

One-through Selective Separation of Copper, Chromium and Zinc Ions by Hollow Fiber Supported Liquid Membrane

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Abstract—The separation of a mixture of Cu(II), Cr(VI) and Zn(II) simultaneously from a sulfate media using two consecutive hollow fiber microporous liquid membrane extraction systems has been studied. The experiments were made in the one-through mode. LIX84-I and Aliquat336 were used as carrier extractants for copper and chromium in the first and second hollow fiber modules, respectively. Pure copper and pure chromium ions are extracted and stripped from first and second hollow fiber modules, respectively, but zinc ions cannot be extracted by both extractants due to pH conditions used in this study and remain in the raffinate. Results indicate that the percentage of extraction is highly dependent on pH of the feed solution and the pH value is 2.5 for the maximum extraction. The percentage of extraction of copper and chromium ions is enhanced when the concentration of LIX84-I and Aliquat336 is increased of which both maximum value is 0.5 M, and these results also occur in stripping phase. The influence of sulfuric acid and sodium hydroxide concentration in strip solution of each column was examined, and it was found that the percentage of extraction and stripping is further increased due to the difference of driving force. The maximum percentage of extraction for copper is 33% and 92% for chromium. The experimental results indicated the feasibility of separation and recovery of these metals from the dilute solution by using membrane technology.

Key words: Extraction, Liquid Membrane, Hollow Fiber, Copper, Chromium, Zinc

INTRODUCTION

The presence of copper, chromium and zinc ions in the environment is a major concern due to their toxicity to many life forms. These heavy metals are widely used in various applications. Chromium has numerous industrial applications including their use in stainless steels, nonferrous alloy, metal plating, refractory material and electroplate coating chromate preservative. Copper is currently used in kitchen utensils, as thermal and electric conductors, and in sanitation. Copper solution is used in various chemical processes, and zinc and its compounds are used in production of alloys (brass, bronze) as anticorrosion coatings (galvanization) of steel and iron products, in electrical apparatus, especially dry cell batteries, in the rubber and textile industry, glass ceramic manufacture, and chemical manufacture [Seiler, 1994]. The major components of effluent/wastes of some metallurgical/plating industries are zinc and copper. Cementates of the zinc industry are obtained during the hydrometallurgical zinc-winning process, and the waste contains Cu (28.6%) and Zn (22.4%). Similarly, the plating industry waste contains zinc, copper and some chromium [Sarangi, 2004].

For this reason, the selective extraction and separation of these metals from their mixed solution is of great interest in hydrometallurgical processes due to the possibility of recovering the metal values, as well as addressing the environmental pollution problems. This separation or removal of copper, zinc and chromium can be achieved by liquid membranes systems that have been widely applied to the extraction and recovery of metal ions from solutions. The simultaneous extraction and stripping operation is very attrac-

tive because metal ions can move from low to high concentration solutions. The membranes contain an extractant or a carrier which possesses the potential for selective permeation by using the facilitated transport mechanism [Gherrou and Hacene, 2002]. This technique has been widely applied to the extraction and recovery of metal ions. One promising technique of liquid membrane is the use of micro porous hollow fiber modules as liquid-liquid phase contactors. The basic principle of hollow fiber supported liquid membrane (HFSLM) is the immobilization of organic extractant into the pores of a hydrophobic membrane [Loiacono et al., 1986; Sheng et al., 2004].

The potential advantages of HFSLMs over traditional separation techniques are: lower capital and operating costs, low energy and low extractant consumption factors and high fluxes compared to solid membranes [Loiacono et al., 1986; Sheng et al., 2004]. Due to these advantages, SLMs may be very useful for the recovery of metals from solutions.

The processes of most of researches that deal with the separation of copper, zinc or chromium or other mixed ions cannot purely separate from their mixed solution: 100% selectivity cannot be obtained [Sarangi and Das, 2004; Kyuchoukov, 2000; Qwusu, 1998].

In this paper, we focused on the separation of three component ions—copper, zinc and chromium—from mixture by using one-through flow. Two modules of hollow fiber supported liquid membrane were connected in series. Because of high selectivity of extractant, pure copper and pure chromium ions were separated from the first and second module, respectively. 100% selectivity could be achieved.

LIX84-I was used for extracting copper (Cu^{2+}) from mixture of three component ions because LIX84-I is a strong copper extractant [Fernado and Haris, 2000]. Aliquat336 was used for extracting chromium (HCrO_4^-) because quaternary ammonium salt is known

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to be an efficient extractant of many solutes, such as anionic species [Berta et al., 2004]. Copper and chromium are extracted selectively and simultaneously, and zinc was in the residue.

THEORY

A liquid membrane an extractant; carrier was immobilized in the pores of a hydrophobic microporous supporter which binds one of the components very selectively from the feed solution. The SLM separated the aqueous feed solution and the strip solution. The species are accumulated in the strip at a concentration generally greater than that in the feed solution. The permeation of the species is due to a chemical potential gradient (the driving force of the process) existing between two opposite sides of the SLM [Schulz, 1988; Ramakul and Pancharoen, 2003].

The transport of metal ions by extractant, the facilitated transport [Alguacil, 2002], is described as follows [Porter, 1990]:

The metal ions are complexed by extractant at the interface feed-phase/membrane and the complex formed diffuses through the membrane phase to the interface membrane/strip-phase where the de-complexation of the metal ions occurs. In the case that the carrier is being an acidic extractant (HA), the simple extraction reaction is shown as follows [Porter, 1990; Ramakul and Pancharoen, 2003]:



The driving force is achieved by the hydronium ion (pH) gradient. The hydronium ion is counter-transported with metal ion. This case, called counter-transport, is presented in Fig. 1. The forward reaction occurs at the feed-membrane interphase and the backward reaction occurs at membrane/strip interphase.

The other case occurs when the metal carrier is a basic or neutral extractant. This process, shown in Fig. 2, called co-transport, is driven by the concentration gradient of the OH^- . The hydroxide ion is counter-transported with metal ion. As a result, hydrogen and metal ions are transported in the same direction, co-transport, and metal ions must be in anion complex form [Porter, 1990]. The chemistry of extraction is shown in Eq. (2). X is denoted as Cl^- for the first cycle of extraction of extractant and denoted as OH^- for the next cycle [Nakararueng, 2004].

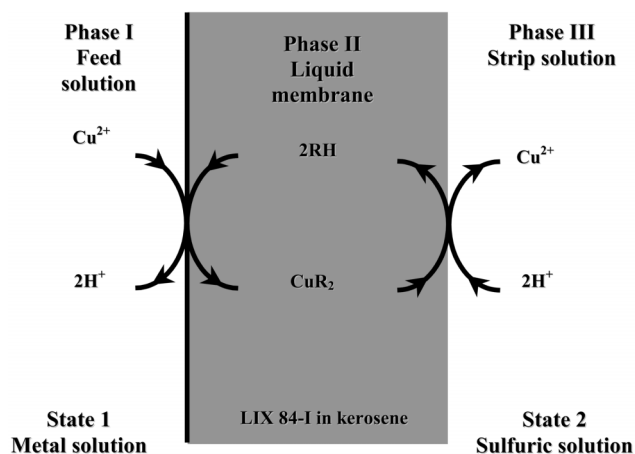


Fig. 1. Counter-transport scheme for acidic extractant.

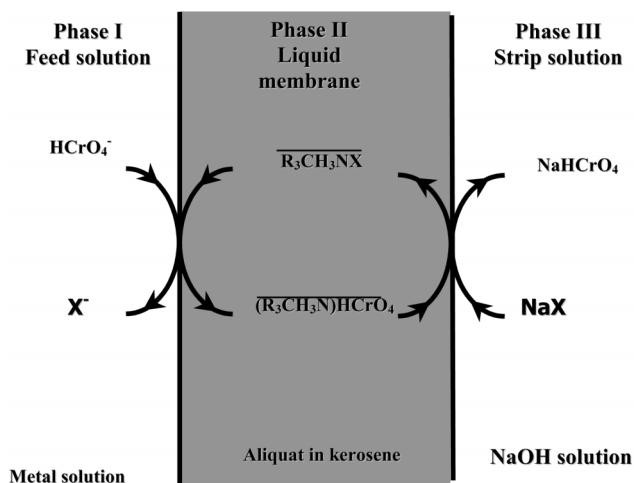


Fig. 2. Co-transport scheme for basic extractant.

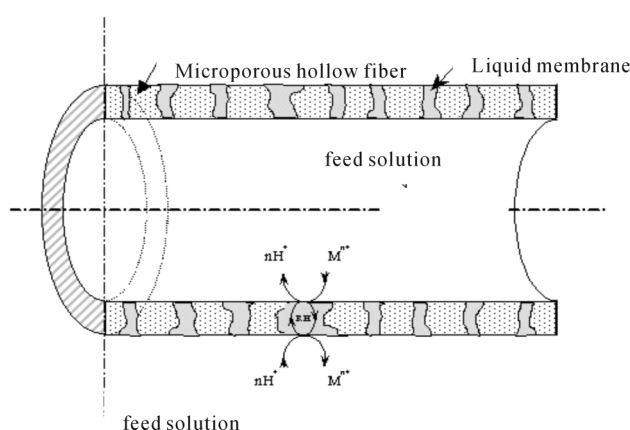


Fig. 3. Flow pattern in hollow fiber supported liquid membrane.



The extraction and stripping steps in Fig. 1 and Fig. 2 occurred in hollow fiber modules as shown in Fig. 3. The hollow fiber module consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane was trapped in hydrophobic micropore due to capillary force [Schulz, 1988] and separated feed and strip solution. Feed solution and strip solution flow countercurrently and liquid membrane was between them [Ramakul and Pancharoen, 2003].

In this work, two kinds of metal ions, copper, zinc and chromium were mixed together in feed solution. Copper and zinc are in cation (Cu^{2+} and Zn^{2+}) but chromium is in an anion complex form (HCrO_4^-). Copper ions can be extracted by an acidic extractant, LIX84-I from first hollow fiber module while HCrO_4^- can be extracted by a basic extractant, Aliquat336, from the second one.

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

$$\% \text{ extraction} = \frac{C_{i,\text{feed}} - C_{i,\text{raf}}}{C_{i,\text{feed}}} \times 100 \quad (3)$$

and the percentage of recovery:

$$\% \text{stripping} = \frac{C_{i,st}}{C_{i,feed}} \times 100 \quad (4)$$

The selectivity is defined as follow:

$$S_i = \frac{C_{i,st}}{\sum_{i=1}^n C_{i,st}} \quad (5)$$

where $C_{i,feed}$, $C_{i,ref}$, $C_{i,st}$ are the concentration of feed, raffinate, outlet strip of component i , respectively.

EXPERIMENTAL

1. Chemicals

For a feed solution, $\text{Cu}(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{SO}_4)_4 \cdot 7\text{H}_2\text{O}$ and K_2CrO_4 were supplied by Merck, LIX84-I from Henkel Thai Ltd. and Methyltriocetylammmonium Chloride (Aliquat336) from Merck were used as liquid membrane. H_2SO_4 and NaOH were used as strip solution. All chemicals were A.R. grade.

2. Apparatus

Two of the Liqui-Cel® Extra-Flow modules offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), were 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 properties of the hollow fiber module are shown in Table 1. The fiber is potted into a solvent-resistant polyethylene tubesheet and shell casing in polypropylene.

The Liqui-Cel® Laboratory Liquid/Liquid Extraction System was

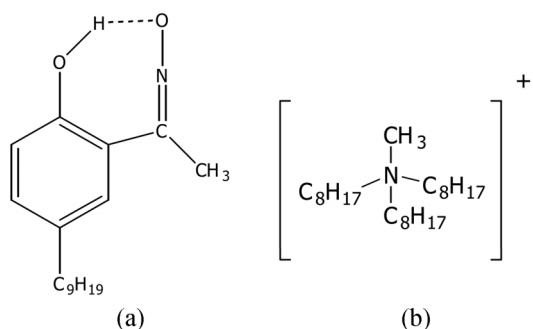


Fig. 4. Chemical structure of the extractant. (a) LIX84-I, (b) Aliquat336.

Table 1. Properties of hollow fiber module [Ramakul, 2002]

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

used. It is composed of three gear pumps, three variable speed controllers, three rotameters and three pressure gauges.

- pH was measured by pH-meter HI8418A.
- The concentrations of three metal ions were measured by Inductively Coupled Plasma Spectroscopy (ICP).

3. Procedure

The feed solution was made by dissolution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, K_2CrO_4 and ZnSO_4 , and pH was adjusted by H_2SO_4 . The liquid membrane phase was prepared by dissolution of LIX84-I for the first hollow fiber module and Aliquat336 for the second hollow fiber module. Both extractants were dissolved in kerosene. The strip solution was H_2SO_4 and NaOH for the first and second hollow fiber modules, respectively. The organic solution which contained LIX84-I and Aliquat336 was circulated in the tube and shell side of the first and second hollow fiber modules, respectively, for 20 minutes. Then, the experiment was started by flowing the feed solution into the tube side of both hollow fiber modules. Simultaneously, the strip solution was pumped into the shell side of hollow fiber module countercurrently and once-through-mode operation was used. The flow diagram is shown in Fig. 5 [Nakararueng, 2004].

RESULTS AND DISCUSSTION

1. The Effect of the pH of Feed Solution

The effect of pH on concentration of stripping solution from the first and the second hollow fiber module and the raffinate is shown in Table 2. Good agreement of a material balance can be obtained. The selectivity was calculated by using Eq. (5) and 100% selectivity of copper and chromium can be achieved.

The percentage of extraction and stripping was calculated by using Eqs. (3) and (4), respectively, as shown in Table 2. The dependence

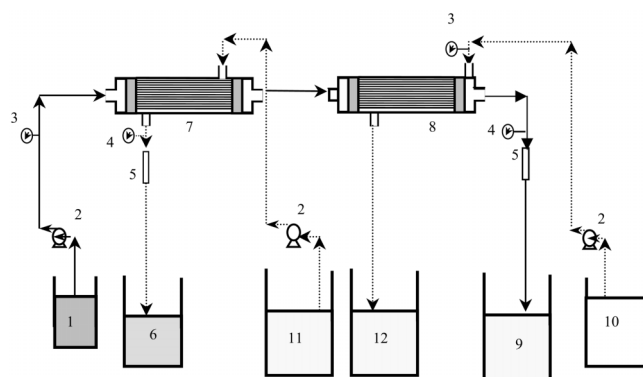
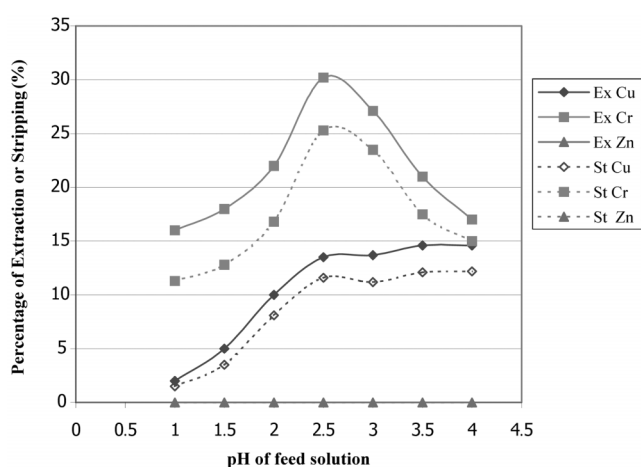


Fig. 5. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.

1. Feed reservoir to first hollow fiber module
2. Gear pump
3. Inlet pressure gauges
4. Outlet pressure gauges
5. Flow meters
6. Strip outlet reservoir for copper extraction
7. First hollow fiber module
8. Second hollow fiber module
9. Raffinate reservoir
10. Inlet strip reservoir for chromium extraction
11. Inlet strip reservoir for copper extraction
12. Strip outlet reservoir for chromium extraction

Table 2. Effect of pH on concentration of stripping solution from first, second column and raffinate while using 1% (v/v) Aliquat336, 100 ppm Cu^{2+} , HCrO_4 and Zn^{2+} , 0.1 M H_2SO_4 and 0.5 M NaOH for Strip solution in the first and second hollow fiber modules, respectively

pH	Concentration of stripping solution from <i>first</i> column (ppm)			Concentration of stripping solution from <i>second</i> column (ppm)			Concentration of raffinate (ppm)			Percentage of extraction (%)			Percentage of stripping (%)		
	Cu	Cr	Zn	Cu	Cr	Zn	Cu	Cr	Zn	Cu	Cr	Zn	Cu	Cr	Zn
1.0	1.5	0	0	0	11.3	0	98	84	100	2	16	0	1.5	11.3	0
1.5	3.5	0	0	0	12.8	0	95	82	100	5	18	0	3.5	12.8	0
2.0	8.1	0	0	0	16.8	0	90	78	100	10	22	0	8.1	16.8	0
2.5	11.6	0	0	0	25.3	0	86.5	69.8	100	13.5	30.2	0	11.6	25.3	0
3.0	11.2	0	0	0	23.5	0	86.3	72.9	100	13.7	27.1	0	11.2	23.5	0
3.5	12.1	0	0	0	17.5	0	85.4	79	100	14.6	21	0	12.1	17.5	0
4.0	12.2	0	0	0	15	0	85.4	83	100	14.6	17	0	12.2	15	0

**Fig. 6. Plot of percentage of extraction and stripping against pH of feed solution for the membrane using mixture of 1% LIX84-I and 1% Aliquat336 and using 100 ppm Cu^{2+} , HCrO_4 and Zn^{2+} in feed solution and 0.1 M H_2SO_4 , 0.5 M NaOH for strip solution in first and second hollow fiber module, respectively.**

of the percentage of extraction and stripping of copper and chromium ions on the pH value of feed solution is shown in Fig. 6.

In the first hollow fiber module, the extractant that carries copper ions from the feed solution through the liquid membrane is acidic extractant (LIX84-I) in which the concentration gradient of hydrogen ion is the driving force, and countercurrent transport occurs. It is evident that the percentage of extraction increases with increasing pH value in the range of 1.0 to 2.5. When pH value is higher than 2.5, the percentage of extraction is constant and all of these results also occur in the stripping phase as shown Fig. 6.

Selectivity of Cu and Cr was calculated by using Eq. (5). The concentration of stripping solution from first and second hollow fiber column is pure Cu and Cr, respectively, as shown in Table 2. The 100% of selectivity can be obtained in both Cu and Cr.

The extracted reaction of copper ions by LIX84-I in the first hollow fiber module can be expressed as in Eq. (1). From Le Chatelier's principle, when hydronium ion concentration decreased (pH increase), the metal ions were extracted more and converted to the product. As LIX84-I is an acidic extractant, it can react with metal

ions in an acid solution only. Therefore, the percentage of extraction reaches a constant when the pH is higher than 2.5.

In the second hollow fiber module, the chromium ions are carried by Aliquat336 from the raffinate solution of the first hollow fiber module through the liquid membrane. Aliquat336 is a basic extractant in which the concentration gradient of hydroxide ion is the driving force and counter-current (or co-current with the hydronium ions) transport occurs. The dependence of the percentage of extraction of ions on the pH value of feed solution is shown in Fig. 6. It is found that the percentage of extraction increases with decreasing pH value in the range of 4.0 back to 2.5. At pH value of 2.5, the percentage of extraction is maximum. When the pH value is lower than 2.5, the percentage of extraction abruptly decreases and these results also occur in the stripping phase.

The extracted reaction of chromium ions in the second hollow fiber module by Aliquat336 can be expressed as in Eq. (2). From Le Chatelier's principle, when the concentration of hydroxide ions was decreased (pH decrease) the chromium ions were extracted more and converted to the product. As Aliquat336 is a basic extractant, it can react with metal ions in a basic or low acidity solution only [Thornton, 1992]. Therefore, the percentage of extraction decreases when the pH is lower than 2.5. From the result of the experiment, the pH for the maximum percentage of extraction of copper and chromium from their mixed solution was 2.5 and the pH of the following experiments was fixed at 2.5.

It should be noted that a high pH value in the aqueous phase may cause the metal ions to precipitate and these would hinder the extraction [Campderrós et al., 1998]. In the first column, copper was extracted by LIX84-I only because LIX84-I is a strong copper extractant which acts by cation exchange in a chelate-type complex formation. Cu(II) is able to form a chelate complex with the oximic extractant and release a hydrogen ion into the aqueous solution from which the metal was extracted. Under the pH conditions used in these experiments, Zn(II) cannot be extracted [Fernado and Haris, 2000]. Hydroxyoximes, the active components of LIX84-I, contain two chemically active groups: a phenolic group of low acidity and oximino group containing nitrogen with a free electron pair. As a result, a stable complex with the structure as shown in Fig. 7 is formed, especially with Cu(II) ions [Francisco and Antonio, 1999]. In the second column, zinc also cannot be extracted by Aliquat336 because Aliquat336 only reacts with anion metal complex. Consequently, zinc

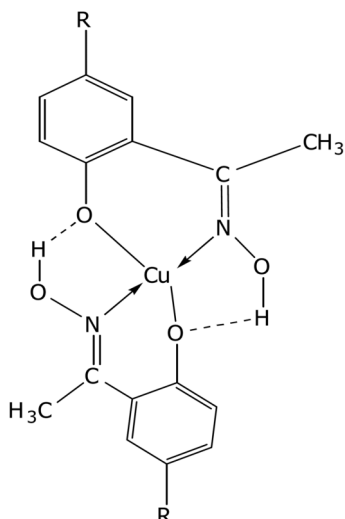


Fig. 7. The structure of the copper-LIX84-I complex [Francisco and Antonio, 1999].

ions remained in the raffinate.

2. The Influence of LIX84-I and Aliquat336 Concentration in Liquid Membrane

The variation of percentage of extraction LIX84-I concentration vs. the extractant concentration is shown in Fig. 8.

When LIX84-I concentration was 1-2.5% (v/v), the percentage of the extraction of copper ions rose abruptly by increasing its concentration, as shown in Fig. 8. As the concentration of LIX84-I was 2.5% (v/v), the percentage of extraction and stripping was maximum. For the extraction of chromium ions in the second column, the percentage of extraction rose gradually when the Aliquat336 concentration increased and LIX84-I concentration was fixed at 2.5% (v/v), as shown in Fig. 9. When the concentration of Aliquat336 was 4% (v/v), the percentage of extraction was maximum. However, with the concentration of LIX84-I and Aliquat336 exceeding 2.5% (v/v) and 4% (v/v), respectively, both percentages of extraction were constant due to the viscosity of membrane being increased according to the molecular kinetic interpretation of Nernst. The diffusion coefficient (D) can be defined as [Schulz, 1988].

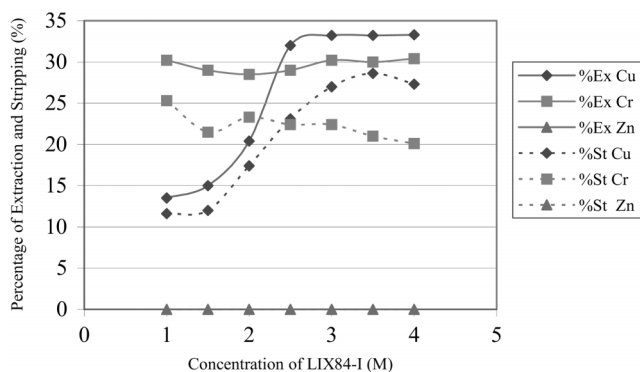


Fig. 8. Plot of percentage of extraction and recovery against LIX84-I concentration while using 1% (v/v) Aliquat336 for the membrane, 100 ppm Cu^{2+} , HCrO_4^- and Zn^{2+} in feed solution and 0.1 M H_2SO_4 , 0.5 M NaOH for Strip solution in the first and second hollow fiber modules, respectively.

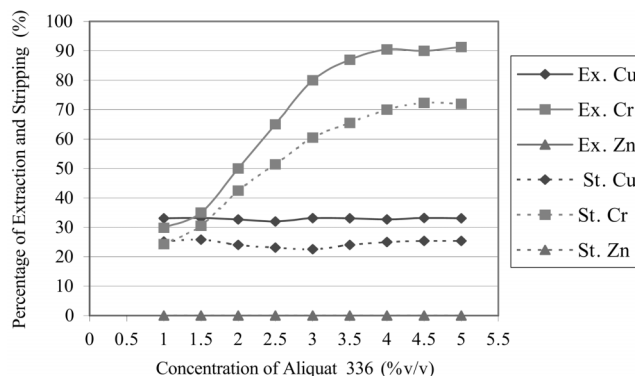


Fig. 9. Plot of percentage of extraction and recovery against Aliquat336 concentration while using 2.5% (v/v) LIX84-I for the membrane, 100 ppm Cu^{2+} , HCrO_4^- and Zn^{2+} in feed solution and 0.1 M H_2SO_4 , 0.5 M NaOH for strip solution in the first and second hollow fiber modules, respectively.

$$D = \frac{RT}{6\pi\eta r} \quad (6)$$

where η is the viscosity of the liquid membrane r ; and T the radius of the diffusion component and process temperature, respectively. Hence, all the following LIX84-I and Aliquat336 concentrations will be fixed at 2.5% (v/v) and 4% (v/v), respectively.

3. The Influence of Sulfuric Acid and Sodium Hydroxide Concentration in Strip Solution

The effect of H_2SO_4 and NaOH concentration in the first and second hollow fiber modules on the stripping was shown in Fig. 10 and Fig. 11, respectively.

The stripping of copper ions by LIX84-I in first hollow fiber module and chromium ions by Aliquat336 in the second hollow fiber module can be expressed as in the backward reaction of Eq. (1) and (2), respectively. From the principle of Le Chatelier, when hydronium ion concentration increases, the concentration difference of hydronium ion between feed and strip solution increases. Therefore,

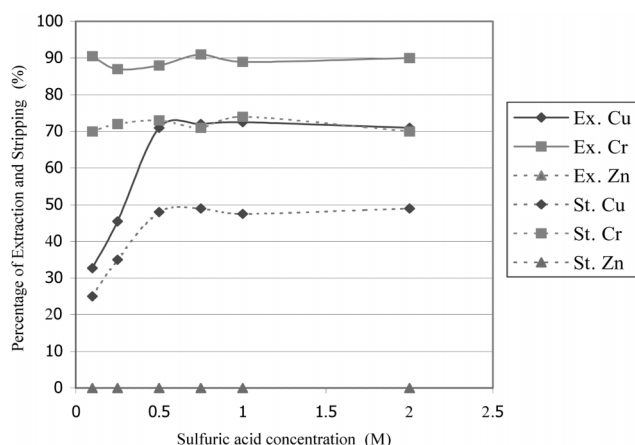


Fig. 10. Plot of percentage of extraction and recovery against sulfuric acid concentration in first hollow fiber module while using 2.5% (v/v) LIX84-I for the membrane, 100 ppm Cu^{2+} , HCrO_4^- and Zn^{2+} in feed solution and 0.1 M H_2SO_4 , 0.5 M NaOH for strip solution in the first and second hollow fiber modules, respectively.

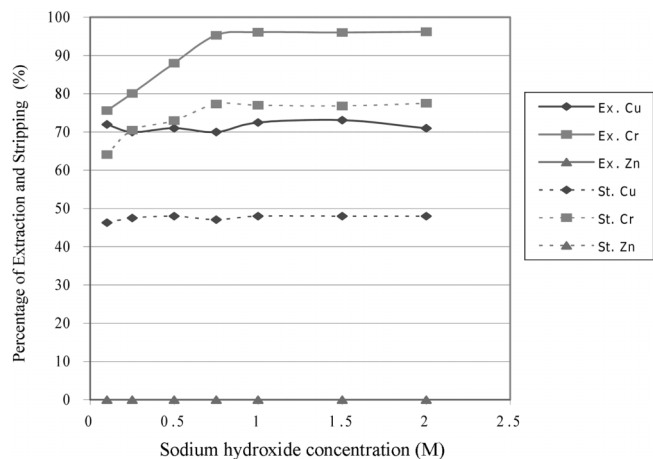


Fig. 11. Plot of percentage of extraction and recovery against sodium hydroxide concentration in second hollow fiber module while using 2.5% (v/v) LIX84-I for the membrane, 100 ppm Cu^{2+} , HCrO_4^- and Zn^{2+} in feed solution and 0.1 M H_2SO_4 , 0.5 M NaOH for strip solution in first and second hollow fiber module, respectively.

more copper ions were extracted into liquid membrane and stripped into the strip solution. Similarly, when the hydroxide ion concentration increased, more chromium ions were extracted and stripped more into its strip solution. However, when the H_2SO_4 and NaOH concentrations were higher than 0.5 M, the percentage of stripping was constant due to the limitation of mass transfer area of hollow fiber [Nakararueng, 2004; Pattawekongka, 2002].

Material balances were not shown for all experiments. However, good material balance agreement can be obtained.

CONCLUSIONS

The hollow fiber supported liquid membrane can be used to extract the copper, chromium ions by one-through flow. Copper ions can be purely extracted by LIX84-I and chromium ions can be purely extracted by Aliquat336, but zinc ions cannot be extracted by any extractants under the experimental conditions investigated in this study.

The percentage of extraction and stripping is highly dependent on pH of feed solution, which has a maximum value of 2.5. The appropriate concentration of LIX84-I and Aliquat336 was 2.5% (v/v) and 4% (v/v), respectively. When sulfuric acid and sodium hydroxide concentration in the strip solution were increased, the copper and chromium ions, respectively, were extracted and stripped more into its strip solution.

NOMENCLATURE

- $C_{i, \text{feed}}$: concentration of feed of component i [ppm]
 $C_{i, \text{raf}}$: concentration of raffinate of component i [ppm]
 $C_{i, \text{st}}$: concentration of outlet strip of component i [ppm]
 HR : acidic extractant
 S_i : selectivity [%]
 X^- : chloride ion or hydroxide ion

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