Korean J. Chem. Eng., **26**(3), 765-769 (2009)

Reduction of concentration polarization at feeding interphase of a hollow fiber supported liquid membrane by using periodic operation

Prakorn Ramakul*,†, Natchanun Leepipatpiboon, Chamaiporn Yamoum*, Uthen Thubsuang*, Sirapop Bunnak*, and Ura Pancharoen*****

*Department of Chemical Engineering, Faculty of Engineering and Industrial Technology Silpakorn University, Nakhon Pathom 73000, Thailand
**Department of Chemistry, Faculty of Science, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand
***Department of Chemical Engineering Faculty of Engineering, Chulalongkorn University Patumwun, Bangkok 10330, Thailand
(*Received 26 June 2008 • accepted 17 December 2008*)

Abstract−An experimental investigation was carried out to reduce the concentration polarization at feeding interphase between feed solution and liquid membrane imposing flow instabilities. The periodic operation of the hollow fiber supported liquid membrane for separation of lanthanide metal by using D2EHPA as extractant dissolved in kerosene. The operating flow rate of the feed solution was varied according to a symmetric square wave function around time-average values of 200, 300 and 400 ml/min. Time periods ranging from 18 to 3 minutes and amplitudes of 50 and 100 ml/min were investigated. The results of these periodic tests were compared with results obtained from the conventional steady-state mode of operation. It has been found that the periodic operation leads to higher stripping concentration or higher ion flux than that obtained from the corresponding steady state operating conditions. This is because periodic operation disturbs concentration polarization in the boundary layer between the feed solution and liquid membrane. It has also been found that the ion flux increases with increasing amplitudes and decreasing time periods of the forcing function. However, when the period is less than 3 minutes the flux decreases because the liquid membrane is peeled out from the pores of hollow fiber.

Key words: Liquid Membrane, Hollow Fiber, Instabilities Flow, Periodic Operation, Concentration Polarization

INTRODUCTION

A number of researchers have studied efficient separation and purification of ions from an aqueous solution by using liquid membranes. This technology combines solvent extraction and stripping processes in a single step. It does not require phase-mixing for good mass transfer. Instead, the two phases come in contact with each other through a rigid, thin and porous membrane, stabilizing the interface between the two phases. These membranes are specially attractive for treatment of dilute solutions, recovery of metal [1,2] and strategic importance, pollutant removal and bioseparation [3,4]. Hollow fiber is one of the most popular membranes used industrially because of its several beneficial features that make it attractive for those industries. Among them are lower amount of extractant than solvent extraction, long life time, low energy and high selectivity [5].

However, it also has some disadvantages which lead to its application constraints. The main disadvantage is concentration polarization, which is more frequent than other membranes [6], especially when the feed concentration is very high [7].

Periodic operation of chemical engineering processes has been the subject of many investigations in the past two decades. In many cases the time-average performance of the process with cyclic or periodic operation was higher than the steady state operations [8-10]. The processes for which periodic operation has been investigated include distillation, solvent extraction, membrane system and heat exchange [11,12]. Periodic operation of chemical reactors has been shown to increase the rate of reactions compared to steady state operation [13-15].

Therefore, improving the performance of membrane processes by imposing flow instabilities has also been the subject of many studies in recent years. A very good work of the process that uses various types of flows was provided by Winzeler and Belfort [16]. The techniques are the use of membranes with steady flow and pulse flow. The unsteady flow tends to produce better mixing and reduce the resistances caused by fouling and concentration polarization [6]. The result is a higher permeate flux. For example, Kennedy obtained about 70% increase in the permeate flux by oscillating the flow of a sucrose solution to a reverse osmosis unit [17]. Ilias and Govind [18] showed that the extra power required to obtain such a gain in transmembrane flux is a minute fraction of power needed to maintain the corresponding steady flow. Several researchers reported higher gains by using periodic flow to operate microfiltration, ultrafiltration [19] and pervaporation [20].

The goal of this work is to study the effect of the periodic operation compared to steady state operation on the performance of hollow fiber supported liquid membrane process. Lanthanum (III) is the representative of metal ion. The operating flow rates were varied in symmetric square waves about a time-average value. The effect of amplitude and period of the wave was investigated.

THEORY

A liquid membrane, which was composed of a diluent and an extractant and served to bind one of the components very selectively

†To whom correspondence should be addressed.
E-mail: korn_mass_transfer@hotmail.com

from the feed solution was immobilized in the pores of a hydrophobic microporous supporter. The supported liquid membrane (SLM) separated the aqueous feed solution and the strip solution. The species were accumulated in the strip at a concentration generally higher than that in the feed solution. The permeation of the species proceeded due to a chemical potential gradient (the driving force of the process) existing between the two opposite sides of the SLM [21,22] where the transport mechanism of metal ions is described as follows. The metal ions form a complex with the extractant at the interface feed phase/membrane. This complex diffuses through the membrane phase to the interface between the membrane and the strip phases where a decomposition of the metal complex takes place. In this case, the carrier is D2EHPA. The transport mechanism of metal ions is shown and described elsewhere [1,2,7,21].

$$La^{3+}+HR_3 \leftrightarrow LaR_3+3H^+ \tag{1}$$

Lanthanum (III) represents the metal ions. Eq. (1) is the extraction reaction equation. Forward reaction occurs at feed-membrane interphase and a backward reaction occurs at membrane - strip interphase. The driving force is achieved by hydronium ion (pH) gradient.

The hollow fiber module consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane, solution of D2EHPA in kerosene, was trapped in hydrophobic micropore due to capillary force [21] and separated feed and strip solution. In this work, lanthanum ion solution as feed phase flowed in tube side and sulfuric acid as stripping phase flowing in shell side [22-24].

EXPERIMENTAL

1. Chemicals

The chemicals used were: $LaCl_2 \cdot 7H_2O$ was used in the feed solution The organic solvent used for soaking the filter membranes was kerosene, and Di(2-ethyl hexyl) phosphoric acid (D2EHPA) is the extractant. Nitric acid was applied as the strip solution. All chemicals were of A.R. grade and supplied by Merck.

2. Apparatus

(1) The hollow fiber, which is manufactured by Hoechst Celanese, Charlotte, NC (Liqui-Cel Extra-Flow module), was used as a support material [1,22] This module uses Celgard microporous polypropylene fibers that are woven into the fabric and wrapped around a central tube feeder that supplies the shell side fluid. Woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers [25]. The fiber is potted into a solvent resistant polyethylene tube sheet and shell casing in polypropylene.

(2) The Liqui-Cel Laboratory Liquid/Liquid Extraction Systems were used. They are composed of two gear pumps, two speed controllers, two rotameters and two pressure gauges. The flow diagram is shown in Fig. 1.

(3) Inductively coupled plasma spectroscopy (ICP) was used to measure the concentrations of Lanthanum (III).

3. Procedure

A microporous hydrophobic PTFE membrane was impregnated with 5% (v/v) Di(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene for 20 minutes. Consequent up on the impregnation, the excess oil was wiped out and then sandwiched between the feed and stripping solutions. In all cases, feed solutions were 600 ppm of lanthanum ion dissolved in 0.1 M nitric acid and the stripping solution was 0.5 M nitric acid. After that, the experiment was started by flowing feed solution in the tube side. Simultaneously, recovery solution was pumped into the shell side counter-currently and one-through mode operation was used. The flow diagram is shown in Fig. 1.

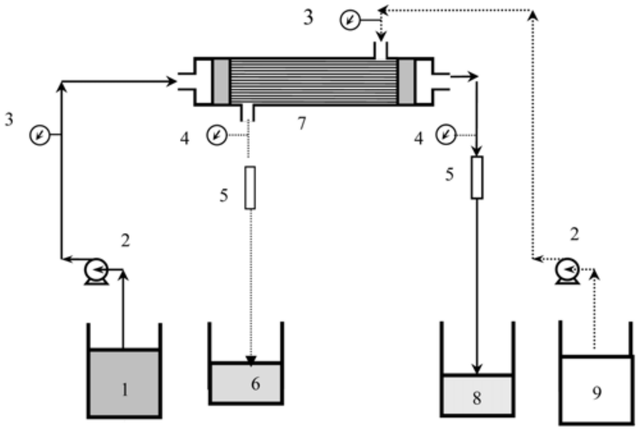

Fig. 1. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.

1. Feed reservoir	6. Stripping outlet reservoir
2. Gear pump	7. Hollow fiber module
3. Inlet pressure gauges	8. Raffinate reservoir
4. Outlet pressure gauges	9. Inlet stripping reservoir
5. Flow meters	

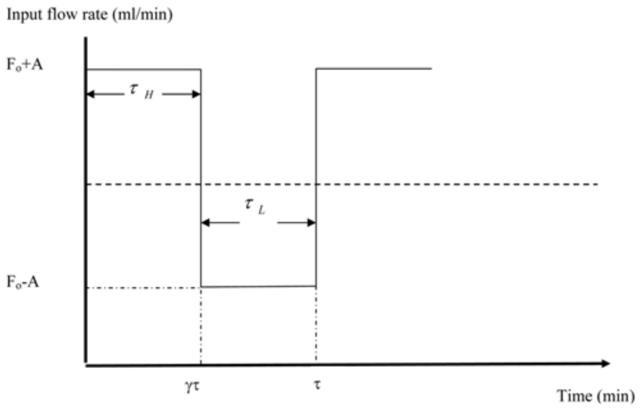

Fig. 2. Symmetric square wave function for periodic operation feed flow.

For periodic operation mode, periodic tests were performed using a square wave forcing function by fluctuating the operating flow rate of feed solution around and average value of flow rate as shown in Fig. 2 where F^H and F^L are the higher and lower operating flow rate, respectively. The time split, γ is the ratio between τ^H and τ^L while τ^H and τ^L are the duration of operation at the higher and lower flow rate, respectively. The effect of amplitude (A) (F^H–F^L) and period (τ) were examined. A number of experiments were performed using a range of γ values, all yielding the same average flow rate, $\overline{F}$; three average flow rates were employed in the present work: 200, 300 and 400 ml/min.

The transport of lanthanum from feed phase to the receiving phase

Table 1. Effect of amplitude and period on the flux of lanthanum ion in difference average flow rate while using 5% (v/v) D2EHPA, 600 ppm of lanthanum in 0.1 M Nitric acid and 0.5 M nitric acid for stripping solution. F is the flux of lanthanum ion, mg/m^2·min and F_N is normalized flux of lanthanum ion, dimensionless

Period (τ)	Average flow rate (ml/min)														
	200					300					400				
	Steady flow	Amplitude of PO (ml/min)				Steady flow	Amplitude of PO (ml/min)				Steady flow	Amplitude of PO (ml/min)			
		50		100			50		100			50		100	
		F	F_N	F	F_N		F	F_N	F	F_N		F	F_N	F	F_N
0	125	125	1.00	125	1.00	112	112	1.00	112	1.00	85	85	1.00	85.0	1.00
3	125	118	0.95	114	0.91	112	98.5	0.88	91.8	0.82	85	72	0.85	72.2	0.85
6	125	146	1.17	148	1.19	112	127	1.14	129	1.16	85	92	1.08	91.8	1.08
9	125	140	1.12	143	1.15	112	120	1.08	123	1.10	85	90	1.05	89.2	1.05
12	125	135	1.08	138	1.10	112	117	1.05	119	1.07	85	87	1.03	87.5	1.03
15	125	128	1.03	134	1.07	112	113	1.01	114	1.02	85	86	1.01	86.8	1.02
18	125	125	1.00	126	1.01	112	112	1.00	112	1.00	85	85	1.00	85.0	1.00

was measured by taking samples from the feed and stripping solutions and analyzed for the transport of lanthanum ion. The concentration of lanthanum ions was measured by inductively coupled plasma spectroscopy (ICP).

RESULT AND DISCUSSION

All of the fluxes of lanthanum ions are shown in Table 1 and they have been normalized by dividing them by the flux obtained through steady operation, which are 125, 112 and 85 mg/m^2·min for the average flow of 200, 300 and 400, respectively. For example, when τ=6 minutes, amplitude (A)=100 ml/min and flow-average=200 ml/min, the flux was 148 mg/m^2·min. So, the normalized values, F_N= 148/125=1.19, which is 19% higher than the rate obtained from steady operation.

Fig. 3 shows the normalized flux of lanthanum ions corresponding to periodic operation around flow-average of 200, 300 and 400 ml/min, respectively. According to Figs. 3-5, the flux of lanthanum ion increased as the frequency and the amplitude increased. Periodic operation of around the flow-average of 300 and 400 ml/min yielded similar trends as shown in Figs. 4 and 5, respectively. When the average flow rate of the feed solution was decreased, the percentage of extraction increased due to the residence time [23], but the average flow rate, which is lower than 200 ml/min, cannot be performed because when the amplitude is 100 ml/min, the flow rate goes down and is too low to operate.

A simplified theoretical model was used to predict the performance of the hollow fiber liquid membrane system. The model incorporates the effect of concentration polarization. The main effect

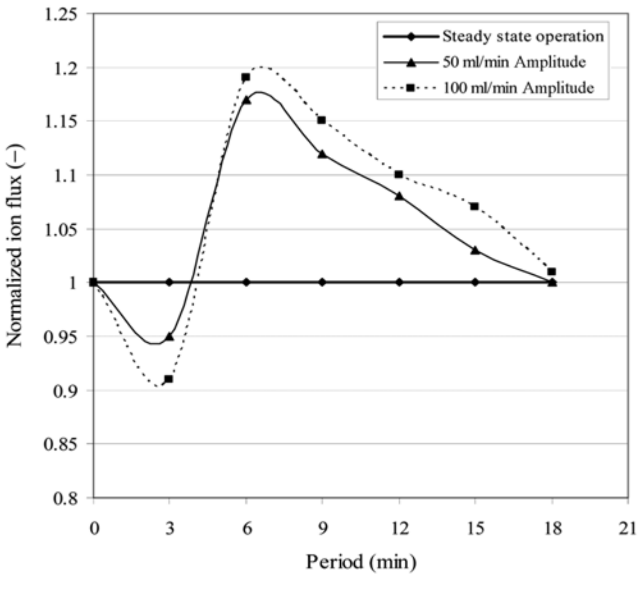

Fig. 3. Normalized lanthanum flux corresponding to periodic operation around average flow rate of feed solution of 200 ml/min.

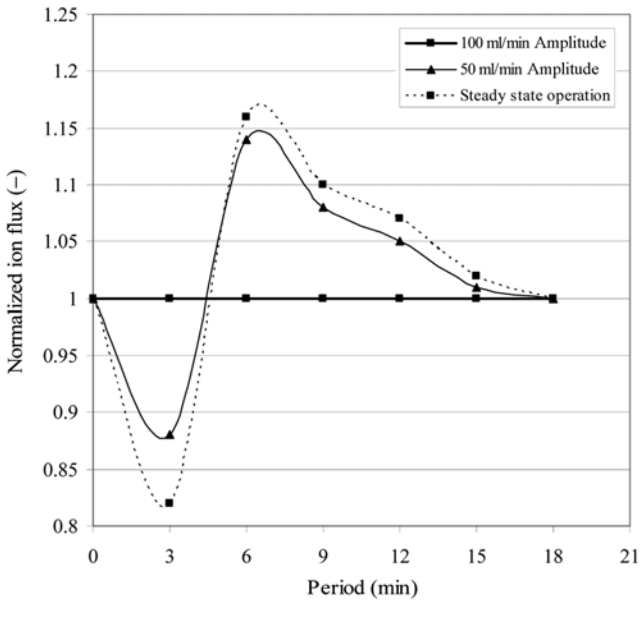

Fig. 4. Normalized lanthanum flux corresponding to periodic operation around average flow rate of feed solution of 300 ml/min.

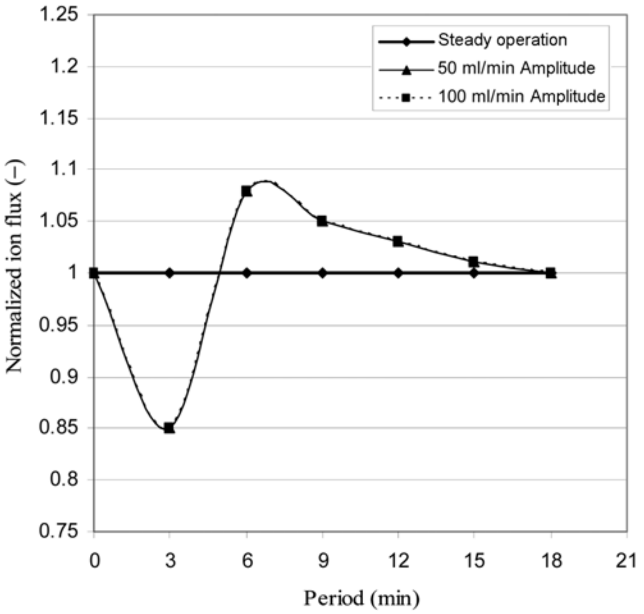

Fig. 5. Normalized lanthanum flux corresponding to periodic operation around average flow rate of feed solution of 400 ml/min.

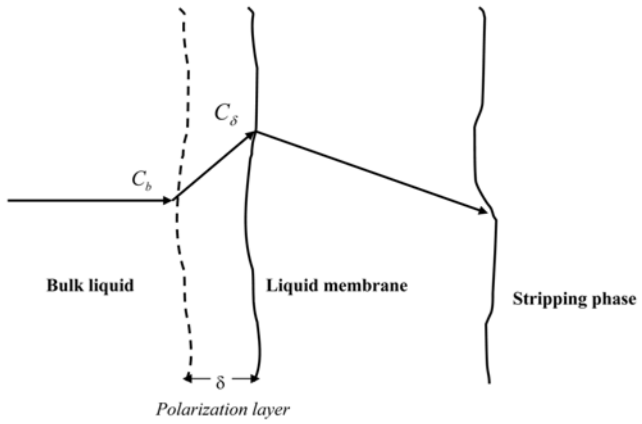

Fig. 6. Concentration profile in liquid membrane process.

of mass transfer is concentration polarization, because it decreases the value of the mass transfer coefficient [6]. A material balance within this layer between the solute carried to the membrane by convection and the solute carried away by diffusion leads to the following equation [26]:

$$J = D\frac{dc}{dx} \tag{2}$$

where J is the flux of metal ion, D is the diffusivity of the solute, c is the solute concentration and y is the distance perpendicular to the membrane wall. Solving this equation by the boundary condition $c=c_b$ at x=0 and $c=c_\delta$ at $x=\delta$, the result is the following expression:

$$J=k(C_\delta-C_b) \tag{3}$$

$$\text{where } k = \frac{D}{\delta} \tag{4}$$

is the mass transfer coefficient, δ is the thickness of the boundary layer, subscript b refers to the bulk. It should be noted that C_δ is not directly known, as it is higher than the concentration in the bulk of the solution, C_b. A thin concentration boundary layer is assumed to exist next to the membrane wall within which the concentration varies from a value of C_b to a maximum value of C_δ.

The discussion for the increasing of lanthanum ion flux with periodic operation may be given in terms of the effect of such an operation mode on polarization. It is known that polarization is caused by a higher ion concentration in the region near the membrane compared to the bulk of the feed. This leads to a higher thickness of the boundary layer, δ. From Eq. (3 and 4), when δ increases, the mass transfer coefficient decreases and the flux of metal ions decreases. Therefore, when periodic operation is being performed, the high concentration in boundary layer between the feed solution and liquid membrane is disturbed (see Fig. 6), leading to a lower thickness of the boundary layer, δ, and hence higher lanthanum ion flux. The higher normalized flow rate can be seen in Figs. 3-5. The low period (high frequency) and high amplitude lead to a different from steady flow due to more disturbances to the concentration polarization layer. Unfortunately, the metal flux decreases when the period is lower than 3 minutes because when the frequency is too high, the period is too low; the capillary force which immobilized the liquid membrane at the pore-mouth was destroyed [19,21]. Thus, the liquid membrane was peeled out from pore-mouth by feed solution. From these results, the optimized period is approximately 6 minutes.

CONCLUSIONS

Cyclic variation or periodic operation on the flow rate of feed solution of a hollow fiber supported liquid membrane processes can increase the mass transfer coefficient and enhance the flux of metal ion. The flux increases more with increasing amplitude and decreasing period of the flow of feed solution. The metal ion flux decreases when the period is lower than 3 minutes (frequency higher than 1/3 minute^{-1}) because when the frequency is too high, organic liquid membrane is peeled out from the pores of the hollow fiber.

ACKNOWLEDGMENT

This work was financially supported from the Thailand Research Fund (TRF) and Commission on Higher Education. The authors wish to thank the Separation Laboratory, Department of Chemical Engineering, Chulalongkorn University, Bangkok, Thailand for apparatus.

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