

## **Extraction and separation of zinc and chromium from electroplating effluent**

**REKHA PANDA, ARCHANA KUMARI, JHUMKI HAIT and MANIS KUMAR JHA\***

Metal Extraction and Forming Division,  
CSIR-National Metallurgical Laboratory, Jamshedpur-831007, India

**Abstract:** Toxicity of industrial effluent is mainly due to the presence of heavy metals like Zn, Cd, Cr, Pb, As, etc. The treatment of these effluents will not only reduce environmental pollution but also conserve the natural resources. Present paper reports selective extraction and separation of zinc and chromium from the electroplating effluent (~15 g/L Zn and ~30 g/L Cr) using solvent extraction technique. Initial studies were carried out from synthetic solution containing Zn (1.78 g/L) and Cr (3.6 g/L) using 10% DE2PHA diluted with kerosene. Various process parameters viz. effect of pH, time, O/A ratio, loading capacity, etc. were studied and optimized. 98.17% Zn gets extracted in 5 min at equilibrium pH 2.5 maintaining O/A ratio 1. 10% H<sub>2</sub>SO<sub>4</sub> was used for stripping the loaded organic. The optimum condition for extraction was validated with the original electroplating effluent supplied by M/s Sinha Electrochemical Plant, Jamshedpur, India. Complete extraction of Zn from the original effluent takes place in 5 min at an equilibrium pH 2.5 and phase ratio (O/A) 1, leaving 99% Cr in the raffinate. From the pure solution obtained, metal or salt could be produced by evaporation, precipitation, electrowinning, crystallization, etc.

**Keywords:** Effluent; Zinc; Chromium; Solvent extraction; D2EHPA.

### **INTRODUCTION**

Rapid industrialization and urbanization has resulted in heavy discharge of toxic pollutants into the water bodies. Billions of wastes are generated every year by the industrial sector which is often pre-treated prior to final disposal in landfills. This practice is leading to resource diminution and creating a harmful inheritance for future generations<sup>[1, 2]</sup>. A massive amount of lethal effluents containing Zn, Cu, Ni, Cr, Cd, Fe, etc. are generated in various process industries viz. electroplating, metal finishing, textile, galvanizing, etc.<sup>[3, 4]</sup>. In general, only 30-40% of all metals used in electroplating processes are effectively utilized i.e. plated on the articles. The rest contaminates the rinse water during the plating process which contains up to 1000 mg/L perilous metals. This waste water is of considerable concern because they are often present at significant levels, are non-biodegradable and probably carcinogen. These toxic contents must be controlled to an acceptable level before being discharged to the environment<sup>[5]</sup>. The discharge of the industrial wastewater into surface water not only causes environmental pollution but also adversely affects the aquatic and human life as well as other living resources as the concentration of these ions is above the pollution norms (1-5 mg/L for Zn)<sup>[3, 6]</sup>. Even acute toxicity of Zn may result in throat dryness, cough, weakness, chills, fever and vomiting<sup>[2]</sup>. So, it is tremendously important to develop feasible ways to recycle industrial sludge if environmental or economical concerns are to be taken into account. Nowadays, a lot of waste producers have begun to pay attention to these effluent problems, trying to solve them as better as possible.

A good way to treat and salvage these materials can be the utilization of numerous hydrometallurgical technologies over the conventional and contemporary ones, since they are economical and environmentally suitable to recover valuable metals. Several methods like

\*Corresponding Authors Email : [mkjha@nmlindia.org](mailto:mkjha@nmlindia.org) / [maniskrjha@gmail.com](mailto:maniskrjha@gmail.com)

chemical precipitation, ion-exchange, evaporation, reverse osmosis, electro-dialysis, ultra filtration and phytoremediation are used for the removal of heavy metals from waste water. But these methods are expensive and inefficient for removal when the metals are at high concentration. The removal of metals to tolerable pollution norms using conventional precipitation process consumes large quantity of chemicals and generates sludge, which needs costly disposal procedure as landfill<sup>[3]</sup>. The evaporation of the rinse water to recycle the metallic value is highly energy intensive. The plant constituents, inorganic and organic materials available in nature were studied for the adsorption of Zn using ion-exchange process [3]. Among the available processing alternatives, solvent extraction is a well established technique in hydrometallurgy that not only meets the strict environmental regulations but also high purity value added products could be produced<sup>[7]</sup>. Nowadays, a very large number of stable extractants is available for use in hydrometallurgy, showing excellent selectivity for particular metal ions, coupled with advances in the engineering and increasing demands for high purity products and more environmentally friendly processing routes.

Several treatment processes have been suggested for the removal of heavy metals from aqueous waste streams. Dermentzis and co-workers presented the performance of electro coagulation with aluminium electrode for simultaneous removal of Ni, Cu, Zn and Cr from synthetic aqueous aliquot solutions and actual electroplating wastewater<sup>[5]</sup>. Best removal was achieved at a current density of 40 mA/cm<sup>2</sup>. The selective extraction of Zn and Fe from Cr (III) passivating baths by the Emulsion Pertraction Technology (EPT), a liquid-liquid extraction process performed in membrane contractors was also investigated. After EPT treatment, the concentration of Zn decreases from 7000 mg/L to 2450 mg/L<sup>[8]</sup>. Sapari and his workers reported the total removal of Zn, Cr (VI), Cr (III) and cyanide from mixed plating rinse wastewater using sand filter and ion exchange columns<sup>[9]</sup>. The recovery of Zn from electroplating effluent using cationic resin, Tulsion T-42 was studied. Complete extraction of Zn took place in 5 min from the aqueous feed containing 0.5 mg Zn/mL at eq. pH 2-4 and aqueous to resin ratio (A/R) ratio 100<sup>[3]</sup>. Cork powder can also be used as adsorbent to remove 91% Zn from electroplating industrial effluents<sup>[2]</sup>.

Different authors studied the extraction of Zn from industrial effluents using solvent extraction process in which different organic extractants such as tri-n-butyl phosphate (TBP), versatic 10 acid, Cyanex 272, LIX984N, etc. The extraction of metal depends on the pH and their separation could be achieved by precisely maintaining the pH of solution<sup>[10]</sup>. Weng Fu and co-workers reported the extraction of Zn from ammoniacal/ammonium chloride solutions using a sterically hindered  $\beta$ -diketone, 4-ethyl-1-phenyl-1, 3-octadione (XI-55, HA) as the extractant in the presence or absence of tri-n-octylphosphine oxide (TOPO, B)<sup>[11]</sup>. Solvent extraction study for the extraction of Zn, Cr (II) and Cr (III) from phosphoric acid solutions by tri-n-butyl phosphate (TBP) in kerosene was also reported<sup>[12]</sup>. Sahu et al. studied the solvent extraction of Cu and Zn using versatic 10, Cyanex 272 and LIX984N from model brass pickle liquor<sup>[13]</sup>. The study for separation of Zn and Cu from leach liquor generated in the treatment of the zinc residue by liquid-liquid extraction has also been described. The selective separation of Zn from Ca using thiophosphinic extractant (Cyanex 302) has also been carried out from rayon waste effluent<sup>[14]</sup>. Organophosphorus extractants D2EHPA, Ionquest 801 and Cyanex 272 were tested for selective extraction of zinc. Among all, D2EHPA was found to be the best<sup>[15]</sup>. D2EHPA has been extensively used for the extraction and separation of transition metals. The extraction of Zn from the leach liquor of Zn plant residue and effluent generated at rayon plant has been carried out using D2EHPA<sup>[16,17]</sup>.

The present study emphasizes on the possibility of extraction and separation of Zn from the electroplating effluent containing impurities in form of Cr by solvent extraction process using D2EHPA. Various process parameters such as effect of pH, time, O/A ratio, loading capacity, etc. were studied and optimized for maximum extraction. The obtained data were validated with the original effluent, where satisfactory mass balance was obtained.

## EXPERIMENTAL

### Materials

The Electroplating effluent containing ~15 g/L Zn and ~30 g/L Cr was supplied by M/s Sinha Electrochemical Plant, Jamshedpur, India, which was used as sample for experimental purpose. A model solution, containing 1.78g/L Zn and 3.6 g/L Cr having similar ratio as the original effluent was prepared by dissolving appropriate amount of their sulfate salt in distilled water. Sulfuric acid ( $H_2SO_4$ ) and sodium hydroxide (NaOH) were used in order to maintain desired equilibrium pH of the solution during extraction. All chemicals used were of analytical grade from E. Merck, Mumbai, India. Organic extractant, Di-2-ethylhexyl phosphoric acid (D2EHPA) procured from Fluka, AG, Buchs was employed for extraction without further purification. Commercial grade kerosene was used as diluent for organic extractant and 2% isodecanol was mixed with D2EHPA to avoid third phase formation and achieve quick phase separation.

### Methods

#### *Solvent extraction method*

Bench scale solvent extraction studies were carried out by mixing equal volume (50 mL) of aqueous and organic extractant with the help of a mechanical stirrer for a fixed time interval. After equilibration, the phases were allowed to settle and separate. The required pH of the aqueous was adjusted using NaOH or  $H_2SO_4$  solution. Stripping of metal ions from the loaded organic phase was carried out with 10% (v/v)  $H_2SO_4$ . Satisfactory material balance was obtained in all the experiments. The regenerated organic showed similar extraction efficiency when reused under the same experimental condition for several cycles of extraction.

#### *Analytical method*

The concentration of metals in the aqueous was determined using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer model, Analyst 200; USA) equipped with single element hollow cathode lamps and in air-acetylene flame. The wavelengths used for analyzing the concentration of Zn and Cr ions were 213.9 nm and 357.9 nm, respectively. Concentration of metal in organic phase was deduced from the difference between initial concentration of metal in aqueous phase and its concentration in the raffinate. CL 46 pH meter (Toshniwal Pvt. Ltd., Ajmer) was used for measuring pH of the solution.

## RESULTS AND DISCUSSION

Experiments were carried out to optimize the parameters for the selective extraction and separation of Zn from the synthetic solution containing 1.78 g/L of Zn and 3.6 g/L Cr in sulfate medium. 10% D2EHPA diluted in kerosene with 2% isodecanol as phase modifier was used for the selective extraction of zinc from the aqueous solution. The optimized condition obtained was validated with the actual electroplating effluent.

### Effect of extractant concentration

Selective extraction of Zn was carried out from its synthetic solution with different concentration of D2EHPA diluted with kerosene varying in the range of 5-20%. Fig. 1 shows that the extraction of Zn increases with increase in the extractant concentration, maintaining O/A ratio 1. It was found that 46.74%, 98.17%, 98.65% and 98.87% Zn was extracted using 5%, 10%, 15% and 20% D2EHPA, respectively at equilibrium pH 2.5, maintaining O/A ratio 1 and mixing time 5 min. As the increase in extractant concentration had negligible effect on the extraction of Zn, thus, 10% D2EHPA was considered as optimum concentration and used for further experimental purpose.

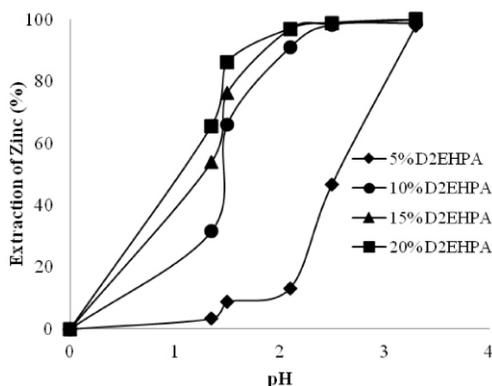


Fig. 1 : Effect of extractant concentration  
(Organic: D2EHPA; Aqueous: 1.78g/L Zn & 3.6 g/L Cr; Time: 5 min; O/A ratio: 1)

### Effect of pH on the extraction of Zn/Cr

Extraction of metals from the aqueous solution is largely affected by the equilibrium pH which is adjusted to desired range by adding  $H_2SO_4$  or NaOH to the aqueous solution. The use of cationic extractants for the extraction of metals, releases  $H^+$  ions which not only lowers the pH but also decreases the extraction of metals. To examine the effect of pH on the extraction of Zn from the sulfate solution containing 1.78 g/L Zn and 3.6 g/L Cr, number of experiments were carried out at different pH using 10% D2EHPA with 2% (v/v) isodecanol in kerosene at phase ratio 1 in a contact time of 5 min. The results presented in Fig. 2 shows that the extraction of Zn increases from 44.99 to 99.7 % with increase in pH from 0 to 3. It was found that 98.17 % Zn

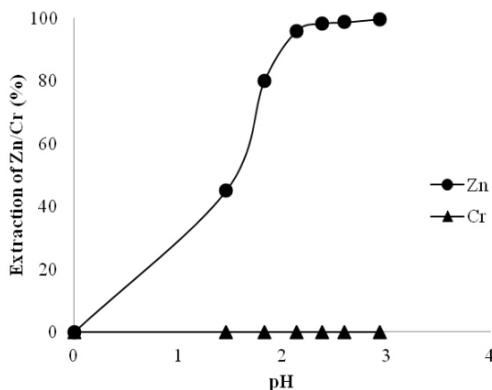


Fig. 2 : Effect of pH on the extraction of Zn/Cr  
(Organic: 10% D2EHPA; Aqueous: 1.78g/L Zn & 3.6 g/L Cr; Time: 5 min; O/A ratio: 1)

was extracted using 10% D2EHPA at O/A ratio 1 in a mixing time of 5 min at equilibrium pH 2.5 in single stage. The extraction of Cr was negligible under the above mentioned experimental condition. A shift towards higher pH value is observed with increase in concentration of Zn in the aqueous feed. This may be due to the fact that at a particular pH an extractant can extract a certain quantity of metal ion.

A plot of log D vs equilibrium pH was plotted for the given aqueous solution. The results presented in Fig. 3 gives a straight line with a slope 1.715 indicating the release of 2 moles of H<sup>+</sup>

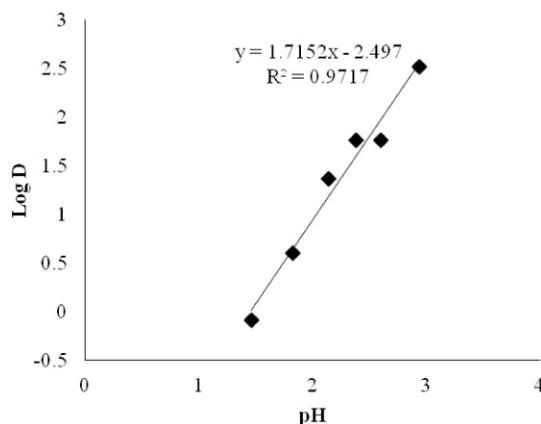
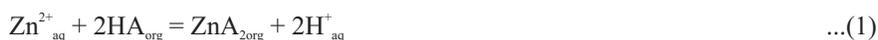


Fig. 3 : Log D vs Log pH

(Organic: 10% D2EHPA; Aqueous: 1.78g/L Zn & 3.6 g/L Cr; Time: 5 min; O/A ratio: 1)

ions for each metal ion. Thus, the extraction equilibrium of zinc (Zn<sup>2+</sup>) with D2EHPA (HA) in kerosene can be expressed as,



The equilibrium constant  $K_{\text{ex}}$  can be given as :

$$K_{\text{ex}} = \frac{[\text{ZnA}_2][\text{H}^+]^2}{[\text{Zn}^{2+}][\text{HA}_{\text{org}}]^2} \quad \dots(2)$$

Equation (2) can be rewritten as

$$K_{\text{ex}} = \frac{[D_M][\text{H}^+]^2}{[\text{HA}_{\text{org}}]^2} \quad \dots(3)$$

where  $D_M$  is the distribution ratio

$$D_M = \frac{[\text{ZnA}_{2\text{org}}]}{[\text{Zn}^{2+}]} \quad \dots(4)$$

Taking logarithm of equation (4) and rearranging

$$\text{Log } D_M = \text{log } K_{\text{ex}} + 2 (\text{log } [\text{HA}] + \text{pH}) \quad \dots(5)$$

or

$$\text{Log } D_M = \text{log } K_{\text{ex}} + 2 \text{log } [\text{HA}] + 2\text{pH} \quad (6)$$

From equation 6 it can be concluded that  $D_M$  is a function of equilibrium pH and concentration of extractant.

### Effect of time on the extraction of Zn

Effect of time on the extraction of Zn from the sulfate medium was studied. Experiments were carried out using 10% D2EHPA diluted in kerosene at different time intervals (1 to 10 min). It was found that percentage extraction of zinc increases from 42.98% to 60.85% with increase in time from 1 to 5 min using 10% D2EHPA at eq. pH 2.5 maintaining phase ratio (O/A) 1 (Fig. 4). Increase in time beyond 5 min had negligible effect on the extraction of Zn, thus 5min was considered optimum for further experimental purpose.

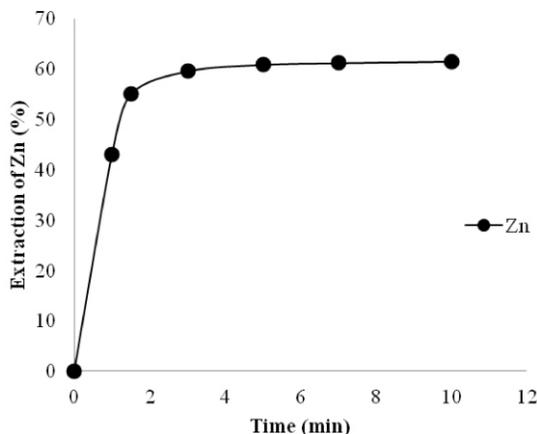


Fig. 4 : Effect of time on the extraction of Zn  
(Organic: 10% D2EHPA; Aqueous: 1.78g/L Zn; pH: 2.5; O/A ratio: 1)

### Effect of phase ratio (O/A) on the extraction of Zn

The effect of phase ratio has also been studied using an aqueous feed containing 1.78 g/L Zn with 10% D2EHPA diluted in kerosene. The results presented in Fig. 5 indicate an increase in extraction of Zn from 92.1 to 99.54 % with increase in O/A ratio from 1:3 to 3:1 using 10% D2EHPA at eq. pH 2.5 in a mixing time of 5 min.

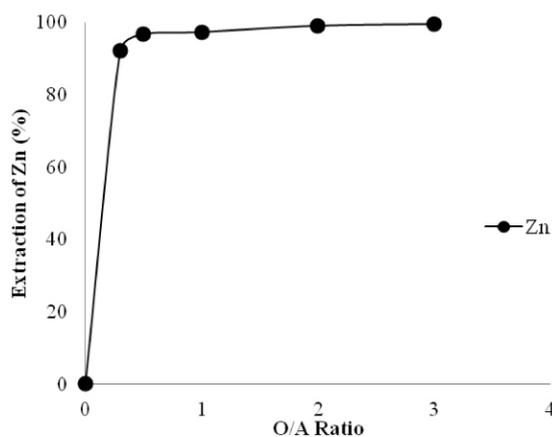


Fig. 5 : Effect of O/A ratio on the extraction of Zn  
(Organic: 10% D2EHPA; Aqueous: 1.78g/L Zn; pH: 2.5; Time: 5 min)

In order to determine the number of theoretical counter current extraction stages required for complete recovery of Zn, McCabe-Thiele plot was drawn from the phase variation data as shown in Fig. 6. The plot suggests that two stages are required for complete extraction of Zn at O/A ratio 1 in a contact time of 5 min.

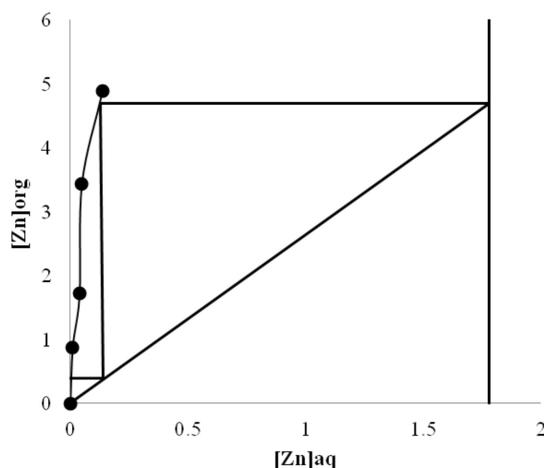


Fig. 6 : McCabe-Thiele diagram  
(Organic: 10% D2EHPA; Aqueous: 1.78g/L Zn; pH: 2.5; Time: 5 min)

#### Loading capacity of D2EHPA

In order to investigate the loading capacity of the solvent, 10% D2EHPA diluted with kerosene was repeatedly contacted with equal volume of fresh aqueous feed maintaining O/A ratio 1 at equilibrium pH 2.5 for 5 min to achieve maximum loading of Zn in the organic phase. The study showed increase in metal concentration in the organic phase with the increase in contact number and achieved equilibrium concentration of 4.97 g/L Zn in fifth contact as shown in Fig. 7.

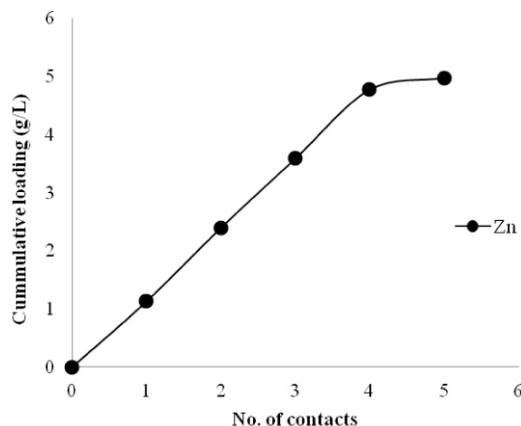


Fig. 7 : Loading capacity of D2EHPA for Zn

#### Stripping of loaded organic

Stripping of Zn from the loaded D2EHPA was carried using sulfuric acid. The ratio of organic to strip solution was maintained at 1:1 for every set of experiment. The stripping of Zn depends

on the concentration of sulfuric acid. The extraction of Zn increases from 71.35 to 93.8% with the increase in sulfuric acid concentration from 1 to 10% (v/v). The results shown in Fig. 8 indicate that, ~94 % Zn was stripped from the loaded organic in a single contact at a phase ratio 1.

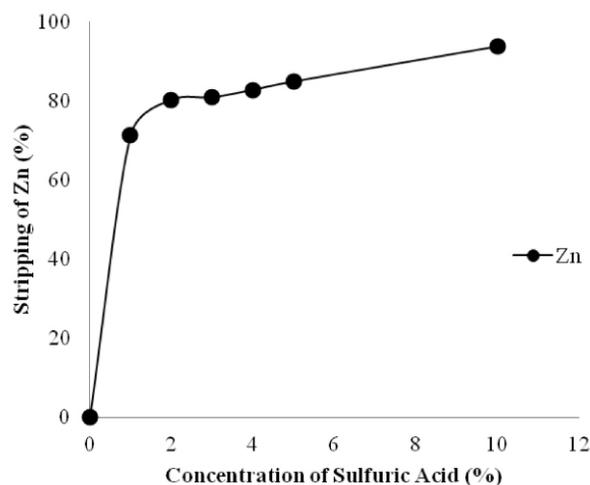


Fig. 8 : Stripping of loaded Zn  
(Organic: 10% D2EHPA; Aqueous: Sulfuric acid; Time: 5 min; O/A ratio: 1)

#### Extraction of Zn/Cr from original effluent

The results obtained from the extraction study of Zn and Cr from their model solution was validated with the actual effluent, supplied by M/s Sinha Electrochemical Plant, Jamshedpur. It was observed that 99.27% Zn was extracted at equilibrium pH of 2.5 using 10% D2EHPA at O/A ratio 1 in a mixing time of 5 min, leaving Cr in the raffinate (Fig. 9). An anionic resin, Amberlite IRA 400 Cl can be used to extract Cr from the raffinate<sup>[18]</sup>. The organic extractant D2EHPA can be regenerated and pure metal or salt can be produced from the stripped solution by the method of evaporation, electrowinning, crystallization, etc. Further increase in pH initiate precipitation of metals from effluent as well as the separation of organic and aqueous phase becomes complicated.

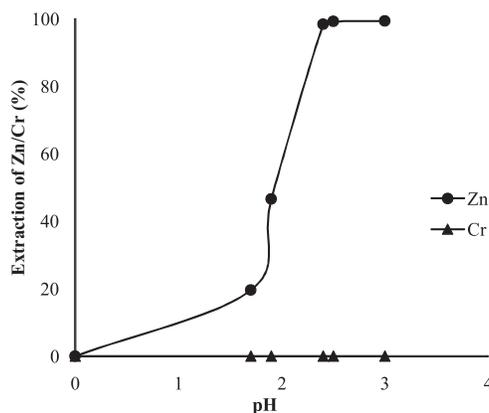


Fig. 9 : Extraction of Zn/Cr from original effluent  
(Organic: 10% D2EHPA; Aqueous: Original Zn/Cr effluent; Time: 5 min; O/A ratio: 1)

## CONCLUSIONS

Based on the above studies for the selective extraction of Zn from the effluent containing Zn/Cr, it can be concluded that:

Almost 98.17% Zn was extracted from the model sulfate solution containing 1.78g/L Zn and 3.6 g/L Cr at pH 2.5 at phase ratio (O/A) 1 using 10% D2EHPA diluted with kerosene whereas more than 90% stripping of the Zn from the loaded organic was achieved using H<sub>2</sub>SO<sub>4</sub> in a single contact. The obtained optimum condition was validated with the original effluent (~15 g/L Zn and ~30 g/L Cr), ~99.27% Zn was extracted under similar experimental conditions in a single stage, leaving Cr in the raffinate. A complete process flow-sheet for the separation of Zn/Cr from industrial effluent is given in Fig. 10.

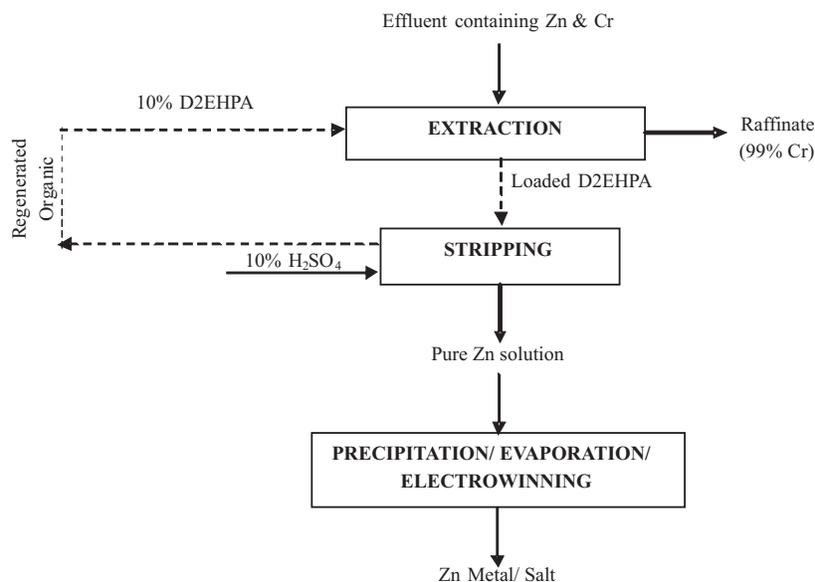


Fig. 10 : A complete process flow-sheet for the extraction and separation of Zn and Cr from electroplating effluent

The data obtained from this basic research will be useful for researchers to plan and determine number of stages required in scale-up studies for selective recovery of Zn as pure solution. This basic studies will also be helpful for further cementation/precipitation to get value added products.

## ACKNOWLEDGEMENTS

This paper is based on research work carried out at CSIR-National Metallurgical Laboratory (CSIR-NML), Jamshedpur, India. Authors are thankful to the Director, CSIR-NML, Jamshedpur for giving permission to publish this paper.

## REFERENCES

- [1] Bachmann R.T., Wiemken D., Tengkiat A.B. and Wilichowski M., (2010), Feasibility study on the recovery of hexavalent chromium from a simulated electroplating effluent using alamine 336 and refined palm oil, Sep. Purif. Technol., **75**, pp. 303-309.
- [2] Kanawade S.M. and Gaikwad R.W., (2011), Removal of zinc ions from industrial effluents by using cork powder as adsorbent, Int. J. of Chem. Engg. App., **2**, pp. 199-201.
- [3] Jha M.K., Upadhyay A.K., Bagchi D. and Kumar V., (2005), Recovery of zinc from electroplating effluent using cationic resins, J. of Met. Mater. Sci., **47**, pp. 177-187.

- [4] Maslii A.I., Belobaba A.G., Pushkareva G.I. and Bobyleva S.A., (2004), Technology of heavy metal ion extraction from industrial waste waters, *J. of Min. Sci.*, **40**, pp. 624-628.
- [5] Dermentzis K., Christoforidis A. and Valsamidou E., (2011), Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation, *Int. J. Environ. Sci.*, **1**, pp. 697-710.
- [6] Kumbasar R.A., (2008), Studies on the extraction of chromium (VI) from acidic solutions containing various metal ions by emulsion liquid membrane using alamine 336 as extractant, *J. Mem. Sci.*, **325**, pp. 460-466.
- [7] Kumar V., Kumar M., Jha M.K., Jeong J. and Lee J.C., (2009), Solvent extraction of cadmium from sulphate solution with di-(2-ethylhexyl) phosphoric acid diluted in kerosene, *Hydrometallurgy*, **96**, pp. 230-234.
- [8] Mediavilla R., Ortiz I. and Urtiaga A., (2010), Selective extraction of zinc and iron from passivating baths, *Desalination*, **250**, pp. 1014-1015.
- [9] Sapari N., Idris A., Hamid N.H. Ab., (1996), Total removal of heavy metal from mixed plating rinse wastewater, *Desalination*, **106**, pp. 419-422.
- [10] Preston J.F., (1983), Solvent extraction of base metals by mixtures of organophosphoric acids and non-chelating oximes, *Hydrometallurgy*, **10**, pp. 187-204.
- [11] Fu W., Chen Q., Wu Q., Hu H. and Bai L., (2010), Solvent extraction of zinc from ammoniacal/ ammonium chloride solutions by a sterically hindered  $\beta$ -diketone and its mixture with tri-n-octylphosphine oxide, *Hydrometallurgy*, **100**, pp. 116-121.
- [12] Mellah A. and Benachour D., (2007), The solvent extraction of zinc, cadmium and chromium from phosphoric acid solutions by tri-n butyl phosphate in kerosene diluent, *Sep. Purif. Technol.*, **56**, pp. 220-224.
- [13] Sahu S.K., Sinha M.K., Meshram P., Pandey B.D. and Kumar V., (2011), Solvent extraction of copper and zinc from a pickling solution using versatic 10 acid, cyanex 272 and LIX 984N, *The Third Int. Cong., Non-Ferrous and Rare Metals Production, (Part-IV)*, pp. 199-205.
- [14] Jha M.K., Kumar V., Bagchi D., Singh R.J. and Lee Jae-chun, Processing of rayon waste effluent for the recovery of zinc and separation of calcium using thiophosphinic extractant, *J Hazard Mater*, **145**, pp. 221-226.
- [15] Gouvea L.R. and Morais C.A., (2010), Development of a process for the separation of zinc and copper from sulfuric liquor obtained from the leaching of an industrial residue by solvent extraction, *Miner. Eng.*, **23**, pp. 492-497.
- [16] Kunzmann M. and Kolarik Z., (1990), Extraction of mono and polynuclear complexes of zinc(II) with di(2-ethylhexyl) phosphoric acid, In: *Proceedings of the International Solvent Extraction Conference, Kyoto, Japan, July 18-21*.
- [17] Reinhard H., Ottertun H. and Troeng T., (1975), Solvent extraction process for the recovery of zinc from weakly acidic effluent, In: *Liquid Effluents Symposium, Chemical Engineering Symposium Series No. 41, Appl. Chem. Eng. Treat. Sewage Ind.*
- [18] Jha M.K., Kumar V. and Lee Jae-chun, (2007), Processing of electroplating effluent for the recovery of zinc and chromium using ion exchange, In *EPD-2007, Proceedings of TMS-2007, Hydrometallurgy: Metal recovery, The Minerals, Metals & Materials Society, USA*, pp.1-10.