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# Treatment of Indium-Tin-Oxide etching wastewater and recovery of In, Mo, Sn and Cu by liquid-liquid extraction and wet chemical reduction: A laboratory scale sustainable commercial green process

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**Abstract:** A laboratory scale sustainable commercial green process for treatment of indium-tin-oxide (ITO) etching wastewater and total recovery of In, Mo, Sn and Cu by combination liquid-liquid extraction and wet chemical reduction has been developed. The ITO etching wastewater is a threat to the ecosystem and human health, containing significant amounts of valuable metals like In and Cu. In metal and 100nm Cu nanopowder with 5N purity has been recovered. The developed process concurrently treats the ITO etching wastewater and recovers pure metals. By the process, Mo and Sn are recovered by liquid-liquid extraction, In is recovered through liquid-liquid extraction followed by wet chemical reduction. Value added semiconductor industry grade Cu nanopowder is recovered through wet chemical reduction using ascorbic acid. After a series of treatment, the wastewater is free of pollutant, worthy to use in the same industry or disposed. The process is a sustainable, green, versatile and flexible process.

[In(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> while tin forms a [SnCl<sub>6</sub>]<sup>2-</sup> complex. In the ITO etching process, unlike the typical electroplating process, the etching wastewater bath must be disposed of after certain number turnovers, as the etching solution degrades because of foreign element that pollute the process after several turnovers.

The ITO etching wastewater containing significant amounts of industrially valuable metals like In and Cu, is an important secondary resource. As typical ITO etching wastewater bath contains several kg/m<sup>3</sup> of Mo, Cu, Al, Sn and In (pollutant metals), disposal of these wastes without treatment can be a potential health hazard to the human and a threat to the ecosystem<sup>5-13</sup>. Cancer risks for humans from exposure to the semiconductor metals have been reported by Fowler et al.<sup>5</sup>. Chonan et al. and Nogami et. al have reported interstitial pulmonary disorders is associated with ITO waste<sup>6, 7</sup>. Mo does have physiological effects and can affect the balance of other trace elements in animal physiology. The harmful effects of exposure to Mo compounds will be most apparent in the bones, liver and kidneys<sup>8, 10</sup>. Environment concern of Cu includes Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and Cu deposition in the cornea<sup>9</sup>. The uptake of Sn is associated with several

## 1. Introduction

Indium-tin-oxide (ITO), due to its optical transparency, electrical conductivity, and ease of deposition in the form of thin films is being extensively used in numerous industrial applications<sup>1-3</sup>. Some of the most common applications of ITO includes field emission displays, electroluminescent displays, electrochromic displays, touch panels, windshields, photovoltaics, optoelectronics, heat reflective coatings, gas sensors, energy efficient windows, and solar cells<sup>4</sup>. ITO films are best prepared by first depositing a film of indium-tin. The indium-tin film is then oxidized in an oxygen plasma or at elevated temperatures in an oxygenating atmosphere. When etched, using customized etching solution, In is soluble as a trivalent hexa-aquo-complex

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long term effects such as, depressions, liver damage, malfunctioning of immune systems, chromosomal damage, shortage of red blood cells and brain damage (causing anger, sleep disorders, forgetfulness and headaches)<sup>12</sup>. Al is also a neurotoxic, able to cause a brain disorder (encephalopathy)<sup>13</sup>. In also a potential health hazards can damage the lungs, liver, kidney and even can damage developing foetus<sup>11</sup>.

ITO is transparent and conducting, widely used as transparent conductive oxide because of its excellent physical properties and chemical properties. According to the latest market report by BCC Research, 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 2018<sup>14</sup>. The ITO accounted for approximately 97% of the overall market for transparent conducting oxides in 2011. The steady growth of transparent and flexible electronics is the major factor, which is propelling the growth of the global ITO market. Worldwide total supply of In was approximately 1200 tons for the year 2010, which includes 570 tons of primary In production and the rest was from secondary resources<sup>15</sup>. Charles et al. forecasted 15% annual growth rate for In demand over the next two years<sup>15</sup>. According to a United States Geological Survey (USGS) report, worldwide total primary production reported at 770 tons in the year 2013<sup>16</sup>. These reports indicate that, In is at critical risk of supply chain. Both the massive demand and use mean massive waste generation during production and massive end-of-life (EOL) waste generation. Hence, the treatment of this etching wastewater generated during the manufacturing process or EOL waste, through recycling is a feasible option. Simultaneously, from this wastewater, recovered metal values (In, Cu, Mo and Sn) can flow into the material flow stream and close the loop.

Several authors have reported In recovery from various waste resources, i.e., ITO-scrap<sup>17-19</sup>, EOL liquid crystal displays<sup>20</sup> and etching waste<sup>21, 22</sup> are the prospective secondary resources for In. Hasegawa et al. reported selective recovery of In from the etching waste solution of the flat-panel display, mostly their research focused on the recovery of In using ion-exchange resin<sup>23</sup>. 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 industry<sup>21</sup>. Liu et al. studied recovery of In from etching wastewater using supercritical carbon dioxide

extraction<sup>22</sup>. Most of the reported research focused on recovery of In from these waste resources. The total recycling process for ITO etching wastewater, recovery of all valuable metals along with removal of all the polluting metals using non-toxic commercial extractant has never been reported. This investigation focused on the development of a commercial process for treatment of ITO etching industry wastewater followed by recovery of metal values using commercially available non-hazardous chemicals. In our current study, Mo and Sn recovered from ITO etching wastewater through scrubbing, using Cyanex 272, followed by sequential selective stripping using NH<sub>4</sub>OH and NaOH, respectively. After scrubbing, In was recovered through liquid-liquid extraction using DP-8R and recovered by wet chemical reduction. Followed by the value added Cu nanopowder has been recovered by direct wet chemical reduction using nontoxic and biocompatible organic acid, i.e. ascorbic acid. Finally, Al has been removed through precipitation. Eventually, the metal content in wastewater is within the permissible limit as recommended by world health organization (WHO). The novelties of the developed process are listed below.

- (i) This paper addresses the gap between research on metal value recovery and wastewater treatment process, commercially applicable process development and fundamental research.
- (ii) Most of the recovery processes reported in the open literature is about a gram to sub-gram metal recovery process, but the developed process offers versatile and flexible approach for mass production capability up to kilogram scale.
- (iii) The developed proposed flow sheet is a clean, green and a techno-economical feasible process for commercial treatment of several tons (m<sup>3</sup>) etching wastewater per day.
- (iv) The proposed process could completely recover the In with 99.999 % (5N) purity, quantitatively recover Mo and Sn with at least 99 % purity and value added Cu nanopowder with 99.999 % (5N) purity.
- (v) Wastewater after treatment is heavy metal free and can be disposed or reused in the same ITO etching process.
- (vi) Regeneration and reuse of all the organic extractant, use of non-hazardous inexpensive chemical in the process, and recovery of industrially valuable metals eventually, make the process an economical clean and green process.

## 2. Materials and Method

## 2.1. Materials

TSM Co. Ltd., the Republic of Korea, supplied the In rich wastewater from ITO etching. The commercial extractant, Bis (2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) was supplied by Cytec Korea Inc., and the commercial acidic extractant Bis (2-ethylhexyl) phosphoric acid (DP-8R) was obtained from Daihachi (Japan), were used without further purification. Commercial extractant Tri-octyl-methyl-ammonium chloride (Aliquat 336) was supplied by Cognis Co., USA, and was used without further purification. The low boiling point kerosene (180-270 °C) was used as diluent. Other chemicals like NaOH, HCl, and NH<sub>4</sub>OH were of analytical grade supplied by Daejung chemical and metal Co, Ltd, the Republic of Korea.

## 2.2. Liquid-Liquid Extraction Procedure

The commercial extractant Cyanex 272, DP-8R, and Aliquat 336 were diluted using kerosene. The requisite pH of the ITO etching wastewater was adjusted by addition of NaOH or HCl solution. Liquid-liquid extraction experiments were carried out using suitable volumes of ITO etching wastewater and extractant solutions. The ITO etching wastewater was equilibrated with organic extractant for 10 minutes, and then the phases were separated through settling by separating funnel. The aqueous raffinate phase was analysed to determine the amount of metal extracted into the organic phase using the extractant. Metal concentration in the organic phase was calculated through mass balance calculation. The time of 10 minutes was found sufficient to attain the equilibrium, which was verified in preliminary tests. The preliminary tests suggested 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 an ambient temperature (25±1°C). Throughout the study, organic phase/aqueous phase volume ratio (O/A) kept constant at one, unless otherwise mentioned. The same batch of ITO etching wastewater was used in each set of experiment, but the raffinate from the first stage of extraction was used as the aqueous feed in the second stage or subsequent stages for liquid-liquid extraction.

## 2.3. Wet Chemical Reduction Methods

In a typical recovery of Cu nanopowder powder, 500 ml of In, Sn and Mo free of ITO etching wastewater containing Cu and Al was stirred using a magnetic

stirrer for requisite periods (30 minutes). The pH of wastewater was monitored and adjusted using NH<sub>4</sub>OH to reach pH (5.00) and ascorbic acid was added as a reductant at stirring condition. Ascorbic acid was used for both wet chemical reduction and dispersion stabilization to control the size of Cu nanopowder. After synthesis completed, the Cu powders were isolated through washing several times with deionized (DI) water. Then by the isolated Cu nanopowders were vacuum dried at 60 °C and stored under nitrogen environment using a glove box.

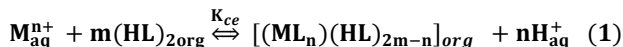
## 2.4. Analytical Procedures

The concentration of metals in the ITO etching wastewater, raffinate and stripped solution was determined using ICP-AES (OPTIMA 4300DV, Perkin-Elmer, USA) after suitable dilution using 5 vol. % of HCl. The instrument parameters were used are those recommended by the manufacturer. The wavelength (nm) selected for the determination of metal concentration were as follows: In (230.606), Sn (189.927), Al (308.222), Cu (324.752), and Mo (202.033). The working linear range for In, Cu and Al was 1.00–25.00 mg/L, and the working linear range for Mo and Sn were 1-10 mg/L. Instrument calibrations were done through 4 point calibration method, where standard first order linear regression calibration line passes through the origin. The R<sup>2</sup> values for linear regression calibration were 0.999 for all the elements. The concentration of each sample was measured thrice and was averaged through ICP-AES machine in-built command. The maximum deviations permitted were about ± 3 % in ICP-AES analysis. The metal concentrations in the organic phases were determined by the mass balance calculation. To minimize the analytical errors associated with the concentrations of metal was estimated by statistical methods (Dixon's Q test, considering its limitation). Synthesized Cu nanopowders were identified and characterized by X-ray diffraction diffractometer (XRD), (Philips Expert PRO MPD) at a scanning rate of 2° min<sup>-1</sup> with 2θ ranging from 10° to 90°, using Cu Kα radiation (λ = 1.5406Å). The XRD peaks were analysed using the Joint Committee on Powder Diffraction Standards (JCPDS) database. Morphologies of the samples were analysed by field emission scanning electron microscopy FE-SEM (S-4700) (JEOL SM5600LV) at 20 kV.



### 3. Theory

The acidic form of Cyanex 272 and DP-8R exists as a dimer at acid equilibrium conditions<sup>24-27</sup>. The cation exchange mechanism of extraction can be represented as follows<sup>28, 29</sup>.



where the subscripts *aq* and *org* denote species in the aqueous and organic phases, respectively. HL stands for either Cyanex 272 or DP-8R, depending upon cases.

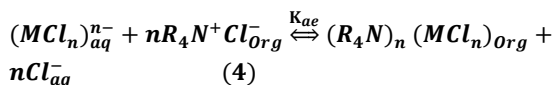
The equilibrium constant for the cation exchange reaction,  $K_{ce}$ , can be written as:

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

$$K_{ce} = \frac{D[H^+]_{aq}^n}{[(HL)_2]_{org}^m} \quad (3)$$

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

The anion exchange mechanism through which a metal ion is extracted from an aqueous chloride solution using Aliquat 336 as follows<sup>30, 31</sup>:



The equilibrium constant for anion exchange reaction ( $K_{ae}$ ) of the extraction reaction [Eq. (4)] can be presented as:

$$K_{ae} = \frac{[(R_4N)_n(MCl_n)_{org}][Cl_{aq}^-]^n}{[(MCl_n)^{n-}]_{aq}[R_4N^+Cl^-]_{org}^n} \quad (5)$$

$$K_{ae} = \frac{D[Cl_{aq}^-]^n}{[R_4N^+Cl^-]_{org}^n} \quad (6)$$

where, the distribution coefficient,

$$D = \frac{[(R_4N)_n(MCl_n)_{org}]}{[(MCl_n)^{n-}]_{aq}} \quad (7)$$

The % metal extraction (E), and the separation factor ( $\beta$ ) were calculated using the equations as explained in our earlier published paper 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<sup>32</sup>

### 4. Results and Discussion

A laboratory scale sustainable green process for treatment of ITO etching wastewater through recovery of In, Mo, and Sn by liquid-liquid extraction and recovery Cu nanopowder through wet chemical reduction has been developed. Various stages involved in the total laboratory scale sustainable commercial green process development are presented in ESI Figure 1†. For the process development following stages are followed: (i) Characterization of ITO etching wastewater and possible speciation analysis through Pourbaix diagrams, (ii) purifications of metal through a selection of extractants for selective extraction and selection of stripping reagent for selective stripping, (iii) optimization of purification process, (iv) metal recovery and remediation of residual metal, and (v) process simulation.

#### 4.1. Characterization ITO Etching Wastewater

The In rich ITO etching wastewater was characterized by the classical qualitative analytical method to understand the anionic content, only chloride medium was confirmed. Metal concentrations of ITO etching wastewater were analysed by ICP-AES. The metal concentrations in the ITO etching wastewater were also analysed both by the standard addition method and calibration curve method. ESI Table 1† shows comparison of metal concentrations those are analysed by both the mentioned methods. As both of these methods provided very similar result, for subsequent studies the metal concentrations in the raffinate were analysed by ICP-AES after suitable dilution. The ITO etching wastewater contains 6.113, 1.806, 0.052, 0.621, and 1.353 kg/m<sup>3</sup> Cu, In, Sn, Mo, and Al, respectively. The pH of the wastewater was 0.7 and was a strong acidic buffer, hardly allows metals to be precipitated. The ITO etching solution is a legally protected custom-made solution, not allow us to go for further investigation. The ITO etching wastewater is highly acidic, having a high chloride concentration along with 9.945 kg/m<sup>3</sup> of various metals. The ITO etching wastewater is a threat to the ecosystem and human health, containing significant amounts of valuable metals like In and Cu. This wastewater needs a treatment, as it poses dangers to aquatic environments

if it is disposed or pollute the soil if it is handled through the waste pond or chemical pond. As In is a valuable metal presence in the wastewater, treatment of wastewater through In recovery should be economical and feasible option. Metal separation, purification and recovery process through liquid-liquid extraction is a vital, versatile and flexible industrial process has been applied for the treatment of wastewater from ITO etching industry.

system where In considered as main element along with Sn (b) Cu-In-Al-Cl-Mo-Sn-H<sub>2</sub>O system where Cu consider as main element along with Mo and Al, were drawn. To avoid the complexity of the Pourbaix diagram it is divided into two parts. (a) In-Al-Cl-Cu-Mo-Sn-H<sub>2</sub>O system for all possible ionic species in chloride media for In and Sn, as an ITO etching solution prior to etching process contains only In and Sn, (b) Cu-In-Al-Cl-Mo-Sn-H<sub>2</sub>O system for all possible ionic species in chloride media for Cu, Mo and Al, as the ITO etching solution accumulates these metal impurities during the etching process. The Pourbaix diagrams were constructed by 7.1 by HSC Chemistry<sup>®</sup> 7.1, Outotec research software, Finland. Considering pH and acidic buffer nature of the ITO etching wastewater, from Figure 1 reasonably concluded that, the metals in the ITO etching wastewater presence in the following states, viz., Al<sup>3+</sup>, Cu<sup>2+</sup>, In<sup>3+</sup>, Mo<sup>2+</sup>, and Sn<sup>2+</sup>. Figure 1 also shows that, all the metals in the ITO etching wastewater are quite stable at higher acidity; hence, reasonably liquid-liquid extraction should be the most versatile technique for recovery of these high pure industrially important metals.

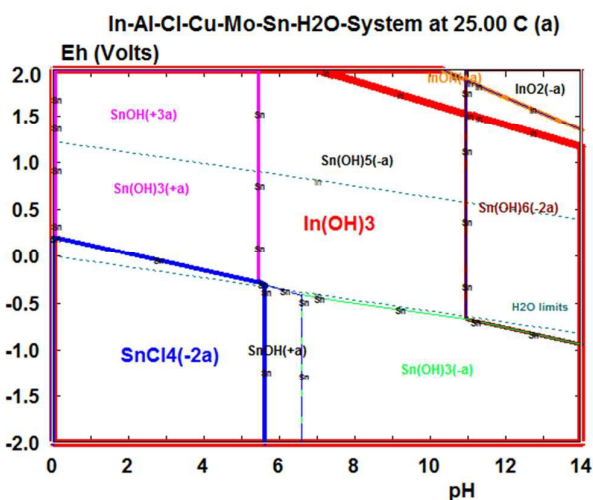
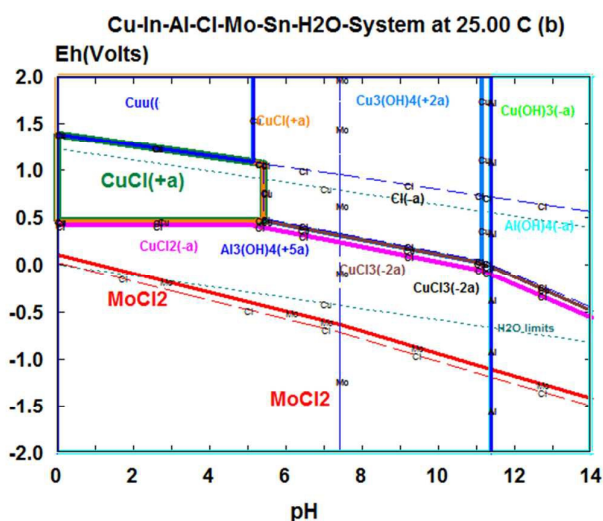


Figure 1: Pourbaix diagrams for (a) In-Al-Cl-Cu-Mo-Sn-H<sub>2</sub>O system where In is considered as main element along with Sn (b) Cu-In-Al-Cl-Mo-Sn-H<sub>2</sub>O system where Cu is considered as main element with Al and Mo.

Figure 1 shows thermodynamic possibility for the presence of different metal ion species, which has been analysed through Pourbaix diagram. Two different Pourbaix diagrams, i.e., (a) In-Al-Cl-Cu-Mo-Sn-H<sub>2</sub>O

## 4.2. Selection of Extractant and Stripping Agent

### 4.2.1. Effect of pH and Selection of Extractant

Three different commercial extractants like; Cyanex 272, DP-8R and Aliquat 336 of 500 mol/m<sup>3</sup> each were selected for the selective extraction or complete removal of metals from ITO etching wastewater. Selectivity of extractants was scanned through pH variation of ITO etching wastewater. Figure 2 shows the percentage of metal extraction as a function of equilibrium pH of ITO etching wastewater. The pH of the wastewater was varied only from zero through 1.5 as beyond that pH, the metal start to colloid formation. After equilibration and phase separation, the equilibrium pH of aqueous phases was measured. Figure 2(a), (b) and (c) depict the extraction behaviour of these three extractants; Cyanex 272, DP-8R and Aliquat 336, respectively. Figure 2(a) shows at all pHs the Mo and Sn extraction is quite efficient, % of Mo extraction was varied from 94.64% to 99.99% and the percentage of Sn extraction was varied from 87.20% to 94.81%. There was no In, Cu and Al extraction from 0 to pH 0.7, even between pH 0.7 to 1.5 the Al and Cu were sparingly co-extracted. The metal co-extraction may be because of the only van der Waals forces of interaction between extractant and metal. As the pH of the wastewater increased from 0-1.5, the In extraction efficiency varied

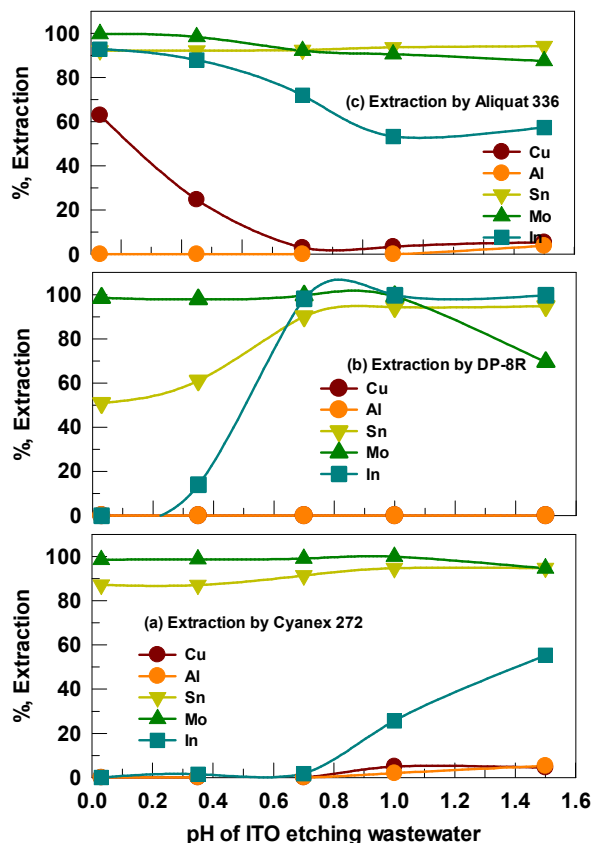


Figure 2: Effect of pH on extraction efficiency and selectivity of extractant for separation of metals. Experimental conditions: extractant concentration  $500 \text{ mol/m}^3$ , organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

from 1.48% to 55.30%. The Figure 2(a) indicates that between 0-0.7 pH, the metals in wastewater can be separated into two different groups, i.e., efficiently extracted Mo and Sn, non-extracted Al, In and Cu. Between pH 0.7-1.5, the metals in wastewater can be separated as three different groups, i.e., efficiently extracted Mo and Sn, non-extracted Al, and Cu, and moderately extracted In.

Figure 2(b), shows that as the pH of wastewater was increased from zero to 1.5, the Sn and In extraction efficiencies was varied from 50.99 to 94.83%, and 0 to 99.77%, respectively, whereas Mo extraction efficiency decreased from 98.55 to 69.49%. There was no extraction at all for Cu and Al. The Figure 2 (b) indicates that the metals from wastewater can be separated as two groups, but complete, selective and sequential extraction of individual metal is impossible. Figure 2(c),

shows that as the pH of wastewater was increased from zero to 1.5 the Cu and In extraction efficiencies decreased from 62.93 to 3.00 %, and 92.88 to 63.30%, respectively and the Mo extraction efficiency was decreased from 99.72 to 87.45%. There was no Al extraction at all. The Figure 2 (c) indicates that the metals from wastewater can be separated as three groups, again complete, selective and sequential extraction of individual metal is impossible.

Separation factors ( $\beta$ ) for Mo over Sn ( $\beta_{\text{Mo/Sn}}$ ), Sn over In ( $\beta_{\text{Sn/In}}$ ) and Mo over In ( $\beta_{\text{Mo/In}}$ ), or vice versa (depending upon a distribution coefficient, whichever appropriate) were calculated using the Equation 7 or 8 as explained in our published paper<sup>32</sup>. As Figure 2 indicated, Mo and Sn together can be separated as a group from In, separation factor of Mo and Sn mixed metals over In ( $\beta_{(\text{Mo+Sn})/\text{In}}$ ) was calculated using Equation 8 or 9 given below.

$$\beta_{(\text{Mo+Sn})/\text{In}} = \frac{D_{\text{Mo}} + D_{\text{Sn}}}{D_{\text{In}}} \quad (8)$$

Provided  $(D_{\text{Mo}} + D_{\text{Sn}}) > D_{\text{In}}$ , otherwise the Equation (9) was used for separation factor calculation.

$$\beta_{\text{In}/(\text{Mo+Sn})} = \frac{D_{\text{In}}}{D_{\text{Mo}} + D_{\text{Sn}}} \quad (9)$$

Table 1 shows the separation factor calculated for  $\beta_{\text{Mo/Sn}}$ ,  $\beta_{\text{Sn/In}}$  and  $\beta_{\text{Mo/In}}$ , or vice versa, with respect to equilibrium pH using different extractant. The table shows when  $500 \text{ mol/m}^3$  of Aliquat 336 or  $500 \text{ mol/m}^3$  of DP-8R were used as an extractant, no significant separation factor was observed either for individual metals or for mixed metals. Hence, separation of individual metal remains the challenge. The same table indicates that, when  $500 \text{ mol/m}^3$  of Cyanex 272 is used as an extractant, the separation factors for individual metal, i.e.  $\beta_{\text{Sn/In}}$  and  $\beta_{\text{Mo/In}}$  were significantly high. The mixed metal separation factor (separation factor for Mo+Sn over In) ( $\beta_{(\text{Mo+Sn})/\text{In}}$ ) using  $500 \text{ mol/m}^3$  of Cyanex 272 as an extractant is also significantly higher, indicates Cyanex 272 can be a better extractant to separate Mo+Sn from other metals in the ITO etching wastewater treatment. Though, Aliquat 336 is a cheaper solvent, can be applied industrially for metal separation process, but Aliquat 336 extraction process associated with the third phase formation and phase disengagement issue. The phase disengagement issues that can be aggravated in the scale up process and can add complicity for the assessment of a

sustainable process. Aliquat 336, associated with the third phase soap formation gets aggravated in the scale up process, which can add complicity for sustainable process. Hence, Aliquat 336 is not considered for the further studies. Figure 2, and Table 1, indicates if Mo, Sn and In could be selectively stripped after extraction, the combination of Cyanex 272 and DP-8R can address the separation and purification issues.

**Table 1: Effect of pH on extraction selectivity and separation factor of metals.**

500 mol/m <sup>3</sup> , Cyanex 272				
<sup>a</sup> Eq. pH	$\beta_{\text{Mo/Sn}}$	$\beta_{\text{Mo/In}}$	$\beta_{\text{Sn/In}}$	$\beta_{(\text{Mo+Sn/In})}$
0.03	9.93	73504.02	7399.88	80903.90
0.35	11.77	5284.57	449.12	5733.69
0.70	10.19	5847.22	574.09	6421.31
1.00	289.41	14974.89	51.74	15026.63
1.50	0.97	14.30	14.80	29.10
500 mol/m <sup>3</sup> , DP-8R				
<sup>a</sup> Eq. pH	$\beta_{\text{Mo/Sn}}$	$\beta_{\text{Mo/In}}$	$\beta_{\text{Sn/In}}$	$\beta_{(\text{Mo+Sn/In})}$
0.03	64.90	288.37	1131.06	74536.81
0.35	29.64	5.16	9.73	298.09
0.70	30.40	0.38	5.89	5.33
1.00	7.84	2.62	20.56	0.43
1.50	0.12	186.13	23.06	0.05
500 mol/m <sup>3</sup> , Aliquat 336				
<sup>a</sup> Eq. pH	$\beta_{\text{Mo/Sn}}$	$\beta_{\text{Mo/In}}$	$\beta_{\text{Sn/In}}$	$\beta_{(\text{Mo+Sn/In})}$
0.03	31.08	28.21	1.10	29.12
0.35	5.05	8.24	1.63	9.88
0.70	4.73	5.51	26.05	31.56
1.00	1.54	8.38	12.88	21.27
1.50	0.42	28.45	11.97	40.42

<sup>a</sup>Eq. pH = Equilibrium pH

Experimental conditions: extractant concentration 500 mol/m<sup>3</sup>, organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

#### 4.2.2. Selection of Stripping Reagent

As extractant selection studies show that individual metal purification is hardly an option, possibility for separation and purification of metals through selective stripping was investigated. Stripping behaviour of extracted metal by both DP-8R and Cyanex 272 were investigated using DI water, 4000 mol/m<sup>3</sup> HCl, 4000 mol/m<sup>3</sup> NaOH and 4000 mol/m<sup>3</sup> NH<sub>4</sub>OH. First, metals were extracted using 500 mol/m<sup>3</sup> Cyanex 272 from ITO itching wastewater directly without changing any acidity at an O/A volume ratio of 1. The loaded organic

generated were stripped using explained reagent and the results are given in Table 2. The metals were extracted from raffinate (raffinate after Mo, Sn scrubbing) using 500 mol/m<sup>3</sup> DP-8R and subsequently stripped with 4000 mol/m<sup>3</sup> HCl and DI water, and results are given in the same Table 2. The table shows NH<sub>4</sub>OH is an efficient stripping reagent for Mo, NaOH is an efficient stripping reagent for both Mo and Sn, and HCl is an excellent stripping reagent for In. The table also shows if Mo is stripped using NH<sub>4</sub>OH prior to Sn stripping using NaOH, the Mo and Sn can be separated efficiently.

**Table 2: stripping behaviour of metals using various stripping reagents.**

Stripping reagent	0.5 M Cyanex 272 loaded from ITO etching wastewater			0.5 M DP-8R loaded from raffinate after Mo, Sn scrubbing		
	[Strip], 4000 mol/m <sup>3</sup>			% Metal stripped		
	Sn	Mo	In	Sn	Mo	In
DI water	12.02	1.39	0.00	na	na	0.00
HCl	3.21	1.66	39.56	na	na	100.00
NaOH	100.00	66.55	100.00	ns	ns	ns
NH <sub>4</sub> OH	4.62	95.71	1.30	ns	ns	ns

na=not applicable, ns=not studied

From the simplicity of the extraction process and process handling perspective, Cyanex 272 and DP-8R were used as extractant as no third phase formation issue or phase disengagement issue was observed. Figure 2, Table 1 and Table 2, indicates that Mo and Sn together can be separated from ITO etching wastewater using Cyanex 272 as an extractant and subsequently Mo can be selectively stripped using NH<sub>4</sub>OH. Then, Sn can be separated through stripping using NaOH. After Mo and Sn recovery as In, Cu, and Al remain in the wastewater raffinate, the In can selectively be extracted using DP-8R and stripped using HCl for purification. Figure 2, Table 1, and Table 2, indicated that by suitable management of acidity in wastewater, the sequential combination of extractant, and the sequential combination of stripping, selective separation of targeted Mo, Sn, and In recovery is absolutely feasible. The ITO etching wastewater is a strongly buffered solution, which resists pH change, needed either very high amount of HCl or NaOH to change requisite pHs. Since, we are looking for sustainable, green, and environmentally friendly technology abstained from pre-



treating the solution prior to liquid-liquid extraction. The possibility of recovery of metal values without adding any chemical, has been investigated, hence, the pH of ITO etching wastewater kept unchanged for our further studies.

### 4.3. Optimization of Purification Process

#### 4.3.1. Effect of Extractant Concentration

Though  $\log D - \log[\text{extractant}]$  analysis has been presented in our earlier publication, but those abstract explanations are not enough to understand and predict the best extractant concentration required for efficient separation and purification<sup>32</sup>. Since, there is no direct explanation given for separation factor and extraction behaviour of other metals like Cu and Al, it is hard to imagine the competitive extraction behaviour of all these five metals, so also purity in the process. As a commercially sustainable green process development is the motto, for more efficient use of extractant, the extraction profile for all the metals at different extractant concentrations need to be well understood. Hence, optimization process for metal extraction with respect to extractant concentration has been presented below. The optimization for the extraction concentration was essentially carried out in terms of extractant concentration at an initial pH of 0.7. The O/A volume ratio was maintained at 1 for each set of studies. Figure 3 shows the effect of Cyanex 272 concentration on % of metal extraction and separation factor. Figure 3(a) shows as Cyanex 272 concentration was increased from 10-1000 mol/m<sup>3</sup>, Sn extraction efficiency was increased from 35.03% to 93.63%, simultaneously Mo extraction also increased from 22.94 % to 100%. Whereas, the In extraction was ranged only from 1.81% to 14.26%. Al and Cu have not extracted at all. Hence, Cyanex 272 has better selectivity towards Mo and Sn, has minimal affinity towards In. The Cyanex 272 rejects Al and Cu in the all ranges of Cyanex 272 concentration. By managing the Cyanex 272 concentration at constant pH of ITO etching wastewater, selectively Mo, and Sn can be scrubbed for the In purification. The same Mo and Sn scrubbing process can be used for the recovery of Mo and Sn. Figure 3(a) clearly indicates that Mo and Sn can be efficiently extracted from wastewater using Cyanex 272, their extraction efficiencies can be managed by changing Cyanex 272 concentrations. Figure 3(b) shows  $\beta_{\text{Mo/Sn}}$ ,  $\beta_{\text{Sn/In}}$ , and  $\beta_{\text{Mo/In}}$  as a function of Cyanex 272 concentration. The figure shows  $\beta_{\text{Mo/Sn}}$  varies from 0.5 to 20 with Cyanex 272 concentration, selective separation

of Mo and Sn during extraction is can hardly be an option. The same Figure 3(b) shows  $\beta_{\text{Sn/In}}$  and  $\beta_{\text{Mo/In}}$  increased from 10 to 573 and 6 to 5850, respectively, as Cyanex 272 concentration increased from 10-500 mol/m<sup>3</sup>, and then separation factor decreased. Significantly, higher  $\beta_{\text{Sn/In}}$  and  $\beta_{\text{Mo/In}}$ , indicates that In and Mo and/or Sn can be separated easily. The Figure 3(b) indicates the  $\beta_{(\text{Mo+Sn})/\text{In}}$  was increased from 16.29 to 6421.77 as Cyanex 272 concentration increased from 10-500 mol/m<sup>3</sup>, then decreased to 1907.58. The high magnitude  $\beta_{(\text{Mo+Sn})/\text{In}}$  at 500 mol/m<sup>3</sup> indicates that Mo and Sn together can be scrubbed from ITO etching wastewater using Cyanex 272. Reasonably, it is concluded that, careful management of Cyanex 272 concentration can scrub Mo and Sn if undesired or selectively separate both if desired.

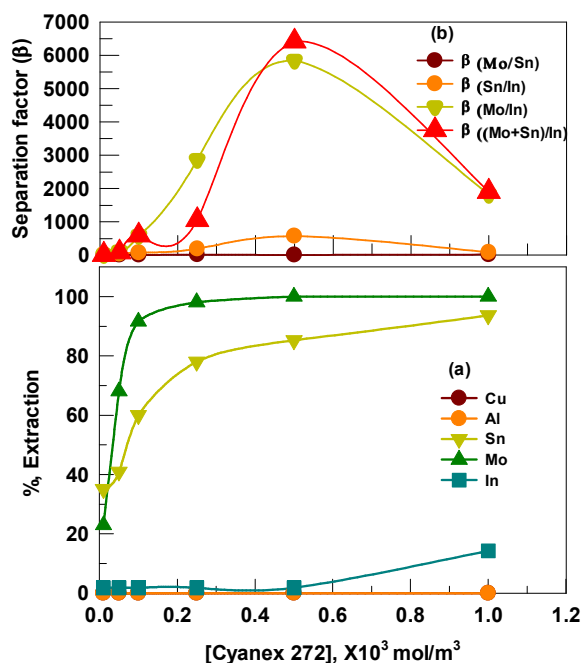


Figure 3: Effect of Cyanex 272 concentration on (a) extraction efficiency and, (b) separation factor. Experimental conditions: wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

Similarly, the extraction behaviour of metals from ITO etching wastewater using various concentrations of DP-8R was investigated at a constant pH. Figure 4(a) shows as DP-8R concentration increased from 10-1000 mol/m<sup>3</sup>, Sn, Mo and In extraction efficiency increased from 47.66% to 94.43%, 28.36% to 99.64% and 5.11%

to 99.54%, respectively. Whereas Al and Cu never been extracted. Although DP-8R has better selectivity towards In, Mo, and Sn, it has no affinity towards Al and Cu, but selective extraction of individual metal is the challenge. If the wastewater treatment was the only motto, all these metals can be selectively extracted to make the wastewater metal free of these pollutants. Since In is one of the valuable metals and In extraction is one of the interest of our project, by the selective combination of extractant and their concentration, In, Mo and/or Sn can be separated. Figure 4(b) shows  $\beta_{\text{Mo/Sn}}$  increased from 0.5 to 30 as the DP-8R concentration increased from 10-500 mol/m<sup>3</sup>, and then  $\beta_{\text{Mo/Sn}}$  decreased to 10.61. The  $\beta_{\text{Sn/In}}$  decreased from 17 to 0.7, indicates that efficient In and Sn separation by DP-8R hardly can be an option. The Figure 4(b) indicates that the  $\beta_{(\text{Mo+Sn})/\text{In}}$ , varied from 38.18 to 0.91 as the DP-8R concentration increased from 50-1000 mol/m<sup>3</sup>. In the case of DP-8R extraction, the mixed metal separation factor is not much different from individual metals. Hence, unlikely Cyanex 272, selective separation of individual metal or mixed metal is not feasible using only DP-8R.

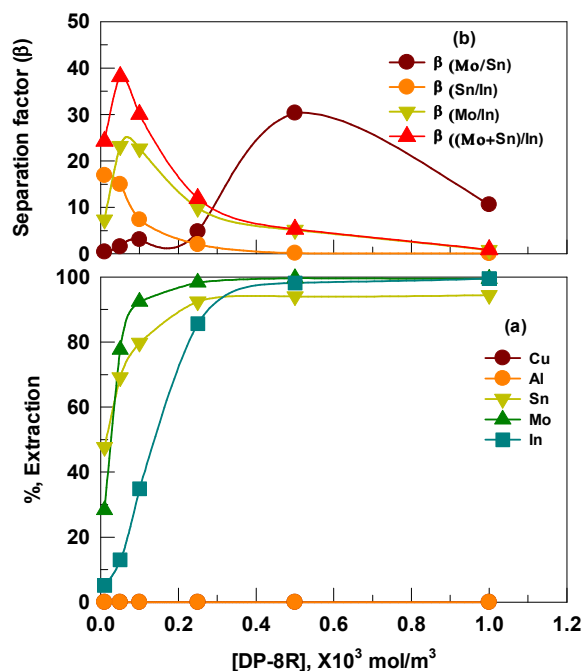


Figure 4: Effect of DP-8R concentration on (a) extraction efficiency and, (b) separation factor. Experimental conditions: wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

#### 4.3.2. Scrubbing Isotherm for Selective Scrubbing of Mo and Sn, and Extraction Isotherm for In

McCabe Thiele diagrams were constructed for scrubbing of Mo and Mo+Sn mixed metal, and selective extraction of In, presented in our earlier publication<sup>32</sup>. The McCabe Thiele diagram for Mo indicated that two stages are required for complete scrubbing of Mo from ITO etching wastewater using 250 mol/m<sup>3</sup> of Cyanex 272 at an O/A volume ratio 1. Similarly, a McCabe Thiele diagram was constructed for the selective scrubbing of Sn using the same condition explained for Mo and depicted in Figure 5. The Figure 5 indicates that Sn also required two stages for complete scrubbing from ITO etching wastewater using 250 mol/m<sup>3</sup> of Cyanex 272 at an O/A volume ratio 1. The McCabe Thiele diagrams for In indicates three stages are required for complete removal of In from ITO etching wastewater using 500 mol/m<sup>3</sup> of DP-8R at an A/O volume ratio of 8.5<sup>32</sup>.

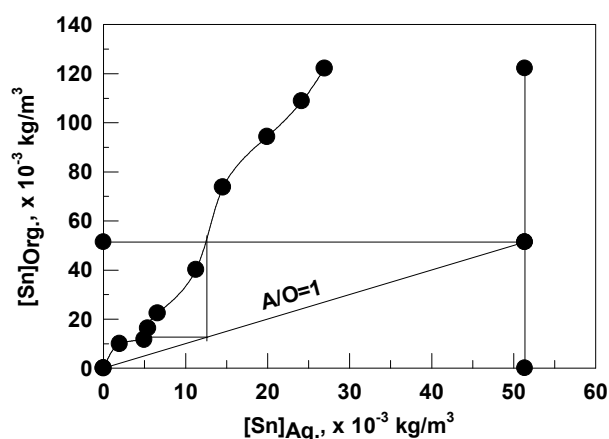


Figure 5: Equilibrium isotherms for scrubbing of Sn from Cyanex 272. Experimental conditions: wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, 250 mol/m<sup>3</sup> Cyanex 272, equilibrium time = 5 min, phase separation through settling time = 1 min.

### 4.3.3. Optimization of Mo, Sn and In Stripping

Equal volume of 250 mol/m<sup>3</sup> Cyanex 272 and ITO etching wastewater equilibrated twice to scrub out Mo and Sn quantitatively from ITO etching wastewater. The raffinate generated was equilibrated with an equal volume of 500 mol/m<sup>3</sup> DP-8R. The Mo and Sn loaded 250 mol/m<sup>3</sup> Cyanex 272 was stripped using various concentrations of NH<sub>4</sub>OH and NaOH, and depicted in Figure 6. Figure 6(a) indicates that as NH<sub>4</sub>OH concentration increased from 500 mol/m<sup>3</sup> to 7000 mol/m<sup>3</sup>, Mo stripping increased from 1.40% to 99.13%, whereas Sn stripping was limited from 1.36% to 10.96%, only. The NH<sub>4</sub>OH has selectivity towards Mo stripping, leaving the Sn in the organic phase. Hence, NH<sub>4</sub>OH can effectively be used as the best stripping reagent for selective stripping of Mo. Figure 6(a) also depicts the purity of Mo stripped as NH<sub>4</sub>OH concentration increased from 500 mol/m<sup>3</sup> to 7000 mol/m<sup>3</sup>. Using 4000 mol/m<sup>3</sup> and 7000 mol/m<sup>3</sup> of NH<sub>4</sub>OH 99.15% and 99.20% Mo has been stripped, respectively.

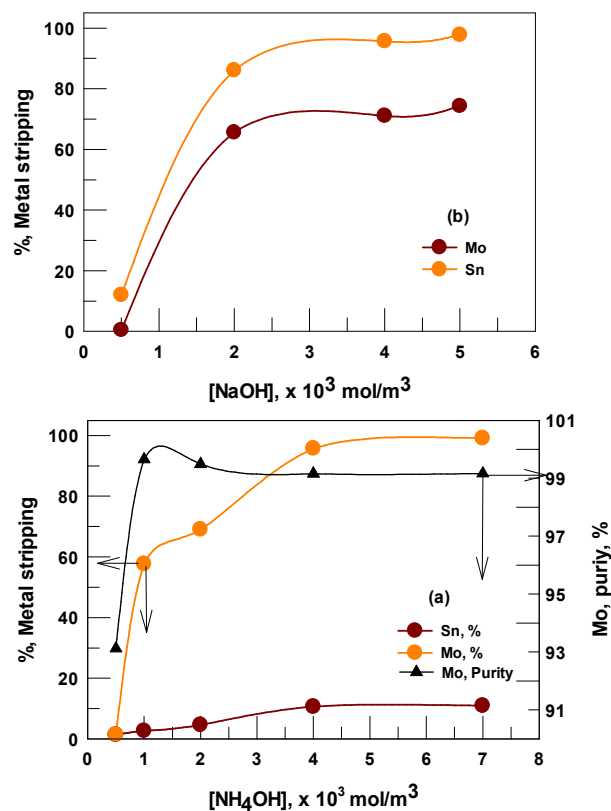


Figure 6: Stripping behaviour of (a) Sn and (b) Mo

from the loaded Cyanex 272. Experimental conditions: wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, loaded from 250 mol/m<sup>3</sup> Cyanex 272 at organic/aqueous volume phase ratio = 1, stripping organic/aqueous volume phase ratio = 1, equilibrium time = 5 min, phase separation through settling time = 1 min.

Figure 6(b) depicts that as the NaOH concentration increased from 500 mol/m<sup>3</sup> to 4000 mol/m<sup>3</sup>, Mo stripping varied from 0.46% to 74.33%, whereas Sn stripping varied from 12.03% to 97.79%. The NaOH has limited selectivity towards either Mo or Sn stripping in the all ranges of NaOH concentration. Hence, only NaOH cannot be used for either pure Sn or Mo recovery. Figure 6(a) and 6(b) indicates that if Mo stripped first using NH<sub>4</sub>OH subsequently, pure Sn can be stripped using NaOH. The same figure suggests that a complete separation of Mo and Sn is possible by the careful sequential management of stripping agents and their concentrations. Followed by Mo and Sn stripping, the Cyanex 272 was regenerated by washing it with an equal volume of DI water (twice) and reused for the Mo and Sn scrubbing. No degradation in Cyanex 272 extraction behaviour was observed. The solvent loss during scrubbing, stripping and regeneration process was insignificant.

The In loaded DP-8R now scrubbed using various concentrations of HCl. Figure 7(a) depicts % of In stripped and ppm of Mo and Sn stripped from In loaded DP-8R. Figure 7(b) depicts the purity of In stripped using various HCl concentrations. Figure 7(a) shows with HCl concentration increased from 500 – 4000 mol/m<sup>3</sup>, the In stripping increased from 0.16% to 100%. Figure 7(b) shows with HCl concentration the % In purity increased from 93.12% to 99.17%. A few ppm of Mo and Sn stripping was detected is associated with instrumental analytical errors. Considering analytical errors reasonably concluded that ultra-pure In recovery is possible from ITO etching wastewater using DP-8R as extractant and HCl as strip. After In stripping, the DP-8R was washed using equal volumes of DI water (twice) and reused for the In extraction purpose. No degradation in DP-8R extraction behaviours was observed. Similar to Cyanex 272 studies the DP-8R loss during the extraction, stripping and regeneration process was insignificant. Solvent loss during the process was less than 1% for both, i.e., DP-8R and Cyanex 272. The solvent loss observed during







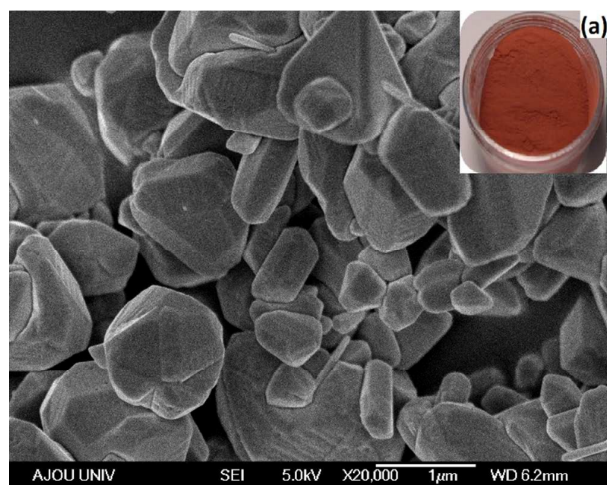
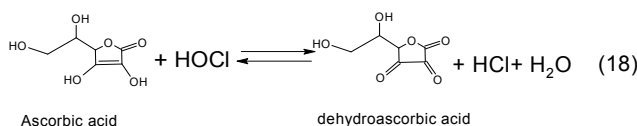


Figure 9: (a) SEM for copper nanopowder and (b) XRD pattern for copper nanopowder synthesized by wet chemical reduction using ascorbic acid as reductant. Experimental conditions: In, Mo and Sn free wastewater from indium-tin-oxide (ITO) etching at pH = 0.70, 60 kg/m<sup>3</sup> of ascorbic acid, 180 l/m<sup>3</sup> of NH<sub>4</sub>OH, 30 minutes stirring.

The ascorbic acid neutralizes both chlorine and chloramines without affecting oxygen levels during the dechlorination process.<sup>36, 37</sup> The chemical reaction of ascorbic acid with chlorine is shown below as Equation (18).



After completion of all the process explained, the wastewater was neutralized using solid NaOH. Most of the Al gets precipitated as Al(OH)<sub>3</sub>. After filtration, the filtrate was analysed and only a trace amount of Al and Cu was detected, which indicate that the treated wastewater is suitable for disposal. After In recovery using aluminium, the AlCl<sub>3</sub> in the waste solution can be neutralized, the same method explained for Al bearing wastewater after series of recovery process.

#### 4.5. Development of Process Flow Sheet and Simulation

For simplifying the complex flow sheet, the flow sheet is presented in two different parts, i.e., (a) a qualitative flow sheet explaining various treatment and recovery process involved and (b) a Quantitative flow sheet explaining process simulation in term of weight, volume

and concentration. Based on the investigation explained above, a qualitative process flow sheet is proposed, and presented in Figure 10. Figure 10 explains first, Mo and Sn were scrubbed from ITO etching industry wastewater using Cyanex 272 followed by sequential Mo and Sn recovery using NH<sub>4</sub>OH and NaOH, respectively. Mo and Sn scrubbing requires two stages using 250 mol/m<sup>3</sup> of Cyanex 272. First the Mo was stripped using 4000 mol/m<sup>3</sup> NH<sub>4</sub>OH followed by Sn was stripped using 4000 mol/m<sup>3</sup> NaOH from Mo and Sn loaded Cyanex 272. Then from the raffinate, In was recovered using 500 mol/m<sup>3</sup> of DP-8R as extractant followed by 4000 mol/m<sup>3</sup> of HCl stripping, finally the In chloride solution was reduced using metallic Al through wet chemical reduction. Three stages of extraction required using A/O=8.5 of 500 mol/m<sup>3</sup> DP-8R and 2 stages of stripping required using O/A =10 of 4000 mol/m<sup>3</sup> HCl. Finally, from the Cu and Al containing wastewater, pure Cu metal was recovered using Ascorbic acid powder as reductant. Cu nanopowder was recovered through filtration after wet chemical reduction using ascorbic acid. The filtrate was neutralized using NaOH to precipitate Al as Al(OH)<sub>3</sub>. Finally, the neutralized water can be disposed of or reused in the same industry.

Based on above optimization studies and information, a process simulation and their reproducibility were investigated for the process at their optimum condition. Figure 11 represents the process simulation at their optimum condition. From Figure 11, complete recovery of metal values from ITO etching wastewater is indicated. As part of project interest, the proposed simulation was carried out both in laboratory scale and pilot scale. For the laboratory-scale simulation study a 2 l/batch process has been investigated. Reproducibility within 95% confidence interval was achieved through the investigations. From the process flow sheet through a laboratory scale simulation, the achievements of the developed process are listed below.

- (i) The process offers flexibility to treat several litters to one m<sup>3</sup>/day and versatile, capable of complete recovery of In with 99.999 % purity (5N).
- (ii) Quantitative recovery of Mo and Sn with at least 99 % purity, value added Cu nanopowder (≈ 100 nm) with 99.999 % purity could be recovered.
- (iii) The developed proposed flow sheet is a clean, green and a techno-economical feasible process for commercial treatment of several m<sup>3</sup> of etching wastewater per day.

- (iv) Wastewater after treatment is heavy metal free (mostly chloride free) can be disposed of or reused in the same ITO etching process.
- (v) Regeneration and reuse of all the organic extractant, no hazardous chemical uses for process make the process a clean and green economical process.
- (vi) A scaled up 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 operating conditions has been investigated and reported elsewhere (Green chemistry)<sup>32</sup>.

- A clean and green, economical wastewater treatment process developed for the treatment of ITO etching industry wastewater through liquid-liquid extraction and wet chemical reduction.
- By the developed process simultaneously the valuable industrial (high pure) metals like In, 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. The use of cheaper commercial extractant and chemicals for expensive metal recovery, justifies the economical, and sustainability of the process. Regeneration and reuse of extractant, justifies the environmentally friendly and green chemistry aspect of the process.
- As the process is a versatile and flexible process, can be used in small, medium and mega-scale industrial wastewater treatment where ITO etching wastewater is a concern.
- The process developed can be used for batch wise treatment process or continuous treatment process. By the process, industrial wastewater disposal limit imposed by WHO can be achieved.
- The developed process is a valorisation process, which convert waste to wealth in true sense.

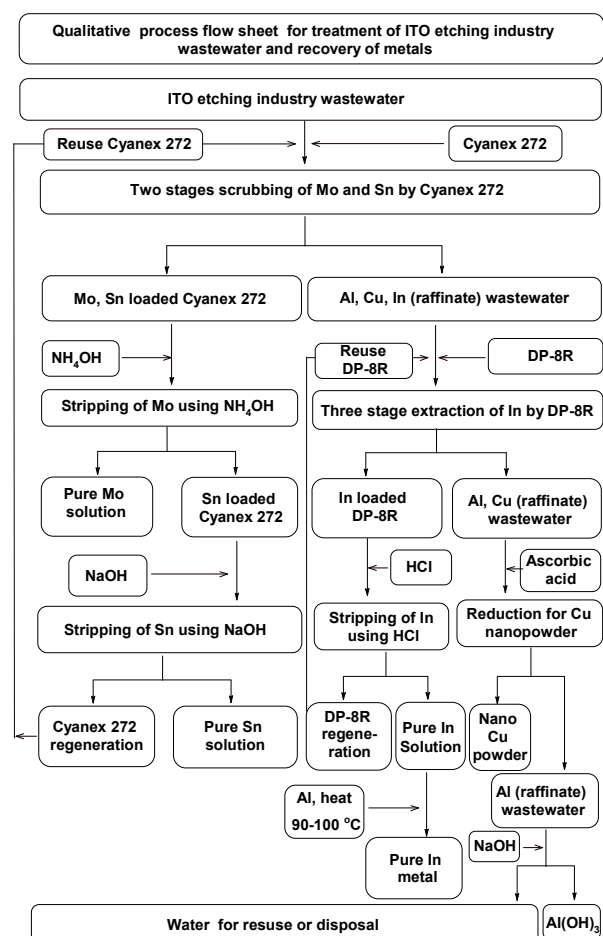


Figure 10: Qualitative process flow sheet for treatment of indium-tin-oxide (ITO) etching wastewater and total recovery of metal values.

## 5. Conclusions

**STATE OF THE ART PROCESS FLOW SHEET FOR TREATMENT OF ITO ETCHING WASTEWATER, AND RECOVERY OF INDIUM, MOLYBDENUM, TIN AND COPPER BY LIQUID-LIQUID EXTRACTION AND WET CHEMICAL REDUCTION: A LABORATORY SCALE SUSTAINABLE COMMERCIAL GREEN PROCESS**

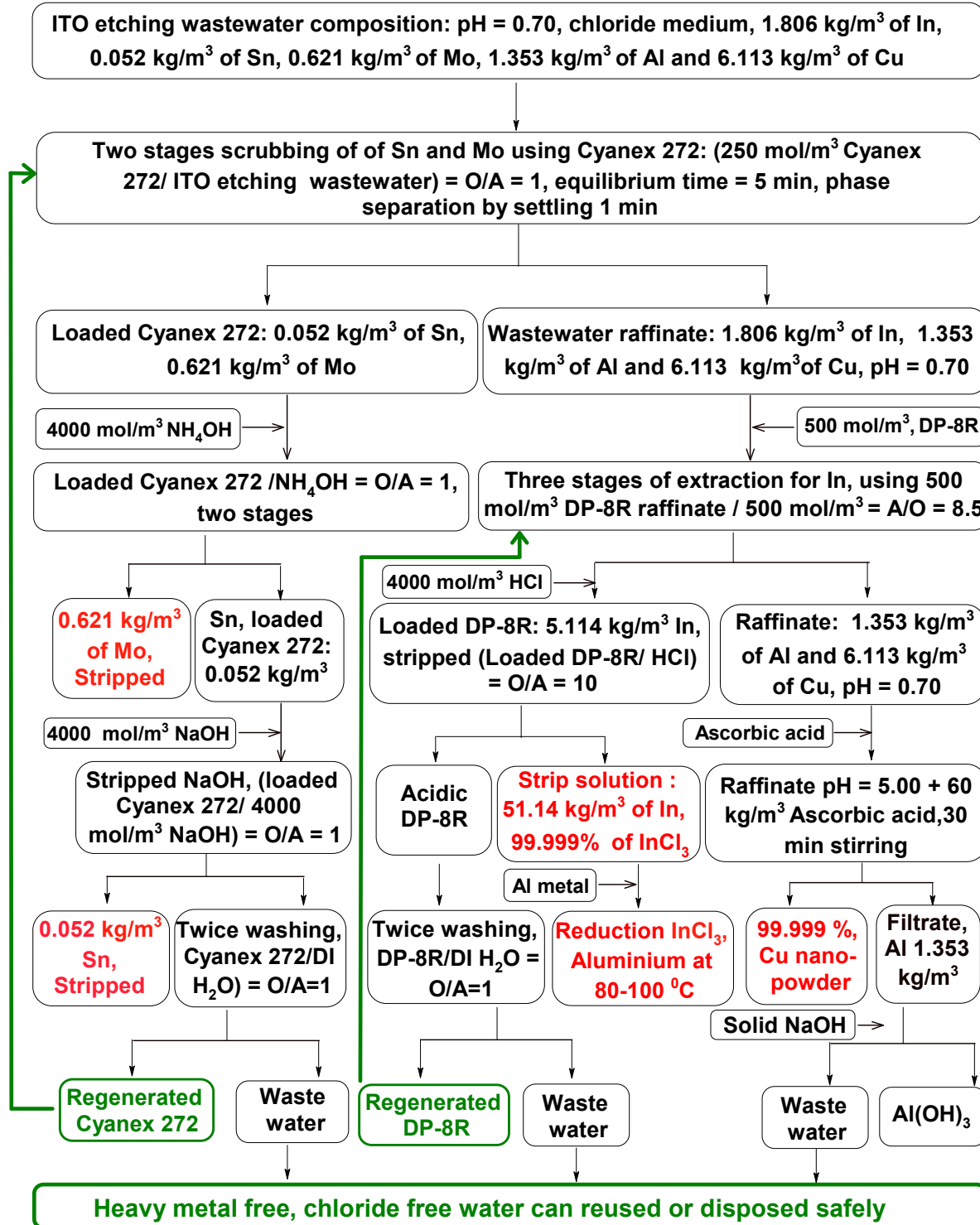


Figure 11: Quantitative simulation for treatment of indium-tin-oxide (ITO) etching wastewater and total recovery of metal values.



## Abbreviations/Nomenclatures

ITO= Indium-tin-oxide  
 Cyanex 272 = Bis (2,4,4,-trimethylpentyl) phosphinic acid  
 DP-8R= Bis (2-ethylhexyl) phosphoric acid  
 Aliquat 336=Tri-octyl-methyl-ammonium chloride  
 Aq. = Aqueous  
 Org. = Organic  
 D = Distribution coefficient of the metal  
 M = Metal  
 K = Equilibrium constant  
 HL = Organic solvent  
 ML= Organometallic complex  
 E = Percentage of extraction  
 $\beta$  = Separation factor

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## FULL PAPER

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FULL PAPER

**Treatment of Indium-Tin-Oxide etching wastewater and recovery of In, Mo, Sn and Cu by liquid-liquid extraction and wet chemical reduction: A sustainable commercial green process**

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

A sustainable commercial green process for treatment of Indium-Tin-Oxide etching wastewater and recovery of In, Mo, Sn and Cu by liquid-liquid extraction and wet chemical reduction has been developed.

