CHAPTER IV

MODEL DEVELOPMENT AND EXPERIMENT

This chapter presents the model development and experimental section. The models are separated to two parts, the first is once through operating mode and the last is recycling mode.

4.1   Model development

4.1.1   Modeling of the mass transfer

In this work, the hollow fiber liquid membrane consists of an aqueous feed solution containing copper (II) ion flowing in the tube side of a hollow fiber supported liquid membrane whose pores are fill with the extractant (bis(2-ethylhexyl) phosphoric acid in kerosene, D2EHPA) and the extractant flowing in the shell side. The flow between the tube side and the shell side is counter-current flow.

A model is presented in this work that consider possible mass transfer steps, including aqueous layer diffusion both in feed and stripping solution, interfacial chemical reaction and membrane diffusion.

The reaction between copper-ion and D2EHPA in kerosene occurs at the membrane interfaces is given by

$$Cu^{2+} + 2(RH)_2 \Leftrightarrow \overline{CuR_2 \cdot 2RH} + 2H^+ \tag{4.1}$$

$$(C + 2E \Leftrightarrow P + 2H)$$
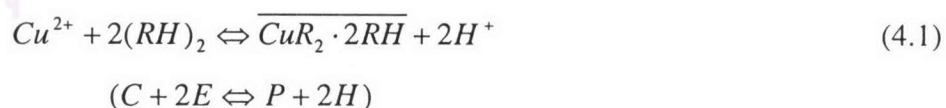
where RH represents D2EHPA and $\overline{CuR_2 \cdot 2RH}$ is the copper-ion complex.

The forward and reverse reaction rates are expressed as (Chien-Yeh Shiau and Pai-Zon Chen, 1993):

$$\text{Forward reaction rate} = k_f(C \cdot E^2/H^2 - P/K_{eq})$$
$$\text{Reverse reaction rate} = k_f(P/K_{eq} - C \cdot E^2/H^2)$$

where k_f is the forward reaction rate constant and K_{eq} is the equilibrium constant.
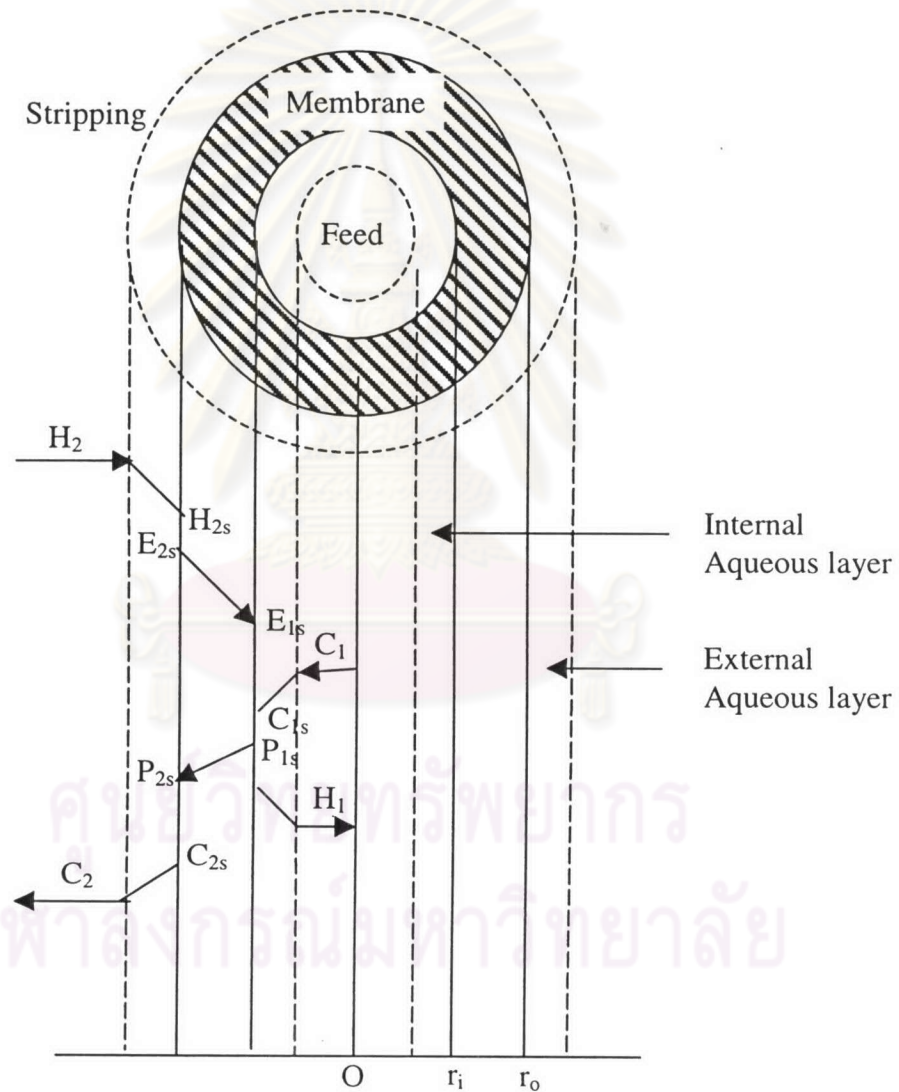

Figure 4.1 Concentration profile of reactive species for the extraction of copper ion with D2EHPA in hollow fiber.

Figure 4.1 shows the concentration profile of the various species around the hollow fiber. When an aqueous feed solution containing copper ions flow through the lumen of a hollow fiber supported liquid membrane, the copper ions are continuously extracted by the extractant(D2EHPA in kerosrne) present in the membrane phase, causing the copper ion concentration of the feed solution to gradually decrease along the hollow fiber.

To develop the model , the mass transfer steps include the diffusion of copper-ion in feed stagnant layer, the reaction between the copper-ion and extractant to form the corresponding complexes at feed-membrane interface, the diffusion of the copper-ion complexes within the membrane stagnant layer, the reaction between the copper-ion complex and hydrogen ion to form the copper-ion at the membrane-stripping interface and the diffusion of copper-ion in the stripping stagnant layer are considered. The description of each elementary mass transfer step is indicated as follows:

Step 1. Due to the driving force of the concentration gradient, the copper-ions in the aqueous feed solution permeate through an aqueous feed layer formed along the hollow fiber wall and move toward the liquid membrane. The mass transfer rate of the copper ions can be generally represented as :

$$J_1 = k_i (C_1 - C_{1s})$$ (4.2)

where k_i is the mass transfer coefficient of copper-ion in the aqueous feed solution.

Step 2. At the feed-membrane interface, the copper-ions react with the extractant present in the membrane phase to form copper complexes. The reaction rate of the copper complexes is

$$J_2 = k_f \left[\frac{C_{1s} \cdot E_{1s}^2}{H_{1s}^2} - \frac{P_{1s}}{K_{eq}} \right]$$ (4.3)

Step 3. The copper complexes formed at the feed-membrane interface then diffuse across the membrane toward the other side. By assuming a linear concentration profile in the membrane, the mass transfer rate of the copper complexes in the membrane can now be expressed as :

$$J_3 = k_m (P_{1s} - P_{2s})$$

(4.4)

where k_m is the mass transfer coefficient of the copper complex in the membrane phase.

Step 4. At the membrane-stripping interface, the copper ions are stripped from the copper complexes by the resistance of the strong acid present in the stripping phase. The reaction rate is

$$J_4 = k_f \left[\frac{P_{2s}}{K_{eq}} - \frac{C_{2s} \cdot E_{2s}^2}{H_{2s}^2} \right]$$

(4.5)

Step 5. The stripped copper ions permeate through an aqueous stagnant layer outside the hollow fiber and enter to the stripping solution. The mass transfer rate is expressed as

$$J_5 = k_o (C_{2s} - C_2)$$

(4.6)

where k_o is the mass transfer coefficient of the copper-ion in the stripping solution.

At steady state, all the mass transfer rate are equal, there for

$$J_1 = J_2 = J_3 = J_4 = J_5 = J$$

(4.7)

The additional constrains for the system are

$$2C_1 + H_1 = 2C_{1s} + H_{1s} = 2C_{10} + H_{10} \qquad (4.8)$$

$$2C_2 + H_2 = 2C_{2s} + H_{2s} = H_{20} \qquad (4.9)$$

$$2P_{1s} + E_{1s} = 2P_{2s} + E_{2s} = E_0 \qquad (4.10)$$

4.1.2 Modeling of copper-ion extraction for the once through mode operation

The once-trough mode operation is indicated in the figure 4.2. The outlet concentration of copper ion at the exit of the hollow fiber can be obtained by making an overall material balance for the feed solution over the hollow fiber.
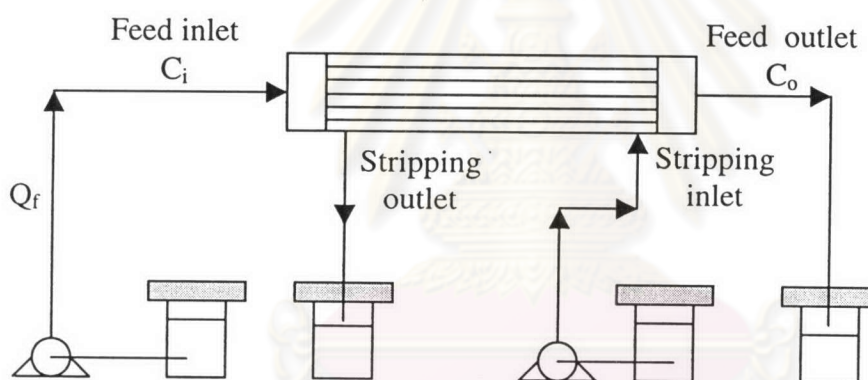

Figure 4.2 Schematic diagram of hollow fiber liquid membrane run in the once through mode

The following assumptions were taken to develop the model :

1. Axial diffusion in the fiber lumen is neglected.
2. All physical and transport properties are constant during the entire extraction process operation.

3. Except in the aqueous stagnant layer which forms along the fiber wall, the concentration profile of copper ions in the fiber lumen is flat at any axial position.

4. The solubility of D2EHPA in stripping solutions is considers to be negligibly small, so the total amounts of D2EHPA in the membrane phase is kept constant.

5. Pseudo steady state operation.

Based on these assumptions, a material balance equation for the copper ions of the feed solution over an element section may be formulated as

$$-Q_f \frac{dC_f}{dx} = J\ (2\pi\bar{r})$$
(4.11)

$$= J\ \pi(r_i + r_o)$$

$$C_{f_{x+\Delta x}} = C_{f_x} - \frac{J\pi(r_i + r_o)}{Q_f}\Delta x$$
(4.12)

where Q_f is the volumetric flow rate of feed solutions, J is mass transfer rate of Cu^{2+} for any axial position in the hollow fiber module.

Mass transfer rate of copper for any given position can be obtained by solving sets of equation (4.2) – (4.10) by using least square method.

4.1.3 Modeling of copper-ion extraction for the recycling mode operation

For the recycling mode, both feed solution and stripping solution are recycled, as shown in figure 4.3.

From the figure 4.3, the following material balance equation for copper ion extraction across the supported liquid membrane module can be formulated for the feed side as :

$$-V_f \frac{dC_i}{dt} = Q_f (C_i - C_o) \tag{4.12}$$

$$[C_i]_{t+\Delta t} = [C_i]_t - \frac{Q_f}{V_f} \{[C_i]_t - [C_o]_t\} \Delta t \tag{4.13}$$

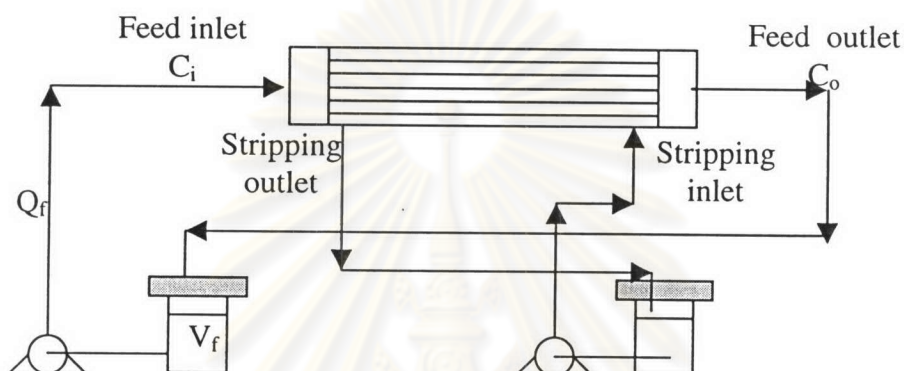where V_f is liquid volume of feed solution in feed tank,

Figure 4.3   Schematic diagram of hollow fiber liquid membrane run in the recycling through mode

To describe the degree of copper-ion extraction in hollow fiber supported liquid membrane, the term "removal efficiency" is proposed. It is defined as the percentage of copper-ion remove from the feed solution.

$$\text{Removal efficiency (\%)} = \frac{C_i - C_o}{C_i} \times 100\% \tag{4.14}$$

4.1.3   Model validation

In order to check the validity of the proposed model for extraction of copper-ion in hollow fiber module, two tools were used as follow

1.   The removal efficiency of copper ion in feed solution was compared with previous experimental results (Itsara, 1998). The absolute error percentage of removal efficiency of copper-ion in feed solution between experimental results and model calculation was proposed. It is define as

$$\text{Absolute error } (\%) = \left| \frac{[Cu^{2+}]^{\exp} - [Cu^{2+}]^{cal}}{[Cu^{2+}]^{\exp}} \right| \times 100 \qquad (4.15)$$

2.   The standard deviation (SD) between calculated and measured results was determined. It is defined in equation (4.15)

$$SD(\%) = 100 \times \sqrt{\frac{\sum \left\{ \left(\frac{[Cu^{2+}]^{cal}}{[Cu^{2+}]^{\exp}} \right) - 1 \right\}^2}{n-1}} \qquad (4.16)$$

4.2   Reagents and Apparatus

4.2.1   Reagents

All reagents used for extraction of copper ion by hollow fiber supported liquid membrane are listed below.

1.   Copper sulfate pentahydrate($CuSO_4 \cdot 5H_2O$)
2.   Sulfuric acid
3.   Bis(2-ethylhexy)phosphoric acid
4.   kerosene

4.2.2 Apparatus

Apparatus for extraction of copper ion can be listed as follows:

1.   Liqui-Cel Laboratory was purchased from Hoechst Celanese Corporation. This apparatus composes of 2 pumps, 2 pressure gauges, 2 pump speed control and 2 flowmeters as indicated in figure 4.4

2.   Hollow fiber modules used were Hoechst Celanese Corporation (model X-30). Characteristics of this module are indicated in table 4.1.

3.   pH meter was bought from Hana Instrument Company (model HI 8417 Microprocessor Bench pH).

4.   Atomic absorption/flame emission spectrophotometer came from Shimazu Company (model AA-670).

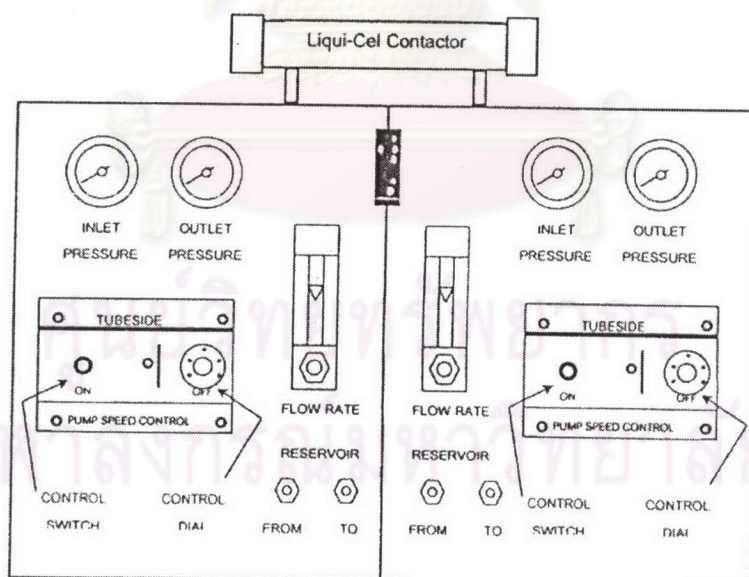5.   AA spectrometer was purchased from Unicam Company (model UNICAM 898 QZ).

Figure 4.4   Liqui-Cel Laboratory (Hoechst Celanese Corporation)

Table 4.1 Characteristics of the hollow fiber module used for extraction experiments (Hoechst Celanese Corporation, 1995)

	Shell character
material	polypropylene
length	20.3 cm
inner diameter	6.3 cm
outer diameter	7.7 cm
	Fiber characteristics
material	Cegard X-30 polypropylene hollow fiber
number of fiber	10,000
effective length	19.8 cm
inner diameter	240 μm
outer diameter	300 μm
effective surface area	1.4 m^2
effective area/volume	29.3 cm^2/cm^3
membrane porosity	30 %
membrane tortuosity	2.6
operating temperature	1 – 60 $^{\circ}$C
The highest pressure drop across the membrane	60 psi

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.3   Simulation Procedures

The mathematics models, which previously developed, are used for studying the parameters that will affect the copper ion extraction. This parameters are copper ion concentration in feed solution, D2EHPA concentration, hydrogen ion concentrations in stripping solution, pH of feed solution and volumetric flow rate in feed solution. The removal efficiency of copper ion is used to compare the effect of parameters.

In this research, the experiments are separated to 2 parts. The first is copper ion extraction for once through mode operation and the last is recycle mode operation.

4.3.1   Once Through Mode Operation

For once through mode, D2EHPA is absorbed in the microporous walls of hollow fiber. The feed solution is circulated through the tube side and the stripping solution on the shell side of the hollow fiber module. The type of flow between feed solution and stripping solution is countercurrent flow.

1.   The effect of D2EHPA concentration in membrane solution

1.1 At the start, the copper ion concentration in feed solution was 100 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 2 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 10 L.

1.2 The copper permeation flux were calculated by solving sets of equation (4.2) – (4.10) simultaneously. The copper ion concentration and removal efficiency of copper ion in feed solution were determined by solving equations (4.11) and (4.14), respectively. The Δx used in the model were 1, 2 and 5 cm.

1.3 D2EHPA concentration was changed from 2 % to 3, 4, 5, 10, 15, 20, 25, 35, 50 and 75 %. The procedures were repeated from step 1.1 to step 1.2.

1.4 The copper ion concentration in feed solution was change from 100 ppm to 10, 50, 300, 500 and 1,000 ppm. The procedures were repeated from step 1.1 to step 1.3. The Δx used in the model was 1 cm.

The values of parameters used for calculation of the permeation flux of copper ion are shown in Table 4.2.

Table 4.2 Values of parameters used for the calculation of the permeation flux of copper ion with D2EHPA

Solute/medium	Diffusivity (m^2/s)	Mass transfer coefficient
Cu^{2+}/feed phase	2.83×10^{-9}	1.75×10^{-5} m/s
Cu^{2+}/stripping phase	2.83×10^{-9}	6.27×10^{-7} m/s
copper ion complex/kerosene	4.04×10^{-10}	6.69×10^{-7} m/s
forward and reward reaction rate	1.80×10^{-8} m	
equilibrium constant	1.80×10^{-3}	

2. The effect of copper ion concentration in feed solution

2.1 At the start, the copper ion concentration in feed solution was 10 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 2 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 10 L.

2.2 The copper permeation flux were calculated by solving sets of equation (4.2) – (4.10) simultaneously. The copper ion concentration and removal efficiency of copper ion in feed solution were determined by solving equations (4.11) and (4.14), respectively. The Δx used in the model were 1.

2.3 The copper ion concentration in feed solution was change from 10 ppm to 50, 100, 300, 500 and 1,000 ppm. The procedures were repeated from step 2.1 to step 2.2.

2.4 D2EHPA concentration was changed from 2 % to 5, 10, 15, 20, 25, 35, 50 and 75 %. The procedures were repeated from step 2.1 to step 2.3.

3. The effect pH in feed solution

3.1 At the start, the copper ion concentration in feed solution was 100 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 2 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 10 L.

3.2 The copper permeation flux were calculated by solving sets of equation (4.2) – (4.10) simultaneously. The copper ion concentration and removal efficiency of copper ion in feed solution were determined by solving equations (4.11) and (4.14), respectively. The Δx used in the model were 1

3.3 pH in feed solution was change from 7 to 1, 2, 3, 4, 5, 6 and 8. The procedures were repeated from step 3.1 to step 3.2.

3.4 D2EHPA concentration was changed from 2 % to 5, 10, 15, 20, 25 %. The procedures were repeated from step 3.1 to step 3.3.

4. The effect of hydrogen ion concentration in stripping solution

4.1 At the start, the copper ion concentration in feed solution was 100 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 2 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 10 L.

4.2 The copper permeation flux were calculated by solving sets of equation (4.2) − (4.10) simultaneously. The copper ion concentration and removal efficiency of copper ion in feed solution were determined by solving equations (4.11) and (4.14), respectively. The Δx used in the model were 1.

4.3 The hydrogen ion in stripping solution was changed from 0.1 to 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 1 and 10 mol/L. The procedures were repeated from step 4.1 to step 4.2.

4.4 D2EHPA concentration was changed from 2 % to 5, 10, 15, 20, 25 %. The procedures were repeated from step 4.1 to step 4.3.

5. The effect of the volumetric Flow rate in feed solution

5.1 At the start, the copper ion concentration in feed solution was 100 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 2 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 10 L.

5.2 The copper permeation flux were calculated by solving sets of equation (4.2) − (4.10) simultaneously. The copper ion concentration and removal efficiency of copper ion in feed solution were determined by solving equations (4.11) and (4.14), respectively. The Δx used in the model were 1.

5.3 The volumetric flow rate in feed solution was changed from 200 to 5, 10, 50, 100, 500 and 1000 ml/min. The procedures were repeated from step 5.1 to step 5.2.

5.4 D2EHPA concentration was changed from 2 % to 5, 10, 15, 20, 25 %. The procedures were repeated from step 5.1 to step 5.3.

The mass transfer coefficient of copper ion in feed and stripping solution for various volumetric flow rate shown in table 4.3.

Table 4.3 The mass transfer coefficient of copper ion in feed and stripping solution

Volumetric flow rate in feed solution (ml/min)	Mass transfer coefficient (m/s)	
	Feed side(k_i)	Stripping side (k_o)
5	5.14×10^{-6}	6.27×10^{-7}
10	6.47×10^{-6}	6.27×10^{-7}
50	1.11×10^{-5}	6.27×10^{-7}
100	1.40×10^{-5}	6.27×10^{-7}
200	1.76×10^{-5}	6.27×10^{-7}
400	2.21×10^{-5}	6.27×10^{-7}
500	2.38×10^{-5}	6.27×10^{-7}
600	2.53×10^{-5}	6.27×10^{-7}
800	2.79×10^{-5}	6.27×10^{-7}
1000	3.00×10^{-5}	6.27×10^{-7}

4.3.2 Recycling Mode Operation

For the recycling mode, both feed solution and stripping solution are recycled, as shown in figure 4.3. Two parameters were studied in this mode, the first was circulation rate of feed solution and the last was circulation time. The experimental procedures for this mode can be listed as below

1. At the start, the copper ion concentration in feed solution was 300 ppm, pH in feed solution was 7, volumetric flow rate of feed solution was 200 ml/min, D2EHPA concentration is 25 % v/v, hydrogen ion concentration in stripping solution was 0.1 mol/L and liquid volume of feed solution was 2 l.

2. The exiting copper-ion concentration (C_o) from the hollow fiber for each cycle path was obtained by solving sets of equation (4.2) – (4.10), the time course of C_i can then be obtained by simultaneously solving equation (4.13) and sets of equation (4.2) – (4.10).

3. The volumetric flow rate in feed solution was changed from 200 to 50, 100, 400 and 600 ml/min. The procedures were repeated from 1 to 2.