

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Commercial process for recovery of metals from ITO etching industry wastewater by liquid-liquid extraction: simulation, analysis of mechanism, and mathematical model to predict optimum operational conditions

Basudev Swain*, Chinmayee Mishra, Hyun-Seon Hong, Sung-Soo Cho, Sung kyu Lee

**Institute for Advanced Engineering (IAE)
Advanced Materials & Processing Center, Yongin-Si 449-863,
Republic of Korea**

Abstract

A commercial process for recovery of metals from Indium-Tin-Oxide (ITO) etching industry wastewater by liquid-liquid extraction has been developed. A suitable cross current simulated batch process was developed; extraction mechanisms involved in the process were analyzed. Mathematical models were proposed to correlate metal extractability with respect to extractant concentrations and metal loading with respect to solvent/solution volume ratio. Optimum conditions required for complete scrubbing of Mo and Sn using Cyanex 272, quantitative extraction of pure In using DP-8R were estimated by a proposed model. A good agreement between proposed model and observed results were indicated. Based on the laboratory scale simulation a pilot plant batch process was developed and simulated. The developed process is a techno economical feasible, environment friendly, occupational safe, clean and green process for the commercial treatment of ITO etching industry wastewater and recovery of metal values through liquid-liquid extraction. In with 99.999 % purity, Cu nanopowder with 99.999 % purity, Mo and In with 99 % purity has been recovered.

Keywords Wastewater treatment: Green process, Indium-Tin-Oxide etching waste, Indium recovery, etching wastewater treatment, crosscurrent simulation

* To whom correspondences should be addressed:

Tel.:82-31-330-7481 Fax: 82-31-330-7113, E mail: Basudev Swain (swain@iae.re.kr)
Basudevswain@yahoo.com

1. Introduction

Indium tin oxide (ITO) is a solid solution typically contains 90% of indium oxide and 10% of tin oxide by weight; in thin layers, it is colorless and transparent. Due to their optical transparency, electrical conductivity, and easier thin film deposition, ITO is a core and critical materials in the electronic information area, mainly for the manufacture of flat panel liquid crystal displays, touch panel, thin film transistors, solar cells, transparent electrodes and multifunction glass. ITO has also several other hi-tech applications like; field emission displays, electroluminescent displays, electrochromic displays, windshields, photovoltaics, optoelectronics, heat reflective coatings, gas sensors, and energy efficient windows¹⁻³. ITO films, thicknesses of 1000-3000 angstroms are normally deposited by physical vapor deposition process such as magnetron sputtering or electron beam deposition, followed by oxidation in an oxygen plasma or at elevated temperatures in an oxygenating atmosphere. Finally, etched, using the customized etching solution in the chloride media. During etching, In is soluble as a trivalent hexa-aquo-complex $[\text{In}(\text{H}_2\text{O})_6]^{3+}$ while tin forms a divalent hexa-chloro-complex $[\text{SnCl}_6]^{2-}$. During, the ITO etching process the customized etching solution gradually enriched with In and Sn along with other undesirable elements makes the etching bath undesirable after several turnovers. The etching wastewater bath must be disposed of after a certain number of turnovers. The ITO etching wastewater contains several kg/m^3 of pollutant metals is a threat to the ecosystem as well as human health. It is also a potential secondary resource for industrially valuable metals like; In and Cu. Recycling/disposal of this industrial wastewater after metal value recovery and treatment can be a feasible option, which can address the environment and resources issues.

Asia is the leading producer and consumer of ITO due to the huge electronics market in China, Japan, and Korea. Currently, global ITO sputtering targets are almost monopolized by a small minority of enterprises such as JX Nippon Mining and Metals, Mitsui Mining, Tosoh, Samsung, Heraeus, and Umicore, in which Japanese and Korean companies account for nearly 80% of the market share^{4,6}. Globally, 70% of the global In is used for ITO sputtering target production, whereas the In resource is very scarce, with basic reserves merely 16,000 tons. The global annual In consumption during 2013-14 was 1,400 tons, whereas worldwide total (primary, 570 tons and secondary) In production was approximately 1200 tons, for year 2010⁷. The United States Geological Survey (USGS) reported, worldwide total primary production was 770 tons in the year 2013⁸. Global ITO sputtering target demand will hit 2,500 tons by 2016, and hence, long-term supply of In will suffer bottlenecks^{5, 6}. BCC

Research reported, the global market for transparent conductive coatings is expected to grow to nearly \$7.1 billion by 2018 from \$4.8 billion in 2013, registering a compound annual growth rate (CAGR) of 8.0% between 2013 and 2018⁹. The ITO accounted for approximately 97% of the overall market for transparent conducting oxides in 2011. All these reports indicate In is at critical risk of supply chain. Massive demand and use mean massive waste generation during production and massive end-of-life (EOL) waste generation. A status report on recycling rates of metals reported by United Nations Environment Programme (UNEP) indicates hardly 1% In bearing EOL waste being recycled^{10,11}. Hence, the treatment of this etching wastewater generated during the manufacturing process or EOL waste, through recycling is a feasible option.

The limited number of information on recovery of In from ITO-scrap has been reported in the literature. Park has reported recovery of In from ITO target scrap by alkaline hydrothermal reaction¹². Hong *et al.* reported recycling of the In from ITO-sputtering waste mostly deals with enrichment of In containing waste powder from sputtering chamber wall¹³. Hsieh *et al.*, and Li *et al.* has proposed pure indium recovery method from ITO scraps using hydrometallurgical route^{14,15}. Several waste resources are studied for the recovery of In are ITO-scrap¹⁴⁻¹⁶, end-of-life liquid crystal displays and etching waste^{17,18} as prospective secondary resources for In. Hasegawa *et al.* reported selective recovery of In from the etching waste solution of the flat-panel display, mostly focused on recovery of In using ion-exchange resin¹⁹. Kang *et al.* reported recovery of In from etching waste by solvent extraction and electrolytic refining, but they have used a solid cake from ITO etching industry¹⁷. Liu *et al.* studied recovery of In from etching wastewater using supercritical carbon dioxide extraction¹⁸. Most of the research reported are focused on recovery of In from these waste resources and laboratory scale. The commercial process to recover metal values by hydrometallurgical route from ITO industry wastewater never been reported. Our current investigation focused on the optimization of a commercial process, laboratory scale simulation of the developed process, verification of reproducibility, analysis of mechanisms, development of a suitable model to predict extractability, and their verification through pilot scale operations. In the current study optimum condition for Mo and Sn scrubbing, using Cyanex 272 followed by In extraction using DP-8R, and their stripping are revealed. The mechanism involved for scrubbing and extraction was analyzed, through mechanism analysis, theoretical (ideal) loading capacity and real loading capacity of each extractant were analyzed. Suitable models were fitted for scrubbing, extraction, and loading behavior. From model possible % extraction, concentrations in McCabe-Thiele extraction isotherm were calculated and

compared with experimental values. Eventually, based on laboratory simulation and models, required optimum condition for a random batch of ITO etching wastewater were calculated and verified in the pilot plant operation and simulation. The novelties of the developed process are listed below.

- (i) This paper addresses the gap between laboratory based process optimization and commercially applicable process development.
- (ii) The developed process is a techno economical feasible, environment friendly, occupational safe, clean and green process for commercial treatment of several tons (m^3) ITO etching wastewater per day.
- (iii) Most of the In recovery processes reported in the open literature are about laboratory scale process; deal with several ml of solution, but our commercial process offers versatile, flexible and robust approach, capability for mass production of In up to kilogram scale.
- (iv) Regeneration and reuse of all the organic extractant, use of non-hazardous chemical in the process, eventually, make the process a clean and green economical process. After treatment, the wastewater is heavy metal free can be disposed of or reused in the same ITO etching process.
- (v) Complete recovery of In with 99.999 % purity, quantitative recovery of Mo and Sn with at least 99 % purity and value added Cu nanopowder with 99.999 % are feasible through our proposed process.

2. Materials and Method

2.1. Materials

TSM Co. Ltd, the Republic of Korea, supplied the In rich wastewater from the ITO etching process, which is no longer suitable for further etching application. Composition of ITO industry etching wastewater used for laboratory scale and pilot plant study is given in Table 1. Anion analysis showed the wastewater was purely a chloride solution. The ITO etching wastewater was used for all experiments as received, unless otherwise mentioned. The commercial acidic extractants, *i.e.*, Bis (2,4,4,-trimethyl pentyl) phosphinic acid (Cyanex 272) was supplied by Cytec Korea Inc., and Bis (2-ethylhexyl) phosphoric acid (DP-8R) was obtained from Daihachi (Japan), were used without further purification. The low boiling point kerosene (180-270 °C) was used as diluent. Other chemicals like NaOH, HCl, and NH_4OH

were of analytical grade supplied by Daejung chemical and metal Co, Ltd, the Republic of Korea.

2.2. Laboratory Scale Liquid-Liquid Extraction Procedure

The extractant Cyanex 272 and, DP-8R were diluted using kerosene as diluent. The requisite pH of the wastewater from ITO etching industry was adjusted by addition of NaOH or HCl solution (for pH variation study only). Liquid-liquid extraction experiments were carried out using suitable volumes of wastewater from ITO etching industry and extractant solutions. The wastewater from ITO etching industry was equilibrated with organic extractant for 10 minutes, and then the phase was separated through settling by separating funnel. The aqueous raffinate was analyzed to determine the amount of metal extracted by organic extractant. Organic phase metal concentration was analyzed through the mass balance calculation. The time 10 minutes was found sufficient to attain the equilibrium, which was verified in preliminary test. The preliminary tests suggest that about 4 to 5 minutes shaking is good enough to get the equilibrium. Metals scrubbed and stripped similarly equilibrating requisite volume of aqueous and organic phase. All experiments were carried out at ambient temperature ($25\pm 1^\circ\text{C}$). Throughout the study, organic phase/aqueous phase volume ratio (O/A) kept constant at one, unless otherwise mentioned.

2.3. Pilot Scale Liquid-Liquid Extraction Procedure

For pilot scale liquid-liquid extraction, an indigenous batch process reactor has been designed to treat 300 L/batch of solution (600 L reactor). Selected volume of wastewater and organic extractant were fed to the reactor container by electrical pumps, and were mixed through the baffle mixture for 1 h. After complete phase separation, the loaded organic and raffinate was separated through an operating valve. Operating windows made up of transparent quartz were attached below the reactor tanks to observe organic and aqueous layer during liquid-liquid separation. Supplementary Figure 1 shows a pilot plant view of batch process ITO etching wastewater treatment plant.

2.4. Analytical Procedures

The concentration of metals in the ITO etching wastewater, the raffinate and stripped solution was determined using ICP-AES (OPTIMA 4300DV, Perkin-Elmer, USA) after suitable dilution using 5 vol. % of HCl. The maximum deviations permitted were about $\pm 3\%$ in ICP-AES analysis. The concentrations in the organic phases were determined by the mass

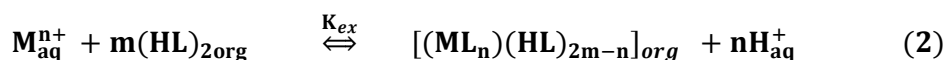
balance calculation. To minimize the analytical errors associated with the concentrations of metal, the concentrations were averaged after several reproducible analyses and were estimated by statistical methods.

3. Theory

The acidic Cyanex 272 and DP-8R exists as a dimer at acid equilibrium conditions²⁰⁻²³. The mechanism of extraction can be represented as follows^{24, 25}.



where, K_d is dimerization constant for the extractants and HL is organic extractant



where the subscripts *aq* and *org* denote species in the aqueous and organic phases, respectively. The equilibrium constant K_{ex} of the reaction can be written as:

$$K_{ex} = \frac{[(ML_n)(HL)_{2m-n}]_{org}[H^+]_{aq}^n}{[M^{n+}]_{aq}[(HL)_2]_{org}^m} \quad (3)$$

$$K_{ex} = \frac{D[H^+]_{aq}^n}{[(HL)_2]_{org}^m} \quad (4)$$

where, distribution coefficient, $D = [(ML_n)(HL)_{2m-n}]_{org} / [M^{n+}]_{aq}$

Equation (4) could be rearranged as:

$$\log D = \log K + m \log [(HL)_2]_{org} + n pH \quad (5)$$

$$\text{Consequently } (\partial \log D / \partial pH)_{[(HL)_2]_{org}} = n \text{ and } (\partial \log D / \partial \log [(HL)_2]_{org})_{pH} = m \quad (6)$$

The separation factor (β) is calculated using Equation (7).

$$\beta_{M1/M2} = D_{M1} / D_{M2} \quad (7)$$

where D_{M1} = Distribution coefficient of the metal 1.

D_{M2} = Distribution coefficient of the metal 2.

Provided $D_{M1} > D_{M2}$, otherwise the Equation (7) reverse as Equation (8).

$$\beta_{M2/M1} = D_{M2} / D_{M1} \quad (8)$$

This Distribution coefficient can be used to calculate the percentage of the extracted metal, E :

$$E = \left[\frac{DV_{org}/V_{aq}}{1 + (DV_{org}/V_{aq})} \right] \times 100 \quad (9)$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases respectively. Since we have used equal volumes this reduces to:

$$E = [D/(1 + D)] \times 100 \quad (10)$$

Based on Equation 6 theoretical loading capacity of the extractant can be defined as

$$\text{Theoretical Loading Capacity} = \frac{M}{m} * \text{Atomic weight } (M^{n+}) \quad (11)$$

where M stands for mol/l of metal, M^{n+} stands for metal with n^{th} valency.

4. Result and Discussion

In an ITO etching industry different batch of etching wastewater generated has a different metal ion concentration, although their basic composition remains the same. For each batch of etching wastewater treatment, optimizing the process technology is time taking, tedious, and cost inefficient. Understanding the reaction mechanism, developing models to predict extraction efficiency and the number of stages required for pure metal extraction, and working through a suitable simulation can overcome the challenge. Hence, through a process optimization, the ion exchange mechanism involved and their behavior has been investigated. Suitable mathematical models correlated with experimental results, based on model value process parameters were selected and were operated through a pilot plant.

4.1. Simulation

Qualitative process flow sheet followed for treatment of ITO etching wastewater and the recovery of metal values from wastewater presented in supplementary Figure 2. Based on the proposed flow sheet a laboratory scale process was optimized and is presented in Figure 1. The Figure1 reflects liquid-liquid extraction cross current simulation process flow sheet, which consists of three cycles. In the first cycle the Mo and Sn were scrubbed from wastewater by liquid-liquid extraction using Cyanex 272, in the second cycle In was recovered by liquid-liquid extraction using DP-8R, and in third cycle the Cu nanopowder was recovered by cementation. Finally, Al was precipitated through neutralization. Eventually, the treated water worthy to be disposed or reused in the same industry. Figure 1 shows Mo and

Sn involved two stages of scrubbing process using 0.25 M Cyanex 272 at a (A/O) volume ratio of one. Then both the scrubbed Mo and Sn were selectively stripped using 7 M NH_4OH and 4 M NaOH , respectively in a series. Mo was stripped as Ammonium polymolybdate and Sn as Sodium stannite using NH_4OH and NaOH , respectively. It should be noted that Mo should be stripped first, followed by Sn as reverse affects the selective recovery of metals. In the second cycle, DP-8R was used as an extractant, through the optimization process followed by McCabe-Thiele study, using 0.5 M DP-8R at A/O ratio 8.5, three stages of extraction were required for complete recovery of In. In this cycle all these loaded organics from three stages were mixed together and stripped using 4 M HCl . Using loaded organic/4 M HCl volume ratio of 10 ($\text{O/A}=10$ or $\text{A/O}=0.1$), In was stripped. From the strip In chloride solution, In was recovered by cementation using metallic Al at 80-100 °C. AlCl_3 solution generated during In cementation can be precipitated as $\text{Al}(\text{OH})_3$, as explained in 3rd cycle. In the third cycle Cu was recovered as Cu nanopowder through reduction using 60 kg/m³ of ascorbic acid. Finally, the wastewater was neutralized using solid NaOH . The proposed process was applied to a specific batch of wastewater generated from ITO etching wastewater or it can be applied for the similar kind of ITO etching wastewater.

From the monitoring throughout the year, we observed that the concentration of metal content varies from -50 % to + 120 % (with respect to Table 1, composition applied for laboratory scale). In these cases, through the proposed concept and simulation process mentioned in Figure 1, total recovery of metals and treatment of ITO etching wastewater is feasible. However, the specific extractant and reagent concentration mentioned may be excess or insufficient, depending upon batch of wastewater to be treated. In both cases, the process may lose its cost effectiveness and metal purity aspect, hence through the mechanism and distribution analysis, it could be easy to decide required extractant/ reagent concentration in each cycle as given in the simulation (Figure 1). The simulation process proposed above was carried out in the laboratory in various volume scales ranging from 20 ml to 2 L volume at least three operations each. Reproducibility of the data in each step was analyzed, on an average ± 2.5 % variation in results was observed. Hence, reasonably, concluded that the proposed process is suitable, feasible and economical one. Important aspects of the current simulation noted below.

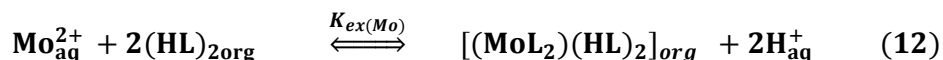
1. During In extraction cycle since the A/O volume ratio used was 8.5 and In stripping O/A volume ratio used was 10 ($\text{A/O}=0.1$), hence, in recovery process In enriched 28 times, the volume of DP-8R and strip acid used are significantly low. Figure 2 shows the

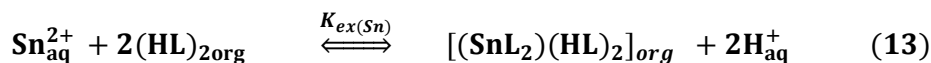
volume reduction during the downstream extraction process at all stages of the extraction process.

2. All extractants like Cyanex 272 and DP-8R are can be regenerated and reused, as extractants are very stable, potentially can be used for decades through proper regeneration ²⁶.
3. Ascorbic acids used for Cu reduction help to make wastewater chlorine free and add value to Cu nanopowder.
4. Suitable for both batch and continuous process operation add flexibility for easier industrial applicability.

4.2. Analysis of mechanism

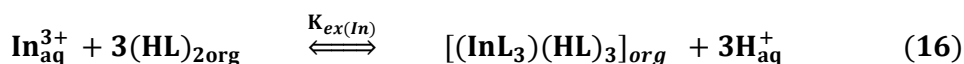
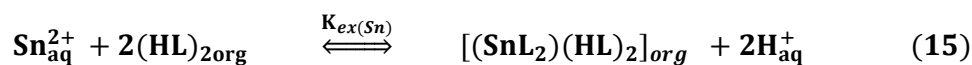
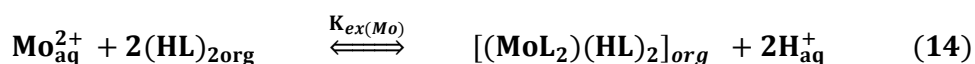
The possible ion exchange mechanism involved in scrubbing Mo, Sn as explained in first simulation cycle in the Figure 1, was analyzed through log-log analysis as proposed in Equation 6. The Mo and Sn scrubbing process were optimized through pH variation, and Cyanex 272 concentration variation. Figure 3a shows logD versus equilibrium pH of ITO etching wastewater using 0.5 M of Cyanex 272. The best-fitted straight line to data can be expressed as $y = 0.91x + 0.60$, $R^2 = 0.97$, $y = 1.68x + 1.53$, $R^2 = 0.86$ and $y = 2.16x - 2.90$, $R^2 = 0.95$, respectively for Sn, Mo and In. The slope values for Sn, Mo, and In are 0.91, 1.68, and 2.16, are approximated to 1, 2, and 2, respectively indicates that one mole of Mo gets efficiently extracted with exchanges of 2 moles of H^+ , but for Sn it was only 1 and for In it was 2. From Equation 6 the slope should be 2 and 3 for Sn and In, respectively, indicates the pH of the feed solution is not as efficient as in the case of Mo. The Figure 3b shows logD versus $\log[\text{Cyanex 272}]$ M, the best straight line fitted to data can be expressed as $y = 2.00x + 1.73$, $R^2 = 0.87$, $y = 1.55x + 2.19$, $R^2 = 0.99$ and $y = 0.27x - 1.08$, $R^2 = 0.39$, respectively for Sn, Mo and In at constant ITO etching wastewater pH=0.7. The slopes for Sn, Mo and In are 2.00, 1.55 and 0.27, respectively, indicating 2 moles of Cyanex 272 required for extraction Sn and Mo each. The poor slope values for In indicates that Cyanex 272 is not a good extractant for In recovery at pH of 0.7, also cause for poor logD-equilibrium pH decencies. The figure also justifies Cyanex 272 can efficiently scrub out all Mo and Sn, helps for In purification and recovery. Hence, the ion-exchange mechanism and stoichiometry involved for Sn and Mo can be explained as below.





Where HL stands for bis(2,4,4-trimethylpentyl)phosphinic acid or Cyanex 272 and L stands for bis(2,4,4-trimethylpentyl)phosphinic anion.

As explained in Figure 1 in the second simulation cycle the In extraction process was optimized through pH variation, and DP-8R concentration variation study. Figure 4a shows logD versus equilibrium pH of ITO etching wastewater using 0.5 M of DP-8R. The best-fitted straight line to data can be expressed as $y = 1.52x - 0.18$, $R^2 = 0.98$, $y = -2.14x + 3.67$, $R^2 = 0.98$ and $y = 3.01x - 0.89$, $R^2 = 0.93$, respectively for Sn, Mo and In. The slope values for Sn, Mo, and In are 1.52, -2.14, and 3.01, are approximated to 2, -2, and 3, respectively. That, indicates that Sn and In get efficiently extracted with exchanges of 2 and 3 moles of H^+ , but the -ve slope for Mo indicates increases in the pH inversely affect the Mo extraction. Figure 4b shows logD versus log[DP-8R], M using at constant ITO etching wastewater pH 0.7. The Figure 4b shows, the best-fitted straight line to data can be expressed as $y = 1.70x + 1.89$, $R^2 = 0.95$, $y = 1.97x + 2.50$, $R^2 = 0.99$, and $y = 2.98x + 1.98$, $R^2 = 0.97$, respectively for Sn, Mo and In. The slope values for Sn, Mo, and In are 1.70, 1.97, and 2.98, are approximated to 2, 2, and 3, respectively indicates that all the three metals get efficiently extracted with exchanges of 2, 2, and 3 moles of DP-8R with one mole of each Sn, Mo and In, respectively. Hence, the ion-exchange mechanism and involving the stoichiometry for Sn, Mo and In can be explained as below.



Where HL stands for Di-(2-ethylhexyl)phosphoric acid and L stands for Di-(2-ethylhexyl)phosphoric acid anion.

In a different experiment, extraction of In was investigated varying pH in constant DP-8R concentration (0.5M) and varying DP-8R at constant pH (0.7) from Mo and Sn scrubbed (Mo and Sn free ITO etching wastewater) ITO etching wastewater. The logD dependencies for equilibrium pH and DP-8R were analyzed. The slope analysis shows the above Equation 6

hold good. The slope values for logD versus equilibrium pH and logD versus equilibrium log[DP-8R]M were approximately 3 and 3, respectively indicates the In extraction mechanism is independent from Mo and Sn, also follows the Equation 16 as explained above.

4.3. Metal extractability behavior and modeling

In extraction behavior, varying DP-8R molar concentration at constant initial pH was investigated. Percentage of In extracted can be considered as a function of the active extractant concentration in the fresh solvent system. The extracted In percentage exhibits an exponentially increases to a maxima as a function of molar concentration of DP-8R. A nonlinear modified exponential function was proposed to predict % In extraction (E) as a function of DP-8R molar concentration in Equation (17),

$$E = 100(1 - \exp^{-b \times [(DP-8R)_2]}) \quad (17)$$

where

$$b = 3 (Equilibrium\ pH + Equilibrium\ \log[(DP - 8R)_2]) + \log K_{ex(In)} + \log K_{d(DP-8R)}$$

$\log K_{ex(In)} = 1.98$ was obtained from Figure 4b, and $\log K_{d(DP-8R)} = 4.50$ for DP-8R was used from the literature²⁷. For the DP-8R concentration as organic phases, the percentage of In extraction from aqueous phase is predicted through proposed equation (Equation 17), and compared with experimental values. Plotting of E versus $[(DP-8R)_2]$ M compared the predicted and observed results graphically as shown in Figure 5a. The Figure shows a very good fit between predicted values and experimental values, indicating through the proposed model, a suitable DP-8R concentration can be selected for quantitative extraction of In from ITO etching wastewater.

In ITO etching wastewater Sn and Mo contain approximately 1: 10 weight ratio. Since, their Sn content is very small, prediction through a modelling of individual metal may not be of appropriate. Hence, a model equation was fitted for mixed metal extraction using Cyanex 272. Since, Mo and Sn scrubbed together by Cyanex 272, predicting their mixture can add values for understanding of the model. Mixed metal scrubbing i.e. both Mo and Sn scrubbing behavior was studied varying Cyanex 272 M concentration at constant initial pH of 0.7. Percentage of mixed metal extracted can be considered as a response to the active Cyanex 272 concentrations in the fresh solvent system. Similar to In extraction, the percentage mixed

metal scrubbing exhibits an exponentially increases to a maxima as a function of molar concentration of Cyanex 272. A nonlinear modified exponential function was proposed to predict % metal mixture extraction (E) as a function of Cyanex 272 molar concentration, in Equation (18),

$$E = 100(1 - \exp(-b \times c \times [(Cyanex\ 272)_2])) \quad (18)$$

where

$$b = 3(Equilibrium\ pH + Equilibrium\ \log[(cyanex\ 272)_2]) + \log K_{ex(Mo)} \\ + \log K_{d(Cyanex\ 272)}$$

$$c = 3(Equilibrium\ pH + Equilibrium\ \log[(cyanex\ 272)_2]) + \log K_{ex(Sn)} \\ + \log K_{d(Cyanex\ 272)}$$

$\log K_{ex(Sn)} = 1.73$ and $\log K_{ex(Mo)} = 2.19$ were obtained from Figure 3b, and $\log K_{d(Cyanex\ 272)} = 2.27$ for Cyanex 272 was used from the literature²⁸. For the Cyanex 272 concentration organic phases, the percentage of mixed metal extraction from the aqueous phase predicted through proposed Equation 18, and compared with observed values. Plotting E versus $[(Cyanex\ 272)_2]$ compared the predicted and observed results graphically as shown in Figure 5b. The Figure shows a very good fit between predicted values and experimental values, indicating through model a suitable Cyanex 272 concentration can be selected for complete scrubbing off Mo and Sn from ITO etching wastewater. Figure 5c shows the experimental distribution coefficient versus model based distribution coefficient. The figure shows, a linear regression line was fitted using global curve fitting wizard, an inbuilt analysis tool used in SigmaPlotTM 12 (SigmaPlotTM, Systat Software, Inc.). The global goodness of fit for DP-8R and Cyanex 272 concentration variations were as such; $R = 0.99$, $R\text{-square} = 0.99$, adjusted $R\text{-square} = 0.99$ and standard error of estimate = 114.65. The statistical parameter values R , $R\text{-square}$, and adjusted $R\text{-square}$ values were accurate and desirable up to two significant numbers after decimal. Through the inbuilt wizard of SigmaPlotTM 12, 95% confidence interval and predicted boundaries were determined and shown in the same figure. The linear dependencies reveal that the proposed model for % metal extraction calculation as a function of extractant concentration holds well and is a robust model within 95% confidence interval. Hence, the validity of the model was good enough to conclude that the model equation can be used as a tool to select extractant concentration appropriate for complete scrubbing of Mo and Sn, and purification of In.

4.4. McCabe-Thiele extraction isotherm and Modelling

For McCabe-Thiele extraction isotherms construction purpose liquid-liquid extraction was investigated varying $(Volume_{aq}/Volume_{org}) = (V_{aq}/V_{org}) = A/O$ volume ratio in the range of 0.2 to 10 for In extraction purpose. The Mo and Sn free ITO etching wastewater-having pH 0.7 was used without any further treatment and 0.5 M DP-8R was used as organic phase. Figure 6 shows In loading behavior in DP-8R with respect to A/O volume ratio variation. The figure shows the In loading in solvent increases exponentially to a maxima. The same figure also shows theoretical loading capacity, which is calculated based on Equation (11) and % of In loaded with respect to theoretical loading capacity. A significant gap between theoretical loading capacity and experimental loading behavior was observed. The maximum experimental (real) loading capacity of 0.5 M DP-8R was 45 % of theoretical loading capacity (ideal). We assumed maximum possible loading is 50% of theoretical loading. From Figure 6, In loading (kg/m^3) in solvent can be considered as a function of the A/O volume ratio. The In loading (kg/m^3) exhibits an exponential growth to a maxima shaped trend as a function of A/O ratio. A modified exponential equation proposed to understand loading capacity, given below in Equation 19.

$$LO_{exp} = LO_{max}(1 - \exp^{-k(V_{aq}/V_{org})}) \quad (19)$$

Where, LO_{exp} is the experimental loading of metal in organic solvent LO_{max} is the maximum possible loading, k is unstructured parameters.

Based on Figure 6 we have assumed $LO_{max} = 50\%$ of theoretical loading, the assumption given LO_{max} can be expressed as:

$$LO_{max} = \text{Theoretical Loading} / 2 \quad (20)$$

Theoretical maximum In loading of DP-8R was also calculated for selected concentration i.e. 0.5 M, based on reaction mechanism proposed in Equation 16.

The model based predicted and observed results were compared graphically by plotting In loading in solvent versus A/O volume ratio as shown in Figure 7a. In this, figure symbols denote experimental points and solid line denotes predicted line using the Equation 19. The 95% confidence interval value, giving a range within a parameter is expected to lie with a certain probability of 95%, is calculated for each case. 'k' the unstructured parameters were estimated by a multivariate nonlinear regression analysis using Trust-Region algorithms. The

parameters estimated by above method are given in Table 2. The random patterns of the residuals indicate that the model is free of systematical errors. The MATLAB® 10.1 program was used for curve fitting purpose. The Interactive Curve Fitting procedure was used to predict and compare for the curve at different an A/O volume ratio of Mo and Sn free ITO etching wastewater and (0.5 M) DP-8R. The best-fit parameters are estimated using nonlinear least squares method, trust-region algorithms and LAR robust method for performing the minimization of the objective function given by the sum of squares due to error (SSE) $\sum_i e_i^2$. The error (e) is the difference between the observed and predicted responses for metal extraction (E). The asymptotic standard error values (SE) were also computed for each best-fit parameter.

From our proposed model (Equation 19) the concentration of In in organic phase, aqueous phase and distribution coefficients were calculated for different A/O volume ratios of DP-8R. For construction of the McCabe-Thiele diagram, the values for In content in organic and aqueous phase were calculated from the Equation 21.

$$Y_{org} = \frac{V_{aq}}{V_{org}}(X_0 - X_n)_{aq} \quad (21)$$

Figure 7b shows the McCabe-Thiele extraction isotherm for experimentally obtained values and model based calculation. The McCabe-Thiele diagram for 0.5 M of DP-8R indicated the same number of stages required for quantitative extraction of In, both by experiment and the proposed model. A very good agreement and correlation was indicated between proposed model and experimentally observed extraction. Hence, the combination of proposed model Equation 19 and Equation 21, can be an accurate tool to predict the number of stages required for quantitative recovery of In from different batches of ITO etching wastewater.

The metal loading behavior of Cyanex 272 was also investigated varying A/O volume ratio in the range of 0.2 to 5 for Mo and Sn scrubbing purpose. The individual metal and their mixture exhibit an exponential growth to a maxima shaped trend as a function of the A/O volume ratio. The same exponential equation proposed for In extraction (Equation 19) is used to understand the loading behavior of Mo, Sn and their mixture. The same curve fitting procedure used for In also used for Mo, Sn and their mixture using the MATLAB® 10.1 program. The set of best-fit parameters were estimated using nonlinear least squares method, trust-region algorithms and LAR robust method for performing the minimization of the objective function given by the sum of squares due to error (SSE) $\sum_i e_i^2$. The model based

predicted and observed results are compared plotting for Mo, Sn and their mixture loading in Cyanex 272 as a function of the A/O volume ratio and shown in Figure 8a. In this, figure symbols denote experimental points and solid line denotes predicted line using the Equation 19. The 95% confidence interval values are predicted for each case as shown Figure 8a. The unstructured parameters ' k ' for Mo, Sn and their mixture are estimated by a multivariate nonlinear regression analysis using Trust-Region algorithms by MATLAB. The parameters estimated by above method are given in Table 2. The random patterns of the residuals indicate that the model is free of systematical errors.

Similarly, the McCabe-Thiele extraction isotherms were investigated for Mo and Sn scrubbing using 0.25M Cyanex 272. As the scrubbing of both these metals is a basic requirement of the proposed process, a mixed metal isotherm was also investigated. Mixed metal isotherm study explained elsewhere²⁹, indicates it can be an important tool applied for our metal scrubbing purpose. Although, both Mo and Sn follow the same ion exchange mechanism with Cyanex 272, but theoretical loading capacity in kg/m^3 for Sn is higher than Mo, because of higher atomic weight of Sn. Hence LO_{max} applies to Sn was used for mixed metal loading calculation purpose. Based on proposed model the metal content in organic phase, the aqueous phase was calculated for different phase ratios. From experimental and calculated values McCabe-Thiele scrubbing isotherms were constructed for Mo and Mo+Sn mixed metal and shown in Figure 8b and 8c, respectively. The Figure 8b-c show there is a very good agreement between experimentally obtained values and model based calculated values for McCabe-Thiele scrubbing isotherm. Even the same number of stage requirement for the same operating line was observed from Figure 8b and c. Hence, it is reasonably concluded that the proposed model is an appropriate tool to determine the number of stage requirement for scrubbing.

4.5. Stripping of Mo and Sn

An equal volume of 0.25 M Cyanex 272 and ITO etching wastewater was equilibrated for 5 minutes, after phase separation the loaded organic and raffinate was separated. The 0.25 M Cyanex 272 loaded of Mo and In was stripped using NH_4OH and NaOH , sequentially, respectively. Table 3 shows stripping behavior of Mo and Sn at a lab-scale optimization study. The Table shows that as NH_4OH concentration increased from 0.5 M to 7 M, Mo stripping varies from 1.41% to 99.13%. The NH_4OH has selectivity towards Mo stripping, leaving the Sn in the organic phase. The same table depicts that as the NaOH concentration increased from 0.5 M to 5 M, the Sn stripping was varied from 12.03% to 97.78%. The

NaOH has limited selectivity towards either Mo or Sn stripping, hence, a sequential stripping is recommended. The Table 3 suggests a complete stripping of Mo and Sn is possible, by careful management of stripping agent and their concentrations.

4.6. Pilot scale commercial process for metal recovery

For a different batch of ITO industry etching wastewater the proposed process was applied through scale up studies. The composition of the ITO etching industry wastewater is given in Table 1. The Table 1 shows the wastewater composition is very different from the etching wastewater was used for lab scale studies. The proposed simulation, model and mechanism, that has been developed in laboratory scale was applied for pilot plant scale up studies. From given composition in Table 1, it was calculated that two stages are required for complete scrubbing of Mo and In using 0.25 M of Cyanex 272 at an A/O phase ratio of 1. Similarly, it was predicted that three stages are required for complete recovery of In using 0.5 M Cyanex 272 at an A/O phase ratio of 8.5. Figure 9 shows a pilot scale simulation for the commercial recovery of metal values and treatment of wastewater. Table 4 shows composition analysis during various stages of simulation explained in Figure 9. The table shows complete recovery of metal values is possible. The proposed model is a robust model can be applied as an accurate predicting tool for any batch of ITO etching wastewater treatment purpose. Of course, continuous mixture settler process is being applied in various industries for metal recovery/separation/purification purpose, but for ITO etching industry wastewater treatment and metal recovery purpose the batch process can be more efficient and appropriate. In etching industry, usually wastewater is generated batch wise; hence, a batch treatment process should be more appropriate. Hence, a batch treatment process has been developed. The designed pilot plant can handle at least one m³ of ITO etching wastewater/day. Considering high pure Indium price, use of cheap commercial extractant and diluent, regeneration and recycling of extractant, and inexpensive chemicals used in the reported process, justifies, the process should be a cost effective and economical process.

5. Conclusion

- A commercial techno economical feasible, environment friendly, occupational safe, clean and green pilot scale wastewater treatment process has been developed for the treatment and recovery of metal values from ITO etching industry wastewater through liquid-liquid extraction.

- Based on the laboratory scale optimization a complete treatment and recovery process has been proposed, for various process parameters suitable working mathematical models were proposed. Through the proposed model-equation, possible operation parameter was decided for pilot scale operation purpose. Validity of model, process and simulation was verified for pilot scale.
- Most of the In recovery processes reported in the open literature are about laboratory scale process; deal with several ml of solution, but our commercial process offers versatile, flexible and robust approach for mass production capability of In up to kilogram scale. A batch process pilot plant capable of handling at least 1 m³ water/day, with potential for continuous operation through automation has been designed.
- By the developed process simultaneously the valuable industrial (high pure) metals like In, Mo, Sn and Cu can be recovered to enter mainstream material flow. After values recovery and treatment, the wastewater is heavy metal free (mostly chloride free) can be disposed of or reused in the same ITO etching process.
- All the organic extractant can be regenerated and reused; no hazardous chemical used for process makes the process a clean and green economical process.
- As the process is a versatile, flexible and robust process capable operating both by batch and by continuous process can be used in small, medium and mega-scale industrial wastewater treatment where ITO etching wastewater is a concern.

Acknowledgement

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project No.: GT-11-C-01-020-0).

Abbreviations/Nomenclatures

ITO = Indium-tin-oxide

Cyanex 272 = Bis (2,4,4,-trimethylpentyl) phosphinic acid

DP-8R = Bis (2-ethylhexyl) phosphoric acid

Aq. = Aqueous

Org. = Organic

D = Distribution coefficient of the metal

M = Metal

K_{ex} = Equilibrium constant

HL = Organic solvent

ML= Organometallic complex

E = Percentage of extraction

β = Separation factor

A/O = Aqueous phase/organic phase volume ratio or vice versa

$K_{ex(Mo)}$ = Equilibrium constant for Mo

$K_{ex(Sn)}$ = Equilibrium constant for Sn

$K_{ex(In)}$ = Equilibrium constant for In

$\log K_{d(Cyanex\ 272)}$ = Dimerization constant for Cyanex 272

$\log K_{d(DP-8R)}$ = Dimerization constant for DP-8R

LO_{exp} = Experimental loading

LO_{max} = Maximum loading

(V_{aq}/V_{org}) = Aqueous volume/Organic volume

b and c = Model parameter

k = Unstructured model parameter

References

1. H. Hartnagel, *Semiconducting Transparent Thin Films*, Taylor & Francis, 1995.
2. G. Oskam, *Semiconductors, Metal Oxides, and Composites: Metallization and Electrodeposition of Thin Films and Nanostructures*, Electrochemical Society, 2010.
3. R. M. Pasquarelli, D. S. Ginley and R. O'Hayre, *Chemical Society Reviews*, 2011, **40**, 5406-5441.
4. Indium Tin Oxide (ITO) Market - Global Industry Analysis, Size, Share, Growth, Trends And Forecast, 2012 - 2018, <http://www.transparencymarketresearch.com/indium-tin-oxide.html>, Accessed 8/2/2015, 2015.
5. Research and Markets: Global and Chinese ITO (Indium Tin Oxide) Sputtering Targets Industry Report, 2013-2016, <http://www.businesswire.com/news/home/20140605006287/en/Research-Markets-Global-Chinese-ITO-Indium-Tin#.VNHVHtKUcdZ>, Accessed 08/02/2015, 2015.
6. Global and China ITO Sputtering Targets Industry Report, 2013-2016, Accessed 08/02/2015, 2015, 2014-05-27.
7. T. H. Charles Gibson, Indium and gallium overview <http://www.edisoninvestmentresearch.com/sectorreports/IndiumGalliumOverview071011.pdf>, Accessed 12/12/2014, 2014.
8. Sally Jewell and S. M. Kimball, USGS Mineral Commodities Summaries: 2014, U.S. Geological Survey, <http://minerals.usgs.gov/minerals/pubs/mcs/2014/mcs2014.pdf>, Accessed 12/12/2014, 2014.
9. R. BCC, Transparent Conductive Coatings: Technologies and Global Markets, <http://www.bccresearch.com/market-research/advanced-materials/transparent-conductive-coatings-avm105a.html>, Accessed 12/12/2014, 2014.
10. T. E. Graedel, J. Allwood, J.-P. Birat, M. Buchert, C. Hagelüken, B. K. Reck, S. F. Sibley and G. Sonnemann, *Journal of Industrial Ecology*, 2011, **15**, 355-366.
11. T. E. Graedel, Recycling rates of metals, a status report, http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf, Accessed 8/2/2015, 2015.
12. J.-C. Park, *Bull. Korean Chem. Soc.*, 2011, **32**, 3796-3978.
13. H. Hong, H. Jung and S.-J. Hong, *Res Chem Intermed*, 2010, **36**, 761-766.
14. S.-J. Hsieh, C.-C. Chen and W. C. Say, *Materials Science and Engineering: B*, 2009, **158**, 82-87.
15. Y. Li, Z. Liu, Q. Li, Z. Liu and L. Zeng, *Hydrometallurgy*, 2011, **105**, 207-212.
16. S. Virolainen, D. Ibana and E. Paatero, *Hydrometallurgy*, 2011, **107**, 56-61.
17. H. N. Kang, J.-Y. Lee and J.-Y. Kim, *Hydrometallurgy*, 2011, **110**, 120-127.
18. H.-M. Liu, C.-C. Wu, Y.-H. Lin and C.-K. Chiang, *Journal of Hazardous Materials*, 2009, **172**, 744-748.
19. H. Hasegawa, I. M. M. Rahman, Y. Umehara, H. Sawai, T. Maki, Y. Furusho and S. Mizutani, *Microchemical Journal*, 2013, **110**, 133-139.
20. G. M. Ritcey, Ashbrook, A.W., *Solvent extraction principles and applications to process metallurgy*, Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1984.
21. N. B. Devi, K. C. Nathsarma and V. Chakravorty, *Hydrometallurgy*, 2000, **54**, 117-131.
22. B. Swain, J. Jeong, J. Lee and G.-H. Lee, *Hydrometallurgy*, 2006, **84**, 130-138.
23. B. Swain, J. Jeong, J.-c. Lee and G.-H. Lee, *Separation and Purification Technology*, 2008, **63**, 360-369.
24. B. Swain and E. O. Otu, *Separation and Purification Technology*, 2011, **83**, 82-90.
25. B. Swain, J. Jeong, K. Yoo and J.-c. Lee, *Hydrometallurgy*, 2010, **101**, 20-27.
26. Brochure for Cyanex 272, <http://www.cytex.com/sites/default/files/datasheets/CYANEX%20272%20Brochure.pdf>, 2015.

27. R. K. Biswas, M. A. Habib and M. N. Islam, *Industrial & Engineering Chemistry Research*, 1999, **39**, 155-160.
28. R. K. Biswas, M. A. Habib and H. P. Singha, *Hydrometallurgy*, 2005, **76**, 97-104.
29. M. V. Rane, R. Sadanandam, K. Bhattacharya, S. K. Tangri and A. K. Suri, *Hydrometallurgy*, 2006, **81**, 1-8.

List of Figures

Fig. 1: Laboratory scale optimization and cross current simulation for recovery of metals and treatment of ITO etching industry wastewater.

Fig. 2: Volume reduction during downstream extraction process at all stages of extraction process.

Fig. 3: (a) Plot of log D versus equilibrium pH at 0.5 M Cyanex 272 (b) log D versus equilibrium log [Cyanex 272] at initial pH=0.7. Experimental conditions: ITO etching industry wastewater versus Cyanex 272, the O/A = 1.

Fig. 4: (a) Plot of log D versus equilibrium pH at 0.5 M DP-8R (b) log D versus equilibrium log [DP-8R] at initial pH=0.7. Experimental conditions: ITO etching industry wastewater versus Cyanex 272, the O/A = 1.

Fig. 5: (a) Extraction of In at different concentration of DP-8R, (b) Scrubbing Mo and Sn by Cyanex 272, (c) Agreement of modeled distribution coefficient with experimental distribution coefficient. Experimental conditions: ITO etching industry wastewater versus extractant, the O/A = 1.

Fig. 6: Loading behavior of In at different volume ratio of DP-8R from Mo and Sn free ITO industry etching wastewater. Experimental conditions: ITO etching industry wastewater at pH=0.7, DP-8R concentration = 0.5 M.

Fig. 7 : (a) Model equation fitting for In loading behavior, (b) McCabe-Thiele extraction isotherm for of In from Mo and Sn free ITO etching industry wastewater. Experimental condition: pH of solution 0.7 and DP-8R concentration 0.5 M.

Fig. 8 : (a) Model equation fitting for Mo, Sn and their mixture loading behavior, (b) McCabe-Thiele scrubbing isotherm for Mo, (c) Mix metal McCabe-Thiele scrubbing isotherm for Mo and Sn mixture. Experimental condition: pH of solution 0.7 and DP-8R concentration 0.5 M.

Fig. 9: Scale up verification and pilot plant cross current simulation for recovery of metals and treatment of ITO etching industry wastewater. Scale up simulation drawn by HSC Chemistry[®] 7.1, Outotec research software, Finland.

List of Tables

Table 1: Composition of ITO etching wastewater for lab scale and pilot scale investigation

Table 2: Estimated model parameters and goodness of fit for In, Mo, Sn, and Mo+Sn mixture

Table 3: Stripping behavior of Sn and Mo from the loaded Cyanex 272

Table 4: Composition analysis of metal content at each stage of extraction as explained in Figure 9

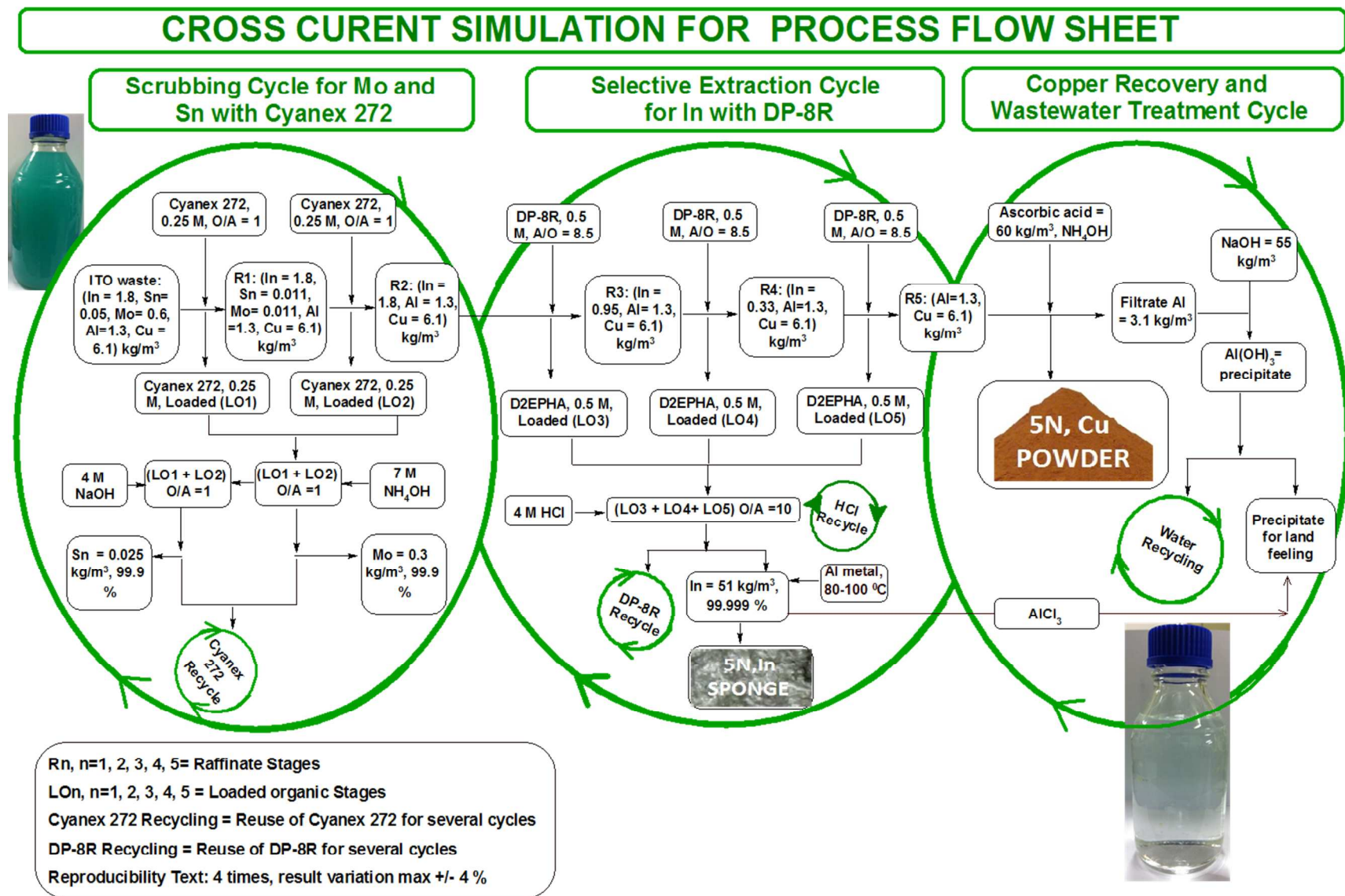
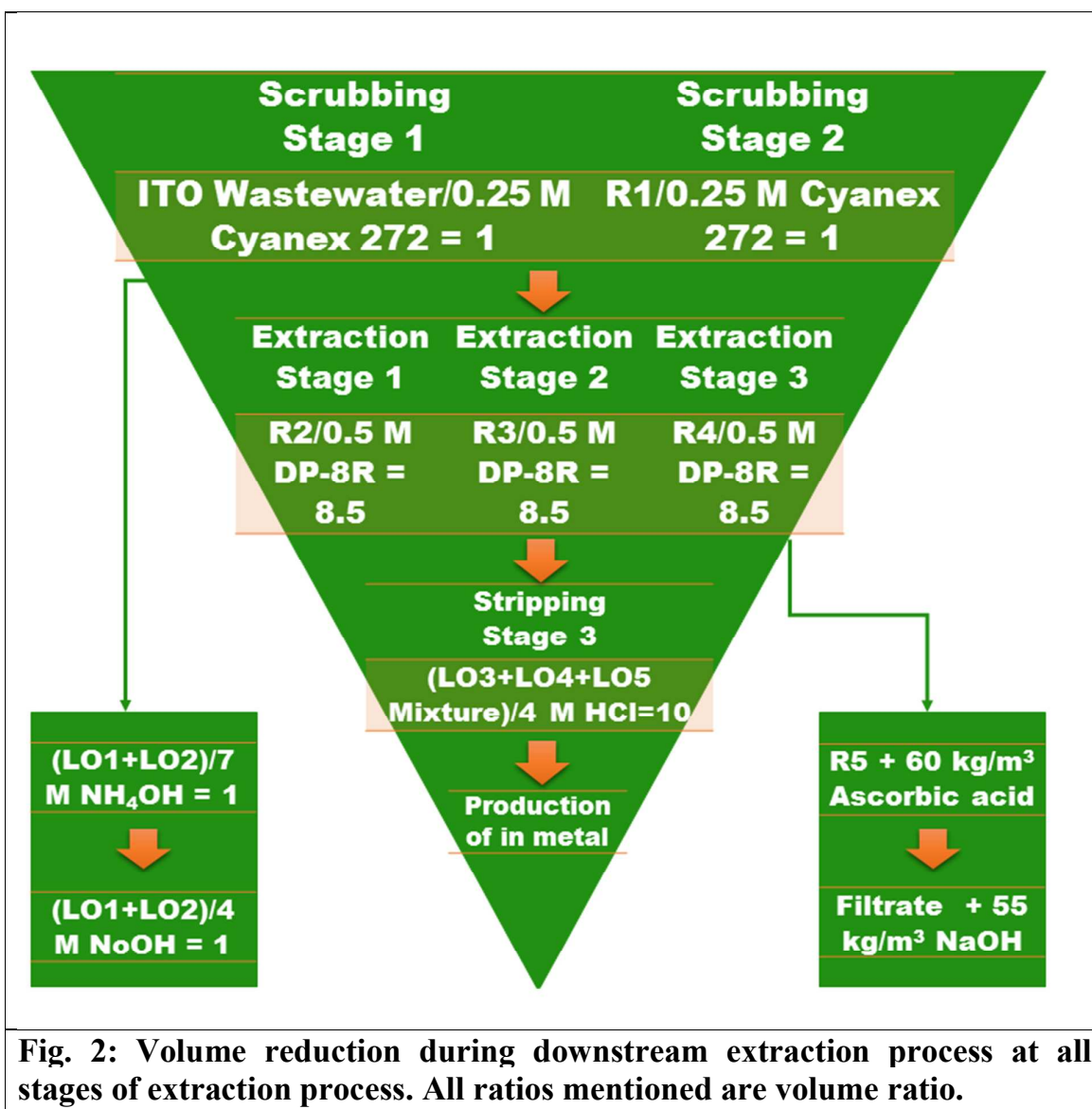
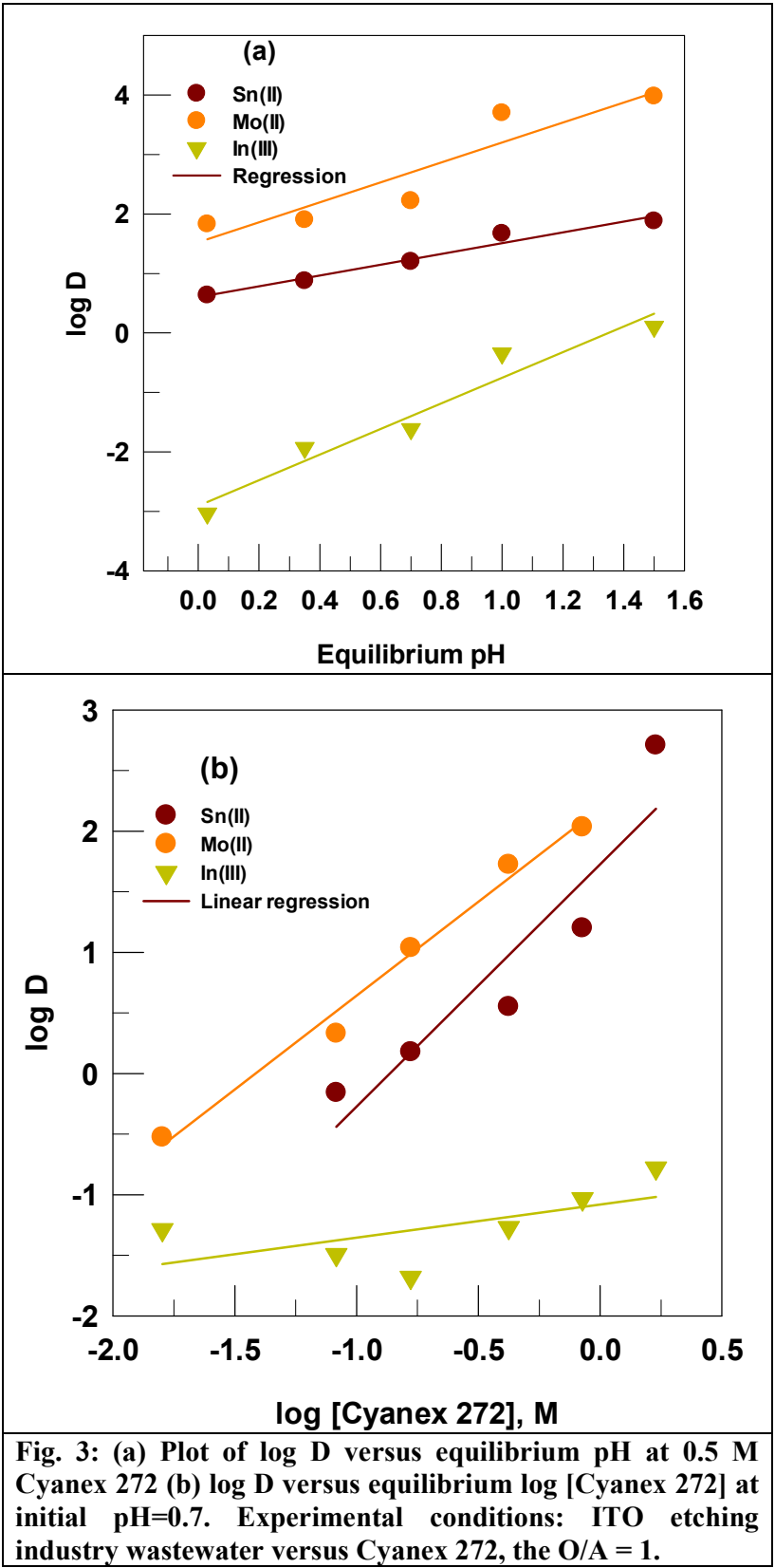


Fig. 1: Laboratory scale optimization and cross current simulation for recovery of metals and treatment of ITO etching industry wastewater.





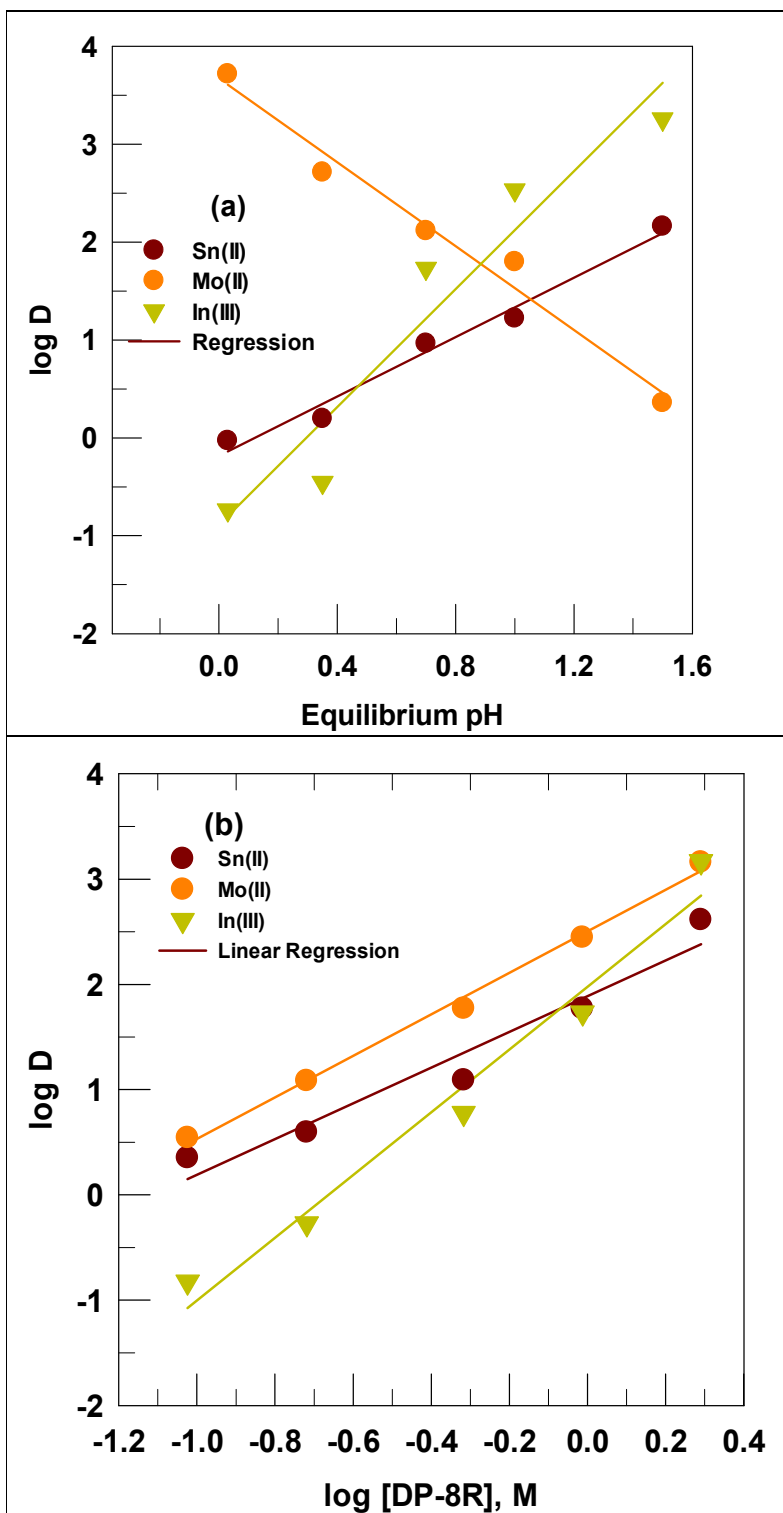
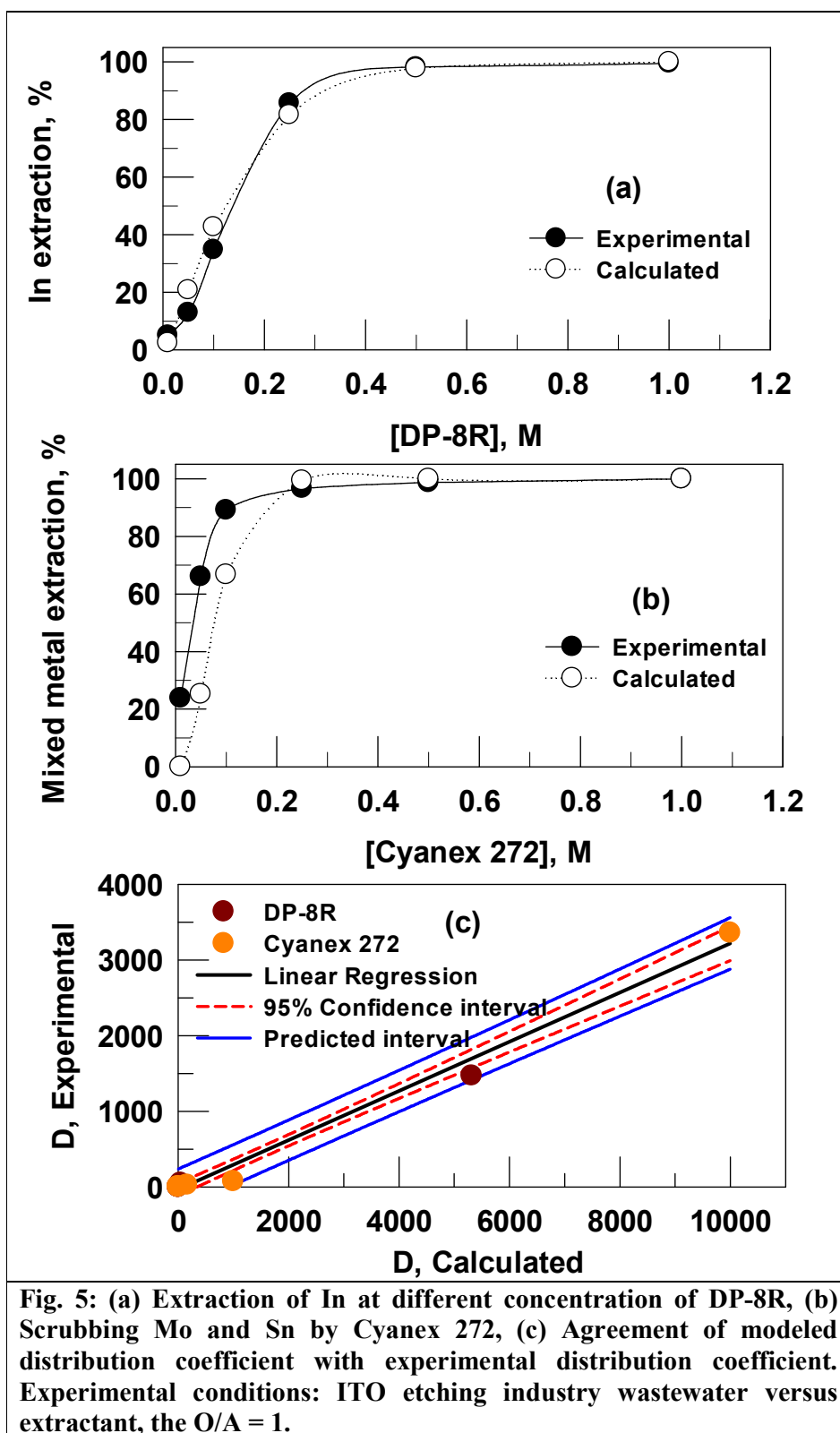
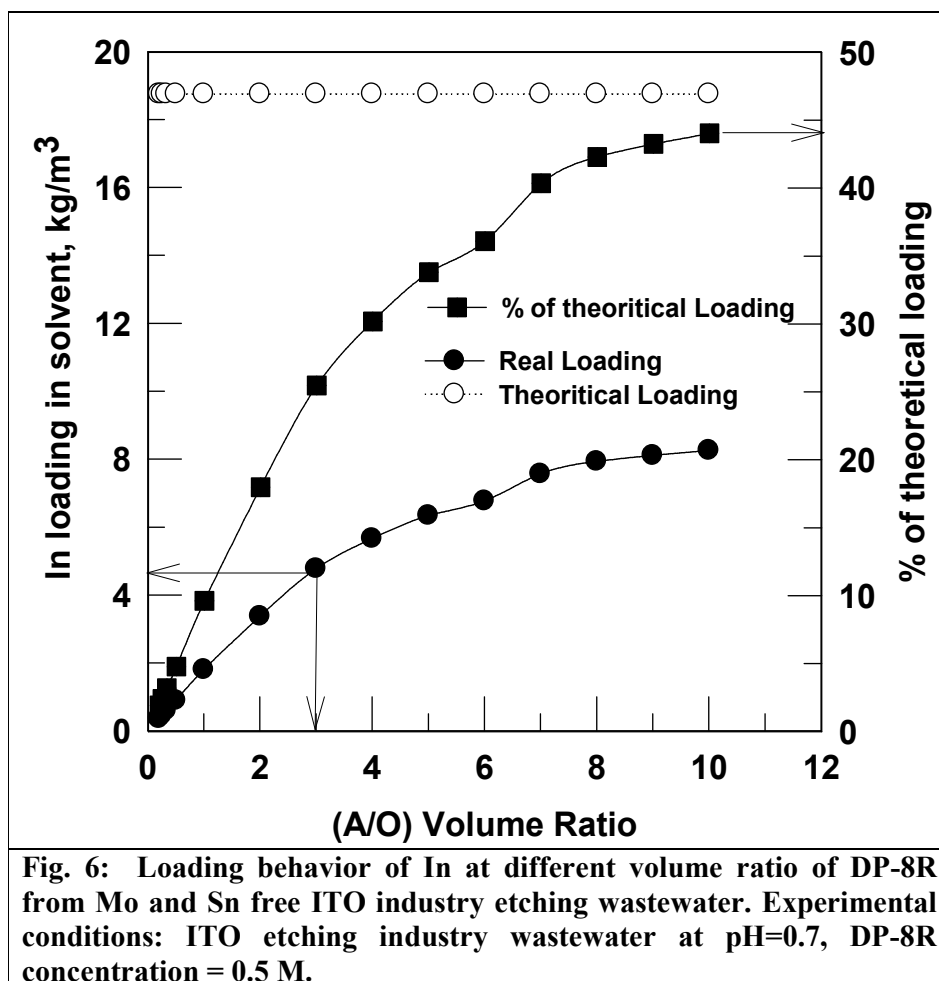
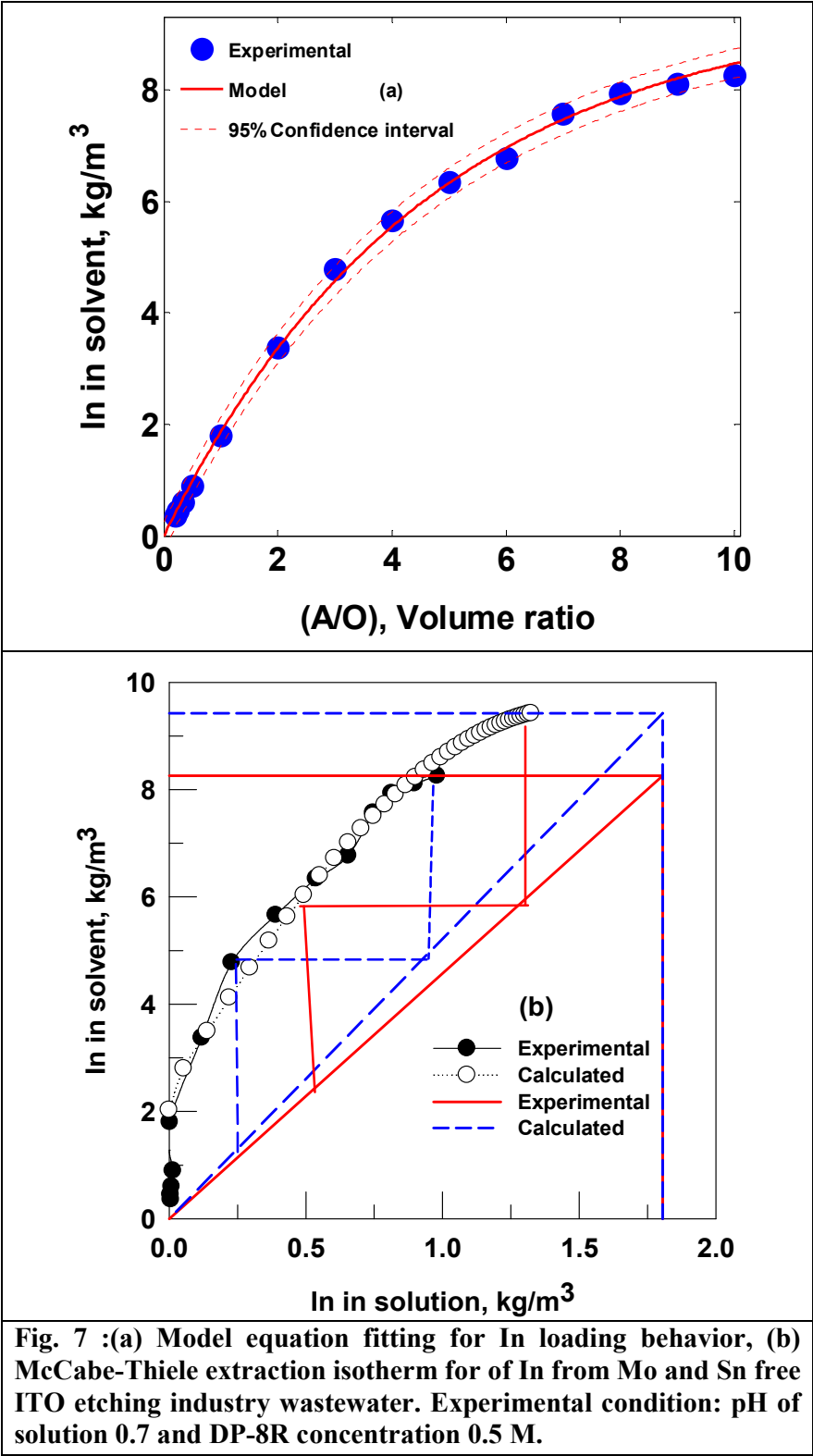


Fig. 4: (a) Plot of $\log D$ versus equilibrium pH at 0.5 M DP-8R (b) $\log D$ versus equilibrium $\log [\text{DP-8R}]$ at initial pH=0.7. Experimental conditions: ITO etching industry wastewater versus DP-8R, the O/A = 1.







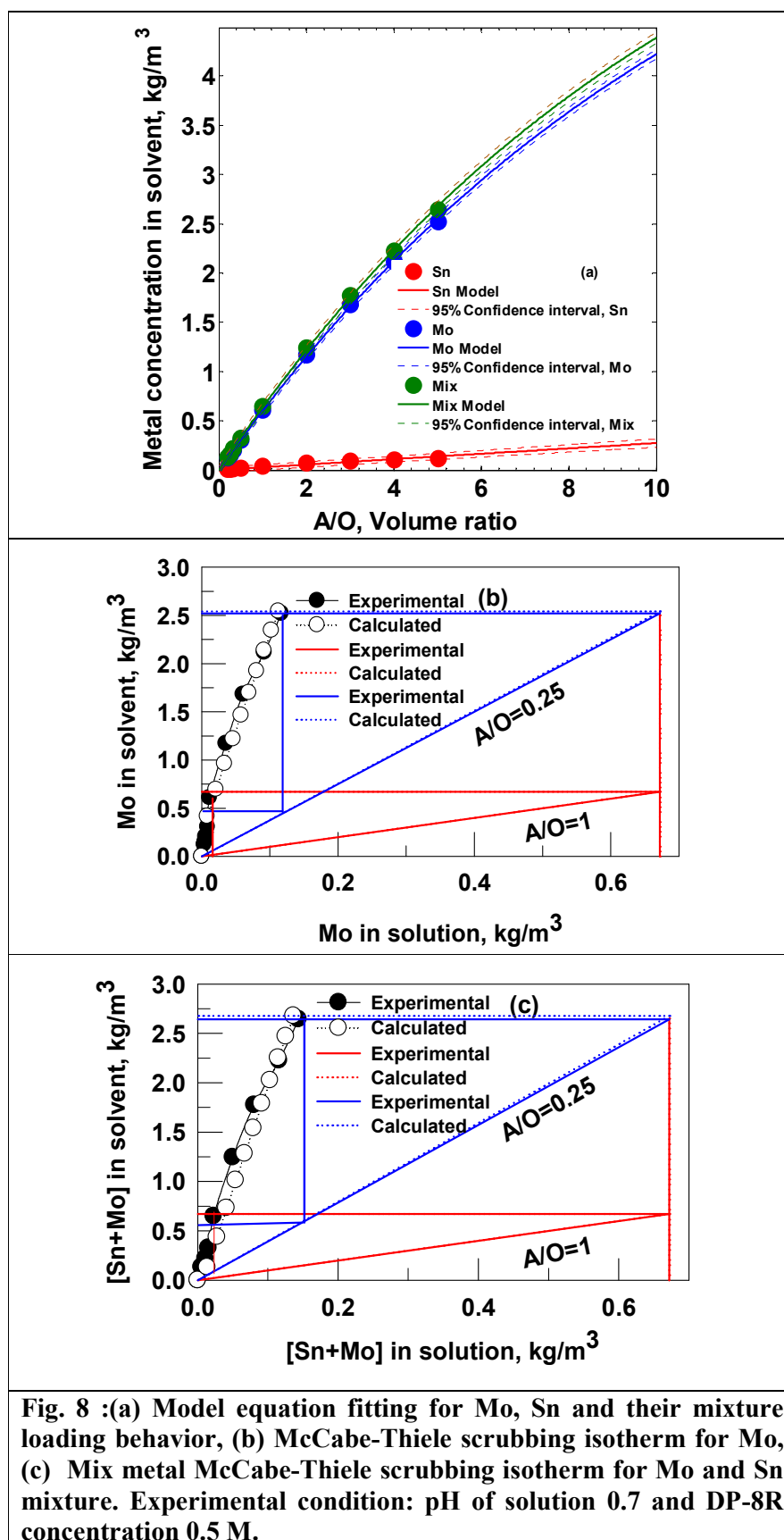




Table 1: Composition of ITO etching wastewater for lab scale and pilot scale investigation

Metal, kg/m ³	Lab scale composition	Scale up (pilot scale) composition
Al	1.353	1.003
Cu	6.113	0.385
In	1.805	3.999
Mo	0.621	0.468
Sn	0.051	0.044

Table 2: Estimated model parameters and goodness of fit for In, Mo, Sn, and Mo+Sn mixture

Metal	k	Goodness of fit			
		SSE	R-square	Adjusted R-square	RMSE
In	0.22±0.006	0.178	0.998	0.998	0.118
Sn	0.004±0.0004	0.001	0.9364	0.9364	0.011
Mo	0.084±0.001	0.002	0.999	0.999	0.016
Mo and Sn Mix	0.089 ±0.001	0.003	0.999	0.999	0.019

Table 3: Stripping behavior of Sn and Mo from the loaded Cyanex 272

[NH₄OH], M	LO/ NH₄OH	Mo, %	[NaOH], M	LO/ NaOH	Sn, %
0.5	1	1.41	0.5	1	12.03
1	1	57.68	1	1	46.68
2	1	69.05	2	1	86.07
4	1	95.72	4	1	95.65
7	1	99.13	5	1	97.78

*LO=loaded organic= Mo and Sn loaded Cyanex 272

Experimental conditions: wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, loaded from 0.25 M Cyanex 272 at organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

Table 4: Composition analysis of metal content at each stage of extraction as explained in Figure 9

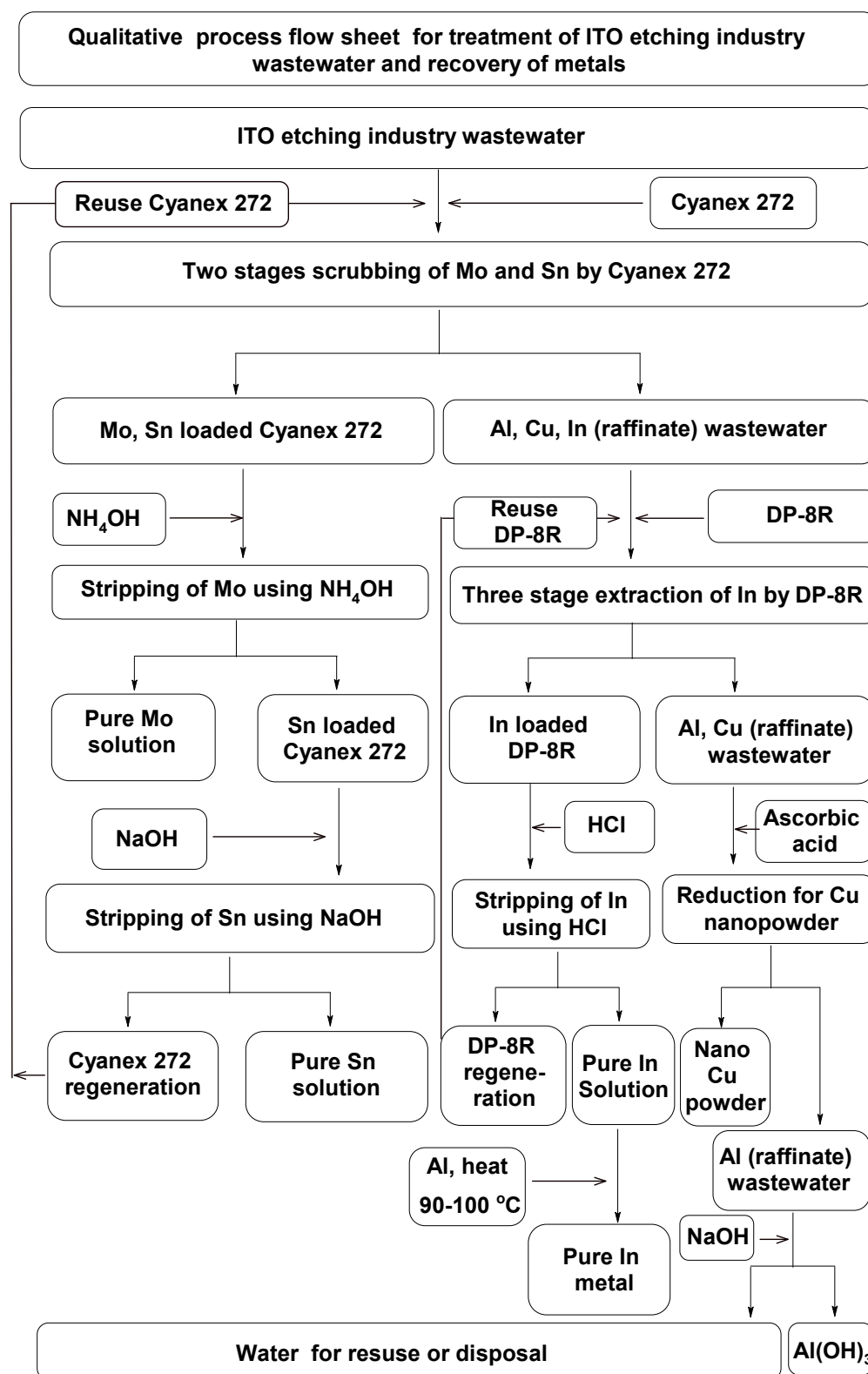
Metal	Etching wastewater		Raffinate (1)		Raffinate (2)		Raffinate (3)		Raffinate (4)		Raffinate (5)	
	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)
Al	1.003	0.05	1.003	0.05	1.003	0.05	1.003	0.05	1.003	0.05	1.003	0.05
Cu	0.385	0.05	0.385	0.05	0.385	0.05	0.385	0.05	0.385	0.05	0.385	0.05
In	3.999	0.05	3.999	0.05	3.999	0.05	2.023	0.05	0.440	0.05	ND	0.05
Mo	0.468	0.05	0.009	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05
Sn	0.044	0.05	0.004	0.05	ND	0.05	ND	0.05	ND	0.05	ND	0.05
	Loaded Cyanex 272 (1)		Loaded Cyanex 272 (2)		Loaded DP-8R (1)		Loaded DP-8R (2)		Loaded DP-8R (3)			
	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)
Al	-	0.05	-	0.05	-	0.006	-	0.006	-	0.006	-	0.006
Cu	-	0.05	-	0.05	-	0.006	-	0.006	-	0.006	-	0.006
In	-	0.05	-	0.05	16.466	0.006	13.192	0.006	3.666	0.006	-	0.006
Mo	0.467	0.05	0.009	0.05	-	0.006	-	0.006	-	0.006	-	0.006
Sn	0.040	0.05	0.004	0.05	-	0.006	-	0.006	-	0.006	-	0.006
Loaded (Cyanex 272 (1)+ Cyanex 272 (1))= 0.1 m ³						Loaded DP-8R (1)+ Loaded DP-8R (2)+ Loaded DP-8R (3)= 0.018 m ³						
	Mo Stripping		Sn Stripping						In Stripping			
	Metal, kg/m ³	Volume, (m ³)	Metal, kg/m ³	Volume, (m ³)					Metal, kg/m ³	Volume, (m ³)		
Al	-	0.1	-	0.1					-	0.0018		
Cu	-	0.1	-	0.1					-	0.0018		
In	-	0.1	-	0.1					111.06	0.0018		
Mo	0.233	0.1	-	0.1					-	0.0018		
Sn	-	0.1	0.021	0.1					-	0.0018		

*ND=Not Detected, ** Discrepancies in mass balance observed marked in color font, these discrepancies associated with analytical values followed by further rounding to significant digits.

Supplementary Figures



Supplementary Fig. 1: Pilot plant view of batch process ITO etching industry wastewater treatment plant: (a) and (c) view of plant, (b) transparent window to watch liquid-liquid separation, and (d) inside view of the baffle mixture reactor.



Supplementary Fig.2: Qualitative process flow sheet for treatment of indium-tin-oxide (ITO) etching wastewater and total recovery of metal values.

Commercial process for recovery of metals from ITO etching industry wastewater by liquid-liquid extraction: simulation, analysis of mechanism, and mathematical model to predict optimum operational conditions

Basudev Swain*, Chinmayee Mishra, Hyun-Seon Hong, Sung-Soo Cho, Sungkyu Lee

Graphical Abstract

