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SIMULATION FOR SYNERGISTIC EXTRACTION OF NEODYMIUM IONS WITH HOLLOW FIBER SUPPORTED LIQUID MEMBRANE

Konaem Wasamon, Kittisupakorn Paisan
Department of Chemical Engineering, Faculty of Engineering
Chulalongkorn University
Bangkok, Thailand

***Abstract*—The modeling of neodymium ions extraction from the mixture of D2EHPA and TOPO by the hollow fiber supported liquid membrane has been studied. The system is operated in an once-through-mode and H_2SO_4 is used as stripping solution. Mathematical models have been developed based on a fluid-flow model including the term of axial convection, axial diffusion, chemical reaction at the feed-liquid membrane and accumulation of neodymium ions. The models are solved by a finite difference method on the MATLAB software. The literature experimental data have been used to validate the models. Simulation carried out shows that the models provide good prediction of the concentration of neodymium ions in the feed at the final time with an average absolute accuracy of 8.95%**.

***Index Terms*— simulation, Neodymium ions, synergistic, Hollow fiber, supported liquid membrane.**

I. INTRODUCTION

Rare earth elements (REEs) are of great importance owing to their unique physical and chemical properties best suited for the creation of advanced materials for high-technology devices. REEs being used alone or in the form of mischmetals are widely used. The performance of alloys can be greatly improved by adding appropriate amount of rare earth metals or their compounds. Therefore, rare earth elements are also known as the vitamin of metallurgical industry. For example, after being added with a number of rare earth elements in steel, the plasticity, heat resistance, toughness, oxidation resistance, abrasive resistance and corrosion resistance of the steel can be increased. REEs have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high-temperature superconductors, secondary batteries and catalysis. Out of the REEs, importance of neodymium has been greatly enhanced in the recent years due to the development of Nd–Fe–B permanent magnet. Neodymium is the raw material used in high-strength permanent magnets (Nd–B–Fe), making it less expensive than samarium-cobalt permanent magnets [1].

The high value of REE depends on their effective separation into high purity compounds. Separating individual REE from concentrates is a very difficult process due to their similar chemical properties. Therefore the separation process for REE need to high separation performance.

Hollow fiber supported liquid membrane (HFSLM) based separation methods have several advantages over conventional solvent extraction method such as dispersion free operation, very high contact surface are a per unit extract or volume, independent control of process flow rates eliminating loading and flooding and non-requirement of density difference of the phases. Furthermore a supported liquid membrane (SLM) are lower capital and operating costs, lower energy consumption, lower maintenance costs due to fewer moving parts. The process combine the extraction, stripping and regeneration process into a simple stage [2,3].

In this present work, The models of Hollow fiber supported liquid membrane that operated in an once-through-mode, using 0.5M D2EHPA and 0.5M TOPO as the mixtures as the synergistic extractant and using H_2SO_4 as the stripping solution were studied. The initial concentration of neodymium ions in wastewater is 100 mg/dm^3. The models of HFSLM were mostly based fluid-flow model including the term of axial convection, chemical reaction at the feed-liquid membrane and accumulation of neodymium ions. The MATLAB software was used to solve the model by finite difference method.

II. THEORY

A. *Transportation mechanism of neodymium ion in HFSLM*

Hollow fiber supported liquid membrane system composes of a feed solution and a stripping solution. Both feed and stripping phase are separated by a supported liquid membrane impregnate with one type of organic extractant or a mixture of two types of extractant to enhance the separation. Figure 1 show the counter current flow pattern for once-through-mode operation in hollow fiber supported liquid membrane. The counter transport is the flux of two ions moves counter to each other across the membrane by the driving force.

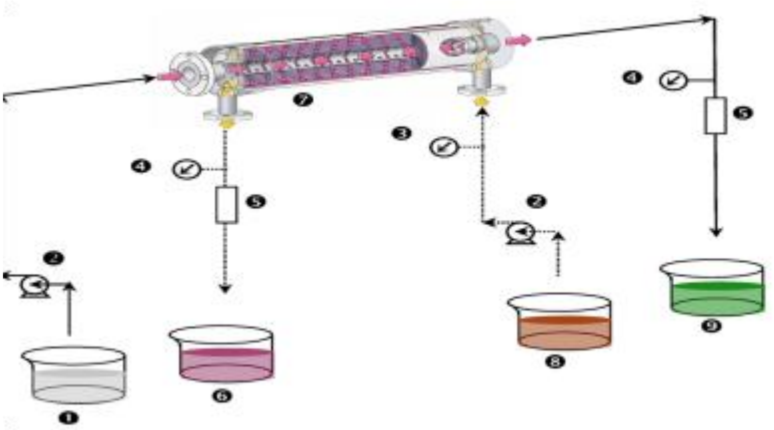

Fig. 1 Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane. (1) Feed reservoir; (2) gear pumps; (3) inlet pressure gauges; (4) outlet pressure gauges; (5) flow meters; (6) outlet stripping reservoir; (7) hollow fiber module; (8) inlet stripping reservoir; (9) outlet stripping reservoir [4].

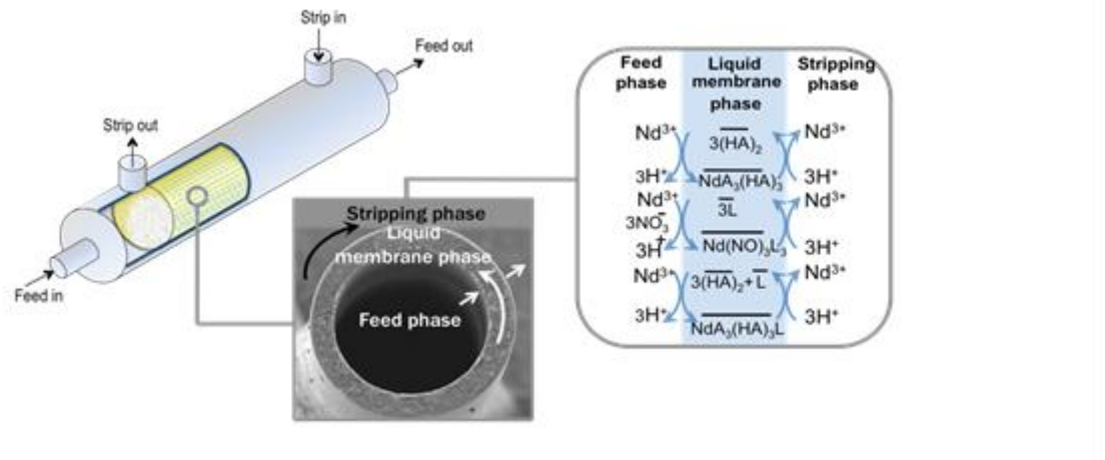

Fig. 2. Transportation mechanism of neodymium ion in HFSLM [5]

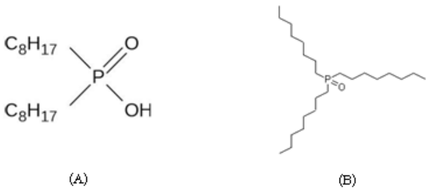

Fig. 3. The molecular structure of extractants (A) D2EHPA (di(2-ethylhexyl) phosphoric acid) and (B) TOPO (trioctyl phosphine oxide)

The transportation of neodymium ion through the HFSLM can be described by fig. 2.

Step 1: Nd(III) ion in the feed solution is transport to a contact surface between feed solution phase and liquid membrane phase. Nd(III) ion is reacted with D2EHPA (di(2-ethylhexyl) phosphoric acid) and TOPO (trioctyl phosphine oxide) yields a stable complex compound. The structure of extractants were shown in Fig. 3.

Equations 1-3 are shown the extraction of Nd(III) with D2EHPA, TOPO) and synergistic extractants (the mixture of D2EHPA and TOPO), respectively [5].

$$\mathrm{Nd^{3+}} + 3\overline{\mathrm{(HA)}_2} \xrightleftharpoons{k_{ex}} \overline{\mathrm{NdA_3(HA)_3}} + 3\mathrm{H^+} \qquad (1)$$

$$\mathrm{Nd^{3+}} + 3\mathrm{NO_3^-} + 3\overline{\mathrm{L}} \xrightleftharpoons{k_{ex}} \overline{\mathrm{Nd(NO_3)_3 \cdot L_3}} \qquad (2)$$

$$\mathrm{Nd^{3+}} + 3\overline{\mathrm{(HA)}_2} + \overline{\mathrm{L}} \xrightleftharpoons{k_{ex}} \overline{\mathrm{NdA_3(HA)_3 \cdot L}} + 3\mathrm{H^+} \qquad (3)$$

Step 2: The neodymium complex compound diffuses from liquid membrane phase to stripping solution phase by the concentration gradient as a driving force.

Step 3: The neodymium complex react with H_2SO_4 solution, a stripping solution, at the liquid membrane-stripping solution interface.

Step 4: $Nd^{3+}$is transferred into the stripping solution while the extractant diffuses back to the feeding solution phase with a concentration gradient as a driving force to react again with Nd^{3+} in feed solution.

Property	**Description**	
	Value	***Unit***
Material	Polypropylene	
Inside diameter of hollow fiber	0.024	cm
Outside diameter of hollow fiber	0.03	cm
Effective length of hollow fiber	15	cm
Number of hollow fibers	35,000	
Average pore size	3 x 10^6	cm
Porosity	30%	
Effective surface area	1.4 x 10^4	cm^2
Area per unit volume	29.3	cm^2/cm^3
Module diameter	6.3	cm
Module length	20.3	cm
Contract area	30%	
Tortuosity factor	2.6	
Operating temperature	273 – 333	K

TABLE I. PROPERTIES OF THE HOLLOW FIBER MODULE

$$\overline{\mathrm{NdA_3(HA)_3}} + 3\mathrm{H}^+ \xrightleftharpoons{k_{st}} \mathrm{Nd}^{3+} + 3\overline{\mathrm{(HA)_2}} \qquad (4)$$

$$\overline{\mathrm{Nd(NO_3)_3 \square L_3}} + 3\mathrm{H}^+ \xrightleftharpoons{k_{st}} \mathrm{Nd}^{3+} + 3\mathrm{NO_3^-} + 3\overline{\mathrm{L}} + 3\mathrm{H}^+ \qquad (5)$$

$$\overline{\mathrm{NdA_3(HA)_3 \square L}} + 3\mathrm{H}^+ \xrightleftharpoons{k_{st}} \mathrm{Nd}^{3+} + 3\overline{\mathrm{(HA)_2}} + \overline{\mathrm{L}} \qquad (6)$$

The reaction involved in the stripping due to extraction reaction Eq. 1 – 3 are summarized in Eq. 4 – 6, respectively.

B. Synergistic extraction theory

The synergistic extraction is the extract metal ion species which use two extractants taken together with much higher efficiency as compared to the normal additive effect of these extractants separately. The optimal extraction of neodymium ion occurred at the mixture of 0.5M D2EHPA and 0.5 M TOPO in heptene served as the extractants [5].

Equations 1 – 3 were involved in this synergistic extraction. The primary extractions from direct reaction with D2EHPA and TOPO when D2EHPA is a proton acceptor and TOPO is a proton donor, as shown in Eq. 1 – 2. The reaction as shown in Eq. 3 was the secondary reaction where the reaction took place in the presence of D2EHPA - TOPO (Acceptor-donor interactions). It produced the complex D2EHPA-TOPO-metal ion. These complexes induce the cooperative transport of metal ion within the liquid membrane, thus increasing the extraction performance.

C. Mathematic model

The laminar transport of neodymium ion in feed phase with reaction flux and axial convection influence. The concentrations of neodymium ion along the hollow fiber tube vary depending on the axial direction and the extraction time corresponding to the accumulation of neodymium ions in the feed phase. The model in feed phase is made according to the following assumption [6]:

- The physical properties in feed phase are constant.
- The concentration of neodymium ions in the radial direction is constant because the inside diameter of hollow fiber is very small. Therefore means that the diffusion fluxes of neodymium ions in the feed phase exist only in the axial direction.
- Perfect mixing occur in the small cross sectional area of the inner tube. Therefore the concentration of neodymium ions in the radial direction is constant.
- Only complex species, not neodymium ions, are transport through the liquid membrane phase.
- The forwards reaction is dominant.

$$
\begin{aligned}
&[\text{Rate of mass transport into the system by convection}]\\
&-[\text{Rate of mass transport out of the system by convection}]\\
&+[\text{Rate of mass transport through the system by diffusion}]\\
&-[\text{Rate of mass extracted by extraction reaction}]\\
&=[\text{Rate of mass accumulation within the system}]
\end{aligned}
$$

For feed phase the mass conservation of neodymium ions in each segment (Δx) is considered by Eq. 8-9 [6]

$$q_f C_{Af}(x,t) - q_f C_{Af}(x+\Delta x,t) + \frac{A_f D_f}{\Delta x}(C_{Af}(x+\Delta x,t) + \Delta x A_f \cdot r_{Af} \qquad (7)$$

$$D_f = \frac{7.4\times10^{-8}(\phi M_w)^{0.5} T}{\eta_w v_{Nd^{3+}}^{0.6}} \qquad (8)$$

∂t

Where

$$r_{Af} = k_{Ex} C_{Af}^n(x,t) \qquad (9)$$

(10)

$$A_f = N \cdot \pi r_i^2 \qquad (11)$$

The percentage of Nd(III) extraction from experiment was calculated by Eq. 12.

$$\text{Extraction (\%)} = \left|\frac{[\mathrm{Nd}^{3+}]_{\mathrm{f,in}} - [\mathrm{Nd}^{3+}]_{\mathrm{f,out}}}{[\mathrm{Nd}^{3+}]_{\mathrm{f,in}}}\right| \times 100 \qquad (12)$$

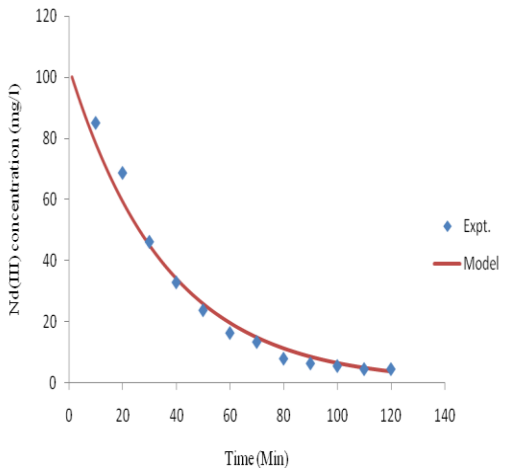

Fig. 4. Experimental and model of concentration of Nd(III) in feed solution (feed = pH 4.5; extractants = 0.5 M D2EHPA and 0.5 F TOPO; stripping =1 M H_2SO_4; flow rate = 100 mL/min for both feed and stripping solution).

The absolute error percentage of the extraction efficiency of Nd(III) obtained by experimental and model simulation is defined as Eq. 13.

$$\text{Absolute error (\%)} = \left| \frac{\left[\mathrm{Nd}^{3+}\right]_{\exp} - \left[\mathrm{Nd}^{3+}\right]_{cal}}{\left[\mathrm{Nd}^{3+}\right]_{\exp}} \right| \times 100 \qquad (13)$$

III. RESULTS AND DISCUSSIONS

A. *Model for concentration extraction of neodymium ions*

Figure. 4 is shown the concentration of Nd(III), at any time, from feed solution as calculated in Eq. 8 – 11 shows the comparison of concentration of Nd(III) in feed solution obtained from experimental results and from the models. It was found that the model provides good estimates of the concentration of Nd(III) in feed solution; the absolute error is 15.68%.

B. *Model for % extraction of neodymium ions*

The percentage of Nd(III) extraction was plotted in Fig. 5 by compare the experimental with predictive by model. The percentage of extraction was calculated by Eq. 12. The modeled results were in good agreement with the experimental data at the average percentage of deviation about 8.37%.

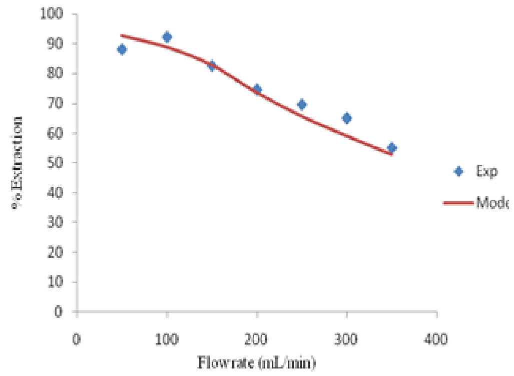

Fig. 5. Experimental and model of percentage extraction of Nd(III) in feed solution (feed = pH 4.5; extractants = 0.5 M D2EHPA and 0.5 F TOPO; stripping =1 M H_2SO_4; flow rate = 100 mL/min for both feed and stripping solution).

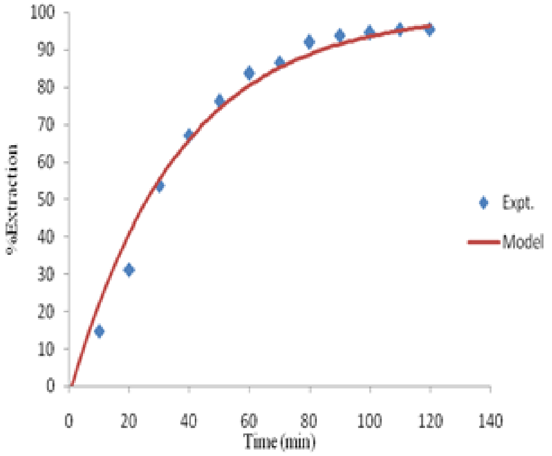

Fig. 6. Effect of volumetric flowrate in feed solution on percentage extraction of Nd(III) in feed solution (feed = pH 4.5; extractants = 0.5 M D2EHPA and 0.5 F TOPO; stripping =1 M H_2SO_4).

C. *Effect of the volumetric flowrate in feed solution*

The volumetric flowrate has an effect on the efficiency of Nd(III) extraction because the residence time and the formation rate of Neodymium complex will be decrease if the volumetric flowrate increase, and the efficiency of extraction will be also decrease. Figure 6 was plotted in feed phase by comparing the extraction results by experiment and predicted by model. We can see that the plot of neodymium extraction in this work predicted by the proposed model had the good agreement with the experiment data. The absolute error is 2.79%.

IV. CONCLUSION

Mathematical models considering the term of axial convection, axial diffusion, chemical reaction at the feed-liquid membrane and accumulation of neodymium ions have been developed to predict the extraction of neodymium ions. A hollow fiber supported liquid membrane system using 0.5M D2EHPA and 0.5M TOPO mixtures as the synergistic extractant and once-through-mode operation has been studied in this work. Simulation results of the developed models are in good agreement with the experimental data reported. The average percentage of absolute error is 8.95%.

NOMENCLATURE

A_f	inside cross-sectional area of the hollow fibers (cm^2)
C	concentration of neodymium ions (mg/dm^3)
C	concentration of neodymium ions (mg/dm^3)
D_f	diffusion coefficient of neodymium ions in feed phases
M_w	Molecular weight of water
n	reaction order of the extraction of neodymium ions
N	number of hollow fibers
q	volumetric flow rate in feed solution (mL/min)
r_{Af}	rate of neodymium ion extraction (mg/cm^3 min)
r_i	inside radius of a hollow fiber (cm)
t	extraction time (min)
T	Temperature of feed phase (K)
$[Nd^{3+}]_{f,in}$	initial concentration of Nd(III) in feed phase (mg/dm^3)
$[Nd^{3+}]_{f,out}$	concentration of Nd(III) in feed phase
$[Nd^{3+}]_{exp}$	concentration of Nd(III)from experimental
$[Nd^{3+}]_{cal}$	concentration of Nd(III) from calculated by model

ϕ association factor of water (=2.6)

η viscosity of water (cP)

ν molar volume of neodymium ions at normal boiling point

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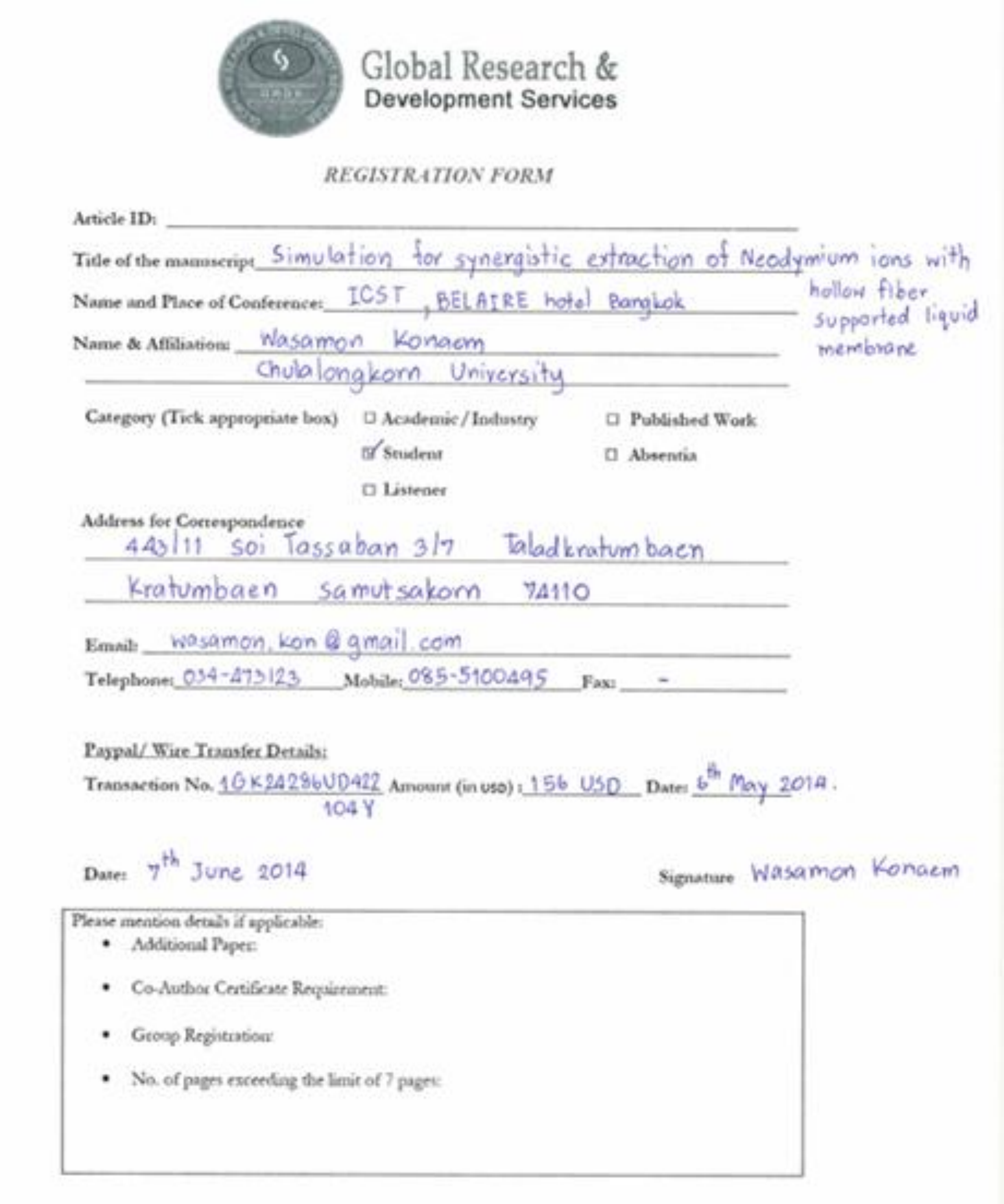

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Address for Correspondence
443/11 soi Tassaban 3/7 Taladkratumbaen
Kratumbaen samutsakorn 74110

Email: wasamon.kon@gmail.com

Telephone: 034-473123 Mobile: 085-5100495 Fax: -

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