Extraction of Heavy Metals from Aqueous Streams and their Recovery as Fine Particles

A thesis submitted
to
The Maharaja Sayajirao University of Baroda
for the award of the degree

Doctor of Philosophy

in
Chemical Engineering

By

KHYATI SHAH

Guided by

Dr. BINA SENGUPTA

Chemical Engineering Department
Faculty of Technology and Engineering
The Maharaja Sayajirao University of Baroda
Vadodara - 390 001
July 2018

Summary of the Report

Introduction

Heavy metals in aqueous streams and water bodies poses considerable health hazard to humankind and it is imperative to treat the wastes to mitigate the hazard. Since metal values are highly recyclable it also provides a good opportunity to earn revenue while cleaning up the environment. Metal laden waste water treatment can be successful only when the three R's are fulfilled i.e recovery, recycle and reuse.

In this investigation the focus is primarily on reclaiming the metal values from acidic pickle liquor and rinse liquor of brass articles manufacturing processes. Gujarat is well known for manufacturing of brass artefacts as well as industrial components. Almost 70% of brass industrial components manufactured in India come from the Jamnagar brass cluster in Gujarat where 5000 manufacturers' are located. Most of the industrial component manufacturers are small scale producers and the decorative artefacts and articles are mostly produced in cottage industries. Such producers are handicapped by ignorance, lack of awareness and lack of resources to effectively treat the wastes.

Brass on exposure to atmosphere undergoes surface discolouration, called tarnish. Cleaning and finishing process to remove tarnish and oxide layer formed on industrial brass components subjected to stages of acid wash and water rinse (Davis, 2001). Acid wash with H_2SO_4 is more common but many processors prefer to use HCl since it reacts quickly, preferentially attacks the oxide layer, prevents pitting and the pickling baths can be operated at ambient temperatures. The pickling bath is used till the acid concentration declines to such a low value that the time required for tarnish removal becomes large and uneconomical for operation, resulting in a substantial metal build up in the pickle liquor.

The third stream from which metal was recovered was ammoniacal etch solution of Printed Circuit Board (PCB) manufacturing. Ammoniacal etchants-ammonium chloride or ammonium sulfate are the most widely used etchants in the PCB industry. Spent etching solutions obtained from the PCB industry contain a large amount of copper, which can be recovered and recycled for further reuse. Almost one billion cubic meter of waste etchant is being generated annually from the PCB industry worldwide accounting for more than 70,000 tons of copper being lost if unclaimed.

Currently we produce less than 1% of global requirements of PCB while China produces more than 40%. It is foreseen that the growth of PCB industry in India in coming years is likely to be explosive. Hence, the need for regeneration of etch solution is going to be of very large volume. However, like in brass processing even in PCB manufacturing there are a very large number of small scale producers, who need appropriate technologies to be able to process their streams and recover the metal values from them.

The present work is focused towards developing processing schemes for the recovery and reclamation of metal values from brass pickle liquors, brass rinse solutions and ammoniacal PCB etch liquors using hydrometallurgical techniques. Focus is also on the use of Precipitation – Stripping (PS) as a tool for metal reclamation from organic solvents as well as a technique for particle synthesis, resulting in the formation of metal oxalate particles that could be calcined at an appropriate temperature to get the commercially valuable oxide particles.

Chapter 2: Heavy Metals in Aqueous Solutions: Sources, Effects and Reclamation

Sources of heavy metals in waste waters and aqueous streams are diverse, but metal related industries are the largest contributors. Metals find their way into aqueous streams from the effluents of metal plating industries (Bode, 1998; Benito et al., 2002; Barakat, 2011), hydrometallurgical applications (Elejalde et al., 1991; Zewail and El-Garf, 2010), battery manufacturing units (Zewail and El-Garf, 2010; Salam et al., 2011), spent catalyst units (Liang, 2004), rayon manufacturing units (Jha et al., 2007), tannery units (Apaydin et al., 2009; Fu et al., 2011)basic steel works, aircraft plating industries, paper and pulp industries, petroleum refining and printed circuit board industries (Kadirvelu and Goel, 2007). The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human. Lead, cadmium, chromium, nickel, and copper etc. are the most hazardous pollutants of freshwater reserves (Zhao et al., 2016). The sources and toxicological effects of heavy metals on human health with their maximum permissible limits are reported by Ravindra et al. (2015).

During the treatment of wastes, the objective is to remove the metals so as to produce a liquid waste stream capable of reuse, or dispose the liquid meeting the environmental discharge limits. Energy savings is the major benefit of recycling A diverse range of treatment techniques such as chemical precipitation (Abdel-Raouf and Abdul-Raheim 2017), membrane filtration (Wang *et al.*, 2017), adsorption (Burakov *et al.*, 2018), ion exchange

(Kurniawan *et al.*, 2006) electrochemical (Hakizimana et al., 2017), flotation (Rubio *et al.*. 2002) are avaliable.

While all these techniques can be employed for the treatment of heavy metal laden wastewater but the selection of the most suitable treatment technique depends on many factors such as; the initial metal concentration, the composition of the wastewater, capital investment and operational cost, plant flexibility, reliability and environmental impact (Stuart and Greenberg, 1999). Over the years numerous approaches have been investigated for the development of more effective and cheaper technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent (Rajasulochana and Preethy, 2015). Numerous investigators have presented comprehensive review papers on wastewater treatment techniques (Carolin *et al.,* 2017; Fu and Wang, 2011; Barakat, 2011).

Solvent extraction, the most important process in hydrometallurgy is an established technique for recovery of heavy metals from low grade, mixed metal, ores and has been widely used as a potential technique for the recovery of metal values from secondary sources (Wilson et al., 2014). The most important metalliferous aqueous streams where solvent extraction can be used are from metal finishing operations, plating, pickling, etching and wash waters arising from cleaning of work pieces (Cox et.al., 2004).

Solvent extraction is a selective separation procedure based on the distribution of a solute between two immiscible liquid phases that are in contact with each other. It is used for isolating and concentrating metals from aqueous solutions with the aid of an immiscible organic solvent and a suitable extractant which selectively loads the metal ions. The organic phase of the solvent extraction mixture consists of an extractant, a diluent and optionally a modifier may also be added to prevent the formation of third phase during extraction

Metal extraction can be achieved using extractants which are classified considering both the extraction mechanism and the physico-chemical properties of the extractant as cationic, anionic and solvating. A comprehensive survey of metal extractant systems are detailed by Cox, (2004); Ritcey, (2006); Chapman, (2009). The salient features of the choice of extractant are detailed by Rao, 2007. Diluent is a liquid or homogeneous mixture of liquids in which extractant and possible modifier dissolve to form the solvent/organic phase (Rydberg *et al.,* 2004). Since kerosene is cheap, available and not very volatile at the temperature of extraction hence, it is most commonly used as a diluent.

In the last decade, a number of research articles have been published focusing of removal of various metal species from aqueous solutions using solvent extraction (Sulaimana and Othman, 2018, Sinha, 2012, Sun *et al.,* 2018). The work on reclamation of metal values from real life wastes is limited. However, there are a number of publications where investigators have attempted to simulate the waste liquor and extract/reclaim the metal values.

Working with the actual waste samples involves a number of challenges viz. inconsistency in the composition of the waste collected from time to time, additional trace impurities present in the actual waste samples that do not manifest in simulated wastes, often industries are very reluctant to share their liquid effluents without a secrecy clause with any research agency / University, publications of real life data is inhibited by the industry generating the waste. On the other hand, a simulated waste does not reveal the true picture nor does it bring out all the effect of various interactions in a complex matrix and at best remains only a pointer towards development of a recovery process.

After a thorough literature survey it is observed that in spite of a huge amount of published work on solvent extraction of metals from aqueous streams there is dearth of literature on real life systems encountered by industry as well as environmental agencies. Most of the work published addresses single solutes extraction, prepared synthetically and existing in a condition different from that which it is encountered in real practice.

Chapter 3 Materials and Methods

Three metal bearing waste water streams from industrial sectors: Brass pickle liquors in chloride media, printed circuit board etching solutions in ammoniacal media and post pickling rinse liquors in chloride media were used as resources for the recovery of metals as fine particles.

Organophosphorous acid D2EHPA and hydroxyoxime extractant LIX 84-I were used to recover the heavy metals from the metal bearing streams. Kerosene was used as a diluent and oxalic acid was used as a stripping and precipitating agent Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used to determine the initial metals present in all the three aqueous solutions. The targeted metal concentration was measured using Atomic Absorption Spectrophotometer (AAS). The chloride, sulfate, nitrate and ammoniacal nitrogen in the aqueous streams were determined by chemical analysis based on the APHA standard methods for examination of water and waste water (APHA 22nd Edition).

Metal extraction was carried out in shake flasks at equal organic and aqueous volume on a rotary shaker at 150 rpm and $30\pm2\ ^0C$. The organic phase consisted of diluent kerosene and extractant. Preliminary experiments were carried out to determine the equilibration time for each of the metal extraction system. After equilibration, both organic and aqueous phase were separated and the pH of the aqueous phase was noted. During extraction there was a decrease in the pH of the aqueous phase. Adjustments in pH during extraction were made using sodium hydroxide. Samples were withdrawn from the aqueous phase and metal concentration in the aqueous phase was determined using an AAS after appropriate dilution. The concentration of the metal in the organic phase was calculated as the difference between concentration of metal in the aqueous phase before and after extraction. The separated metal loaded organic phase was scrubbed with water to remove the adhering aqueous phase prior to precipitation-stripping.

Precipitation-stripping was carried out in shake flasks by contacting the metal loaded organic phase at equal organic and aqueous volume on a rotary shaker at $30\pm2\ ^0C$ and 150 rpm. Effect of parametric variations viz. oxalic acid concentration, time of contact, agitation speed on stripping and precipitation was also investigated. After stripping, the organic phase and aqueous phase containing the metal oxalate was separated. Thereafter, the metal oxalate precipitate was separated from the aqueous phase by centrifugation at 6500-7000 rpm for 10 min. The metal oxalate particles were washed with ethanol and water and dried in an air oven at $60\ ^0C$. The organic phase was further stripped with sulfuric acid to recover any residual metal present so as to recycle the organic phase. The oxalate precipitates were calcined under controlled conditions in a horizontal tube furnace which can operate up to a maximum temperature of 1200^0C to obtain the respective metal oxides. The heating rate was 5^0C/min. After attaining the desired temperature, the material was soaked for requisite time interval to convert the oxalate to oxide. Figure 1 shows the sequence of steps used to recover the metal from aqueous streams as particles.

Material characterization of the particles obtained was carried out by XRD, FTIR, and EDX. Thermal decomposition studies were carried on a TGA. Particles sizes were measured on a

Laser diffraction particle size analyser and surface charges on the particles were determined on a Zeta sizer. Interfacial tension measurements between the organic phase and aqueous phase were carried on a Du Nouy Tensiometer. Morphology of particles were observed on a Field Emission Scanning Electron Microscopy. Figure 1 shows the processing steps adopted for the recovery of metal values from the aqueous streams.

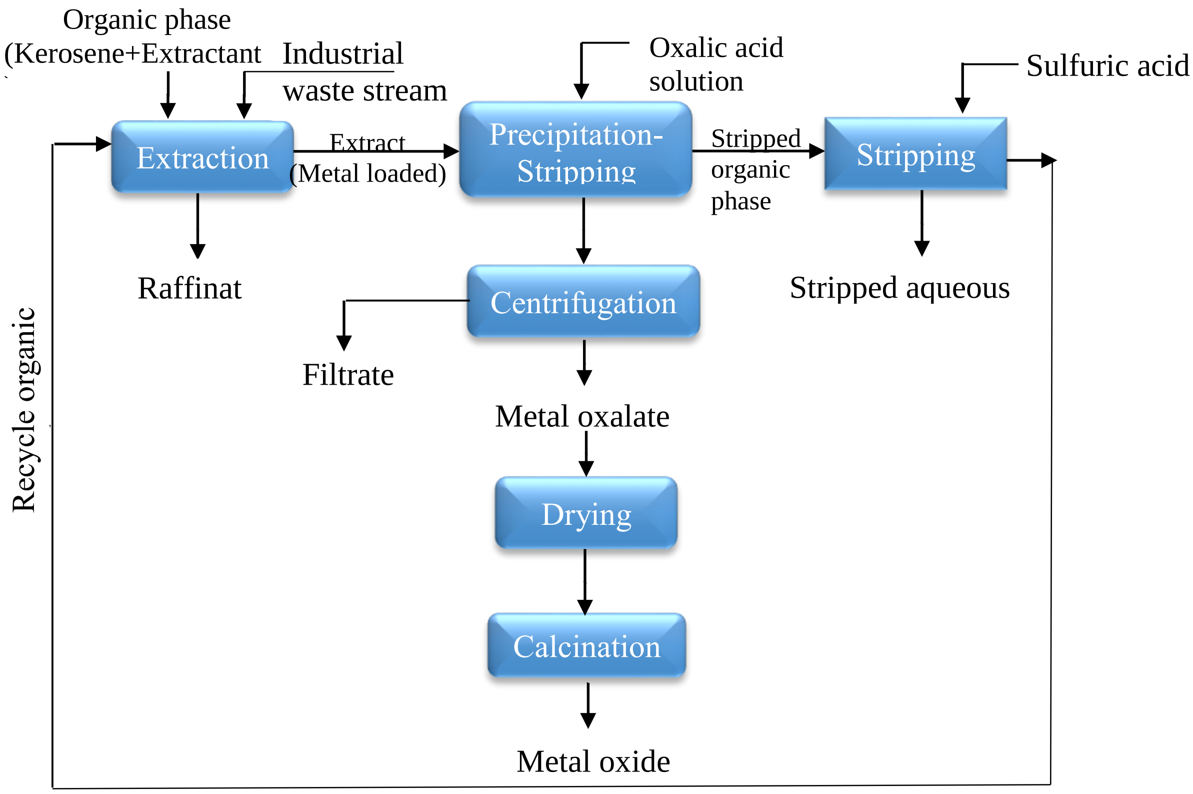

Fig.1 Processing steps for metal recovery

Chapter 4: Recovery of Copper and Zinc from Spent Brass Pickle Liquors

Spent pickle liquor used in this investigation was collected from a brass component manufacturing industry in Rajkot, Gujarat. Pickle liquor contained 20g/l copper and 12.6 g/l of zinc along with small amount of other metals The initial pH of the liquor was 0.25 and the chloride concentration was 10.968g/L.

The speciation of the pickle liquor was evaluated using *Visual MINTEQ 3.1* operating platform. At chloride concentration of 10.968g/L (0.308M) both copper and zinc exist largely as the bivalent cationic species (Cu^{2+}, Zn^{2+}) followed by the monovalent specie ($CuCl^{+}$ and $ZnCl^{+}$) and a very small fraction as the neutral specie $CuCl_2$ and $ZnCl_2$. (Figure 2)

The extraction cycle was designed to initially selectively extract copper using hydroxyoxime LIX 84-IC. After copper extraction, the pH of the pickle liquor was around 2.5 this was directly subjected to zinc extraction using D2EHPA.

Copper extraction was carried out using LIX 84-IC at concentrations ranging from 7.5% (v/v) to 30% (v/v). An increase in the extractant concentration resulted in an increase in copper extraction and at 30% v/v extractant concentration, 98.8% of initial copper present was extracted at an equilibrium pH of 2.5 (Figure 3). It was also observed that of the 131 mg/L iron initially present 77% was extracted. Other than copper and iron none of the other metals initially present in the liquor were extracted under the operating conditions.

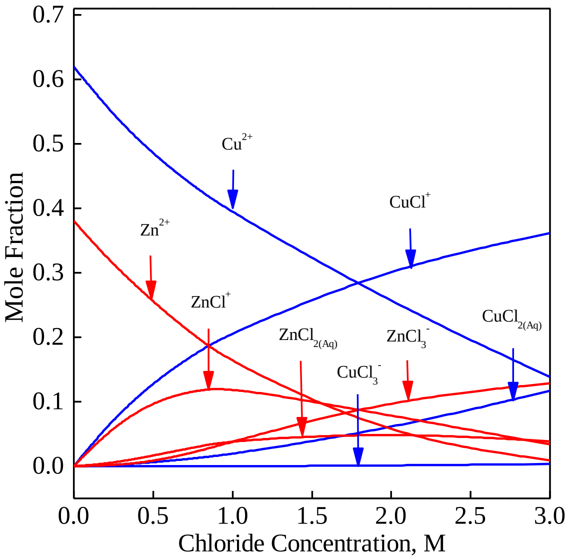

Fig.2: Speciation diagram of copper and zinc in pickle liquor as a function of chloride concentration

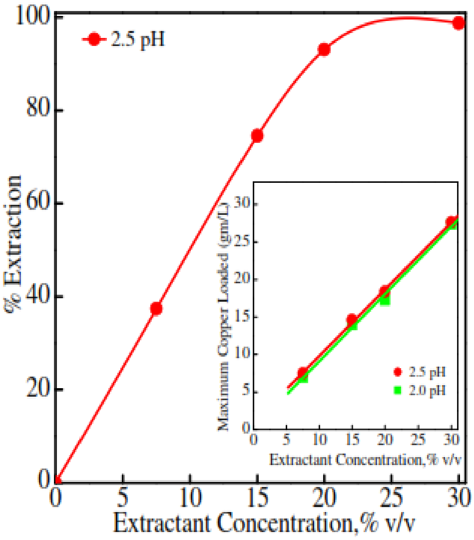

Fig. 3. Effect of LIX 84-IC on copper extraction. (Inset: Maximum copper loading for LIX84-IC in kerosene).

The maximum loading capacity of LIX 84I-C at an equilibrium pH value of 2 was 0.9 g/L per 1% (v/v) of extractant (Figure 3,inset). The plots of distribution coefficient vs equilibrium pH were linear at all extractant concentrations, but the slope values are considerably lower than the theoretical value of 2. Reduction in slope values could be attributed to the transfer of the monovalent ions ($CuCl^+$) along with the bivalent ions (Cu^{2+}). Navaroo and Ruiz (2001) reported that low pH value, $CuCl^+$competes with Cu^{2+} whereas at higher pH values only Cu^{2+} is extracted.

IR studies revealed that the oxime extractant in organic phase existed both as a monomer and dimer at the extractant concentrations investigated and both were involved in the complexation process.

After copper extraction at equilibrium pH of 2.5, zinc was extracted using 15% (v/v) D2EHPA at an equilibrium pH of 2.0. IR studies revealed that D2EHPA was fully complexed with zinc and free extractant was not present in the organic phase. Slope analysis revealed two extractant molecules participated in the complexation process extracting zinc as the specie ZnR_2.

Precipitation - Stripping of copper and zinc from loaded organic phase:

Precipitation - stripping of copper from the organic phase involves a reaction between the loaded organic phase with an aqueous solution of oxalic acid. Precipitation-stripping of the loaded metal using 1 M oxalic acid resulted in formation of sparingly soluble oxalate precipitates. Solubility diagrams were developed theoretically for both copper and zinc-oxalic acid system, using appropriate values of equilibrium constants. Figure 4 shows the solubility diagrams and the distribution of soluble copper/zinc species present in the solution based on theoretical consideration.

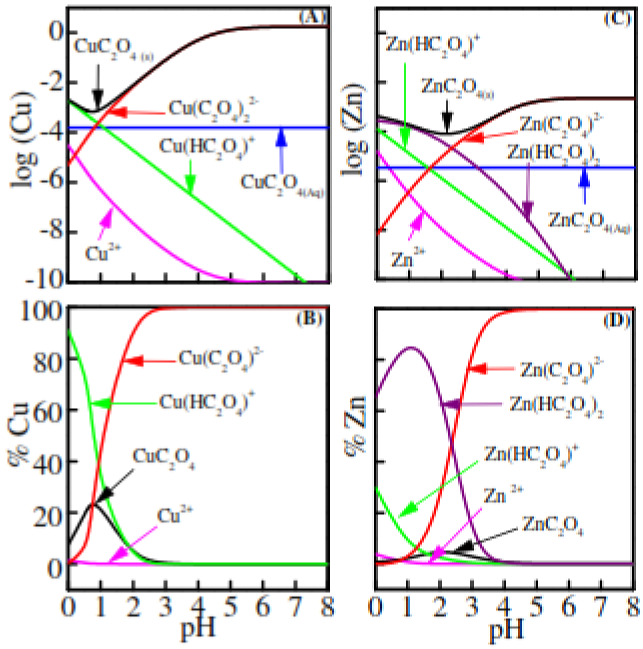

Fig. 4 Solubility diagram: (a) Copper-oxalic acid (b) Zinc-oxalic acid Soluble specie distribution curves: (c) Copper oxalate, (d) Zinc oxalate.

The experimental yield and the predicted yield considering dissolved copper/zinc obtained from solubility diagram are in close agreement with high degree of accuracy (99%). It was coincidental that both copper and zinc recovered as copper oxalate and zinc oxalate accounted for 97.3% of the initial copper and zinc present in the pickle liquor.

The precipitates of copper oxalate and zinc oxalate obtained were characterized by XRD, FTIR and EDX. FESEM analysis was used to study the morphology of oxalate particles. Calcination of the oxalates under controlled conditions converted them to their corresponding oxides. Figure 5 shows the XRD patterns of copper oxide matched with

JCPDS No. 05-661 and zinc oxide matched with JCPDS 36-1451. Chemical analysis revealed that copper was recovered as pure copper oxide, while zinc oxide was obtained with a purity of 99.1%. EDX analysis of copper oxide also showed the presence of zinc (Figure 6). The unextracted residual copper had slipped into the zinc circuit and was extracted by D2EHPA as a result copper manifested as an impurity in Zn oxide.

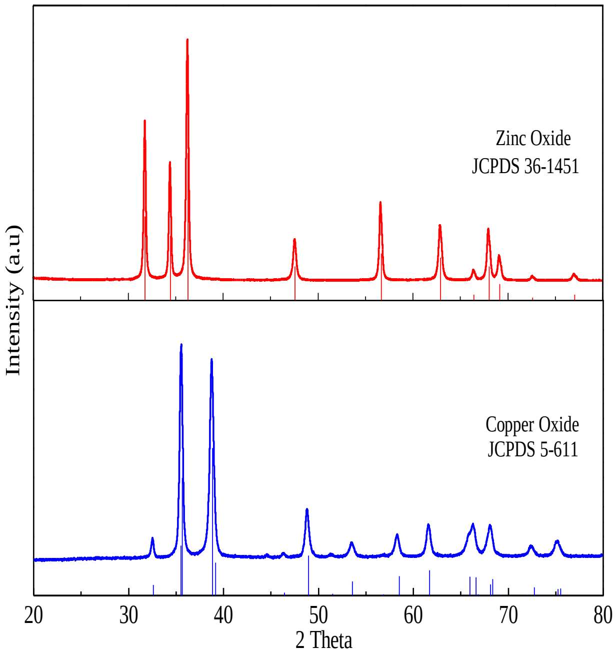

Fig. 5: XRD spectra of copper oxide and zinc oxide

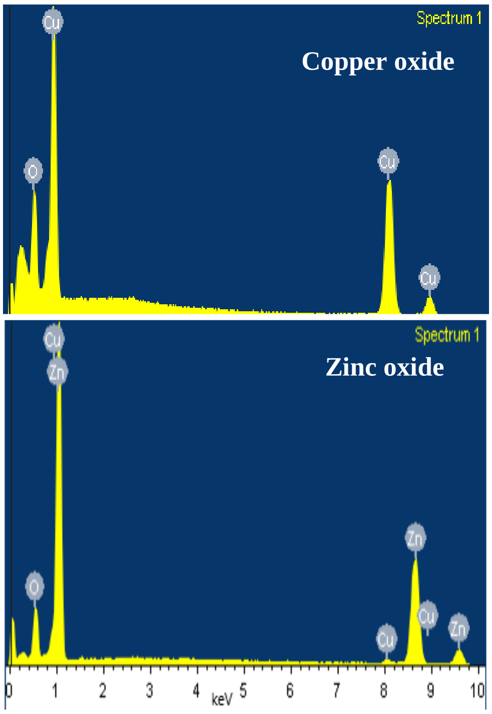

Fig. 6: EDX of copper oxide and zinc oxide

FESEM image of the oxalates revealed that copper oxalate particles were disc shaped, smaller in size and lacked sharp edges whereas zinc oxalate particles were more defined layered structures with sharp edges FESEM images of the oxides show that on calcination oxalates were transformed to their respective oxides without losing their ordered structure.

It was found that the organic phase could be reused without any significant decline in the extractability of the metal ion, and even after 5 cycles 98.3% of the copper could be extracted using LIX84-IC and 97.7% zinc using D2EHPA. A detailed processing scheme (Figure 7) is developed wherein after recovery of copper and zinc to the extent of 98.8% and 98.2% by extraction the residual metals and other trace elements in the aqueous stream was subjected to flocculation and coagulation to obtain a sludge containing the residual metal values and the treated water free of metals could be discharged into municipal water bodies.

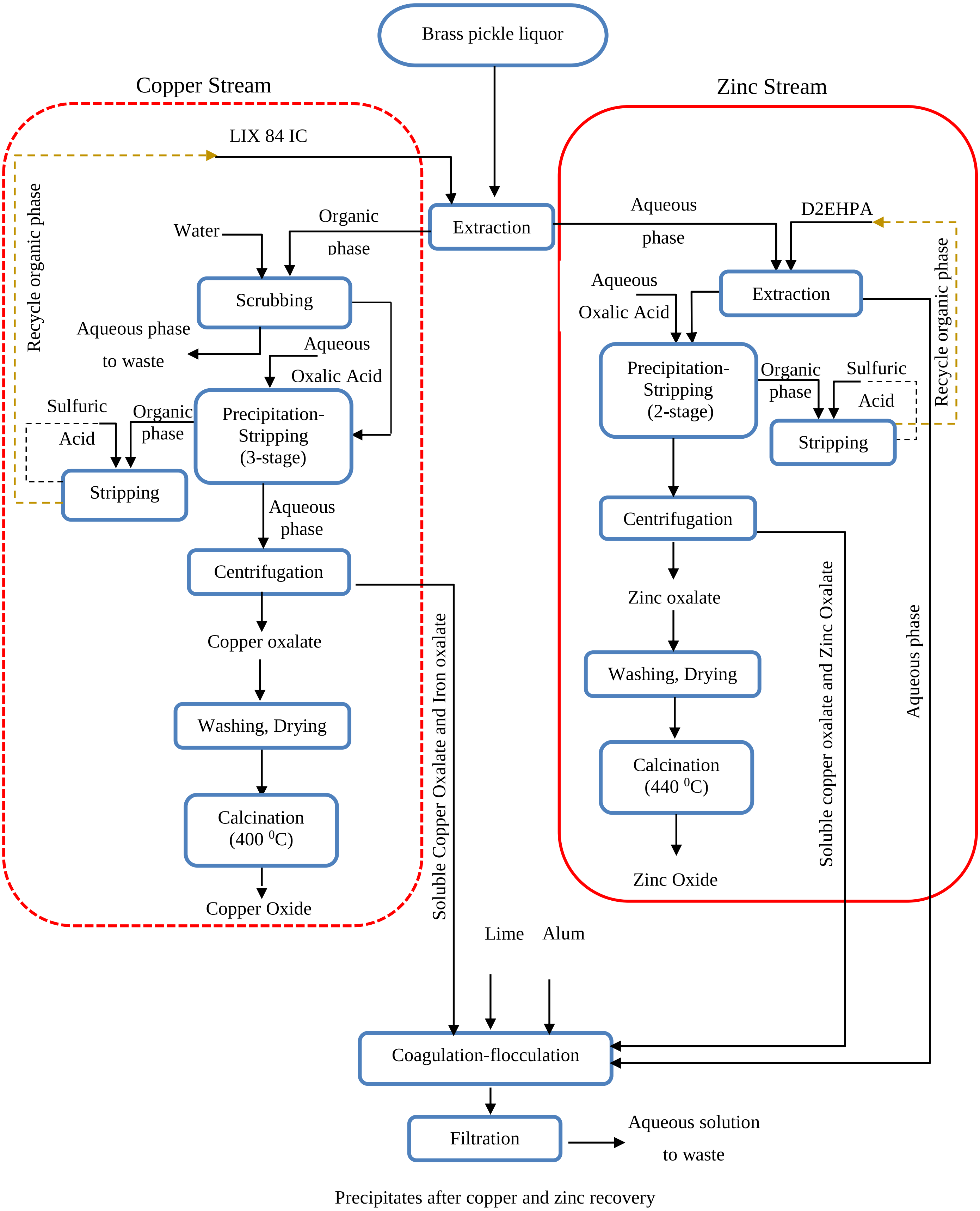

Fig. 7: Process scheme for the recovery of copper and zinc from pickle liqour

Metal reclamation by hydrometallurgical route from chloride media invariably involves transfer of chloride to the stripping phase resulting in chlorine liberation at the anode during electrowinning. Further, copper, iron and zinc often coexist in chloride leach solutions from industrial effluents. Separation of iron from the two metals is problematic as iron is co-extracted during extraction with most of the extractants. This problem can be circumvented if precipitation stripping is adopted, since the co-extracted iron gets removed in the form of soluble oxalate, removing it from the process mainstream.

Chapter 5: Reclamation of copper from spent ammoniacal Printed Circuit Board (PCB) etch solutions

An extraction-stripping scheme was developed to recover copper from spent ammoniacal etching solution collected from a PCB manufacturing industry in Vadodara containing 51.8 g/L copper having an initial pH value of 8.5 using LIX 84-I as the extractant in kerosene. PS technique was used for regenerating the extractant and simultaneously producing copper oxalate particles. The copper oxalate thus obtained was calcined to obtain copper oxide that has considerable commercial potential.

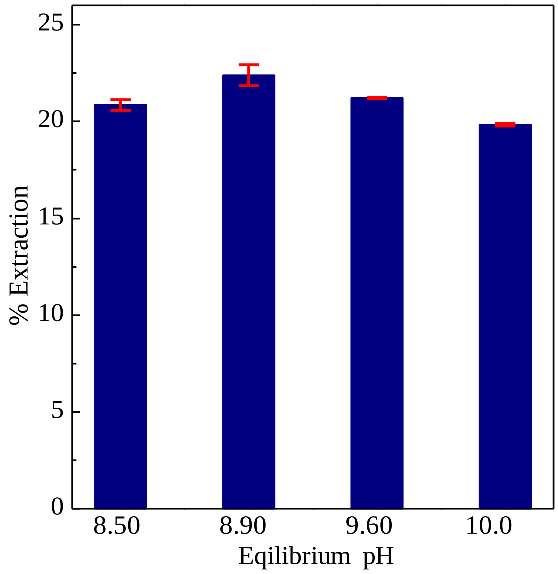

Fig.8: Effect of equilibrium pH on percentage extraction (LIX 84-I=20% (v/v), O/A= 1)

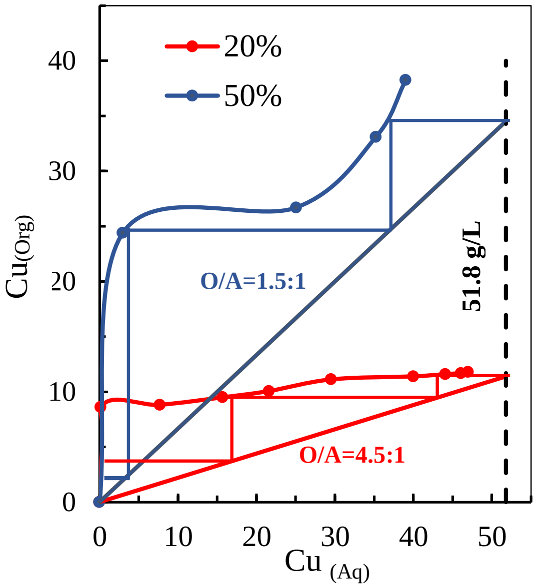

Fig.9: McCabe–Thiele plot for copper extraction using LIX 84-I

Effect of pH on copper extraction was investigated and a maximum extraction was obtained at a pH value of 8.9 (Figure 8). Extraction using 20% (v/v) and 50% (v/v) were investigated at organic to aqueous ratios of 4.5:1 and 1.5:1 respectively. In both the cases three equilibrium stages are required as indicated by McCabe -Thiele plots (Figure 9).

Stripping of the metal loaded organic phase with 1 M ethanolic oxalic acid solution required just one stripping stage when ethanol content was 25%, E(25) and more 50%, E(50). However, when oxalic acid solution (AQ) and 10% ethanolic oxalic acid solution, E(10) was used two stripping stages was necessary. The stripping was complete in all cases in one hr contact between oil phase and oxalic acid. Figure 9 shows the scheme for extraction/stripping and recovery of copper as copper oxide from the spent etchant The particles produced in aqueous oxalic acid were of wide size distribution and quite aggregated while particles formed in 50% ethanolic oxalic acid were not only very small in size but had a very narrow distribution as well. (Figure 10)

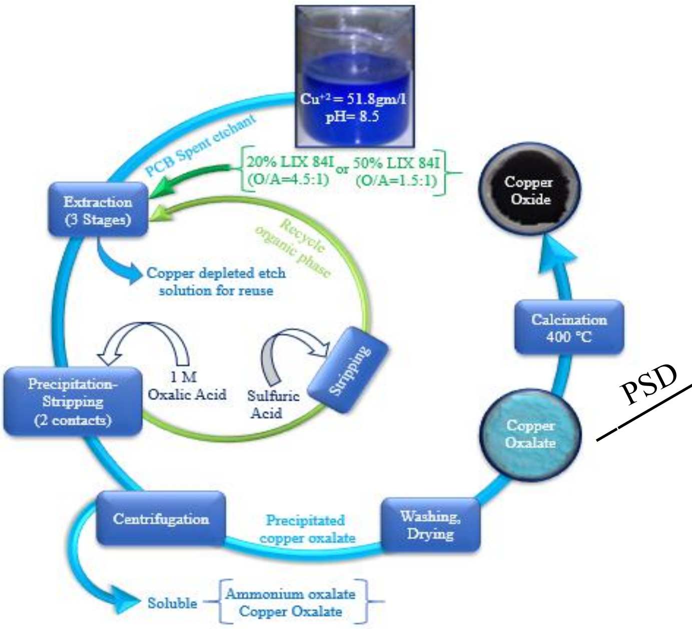

Fig. 9: Process scheme for copper recovery from spent PCB etch solutions

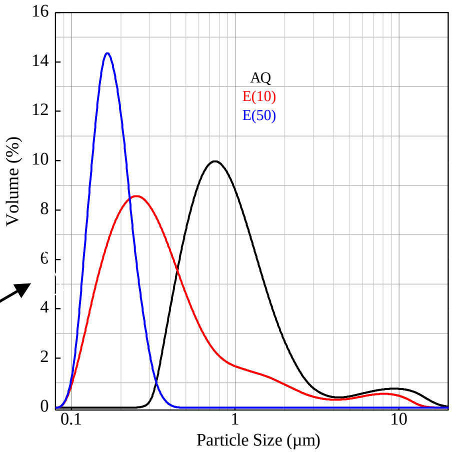

Fig. 10: Particle size distribution of copper oxalate

Particles were characterized by XRD, FTIR, FESEM etc. and were identified as pure copper oxalate matching with JCPDS No. 21-297. TGA of particles identified the decomposition patterns and copper oxalate. The oxide particles were also characterized by XRD, EDX, FTIR, the morphology was observed by FESEM, particle size distribution was determined, surface charge zeta potential were measured. CuO particles obtained matched JCPDS No. 5-661, no impurities were observed.

The copper oxide prepared was used to catalyze the reduction of nitrobenzene to aniline and the effects of various parameters were investigated. The overall conversion was found to be over 98% with 100% selectivity. The catalyst could be reused a number of times without any loss of activity.

Chapter 6 Particle formation during precipitation-stripping

Brass rinse liquors were used to recover copper and zinc on the same lines as brass pickle liquors for the recovery of these metals. The concentration of the metals in the rinse solution was significantly lower than the concentration of metals in the brass pickle liquor. Hence, the extraction circuits were designed to recover copper using 10% (v/v) LIX 84I-C and subsequently zinc was recovered using 10% (v/v) D2EHPA. The recovery of copper was quantitative at an equilibrium pH of 2.5. While 98.8% zinc was recovered at an equilibrium pH of 3.

The metal values were reclaimed by PS that regenerated the solvent for reuse. The efficacy of PS was explored over a wide range of parametric space and the nature of the particles obtained under different precipitating conditions was investigated. Key parameters varied were rate of agitation, precipitation time, concentration of oxalic acid and initial metal concentration. For all these situations the PSD were obtained and an attempt is made to interpret the precipitation patterns.

Striping mechanism of copper from LIX 84-IC and zinc from D2EHPA are significantly different since copper is held as a chelate while zinc could be bonded as well as solubilized by D2EHPA. Precipitation of particles in Cu-LIX 84-IC system takes place at the interface while in the case of D2EHPA because of its phase transfer behavior stripping also takes place in the aqueous film surrounding the oil phase. It was observed that copper stripping is much better defined than the stripping of zinc. Increasing the agitation increased % yield of particle (Figure 12 and Figure 13).

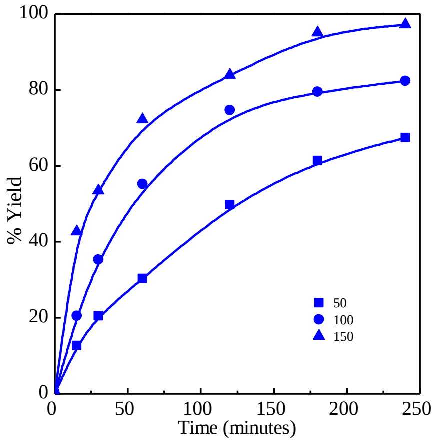

Fig.12: Effect of RPM on copper stripping (Cu- 4.365 g/L, oxalic acid 1M)

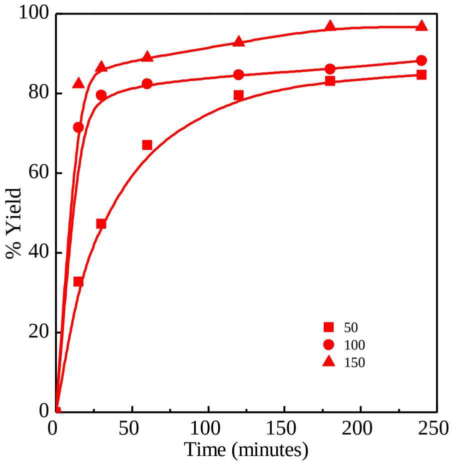

Fig. 13: Effect of RPM on zinc stripping (Zn- 2.73 g/L, oxalic acid 1M)

In both the cases the precipitation yields consistently increased with concentration of oxalic acid. With an increase in degree of agitation and contact time, the PSD narrows and there is a shift towards smaller particle sizes and more stable size distribution patterns emerge.

The effect of concentration of oxalic acid on copper stripping is not very pronounced although there are differences in particle sizes when oxalic acid concentration is changed from 0.078 to 1M (Figure 14). For the case of zinc oxalate there is a drastic reduction in particle size with increase in oxalic acid concentration (Figure 15). The $d_{0.5}$ shifts from 18.26 mm at 0.057M to 3.07 mm at 1M concentration. A four to fivefold increase in concentration of the metal in the organic phase did not make any significant difference in the PSD obtained.

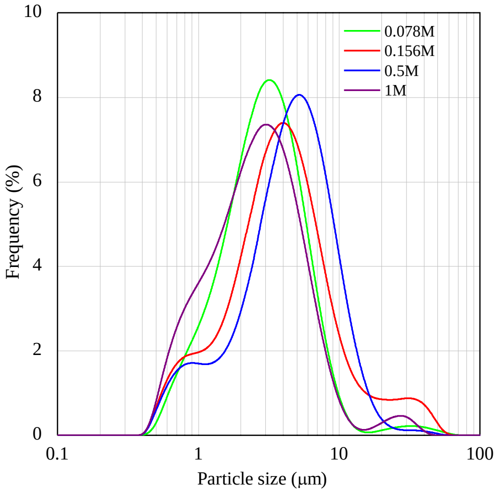

Fig.14: Effect of oxalic acid concentration on copper oxalate (Cu= 4.365 g/L, t=3 hr)

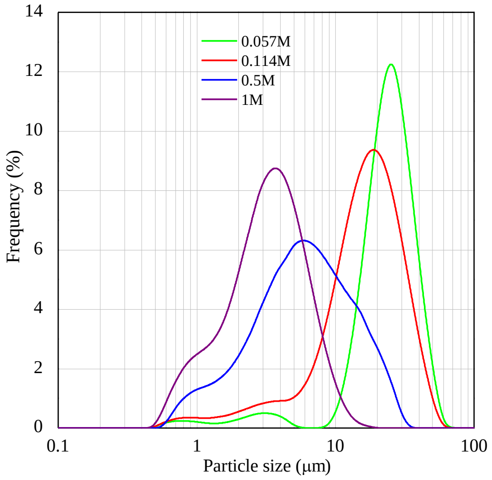

Fig.15: Effect of oxalic acid concentration on zinc oxalate (Zn= 2.73 g/L, t=3 hr)

The particles obtained were characterized by XRD, FTIR, EDX and XRF studies and results indicated that pure copper and zinc oxalate were obtained. Morphology of the copper oxalate particles were cushion shaped (Figure 16) whereas zinc oxalate particles had sharp edges which were built layer by layer (Figure 17)

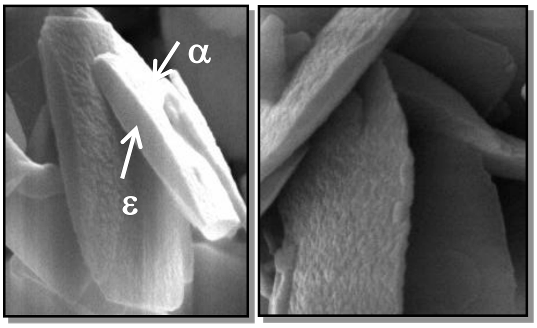

Fig.16: FESEM of copper oxalate (Cu=4.365 g/L, t=3hr)

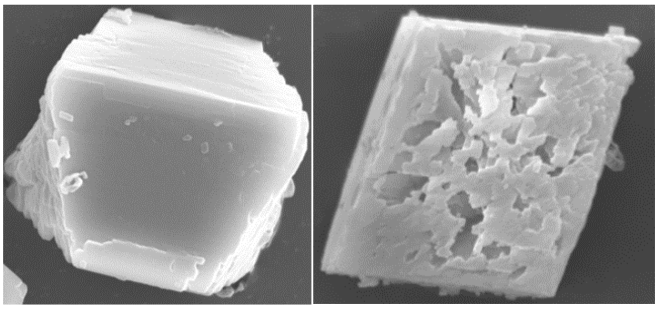

Fig.17: FESEM of zinc oxalate Zn=2.73 g/L, t=15 min

transformation to the oxide did not lose its ordered structure. XRD analysis revealed that pure copper oxide and zinc oxide were obtained. For both copper and zinc oxide the metal-oxygen ratios were in stoichiometric proportions.

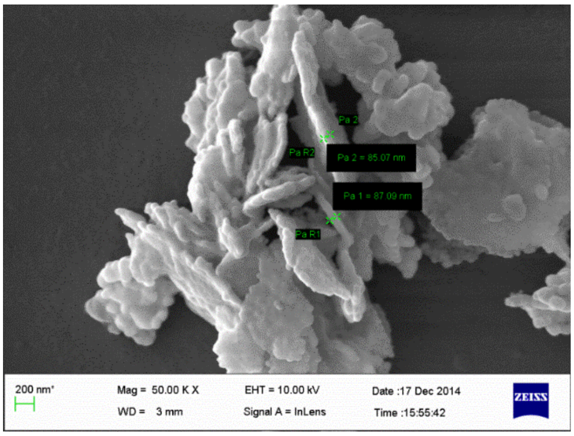

Fig. 18:FESEM image of copper oxide

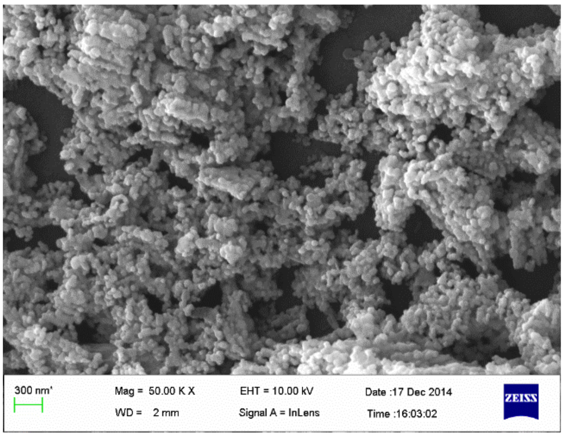

Fig. 19: FESEM image of zinc oxide

The antibacterial activity of copper oxide and zinc oxide were evaluated against four Gram-negative and one gram positive bacteria. Both the oxides exhibited antibacterial activity when tested against the five organisms. The diameter of the inhibition zone which reflects the susceptibility of the microorganism was higher for copper oxide.

Conclusions

Processes have been developed to recover copper and zinc from three different industrial waste streams containing copper in the range of ~50g/L to 4.38 g/L and zinc 12.6 g/l to 2.78g/L. Almost 99% recovery was achieved in all the cases and the residual metal values could be precipitated out thereby releasing the aqueous streams free of metals as effluents from the brass units while recirculating the ammoniacal etch solution back to the process in PCB units. Copper and zinc where finally obtained as pure oxides and applications of copper oxide as a catalyst for reduction reactions and both copper and zinc oxide as antibacterial agents were investigated. However, numerous other applications of these oxides as gas sensors, in photovoltaic cells, ceramics, catalysts etc. need to be specifically explored and tailoring of the recovery processes towards specific outcome should be attempted in the future. Developing appropriate technologies to process such metal containing effluent streams gives us an opportunity to fulfill the twin goals of environmental sustainability and economic gain.

References:

- Davis JR. Surface Engineering. In: Copper and copper alloys. ASM Specialty Handbook. 2001; 320-321. Davis JR. (ed.), ASM International, Materials Park.
- Bode H. Control of heavy metal emission from metal plating industry in a German river basin. *Water Sci Technol.* 1998; 38: 4-5, 121-129.
- Benito Y, Ruiz ML. Reverse osmosis applied to metal finishing wastewater. *Desalination.* 2002; 142: 229–234.
- Barakat MA. New trends in removing heavy metals from industrial wastewater. *Arab J Chem.* 2011; 4: 361–377.
- Elejalde C, Romero F,Diaz JM. Separation and recovery of heavy metals from hydrometallurgical effluents by solvent extraction. *Fresenius J Anal Chem.* 1991; 340: 182-185.
- Zewail TM, El-Garf SAM. Preparation of agriculture residue based adsorbents for heavy metal removal. *Desalin Water Treat.* 2010; 22: 363-370.
- Abdel Salam OE, Reiad NA, ElShafei MM. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *J Adv Res.* 2011; 2(4): 297-303.
- Chen Hsiu-Liang, Tseng Yun-Sheng, Hsu Kung-Chung. Spent FCC catalyst as a pozzolanic material for high-performance mortars. *Cem Concr Composites.* 2004; 26: 657–664.
- Jha MK, Kumar V, Bagchi D, Singh RJ, Lee J chun. Processing of rayon waste effluent for the recovery of zinc and separation of calcium using thiophosphinic extractant. *J Hazard Mater.* 2007; 145(1-2): 221-226.
- Apaydin O, Kurt U, Gonullu MT. An investigation on the treatment of tannery wastewater by electrocoagulation. *Water.* 2009; 11(4): 546-555.
- Fu F, Wang Q. Removal of heavy metal ions from waste water: a review. *J Environ Manage.* 2011; 92 (3): 407-418.
- Kadirvelu K, Goel J. Eco-friendly technology for removal of hazardous heavy metal from water and industrial wastewater. In: *Hazardous Materials and Wastewater:* Treatment, Removal and Analysis. Lewinsky AL. (ed.) Nova Publishers, New York.
- Zhao M, Xu Y, Zhang C, Rong H, Zeng G. New trends in removing heavy metals from wastewater. *Appl Microbiol Biotechnol.* 2016; 100 (15): 6509-6518.

- Ravindra KG, Sharma SK, Mahiya S, Chattopadhyaya CM. Contamination of heavy metals in aquatic media: Transport, toxicity and technologies for remediation. In: *Heavy Metals in Water:* Presence, Removal and Safety. 2015; Sharma SK. (Ed.) RSC.
- Abdul-Raouf MS, Abdul-Raheim ARM. Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review. *J Pollut Eff Control*. 2017; 5(1): 1-13.
- Wang X, Zhou K, Ma Z, Lu X, Wang L, Wang Z, Gao X. Preparation and characterization of novel polyvinylidene fluoride/2-aminobenzothiazole modified ultrafiltration membrane for the removal of Cr(VI) in wastewater. *Polymers*. 2017; 10(1): 1-10.
- Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicol Environ Saf*. 2018; 148: 702-712.
- Kurniawan TA, Chan GYS, Lo WH, Babel S. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chem Eng J*. 2006; 118 (1-2): 83-98.
- Hakizimana JN, Gourich B, Chafi M, Stiriba Y, Vial C, Drogui P, Naja J. Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination.* 2017; 404: 1-21.
- Rubio J, Smith RW. Overview of flotation as a wastewater treatment technique. *Miner Eng*. 2002; 15(15): 139–155.
- Stuart LG, Greenberg LA. Optimized wastewater treatment for a printed circuit board facility.1999; 1-10.
- Rajasulochana P, Preethy V. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. *Resour Technol*. 2016; 2(4): 175-184.
- Carolin CF, Kumar PS, Saravanan A, Joshiba GJ, Naushad M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J Environ Chem Eng.* 2017; 5 (3): 2782-2799.
- Wilson AM, Bailey PJ, Tasker PA, Turkington JR, Grant RA, Love JB. Solvent extraction: The coordination chemistry behind extractive metallurgy. *Chem Soc Rev*. 2014; 43(1): 123-134.

- Cox M. The use of solvent extraction in the recovery of waste. In: *Solvent extraction principles and practices*. 2004.609-649. Rydberg J, Cox M, Musikas C, Choppin G. (eds.) CRC Press.
- Ritcey GM. Solvent extraction in hydrometallurgy: Present and future. *Tsinghua Sci Technol.* 2006; 11(2): 137-152.
- Chapman TW. Extraction-Metal processing. In: Handbook of Separation Process Technology. Rousseau RW. (ed.) 2009; 467-499. John Wiley & Sons.
- Ramachandra Rao S. Resource Recovery and Recycling from Metallurgical Wastes. 2007; 7: 71-108. Elsevier Science.
- Rydberg J, Cox M, Musikas C, Choppin G. Solvent extraction principles and practice. Revised and Expanded. 2004. CRC press.
- Sulaimana RNR, Othman N. Solvent extraction of nickel ions from electroless nickel plating wastewater using synergistic green binary mixture of D2EHPA-Octanol system. *J Environ Chem Eng.* 2018; 6(2): 1814-1820.
- Sinha MK, Sahu SK, Meshram P, Pandey BD, Kumar V. Solvent extraction and separation of copper and zinc from a pickling solution. *Int J Metall Eng*. 2012; 1(2): 28–34.
- Sun Q, Wang W, Yang L, Huang S, Xu Z, Ji Z. Separation and recovery of heavy metals from concentrated smelting wastewater by synergistic solvent extraction using a mixture of 2-hydroxy-5-trimethylpentyl-phosphinic acid. *Solvent Extr Ion Exch.* 2018; 36(2): 175-190.
- Standard Methods for the Examination of Water and Wastewater, 22nd ed., APHA, AWWA, WEF, Washington, DC, USA, 2012, pp. 4.72-4.190.
- Standard Methods for the Examination of Water and Wastewater, 16th ed., APHA, AWWA, WEF, Washington, DC, USA, 1985, pp. 397-398.
- Navaroo C, Ruiz M. Solvent extraction of copper from chloride solutions with LIX 860N-IC and LIX 84-IC. *Rev Metal Madrid.* 2001; 37: 483-491.