SUPPORTED LIQUID MEMBRANE WITH STRIP DISPERSION FOR RECOVERING INDIUM FROM ETCHING SOLUTION OF LCD INDUSTRY: INFLUENCE OF FACTORS ON PERFORMANCE

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Abstract. Supported liquid membrane with strip dispersion (SLMSD) is a promising process for metal recovery from e-waste or waste streams because of many advantages such as the ability to combine extraction and stripping into one single step and thus have non-equilibrium mass transfer characteristics and maximum driving force. This paper investigated the effect of important factors on SLMSD performance to recover indium from etching solution such as: pH of feed solution, extractant (Di-(2-ethylhexyl) phosphoric acid (D2EHPA)) concentration, oxalic acid concentration. It was found that 99.5 % In^{3+} was removed from feed solution in about 20 minutes with high concentration factor (4.5) under suitable conditions (pH 1; 0.6M Di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2 wt% oxalic acid).

1. INTRODUCTION

Using liquid membrane, the extraction and stripping process can be combined into one step, that normally carried out in two separate stages in conventional solvent extraction. This technique has been applied mainly for ions separating and concentrating. The membrane here is an organic solution which consists of an extractant, a diluent and a modifier in some cases. The desired ion forms complex with extractant at one side of membrane, then the complex diffuses across the membrane to the opposite side, where the reaction is reversed under appropriate conditions of stripping solution. The regenerated extractant then diffuses back across the membrane to react with more desired ion.

The first liquid membrane system includes an U-shape tube with the organic solution placing between feed and strip solution for metal ion separations. Because the obtained flux is too low to compete with conventional separation processes, the liquid membrane was improved by several ways: (i) dissolving organic solutions in a polymer matrix; (ii) immobilizing the organic solution in pores of a hydrophobic membrane (supported liquid membrane); (iii)

forming the wall of the emulsion droplets by organic solution to separate aqueous feed and aqueous strip solution (emulsion liquid membrane) [1].

Among them, supported liquid membrane is more attractive due to the well-defined geometry and decreasing cost of polymer membrane; easy to independently control working condition in two sides of membrane, very small amount of organic solution [2]. However, the long - term instability of this system due to the loss of organic phase hindered its upscale ability [1 - 3].

To solve this problem, SLMSD scheme was introduced in which the aqueous strip solution was dispersed in organic solution and then brought to contact with the hydrophobic membranes [3]. With this technique, the extractant contained in the membrane pores can be replenished from the strip side in case it is lost to the feed due to its solubility in water or other reasons. Overcoming instability issue, SLMSD can be considered a promising technology for ion separation and concentration.

Recovery of indium from etching solution can be of great help for balancing the demand and supply of indium and as well for environmental pollution control [4 - 6]. One of potential techniques for indium recovery is SLMSD [4, 5, 7]. To understand the mass transfer mechanism as well as to establish a suitable model to describe this process, important factors affecting SLMSD performance must be evaluated. Theoretically, SLMSD performance depends on many parameters, such as: type of extractant, type of diluent, stripping solution type and concentration, temperature, hydrodynamic conditions in feed and permeate side, pH of feed solution, extractant concentration, the presence of oxalic acid. To save the time, some parameters would be fixed based on literature review [5, 8 - 10] and previous research in our lab as following: Organic phase: (Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (extractant), Isopar-L (diluent), 2 % 1 - dodecanol (modifier); Stripping solution: HCl 5M; Feed flowrate: 1l/min.; Strip flowrate: 1l / min.; The ratio between volume of feed and strip solution: 5/1; All experiments were conducted at room temperature. Other parameters such as feed pH (from 0.25 to 1), extractant concentration (from 0.08M to 1M), oxalic acid concentration (from 0 wt% to 2 wt%) were investigated. Etching solution of LCD industry usually contains about 200 ppm In^{3+} and 2 % oxalic acid. Therefore, in this paper, SLMSD has been investigated to recover indium from simulated solution with similar composition.

2. EXPERIMENTALS

2.1. Materials and solution preparation

Feed solutions: $In_2(SO_4)_3$ (Sigma-Aldrich) was dissolved in water to prepare feed solution containing about 200 ppm of In^{3+}. 2 wt% of oxalic acid was added to the feed solution in order to simulate the waste etching solution from LCD industries. H_2SO_4 (Sigma-Aldrich) was used to adjust pH of the feed solution to 1 (otherwise it would be noted).

Organic solutions: includes extractant (Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Merck)), diluent (Isopar-L (Exxon Mobil Chemical)) and modifier (1-dodecanol (Acros)).

Strip solutions: 5 M of hydrochloric acid (HCl) (Sigma-Aldrich).

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

2.2. Membrane modules

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Hydrophobic hollow-fiber modules with 6.35 cm in diameter and 20.3 cm in length were used. The membrane surface area of the module was 1.4 m^2. The hollow fibers had outside diameters of about 300 μm and inside diameters of about 220 μm. The membrane has 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 presented the SLMSD set-up. The feed solution was circulated in the tube side of the membrane module by a feed pump; the strip solution was dispersed in the extractant-containing oil and then circulated in the shell side of the membrane module by a strip pump.

The indium concentration in the aqueous phase was then determined by using atomic absorption spectroscopy (Perkin Elmer AAnalyst200). All the experiments were conducted with the same stirring rate at room temperature.
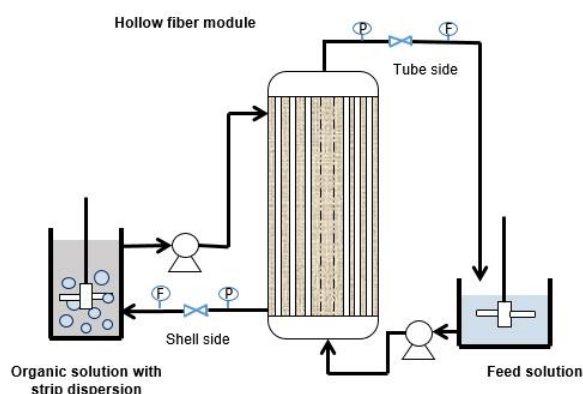

Figure 1. Schematic presentation of the experimental set-up.

3. RESULTS AND DISCUSSION

3.1. Effect of feed pH

The effect of feed pH on SLMSD performance was shown in Figure 2. When pH increased from 0.25 to 0.5, the separation of indium from feed solution was more completed in shorter time. However, this change is insignificantly when pH increases from 0.5 to 1. It could be explained as following.

The extraction reaction between In^{3+} and D2EHPA can be described as [9, 11]:

$$2In_{(aq)}^{3+} + 5(HR)_{2(org)} \rightleftharpoons In_2R_{10}H_{4(org)} + 6H_{(aq)}^{+} \tag{1}$$
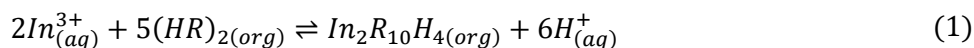
Besides, In^{3+} can form complex with oxalic acid as following [12]:

$$In^{3+} + HC_2O_4^- \rightleftharpoons In(HC_2O_4)^{2+} \tag{2}$$

Under higher pH condition (i.e., lower H$^+$ concentration), the equilibrium of reaction (1) shifts to right side according to Le Chatelier's principle. As a result, more complex is formed which means more In^{3+} is extracted.
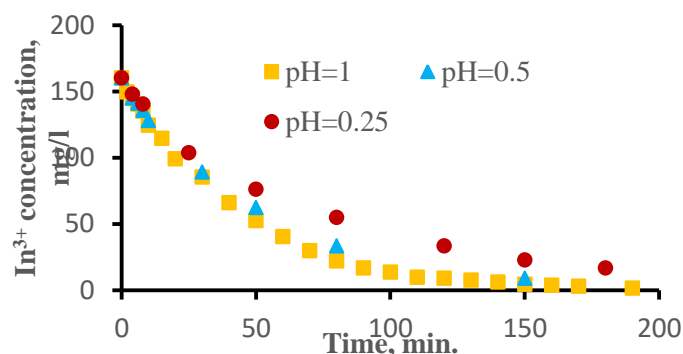
Figure 2. Effect of feed pH on time dependence of indium in feed solution ([D2EHPA] = 0.2 M).

In the industry, the etching wastes usually have pH about 1. Therefore, pH = 1 was chosen for conducting next experiments.

3.2. Effect of D2EHPA concentration

When extractant concentration increased from 0.08M to 1M, extraction rate also increased according to equation (1). However, theoretically, solution viscosity is also increased with D2EHPA concentration which make the diffusivity of solution slower. Because of this opposite influencing, extraction rate increased quickly with D2EHPA concentration from 0.08 M to 0.6 M, but almost remained unchanged with D2EHPA concentration from 0.6 M to 1 M (Figure 3).
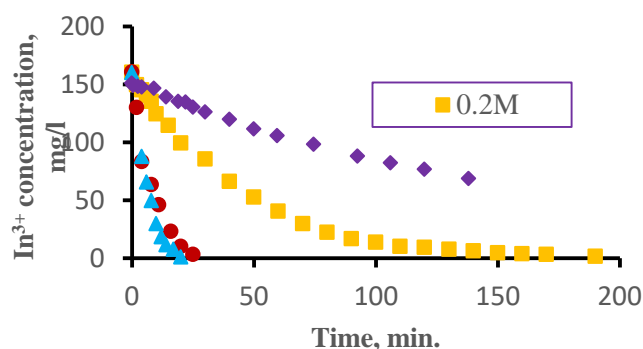

Figure 3. Effect of D2EHPA concentration on time dependence of indium in feed solution.

It can be concluded that, increasing extractant concentration to a specific point increases membrane permeability which leads to more indium removal in feed solution. However, exceeding the concentration over that point might decrease the permeability due to the elevated viscosity of organic phase.

3.3. The presence of oxalic acid

According to equation (2), the presence of oxalic acid would slow down the extraction rate. To know how the concentration of oxalic acid affected the indium extraction performance, SLMSD experiments were performed with the feed solutions having different concentrations of oxalic acid. The results are presented in Figure 4.
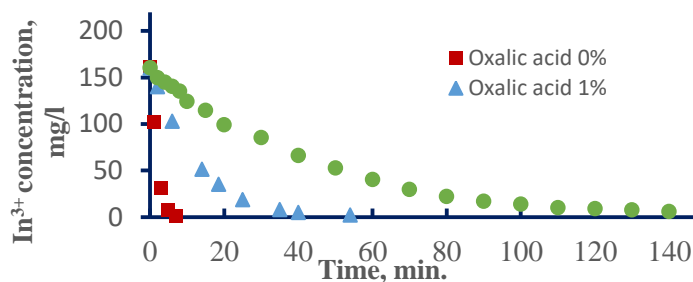
Figure 4. Effect of oxalic acid concentration on performance of SLMSD.

The higher the oxalic acid concentration was, the lower extraction rate of indium became. The results can be explained by that more $In(HC_2O_4)^{2+}$ was formed with higher oxalic acid concentration (according to reaction (2)), leading to more indium stay in aqueous feed phase.

3.4. SLMSD performance

SLMSD was investigated under following conditions: pH of feed solution was 1; D2EHPA concentration was 0.6M, oxalic acid concentration was 2 wt%. The results were shown in Fig. 5.
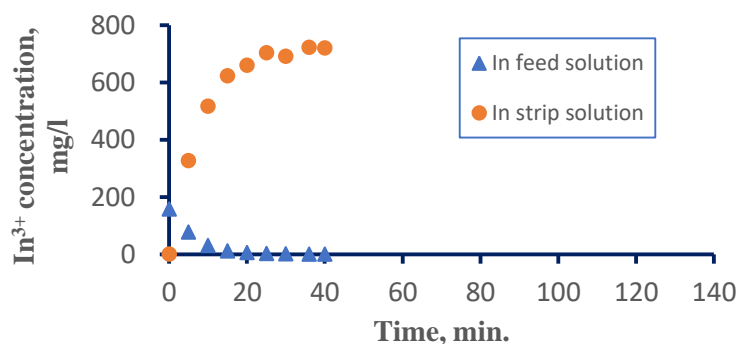

Figure 5. The dependence of In^{3+} concentration in feed side and strip side on time in SLMSD.

Under above conditions, 99.5 % In^{3+} could be removed from feed solution in about 20 minutes with concentration factor of 4.5.

4. CONCLUSIONS

Influence of parameters such as pH, extractant concentration, oxalic acid concentration on SLMSD performance were investigated. It was found that higher pH of feed solution, suitable D2EHPA concentration, less oxalic concentration would lead to more complete separation of indium from wastewater in shorter time.

The results suggested that, using an appropriate pretreatment method in order to reduce the amount of oxalic acid in feed solution can be great of help in improving SLMSD performance. For example, decomposition of oxalic acid using strong oxidizes such as H_2O_2. Almost In^{3+} (99.5 %) was removed from feed solution in about 20 minutes with high concentration factor (4.5)

under suitable conditions (pH 1; 0.6 M D2EHPA, 2 wt% oxalic acid). It indicated that SLMSD could be a promising technology for recovery In^{3+} efficiently from etching waste solution of LCD industry.

CRediT authorship contribution statement. Author 1: Methodology, Investigation, Formal analysis. Author 2: Funding acquisition, Supervision. Author 3: Supervision.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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