For the stripping solution:

1. module mass balance

$$\frac{\partial C_s^m}{\partial t} = -\upsilon_s \frac{\partial C_s^m}{\partial z} + \left(\frac{A}{V_m}\right)_{out} P_U (C_f^m - C_s^m) \tag{7}$$

2. tank mass balance

$$\frac{dC_s^T}{dt} = \frac{Q_s}{V_s}(C_{s,z=L}^m - C_{s,z=0}^m) \tag{8}$$

where P_U is the overall permeability coefficient (cm/s), C is the solute concentration (g/cm^3), L is the fiber length (cm), Q is the flow rate (cm^3/s), υ is the linear velocity (cm/s), and V is the tank volume (cm^3). The subscripts f and s refer to the feed and stripping solutions respectively. The superscripts m and T refer to the membrane module and phase tank respectively.

A/V_m is the ratio of the area to the volume of mass transfer of the fiber:

1. for the feed phase circulating through the inside of the fiber

$$(A/V_m)_{in} = \frac{2\pi n_f r_i L}{\pi n_f r_i^2 L} = \frac{2}{r_i} \tag{9}$$

2. for the stripping phase circulating along the outside of the fiber

$$(A/V_m)_{out} = \frac{2\pi n_f r_0 L}{\pi(R_c^2 - n_f r_o^2)L} = \frac{2 r_o n_f}{R_c^2 - n_f r_o^2} \tag{10}$$

where n_f is the number of fibers contained in the membrane module, R_c is the inner radius of the module cell, and r_i and r_o are the inner and outer radii of the hollow fiber respectively.

The integration of differential equations 5–8 for concurrent flow can be obtained by numerical methods. When 0.01 M HNO_3 solution is used as the stripping agent, an instantaneous reaction (due to shift of equilibrium with dilute HNO_3) is assumed to occur on the outside of the fiber, leading to $C_s^m = 0$ and $C_s^T = 0$. In this case, the solution to Equations 5–8 is simplified to:

$$V_f \ln\left(\frac{C_{f,t=0}}{C_f}\right) = Q_f\left\{1 - \exp\left(\frac{2P_U L}{\upsilon_f r_i}\right)\right\}t \tag{11}$$

Experimental results can thus be fitted to a first-order kinetic law:

$$V_f \ln\left(\frac{C^f_{A,t=0}}{C_A}\right) = St \tag{12}$$

Where S is the factor dependent on the geometry of the fibers and the module, the linear velocity of the fluids, and the overall permeability of the system. The overall permeability coefficient can easily be obtained from the experimental value of the slope S as follows

$$P_U = \frac{-\upsilon_f r_i}{2L}\left[\ln\left(1 - \frac{S}{Q_f}\right)\right] \tag{13}$$

or for a system running in a recycling mode:

$$P_U = \frac{-Qf}{2\Pi riLN}\left[\ln\left(1 - \frac{S}{Q_f}\right)\right] \tag{14}$$

The design of the hollow fiber supported liquid membrane modules for the separation-concentration of uranium using overall permeability coefficient P_U centers on three mass transfer resistances. One of them occurs in the liquid flowing through the hollow fiber lumen. The second corresponds to the uranium-complex diffusion across the liquid membrane immobilized on the porous wall of the fiber. The third resistance is due to the aqueous interface created on the outside of the fiber.

The reciprocal of the overall permeability coefficient is given by:

$$\frac{1}{P_U} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_o}\frac{1}{k_o} \tag{15}$$

where r_{lm} is the hollow fiber log mean radius, and k_i and k_o are the interfacial coefficients corresponding to the inner and outer aqueous boundary layers. P_m is the membrane permeability, which is related to the partition coefficient of uranium (D_r) with TBP (7) by the following:

$$P_m = D_r k_m = K_{ex}[H^+][TBP]k_m \tag{16}$$

where partition coefficient D_U is defined by:

$$D_U = [UO_2(NO_3)_2 \cdot 2TBP]_{org}/[UO_2^{2+}]aq \tag{17}$$

Inserting Eq. (17) in Eq. (15) gives P_U:

$$\frac{1}{P_U} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{k_m K_{ex}\left[NO_3^-\right]^2 [TBP]^2} + \frac{r_i}{r_o}\frac{1}{k_o} \tag{18}$$

When the reaction is instantaneous on the stripping side, the contribution of the outer aqueous phase is removed from Eq. (18) and P_U is determined from:

$$\frac{1}{P_U} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{k_m K_{ex}\left[NO_3^-\right]^2 [TBP]^2} \tag{19}$$

Membrane Diffusion

The effective diffusion coefficients (D_{eff}) of U(VI) extractant complexes through the organic membrane phase were determined using the PEHFSD model. An effective diffusion coefficient (D_{eff}) for the solute in the immobilized organic liquid membrane can be defined as follows:

$$D_{eff=k_m t_m \tau} \tag{20}$$

where k_m is the membrane mass transfer coefficient, t_m is membrane thickness and τ is tortousity.

Reproducibility and Statistical Error Associated with Permeability Coefficients

Based on five observations, the permeability value (percent extraction of U(VI) at about 90%) exhibits a coefficient of variation of ±1%.

As far as the reproducibility of data are concerned, initially several experiments were performed to check the feasibility and consistency of results under the same experimental conditions. Reproducibility was found to be satisfactory for the results obtained for a fixed period of time using three sets of data.

RESULTS AND DISCUSSION

Permeation of U(VI) has been studied with hollow-fiber supports assembled in laboratory-scale modules. A schematic diagram of the system is given in Fig. 4 (30). Detailed investigations were undertaken to define the best operating conditions and to consider how the selectivity and the durability of operation could be ensured. Experiments were conducted for the operation of PEHFSD in different conditions such as the effect of feed acidity, carrier concentration in pseudo-emulsion phase, variation of O/A ratio, and variation of metal ion concentration in feed phase These factors significantly affect the transport of metal ion. Metal ion recovery was carried out with actual oxalate supernatant solution (both untreated and treated with $KMnO_4/H_2O_2$). A comparative study with SLM technique was also initiated.

The stability of pseudo emulsion was found to be quite good during the experimental run. This is well supported by literature (9,16,28). Some of the initial experiments were conducted to confirm the same phenomenon but pseudo-emulsion was intact during one pass of a solution. Also, the length of the tube is maintained in such a way that pseudo-emulsion reaches back to reservoir within a short time interval.

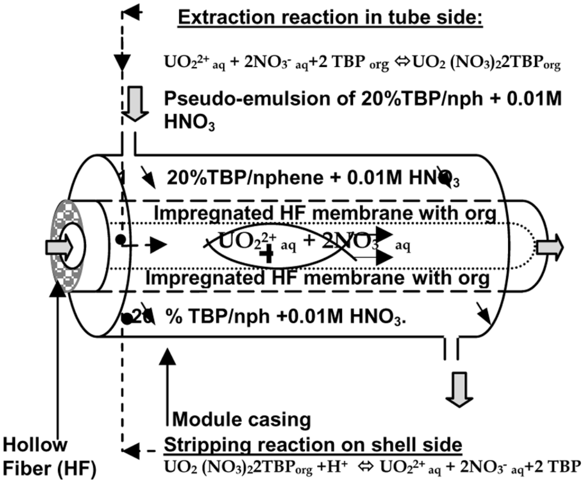

Figure 4. Extraction mechanism of U(VI) from nitric acid with 20% (0.73 M) TBP/nph impregnated in hollow fiber membrane module, flowing pseudo-emulsion of 20% TBP/nph and $0.01 M HNO_3$ as receiving phase in shell side and feed containing U(VI) flowing in tube side.

Optimization of Hydrodynamics and Chemical Parameters

On the basis of previous studies performed, an aliphatic diluent, nph was selected as diluent for PEHFSD system (18,19). The details of hollow-fiber module, hollow fiber membrane characteristics are presented in Table 1.

Working in the recycling mode, the feed solution, which consisted of 300 cm^3 of an aqueous solution with an initial U(VI) concentration of 14.72 $g\,dm^{-3}$ was circulated into tube side hollow fiber module. The flow rate of feed was maintained at 3.33 cm^3/s (Q_f) (linear flow velocity 13.09 cm/s (V_f)). For facilitating stripping of uranium, 200 cm^3 of 0.01 M HNO_3 was used as stripping solution (in the form of pseudo emulsion with TBP in nph) and passed to the shell side at the flow rate of 1.4 cm^3/s (Q_s) (linear flow velocity = 5.4 cm/s (V_s)). Experimental results have been expressed as the U(VI) concentration in the feed, strip and organic phase against time (refer to Fig. 5). Almost complete transport of U(VI) was obtained in ~150 minutes. The feasibility of recovering U(VI) with PEHFSD using TBP in nph as liquid membrane was thus proved.

Influence of HNO_3 Concentration on Permeation Coefficient (P_U) of U(VI)

To study the influence of the HNO_3 concentration on extraction of U(VI), experiments were performed at various HNO_3 concentrations.

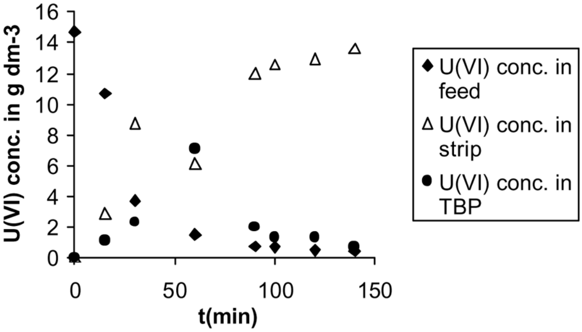

Figure 5. Concentration of U(VI) in the feed, strip and organic phase as a function of time in recycle mode. Experimental conditions: Feed phase: 300 ml of aqueous solution of U(VI) . Pressure difference applied: 0.2 bar, feed flow rate = 3.33 cm^3/s. Pseudo-emulsion: 100 ml of 20% TBP/nph and 200 ml 0.01 M HNO_3 as stripping solution. Stripping flow rate: Strip flow rate = 1.4 cm^3/s.

In these experiments, TBP concentration and strippant concentration in the pseudo-emulsion phase was maintained constant. The results are presented in Table 2. The percentage of U(VI) extraction increased up to 4 M HNO_3 (maximum 82% extraction was obtained in 90 minutes) and thereafter it decreased. This may be due to the fact that initially the nitrate ion helps as a salting out agent as follows:

$$D_U \propto [NO_3^-]^2[TBP]^2 \tag{21}$$

The D_u (partition coefficient defined as the ratio of concentration of uranium in organic and aqueous phase) is directly proportional to the second power of NO_3^-, later it competes with TBP to form complex in 1:1 ratio as under:

$$\mathrm{TBP} + \mathrm{HNO_3} \Rightarrow \mathrm{TBP\,.\,HNO_3} \tag{22}$$

This may be due to the formation of the $TBP\,.\,mHNO_3$ complex inside the membrane adjacent tothe aqueous solutions interfacing it. This depends on the distribution coefficient of U(VI) ions between the membrane and aqueous phases. Uranium ion extraction is associated with free NO_3^- and UO_2^{2+} ions present in the feed phase. The ratio of dissociated nitrate ions to undissociated HNO_3 decreases with increase in nitric acid concentration.

Figure 6 presents the experimental courses of $Ln(C_o/C)$ v/s time and results revealed that the P_U ($\times 10^{-3}$ cm/s) increases from 13.55 to 57.94 as a function of feed acidity which increased from 1 M HNO_3 to 4 M HNO_3, and thereafter decreases to 30.29 at 5 M HNO_3. These results are similar to those previously observed with the flat sheet supported liquid membrane studies of U(VI) from nitric acid media (5,6,18–20)

Table 2. Experimental values of the % recovery of U(VI) for the recycling system using different initial feed acidity (Receiving phase, 0.01 M HNO_3; Feed volume = 300 cm^3, Feed flow rate = 3.33 cm^3/s, Feed linear flow velocity = 13.09, Strip flow rate = 1.4 cm^3/s , 20% TBP/nph as carrier for U(VI))

Time (min)	1 M HNO_3	2 M HNO_3	3 M HNO_3	4 M HNO_3	5 M HNO_3
	%Recovery	%Recovery	%Recovery	%Recovery	%Recovery
0	0	0	0	0	0
15	16.2	19.7	19.4	19.7	28.9
30	27.0	30.2	36.2	32.6	39.2
60	28.9	48.3	64.8	61.8	61.0
90	40.1	60.3	77.5	81.6	70.4

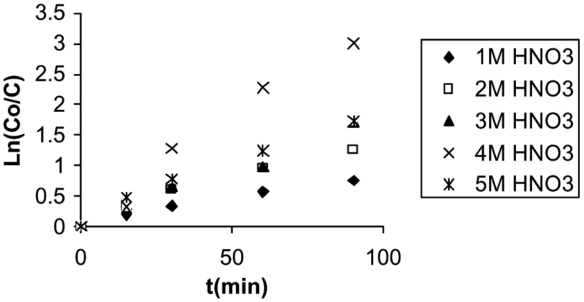

Figure 6. Influence of the feed acidity on the permeability of U(VI) in the feed phase as a function of time in recycle mode.

(with the same feed composition). So, the feed acidity 4 M HNO_3 was selected to carry out further experiments.

Influence of TBP/nph Concentration in Pseudo-emulsion Phase on U(VI) Transport

Experimental conditions were established as pseudo-emulsion phase of various concentration of TBP (up to 40%) in nph mixed with 0.01 M HNO_3 as strippant and feed containing uranium 26.77 gm dm^{-3} in 300 ml of 4 M HNO_3. As shown in Fig. 7, plotted as $Ln(C_o/C)$ v/s time, the permeability of U(VI) transport increases with increasing TBP concentration. Table 3 shows permeability values for the transport of

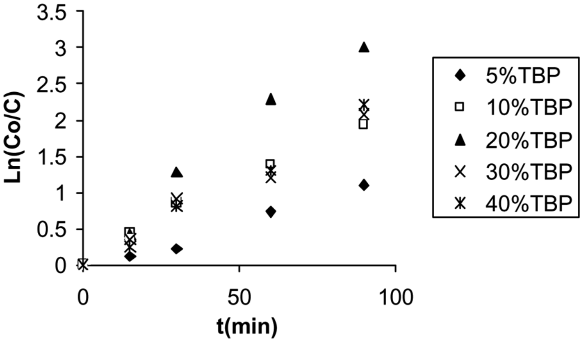

Figure 7. Influence of the TBP conc. on the permeability of U(VI) in the pseudo-emulsion phase as a function of time in recycle mode.

Table 3. Experimental values of the overall permeability coefficient (P_U) for the recycling system using different TBP conc. in pseudo-emulsion (Receiving phase, 0.01 M HNO3; feed acidity = 4 M HN03, Feed volume = 300 cm^3, Feed flow rate = 3.33 cm^3/s, Feed linear flow velocity = 13.09 cm/s, Strip flow rate = 1.4 cm^3s, 20% TBP/nph as carriet for U(VI)

TBP conc (%)	TBP conc (M)	S (slope) (cm^3/s) ($\times 10^{-3}$)	r^2	P_U ($\times 10^{-3}$, cm/s)
5	0.18	12.8	0.9821	21.2
10	0.37	21.1	0.9883	34.9
20	0.73	34.9	0.9768	57.9
30	1.10	21.9	0.9709	38.9
40	1.50	23.5	0.9875	36.3

uranium through the PEHFSD with various solutions of TBP (0.182–1.461 M) in nph. It can be seen from Fig. 10 that the permeability increased with TBP concentration up to 20% TBP and P_U value was observed to decrease at higher carrier concentration in pseudo-emulsion phase. The rate of transport is therefore limited by diffusion through the aqueous film on the feed side of the membrane in this region. The optimum concentration 20% TBP was selected for further experiments. But adhering to the PUREX (Plutonium Uranium Recovery by Extraction) process conditions and the increasing viscosity problem at higher TBP concentration, 20%TBP was selected as optimum extractant concentration to evaluate various parameters.

As is evident from equation 4, D_U is directly proportional to the square of TBP concentration and U(VI) extraction increased rapidly with increase in TBP concentration. At lower concentrations of TBP, mass transfer control is in the membrane. Furthermore, P_U remained constant for higher concentration of TBP. This behaviour could be due to the following reasons:

1. At higher concentrations of TBP, mass transfer control is shifted to the aqueous phase, so increase in TBP concentration does not influence the mass transfer significantly.
2. The higher concentration of TBP results in higher viscosity of organic solution which leads to lower diffiusion coefficient of the TBP-Uranium complex and can be estimated by Stokes-Einstein equation (13):

$$D = \frac{kT}{6\pi r\eta} \tag{23}$$

where k is the Boltzmann constant, T is the absolute temperature, r is the molecular radius of the uranium complex and η is the viscosity of the organic phase equilibrated with the aqueous phase. This will finally result in a lower level of uranium extraction.

Influence of U(VI) Concentration in Feed Phase

The influence of the initial uranium concentration on the transport of U(VI) by TBP/nph was investigated. Figure 5 shows how U(VI) is transported through the PEHFSD membrane. Permeability (P_U) has been calculated using eq. (13) and eq. (14) with results shown in Fig. 8 and Table 4. The highest percentage of U(VI) transport was obtained when the feed phase had an initial concentration of 14.72 gdm^{-3} uranium. Thereafter U(VI) extraction decreased as concentration increased.

Figure 4 schematically shows how U(VI) diffuses through the membrane. The mass transfer of U(VI) across the membrane is described using only diffusional parameters. The interfacial transport of U(VI) to the chemical reaction has been neglected as the chemical reactions seems to take place at the aqueous feed solution-membrane interface and membrane-pseudo-emulsion phase interface. Therefore, the U(VI) transport rate is determined by the rate of diffusion of uranium-containing species through the feed diffusion layer and the rate of uranium-TBP/nph ($UO_2(NO_3)_2 . 2TBP_{org}$ species through the membrane.

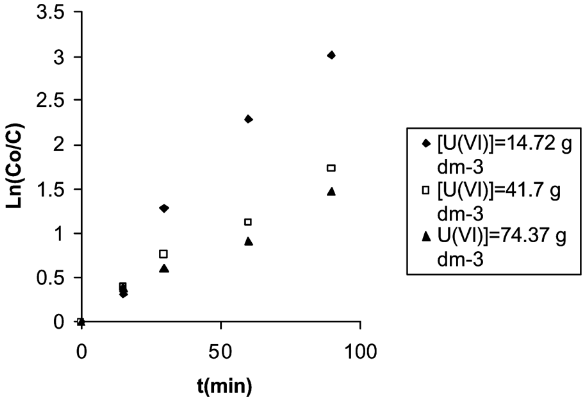

Figure 8. Influence of the U(VI) conc. on the permeability of U(VI) in the feed phase as a function of time in recycle mode.

Table 4. Experimental values of the overall permeability coefficient (P_U) for the recycling system using different U(VI) conc. in feed (Receiving phase, 0.01 M HNO_3; Feed volume = 300 cm^3, Feed flow rate = 3.33 cm^3/s, Feed linear flow velocity = 13.09 , Strip flow rate = 1.4 cm^3/s , 20% TBP/nph as carrier for U(VI)

U(VI) conc. gm dm^{-3}	conc (M) ($\times 10^{-2}$)	S (slope) (cm^3/s) ($\times 10^{-3}$)	r^2	P_U($\times 10^{-3}$, cm/s)
14.7	6.2	0.0349	0.9768	57.9
41.7	17.5	0.0183	0.9834	30.3
74.4	31.2	0.0152	0.9794	25.2

Mass Transfer Modelling and Evaluation of Diffusional Parameters and Rate Controlling Steps

At Low Uranium Concentration

The aqueous phase mass transfer coefficient (k_i), the membrane mass transfer coefficient (k_m) and the diffusivity of U(VI) across the membrane may be derived by eq. (19) (17–20). By plotting $1/P_U$ v/s $1/ K_{ex} . [NO_3^-]^2 . [TBP]^2$ for different extractant concentrations of TBP (Fig. 9) and as shown in Table 3 (at feed acidity = 4 M HNO_3 and varying feed acidity with 20% TBP concentration), a straight line is obtained with slope $r_i/rl_m . k_m$ and an ordinate to calculate the value of k_i and k_m.

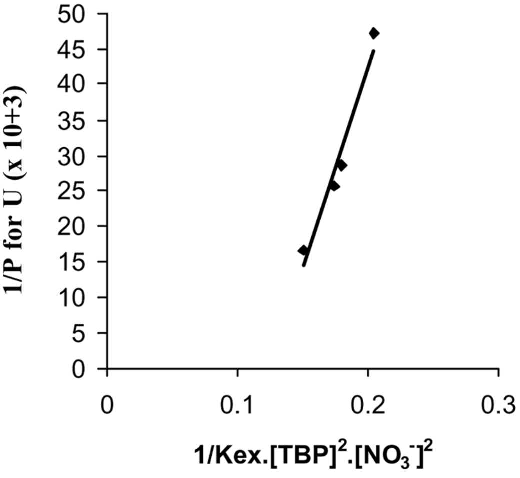

Figure 9. Plot of $1/P_U$ as a function of $1/Kex.[TBP]^2.[NO_3^-]^2$.

The values of $k_i = 1.4 \times 10^{-2}$ cm/s, $k_m = 8.5 \times 10^{-5}$ cm/s and and overall permeability coefficient $P_U = 1.93 \times 10^{-3}$ cm/s were calculated from the proposed model. The calculated value of the effective diffusion coefficient (D_{eff}) (eq. 20) was $D_{eff} = 3.4 \times 10^{-6}\,cm^2\ s^{-1}$ in examined conditions.

At High Uranium Concentration

By plotting $[U(VI)]_o - [U(VI)]_{in}$ v/s time (t) for different U(VI) concentrations, a straight line is obtained with a slope $[U(VI)]_o - [U(VI)]_{in}/t$ (at 20% TBP/nph feed acidity and 0.01 M HNO_3 as strippant) (Fig. 10). An ordinate for calculating the value of K_m and D_{eff} should also be obtained. The membrane permeability (P_m) was calculated by using Equation (16). The calculated value of P_m was 1.20×10^{-5} cm/s.

$$p = \frac{J}{C} = \frac{[TBP]k_m}{nC} \tag{24}$$

$$[U(VI)]_o - [U(VI)]_{in} = \frac{[TBP]k_m A}{nV} t \tag{25}$$

$[U(VI)]_o$ and $[U(VI)]_{in}$ are metal concentration at time, t and at 0 hrs. The values of $k_m = 2.1 \times 10^{-6}$ cm/s and $D_{eff} = 1.00 \times 10^{7}\,cm^2/s$. (Eq. 25) were obtained from the proposed model under the conditions examined.

Equation (19) indicates that the local value of the total resistance is a sum of the local values of the individual resistances. Therefore, in the

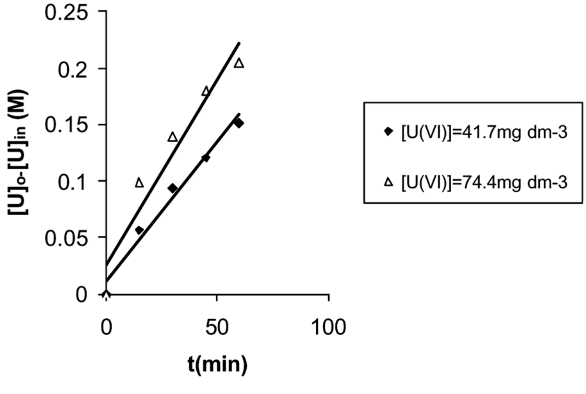

Figure 10. Influence of the conc. difference of U(VI) in the feed against time (min) in recycle Mode.

right hand side of eq. (19), the first term is around 70 s/cm and the second term is around 650 s/cm. The overall resistance in the experiments calculated from eq. (13) was observed to be around 720 s/cm. The overall resistance estimated from the model was 518 s/cm which shows that resistance due to the membrane is dominant under the experimental conditions studied. The difference between the estimated value from the model and the experimental value is due to the error associated in determining diffusion coefficient of metal species in membrane and correctness of porosity and tortuosity of the hollow fiber membranes. When uranium concentration is high, resistance due to the membrane remains to be dominant under the experimental conditions studied as k_m decreased from 8.5×10^{-5} cm/s to 2.1×10^{-6} cm/s (approximately 40 times).

Influence of O/A Ratio on Permeation Coefficient (P_U) of U(VI) in the Feed Phase

To study the influence of the O/A ratio, experiments were performed at various O/A ratios ranging from 0.09 to 0.5. It was found that an O/A ratio of, 0.5 resulted in maximum permeation of U(VI) (81.6%). When the volume of organic was decreased, metal recovery was decreased under similar experimental conditions.

Table 5, Fig. 11 show the effect of variation of volume ratios. U(VI) transport increased with an increase in the O/A ratio and the value of P_U also increased from 18.13×10^{-3} cm/s to 57.94×10^{-3} cm/s. The U(VI) value in the stripping phase was found to increase from 2.9 to 12.02 gms dm^{-3} indicating that higher ratios of TBP to the strippant (from 0.09 to 0.5) increased the U(VI) extraction. This is due to the larger volume of TBP available for fixed volume of strippant.

Table 5. Experimental values of the overall permeability coefficient (P_U) for the recycling system using different strippant volume (O/A ratio) in pseudo-emulsion phase (Receiving phase, 0.01HNO$_3$; Feed volume = 300 cm^3, Feed flow rate = 3.33 cm^3/s, Feed linear flow velocity = 13.09 cm/s, Strip flow rate = 1.4 cm^3/s, 20% TBP/nph as carrier for U(VI)

Volume of strippant (ml)	O/A ratio	S (slope) (cm^3/s) ($\times 10^{-3}$)	r^2	P_U($\times 10^{-3}$, cm/s)
200	0.5	34.9	0.9768	57.9
225	0.3	19.5	0.9787	32.3
250	0.2	1.3	0.9939	25.2
275	0.1	1.1	0.9898	18.2

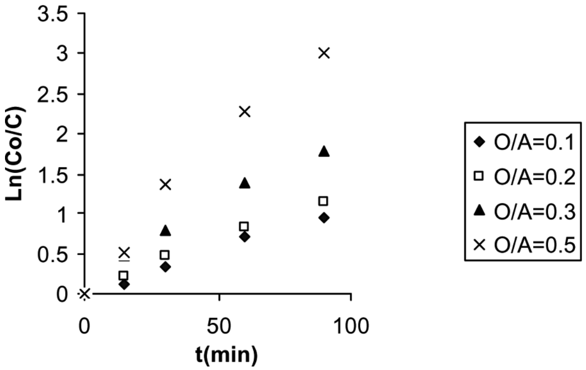

Figure 11. Ln(Co/C) against elapsed time for U(VI) transported for different O/A ratio in the pseudo-emulsion phase from the experimental results in recycle mode. Experimental conditions: Feed phase: 300 ml of aqueous solution at 4 HNO_3, Pressure difference applied: 0.2 bar, feed flow rate: 3.33 cm^3/s. Stripping flow rate: 1.4 cm^3/s.

Comparative Performance of PEHFSD and HFSLM Technique

The feasibility of direct recovery of U(VI) by PEHFSD and by HFSLM under the same experimental conditions was studied. Results are shown in Fig. 12 with ~82% recovery of U(VI) by the PEHFSD technique and ~46% by SLM under the same experimental conditions after 90 minutes. Both the experiments were run in counter-current and in

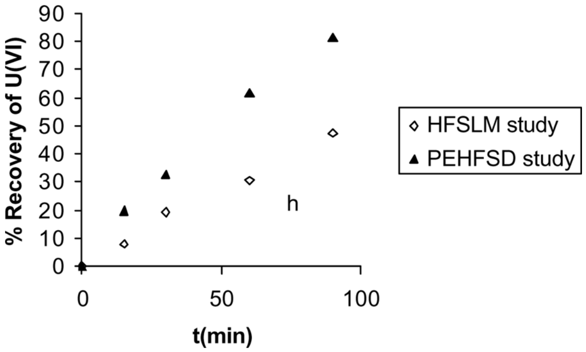

Figure 12. Experimental values of the % Recovery of U(VI) for the recycling system for comparative study of SLM and HFSD under same experimental conditions (Receiving phase, 0.01 M HNO_3; Feed volume = 300 cm^3, 20% TBP/nph as carrier for U(VI).

recirculation mode for 90 minutes maintaining O/A ratio of 0.5. Repeat runs with the same feed in HFSLM mode produced only ~ 67% metal ion recovery whereas it was 82% in the PEHFSD mode in a single run. The main reason for this efficiency could be the large surface area provided for stripping in the PEHFSD technique. Merits of ELM and high surface area of the HF membrane attributed to the better performance of the PEHFSD technique. On the contrary, recovery of uranium in HFSLM was quite slow and stability of the technique was at question.

Concentration Profile Study of U(VI) in Stripping Phase by PEHFSD

To maximize the concentration of uranium in the stripping phase, three sets of experiments were carried out in which the feed solution was replenished with fresh feed while keeping the same strippant in recirculation mode. As a result, small increments in the metal ion concentration profile in the strippant phase was observed. Table 6 (a–c) shows that, from three sets of feed solution [each set contains $\sim 8.1 \times 10^{-2}$ mol dm^{-3} of U(VI)] ~ 54% of feed could be concentrated in the same strippant, though strippant solution was not saturated. These experiments were continued for 24 hours and it was observed that concentration of uranium reached around 10 times that of the initial feed concentration. Thus, the concentration factor was around 10 under the studied experimental conditions. This shows that the PEHFSD technique is useful for concentrating dilute uranium streams (micro concentration) and also have potential for extracting macro concentration (described in section 4.4).

Applicability of PEHFSD for Recovery of U(VI) from Real Oxalate Waste

The feasibility of direct recovery of U(VI) from the oxalate supernatant without adjusting acidity and using 20% TBP/nph as extractant was also studied using PEHFSD technique. Experiments were performed separately with treated (for oxalate ion destroyed by $KMnO_4/H_2O_2$) and untreated (without oxalate decomposition) waste. The recovery of U(VI) was well above 84% in case of untreated waste and in case of treated waste it was more than 88% (Fig. 13) after 90 mins. Both the experiments were run in a counter-current recirculation mode for 90 minutes, with an O/A ratio of 0.5. The plutonium present in the waste (~25 mg/L) was also extracted by TBP but stripping was not possible by 0.01 M HNO3. On the contrary, uranium stripping was fast because

Table 6. (a): Concentration profile study of strippant using PEHFSD mode; Ist run. (b): concentration profile study of strippant using PEHFSD mode; II run. (c): concentration profile study of strippant using PEHFSD mode; III run, Acidity: 4 M HNO_3; extractant: 20% TBP in nph; feed volume: 300 cm^3 in each run; volume of pseudo emulsion: 300 cm^3 (organic 100 cm^3 + strippant 200 cm^3); feed linear flow velocity: 13.1 cm/s; linear flow velocity of pseudo emulsion: 5.5 cm/s; stirring rate ~600 rpm; time: 90 min

(1st run)

Time (min.)	U(VI) conc. in feed Ist run (10^{-2} M)	U conc. in stripping phase (10^{-2} M)
0	8.1	0
5	7.5	0.5
15	5.6	1.2
30	3.8	3.1
60	1.2	6.3
90	1.0	6.9

(2nd run)

Time (min.)	U(VI) conc. in feed IInd run(10^{-2} M)	U conc. in stripping phase (10^{-2} M)
0	8.1	0
5	6.2	6.9
15	5.6	6.9
30	4.4	7.3
60	3.8	8.1
90	1.9	8.8

(3rd run)

Time (min.)	U(VI) conc. in feed IIIrd run(10^{-2} M)	U conc. in stripping phase (10^{-2} M)
0	8.1	0
5	7.5	8.8
15	6.9	9.4
30	5.6	10.0
60	3.8	11.3
90	3.1	13.1

of simple equilibrium shift (extremely poor partition coefficient of uranium (D_U) value at 0.01 M HNO_3).

The permeability coefficients for the extraction as well as stripping of U(VI) were calculated using equation (13 or 14). The results indicated

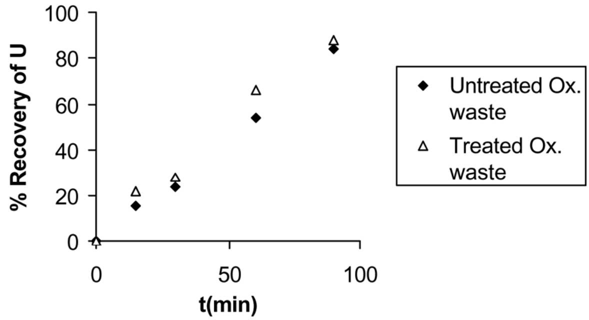

Figure 13. % Recovery against elapsed time for U(VI) transported for actual untreated and treated oxalate supernatant solution in the feed phase from the experimental results in recycle mode.

that the permeability coefficient increases for untreated to treated solution under the same experimental conditions. The values of the permeability coefficient for actual oxalate supernatant solution (treated with $KMnO_4/H_2O_2$) is 51.08×10^{-3} cm/s and for untreated solution 45.42×10^{-3} cm/s. This difference in permeability value for treated and untreated is due to the interference of oxalate ions in case of untreated waste.

CONCLUSION

The present study is the first of its kind ever carried out in radioactive environment and experimental results have clearly demonstrated that this novel technique, PEHFSD, is a valuable alternative to conventional decontamination processes for metal recovery from acidic streams.

1. This method is suitable for extraction as well as stripping of macro quantities of metal ions in a single contactor which is an added advantage compared to traditional liquid-liquid extraction and non-dispersive solvent extraction (NDSX) where two contactors are required.
2. Metal ion extraction results from this study show optimal operating conditions at an O/A ratio of 0.5, 20% TBP as carrier concentration, 4 M HNO_3 as feed acidity, strippant flow rate of 1.4 cm^3/s and feed flow rate of 3.33 cm^3/s
3. Another configuration of the liquid membrane (LM) ie. SLM (supported liquid membrane) was also operated to compare the enhanced stability of the new system (no leakage of organic from extractant support and consistent supply of organic to the membrane). Evaluation

of the permeation data from the PEHFSD system has proved its efficiency in extraction and improved stability of this novel system.

4. The strip dispersion method was carried out to concentrate uranium ion in the raffinate of the process stream after repeated experimental runs with fresh feed while keeping the same strippant. Mass transfer calculations pertaining to U(VI) permeation was carried out. The calculated values of the effective diffusion coefficient (D_{eff}) (equation-19) and membrane mass transfer coefficient (K_m) were $3.4 \times 10^{-6}\,cm^2\,s^{-1}$ and $8.5 \times 10^{-4}\,cm/s$ respectively.
5. Overall the PEHFSD with 20% TBP/nph system can be successfully utilized for the recovery of U(VI) from dilute solutions as well as waste streams. Recovery of U(VI) from waste solutions, even in presence of oxalate ions, across PEHFSD using 20% TBP/nph as extractant and 0.01 M HNO_3 solution as strippant has been clearly demonstrated and this technique was found to be an alternative to other conventional methods.

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NOMENCLATURE

Co/C	metal concentration at time 0 and time t (M)
D_{eff} or D	effective membrane diffusion coefficient of the uranium containing organic species (cm^2/s)
k_m	membrane mass transfer coefficient (cm/s)
K_{ex}	extraction constant derived from equation 4
L	fiber length (cm)
M	mol dm^{-3}
N	number of fibers
P_U	permeability coefficient for uranium (cm/s)
r_i and r_o	inner and outer hollow fiber radius (cm)
d_a	thickness of the aqueous boundary layer (cm)
t_m	thickness of the fiber membrane (cm)
V_f	volume (cm^3)
J_m	flux (mol/ cm^2/ s)

Subscripts

t	refer to time t
f and s	refer to feed and stripping solution respectively

i	for inner radii
o	for outer radii
M	metal ion
aq	aqueous
org	organic

Superscript

0	refer to time zero
n	number

Greek letter

τ	tortuosity of the membrane
v_f	linear flow velocity
ε	porosity of the hollow fiber membrane
η	viscosity

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