A process intensified technique of liquid membrane employed in in-house hollow fiber contactor

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ABSTRACT

Facilitated transport through liquid membrane is advantageous over conventional processes for separation of valuable metals such as uranium from lean streams. Dispersion liquid membrane in hollow fiber contactor has the advantage of simultaneous extraction and stripping, continuous replenishment of organic phase immobilized in pores of polymeric membrane and fast disengagement of loaded dispersion after the mass transport operation. In liquid membrane based transport process, diffusion path length inside the wetted pore is important in deciding the rate of extraction. Diffusion path length is related to the fraction of the pore length wetted by the organic liquid membrane phase. Hence, estimation of fraction of the pore length wetted by the organic phase is beneficial for design and scale up of this process. In the present work, a mathematical model has been developed for determining the rate of transport through the membrane and the extent of extraction through the contactor. A novel approach for estimation of fraction of the pore length wetted by the organic membrane phase has been suggested through developed model. This estimation is also helpful to get an idea of the stability of liquid membrane phase to the given polymeric membrane. The data has been generated for extraction of uranium from nitrate medium in counter current once-through mode using hollow fiber dispersion liquid membrane. Water-in-oil dispersion of 1 M NaHCO$_3$ in dodecane, containing 30 % v/v Tri-n-butyl phosphate (TBP), is used as extractant. Using polypropylene contactor, uranium extraction of 98 % has been achieved in single pass of the feed solution. The model is validated for contactors made of lumens of different materials viz. polysulfone and polypropylene. For polysulfone lumen, the model estimates the fraction of the pore length wetted by the organic membrane phase as 40%. Similarly, estimation has been made for polypropylene lumen and the entire pore length has been found wetted by the organic membrane phase. The model has also been found beneficial for prediction of the performance of polysulfone and polypropylene hollow fiber contactors regarding their scale up.

Keywords: Modelling; Hollowfiber; Uranium; Membrane; Scale up

1. Introduction

Recovery of valuable metals such as uranium from lean acidic raffinate is a major task in nuclear industry in view of limited resources and strict environmental regulations [1]. The existing methods used for this purpose viz. solvent extraction and ion exchange have their own limitations. The solvent extraction process needs separate extraction and stripping step, multistage contactor for recovery from lean streams, large density difference between the phases (for efficient phase separation) and large solvent inventories. Moreover, there are emulsification losses. In ion exchange process, there are problems such as resin fouling, through-

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put limitations and poor selectivity, which limit its applicability. In addition, the driving force for mass transfer in these processes is low due to equilibrium limitations [2]. On the other hand, liquid membrane process facilitates simultaneous extraction and stripping and has no moving parts. The process has low energy consumption and less entrainment losses [3–5]. Since the organic phase is stripped as soon as it is loaded, the driving force for extraction is substantially increased and equilibrium limitation is overcome. The organic phase is, therefore, able to extract solutes from very lean solutions.

Among the major liquid membrane configurations [6,8], the supported liquid membrane (SLM) comprises a micro-porous polymeric membrane in which the organic liquid is immobilized in its pores. The aqueous feed and the strip phases are confined to the two sides of a membrane pore. The organic phase immobilized in the pores, acts as a selective barrier for solute transport. Since the organic phase is confined to the pores of polymeric membrane, its total volume is limited by the pore volume of the membrane, which is very small. Moreover, any pressure imbalance on the two sides of the polymeric membrane can cause washout of the organic phase from the pores and irreversible breakthrough of one phase into the other phase [9–11]. In another configuration called dispersion liquid membrane (DLM), a dispersion of strip phase in a continuous organic phase is confined to one side, and the aqueous feed phase to the other side of a membrane pore. The organic phase fills the pores of the microporous polymeric membrane and acts as a liquid membrane. In DLM, continuous replenishment of the pores by the membrane liquid allows elimination of the problem of stability faced by SLM due to loss of the liquid membrane from the pores [12]. Due to short residence times of the dispersion in the contactor, DLM does not require the use of surfactant to stabilize the dispersion. This eases the product recovery process. The dispersion of strip phase in the organic phase is created externally in a mixer device.

Both SLM and DLM configurations can be operated in the hollow fiber modules. These are shell and tube type contactors having micro porous polymeric lumens packed in a cylindrical shell. One of the aqueous solutions passes through the lumen and the other passes through the shell side. Hollow fiber (HF) contactor provides the advantages such as non-dispersive contact, high mass transfer area per unit contactor volume and modular design for easy scale up [13,14]. Hollow fiber dispersion liquid membrane (HFDLM) process employs DLM in HF contactor. Here, a dispersion of the strippant in the organic extractant is passed through the shell side of the hollow fiber contactor, while the feed solution is passed through the lumen side [15,16].

The interface between the organic phase and feed phase lies within the pore of the membrane. Location of this interface is important in deciding the rate of extraction. Since the diffusion coefficient of the metal cation in the aqueous feed phase is much higher than that of the metal-carrier complex in the organic phase, a higher rate of extraction can be achieved by maintaining the interface as near the shell end of the pore as possible so that diffusion path length in the organic phase is kept as low as possible. The wettability of the organic phase to the membrane material is very important. Low wettability results in shorter transport path in the organic phase and better rates of extraction. On the other

hand, low wettability causes reduction of the breakthrough pressures and therefore requires more stringent control of the differential pressure across the membrane. Adequate wettability of polymeric membrane is essential for its ability to perform carrier-facilitated transport of metal species. Between the two polymeric membrane materials used in these studies, polysulfone (PS) is less hydrophobic than polypropylene (PP) [17–19], and would provide shorter path length in the organic phase. PS is a better material for working in nuclear environment due to its toughness, stability to nuclear radiation and resistance to oxidation.

In the present work, applicability of hollow fiber contactors, with micro-porous PS and PP fibers has been studied using HFDLM technique for recovery of uranium from lean acidic nuclear waste streams. Water-in-oil dispersion of 1 M $NaHCO_3$ in dodecane containing 30% v/v tri-n-butyl phosphate (TBP) is used as extractant. It is demonstrated here that hollow fiber contactor is a promising device for application in recovery of values like uranium from dilute streams using DLM configuration. This separation process can be applied for treatment of lean acidic streams such as raffinate from uranium refining plant. A mathematical model has been developed for determining the rate of transport through the membrane and the extent of extraction through the contactor. Model also estimates the fraction of the pore length wetted by the organic membrane phase. The model is validated for extraction of uranium from nitrate medium in once-through mode using dispersion liquid membrane employed in PS and PP contactors. The model has also been utilized for prediction of the performance of hollow fiber contactor on scale up for both polysulfone and polypropylene lumens.

2. Methodology

The organic phase was prepared by dissolving the 30% v/v tri-n-butyl phosphate (TBP) in n-dodecane. TBP and n-dodecane were supplied by Heavy Water Board, Mumbai. Pure uranyl nitrate solution (50 g/L of U^{6+}) is obtained internally from BARC. From this solution, feed of 0.5 g/L U^{6+} was prepared by dissolving it in 1 N HNO_3 (from Thomas Baker Chemicals Pvt. Ltd.). Raffinate stream of a uranium refining plant having acidity 1 N was also used as the feed. Raffinate contains mainly U^{6+} (around 200 ppm) along with some other ions in trace quantities. Aqueous solution of 1 M sodium bicarbonate (from Merck Specialties Pvt. Ltd.) was used as the strippant. The dispersion was prepared by adding an equal volume of strippant to the organic phase in dropwise manner, while agitating the organic phase at 3000 RPM [20]. REMI RQ-127 4 CROSS BLADE emulsifier was used as the agitator and mixing was performed in 20 min.

Five different hollow fiber contactors were used. Two contactors with PS lumens, PS1 and PS2, were supplied by Desalination Division, BARC. The other three contactors, consisting of polypropylene lumens, PP1, PP2 and PP3 (make: Liqui-Cel® 2.5 × 8") were purchased from Membrana, Germany. Dimensional details for the contactors are presented in Table 1.

The HFDLM system is shown in Fig. 1. It consists of a hollow fiber module, a feed and dispersion reservoirs, a feed and dispersion pumps and an agitator for dispersing the strippant into the organic phase. The feed was passed

Table 1
Dimensional details for the contactors

Module	PS1	PS2	PP1	PP2	PP3
Diameter of the shell (cm)	5.0	5.5	5.0	8.5	8.8
Effective length, l (cm)	40	42	16	25	62
Fiber MOC	PS	PS	PP	PP	PP
Fiber OD, $2r_2$ (cm)	0.15	0.15	0.03	0.03	0.03
Fiber ID, $2r_1$ (cm)	0.125	0.10	0.024	0.024	0.024
Fiber log mean diameter, $2r_{lm}$ (cm)	0.14	0.12	0.027	0.027	0.027
Fiber wall thickness, L (=$r_2 - r_1$)(cm)	0.0125	0.025	0.003	0.003	0.003
Pore diameter (nm)	9	9	50	50	50
Porosity, ε %	70	70	40	40	40
Number of fibers, n_f	250	520	10,000	30,000	31800
Mass transfer area ($2\pi r_{lm} l \varepsilon n_f$) (m²)	0.302	0.592	0.543	2.54	6.69
Contactor volume (m³)	7.85×10^{-4}	9.98×10^{-4}	3.14×10^{-4}	1.42×10^{-3}	3.77×10^{-3}
Mass transfer area/contactor volume (m²/m³)	385	593	1729	1789	1774.5
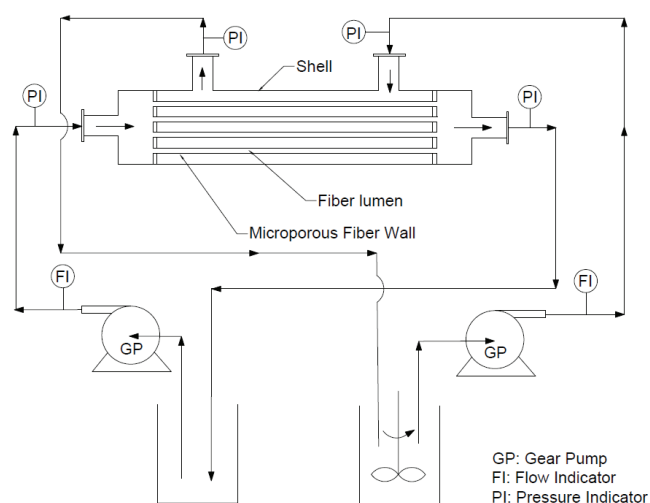
Fig. 1. Schematic of HFDLM process in re-circulating mode.

(a) Experimental set up with polysulfone contactor

(b) Experimental set up with polypropylene contactor

Fig. 2. Experimental set up of HFDLM process; (a) PS1 contactor, (b) PP1 contactor.

through the lumen side and the water-in-oil dispersion (1 M NaHCO$_3$ dispersed in dodecane containing 30% v/v tri-n-butyl phosphate) was circulated through the shell. The organic phase partially fills the micropores of the hollow fibers through capillary action. Positive pressure differential was maintained between the lumen-side of hollow fibers and the shell in order to prevent seepage of the organic phase into the lumen. At the end of the experiment, the agitator was turned off and the dispersion was allowed to separate into two phases viz. the lean organic solution and the loaded strip solution. Phase separation was rapid. Uranium content in the aqueous solutions was determined using ICP-OES. All the data are generated at least in duplicate and the standard deviation of the accepted data was within ±5%.

The photograph of the experimental setup is shown in Fig. 2.

A mathematical model of the transport process was developed for estimating the rate of transport through the

membrane and the extent of extraction through the contactor. The model would be useful in optimization and scale-up of the process using a limited number of experiments.

2.1. Model development

In carrier-facilitated transport through liquid membrane in hollow fiber contactor, the metal ion, UO_2^{2+} is first transported from the feed phase to the interface of feed-organic phase (liquid membrane phase) located in the pores of the fiber. At the interface, UO_2^{2+} reacts with the carrier species, *TBP*, and nitrate ions, to form the metal-carrier complex, $UO_2(NO_3)_2 \cdot 2TBP$. The reaction is represented by the following equation.

$$UO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(org) \xleftrightarrow{K_{eq}} UO_2(NO_3)_2 \cdot 2TBP(org) \quad (1)$$
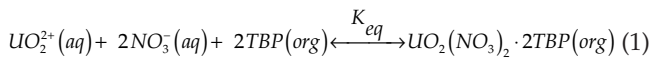
The reaction is fast enough to allow us to assume that it attains equilibrium at the interface. The equilibrium constant for this reaction can be related to the concentrations of the reacting species at the interface by the following equation.

$$K_{eq} = \frac{\left[UO_2(NO_3)_2 \cdot 2TBP\right]_{org}}{\left[UO_2^{2+}\right]_{aq}\left[NO_3^-\right]_{aq}^2\left[TBP\right]_{org}^2} \quad (2)$$

The metal-carrier complex diffuses through the organic phase, till it reaches the organic-strip interface, where it releases the metal ion [3]. The regenerated *TBP* diffuses back towards feed-organic phase interface and the cycle repeats itself.

Differential mass balance for a UO_2^{2+} along a single fiber lumen, at steady state condition, gives

$$-v\pi r_1^2 \frac{dC_f}{dz} = 2\pi r_{lm}\varepsilon J \quad (3)$$

Here, v is the linear velocity of the feed solution through the lumen, C_f is the concentration of the metal ions in the feed and z is the distance measured along the fiber. J is the flux of ions across the fiber, ε is the fraction of the fiber surface which is occupied by pores, and r_{lm} is the log-mean radius of hollow fiber, and is related to the inner radius (r_1) and the outer radius (r_2) of the fiber as, $r_{lm} = (r_1 - r_2)/\ln\left(\dfrac{r_1}{r_2}\right)$

The rate of transport of the metal ions across unit length of the fiber bundle is $2\pi n_f r_{lm}\varepsilon J$, where n_f is number of fibers in the bundle. At steady state, these metal ions are captured by the strip phase. Hence, we can write

$$V_s \frac{dC_s}{dz} = n_f 2\pi r_{lm}\varepsilon J \quad (4)$$

Here, V_s is the volumetric flow rate of the strip phase and C_s is the concentration of metal ions in the strip phase.

In order to obtain the flux J, we consider various transport processes occurring across the wall of a fiber. Schematic diagram of a fiber wall is presented in Fig. 3. It shows a single pore. The interface between the feed and the organic phase lies within this pore. The total length L
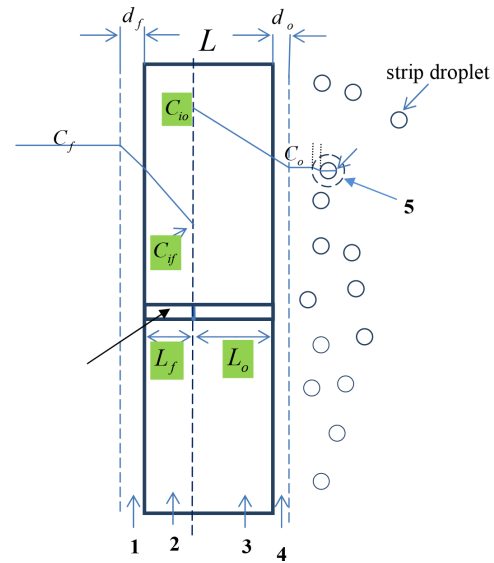

Fig. 3. Schematic representation of transport of metal ion through the hollow fiber membrane; 1 – diffusion film at the feed-membrane interface, 2 – region of the pore filled with feed solution, 3 – region of the pore filled with organic liquid, 4 – diffusion film at the organic membrane interface, 5 – diffusion film at strip-organic interface.

of the pore therefore partially filled by the feed solution on one side (length L_f) and the organic phase on the other side (length L_o).

Metal cations UO_2^{2+} are transported across the diffusion film of thickness d_f, adjacent to the inner side of the fiber wall, before they enter the pore. They are then transported through the pore until they arrive at the feed-organic phase interface. The concentration of the metal ions in the feed solution at the interface is denoted by C_{if}. At the interface, metal ions react with *TBP* to form the complex. The reaction is instantaneous and reversible, so that, the concentration C_{io} of the complex (i.e. $\left[UO_2(NO_3)_2 \cdot 2TBP\right]_{org}$) is in equilibrium with C_{if} (i.e. $\left[UO_2^{2+}\right]_{aq}$). The complex diffuses through the organic phase to the pore mouth on the outer surface of the fiber and then through the diffusion film into the bulk organic phase. The concentration of the complex is uniform in the bulk organic phase. It again falls in the diffusion film surrounding the drop of the strip phase, till it reaches the organic phase-strip phase interface, where its concentration drops to C_{so}. It is then captured by the strip phase. We assume that the complex breaks instantaneously at the interface between the organic and the strip phase and that the resulting metal ions cannot be recaptured by the carrier species. This allows us to assume that $C_{so} = 0$.

At steady state, all fluxes should match. This fact is depicted by the following equations

$$J = k_f\left(C_f - C_{if}\right) = k_o\left(C_{io} - C_o\right) = k_s\left(\frac{a_s}{a_{lm}}\right)\left(C_o - C_{so}\right) \quad (5)$$

Once uranyl ion enters the strip phase, it is immobilized there. Hence, it's back driving force must be zero and thus C_{so} can be taken as zero in Eq. (5),

$$J = k_f \left(C_f - C_{if} \right) = k_o \left(C_{io} - C_o \right) = k_s \left(\frac{a_s}{a_{lm}} \right) C_o \qquad (6)$$

where

$$k_f = \frac{D_f}{d_f + L_f} \qquad (7)$$

$$k_o = \frac{D_o}{d_o + L_o} \qquad (8)$$

$$k_s = \frac{D_o}{d_s} \qquad (9)$$

The relation between the concentrations C_{if} and C_{io} is obtained using Eq. (2) as

$$\frac{C_{io}}{C_{if}} = K_{eq} \left[NO_3^- \right]_{aq}^2 \left[TBP \right]_{org}^2 \qquad (10)$$

The terms on the right-hand side remain constant along the length of the fiber and hence the ratio C_{io}/C_{if} is denoted by K_{Df} and is called the distribution coefficient.

Combining Eqs. (6) and (10), we get

$$J = \frac{K_{Df} C_f}{\dfrac{K_{Df}}{k_f} + \dfrac{1}{k_o} + \dfrac{a_{lm}}{k_s a_s}} \qquad (11)$$

Noting that the last term in the denominator of Eq. (11) is very small compared to the rest of the terms since $a_s \gg a_{lm}$, we can simplify Eq. (11) to

$$J = \frac{K_{Df} C_f}{\dfrac{K_{Df}}{k_f} + \dfrac{1}{k_o}} \qquad (12)$$

For the lumen side, from Eqs. (3) and (12)

$$\frac{dC_f}{dz} = \frac{-2 r_{lm} \varepsilon K_{Df} C_f}{v r_1^2 \left(\dfrac{K_{Df}}{k_f} + \dfrac{1}{k_o} \right)} \qquad (13)$$

Similarly combining Eqs. (4) and (12) we get

$$\frac{dC_s}{dz} = \frac{2 \pi r_{lm} \varepsilon n_f K_{Df} C_f}{V_s \left(\dfrac{K_{Df}}{k_f} + \dfrac{1}{k_o} \right)} \qquad (14)$$

Eq. (13) can be integrated using the initial condition $C_f = C_{f0}$ at $z = 0$ to yield the following expression

$$\ln \left(\frac{C_f}{C_{f0}} \right) = \frac{-2 r_{lm} \varepsilon K_{Df} z}{v r_1^2 \left(\dfrac{K_{Df}}{k_f} + \dfrac{1}{k_o} \right)} \qquad (15)$$

Combining Eqs.(13) and (14) we get

$$\frac{dC_s}{dz} = -\pi n_f r_1^2 \frac{v}{V_s} \frac{dC_f}{dz} \qquad (16)$$

Eq. (16) on integration gives

$$C_s = \pi n_f r_1^2 \frac{v}{V_s} \left(C_{f0} - C_f \right) \qquad (17)$$

where C_{f0} is the initial uranium concentration of feed. It is assumed that strip phase is free from metal ion at the inlet. Distribution coefficients, K_{Df} and K_{Ds} have been generated through independent liquid-liquid extraction experiments. Using Eq. (15), fraction of the pore length wetted by the organic membrane phase has been estimated for lumens made of polysulfone and polypropylene.

Developed mathematical model can be used for prediction of extraction rate of other ions and other types of polymeric membrane. The data needed for the design are, the carrier mediated distribution coefficient of the ion in the organic phase, diffusion coefficient of the ion in the aqueous phase and diffusion coefficient of the ion-carrier complex in the organic phase. Along with pore diameter, pore length and pore area, fraction of the pore length wetted by the organic phase is also needed. This length will be determined by wettability of the polymeric membrane for organic liquid membrane phase.

3. Results

Hollow fiber dispersion liquid membrane process has been employed for transport of uranium using feed phase as pure uranyl nitrate solution containing 0.5 g/L U[6+] in 1 N HNO$_3$, organic phase as 30% v/v TBP in dodecane and strip phase as 1 M NaHCO$_3$. Flow rate of feed phase through fiber lumen and flow rate of dispersion through shell has been maintained at 200 ml/min. Equal volumes of the organic and the strip phases are used for preparing the dispersion. Mass transfer coefficients for aqueous and organic phases are estimated below through available correlations in literature.

3.1. Estimation of mass transfer coefficient of feed phase

The Wilke-Chang correlation can be used for estimation of diffusivity of uranyl ion in the aqueous phase as following [21] for solute molar volume less than 0.5 m³/kmol,

$$D_f = 1.173 \times 10^{-16} \frac{(\varphi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \qquad (18)$$

where M_B is the molecular weight of solvent B, μ_B is the viscosity of solvent in Pa·s, V_A is the solute molar volume in m³/kmol and φ is an association parameter of the solvent. Substituting, $M_B = 63$ kg/kmol, $\varphi = 1$ for nitric acid medium, T = 298 K, $\mu_B = 1 \times 10^{-3}$ Pa·s and $V_A = 9.35 \times 10^{-2}$ m³/kmol [22] in Eq. (18), K_{Df} is estimated as 1.15×10^{-9} m²/s. The mass transfer coefficient inside the fibers is described by the Leveque equation (for Graetz number greater than four) considering fast chemical reaction under laminar flow as following [13],

$$Sh = 1.62 \, (4 r_1^2 v / (l K_{Df}))^{1/3} \qquad (19)$$

where Sh is the Sherwood number (= $2 k_{fl} r_1 / K_{Df}$), k_{fl} is mass transfer coefficient of aqueous feed film, r_1 is the internal radius of fiber, v is the linear flow velocity of the feed solution through fiber lumen, l is the length of fiber and K_{Df} is the diffusion coefficient of uranyl ion in the aqueous phase. Substituting K_{Df} (= 1.15×10^{-9} m²/s) along with fiber char-

acteristic properties (r_1 and l) and feed flow velocity (v) in Leveque equation, k_{f1} has been estimated for PS and PP contactors and listed in Table 2.

3.2. Estimation of mass transfer coefficient of organic membrane phase

The diffusion coefficient of uranyl complex, D_{oeff}, in dodecane containing TBP has been calculated using Stokes-Einstein equation for porous medium as following [21] for solute molar volume greater than 0.5 m³/kmol,

$$D_{oeff} = D_o(\varepsilon / \tau) = \frac{9.96 \times 10^{-16}\ T}{\mu V_A^{1/3}}(\varepsilon / \tau) \tag{20}$$

where D_o is the diffusion coefficient of $UO_2(NO_3)_2 \cdot 2TBP$ in the bulk organic phase and μ is the viscosity of organic liquid membrane in Pa·s. Substituting $V_A = 0.64$ m³/kmol [22], μ for Dodecane containing 30 % v/v $TBP = 1.75 \times 10^{-3}$ Pa·s and T = 298 K in Eq. (20), D_o is estimated as 1.968×10^{-10} m²/s. Calculated values of D_f and D_o are in accordance with that found in the literature [23].

Viscosity of organic liquid membrane for varying composition is measured using Ostwald viscometer and presented in Fig. 4. Viscosity is used for estimation of mass transfer coefficient.

3.3. Estimation of mass transfer coefficient of diffusion film at the organic membrane interface shell side

Average shell side velocity, v_s is estimated using superficial velocity divided by free flow area $(1 - \varphi)$. Shell side equivalent diameter, d_e is estimated through 4× flow area/total fiber circumference. Using d_e and v_s along with density and viscosity of shell side liquid, reynolds number has been calculated and shown in Table 2. At low reynolds number, mass transfer coefficients around a stationary cylinder can be obtained through following correlation [24–25],

$$St\ Sc^{0.67} = 3.42\,\mathrm{Re}^{-0.672} \tag{21}$$

where $St = k_{o1}/v_s$

Mass transfer coefficient of diffusion film at the organic membrane interface, k_{o1} is thus estimated for PS and PP contactors and presented in Table 2. All parameters along with the estimated are summarized in Table 2.
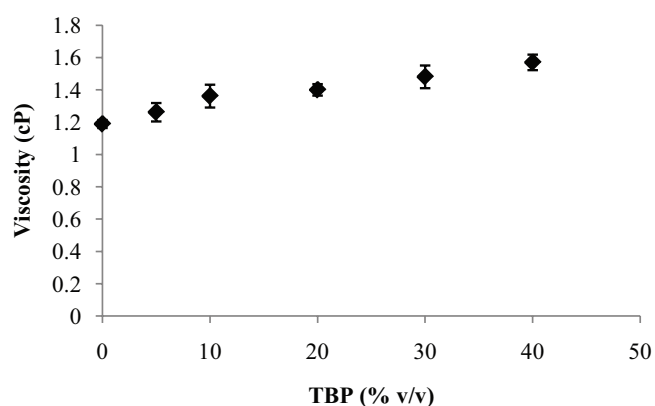

Fig. 4. Viscosity of organic phase for varying concentration of TBP dissolved in dodecane.

Table 2
List of parameters for contactors

Parameters	PS1	PS2	PP1	PP2	PP3
Fiber inner diameter, $2r_1$ (cm)	0.125	0.10	0.024	0.024	0.024
Fiber outer diameter, $2r_2$ (cm)	0.15	0.15	0.030	0.030	0.030
Fiber wall thickness, L (cm)	0.0125	0.025	0.003	0.003	0.003
Effective length of fiber, l (cm)	40	42	16	25	62
Diameter of the shell (cm)	5	5.5	5	8.5	8.8
Fiber packing fraction, φ	0.225	0.387	0.45	0.45	0.45
Feed velocity, v (cm/s)	1.087	0.82	0.74	1.23	1.16
No of fibers, n_f	250	520	10000	30000	31800
Porosity, ε		0.7		0.4	
Tortuosity, τ		1.5		2	
Diffusion coefficient in aqueous phase, D_f (cm²/s)			1.15×10^{-5}		
Diffusion coefficient in bulk organic phase, D_o (cm²/s)			1.97×10^{-6}		
Aqueous phase mass transfer coefficient, k_{f1} (cm/s)	9.93×10^{-4}	9.58×10^{-4}	2.05×10^{-3}	2.10×10^{-3}	7.05×10^{-3}
Average velocity shell side, v_s (cm/s)	0.219	0.229	0.38	0.40	0.55
Equivalent diameter shell side, d_e (cm)	0.517	0.24	0.036	0.058	0.039
Re_{shell} ($= d_e v_s \rho / \mu$)	8.47	4.07	1.03	1.735	1.65
Sc_{shell} ($= \mu/\rho D_o$)		6794		1163	
Organic phase mass transfer coefficient shell side, k_{o1} (cm/s)	4.88×10^{-4}	8.29×10^{-4}	3.50×10^{-3}	2.59×10^{-3}	3.68×10^{-3}

3.4. Transport of Uranium in once through mode operation of hollow fiber contactor

Polysulfone contactors (PS1 and PS2) have been employed for recovery of uranium from nitrate medium through HFDLM process using 30% v/v TBP in dodecane. Using PS1 and PS2 contactor, percent extraction of 28% and 40% has been achieved, respectively, in single pass of the feed solution. Prediction has been made by developed model using parameters from Table 2 and shown in Fig. 5 along with the data. Prediction agrees with the data.

Similar studies have been conducted using microporous contactors with polypropylene lumen (PP1, PP2 and PP3) and percent extraction of 55%, 75% and 95% has been observed, respectively. Model prediction,using parameters from Table 2, is shown in Fig. 6 along with the data. Prediction ties in well with the data.

At $z = l$, Eq. (15) can be written as

$$\ln\left(\frac{C_f}{C_{f0}}\right) = \frac{-2r_{lm}\varepsilon K_{Df}l}{vr_1^2\left(\frac{K_{Df}}{k_f} + \frac{1}{k_o}\right)} \tag{22}$$

Eq.(22) can be rearranged as

$$\frac{K_{Df}}{k_f} + \frac{1}{k_o} = \frac{-2r_{lm}\varepsilon K_{Df}l}{vr_1^2\ln\left(C_f / C_{f0}\right)} \tag{23}$$

The extraction of uranium is defined as

$$E = \left(1 - \frac{C_f}{C_{f0}}\right) \tag{24}$$

Combining Eqs.(23) and (24)

$$\frac{K_{Df}}{k_f} + \frac{1}{k_o} = \frac{-2r_{lm}\varepsilon K_{Df}l}{vr_1^2\ln\left(1 - E\right)} \tag{25}$$

Substituting $L_f = L(1 - \alpha)$ & $L_o = L\alpha$, Eqs.(7) and (8) can be rewritten as

$$\frac{1}{k_f} = \frac{d_f + L(1 - \alpha)}{D_f} \tag{26}$$

$$\frac{1}{k_o} = \frac{L\alpha}{D_{oeff}} + \frac{d_o}{D_o} \tag{27}$$

Substituting k_f and k_o from Eqs. (26) and (27) in Eq. (25)

$$\frac{K_{Df}\left(d_f + L(1 - \alpha)\right)}{D_f} + \frac{L\alpha}{D_{oeff}} + \frac{d_o}{D_o} = \frac{-2\,r_{lm}\varepsilon\,K_{Df}l}{vr_1^2\ln\left(1 - E\right)} \tag{28}$$

Substituting $k_{f1} = D_f/d_f$ and $k_{o1} = D_o/d_o$, Eq. (28) can be rewritten as

$$K_{Df}\left(\frac{1}{k_{f1}} + \frac{L(1 - \alpha)}{D_f}\right) + \frac{L\alpha}{D_{oeff}} + \frac{1}{k_{o1}} = \frac{-2r_{lm}\varepsilon K_{Df}l}{vr_1^2\ln\left(1 - E\right)} \tag{29}$$

Simplifying Eq. (29)

$$\frac{-2r_{lm}\varepsilon l}{vr_1^2\ln\left(1 - E\right)} = \left(\frac{1}{K_{Df}D_{oeff}} - \frac{1}{D_f}\right)L\alpha + \left(\frac{1}{k_{f1}} + \frac{L}{D_f} + \frac{1}{K_{Df}k_{o1}}\right) \tag{30}$$

Since the diffusion coefficient of the metal-carrier complex in the organic phase is much lower than that of the metal ion in the aqueous feed phase (as per Table 2), mass transfer resistance inside membrane is controlling. Hence, estimation of fraction of the pore length wetted by the organic phase is necessary for estimation of the rate of extraction. Eq. (30) has been used for estimation of the fraction of the pore length wetted by the organic phase for known extraction in PS and PP contactors. It is found that 40% of the pore length is wetted by the organic phase in PS2 contactor. Similarly, for PP1, consisting hydrophobic polypropylene lumen, α is estimated to be 1.1. This implies that in the case of PP membrane, the entire length of the pore is wetted by the organic phase. Value of α greater than one, implies that part of the liquid protrudes out from the pore in the form of convex meniscus. A small extent of leakage of the organic phase in the feed is also expected. It was indeed observed in PP membrane, whereas no perceptible leakage was detected with PS membrane. In spite of this drawback, PP1 module is found to exhibit greater extent of extraction than PS1 and PS2. This is because, the fiber wall thickness (L) of PP lumen is one
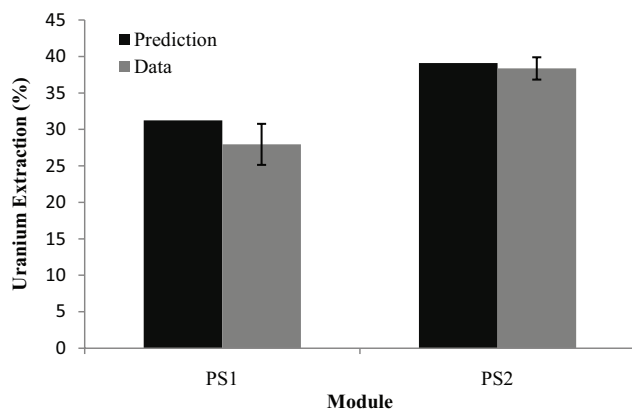

Fig. 5. Extraction of uranium from nitrate medium using polysulfone (PS) contactors in once-through mode; organic: 30% v/v TBP dissolved in dodecane, aqueous strip: 1 M NaHCO$_3$, W/O ratio in dispersion is 1:1 v/v; agitation 3000 rpm.
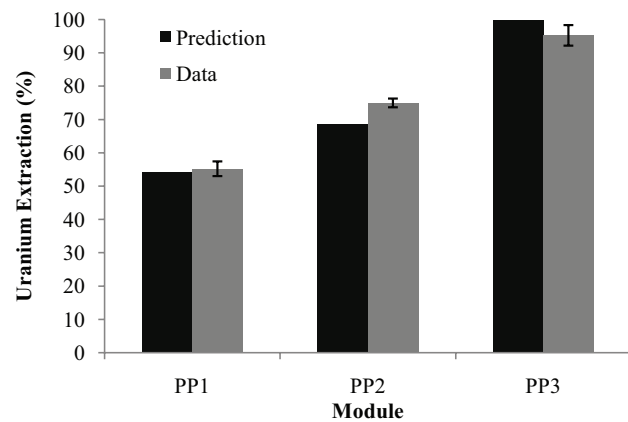

Fig. 6. Extraction of uranium from nitrate medium using polypropylene (PP) contactors in once-through mode; organic: 30% v/v TBP dissolved in dodecane, aqueous strip: 1 M NaHCO$_3$, W/O ratio in dispersion is 1:1 v/v; agitation 3000 rpm.
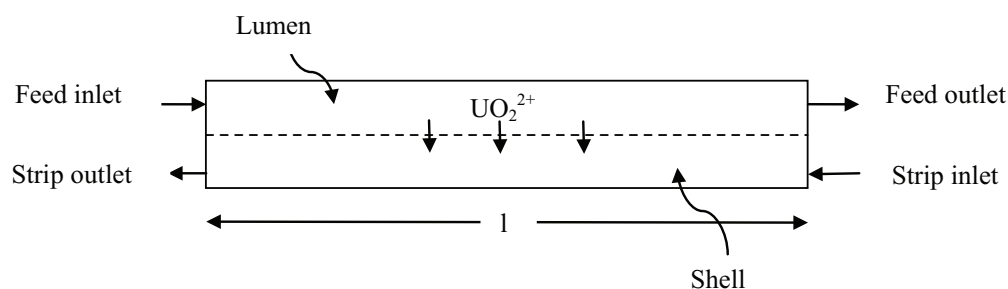
Fig. 7. Schematic of the separation process showing a hollow fiber lumen of length, l.

Table 3
Effect of increase in lumen length on uranium extraction, (a) PS contactor (b) PP contactor

(a)

Length of the fiber, l (cm)	Extraction % (prediction)	Extraction % (data)
40	31.25	28 (generated using PS1)*
42	41.28	39.9 (generated using PS2)*
45	43.47	
50	46.94	
55	50.20	
60	53.26	

*Effective length of lumen, l in PS1 and PS2 contactors are 40 and 42 cm, respectively.

(b)

Length of the fiber (cm)	Extraction % (prediction)	Extraction % (data)
16	54.21	55.21 (generated using PP1) #
20	62.33	
25	70.49	73.64 (generated using PP2) #
30	76.88	
40	85.81	
50	91.29	
62	98.56	98.30 (generated using PP3) #

#Effective length of lumen, l in PP1, PP2 and PP3 contactors are 16, 25 and 62 cm, respectively.

order of magnitude less than that of the PS lumen as mentioned in Table 1. Hence, the reduction in the rate of diffusion of uranium ions due to higher value of α in PP lumen is overcompensated by its shorter pore length, L.

It has also been understood through Eq. (30) that gradient of $L\alpha$ depends upon diffusion coefficient of solute in organic liquid membrane phase sitting inside the pores, D_{oeff} (= $D_o(\varepsilon/\tau)$). This diffusion coefficient will vary among different polymeric membranes because it depends on the characteristic properties of porous polymeric support such as its porosity, ε and tortuosity, τ. Thus, for polymeric membranes with higher ε/τ (i.e. higher D_{oeff}), result in low gradient of $L\alpha$. Hence, for those membranes, extraction of solute (E) will be less dependent on the fraction of the pore length wetted by the organic membrane phase, L_o (= $L\alpha$).

3.5. Utilization of the model for scale up of the process

The model has been utilized to predict the performance of PS and PP hollow fiber contactors, respectively, on their scale up. Parameters conserved during scale up are feed flow velocity, mass transfer coefficients of aqueous and organic phases and fiber characteristic properties. Parameters scaled up are mass transfer area and throughput. Fig. 7 presents the schematic of the separation process showing a hollow fiber lumen of length l. Prediction of extraction made using PS1 and PP1 with parameters conserved as above has been shown in Table 3. PS1 predicts the performance of PS2 for increased lumen length of 42 cm. Prediction made using PS1 ties in well with the data generated using PS2 and shown in Table 3a. Similarly, PP1 predicts the performance of PP2 and PP3 for increased lumen length of 25 cm and 62 cm. Predictions made using PP1 have found in agreement with the data generated using PP2 and PP3 and shown in Table 3b. Hence, the present model can be easily utilized for scale up of HFDLM process with limited experimental trials.

4. Conclusions

Our study has presented a mathematical model for estimation of the wetted length of the fiber pore. Developed model is not system specific and can be used for prediction of extraction rate of other ions and other types of polymeric membranes. It is found that 40% of the pore length is wetted by the organic phase in polysulfone contactor. Similarly, for polypropylene contactor, consisting hydrophobic polypropylene lumen, α is estimated to be 1.1. This implies that in the case of polypropylene membrane, the entire length of the pore is wetted by the organic phase. Polypropylene module is found to exhibit greater extent of extraction than polysulfone. This is because, the fiber wall thickness of PP lumen is one order of magnitude less than that of the PS lumen. Hence, the reduction in the rate of diffusion of uranium ions due to higher value of α in PP lumen is overcompensated by its shorter pore length. It has also been understood that for polymeric membranes with higher ε/τ, extraction of solute will be less dependent on the fraction of the pore length wetted by the organic membrane phase. The model has been utilized to predict the performance of PS and PP hollow fiber contactor, respectively, on their scale up. Prediction is found in agreement with the data.

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