CHEMICAL ENGINEERING TRANSACTIONS
VOL. 122, 2025
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Bohong Wang, Guo Ren Mong, Petar S. Varbanov

ISBN 979-12-81206-23-6; **ISSN** 2283-9216
DOI: 10.3303/CET25122062

Recovery of Indium from Etching Wastewater using Supported Liquid Membrane with Strip Dispersion with Vegetable Oil as Diluent

Ngan Thi Tuyet Dang[a], Da-Ming Wang[b] , Kien Trung Tran[a] , Son Nghiem Xuan[a,*]

[a]Department of Chemical Engineering, School of Chemistry and Life Sciences, Hanoi University of Science and Technology, Hanoi, Vietnam
[b]Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
son.nghiemxuan@hust.edu.vn

Supported Liquid Membrane with Strip Dispersion (SLMSD) is an effective and cost-efficient method for recovering precious metals. Traditionally, petroleum-based diluents such as kerosene or Isopar-L are employed; however, their use raises environmental and safety concerns. This study investigates sunflower oil, a green and renewable alternative, as a diluent in SLMSD for recovering In^{3+} from etching waste solution. Results indicate effective Indium recovery using 0.4 M D2EHPA as the extractant with the permeability of In^{3+} was 9.5×10^{-6} $m.min^{-1}$. A model-based estimation suggests that 99 % removal of In^{3+} could be achieved within 1.22 h using a 1.4 m^2 membrane. This highlights vegetable oil's potential as a sustainable diluent in SLMSD applications.

1. Introduction

Supported Liquid Membrane (SLM) enables the separation of valuable substances by extraction without the need for multiple mixer - settler stages. As the combination of solvent extraction and membrane technology, it does not require much energy for agitating and pressurizing. The introduction of Supported Liquid Membrane with Stripped Dispersion (SLMSD), as proposed by Ho and Poddar (2001), significantly improved process stability, facilitating continous and long-lasting operation. High efficiency was achieved for metals extraction (Ho, 2003). This approach involves placing a hydrophobic membrane, impregnated with an extractant, between the feed solution and a strip solution dispersed in the extractant (emulsion). The metal ion interacts with the extractant on the membrane surface, forming a complex that diffuses through the membrane into the emulsion, where it subsequently reacts with the strip solution. This configuration enables concurrent extraction and stripping, significantly enhancing process efficiency. Additionally, any extractant lost to the feed is replenished from the emulsion, maintaining stable and continuous operation. SLMSD offers numerous advantages, such as a stable and well-defined interfacial area, a compact system footprint, reduced equipment needs, modular scalability, low energy consumption, and the ability to operate without the need for separating the feed solution and extractant. These features make SLMSD a highly potential technology for the efficient recovery of metals such as copper and zinc (Ho et al., 2002), cobalt, chromium and strontium (Ho, 2003), europium, yttrium (Dang et al., 2022a).

Despite its advantages, traditional diluents used in SLMSD, such as petroleum derivatives like kerosene and hexane, pose several challenges. These include their non-renewable nature, high flammability, volatility, and toxicity to living organisms, which have raised concerns about their environmental impact (Chang, 2014). Consequently, there is growing interest in finding more sustainable, safer alternatives for diluents in the SLMSD process.

Indium, a critical element in the semiconductor industry, plays a central role in the production of electronic devices like smartphones and LCD screens. However, its limited availability in the Earth's crust and high demand make its recycling crucial. Wastewater from the etching process, which can contain up to 70 % of the input indium, offers a valuable source for recovery (Chou et al., 2016). Thus, recovering indium from etching waste solutions not only helps balance supply and demand but also reduces environmental pollution (Dang et al.,

Paper Received: 26 August 2025; Revised: 20 October 2025; Accepted: 14 December 2025
Please cite this article as: Dang N.T.T., Wang D.-M., Tran K.T., Xuan S.N., 2025, Recovery of Indium from Etching Wastewater using Supported Liquid Membrane with Strip Dispersion with Vegetable Oil as Diluent, Chemical Engineering Transactions, 122, 367-372 DOI:10.3303/CET25122062

2020). SLMSD has been successfully employed to recover indium from such waste solutions, particularly using Isopar-L as a diluent (Dang et al., 2022b).
In recent years, vegetable oils have emerged as promising alternative diluents in the extraction as well as process due to their renewable, bio-origin properties and good compatibility with extractants. Muthuraman and Palanivelu (2006) demonstrated the successful use of vegetable oils, such as palm oil, sunflower oil, and coconut oil, for extracting textile dyes through supported liquid membranes, achieving an extraction efficiency of 97 % after 5 h. Another research by Hajarabeevia et al. (2009) showed that cationic dyes could be effectively transported using coconut oil as the solvent and D2EHPA as the carrier, achieving extraction rates of 94.2 % for MV and 90 % for RB dyes. Additionally, palm oil has been shown to effectively extract nickel ions in a green, sustainable manner (Sulaiman, 2017). Following the principles of Green Chemistry, vegetable oils could be an effective and eco-friendly alternative solvent for extracting compounds, as well as for purifying, enriching, and cleaning up pollution (Yara-Varón et al., 2017).
This paper explores the potential of sunflower oil as an alternative diluent for indium recovery from etching waste solutions by classical solvent extraction as well as SLMSD. Furthermore, it will compare the performance of sunflower oil with Isopar-L, a conventional petroleum-based diluent, to evaluate the viability of vegetable oils as a sustainable solution for metal recovery. Apart from duration, temperature is usually an important factor of extraction since it may change the liquid – liquid equilibrium between the feed and the extractant and pH is also an important factor in case of metal extraction by D2EHPA thanks to the ion-exchange mechanism. All the three factors will be investigated in this research.

2. Methods

2.1 Materials and solution preparation:

Feed solutions: In2(SO4)3 (Sigma-Aldrich) was dissolved in water to prepare feed solution containing about 200 mg/L of In^{3+} . To simulate the waste etching solution from LCD industries, 2 wt% of oxalic acid (Sigma-Aldrich) was added to the feed solution and H2SO4 (Sigma-Aldrich) was added to adjust the feed solution pH to desired value. To investigate the effect of oxalic acid, additional experiments were carried out with oxalic-free feed.
Organic solutions: Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Merck) was used as extractant. Isopar-L (Exxon Mobil Chemical) was used as conventional diluent. Sunflower oil (Simply) was used as alternative diluent. 2 vol% of 1-dodecanol (Acros) was added as modifier to increase the solubility of indium-D2EHPA complexes in organic phase.
Strip solutions: 5 M of hydrochloric acid (HCl) (Sigma-Aldrich) aqueous solution was used as strip solution for In^{3+} receovery.
All the reagents were used as received, without any additional purification, and the de-ionized water was employed in the experiments.

2.2 Membrane modules

A flat-sheet glass membrane module containing a hydrophobic polypropylene membrane was used, with a membrane surface area of 20 cm^2 (as shown in Figure 1).

Figure 1: SLMSD system

2.3 Analysis

Indium concentration in the aqueous phase was assayed using ICP-OES (Agilent Technologies).

2.4 Solvent extraction (SX):

Aqueous feed solution and extractant-containing organic solution with a ratio of 1:1.5 were mixed and kept well stirred at room temperature in most experiment. Preliminary experiments with D2EHPA concentration of 0.08 M, under the presence of oxalic acid, took approximately 1 h to reach maximum efficiency. To ensure equilibrium condition, all extraction experiments were carried out in 3 h. Three mililitres of samples were taken every hour, centrifuged to allow for the separation of organic and aqueous phases.

2.5 Supported liquid membranes with strip dispersion

210 mL of feed solution containing In^{3+} in the presence of 2 %wt oxalic acid at pH 1 was filled in the feed side and stirred well (with the speed of 300 rpm). ; 30 mL strip solution dispersed in 120 mL organic solution was filled in the strip side.
Depicted in Figure 1 is the experimental set up of the SLMSD. It included a feed vessel, a stripping vessel and a hydrophobic flat sheet membrane between the two vessels. Initially, the feed vessel was filled with 210 mL of aqueous feed solution, while the strip vessel contained 120 mL of aqueous strip solution and 30 mL of organic solution. Stirring was performed in both vessels with the speed of 300 rpm. At various times, 0.5 mL of samples were taken in the feed side and analyzed using ICP-OES (Agilent Technologies). All experiments were performed under the consistent stirring conditions at room temperature.

3. Results and Discussion

Before any further investigation, the solubility of D2EHPA in sunflower oil was verified by mixing these two substances at various ratio. Homogeneous solutions with D2EHPA concentration upto 0.6 M was obtained (as shown in Figure 2), assuring the compatibility between them.

Figure 2: Mixture of D2EHPA 0.6 M and sunflower oil

Preliminary experiments using 0.08 M D2EHPA in sunflower oil, under the presence of oxalic acid, took approximately 1 h to reach maximum efficiency, three times longer than it took for extraction using 0.08 M D2EHPA in Isopar-L to reach maximum efficiency as reported in previous study (Dang et al., 2020). Such a lower mass transfer rate can be attributed to the significant higher viscosity of sunflower (> 40 mPa.s) compared to Isopar-L (~1.2 mPa.s) which would lower diffusion rate through membrane according to Eq(1) (Kislik, 2010):

$$D_m = \frac{k.T.\rho}{6\pi.\mu.r}.\frac{\varepsilon}{\tau} \quad (1)$$

Where: k is Boltzmann's constant; T is temperature; μ is dynamic viscosity; ρ is density; r is radius of the solute; ε is membrane porosity; τ is membrane tortuosity.

For every solvent extraction experiment, all three concentrations sampled at 1, 2 and 3 h, apart from the initial one, were the same, assuring the equilibrium condition. Extraction efficiency of 0.08 M D2EHPA diluted in sunflower oil or Isopar-L at various initial pH and feed composition are recorded in Table 1. Experiment no. 1 proved that D2EHPA diluted in sunflower oil can extract Indium from oxalic-free feed very effectively, as well as D2EHPA diluted in Isopar-L reported in previous study (Dang et al., 2020). However, D2EHPA diluted in sunflower oil is more affected by oxalic acid than D2EHPA diluted in Isopar-L: the extraction efficiency drop to 62.7 % in experiment no.2 (sunflower oil dilution), significantly lower than 88.89 % in experiment no. 9 (Isopar-L dilution). The effect of oxalic acid can be explained as the competition between oxalic acid and D2EHPA for complexation with In^{3+} (Dang et al., 2020), as illustrated by Eq(2) and Eq(3):

$$2In^{3+}_{(aq)} + 5(HR)_{2(org)} \rightleftharpoons In_2R_{10}H_{4(org)} + 6H^{+}_{(aq)} \quad (2)$$

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

The most direct solution to improving competitiveness of Eq(2) is raising D2EHPA concentration. Results from experiment no. 6 – 8 showed its effectivity: by increasing D2EHPA concentration less than three times, the effect of oxalic acid was negated almost completely while fivefolds increasing of D2EHPA concentration even yielded extraction efficiency higher than the base case (experiment no. 1); further rising of D2EHPA concentration did not bring much benefit although distribution coefficient was doubled.

Other efforts to boost reaction (1) were not effective: raising temperature from 25 °C to 50 °C (experiment no. 3) or initial pH from 1 to 2.5 (experiment no. 4) only produced about 2 % additional extraction efficiency. Further increase of temperature is limited by economical and safety concerns while further increase of pH made the situation even worse (experiment no. 5) because indium hydroxide will precipitate thanks to its very big pK_{sp} = 33.2. The insensitivity of D2EHPA as extractant toward temperature has been reported in previous study (Ren et al., 2007) while the effect of initial pH was shadowed by the extra proton released during extraction.

Table 1: Effect of pH on extraction efficiency

Experiment No.	Temperature	Initial pH of feed solution	Aqueous feed phase	Organic phase	Extraction efficiency, %
1	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4	0.08 M D2EHPA in sunflower oil	99
2	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.08 M D2EHPA in sunflower oil	62.7
3	50 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.08 M D2EHPA in sunflower oil	64.8
4	25 °C	2.5	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.08 M D2EHPA in sunflower oil	64.98
5	25 °C	3.7	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.08 M D2EHPA in sunflower oil	58.66
6	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.2 M D2EHPA in sunflower oil	97.23
7	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.4 M D2EHPA in sunflower oil	99.60
8	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.6 M D2EHPA in sunflower oil	99.79
9	25 °C	1	$In_2(SO_4)_3$ + H_2SO_4 + oxalic acid	0.08 M D2EHPA in Isopar-L	88.89

Based on the results above, it is evident that extraction efficiency can be improved through various methods, such as reducing oxalic acid concentration, increasing temperature, adjusting the pH of the feed solution, and increasing D2EHPA concentration. However, the most practical approach is to increase the extractant concentration. Therefore, the following operating conditions were chosen for the SLMSD experiment:

Feed solution contained 200 mg/L In^{3+}, 2 wt% OA and pH was adjust to 1, closely resembling the composition of actual etching waste;

Organic solution: based on the results summerized in Table 1, D2EHPA concentration was set at 0.4 M. Sunflower oil was modified by mixing it with 1-dodecanol in a 100:2 ratio, similar to the procedure used for Isopar-L (Dang et al., 2020).

Stripping solution: A 5 M HCl solution was selected as described in the study by Dang et al., (2020).

To determine In^{3+} permeability in SLMSD, following model can be derived (Li et al., 2017) as Eq(4):

$$ln\frac{C}{C_0} = -\frac{A.P}{V}t \quad (4)$$

Where C_0 denotes the initial Indium concentration in the feed solution (mg/L), A represents the oil - water contact surface area (m^2), V is the total volume of the feed solution (m^3), P is ion permeability (m/min). By assuming A, P, V are constant, plotting $ln\frac{C}{C_0}$ versus t would give a line of which the slope is $-\frac{A.P}{V}$.

Figure 3 represents the results of SLMSD on a logarithmic scale in order to determine the permeability of In^{3+} in two cases: (i) using IsolarL as diluent; (ii) using sunflower oil as diluent.

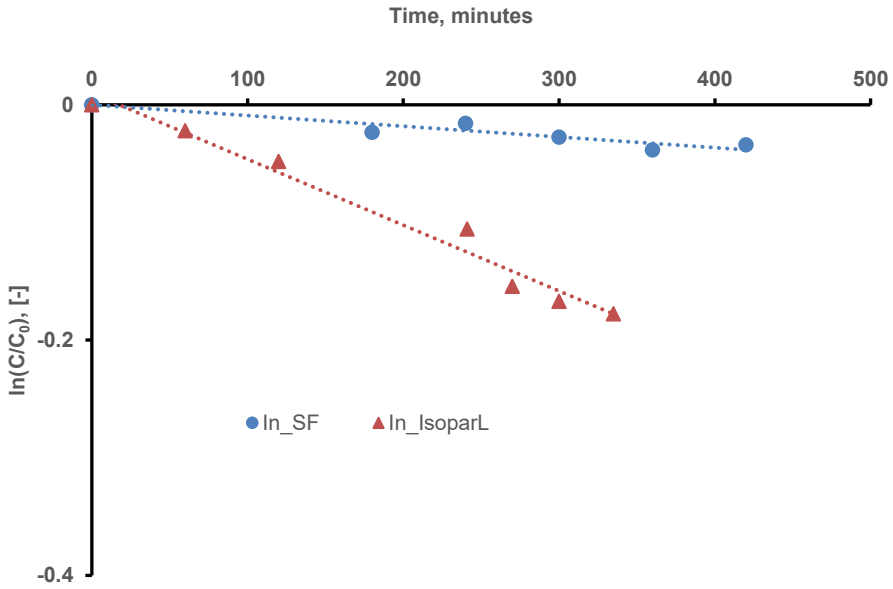

Figure 3: Time dependence of In^{3+} concentration in feed solution

From Figure 3, the permeability (P) of In^{3+} with sunflower oil was determined with the value of 9.5 x 10^{-6} m/min According to this model, the time required to achieve 99 % recovery of Indium is estimated to be 852.8 h. This time can be reduced by increasing the membrane area. For example, using a commercial membrane with an area of 1.4 m² can shorten the recovery time to 1.22 h.

Moreover, the slopes of the two lines in Figure 3 indicate that the permeability of In^{3+} is higher when Isopar-L is used as the diluent compared to sunflower oil. The calculated permeability values are presented in Table 2.

Table 2: Permeability of In^{3+} with two diluents: (i) Isopar-L and (ii) sunflower oil

	Permeability, m/min
In 200 ppm+D2EHPA 0.4 M+Isopar-L	$7.5x10^{-5}$
In 200 ppm+D2EHPA 0.4 M+SF oil	$9.5x10^{-6}$

It can be observed that replacing Isopar-L with sunflower oil slows down the mass transfer rate by a factor of 8. This reduction is likely due to the higher viscosity of the organic phase when sunflower oil is used.

4. Conclusion

This study explored the recovery of Indium from etching waste solutions using Supported Liquid Membrane with Stripped Dispersion (SLMSD), employing sunflower oil as an alternative diluent in the organic phase. The results indicated that D2EHPA diluted in sunflower oil effectively extracted Indium from an oxalic acid-free feed, achieving an impressive extraction efficiency of 99 %. However, the presence of oxalic acid significantly reduced the extraction efficiency when sunflower oil was used, with only 62.7 % of In^{3+} being extracted, compared to

88.89 % extraction using Isopar-L as the diluent. Various strategies, such as reducing oxalic acid concentration, increasing temperature, adjusting pH, and enhancing D2EHPA concentration, could potentially improve extraction efficiency. However, the most practical approach would be to increase the extractant concentration. The SLMSD process, utilizing 0.4 M D2EHPA diluted in sunflower oil, demonstrated effective recovery of In^{3+} from simulated etching waste (200 mg/L In^{3+}, 2 wt% oxalic acid, at pH 1), with a permeability of 9.5×10^{-6} $m.min^{-1}$. Based on the SLMSD model, a commercial membrane with an area of 1.4 m^2 would require approximately 1.22 h to remove 99 % of In^{3+}. While replacing Isopar-L with sunflower oil in the SLMSD process offers notable environmental benefits, it results in a significant reduction of the mass transfer rate, attributed to the high viscosity of sunflower oil. Future studies should focus on identifying more suitable vegetable oils with lower viscosity or exploring combinations of traditional and alternative diluents to optimize mass transfer and extraction efficiency in SLMSD processes.

Acknowledgments

This work was supported by the Program 2395 (Ministry of Science and Technology, Vietnam) and the Asahi Glass Foundation (Japan).

References

Chang S. H., 2014, Vegetable oil as organic solvent for wastewater treatment in liquid membrane processes, Desalination and Water Treatment, 52(1-3), 88-101.

Chou W.-S., Shen Y.-H., Yang S.-J., Hsiao T.-C., Huang L.-F., 2016, Recovery of Indium from the Etching Solution of Indium Tin Oxide by Solvent Extraction, Environmental Progress & Sustainable Energy, 35(3), 2-22.

Dang N. T. T, Wang D. M., Huang S. Y., Tran K. T., 2020, Indium Recovery from Aqueous Solution Containing Oxalic Acid – Enhancement by Using Hydrophobic Membranes, Separation and Purification Technology, 235, 116300.

Dang N. T. T, Wang D. M., Huang S. Y., Nghiem S.X., Pham N. T. B., Dinh G. T., Tran K. T., 2022a, Capability of Supported Liquid Membrane with Strip Dispersion for Precious Metals Recovery from E-waste and Wastewater, Chemical Engineering Transactions, 97, 223 – 228.

Dang N. T. T, Wang D. M., Nghiem S. X., Tran K. T., 2022b, Mass Transfer Performance Comparison between Conventional Solvent Extraction and Supported Liquid Membrane with Strip Dispersion for Indium Recovery from Waste Stream, Chemical Engineering Transactions, 97, 127 – 132.

Hajarabeevi N., Mohammed Bilal I., Easwaramoorthy D., Palanivelu K., 2009, Facilitated transport of cationic dyes through a supported liquid membrane with D2EHPA as carrier, Desalination, 245, 19–27.

Ho W.S.W., Poddar T.K., 2001, New Membrane Technology for Removal and Recovery of Chromium from Waste Water, Environmental Progress, 20(1), 44 – 52.

Ho W. S. W., Poddar T. K., Neumuller T. E., 2002, Removal and recovery of copper and zinc by supported liquid membranes with strip dispersion, J. Chin. Inst. Chem. Engrs., 33, 67 - 76.

Ho W.S.W., 2003, Removal and recovery of metals and other materials by supported liquid membranes with strip dispersion, Ann. N. Y. Acad, 984, 97 - 122.

Kislik V.S., 2010, Liquid membranes: Principles and applications in chemical separations and wastewater treatment, Elsevier B.V.

Li Y.H., Wang D.M., Hsien T.Y., Chan K.Y., Lai J.Y., 2017, Polymer inclusion membranes with strip dispersion, Water, 9, 399.

Muthuraman G., Palanivelu K., 2006, Transport of textile dye in vegetable oils based supported liquid membrane, Dyes and Pigments, 70, 99 – 104.

Ren Z., Zhang W., Meng H., Liu Y. M., and Dai Y., 2007, Extraction Equilibria of Copper(II) with D2EHPA in Kerosene from Aqueous Solutions in Acetate Buffer Media, J. Chem. Eng. Data, 52, 438-441.

Sulaiman R. N. R., 2017, Synergistic green extraction of nickel ions from electroplating waste via mixtures of chelating and organophosphorus carrier, Journal of Hazardous Materials, 340, 77–84.

Yara-Varón E., Li Y., Balcells M., Canela-Garayoa R., Fabiano-Tixier A.-S., Chemat F., 2017, Vegetable Oils as Alternative Solvents for Green Oleo-Extraction, Purification and Formulation of Food and Natural Products, Molecules; 22(9),1474.