

Mass Transfer Performance Comparison between Conventional Solvent Extraction and Supported Liquid Membrane with Strip Dispersion for Indium Recovery from Waste Stream

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Solvent extraction is one of the most popular methods to recovery indium from wastewater. Multistage operation of conventional solvent extraction requires many extraction and stripping stages which leads to large foot print requirement and large amount of chemical usage. Supported liquid membrane with strip dispersion (SLMSD) allows simultaneous extraction and stripping which would lead to much more compact system as well as less solvent consumption. In this paper, the mass transfer rate of conventional solvent extraction (SX) and hollow fiber membrane contactor (SLMSD) were compared in different cases. Moreover, $k.A$ values of SX and SLMSD in each case were also calculated (k is mass transfer coefficient and A is water – oil contact interfacial area). The results showed that mass transfer rate in SLMSD is slower than in solvent extraction due to smaller surface area of membrane contactor compared to interfacial area supplied by dispersion but the mass transfer coefficient is higher in SLMSD. The effect of oxalic acid – the co-occur inhibitor – is also investigated.

1. Introduction

Indium plays a vital role in semiconductor industry, mainly used in etching process for producing smart phone, LCD screen and so on. The high demand and limited reserve in earth crust of indium make its recycling important with many efforts on recovering indium from waste equipment (Dodbiba et al., 2012). The techniques usually begin with strong acid leaching, then indium will be separate from leachate either by reduction (Rocchetti et al., 2015) or organic solvent extraction (Ruan et al., 2012). Another source of indium for recovering is wastewater from etching process which contains 70 % of feeding indium (Chou et al., 2016). Hence, indium recovery from waste stream is also beneficial in terms of environment protection as well as economic value.

Liquid extraction is one of the most popular methods to recovery indium from wastewater. Among them, counter – current multistage extraction shows highest performance: (i) most diluted raffinat means high recovery; (ii) most concentrated extract requires less stripping solution and save energy in electrolysis step (in case of indium recovery). Multistage operation can also enhance performance of stripping whose mechanism is similar to extraction. Utilisation of multistage equipment (like extraction column) is limited due to difficult operation and the requirement that feed solution and extractant have very different densities and low viscosities (McCabe et al., 2004). Therefore, multistage operation usually utilizes multiple stirrer tanks and pumps. Since the performance of multistage process increases with number of stages, high performance counter current multistage extraction requires many tanks, stirrers and pumps. Such a complicated system is difficult to operate in batch mode and continuous process is the choice. Continuous process is more economical at large scale but the flow rate of indium contained waste stream is not much. Therefore, another compact and versatile process is desired.

Liquid membrane was proposed as the method for extracting substances from wastewater (Taoualit et al., 2020). A process called supported liquid membrane with stripped dispersion (SLMSD) was introduced by Ho and Poddar (2001) as the specific solution for metals. In this scheme, a hydrophobic membrane which contains extractant can be set up between feed solution and strip solution dispersed in extractant (emulsion). Indium

reacted extractant on the membrane surface to form complex. The indium (in complex with extractant) diffuses through membrane to emulsion then reacts with strip solution. Thanks to this membrane contactor, extraction and stripping can be operated simultaneously. The extractant in emulsion will fill in the membrane once the extractant there is lost to the feed solution. With many advantages such as stable and known interfacial area, compact system footprint which is equivalent to one stage conventional extraction – stripping, less equipment, modular form so easy scale up, small energy consumption, no need to separate after extraction therefore require no different between feed solution and extractant density and so on, SLMSD is promising in industry. Theoretically, SLMSD is stable and would allow almost completely metal ions in wastewater (Ho et al., 2002) as well as high metal ions concentration achievement by adjusting the ratio between volume of feed and stripping solution.

Application of SLMSD is not without challenge. The popular etching solution is changing from inorganic acids to organic acids such as oxalic acid (OA) (Tsai and Wu, 2006). Oxalic acid will compete with extractant to form complex with indium according to Eq(1), hence slow down the extraction rate:



However, its effect on the performance of Indium recovery processes has not been reported. Therefore, more closely investigation on mass transfer rate of SLMSD in the presence of oxalic acid is necessary. In this manuscript, we used a dynamic mass transfer model to describe SLMSD process. Parameters of the model were determined experimentally in both cases: with and without the presence of oxalic acid. The mass transfer of conventional solvent extraction was also investigated for comparison.

2. Methods

2.1 Mass transfer model

For Indium extraction, di-(2-ethylhexyl) phosphoric acid (D2EHPA) is one of the most common extractant with high distribution ratio, high stability, high selectivity and low water solubility (Yen et al., 2016). The extraction reaction can be described by Eq(2) (Sato, 1975):



where HR represents the chemical formula of D2EHPA. Indium – D2EHPA complex will be transferred through the membrane. Overall mass transfer rate can be described by Eq(3):

$$G = k \cdot A (C_f - C_f^*) \quad (3)$$

Where: G is mass transfer capacity, mg/min; C_f is Indium concentration in feed solution, mg/L; C_f^* is feed indium concentration in equilibrium with strip solution, mg/L; k is mass transfer coefficient, L/m².min; A is interfacial area in feed side, m². For SX process, A is total area of emulsion drops. To evaluate process performance, k.A is used to evaluate mass transfer rate. For SLMSD, A is membrane area (in this experiment A = 1.4 m²), k is termed as permeability P. Mass balance for aqueous phase in feed tank is described by Eq(4):

$$V_f \cdot \frac{dC_f}{dt} = -k \cdot A \cdot (C_f - C_f^*) \quad (4)$$

Where: V_f is feed volume, L; t is extraction time, min

With assumption $C_f \gg C_f^*$ which can be acceptable when oil regeneration rate is much more significant than extraction rate or the first stage of extraction, Eq(4) can be simplified to Eq(5):

$$V_f \cdot \frac{dC_f}{dt} = -k \cdot A \cdot C_f \quad (5)$$

Integrating Eq(5) with initial condition: t = 0, $C_f = C_f^0$ leads to Eq(6):

$$\ln \frac{C_f}{C_f^0} = -\frac{k \cdot A}{V_f} \cdot t \quad (6)$$

If $V_f = \text{const}$, $k \cdot A = \text{const}$, the graph $\ln \frac{C_f}{C_f^0} - t$ or $V_f \cdot \ln \frac{C_f}{C_f^0} - t$ is a straight line with a slope $-k \cdot A / V_f$ or $-k \cdot A$ consequently. From above graph, k can be determined. Then, a model which predicts the change of C_f according to time when $k \cdot A = \text{const}$ and $C_f \gg C_f^*$ is described in Eq(7):

$$C_f = C_f^0 \cdot \exp\left(-\frac{k \cdot A}{V_f} \cdot t\right) \quad (7)$$

2.2 Experiment

2.2.1 Materials and solutions preparation

Feed solutions: $\text{In}_2(\text{SO}_4)_3$ (Sigma-Aldrich) was dissolved in water to prepare feed solution containing about 200 mg/L of In^{3+} . H_2SO_4 (Sigma-Aldrich) was added to adjust the feed solution pH to 1. For the case with oxalic acid, 2 wt% of oxalic acid was added to the feed solution.

Organic solutions: Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Merck) was used as extractant and Isopar-L (Exxon Mobil Chemical) was used as diluent. 2 vol% of 1-dodecanol (Acros) was added as modifier to increase the solubility of indium-D2EHPA complexes in Isopar-L. The D2EHPA concentration in the organic solution was 0.08 M or 0.2 M.

Strip solutions: 5 M of hydrochloric acid (HCl) (Sigma-Aldrich) aqueous solution was used as strip solution.

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

2.2.2 Membrane modules

Hydrophobic hollow-fibre modules with 6.35 cm in diameter and 20.3 cm in length were purchased from Membrana. The membrane surface area of the module was 1.4 m^2 . The hollow fibres had outside diameters of about $300 \mu\text{m}$ and inside diameters of about $220 \mu\text{m}$, and the fibre walls contained pores with an average pore size of $0.03 \mu\text{m}$ and a porosity of approximately 40 %.

2.2.3 Solvent extraction (SX)

360 mL of aqueous feed solution and 540 mL of extractant-containing organic solution were mixed and kept well stirred. At various extraction times, 3 mL of samples were taken, centrifuged to allow for the separation of organic and aqueous phases. The indium concentration in the aqueous phase was then assayed by using atomic absorption spectroscopy (Perkin Elmer AAnalyst200). All the extraction experiments were conducted with the same stirring rate at room temperature.

2.2.4 Supported liquid membranes with strip dispersion

Depicted in Figure 1 is the experimental set up of SLMSD. In this scheme, extraction of indium occurred only at the membrane surface. The role of the membrane module in this scheme was to provide stable contact interface for the aqueous and organic phases. During the operation, the aqueous feed was pumped through the tube side of the membrane module while the strip dispersion was circulated in the shell side. A pressure difference of 0.2 to 0.5 bar between feed and strip sides was maintained to prevent the organic solution in the strip dispersion from passing through the pores to come to the feed side. All experiment was conducted with recirculation flowrate in both feed side and strip side are 1 L/min under room temperature ($25^\circ\text{C} \pm 1$) which is maintained by air conditioner, the feed volume was 360 mL, organic solution volume is 540 mL.

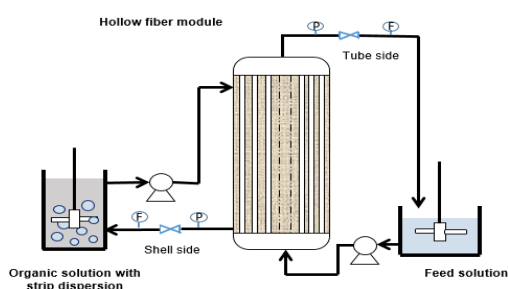


Figure 1: Schematic presentation of the experimental set-up of SLMSD

3. Results and discussions

3.1 SLMSD with and without OA

SLMSD was used to recover indium from 200 mg/L feed solution using 0.08 M D2EHPA in two cases: (i) without OA; (ii) with 2 wt% OA (Figure 2). In the beginning, strip solution was free of indium. Therefore, $C_f^* = 0$ and $C_f \gg C_f^*$. From Figure 2b, the slope of graph $V_f \ln \frac{C_f}{C_f^*}$ vs. t without the presence of OA can be identified.

Substitute this value and $V_f = 360 \text{ mL}$, $C_f^0 = 200 \frac{\text{mg}}{\text{L}}$, $A = 1.4 \text{ m}^2$ into equation (6), k can be calculated as $0.11 \text{ L} \cdot \text{min}^{-1} \cdot \text{m}^{-2}$.

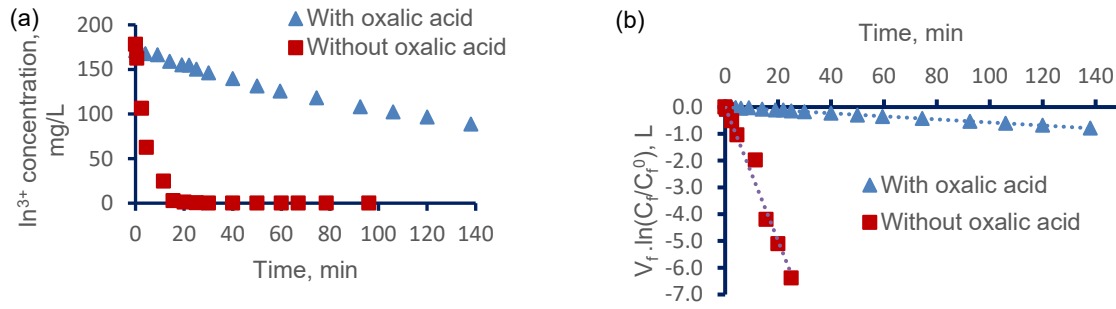


Figure 2: SLMSD with and without oxalic acid: (a) Time dependence of indium concentration in feed solution, (b) Time dependence of $V_f \cdot \ln \frac{C_f}{C_f^0}$

Similarly, the apparent value of k with the presence of OA is $0.0031 \text{ L} \cdot \text{min}^{-1} \cdot \text{m}^{-2}$ which is much smaller than value of k without OA. This can be explained by the decrease of In^{3+} concentration: With the presence of OA, the indium concentration reported in the experiment – C_f – is the total concentration of In^{3+} and $\text{In}(\text{HC}_2\text{O}_4)_2^{2+}$. The relationship between these two concentrations, assuming chemical equilibrium, is described in Eq(8):

$$\frac{[\text{In}^{3+}][\text{H}_2\text{CO}_4^-]}{[\text{In}(\text{HC}_2\text{O}_4)_2^{2+}]} = k_1 \quad (8)$$

with k_1 is the rate constant of reaction (1). Since the concentration of H_2CO_4^- doesn't change during the experiment, so does the ratio between C_f and In^{3+} concentration: the higher $\text{In}(\text{HC}_2\text{O}_4)_2^{2+}$ concentration the lower In^{3+} concentration. This decrease greatly slows down overall mass transfer rate because the rate of reaction (2) is proportional to the square of In^{3+} concentration. Based on experimental data, it can be estimated that 2 %wt of OA decreases In^{3+} concentration by 6 times approximately.

3.2 Compare SX and SLMSD at different conditions

3.2.1 Without OA

Figure 3 represented time dependence of feed concentration for SX and SLMSD at 0.08 M D2EHPA in without oxalic acid case. After very short time (1.5 min), almost all Indium was removed completely. From Figure 3a, the slope of graph $V_f \cdot \ln \frac{C_f}{C_f^0}$ vs. t in case of SX can be identified and $k \cdot A$ can be calculated as $1.341 \text{ L} \cdot \text{min}^{-1}$.

Since interfacial area is undetermined in SX process, k cannot be calculated precisely. However, in comparison with SLMSD, the product $k \cdot A$ is more than 8 times higher ($k \cdot A = 0.153 \text{ L} \cdot \text{min}^{-1}$ in SLMSD process).

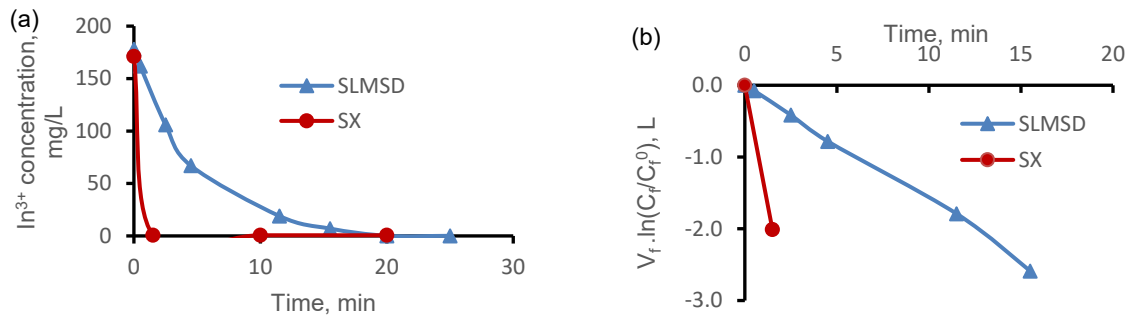


Figure 3: SX and SLMSD without oxalic acid using 0.08 M D2EHPA: (a) Time dependence of indium concentration in feed solution, (b) Time dependence of $V_f \cdot \ln \frac{C_f}{C_f^0}$

3.2.2 With OA

Figure 4 represented time dependence of feed concentration for SX and SLMSD at 0.08 M D2EHPA. It was shown that for SX, indium concentration decreased quite fast in the first 15 min, then decreased more slowly

and reach constant value after 90 min when the process reached equilibrium state (Figure 4a). The graph $V_f \cdot \ln \frac{C_f}{C_f^0}$ vs. t included at least two straight lines with decreased slope (Figure 4b).

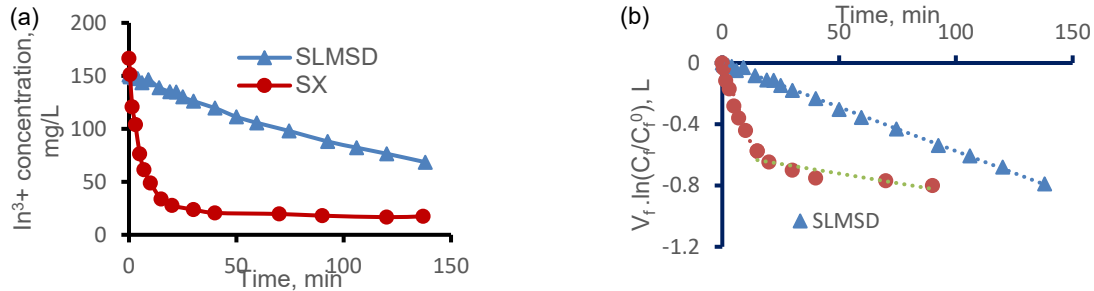


Figure 4: SX and SLMSD with oxalic acid using 0.08 M D2EHPA: (a) Time dependence of indium concentration in feed solution, (b) Time dependence of $V_f \cdot \ln \frac{C_f}{C_f^0}$

To calculate $k.A$, slope of the straight line obtained in first 15 min was used. From Figure 4b, $k.A$ can be calculated as $0.049 \text{ L} \cdot \text{min}^{-1}$. In comparison with SLMSD, the product $k.A$ is more than 11 times higher ($k.A = 0.0043 \text{ L} \cdot \text{min}^{-1}$ in SLMSD process). Compared to the case without OA, the mass transfer rates of both processes are reduced about 30 times.

Figure 5a represented time dependence of feed concentration for SX and SLMSD at 0.2 M D2EHPA. Similarly, from Figure 5b, $k.A$ can be calculated as $0.139 \text{ L} \cdot \text{min}^{-1}$. In comparison with SLMSD, the product $k.A$ is more than 5 times higher ($k.A = 0.0239 \text{ L} \cdot \text{min}^{-1}$ in SLMSD process). It can be seen that, by adding more D2EHPA in extractant (from 0.08 M to 0.2 M), the mass transfer rates of both processes increase because the rate of reaction (2) increase with D2EHPA concentration: 2.8 times with SX and 5.5 times with SLMSD. The improvement is less pronounced in case of SX means some drawback occur with the increase of D2EHPA in SX process but this drawback doesn't affect SLMSD process. Considering the mechanism of the two processes, this drawback is probably the reduction of interfacial area. Under the same agitation, droplets size increase with D2EHPA concentration and interfacial area is decreased in case of SX process while it's fixed as membrane area in case of SLMSD.

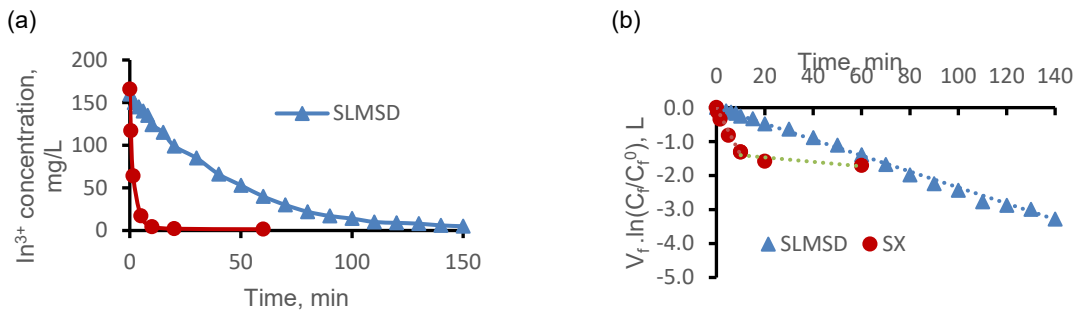


Figure 5: SX and SLMSD with oxalic acid using 0.2 M D2EHPA (a) Time dependence of indium concentration in feed solution, (b) Time dependence of $V_f \cdot \ln \frac{C_f}{C_f^0}$

It can be seen that, $k.A$ of SLMSD in all investigated cases was significantly smaller than SX. Similar results were observed by Raghuraman and Wiencek (1993) for copper recovery by SLM. According to this author, it was caused by smaller interfacial area creating by membrane compared to by mixing.

3.3 Estimation of interfacial area in conventional extraction process

According to experimental condition of SX: $V_f = 0.36 \text{ L}$. Assume diameter of each spherical emulsion drop is $100 \mu\text{m}$ (the typical size of emulsions) (Ho, 2003), interfacial area of each emulsion drop is calculated by Eq(9):

$$A_1 = \pi \cdot d^2 = 3.14 \times 10^{-8} \text{ m}^2 \quad (9)$$

Volume of each spherical emulsion drop is calculated by Eq(10):

$$V_1 = \frac{4}{3} \pi \cdot r^3 = 5.23 \times 10^{-13} \text{ m}^3 \quad (10)$$

The number of drops is calculated by Eq(11):

$$A = n \cdot A_1 = 21.6m^2 \quad (11)$$

Therefore, interfacial area between oil – water phase is calculated by Eq(12):

$$n = \frac{V_f}{V_1} = 6.88 \times 10^8 \text{ drops} \quad (12)$$

Estimation shows that interfacial area of SX is about 15 times more than SLMSD. However, the product k.A in SX process is only 5 to 11 times higher than in SLMSD process. That means the mass transfer coefficient of SLMSD process is slightly higher than SX process. The presence of OA greatly hampers both process but it can be mitigated by increasing D2EHPA concentration, the effect is more pronounced for SLMSD.

4. Conclusions

In this paper, the mass transfer performance of conventional extraction and SLMSD were investigated in both cases: with and without oxalic acid. For comparison, the mass transfer coefficient of SLMSD is higher while SX provided higher interfacial area. These advantages are not free of charge: SLMSD requires continuous circulation pumping to enhance mass transfer coefficient while SX requires continuous stirring to maintain fine dispersion of extract droplets, resulting in high interfacial area. As pump power is proportional to flowrate and stirrer power in case of turbulence is proportional to 5th power of tank diameter, energy consumption by SX process will increase faster than SLMSD process when scaling up from laboratory scale.

The presence of oxalic acid greatly hampers both process but in case of SLMSD, it is easier to deal with by increasing D2EHPA concentration in extractant.

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References

- 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.
- Dodbiba G., Nagai H., Wang L.P., Okaya K., Fujita T., 2012, Leaching of indium from obsolete liquid crystal displays: Comparing grinding with electrical disintegration in context of LCA, *Waste Management*, 32, 1937-1944.
- 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, *Journal of the Chinese Institute of Chemical Engineers*, 33, 67 – 76.
- Ho W.S.W., 2003, Removal and recovery of metals and other materials by supported liquid membranes with strip dispersion, *Annals of the New York Academy of Sciences*, 984, 97 – 122.
- McCabe W. L., Smith J. C., Harriott P., 2004, *Unit operations of chemical engineering*, 7th edition, McGraw-Hill.
- Raghuraman B., Wiencek J., 1993, Extraction with Emulsion Liquid Membranes in a Hollow - Fiber Contactor, *AIChE Journal*, 39, 1885 – 1889.
- Rocchetti L., Amato A., Fonti V., Vegliò, Beolchini F., 2015, Innovative method to extract indium from LCD panels, *Chemical Engineering Transactions*, 43, 1987 – 1992.
- Ruan J., Guo Y., Qiao Q., 2012, Recovery of indium from scrap TFT-LCDs by solvent extraction, *Procedia Environmental Sciences*, 16, 545-551.
- Sato T., 1975, The extraction of Indium (III), Lanthanum (III) and Bismuth (III) from sulphuric acid solutions by Di-(2-ethylhexyl)-phosphoric acid. *Journal of Inorganic and Nuclear Chemistry*, 37, 1485 – 1488.
- Taoualit N., Boutemak K., Bensacia N., Chemlal S., Irriri N., Hadji-Boussaad D.-E., 2020, Extraction and Transport of Methylene Blue Dye through a Plasticized Liquid Membrane containing Trioctyl Phosphine Oxide (TOPO) as the Carrier: Parametric Study, *Chemical Engineering Transactions*, 80, 349 – 354.
- Tsai T.-H., Wu Y.-F., 2006, Organic Acid Mixing to Improve ITO Film Etching in Flat Panel Display Manufacturing, *Journal of the Electrochemical Society*, 153(1), 86 – 90.
- Yen F.-C., Chang T.-C., Laohaprapanon S., Chen Y.-L., You S.-J., 2016, Recovery of Indium from LCD waste by solvent extraction and the SLMSD using D2EHPA as the extractant, *Solvent Extraction Research and Development*, 23(1), 63 – 73.