

Capability of Supported Liquid Membrane with Strip Dispersion for Precious Metals Recovery from E-waste and Wastewater

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A large amount of precious metals containing e-waste and wastewater is discharged into environment every day. Recovery of these metals can help not only protecting environment but also balancing their supply and demand. Supported liquid membrane with strip dispersion (SLMSD) is among the promising methods to recover metals from waste sources. Theoretically, simultaneous extraction and stripping using hydrophobic membrane would allow zero-waste as well as high metal concentration in receive phase. This research investigated the ability of recovering different metals such as indium, europium, yttrium using SLMSD. The investigation proved that SLMSD was able to remove more than 99.5 % metal ions from wastewater or leaching solution. High metal concentration was obtained by adjusting feed to strip volume ratio.

1. Introduction

Semiconductor and electronics industries consume many types of metals such as indium, europium, yttrium. Their limited reserve and low grade ore (Taylor and McLennan, 1985) put a large burden on mining and extracting these precious metals – the mining and extracting sites are usually big sources of pollution. The environmental impacts of zinc (indium is a by-product of zinc ore processing) mining and processing in China were discussed by Zhang et al. (2012) and rare earth mining and processing in China were discussed by Yang et al. (2013) (China is the leading indium and rare earth producer (USGS, 2022)). Their uneven distribution also creates some difficulties to supply chain: in 2020, top ten countries produce more than 99.8 % of global production with Chinese share more than 50 % in case of rare earth metals and 33 % in case of zinc (USGS, 2022). Because of their wide applications, these elements also present frequently in wastes and pose a threat to environment. In cases such as indium, the concentration of the metal in e-waste is even higher than in its primary ore (Dodbiba et al., 2012). This high concentration make it be important to recover these elements in waste streams.

While there are many works about leaching metals from waste electrical and electronic equipment: Hasegawa et al. (2013) extracted indium from end-of-life liquid-crystal display panels using aminopolycarboxylate chelants, Rocchettia et al. (2015) extracted indium from LCD panels using cross - current leaching, Trucillo et al. (2021) extracted other metals from electrical and electronic equipment using hydrochloric acid, further processing of the leachate is discussed less often. This paper focuses on separating precious metals from aqueous solutions using membrane enhanced extraction method. The technique was proved effective in separating other metals from wastewater (Ho and Poddar, 2001). The key for separation processes (such as adsorption, absorption) is selective mass transfer where the desired components transport into another phase while others cannot and remain in the original phase. From technical point of view, separating metals from solutions can be easily achieved by evaporation: solvent transports to gas phase while metals cannot. This method is economically unfeasible due to high energy consumption, especially for diluted solution because of too much solvent evaporation. In the focused method, organic solvent which can form metal complexation filled in a hydrophobic

membrane provides an energy saving method of separation: metal ions can pass through thanks to its reaction with organic solvent while water is repelled by the hydrophobicity of the membrane. The situation is not so simple with the presence of extra components. These components can ruin the mass transfer selectivity in various ways: they can either prevent the transportation of metal ions or transport along with desired metals through the barrier and contaminate the products.

In the following sections, experimental investigation on two cases using supported liquid membrane with strip dispersion (SLMSD) will be presented: (1) indium recovery from etching solution contains oxalic acid as a chelating agent and (2) europium recovery from aqueous solution with yttrium.

2. Experimental

2.1 Materials and solution preparation

Indium recovery:

- Feed solutions: Indium(III) sulfate ($\text{In}_2(\text{SO}_4)_3$) was dissolved in water to prepare feed solution containing 200 mg/L of In^{3+} . To simulate the waste etching solution from liquid crystal display (LCD) industries, 2 wt% of oxalic acid was added to the feed solution and sulfuric acid (H_2SO_4) was added to adjust the feed solution pH to 1.
- Organic solutions: Different solvent for indium extraction such as Di-(2-ethylhexyl) phosphoric acid (D2EHPA), di-(2-ethylhexyl) phosphonic acid (EHEHPA) has been investigated by Sato and Sato (1989). Among them, D2EHPA was chosen thanks to its higher extraction efficiency (Sato and Sato, 1992). Depend on the D2EHPA concentration, distribution coefficient of indium between D2EHPA and inorganic acids can reach up to 100, this value is lower in case of hydrochloric acid (HCl) in compare with sulfuric acid and nitric acid (HNO_3) (Sato and Sato, 1992). The efficiency of D2EHPA in extracting indium from hydrochloric acid solution was also confirmed by other reseachers (Chou et al., 2016). In the above mentioned work (Sato and Sato, 1992), kerosene was used as the diluent but in our current study, Isopar-L was selected instead of kerosene due to environmental concern. 2 vol% of 1-dodecanol was added as modifier to increase the solubility of indium-D2EHPA complexes in Isopar-L.
- Strip solutions: 5 M of hydrochloric acid (HCl) aqueous solution was used as strip solution.

Europium recovery:

- Feed solutions: Leaching solution of waste fluorescent lamp.
- Organic solutions: Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used as extractant and Isopar-L was used as diluent. 2 vol% of 1-dodecanol was added as modifier to increase the solubility of indium-D2EHPA complexes in Isopar-L.
- Strip solutions: nitric acid (HNO_3) 3 M solution was used as strip solution.

All the reagents were used as received without further purification, and the water used was all de-ionized.

2.2 Membrane modules

Hydrophobic hollow-fibre modules with 6.35 cm in diameter and 20.3 cm in length were used. The membrane surface area of one module was 1.4 m^2 . The hollow fibres had outside diameters of 300 μm and inside diameters of 220 μm , and the fibre walls contained pores with an average pore size of 0.03 μm and a porosity of approximately 40 %.

2.3 Supported Liquid Membrane with Strip Dispersion (SLMSD)

Figure 1 is the schematic presentation of the SLMSD set-up used in the present study.

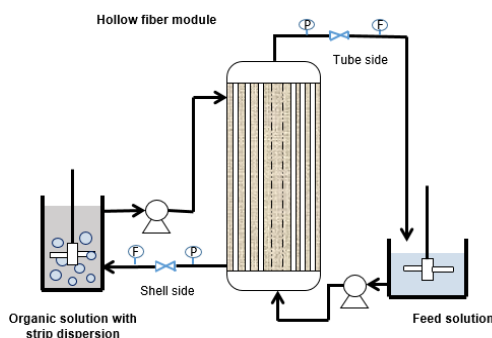


Figure 1: Schematic presentation of the experimental set-up

A commercial polypropylene (PP) hollow fibre module (Liqui-Cel, membrane surface area 1.4 m²) was used for the set-up. The feed solution was pumped into the tube side of the membrane module and the strip solution was dispersed in the extractant-containing oil and then pumped into the shell side. The principle of SLMSD and the details of this scheme were presented in the previous paper (Dang et al., 2020).

2.4 Analytical method

The concentration of indium, europium, yttrium in the aqueous phase were assayed using atomic absorption spectroscopy.

2.5 Data processing

The mass transfer coefficient k was calculated by Eq(1) according to a dynamic mass transfer model (Dang et al., 2020):

$$\ln \frac{C_f}{C_f^0} = -\frac{k \cdot A}{V_f} \cdot t \quad (1)$$

Where: V_f is the total volume of the feed solution, L; C_f^0 denotes the initial indium ion concentration in the feed, mg/L; t is extraction time, min; k is mass transfer coefficient, L/m².min; A is membrane area, $A = 1.4$ m²; C_f is indium ion concentration in the feed at time t , mg/L.

If $V_f = \text{const}$, $k \cdot A = \text{const}$, the graph $\ln \frac{C_f}{C_f^0}$ vs. t is linear with a slope of $-k \cdot A/V_f$. Mass transfer coefficient k can be determined from the slope of this line.

The recovery of metals was calculated by Eq(2):

$$R = \frac{C_f^0 - C}{C_f^0} \times 100 \% \quad (2)$$

With C is final metal concentration in feed solution, mg/L

The selectivity of metals was calculated by Eq(3):

$$S_{Y/Eu} = \frac{k_Y}{k_{Eu}} \quad (3)$$

With k_Y, k_{Eu} is mass transfer coefficient of yttrium and europium, consequently.

3. Results and discussions

3.1 Recovery of Indium from etching solution of LCD industry

Indium was recovered from both pure Indium(III) sulfate solution (200 mg/L) and Indium(III) sulfate solution with 2 wt% oxalic acid. The low mass transfer rate in the second case showed the significant impact of chelating agent on the recovery process. This obstacle was overcome by using more concentrated extractant with higher cost and viscosity as the trade-off.

3.1.1. Recovery of Indium from etching solution without chelating agent

The complexation reaction can be described by Eq(4) (Sato, 1975):



with an equilibrium constant (K_{e1}) of 1.6×10^3 (Tsai and Tsai, 2012), where HR represents the chemical formula of D2EHPA.

Because of the high loading capacity of D2EHPA for indium (Sato and Sato, 1992), the mass transfer rate is high (mass transfer coefficient is 0.11 L.min⁻¹.m⁻² in this experiment) and most indium ions in the feed can be transported to the organic solution (99.8 % after 25 min in this experiment, Figure 2).

3.1.2. Recovery of Indium from etching solution with chelating agent

In the presence of chelating agent in feed solutions such as: EDTA in cobalt solution, OA in indium solution the extraction will be much more difficult and the metals cannot be removed completely. The reason is the competing complexation of chelating agent with metal that keep metal remain in the feed solution. For example, oxalic acid can form complex with indium by Eq(5):



with an equilibrium constant (K_{e2}) of 1.2×10^3 . This formation reduces the concentration of In^{3+} , preventing reaction (4) from happening.

As shown on Figure 2, because $K_{e1} \approx K_{e2}$, oxalic acid competes with D2EHPA for indium; the presence of oxalic acid slows down indium extraction: mass transfer coefficient reduced to $0.0031 \text{ L}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$ in this experiment. More than 30 times reduction of mass transfer coefficient makes the process so slow that only 48 % indium is recovered after 140 min. Extrapolation based on Eq(1) predicts that 15 h is needed for 99.8 % recovery.

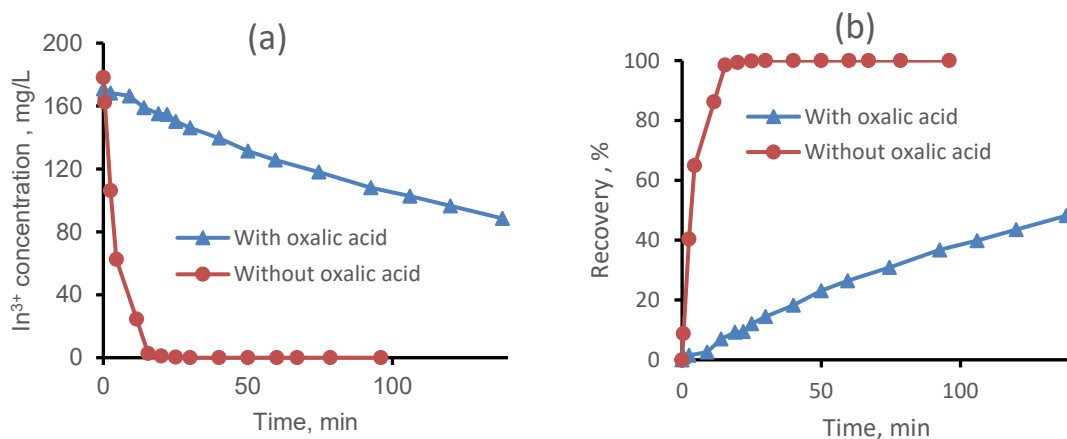


Figure 2: Extraction of indium by 0.08 M D2EHPA (with and without oxalic acid) (a) Feed concentration vs. time, (b) Recovery vs. time

3.1.3. Improving indium recovery

Indium recovery can be improved with higher extractant concentration. Figure 3 showed the results when D2EHPA 0.6 M was used. According to Eq(4), D2EHPA concentration greatly affects the reaction rate. By increasing it almost 8 times, the inhibition effect of low In³⁺ concentration was compensated.

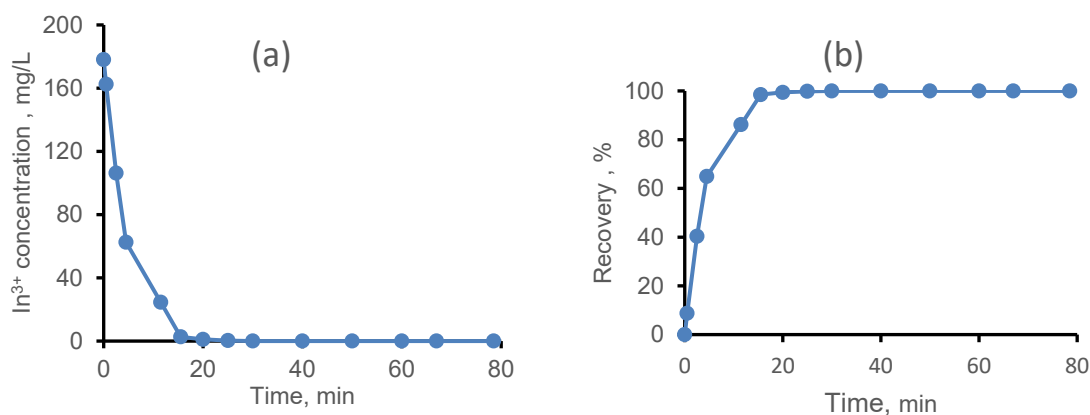


Figure 3: Extraction of indium by 0.6 M D2EHPA (with oxalic acid): (a) Feed concentration vs. time; (b) Recovery vs. time

Due to high concentration of D2EHPA, the mass transfer rate is again very high despite the presence of OA (mass transfer coefficient is $0.08 \text{ L}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$ in this experiment) and most indium ions in the feed can be transported to the organic solution (99.8 % after 25 min in this experiment, Figure 3).

3.2 Europium and Yttrium recovery from waste fluorescent lamp

The leaching solution of waste powder from fluorescent lamp contained 46.6 mg/L europium and 346.5 mg/L yttrium. Since yttrium forms complex with organic solvent more readily than europium, it must be separated first in order to obtain pure europium in the product. Previous study shows that solubility of yttrium and europium in organic solution depends significantly on pH of feed solution (Le, 2017).

As illustrated on Figure 4 (derived from Le, 2017), the solubility of yttrium and europium varies greatly in a narrow range of pH. Yttrium is soluble at pH higher 0.5, europium is soluble at pH higher than 1 but almost insoluble at a pH condition lower than 0.5.

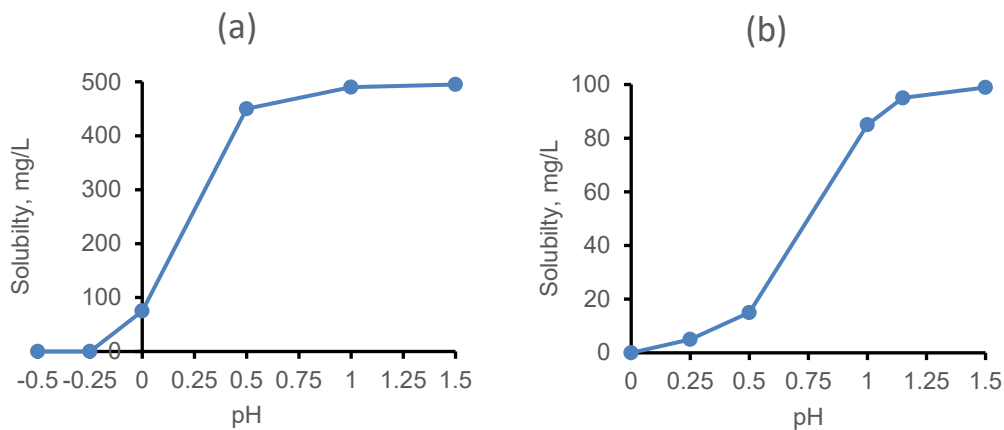


Figure 4: Effect of pH on solubility: (a) Yttrium; (b) Europium

The dependence of solubility on pH suggested a strategy for obtaining pure europium with two consecutive steps: (i) Run SLMSD at feed solution pH = 0.5 until yttrium is removed completely; (ii) Adjust feed solution pH to 1 and run the system to recover pure europium.

The strategy was proven experimentally as illustrated in Figure 5: SLMSD process was first conducted in 120 min at feed solution pH = 0.5, then 120 min more at feed solution pH = 1. As a result, 99.9 % yttrium was removed in 80 min while only 4.8 % europium was co-separated. After switching to pH = 1, 99.9 % of remaining europium was recovered in 30 min. According to Eq(1), mass transfer coefficient of europium and yttrium at pH = 0.5 are $4.29\text{E-}04 \text{ L}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$ and $8.45\text{E-}02 \text{ L}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$. Similarly, $k_{\text{Eu}} = 3.89\text{E-}02 \text{ L}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$ at pH = 1. The selectivity of yttrium compared to europium at feed solution pH = 0.5 is: $S = 97$. The overall europium was obtained with 99.2 % purity and 95.1 % recovery.

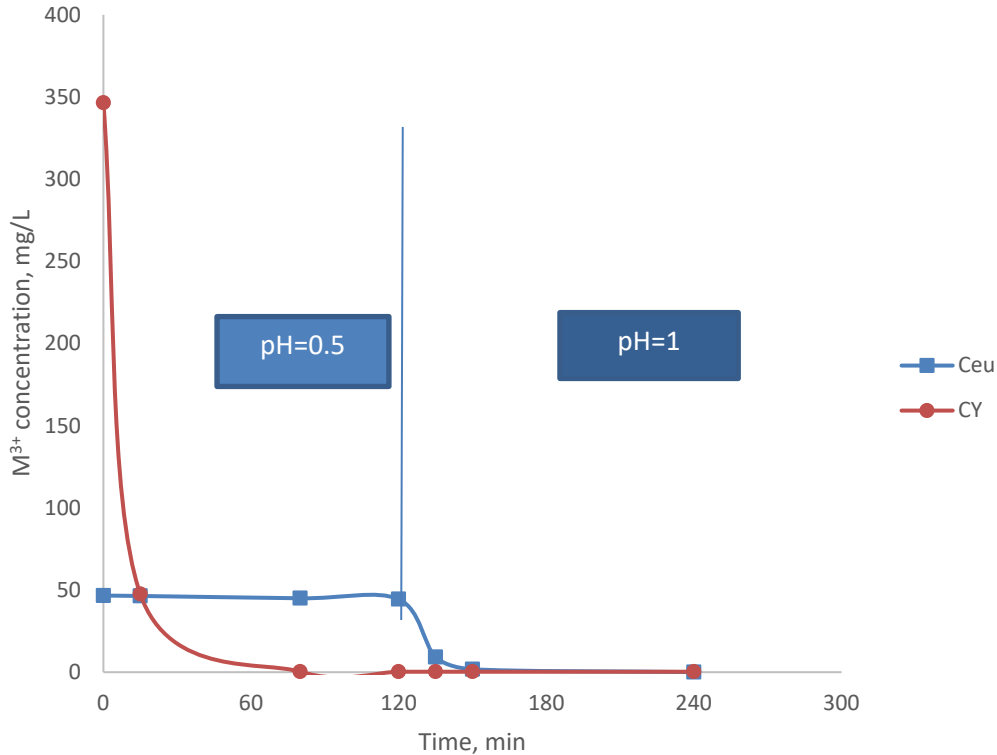


Figure 5: Time dependent of Europium concentration (CeU) and Yttrium concentration (CY) in feed solution

4. Conclusions

Capability of supported liquid membrane with strip dispersion for precious metals recovery from e-waste and wastewater was experimentally demonstrated with both simulated and actual waste water from industry. Despite the fact that extra components impose many difficulties on the separation process, they can be overcome by adjusting operating conditions such as extractant concentration or solution pH. Although further investigations are necessary for SLMSD to be applicable in industry, the method is already demonstrated to be very promising for recovering precious metals from wastewater.

Acknowledgement

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