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Roles of Facilitated Transport Through HFSLM in Engineering Applications

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1. Introduction

For a number of manufacturing processes, separation, concentration and purification are important to handle intermediates, products, by-products and waste streams. In this regards mass and heat transfer play a significant role to attain efficient results. Concern to the separation operations, they can be classified as energy-intensive interphase mass transfer processes and less energy- or less material-intensive intraphase mass transfer processes (Henley & Seader, 1981). With environmental and energy constraints in these days, for sustainability it is of much concern the requirements of process intensification and looking for the most effective operation based on green chemistry concepts (Badami, 2008; Escobar & Schäfer, 2010; Matthews, 2007). Membrane technologies are a potential sustainable solution in this point of view. In contrast to the energy-intensive interphase mass transfer processes as distillation and extraction, membrane separation is an intraphase-mass-transfer process without the energy-intensive step of creating or introducing a new phase. It involves the selective diffusion of target species through the membrane at different rates. Although membrane operations are a relatively new type of separation process, several of them are fast-growing and successfully not only in biological systems but also a large industrial scale, e.g., food and bioproduct processing (Jirjis & Luque, 2010; Lipnizki, 2010). They can apply for a wide range of applications and provide meaningful advantages over conventional separation processes. In applications of controlling drug delivery, a membrane is generally used to moderate the permeation rate of a drug from its reservoir to the human body. In applications for safety regulations of food packaging, the membrane controls the permeation of undesirable constituents completely. In separation purposes, the membrane allows one component in a feed mixture to permeate itself but prohibits permeation of others. Among several membrane types, supported liquid membranes (SLMs) or immobilized liquid membranes (ILMs) containing carriers or extractants to facilitate selective transport of gases or ions draw high interest of the researchers and users in the industry as they are advanced economical feasible for pre-concentration and separation of the target species. So far, four types of supported liquid membrane modules (spiral wound, hollow fiber, tubular and flat sheet or plate and frame) have been used in the industry (Baker, 2007; Cui et al., 2010). The

hollow fiber supported liquid membrane (HFSLM) is renowned as a favorable system to separate valuable compounds or pollutants at a very low concentration and has specific characteristics of simultaneous extraction and stripping of the low-concentration target species in one single stage, non-equilibrium mass transfer, high selectivity and low solvent used.

This chapter describes transport mechanisms in HFSLM and shows some applications with reference to our up-to-date publications, for example

- the effective extraction and recovery of praseodymium from nitrate solutions of mixed rare earths, $RE(NO_3)_3$. Mass transfer phenomena in the system, the extraction equilibrium constant (K_{ex}), distribution ratio (D), permeability coefficient (P), aqueous-phase mass-transfer coefficient (k_i) and organic-phase mass-transfer coefficient (k_m) were reported (Wannachod et al., 2011).

- the enhancement of uranium separation from trisodium phosphate (a by-product from monazite processing) by consecutive extraction with synergistic extractant via HFSLM (Lothongkum et al., 2009).

- a mathematical model describing the effect of reaction flux on facilitated transport mechanism of Cu(II) through the membrane phase of the HFSLM system. The model was verified with the experimental separation results of Cu(II) in ppm level by LIX84I dissolved in kerosene. The model results were in good agreement with the experimental data at the average percentage of deviation of 2%. (Pancharoen et al., in press).

2. Principles of liquid membranes

New technologies and developments in membranes can be accessed from journals (e.g., J. Membr. Sci., Sep. Sci. Technol., Sep. Purif. Technol., J. Alloy. Compd.), vendor communications (via websites), patents and conference proceedings, e.g., annual ACS (Prudich et al., 2008). Theories and applications of liquid membranes (LMs) are stated in (Baker, 2007; Baker & Blume (1990); Kislik, 2010; Scott & Hughes, 1996). Refer to Kislik (Kislik, 2010), LMs are classified in different criteria as follows:

- Classification based on module design configurations
1. Bulk liquid membrane (BLM)
2. Supported or immobilized liquid membrane (SLM or ILM)
3. Emulsion liquid membrane (ELM)
- Classification based on transport mechanisms
1. Simple support
2. Facilitated or carrier-mediated transport (The chemical aspects of complexation reactions to the performance of facilitated transport will be discussed later.)
3. Coupled counter- or cotransport
4. Active transport
- Classification based on carrier types
1. Water-immiscible, organic carriers
2. Water-soluble polymers
3. Electrostatic, ion-exchange carriers
4. Neutral, but polarizable carriers
- Classification based on membrane support types
1. Neutral hydrophobic, hydrophilic membranes
2. Electrically charged or ion exchange membranes

3. Flat sheet, spiral wound module membranes
4. Hollow fiber membranes
5. Capillary hollow fiber membranes
- Classification based on applications
1. Metal-separation concentration
2. Biotechnological products recovery-separation
3. Pharmaceutical products recovery-separation
4. Organic compounds separation, organic pollutants recovery from wastewaters
5. Gas separations
6. Fermentation or enzymatic conversion-recovery-separation (bioreactors)
7. Analytical applications
8. Wastewater treatment including biodegradable-separation techniques

2.1 Membrane structures, materials and modules

The performance of membrane relates closely to its structure, material and module. It is known that porous membranes can be classified according to their structures into microporous and asymmetric membranes. Microporous membranes are designed to reject the species above their ratings. They can get blocked easily compared to asymmetric membranes.

In case of membrane materials, polymeric or organic membranes made of various polymers (e.g., cellulose acetate, polyamide, polypropylene, etc) are cheap, easy to manufacture and available of a wide range of pore sizes. However, some limitations like pH, temperature, pressure, etc can impede the applications of polymeric membranes. On the other hand, ceramic or inorganic membranes have advantages of high mechanical strength, high chemical and thermal stability over the polymeric membranes but they are brittle and more expensive.

In terms of membrane modules, the development of membrane module with large surface areas of membrane at a relatively low manufacturing cost is very important. Resistance to fouling, which is a particularly critical problem in liquid separation, depends on the membrane module. Of four types of the SLM modules (spiral wound, hollow fiber, tubular and flat sheet or plate and frame), hollow fiber module (Fig.1) has the greatest surface area-to-volume ratio resulting in high mass transfer coefficient and is the most efficient type of
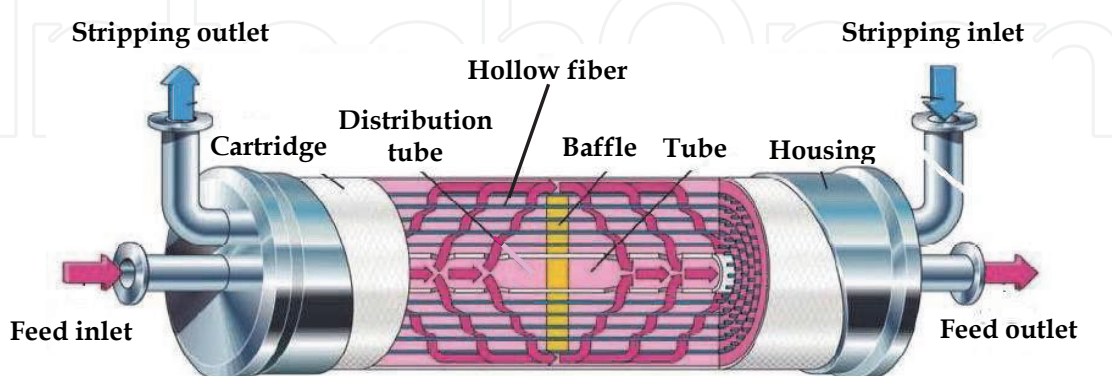

Fig. 1. The hollow fiber module (http://www.liquicel.com/product-information/gas-transfer.cfm)

membrane separation. Hollow fiber module is obviously the lowest cost design per unit membrane area. Compared to flat sheet modules, hollow fiber modules can be operated at higher pressure operation and their manufacturing cost is lower. However, the resistance to fouling of the hollow fibers is poor so the module requires feed pretreatment to reduce large particle sizes. The properties of module designs are shown in Table 1.

Properties	Hollow fibers	Spiral-wound	Flat sheet	Tubular
Manufacturing cost	moderate	high	high	high
Resistance to fouling	very poor	moderate	good	very good
Parasitic pressure drop	high	moderate	low	low
High pressure operation	yes	yes	difficult	difficult
Limit to specific membranes	yes	no	no	no

Table 1. Properties of membrane module designs (modified from Table 2. p. 419, Baker, 2007)

In principle, important performance characteristics of membranes are 1) permeability, 2) selectivity and retention efficiency, 3) electrical resistance, 4) exchange capacity, 5) chemical resistance, 6) wetting behavior and swelling degree, 7) temperature limits, 8) mechanical strength, 9) cleanliness, and 10) adsorption properties (Kislik, 2010). We will discuss in section 3 relevant to permeability, resistance and mass transfer across the HFSLM.

2.2 Hollow fiber supported liquid membrane (HFSLM)
The characteristics of the hollow fiber module are shown in Table 2.

Characteristics	Description
Material	Polypropylene
Fiber ID (μm)	140
Fiber OD (μm)	300
Number of fibers	10,000
Module diameter (cm)	6.3
Module length (cm)	20.3
Effective surface area or contact area (m²)	1.4
Area per unit volume (cm² /cm³)	29.3
Pore size (μm)	0.03
Porosity (%)	30
Tortuosity	2.6

Table 2. Characteristics of hollow fiber module

Hollow fiber modules are recommended to operate with the Reynolds number from 500-3,000 in the laminar flow region. They are one of high economical modules in terms of energy consumption. Other advantages of HFSLM over conventional separations are:
1. high selectivity based on a unique coupled facilitated transport mechanisms and sometimes by using synergistic extractant;

2. simultaneous extraction and stripping of very low-concentration target species (either precious species or toxic species) in one single stage;
3. mild product treatment due to moderate temperature operation;
4. compact and modular design for easy installation and scaling up for industrial applications;
5. low energy consumption;
6. lower capital cost;
7. lower operating cost (consuming small amounts of extractant and solvent and low maintenance cost due to a few moving parts);
8. higher flux;
9. non-equilibrium mass transfer.

As stated, the extremely important disadvantage of HFSLM is the fouling of the hollow fibers causing a reduction in the active area of the membrane and therefore a reduction in flux and process productivity over time. Fouling can be minimized by regular cleaning intervals. The concepts of membrane fouling and cleaning were explained by Li & Chen (Li & Chen, 2010). Active research includes, for example, membrane surface modification (to reduce fouling, increase flux and retention), new module designs (to increase flux, cleanability), etc should be further studied. In short, flux enhancement and fouling control were suggested by different approaches separately or in combination (Cui et al., 2010; Scott & Hughes, 1996):

1. hydrodynamic management on feed side;
2. back flushing or reversed flow and pulsing;
3. membrane surface modification;
4. feed pretreatment;
5. flux control;
6. regular effective membrane cleaning.

3. Mass transfer across HFSLM

Mass transfer plays significant role in membrane separation. The productivity of the membrane separation processes is identified by the permeate flux, which represents rate of target species transported across the membrane. In general practice, high selectivity of membranes for specific solutes attracts commercial interest as the membranes can move the specific solutes from a region of low concentration to a region of high concentration. For example, membranes containing tertiary amines are much more selective for copper than for nickel and other metal ions. They can move copper ions from a solution whose concentration is about 10 ppm into a solution whose concentration is 800 times higher. The mechanisms of these highly selective membranes are certainly different from common membranes which function by solubility mechanism or diffusion. The selectivity of these membranes is, therefore, dominated by differences in solubility. These membranes sometimes not only function by diffusion and solubility but also by chemical reaction. In this case, the transport combines diffusion and reaction, namely facilitated diffusion or facilitated transport or carrier-mediated transport (Cussler, 1997).

For an in-depth understanding of the facilitated transport through liquid membrane, we recommend to read (Kislik, 2010). The facilitated transport mechanisms can be described by solute species partitioning (dissolving), ion complexation, and diffusion. The detailed steps are as follows:

Step 1. Metal ions or target species in feed solution or aqueous phase are transported to a contact surface between feed solution and liquid membrane, subsequently react with the organic extractant at this interface to form complex species.

Step 2. The complex species subsequently diffuse to the opposite side of liquid membrane by the concentration gradient. It is assumed that no transport of target species passes this interface.

Step 3. The complex species react with the stripping solution at the contact surface between liquid membrane and the stripping solution and release metal ions to the stripping phase.

Step 4. Metal ions are transferred into the stripping solution while the extractant moves back to liquid membrane and diffuses to the opposite side of liquid membrane by the concentration gradient to react again with metal ions in feed solution.

The facilitated transport mechanisms through the hollow fiber module are shown in Fig. 2. The facilitated transport through an organic membrane is used widely for the separation applications. The selectivity is controlled by both the extraction/ stripping (back-extraction) equilibrium at the interfaces and the kinetics of the transported complex species under a non-equilibrium mass-transfer process (Yang, 1999).
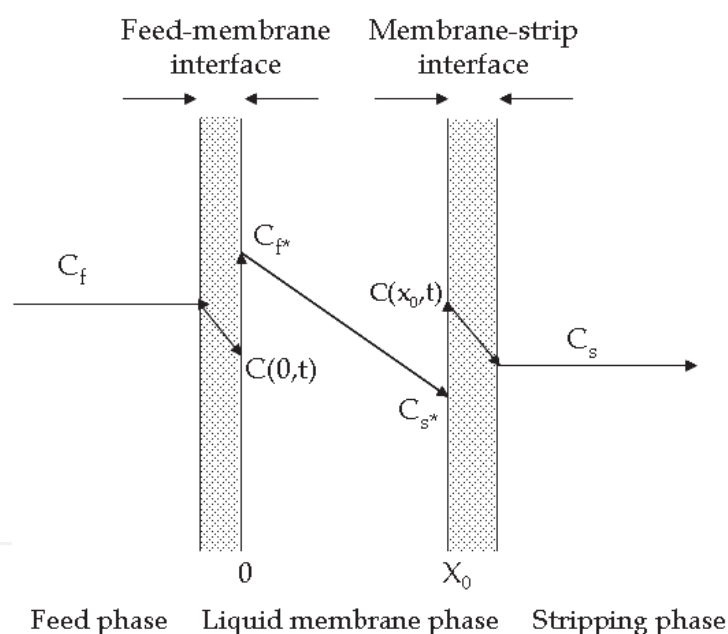

Fig. 2. Facilitated transport mechanisms through the HFSLM

The chemical reaction at the interface between feed phase and liquid membrane phase takes place when the extractant $(\overline{RH})$ reacts with the target species (M^{n+}) in the feed Eq. (1).

$$M^{n+} + \overline{nRH} \rightleftharpoons \overline{MR_n} + nH^+ \tag{1}$$

$\overline{MR_n}$ is the complex species in liquid membrane phase.
The extraction equilibrium constant (K_{ex}) of the target species is

$$K_{ex} = \frac{[\overline{MR_n}] \cdot [H^+]^n}{[M^{n+}] \cdot [\overline{RH}]^n} \tag{2}$$

The distribution ratio (D) is

$$D = \frac{\overline{[MR_n]}}{[M^{n+}]} \qquad (3)$$

The distribution ratio should be derived as a function of the extraction equilibrium constant as

$$D = \frac{K_{ex}\overline{[RH]}^n}{[H^+]^n} \qquad (4)$$

Mass transfer through HFSLM for the separation of the target species in terms of permeability coefficient (P) depends on the overall mass transfer resistance. To determine the overall mass transfer coefficient for the diffusion of the target species through HFSLM, the relationship between the overall mass transfer coefficient and the permeability coefficient is deployed. The permeability coefficient is reciprocal to the mass transfer coefficients as follows (Urtiaga et al., 1992; Kumar et al., 2000; Rathore et al., 2001)

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_o}\frac{1}{k_s} \qquad (5)$$

where k_i and k_s are the feed-phase and stripping-phase mass transfer coefficients, r_{lm} is the log-mean radius of the hollow fiber in tube and shell sides, r_i and r_0 are the inside and outside radius of the hollow fiber, P_m is membrane permeability coefficient relating to the distribution ratio (D) in Eq. (4) and can be defined in terms of the mass transfer coefficient in liquid membrane (k_m) as

$$P_m = Dk_m \qquad (6)$$

Three mass transfer resistances in Eq. (5) are in accordance with three steps of the transport mechanisms. The first term represents the resistance when the feed solution flows through the hollow fiber lumen. The second resistance relates to the diffusion of the complex species through liquid membrane that is immobilized in the porous wall of the hollow fibers. The third resistance is due to the stripping solution and liquid membrane interface outside the hollow fibers. The mass transfer resistance at the stripping interface can be disregarded as the mass transfer coefficient in the stripping phase (k_s) is much higher than that in the feed phase (k_i) according to the following assumptions (Uedee et al., 2008):
1. The film layer at feed interface is much thicker than that at the stripping interface. This is because of a combination of a large amount of target species in feed and co ions in buffer solution at the feed interface while at the stripping interface, a few target species and stripping ions exist. In Eqs. (7) and (8), thick feed interfacial film (l_{if}) makes the mass transfer coefficient in feed phase (k_i) much lower than that in the stripping phase (k_s).

Feed-mass transfer coefficient $\qquad k_i = \frac{D}{l_{if}} \qquad (7)$

Stripping-mass transfer coefficient $\qquad k_s = \frac{D}{l_{is}} \qquad (8)$

2. The difference in the concentration of target species in feed phase (C_f) and the concentration of feed at feed-membrane interface (C_f^*) is higher than the difference in

the concentration of stripping phase at membrane-stripping interface (C_s^*) and the concentration of target species in stripping phase (C_s). At equal flux by Eq. (9), k_i is, therefore, much lower than k_s.

$$J = k_i(C_f - C_f^*) = k_s(C_s^* - C_s) \qquad (9)$$

3. From Eq. (5), we can ignore the third mass transfer resistance. This is attributed to the direct contact of stripping ions with the liquid membrane resulting in rapid dissolution and high mass transfer coefficient of the stripping phase.

P_m in Eq. (5) can be substituted in terms of the distribution ratio (D) and the mass transfer coefficient in liquid membrane (k_m) in Eq. (6) as

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \frac{1}{Dk_m} \qquad (10)$$

In addition, from the permeability coefficient (P) by Danesi (Danesi, 1984):

$$-V_f \ln\left(\frac{C_f}{C_{f,0}}\right) = AP \frac{\beta}{\beta + 1} t \qquad (11)$$

where
$$\beta = \frac{Q_f}{PLN\varepsilon \pi r_i} \qquad (12)$$

We can calculate the permeability coefficient from the slope of the plot between $-V_f \ln\left(\dfrac{C_f}{C_{f,0}}\right)$ against t.

Table 3 shows some applications of HFSLM and their mass transfer related.

4. HFSLM in engineering applications

Compared to conventional separations, membrane separations are attractive for the processing of food, bioproducts, etc where the processed products are sensitive to temperature since most membrane separations involve no chemical, biological, or thermal changes (or moderate temperature changes) of the target component during processing. For environmental-related applications, membrane separation has developed into an important technology for separating volatile organic compounds (VOCs), e.g., acetaldehyde, BTXs, ethylene oxide, trichloroethylene, etc and other gaseous air pollutants from gas streams (Schnelle and Brown, 2002; Simmon et al., 1994).

The following works show the applications of using HFSLM and the role of facilitated transport in separation of praseodymium from nitrate solution of mixed rare earths RE(NO$_3$)$_3$ (Wannachod et al., 2011), separation of uranium from trisodium phosphate from monazite ores processing (Lothongkum et al., 2009) supplied by the Rare Earth Research and Development Center, Office of Atoms for Peace, Bangkok, Thailand, and separation of Cu(II) by LIX84I.

4.1 Effective extraction and recovery of praseodymium from mixed rare earths

Praseodymium (Pr), one of the elements recovered from mixed rare earths (REs), is very useful, e.g., as a composition in mischmetall alloy and a core material for carbon arcs in film

Authors	Species	Extractants	Solvents	P (10^5 m/s)	D 10^3 (-)	k_i (10^3 m/s)	k_m (10^5 m/s)	Results
(Ortiz et al., 1996)	Cr(VI) in synthetic water	Aliquat 336	Kerosene	-	-	-	0.0022	The model results agree well with the experiment
(Marcese & Camderros, 2004)	Cd(II) in synthetic water	D2EHPA	Kerosene	0.1-0.26	-	-	-	The model results reasonably agree with the experiment
(Huang et al., 2008)	D-Phe and L-Phe in synthetic water	Cu(II) N-decyl-(L)-hydroxy proline	Hexanol/ Decane	-	-	4.5x10^{-5}	Rapid diffusion (very low k_m)	The model results agree well with the experiment
(Prapasawat et al., 2008)	As(III), As(V) in synthetic water	Cyanex 923	Toluene	-	-	0.072 0.107	34.5 17.9	The mass transfer in the film layer between the feed phase and liquid membrane is the rate controlling step
(Wannachod et al., 2011)	Pr(III) from RE(NO$_3$)$_3$ solution	Cyanex 272	Kerosene	27-77.5	4.6-15.5	0.103	7.88	The mass transfer in the membrane is the rate controlling step
(Lothongkum et al., 2011)	As from produced water	Aliquat 336 Bromo-PADAP, Cyanex 471, Cyanex 923	Toluene	5.5-11.5	0.63-1.5	0.392	0.102	The mass transfer in the membrane is the rate controlling step
	Hg from produced water	Aliquat 336 Bromo-PADAP, Cyanex 471, Cyanex 923	Toluene	34-53.1	4.5-8.7	22.1	0.013	The mass transfer in the membrane is the rate controlling step

Table 3. Applications of HFSLM and mass transfer related

studio light and searchlights. Praseodymium produces brilliant colors in glasses and ceramics. The composition of yellow didymium glass for welding goggles derived from infrared-heat absorbed praseodymium. Currently, the selective separation and concentration of mixed rare earths are in great demand owing to their unique physical and chemical properties for advanced materials of high-technology devices. Several separation techniques are in limitations, for example, fractionation and ion exchange of REs are time consuming. Solvent extraction requires a large number of stages in series of the mixer settlers to obtain high-purity REs. Due to many advantages of HFSLM and our past successful separations of cerium(IV), trivalent and tetravalent lanthanide ions, etc by HFSLM (Pancharoen et al., 2005; Patthaveekongka et al., 2006; Ramakul et al., 2004, 2005, 2007), we again approached the HFSLM system for extraction and recovery of praseodymium from mixed rare earth solution. The system operation is shown in Fig. 3. Of three extractants, Cyanex 272 in kerosene found to be more suitable for high praseodymium recovery than Aliquat 336 and Cyanex 301 as shown in Fig. 4. Higher extraction of 92% and recovery of 78% were attained by 6-cycle continuous operation about 300 min as shown in Fig. 6.

In this work, the extraction equilibrium constant (K_{ex}) obtaining from Fig. 7 was 1.98 x 10^{-1} (L·mol^{-1})^4. The distribution ratio (D) at Cyanex 272 concentration of 1.0-10 (%v/v) were calculated and found to be increased with the extractant concentration and agreed with Pancharoen et al., 2010. We obtained the permeability coefficients for praseodymium at Cyanex 272 concentration of 1.0-10 (%v/v) from Fig.8. The mass transfer coefficients in feed phase (k_i) and in liquid membrane (k_m) of 0.0103 and 0.788 cm s^{-1}, respectively were

obtained from Fig.9. Because k_m is much higher than k_i, it indicates that the diffusion of praseodymium ions through the film layer between the feed phase and liquid membrane is the rate-controlling step.
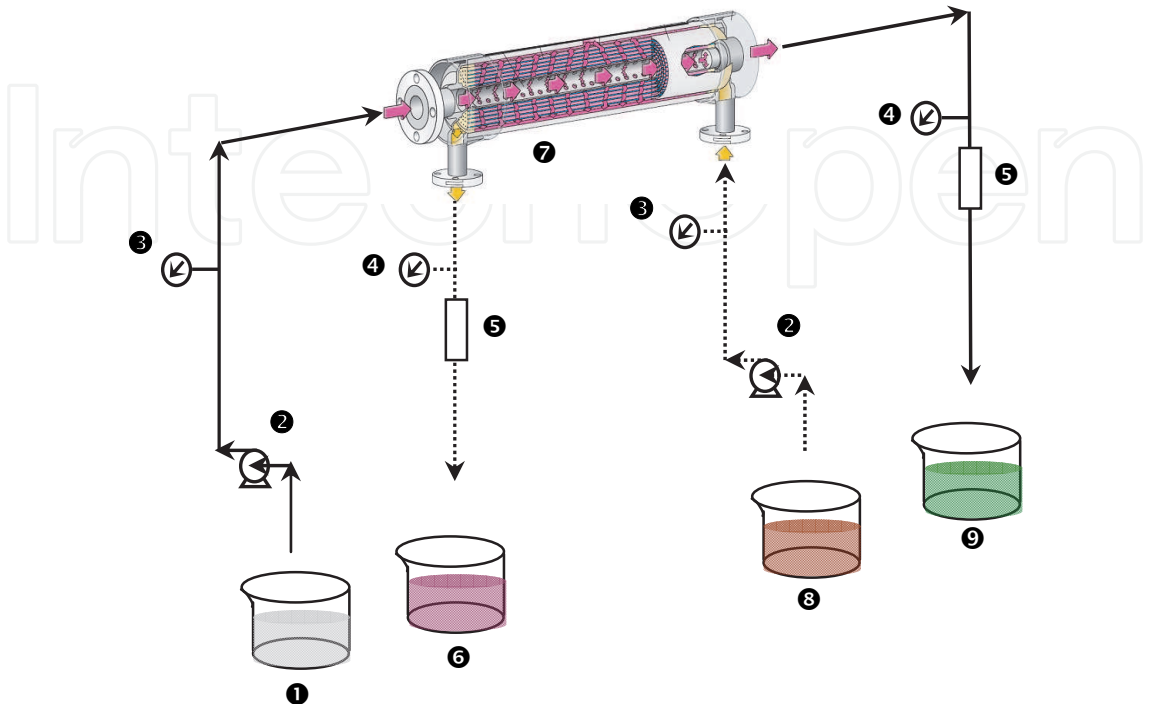

Fig. 3. Schematic counter-current flow diagram for one-through-mode operation of the HFSLM system (❶ inlet feed solution, ❷ gear pumps, ❸ inlet pressure gauges, ❹ outlet pressure gauges, ❺ outlet flow meters, ❻ outlet stripping solution, ❼ the hollow fiber module, ❽ inlet stripping reservoir, and ❾ outlet feed solution)
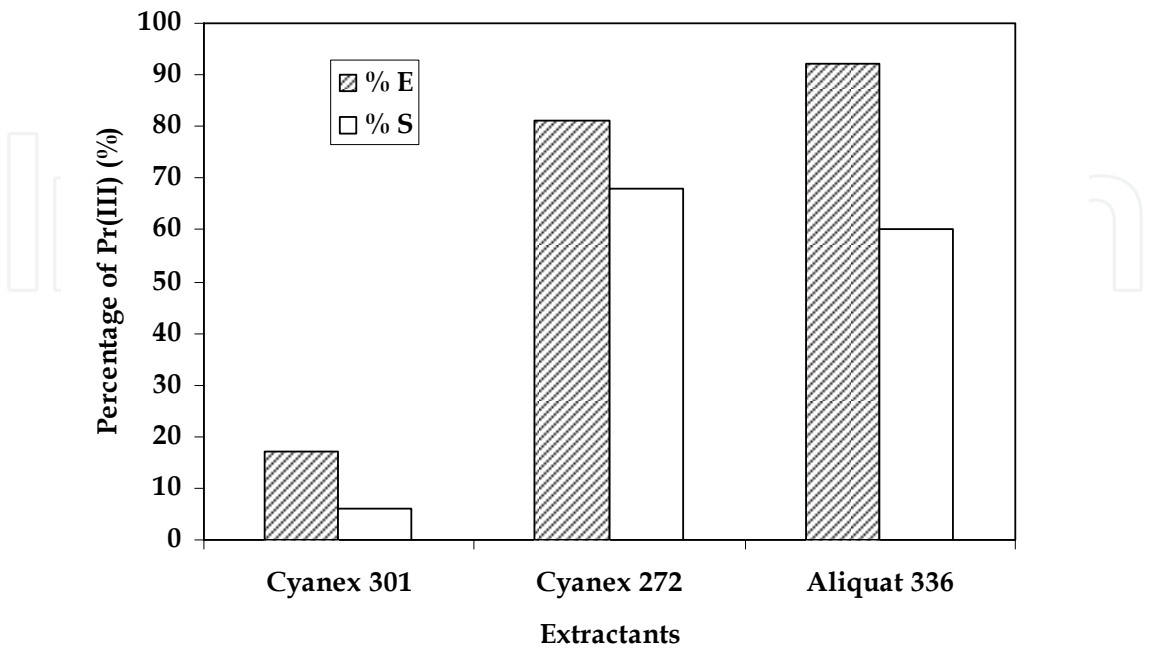
Fig. 4. The percentages of the Pr(III) extraction and stripping from one-through-mode operation
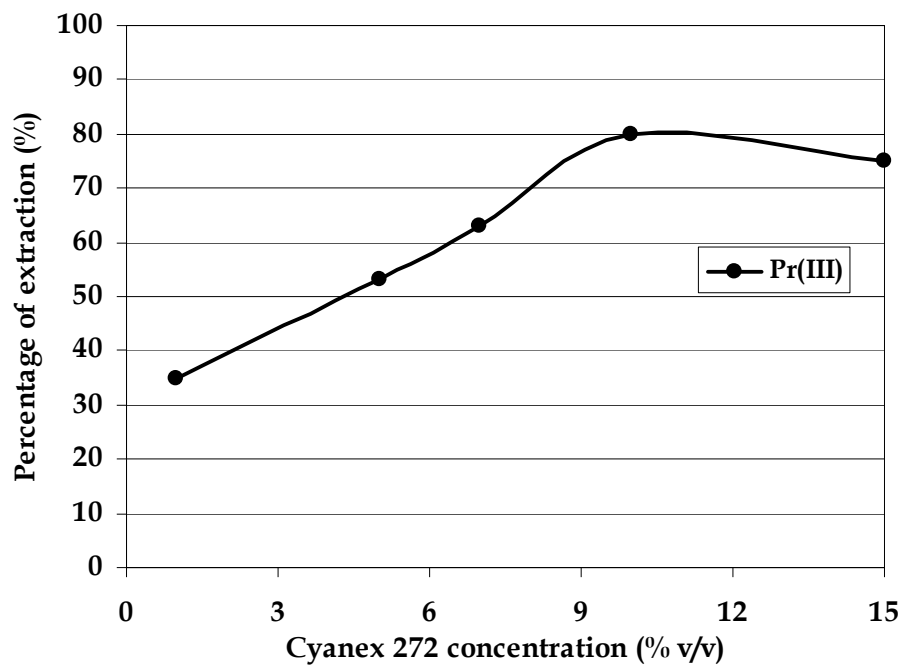
Fig. 5. The percentage of Pr(III) extraction against Cyanex 272 concentration
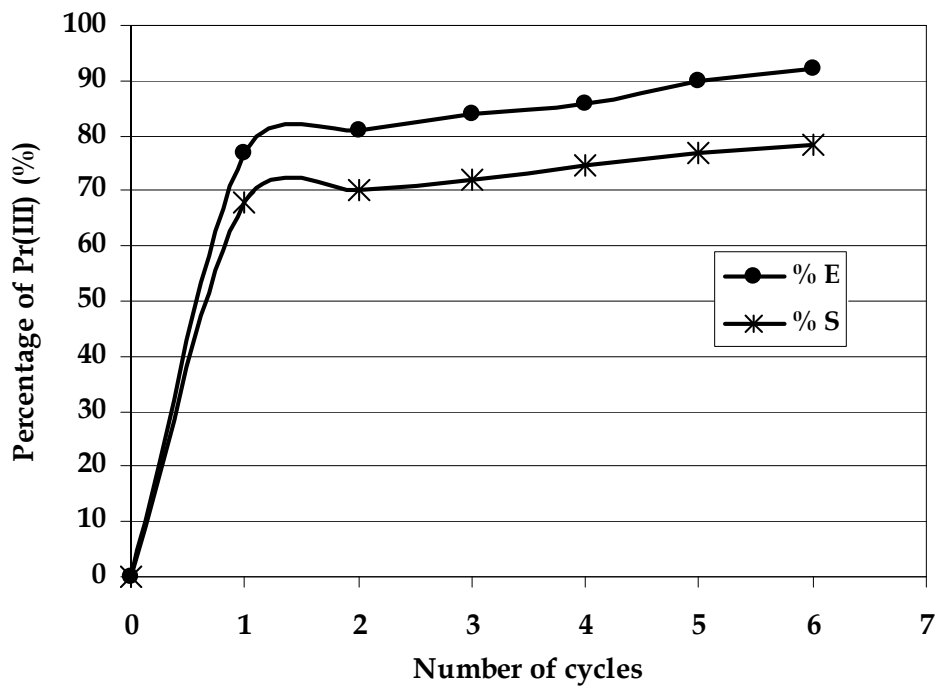
Fig. 6. The percentages of Pr(III) extraction by 10 (%v/v) Cyanex 272 and stripping against the number of separation cycles
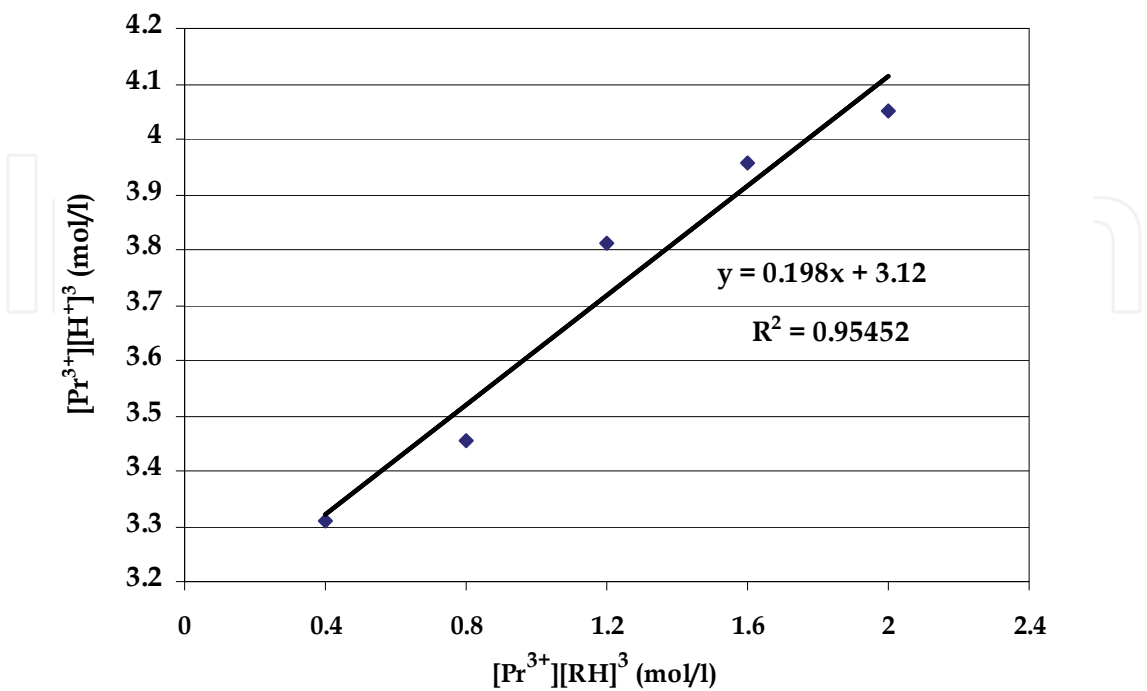
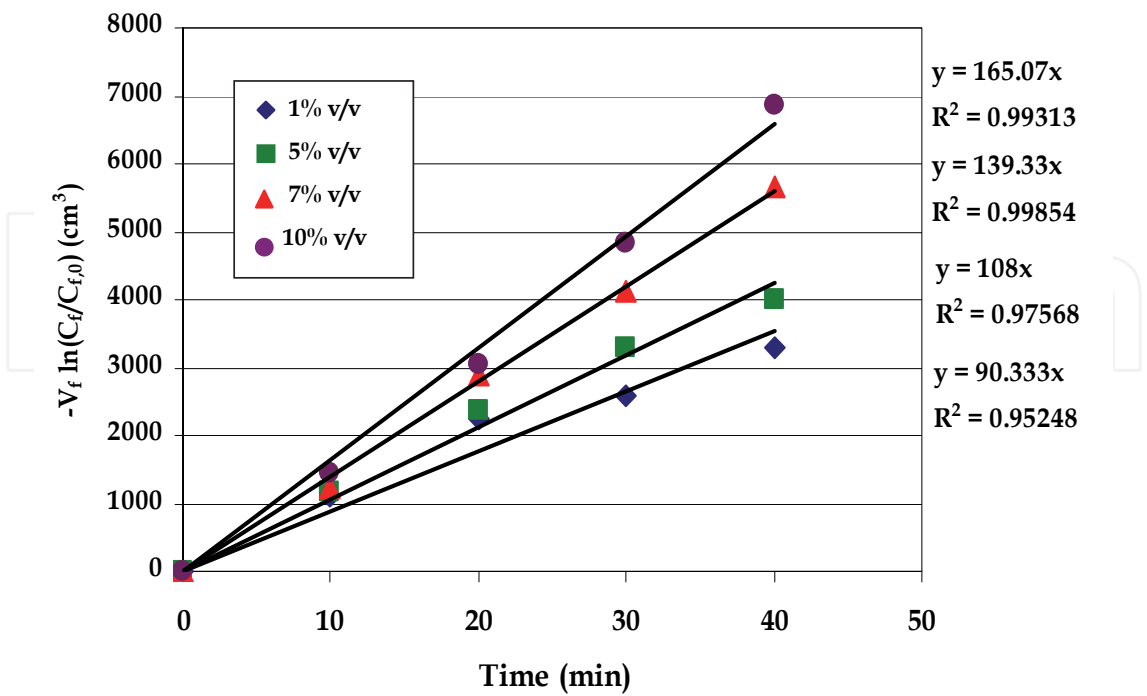Fig. 7. Extraction of Pr(III) by Cyanex 272 as a function of equilibrium $[Pr^{3+}][RH]^3$

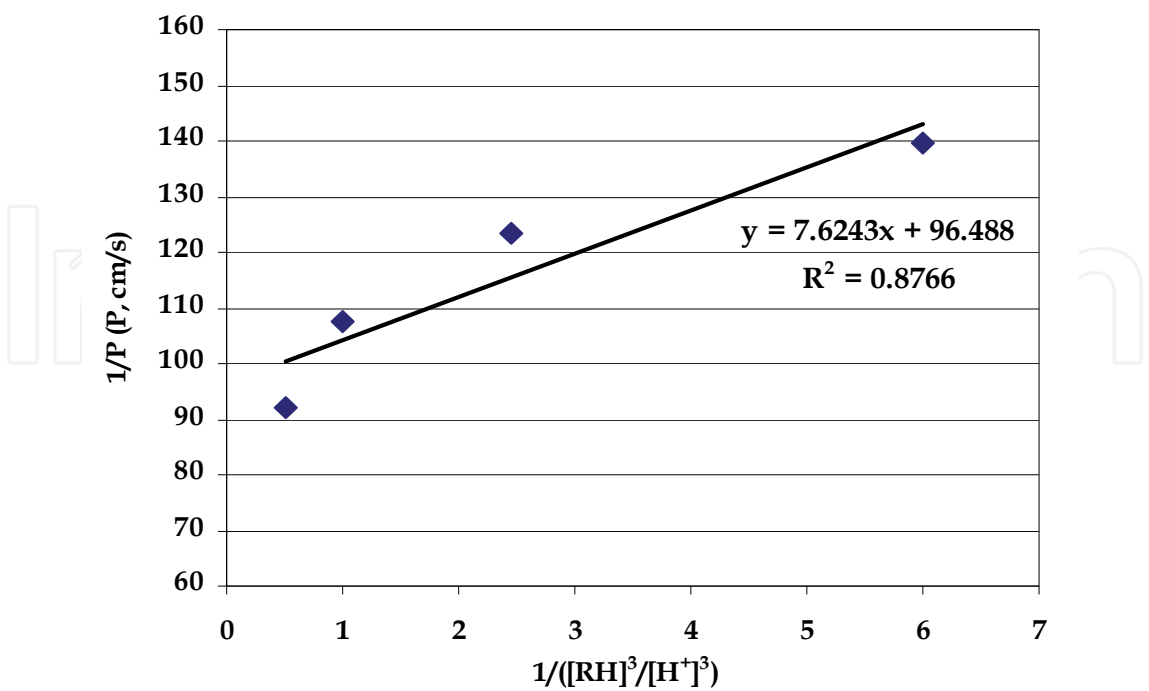Fig. 8. Plot of $-V_f \cdot \ln(C_f / C_{f,0})$ of Pr(III) at different Cyanex 272 concentrations against time
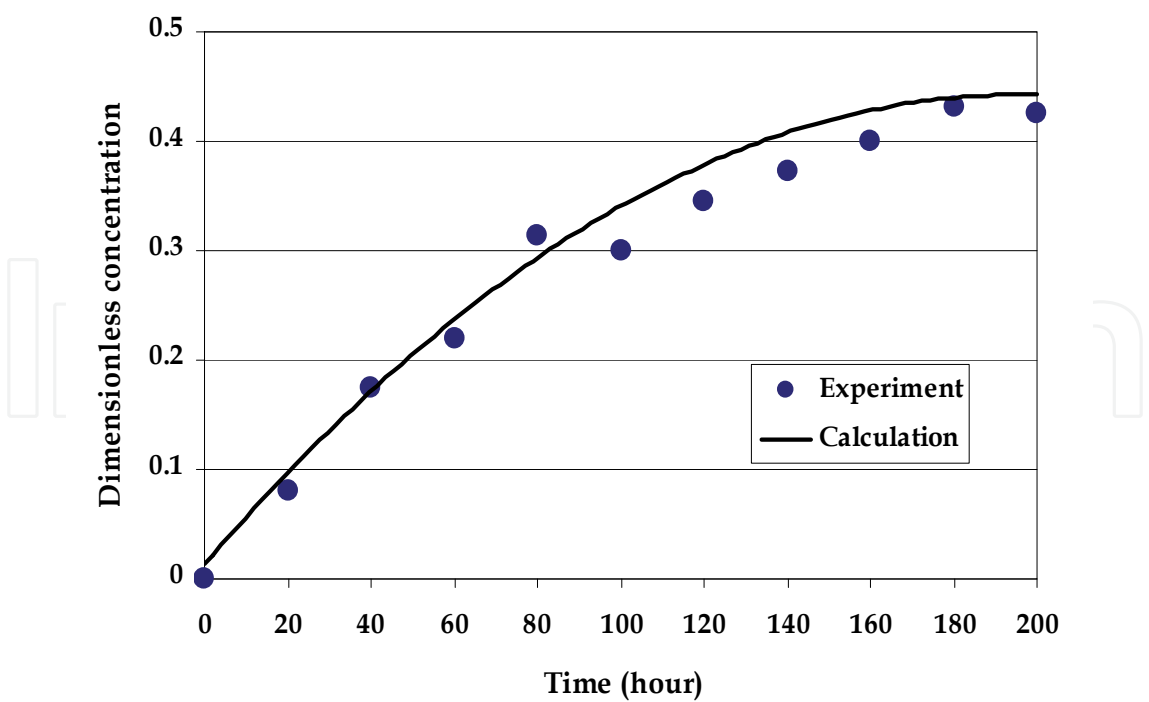
Fig. 9. Plot of $1/P$ as a function of $1/([RH]^3 / [H^+]^3)$

Fig. 10. The model prediction of dimensionless recovery concentration of Pr(III) and experimental results
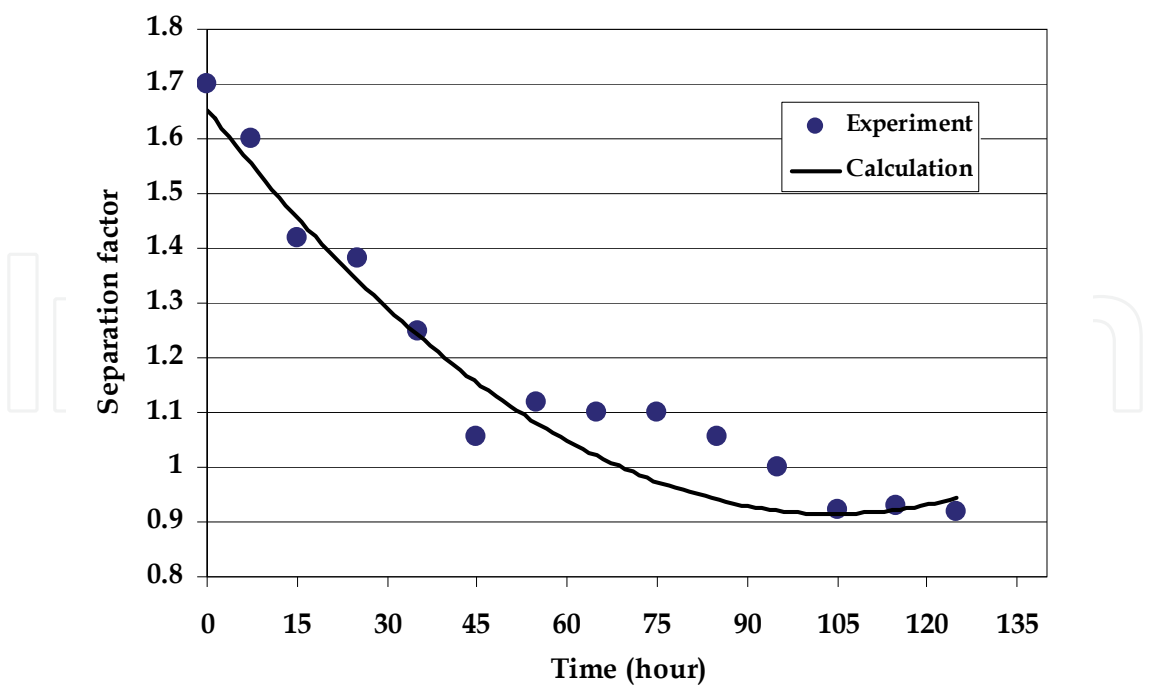
Fig. 11. The model prediction of separation factor and experimental results

From Figs. 10 and 11, we can see that the predictions of dimensionless concentration in stripping phase and the separation factor agreed with the experimental results.

4.2 Enhancement of uranium separation from trisodium phosphate

Two grades of trisodium phosphate, food and technical grades, are extensively used for various purposes. Food grade is used as an additive in cheese processing. Technical grade is used for many applications, e.g., in boiler-water treatment, testing of steel parts after pickling, industrial detergents such as degreasers for steels, and heavy-duty domestic cleaners. As trisodium phosphate is a by-product from the separation of desired rare earths in monazite processing, it is contaminated by some amount of uranium which is often found with the monazite. Uranium is a carcinogen on the other hand it is useful as a radioactive element in the front and back ends of the nuclear fuel cycle, therefore the separation method to recover uranium from trisodium phosphate is necessary. For 45-ppm-uranium-contaminated trisodium phosphate solution, HFSLM is likely a favorable method as it can simultaneously extract the ions of very low concentration and can recover them in one single operation. Undoubtedly, the facilitated transport across the HFSLM accelerates the extraction and recovery of uranium.

Eq. 13 shows that uranium species form complex species with Aliquat 336 (tri-octyl methyl ammonium chloride: $CH_3R_3N^+Cl^-$) in modified leaching and extraction of uranium from monazite (El-Nadi et al., 2005).

$$[UO_2(CO_3)_3]^{4-} + \overline{2(NR_4)^+Cl^-} \rightleftharpoons \overline{(NR_4)_2[UO_2(CO_3)_2^{2-}]} + 2Cl^- + CO_3^{2-} \qquad (13)$$

$[UO_2(CO_3)_3]^{4-}$ represents the uranium species, $\overline{2(NR_4)^+Cl^-}$ represents general form of Aliquat 336 in liquid membrane and $\overline{(NR_4)_2[UO_2(CO_3)_2^{2-}]}$ represents the complex species of Aliquat 336 and uranium species in liquid membrane.

Fig. 12 shows percentage of uranium extraction by different extractants. We can see that D2EHPA (di (2-ethylhexyl) phosphoric acid) obtained high percentage of extraction, however its extractability abruptly decreased with time. Thus, Aliquat 336, of which its extractability followed D2EHPA and decreased slightly with time, was considered the most appropriate extractant for uranium. It can be attributed that uranium ions in trisodium phosphate solution are in $[UO_2(CO_3)_3]^{4-}$ and Aliquat 336, a basic extractant, is good for cations while D2EHPA, an acidic extractant, is good for anions form of UO_2^{2+}. The percentage of uranium extraction at different concentrations of Aliquat 336 is shown in Fig. 13.
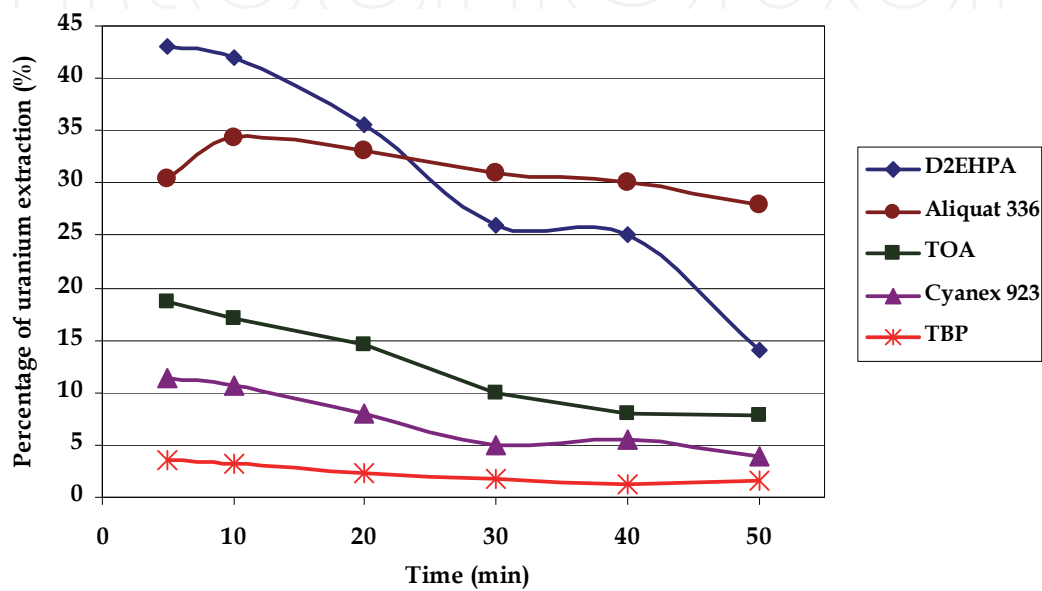

Fig. 12. Percentage of uranium extraction against time using different extractants of 0.1 M, stripping solution [HNO$_3$] of 0.5 M, equal Q$_{feed}$ and Q$_{stripping\ solution}$ of 100 ml/min
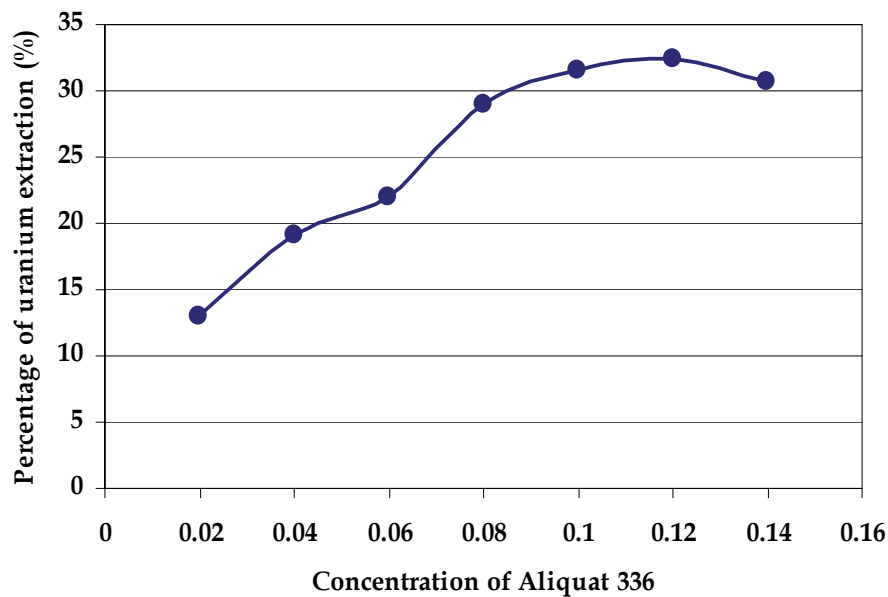

Fig. 13. Percentage of uranium extraction at different concentrations of Aliquat 336, stripping solution [HNO$_3$] of 0.5 M, equal Q$_{feed}$ and Q$_{stripping\ solution}$ of 100 ml/min

To enhance the extraction of uranium, a mixture of Aliquat 336 and TBP (tributylphosphate) showed synergistic effect as can be seen in Fig. 14. The percentage of uranium extraction using the synergistic extractant was higher than that by a single extractant of Aliquat 336 and TBP. The highest extraction of uranium from trisodium phosphate solution was obtained by a synergistic extractant of 0.1 M Aliquat 336 and 0.06 M TBP. (The extraction increased with the concentration of TBP upto 0.06 M.)
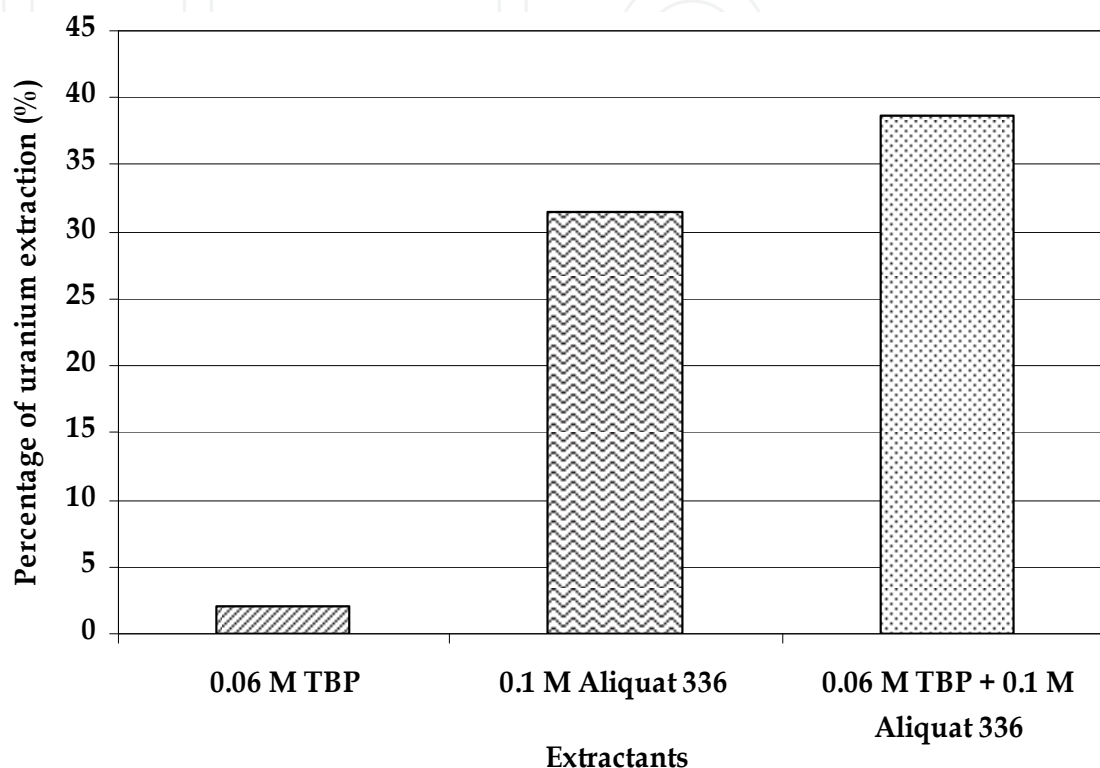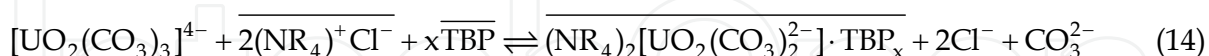

Fig. 14. Percentage of uranium extraction against single and synergistic extractants: stripping solution [HNO$_3$] of 0.5 M, equal Q$_{feed}$ and Q$_{stripping\ solution}$ of 100 ml/min

The reaction by the synergistic extractant of Aliquat 336 and TBP is proposed in this work.

$$[UO_2(CO_3)_3]^{4-} + \overline{2(NR_4)^+Cl^-} + x\overline{TBP} \rightleftharpoons \overline{(NR_4)_2[UO_2(CO_3)_2^{2-}] \cdot TBP_x} + 2Cl^- + CO_3^{2-} \qquad (14)$$

From Fig. 15, by using the synergistic extractant of 0.1 M Aliquat 336 mixed with 0.06 M TBP, the stripping solution of 0.5 M HNO$_3$ with equal flow rates of feed and stripping solutions of 100 ml/min, the percentages of extraction and stripping reached 99% (equivalent to the remaining uranium ions in trisodium phosphate solution of 0.22 ppm) and 53%, respectively by 7-cycle separation in 350 min. The percentage of uranium stripping was much lower than the percentage of extraction presuming that uranium ions accumulated in liquid membrane phase of the hollow fiber module. This is a limitation of the HFSLM applications. For higher stripping, a regular membrane service is needed. In conclusion, the remaining amount of uranium ions in trisodium phosphate solution was 0.22 ppm, which stayed within the standard value 3-ppm uranium of the technical-grade trisodium phosphate. Further study on a better stripping solution for uranium ions is recommended.
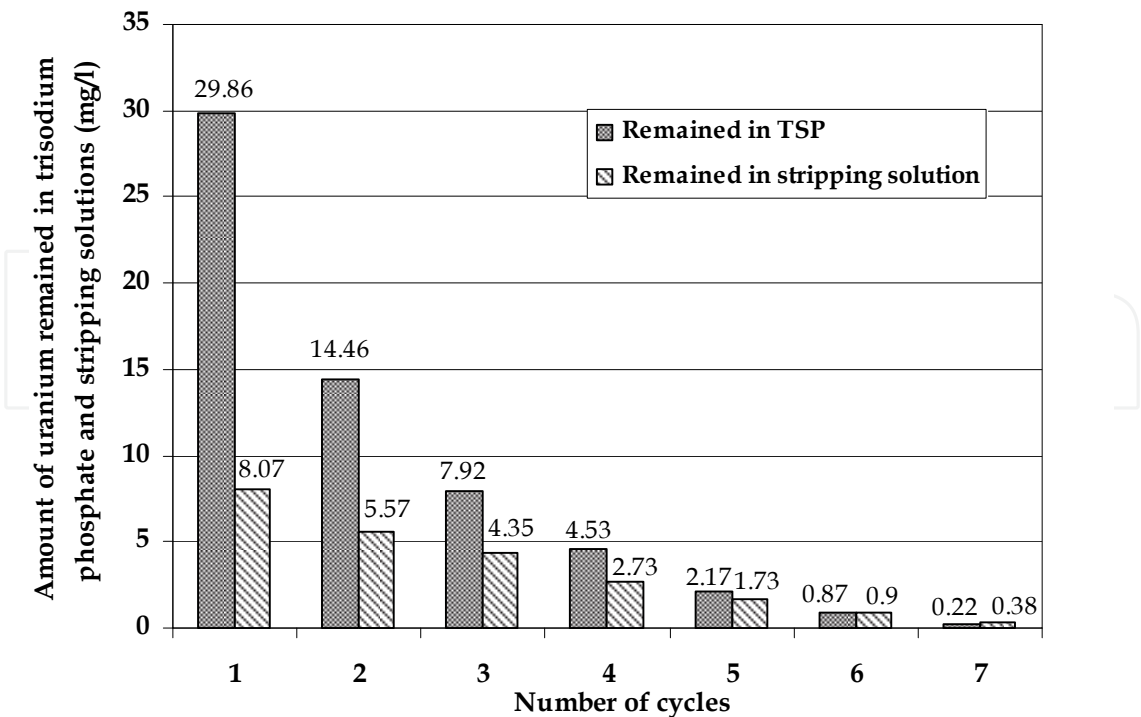
Fig. 15. Amount of uranium ions remained in trisodium phosphate and stripping solutions of one-module operation against the number of separation cycles by 0.1 M Aliquat 336 mixed with 0.06 M TBP, stripping solution [HNO₃] of 0.5 M, equal Q_{feed} and $Q_{stripping\ solution}$ of 100 ml/min

4.3 Reaction flux model for extraction of Cu(II) with LIX84I

In regard to apply the hollow fiber contactor for industrial scale, the reliable mathematical models are required. The model can provide a guideline of mass transfer describing the transport mechanisms of the target species through liquid membrane, and predict the extraction efficiency. Normally, different types of the extractants, their concentration and transport mechanisms (diffusion and facilitated transport or carrier-mediated transport) play important roles on the extraction efficiency. The facilitated transport mechanism relates to the reaction flux of chemical reaction between the target species and the selected single extractant or synergistic extractant to form complex species (Bringas et al., 2009; Kittisupakorn et al., 2007; Ortiz et al., 1996). In principle, the metal-ion transport through the membrane phase occurs when the metal ions react with the selected extractant at the interface between feed phase or aqueous phase and liquid membrane phase, consequently the generated complex species diffuse through the membrane phase. In this work, we developed a mathematical model describing the effect of reaction flux on facilitated transport mechanism of copper ions through the HFSLM system because copper is used extensively in many manufacturing processes, for example, electroplating, electronic industry, hydrometallurgy, etc. Therefore, copper ions, which are toxic and non-biodegradable, may contaminate wastewaters and cause environmental problems and health effects if no appropriate treatment is taken (Lin & Juang, 2001; Ren et al., 2007). The model was verified with the experimental extraction of copper ions in ppm level using LIX84I dissolved in kerosene by continuous counter-current flow through a single-hollow

fiber module. It is known that LIX-series compounds are the most selective extractants of high selectivity and widely used for copper ions (Breembroek et al., 1998; Campderros et al., 1998; Lin & Juang, 2001; Parhi & Sarangi, 2008; Sengupta, et al., 2007). The schematic flow diagram of the separation via HFSLM is shown in Fig. 16. The transport mechanism of copper ion in micro porous hollow fiber is presented schematically in Fig. 17. The chemical reaction at the interface between feed phase and liquid membrane phase takes place when the extractant $(\overline{RH})$ reacts with copper ions in feed (Eq. (15)).

$$Cu_{(aq)}^{2+} + 2\,\overline{RH}_{(org)} \rightleftharpoons \overline{CuR}_{2(org)} + 2H_{(aq)}^{+} \tag{15}$$
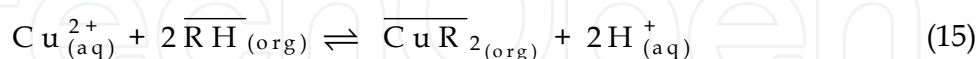
$(\overline{RH})$ is LIX84I in liquid membrane phase.
$\overline{CuR_2}$ is the complex species of copper ion in liquid membrane phase.
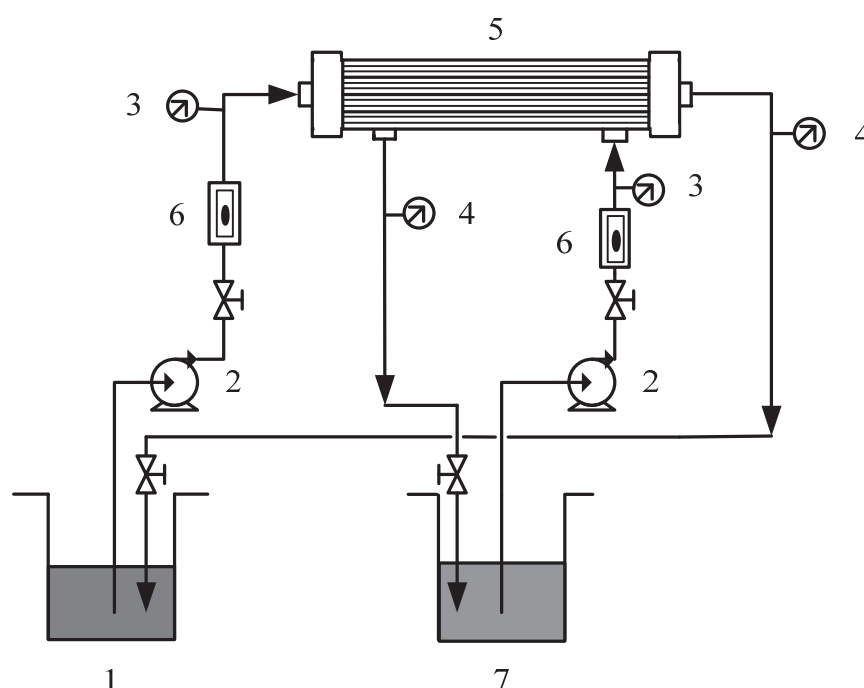

Fig. 16. Schematic diagram for counter-current flow of Cu(II) separation by a single-hollow fiber module (1 = feed reservoir, 2 = gear pumps, 3 = inlet pressure gauges, 4 = outlet pressure gauges, 5 = hollow fiber module, 6 = flow meters and 7 = stripping reservoir

Eq. (15) can be simplified as follows:

$$aA + bB \xrightarrow{\ k_f\ } cC + dD \tag{16}$$

where   A is copper ion, B is LIX84I, C is complex species of copper ion and LIX84I, D is hydrogen ion, and a, b, c, d are stoichiometric coefficients of A, B, C and D, respectively.
The reaction rate (r_A) is

$$-r_A = k_f C_{A\ (x,t)}^{n} \tag{17}$$

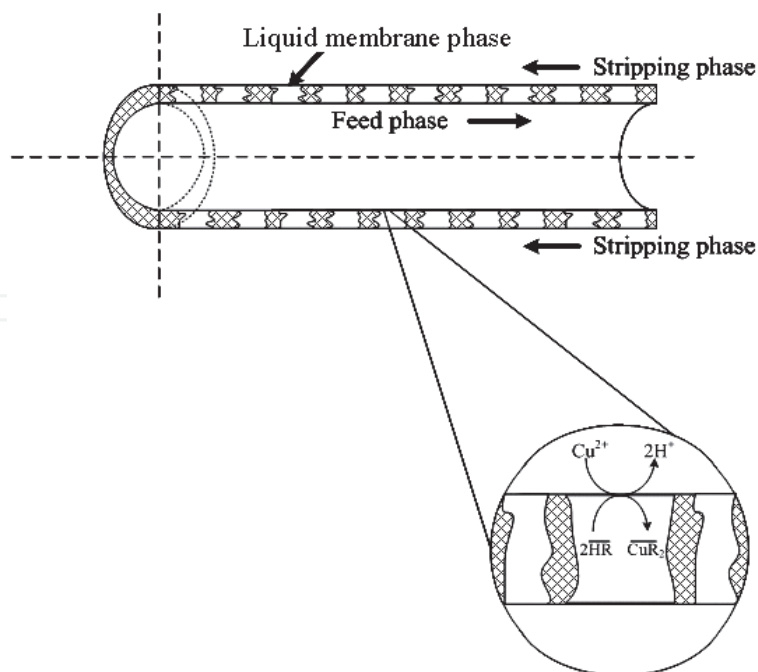k_f is the forward reaction rate constant and n is the order of reaction.

Fig. 17. Schematic transport mechanism of copper ion in liquid membrane phase

The transport of copper ions through a cylindrical hollow fiber is considered in the axial direction or bulk flow direction and radial direction. In order to develop the model, the following assumptions are made:

1. The inside and outside diameters of a hollow fiber are very small. Thus, the membrane thickness is very thin; therefore the radial concentration profile of copper ions is constant.
2. Only the complex species occurring from the reaction, not copper ions, diffuse through liquid membrane phase.
3. The extraction reaction is irreversible that means only the forward reaction of Eq. (15) is considered.
4. Due to very thin membrane thickness, it is presumed that the reaction occurs only in the axial direction of the hollow fibers. Mass flux of copper ions exists in the axial direction.

The conservation of mass for copper ion transport in the hollow fiber is considered as shown in Fig. 18.
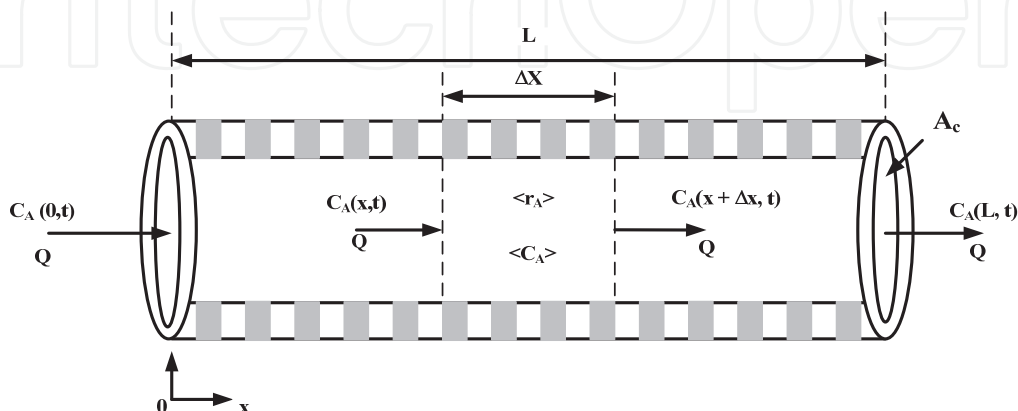

Fig. 18. Transport of copper ions in the hollow fiber

At a small segment Δx, the conservation of mass can be described below:

$$QC_{A\ (x,t)} - QC_{A\ (x+\Delta x,t)} - \langle r_A \rangle \Delta x A_c = \frac{d\langle C_A \rangle}{dt} \Delta x A_c \tag{18}$$

$\langle r_A \rangle$ and $\langle C_A \rangle$ are the average values of the reaction rate and the concentration of copper ions, respectively
Dividing Eq. (18) by $\Delta x A_c$ and taking a limit $\Delta x \to 0$, obtains

$$-\frac{Q}{A_c}\frac{\partial C_{A\ (x,t)}}{\partial x} - r_{A\ (x,t)} = \frac{\partial C_{A\ (x,t)}}{\partial t} \tag{19}$$

At the initial condition (t = 0), the conservation of mass in Eq. (19) is considered with regard to 3 cases of the reaction orders as follows:
Case 1: n = 0

$$C_{A\ (L,0)} = C_{A\ (0,0)} + \frac{k_f A_c}{Q}L \tag{20}$$

Case 2: n = 1

$$C_{A\ (L,0)} = C_{A\ (0,0)}e^{\frac{k_f A_c}{Q}L} \tag{21}$$

Case 3: n ≠ 0, 1

$$C_{A\ (L,0)} = \left[C_{A\ (0,0)}^{1-n} + \frac{(1-n)k_f A_c}{Q}L \right]^{\frac{1}{1-n}} \tag{22}$$

At time t (t ≠ 0), the conservation of mass in Eq. (19) in the differential form is

$$-\frac{Q}{A_c}\frac{\partial \overline{C}_{A\ (x,t)}}{\partial x} - \overline{r}_{A\ (x,t)} = \frac{\partial \overline{C}_{A\ (x,t)}}{\partial t} \tag{23}$$

where $\overline{C}_{A\ (x,t)} = C_{A\ (x,t)} - C_{A\ (x,0)}$

$$\overline{r}_{A\ (x,t)} = r_{A\ (x,t)} - r_{A\ (x,0)} = -\left(\frac{k_f n}{\lambda - \gamma x} \right)\overline{C}_{A\ (x,t)}$$

Linearize Eq. (23) by taking Laplace transforms and considering 3 cases of reaction orders, we obtain:
Case 1: n = 0

$$\overline{C}_{A\ (L,t)} = \overline{C}_{A\ (0,t-\tau_0)} + k_f(t - \tau_0) - k_f t \tag{24}$$

Case 2: n = 1

$$\overline{C}_{A\ (L,t)} = e^{\alpha}\overline{C}_{A\ (0,t-\tau_0)} \tag{25}$$

Case 3: $n \neq 0, 1$

$$\overline{C}_{A\ (L,t)} = e^{\beta}\overline{C}_{A\ (0,t-\tau_0)} \tag{26}$$

Let $\tau_0 = \dfrac{A_cL}{Q}$, $\alpha = \dfrac{k_fA_cL}{Q}$, $\beta = \left(\dfrac{A_ck_fn}{Q\gamma}\right)\ln\left(\dfrac{\gamma L + \lambda}{\lambda}\right)$, $\gamma = \dfrac{(1-n)k_fA_c}{Q}$ and $\lambda = C_{A(0,0)}^{1-n}$
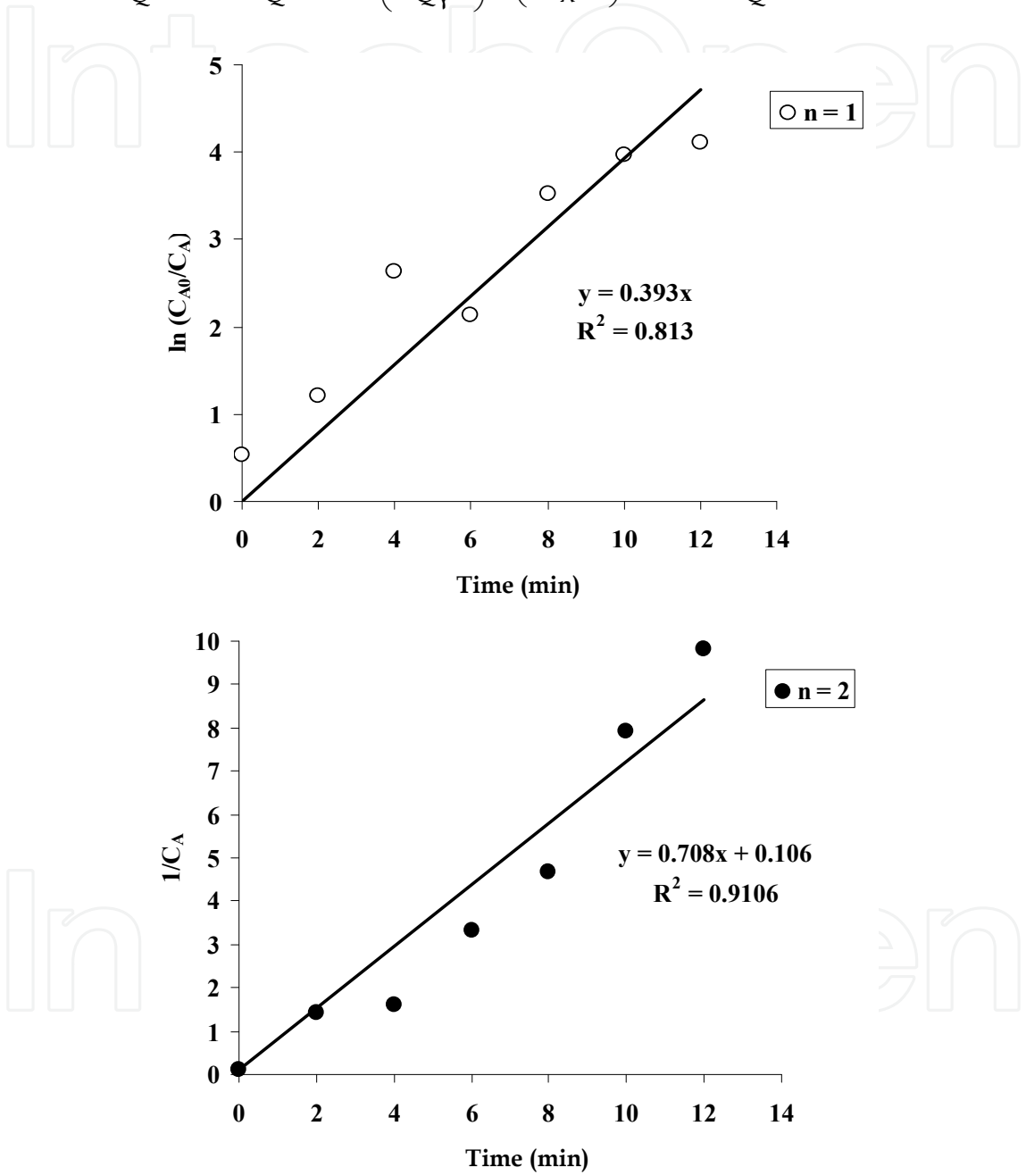

Fig. 19. The integral concentrations of Cu(II) and separation time, ○ for n = 1 and ● for n = 2

The reaction rate constant of the second order is taken into consideration for a better curve fitting between the model and the experimental results, as shown in Table 4 by higher R-squared and less deviation.

The optimum separation time and separation cycles of the extraction can be estimated. The model was verified with the experimental extraction results and other literature.

Fig. 19 is a plot of the integral concentrations of Cu(II) against time to determine the reaction order (n) and the forward reaction rate constant (k_f). The rate of diffusion and/or rates of chemical changes may control the kinetics of transport through liquid membrane depending on transport mechanisms (diffusion or facilitated). The reaction rate constants of first-order (n = 1) and second-order (n = 2) are 0.393 min^{-1} and 0.708 L/mg·min, respectively.

Reaction order (n)	Reaction rate constant (k_f)	R-squared	% Deviation
First-order	0.393 min^{-1}	0.813	61.233
Second-order	0.708 L/mg·min	0.911	1.453

Table 4. R-squared and percentages of deviation for first-order and second-order reactions

The percentage of copper ion extraction is calculated by Eq. (27). The percentage of deviation is calculated by Eq. (28).

$$\% \text{ extraction} = \frac{C_{f,in} - C_{f,out}}{C_{f,in}} \times 100 \tag{27}$$

$$\% \text{ deviation} = \frac{\sum_{i=1}^{j}\left(\frac{C_{Expt.} - C_{Theo.}}{C_{Expt.}}\right)_i}{j} \times 100 \tag{28}$$

The optimum separation time for the prediction of separation cycles can be estimated by the model based on the optimum conditions from the plot of percentage of extraction as a function of initial concentration of the target species in feed and also feed flow rate.

In this work, at the legislation of Cu(II) concentration in waste stream of 2 mg/L, the calculated separation time is 10 min for about 15-continuous cycles. The percentage of extraction calculated from this reaction flux model is much higher than the results from other works which applied different extractants and transport mechanisms. Types of extractants and their concentrations are significant to the separation of metal ions. For example, a hard base extractant can extract both dissociated and undissociated forms in a basic or weak acidic condition but dissociated forms are high favorable. While a neutral extractant normally reacts with undissociated forms, but in an acidic condition it can react with dissociated forms. It is noteworthy to be aware that not only types of the extractants (single or synergistic), in this case LIX84I for Cu(II), but also the transport mechanism, e.g., facilitated transport mechanism attributes to the extraction efficiency. The model results are in good agreement with the experimental data at the average percentage of deviation of 2%.

5. Conclusions

Facilitated transport of the solutes or target species benefits the separation process by liquid membrane with a non-equilibrium mass transfer and uphill effect. It is more drastic chemical changes of the target species with the presence of a suitable extractant or carrier (sometimes by synergistic extractant) in liquid membrane to form new complex species

(dissociated and undissociated forms) to diffuse through the liquid membrane phase. As a result, the efficiency and selectivity of the transport across liquid membrane markedly enhance. Factors that affect the facilitated transport and diffusion through the membrane are, for example, extractant types and properties (e.g., proton donors, electron donors), solvent characteristics, stripping types and properties, life time of membrane due to fouling, operating temperature. Many outstanding advantages of the HFSLM make it the most efficient type of membrane separation for several applications. It is worth to note that the HFSLM can simultaneously extract the target species of very low concentration and recover them in one single operation. For favorable ions (e.g., precious metals), high percentage of recovery is desirable.

Despite many advantages, at present the HFSLM is not often used in a large-scale industry because the major drawbacks of hollow fibers are not only fouling but also mechanical stability of the support. However, in regard to apply the HFSLM in industrial scale, the reliable mathematical model is required as the model can foretell the effect of mass transfer as the functions of operating parameters, membrane properties and feed properties on the separation efficiency. However, due to the limitations of applications or unclear phenomena around the membrane surface, no model so far is fully satisfactory and universally applicable. Even though, the model can help to understand and predict the operation as well as the separation performance. In case the separation of metal ions by the HFSLM, as there are several parameters involved, e.g., types of metal ions, extractants and stripping solutions, and the transport mechanisms, therefore the model probably has implications for other metals but it may need some modifications corresponding to such parameters.

6. Acknowledgments

7. Nomenclature

A	Membrane area (cm^2)
A_C	Cross-sectional area of hollow fiber (cm^2)
BLM	Bulk liquid membrane
BTXs	Benzene, toluene, xylenes
C_A	Concentration of copper ions
$<C_A>$	Average value of the concentration of copper ions
C_f	Concentration of target species in feed phase (moles per unit volume)
C_{f*}	Concentration of target species at feed-membrane interface (moles per unit volume)
$C_{f,0}$	Initial concentration of target species in feed phase (moles per unit volume)
$C_{f,in}$, $C_{f,out}$	Concentration of target species at feed inlet and feed outlet (moles per unit volume)

C_s	Concentration of target species in the stripping solution (moles per unit volume)
C_{s*}	Concentration of target species at membrane-stripping interface (moles per unit volume)
$C(0,t)$	Concentration of target species at liquid membrane thickness = 0 and any time (moles per unit volume)
$C(x_0,t)$	Concentration of target species at liquid membrane thickness of x_0 and any time (moles per unit volume)
D	Distribution ratio
ELM	Emulsion liquid membrane
H^+	Hydrogen ion representing pH gradient
HFSLM	Hollow fiber supported liquid membrane
ILM	Immobilized liquid membrane
J	Flux (mol/cm^2 s)
K_{ex}	Extraction equilibrium constant
k_f	Forward reaction rate constant (cm^3/mg·min)
k_i	Feed- or aqueous-phase mass transfer coefficient or mass transfer coefficient in feed phase
k_m	Organic-phase mass transfer coefficient or mass transfer coefficient in liquid membrane phase
k_s	Stripping-phase mass transfer coefficient or mass transfer coefficient in stripping phase
L	Length of the hollow fiber (cm)
LMs	Liquid membranes
l_{if}	Feed interfacial film thickness
l_{is}	Stripping interfacial film thickness
M	Target species
$\overline{MR_n}$	Complex species in the membrane phase
N	Number of hollow fibers in the module
n	Order of the reaction
P	Permeability coefficient
P_m	Membrane permeability coefficient
Q	Volumetric flow rate (cm^3/min)
Q_f, Q_{feed}	Volumetric flow rate of feed solution (cm^3/s)
Q_s, $Q_{stripping\ solution}$	Volumetric flow rate of stripping solution (cm^3/s)
r_A	Reaction rate
$<r_A>$	Average value of the reaction rate of copper ions
$\overline{RH}$	General form of the extractant
r_i	Inside radius of the hollow fiber (cm)
r_{lm}	Log-mean radius of the hollow fiber
r_o	Outside radius of the hollow fiber (cm)
SLMs	Supported liquid membranes
t	Time (min)
V_f	Volume of the feed phase (cm^3)
VOCs	Volatile organic compounds
x	Spatial coordinate, direction of fiber axis

x_0	Membrane thickness (cm)

Greek letters

ε	Porosity of the hollow fibers (%)
α	Parameter in Eq. (25)
β	Parameter in Eqs. (11-12) and (26)
γ, λ	Parameters for β in Eq. (26)
τ_0	Parameter in Eqs. (24)-(26)

Symbol

< >	average value
Δ	difference between exit and entry values

Subscripts

| aq	In aqueous phase
f	At feed phase
f,in and f,out	At feed inlet and feed outlet
h	Hollow fiber
m	At liquid membrane phase
org	In organic phase (liquid membrane phase)
s	At stripping phase
Expt.	Experimental values
Theo.	Modeled or theoretical values

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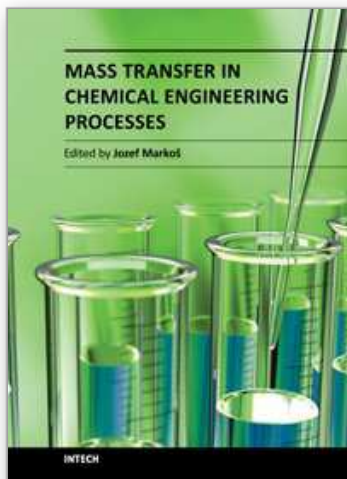
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