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Synergistic Extraction and Separation of Mixture of Lanthanum and Neodymium by Hollow Fiber Supported Liquid Membrane

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Abstract−Separation of lanthanum and neodymium by supported liquid membrane has been studied. Synergistic extraction and recovery of lanthanum and neodymium with thenoyltrifluoroacetone (HTTA) in benzene have been found by the addition of Trioctylamine (TOA). Results indicate that percentage of extraction is highly dependent on pH of feed solution, which the maximum value is 2.5. When TOA was added to HTTA, the percentage of extraction and recovery considerably increased due to synergism. Lanthanum can be extracted and recovered more than neodymium because of the adduct formation constant, β_1. The β_1 values decreased with an increase in atomic number of lanthanide and showed a difference between lanthanum and neodymium. Percentage of extraction and recovery is enhanced when the HTTA concentration is increased, but its difference is larger when TOA concentration is increased. Finally, multi-column module of supported hollow fiber membrane was used and the percentage and difference of extraction and recovery was found to be more increased due to resident time.

Key words: Liquid Membrane, Synergistic, Extraction, Recovery, Hollow Fiber

INTRODUCTION

Lanthanide metals have recently drawn considerable attention in various applications exploiting their fluorescent, magnetic, optical, catalytic and laser properties. Lanthanum and neodymium are two lanthanide metals found in a large part of monazite and basnasite ores [Cotton, 1988]. However, they tend to come in a mixture form. Therefore, there has been a great interest in trying to purify these elements. The liquid membrane separation process is an attractive method to separate metal ions from the solution. Liquid membranes have been widely applied to the extraction and recovery of metal ions. The membranes contain an extractant or a carrier which possesses the potential for the selective permeation by using the facilitated transport [Porter, 1990] mechanism. This technique has been widely applied to the extraction and recovery of metal ions. In general, liquid membranes come either in an emulsion or a supported form. Emulsion liquid membrane (ELM) has a large transport area with a thin membrane [Ching-Yet and Pai-Zon, 1993]. Hence there is a fast solute extraction. Nonetheless, the complicated demulsification process for recovery of the concentrated solute as well as of the membrane liquid makes the Emulsion Liquid Membrane process very difficult to commercialize. In addition, ELM suffers from swelling instability of the inner phase. As for supported liquid membrane (SLM), the membrane is held in porous structure which is usually in porous membrane. The metal is extracted into a pore liquid at the feed solution-membrane interface. At the stripping solution-membrane interface, the metal is extracted back and concentrated in the stripping solution [Yi, 1995; Chaudry et al., 1997; Yang and Fane, 1999]. Although the low permeation rate and degradation of liquid membranes are the weak points of this method, the utilization of hollow fibers in the liquid membrane surface area is still available. The degraded membranes can be easily regenerated.

There are many kinds of supported liquid membrane, flat-plate-type, spiral-type and hollow fiber supported liquid membrane. Because there are several advantages of hollow fiber supported by liquid membrane such as lower amount of extractant than solvent extraction, long life time, low energy and high selectivity [Loiacono et al., 1986]. Therefore, in the present paper, the process of hollow fiber supported liquid membrane was examined experimentally for separation of a mixture of lanthanum and neodymium ions from aqueous solution. Here the liquid membrane is contained on the porous of hollow fiber. The aqueous feed solution flows inside of the tube side of the hollow fiber module and aqueous stripping solution flows inside of the shell side. Each aqueous-organic interphase is immobilized at the pore-mouth with capillary force. Both metal ions were transported through liquid membrane but each flux was not equal. Therefore, the lanthanum and neodymium were separated.

1. Theory

1-1. Liquid Membrane Mechanism

A supported liquid membrane (SLM) consists of an organic solution of an extractant (carrier), which is held in polymeric micropore by capillary force [Schultz, 1988]. Mechanism which transports the metal ions through liquid membrane is schematically illustrated in Fig. 1. The supported liquid membrane is between the aqueous solution initially containing metal ions (feed solution) and the aqueous solution initially containing no metal ions (strip solution). Transportation of ions is due to the driving force between the two opposite side of aqueous phase. In the case of metal carrier such as an acidic extractant (HR), the simple extraction reaction is as follows [Porter, 1990]:

$$M^{n+} + n\overline{HR} \xrightleftharpoons{k_{ex,1}} \overline{MR}_n + nH^+ \tag{1}$$

The driving force is achieved by hydronium ion (pH) gradient. The transport mechanism of metal ions that occurs in this case, called

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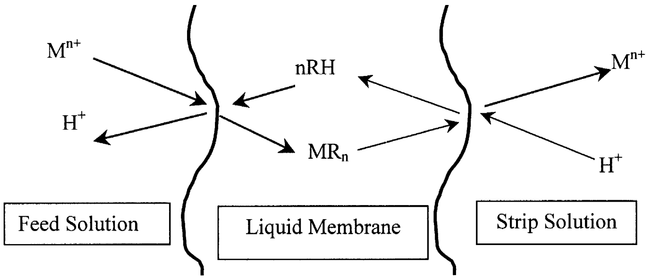

Fig. 1. Counter-transport scheme for acidic extractant.

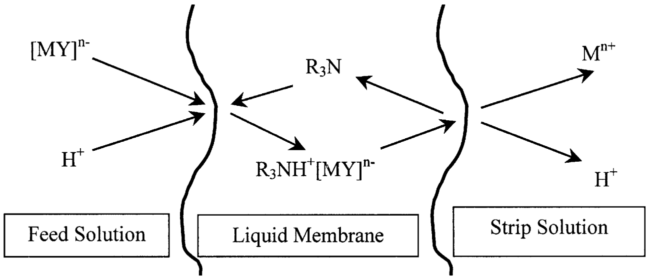

Fig. 2. Co-transport scheme for basic extractant.

counter-transport, is shown in Fig. 1. Forward reaction occurs at feed-membrane interphase and backward reaction occurs at membrane-strip interphase. The other case, called co-transport, shown in Fig. 2, occurs when the metal carrier is basic or neutral extractant (A)

$$M^{n+} + n\overline{X}^- + A \overset{k_{ex,2}}{\rightleftharpoons} \overline{MX_nA} \tag{2}$$

This process is driven by concentration gradient of the H^+ but M^{n+} and H^+ ions are transported in the same direction.

The extraction and stripping processes in Fig. 1 and 2 were occurring in hollow fiber module as shown in Fig. 3. Inside of hollow fiber module, it consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane is trapped in hydrophobic micropore and this liquid membrane separate the feed and stripping solutions, feed solution and strip solution flow counter-currently and liquid membrane is formed between them.

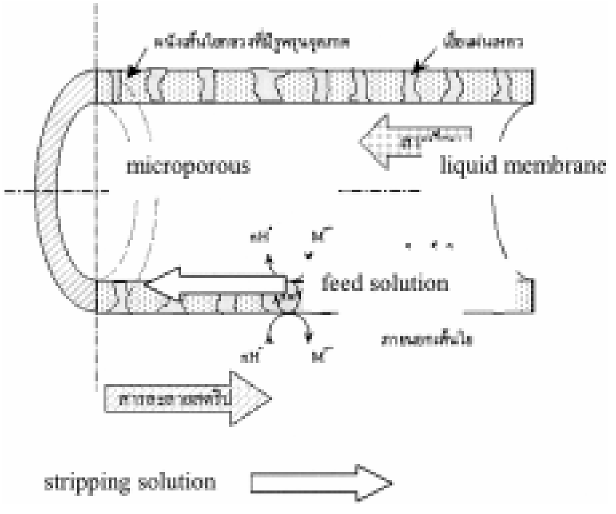

Fig. 3. Flow pattern in hollow fiber supported liquid membrane.

But in this work, two extractants were mixed together, synergistic, acidic and basic extractant. They cooperated to extract lanthanum and neodymium from mixture and extract by liquid membrane system [Jeong and Ju, 2002].

1-2. Synergistic Extraction

The phenomenon in which two extractants taken together extract a metal ion species with much higher efficiency as compared to the normal additive effect of these extractants (separately) is called synergism [Mathur, 1983]. Therefore, in this work, two extractants were mixed together, Thenolytrifluoroacetone (HTTA) and Trioctylamine (TOA), for enhancing the efficiency of extraction and also separating lanthanum from neodymium. Synergistic extraction has been only performed in solvent extraction process. Therefore, another objective in this study was to investigate the possibility that synergistic extraction was applied for liquid membrane process.

The extraction of metal ion (M^{n+}) by a mixture of monoacidic chelating agent (HR) and a neutral donor ligand [Peppard, 1969] shows the synergistic enhancement, it is due to the formation of one or several adduct complexes between the chelate MR_n and the donor ligand S in organic phase. Thus, if X^- denotes an inorganic anion in aqueous phase, at least three species can be assumed to be simultaneously present in the organic phase, i.e., MX_nS_p, MR_n and MR_nS_x and various equilibria involved can be written as [Duyckaerts and Desreux, 1977].

$$M^{n+} + n\overline{HR} \overset{k_{ex,1}}{\rightleftharpoons} \overline{MR_n} + nH^+ \tag{3}$$

$$M^{n+} + n\overline{X}^- + p\overline{S} \overset{k_{ex,2}}{\rightleftharpoons} \overline{MX_nS_p} \tag{4}$$

$$M^{n+} + n\overline{HR} + x\overline{S} \overset{k_{ex,1+2}}{\rightleftharpoons} \overline{M(HR)_nS_x} + nH^+ \tag{5}$$

where $k_{ex,1}$, $k_{ex,2}$ and $k_{ex,1+2}$ refer to equilibrium constant in presence of monoacidic extractant alone and in presence of neutral ligand, S, alone and in presence of both extractants, respectively. The value of $k_{ex,1}$, $k_{ex,2}$ and $k_{ex,1+2}$ can be given as

$$k_{ex,1} = \frac{[H^+]^n[\overline{MR_n}]}{[M^{n+}][\overline{HA}]^n} \tag{6}$$

$$k_{ex,2} = \frac{[\overline{MX_nS_p}]}{[M^{n+}][X^-]^n[\overline{S}]^p} \tag{7}$$

$$k_{ex,1+2} = \frac{[H^+][\overline{MX_nS_x}]}{[M^{n+}][\overline{S}]^x[\overline{HA}]^n} \tag{8}$$

The neutral ligand, S, is often very weak extractant by itself. Therefore, $k_{ex,1}$ and Eq. (3) can be neglected. When Eq. (4) is subtracted by Eq. (3)

$$\overline{MR_n} + x\overline{S} \overset{\beta_{n,x}}{\rightleftharpoons} \overline{MR_nS_x} \tag{9}$$

Eq. (9) becomes the synergistic reaction in organic phase (liquid membrane). Where

$$\beta_{n,x} = \frac{k_{ex,1+2}}{k_{ex,1}} \tag{10}$$

represents the stability constant of the synergistic reaction in organic phase and $\beta_{n,x}$ is the ratio of equilibrium constant in presence of both extractants and equilibrium constant in presence of monoacidic extractant alone [Duyckaerts and Desreux, 1977].

In this experiment, the percentage of extraction was determined as follows:

$$\%\ \text{extraction} = \frac{C_{in} - C_{raf}}{C_{in}} \times 100 \tag{11}$$

and percentage of recovery:

$$\%\ \text{recovery} = \frac{C_{st,out} - C_{st,in}}{C_{in}} \times 100 \tag{12}$$

where C_{in}, C_{raf}, $C_{st,in}$, $C_{st,out}$ are concentrations of feed, raffinate, inlet strip and outlet strip, respectively.

EXPERMENTAL

1. Chemicals

For liquid membrane, Thenoyltrifluoroacetone (HTTA) and. Tri-n-octylamine (TOA) supplied by Sigma and Merck were used. $LaCl_2 \cdot 7H_2O$ and Nd_2O_3 from Merck and Aldrich were used as feed solution. HNO_3 was used as stripping solution. All chemicals were A.R grade.

1-1. Apparatus

- The Liqui-Cel® Laboratory Liquid/Liquid Extraction System which is composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges was used.
- The Liqui-Cel® Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), shown in Fig. 4, was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into fabric and wrapped around a central tube feeder that supplies the shellside fluid. Woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The property of hollow fiber module was shown in Table 1. The fiber is potted into a solvent-resistant polyethylene tubesheet, and shell casing in polypropylene.
- pH was measured by pH-meter HI8418A , Hanna Instrument.
- Concentration of Lanthanum and neodymium were measured by Inductively Couples Plasma Spectroscopy (ICP).

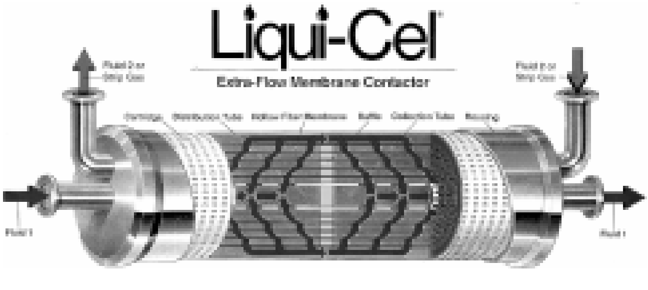

Fig. 4. Schematic representation of the structure of Liqui-Cel liquid membrane contractor.

Table 1. Property of hollow fiber module

Properties	Description
Materials	Polypropylene
Inside diameter of hollow fiber	240 μm
Outside diameter of hollow fiber	300
Size of pore	0.05
Porosity	30%
Maximum pressure drop	4.2 Kg/cm^2 (60 psi)
Contact area	139 m^2
Dimension of module	(2.5×8 inch)

1-2. Procedure

The feed solution was made by dissolution of $LaCl_2 \cdot 7H_2O$ and Nd_2O_3 in 0.5 M HNO_3 and pH was adjusted by LiOH. The liquid membrane was made by dissolution of HTTA and dilute of pure

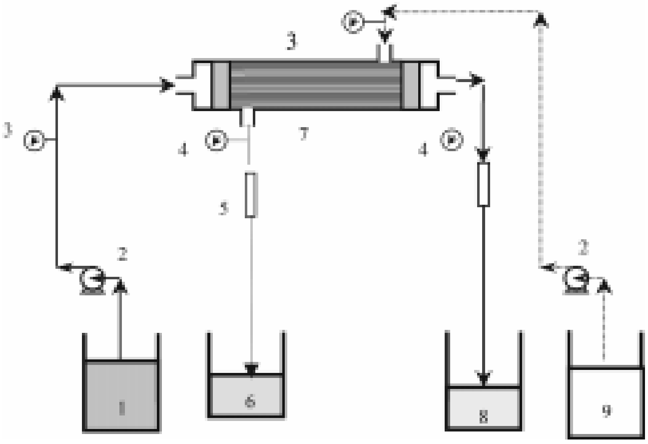

Fig. 5. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.

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

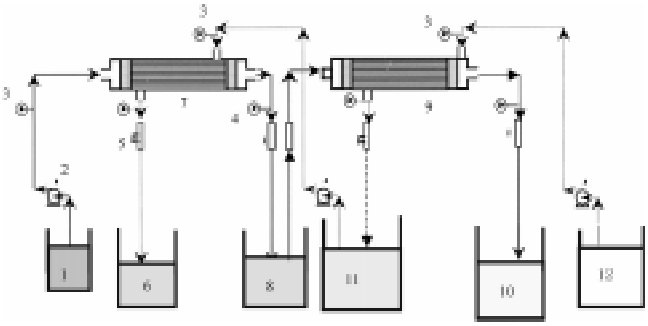

Fig. 6. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.

1. Feed reservoir to module no. 1
2. Gear pump
3. Inlet pressure gauges
4. Outlet pressure gauges
5. Flow meters
6. Strip outlet reservoir from module no. 1
7. Hollow fiber module no. 1
8. Raffinate reservoir from module no. 1 and feed to module no. 2
9. Hollow fiber module no. 2
10. Raffinate reservoir from module no. 2
11. Outlet strip reservoir from module no. 2 to module no. 1
12. Inlet strip reservoir to module no. 2

TOA in benzene. In all cases, the stripping solution was 0.5 M HNO_3 and the organic solution containing HTTA and TOA was circulated in tube and shell side of hollow fiber for 20 minutes. Then, experiment was started by flowing feed solution in the tubeside. Simultaneously, stripping solution was pumped into the shellside countercurrently and once-through-mode operation was used. The flow diagram was shown in Fig. 5 [Ramakul, 2002].

In a double-column operation, the system in Fig. 6 was used [Ramakul, 2002]. When the feed solution passes the first module, pH dropped drastically. Hence, some amount of LiOH was added to the raffinate to adjust the pH in order to increase driving force of feed solution in the second module.

RESULTS AND DISCUSSTION

1. Synergistic Effect in the HTTA+TOA System

From synergism theory, Eq. (3), extraction of metal by HTTA alone can be presented by

$$Ln^{3+} + 3\overline{HTTA} \overset{k_{ex,1}}{\rightleftharpoons} \overline{Ln(TTA)_3} + 3H^+ \tag{13}$$

From Eq. (5), the synergistic effect in the HTTA+TOA system arise from the reaction

$$Ln^{3+} + 3\overline{HTTA} + x\overline{TOA} \overset{k_{ex,1+2}}{\rightleftharpoons} \overline{Ln(TTA)_3TOA_x} + 3H^+ \tag{14}$$

Because TOA is a basic extractant and reacts with anion, extract reaction in Eq. (4) does not occur and synergistic effect in organic phase is

$$\overline{Ln(TTA)_3} + x\overline{TOA} \overset{\beta_{3,x}}{\rightleftharpoons} \overline{Ln(TTA)_3TOA_x} \tag{15}$$

From the result, lanthanum ions can be extracted and stripped more than neodymium ions due to the fact that β_1 value of lanthanum ions is higher than neodymium ions.

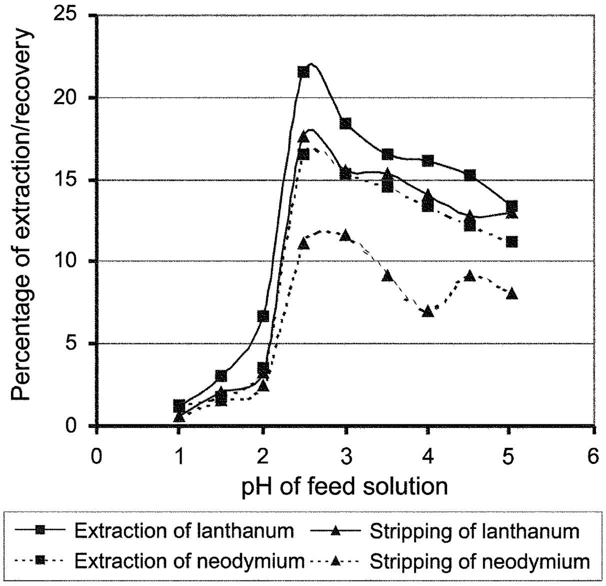

Fig. 7. Plot of percentage of extraction and recovery against pH of feed solution for the membrane using mixture of 0.01 M HTTA and 1% TOA and using 10 ppm La^{3+} and Nd^{3+} in feed solution.

The β_1 values decrease as the atomic number of lanthanide increases [Farbu Alstad, 1977] and showed a difference between lanthanum and neodymium with atomic number of 57 and 60, respectively.

The effect of operating conditions (pH of feed solution, concentration of extractant and its composition, number of columns and concentration of lanthanide ions in feed solution) on the extraction and separation of Lanthanum and Neodymium was examined.

2. Effect of pH of Feed Solution

The transport of La^{3+} and Nd^{3+} from feed solution through liquid membrane that contains acidic extractant is a counter-transport process in which the concentration gradient of hydrogen ion is the driving force. The dependence of the percentage of extraction of La^{3+} and Nd^{3+} on the pH value of feed solution is shown in Fig. 7. It is evident that percentage of extraction increases with increasing pH value in the range of 1.0 to 2.5. At pH value of 2.5, percentage of extraction is maximum. When pH value is more than 2.5, percentage of extraction is gradually decreased and all of these results also occur in stripping phase.

The extraction of lanthanum and neodymium ions by HTTA alone and by synergistic effect can be expressed as in Eqs. (13) and (14), respectively. From both equations, the principle of Henryi Louis Le Chatelier, when hydronium ions concentration was decreased more (pH increase), the metal ions were extracted more and converted to the product. However, the HTTA is an acidic extractant. It can react with metal ions in an acid solution only. Therefore, the percentage of extraction decreases when the pH is higher than 2.5.

3. Effect of HTTA Concentration in Liquid Membrane

The percentage of extraction rises abruptly by increasing the HTTA concentration while TOA concentration was 1%, as shown in Fig.

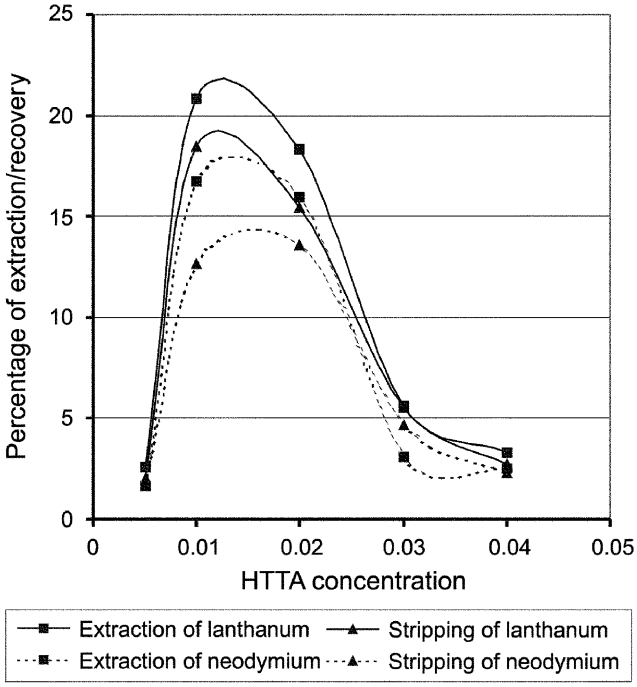

Fig. 8. Plot of percentage of extraction and recovery against HTTA concentration which mixed with 1% TOA for the membrane and using 10 ppm La^{3+} and Nd^{3+} and pH 2.5 for feed solution.

8. When HTTA concentration was higher, the metal ions reacted more and converted to complex compound in membrane and backward reacted at membrane-strip phase; therefore, the percentage of recovery was higher too. As concentration of HTTA was 0.01 mol/dm^3, the percentage of extraction and recovery are maximum. However, with the HTTA concentration exceeding 0.01 mol/dm^3, the percentage of extraction is decreased due to the viscosity of membrane being increased according to the molecular kinetic interpretation of Nernst. The diffusion coefficient D can be defined as [Schultz, 1988].

$$D=\frac{RT}{6\pi\eta r} \tag{16}$$

where η is the viscosity of the liquid membrane r and T the radius of the diffusion component and process temperature, respectively. Moreover, the difference between lanthanum and neodymium is smaller because of higher HTTA concentration than TOA concentration also, Eq. (13) occurs more than Eq. (14).

4. Effect of TOA Concentration in Liquid Membrane

In Fig. 9, at concentration of TOA in membrane is zero or HTTA extracts metal ions alone. Percentages of extract and recovery were very small, about 2%. When TOA was added in 0.01 M HTTA in membrane, the percentage of extract and recovery abruptly increased. This phenomenon is called synergistic extraction. Moreover, the difference between Lanthanum and neodymium is increased with increased TOA concentration because extraction reaction in Eq. (14) occurs more. And Eq. (14) is bound to extract lanthanum more than neodymium ions due to β_1 value of lanthanum ions is higher than neodymium ions. However, when TOA concentration is more than 1%, the percentage of extract and recovery of both ions decreases because viscosity of membrane is too high [Schultz, 1988].

5. Effect of Number of Hollow Fiber Module

In hollow fiber modules, the extract reaction or the exchanging of metal and hydrogen occurred. So, pH of raffinate is usually less than that of feed solution and the driving force is lower. When the double-column (hollow fiber module) was used, the pH of raffinate

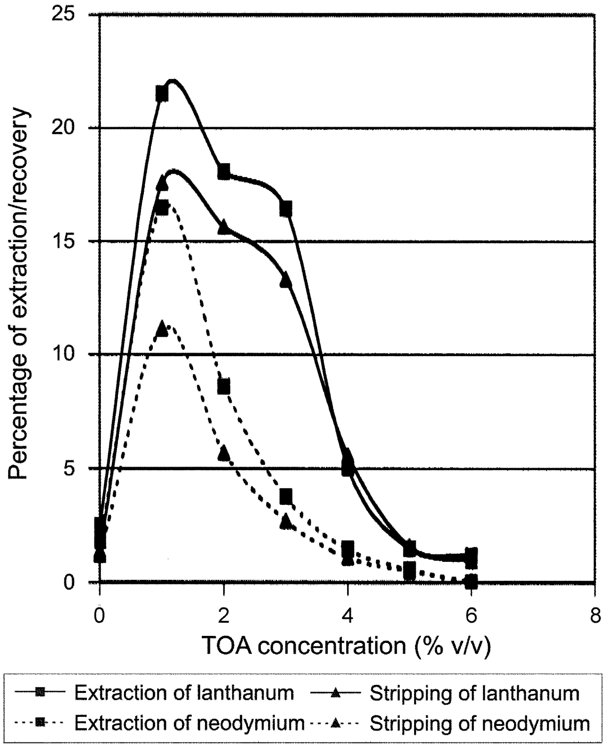

Fig. 9. Plot of percentage of extraction and recovery against TOA concentration which mixed with 0.01 M HTTA for the membrane and using 10 ppm La^{3+} and Nd^{3+} and pH 2.5 for feed solution

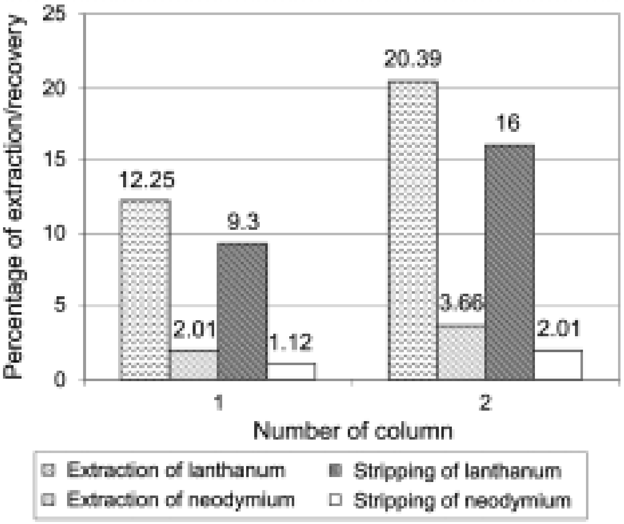

Fig. 10. Relation of number of hollow fiber module and percentage of extraction and recovery at 0.01 M HTTA, 3% TOA, 10 ppm La^{3+} and Nd^{3+} of feed solution.

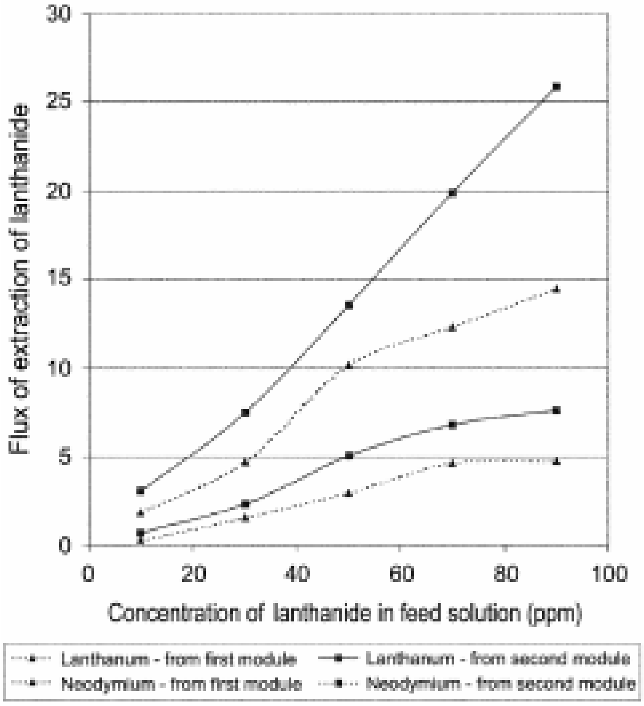

Fig. 11. Plot of flux of extraction against feed concentration for the membrane using mixture of 0.01 M HTTA and 3% TOA and pH 2.5 for feed solution.

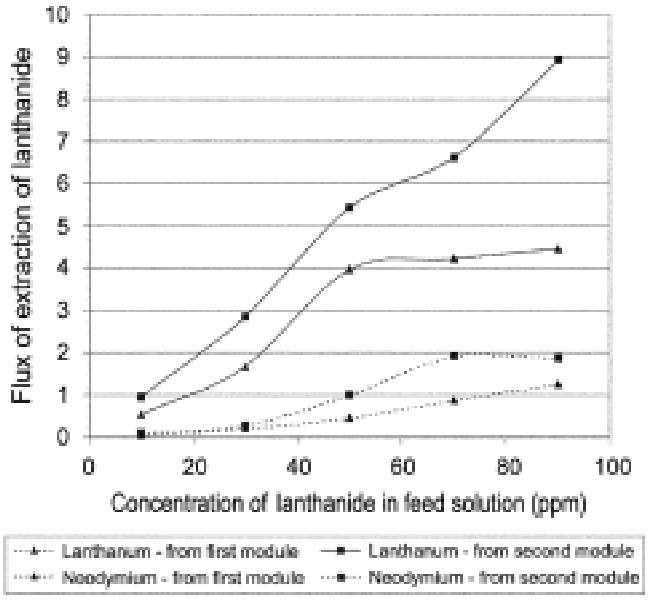

Fig. 12. Plot of flux of recovery against feed concentration for the membrane using mixture of 0.01 M HTTA and 3% TOA and pH 2.5 for feed solution.

from first module was adjusted to 2.5 again by LiOH and fed as feed solution to second module continuously. The result is shown in Fig. 10. Obviously, when the double-column was used, percentage of extraction and recovery increased because driving force was recovered.

6. Effect of Concentration in Feed Solution

When the concentration of lanthanum and neodymium ions in feed solution increased from 10 ppm to 30, 50, 70 and 90 ppm, there was no changing of percentage of extraction and recovery but flux was increased. This result corresponded to the theoretical model proposed by Rovira and Sastre [1998] that the extraction flux of metal ions in the supported liquid membrane is proportional to the concentration of metal ions in the feed solution when the concentration is extremely small. The result is shown in Fig. 11. From Eqs. (13) and (14), increasing the concentration of lanthanide ions in feed solution results in the increase in the transport of the lanthanide ions to stripping solution, which enhances the decrease in pH of feed solution because of the counter-transport of hydrogen ions. Moreover, the double-column was used for each experiment to prove that it can increase the percentage of extract and recovery from single column.

CONCLUSIONS

Hollow fiber supported liquid membrane can be used to extract lanthanum and neodymium ions. When TOA was added to HTTA, the percentage of extraction and recovery considerably increased. The appropriate pH was 2.5 and lanthanum could be extracted and recovered more than neodymium ions. Percentage of extraction and recovery rises when the HTTA concentration is increased, but its difference is larger when TOA concentration is increased. Double-column module of supported hollow fiber membrane can increase percentage and difference of extraction and recovery.

NOMENCLATURE

A : neutral extractant
C_{in} : concentration of feed
C_{raf} : concentration of raffinate
$C_{st,\ in}$: concentration of inlet strip
$C_{st,\ out}$: concentration of outlet strip
HR : acidic extractant
$k_{ex,\ 1}$: equilibrium constant of extraction reaction in presence of monoacidic extractant alone
$k_{ex,\ 2}$: equilibrium constant of extraction reaction in presence of neutral ligand alone
$k_{ex,\ 1+2}$: equilibrium constant of extraction reaction in presence of both extractants
Ln^{3+} : trivalent lanthanide ions
M^{n+} : metal ions
R : gas constant
S : ligand or basic extractant
T : temperature of process

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