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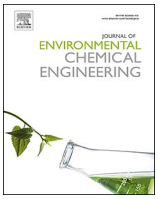

Research Paper

Selective separation of copper and zinc from spent chloride brass pickle liquors using solvent extraction and metal recovery by precipitation-stripping

Khyati Shah, Kamalesh Gupta, Bina Sengupta*

Chemical Engineering Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, India

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ABSTRACT

Copper and zinc were recovered from spent chloride brass pickle liquor using solvent extraction and precipitation-stripping. Speciation diagrams reveal that bivalent copper and zinc and their monovalent chlorocomplexes were present in the liquor. Copper was extracted by hydroxyoxime LIX84IC in kerosene while zinc was extracted using D2EHPA. 98.8% copper was extracted at an equilibrium pH of 2.5 using 30% v/v LIX 84IC whereas 98.3% zinc was extracted at an equilibrium pH of 2 using 15% v/v D2EHPA. Precipitation-stripping of loaded organic phase using oxalic acid resulted in recovery of copper and zinc as water insoluble oxalates. Solubility plots developed on theoretical considerations for copper-oxalic acid and zinc-oxalic acid system predicted the yield of precipitates in close agreement with experimental values. 97.3% of both copper and zinc present in the pickle liquor were recovered as their oxalates. The organic phase could be used for multiple cycles. Calcinations of the oxalates to their oxides did not induce any change in the ordered structure observed in oxalates. Morphology of the precipitates revealed highly agglomerated particles. Copper oxide 100% pure and zinc oxide with 99.1% purity were obtained as value added products. A process flow diagram of the proposed scheme is presented that could be implemented to generate wealth from waste.

1. Introduction

Brass, an alloy of copper and zinc finds wide application due to its unique combination of properties such as strength, malleability, and good thermal conductivity. It can be easily cast to shape and used for costume jewellery, decorative trims and other similar applications because of its bright gold like appearance. India is well known for its brass jewellery, artefacts and industrial components. Brass on exposure to atmosphere undergoes surface discolouration, called tarnish, due to formation of a thin oxide layer that needs to be removed to impart its lustrous look. Cleaning and finishing process to remove tarnish and oxide layer formed on industrial brass components subjected to heat treatment process involves stages of acid wash and water rinse [1]. 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 metal loaded pickle liquor and rinse waters are often discharged to sewers without any treatment. Heavy metals in discharge waters pose considerable threat as they enter the aquatic ecosystem where they bio-accumulate and bio-magnify in the food chain and become toxic for living organisms at higher tropic levels in nature [2]. Although copper and zinc are essential nutrients for various enzymatic reactions, but at high concentrations both aquatic as well as human life are adversely affected. Hence, recovery of these metals is not only important from the point of view of pollution abatement but also results in profit by recycling of the metals.

A continuous research effort is focussed on developing options for the recovery of metals from aqueous waste streams and a number of processes are also available [3]. Around 30% of zinc and 40% of copper produced in the world arises from recycling of secondary sources. Recovery of copper and zinc from brass ash, brass dross and slag, brass flue dust, soil contaminated from brass industry and brass pickle liquors using different techniques is reported in Table 1 [4–15].

Solvent extraction (SX) is the dominant hydrometallurgical process to recover copper from ores as well as secondary sources. Selective extraction of copper using chelating extractants is well known from

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* Corresponding author.
E-mail address: bina_msu@yahoo.co.in (B. Sengupta).

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Table 1
Recovery of copper and zinc from brass components/pickle liquors.

Sr. No.	Brass component	Treatment technique	Recovered as	Reference
1.	Brass ash	Leaching with Ionic liquid	Copper and zinc solution in Ionic liquid	[4]
		Carbothermal recovery by graphite treatment of ash in temperature controlled tube furnace	Metallic zinc and zinc oxide	[5]
		Beneficiation by acidic or/and alkaline leachant	Cement copper and zinc sulphate solution	[6]
		Solvent extraction using 20% LIX84 and 0.25 M NH_4D2EHPA in kerosene	Copper and zinc pregnant electrolyte	[7]
2.	Industrial brass dross	Ionic liquid oxidative leaching	Copper and zinc	[8]
3.	Brass Slag	Leaching with sulfuric acid	Spongy copper powder, zinc sulphate crystals	[9]
		Hydrometallurgical treatment using acid or alkali leachant	Copper salts and zinc salts	[10]
4.	Brass flue dust	Briquetting with coke and reduction in tube furnace to recover zinc using vaporization and condensation	Zinc and zinc oxide	[11]
5.	Industrial brass wastes, brass ash and flue dust	Combined pyro-hydrometallurgical treatment	Copper master alloy, metallic zinc	[12]
6.	Brass filings	Acid leaching with an oxidizing agent	Copper oxychloride and zinc hydroxide	[13]
7.	Brass pickle liquor	Solvent extraction using 30% LIX 984N in kerosene	Copper and zinc oxide powder	[14]
		Solvent extraction using 30% Versatic acid and 20% CYANEX 272 in kerosene	Copper sulphate solution, zinc sulphate solution	[15]

sulphate, chloride and nitrate media [16]. Copper hydrometallurgy and extraction from chloride media is discussed in detail by Szymanowski [17]. Chelating extractants LIX64N [18], LIX 65NHS [19], and LIX 860N IC and LIX84 IC [20,21] have been reported for copper extraction from chloride media.

SX techniques are widely used for upgrading and purification of zinc streams. Zincex and the modified Zincex process used for the extraction of zinc from sulphate media are also suited for recovery of zinc from secondary sources such as zinc ash and brass ash [22]. Extraction of zinc using acidic, basic, solvating and mixed extractants from chloride solutions is reviewed by Jha et al. [23]. Zinclor process for zinc recovery from chloride media is used for the treatment of pickle liquors and effluents from surface treatment plants [24]. Both copper and zinc have also been extracted from chloride media using alkyl-8-hydroxyquinoline [25], Kelex 100 [26,27] and mixed extractants [28].

In conventional SX, metal reclamation from organic phase is by stripping with a strong acid followed by electrowinning. However, if loaded metal ions are stripped from the organic phase using oxalic acid, it results in precipitating the metal as a water insoluble metal oxalate. The metal gets stripped by hydrogen ions and is subsequently precipitated by oxalate anions. A combination of precipitation-stripping stages achieves complete stripping of metal ions at lower acidity than conventional stripping [29]. This method has been used for preparation of rare earth oxalates [30,31], nickel oxalate [32] and zinc oxalate [33]. Oxalates are often used as precursors for oxides in the synthesis of nanomaterials and high temperature superconductive ceramic materials as they can retain the nanostructure, particle shape and crystalline arrangement after thermal decomposition [34].

The present investigation is focused on recovery of copper and zinc from spent chloride pickle liquors generated from brass artefacts manufacturing units using solvent extraction and precipitation-stripping. The extracted metal values were precipitated as their oxalates and subsequently calcined and converted to their respective oxides. The optimum conditions for the maximum recovery of the metals as their oxalates were also determined. Metal oxalates and oxides were characterized for their morphology and purity. Flow sheet of the process for the recovery of copper and zinc as their respective oxides is proposed.

2. Materials and methods

2.1. Materials

Brass pickle liquor was collected from an industry in Rajkot, India. LIX 84 IC (Cognis, Ireland) and D2EHPA (Merck Specialties Private Limited, Germany) were used as metal extractants. Commercial kerosene (B.P- 152–271 °C) used as the solvent was supplied by Indian Oil Corporation Limited. Other reagents, sodium hydroxide, oxalic acid and sulphuric acid used were of AR grade.

2.2. Methods

The metal composition of the pickle liquor was determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 5300 DV). The chloride, sulphate and nitrate concentrations were determined by chemical analysis based on the APHA standard methods for examination of water and waste water. Argentometric method was used for chloride determination as per APHA: (4500 Cl^- B) [35], Turbidimetric method was used for sulphate determination as per APHA (4500 SO_4^{2-} E) [35] and Chromotropic acid method was used for nitrate determination as per APHA: (418-D) [36]. The values of the chloride, sulphate and nitrate concentrations determined are reported in Table 2. Extraction was carried out in shake flasks at equal organic and aqueous volumes (100 ml each) on a rotary shaker (Remi-RS 24BL) at 150 rpm and 30 °C. The organic phase for copper extraction consisted of LIX 84IC (7.5–30% v/v) in kerosene as diluent while for zinc extraction the organic phase was D2EHPA (5–15% v/v) in kerosene. Sodium hydroxide was added for pH adjustment before each equilibrium condition. The concentration of the metals was determined using Atomic Absorption Spectrometer (Chemito AA203) for copper at 324.7 nm, zinc at 213.86 nm and iron at

Table 2
Composition of brass pickle liquor.

Component	Concentration (g/L)
Cu	20
Zn	12.6
Fe	0.131
Ni	0.1
Na	7.4
Ca	0.226
Mg	0.099
Al	0.118
Sn	0.124
Chlorides	10.968
Sulphates	0.009
Nitrates	< 0.1 mg/L
pH	0.25

248.3 nm.

After extraction the organic phase was separated, scrubbed with water and contacted with an equal volume of oxalic acid at concentrations ranging from 0.3 M to 1.0 M. Precipitation-stripping was carried out in shake flasks with equal volume of organic and aqueous phase (100 ml each) on a rotary shaker (Remi-RS 24BL) at 30 °C and 150 rpm. After stripping, the organic phase and aqueous phase containing the metal oxalate was separated. The metal oxalate precipitate was separated from the aqueous phase by centrifugation, washed with 2-propanol and dried in an air oven at 60°C. The organic phase was further stripped with sulphuric acid to recover any residual metal present and contacted with fresh pickle liquor a number of times to evaluate the efficacy of extraction in different cycles. The oxalate precipitates were calcined under controlled conditions in a tube furnace (Ants Ceramics) to obtain the respective metal oxides. The heating rate was 5 °C/min. After attaining the desired temperature the material was soaked for three hours. Copper oxalate calcinations were carried out at 400 °C while zinc oxalate calcinations were at 440 °C.

2.3. Analytical techniques

Precipitated metal oxalates and their respective oxides were characterized by powder X-ray diffraction (XRD) on a PAN Analytical Xpert Pro diffractometer using Cu-Kα radiation at λ value of 1.54°A. Infrared spectroscopic analysis of the metal oxalate and oxide and the organic phase before and after extraction was performed over a frequency range of 400–4000 cm^{-1} with 32 scans using Thermo Scientific Nicolet iS5 spectrophotometer with iD1 transmission. Thermogravimetric analysis of the oxalates was performed at a heating rate of 20 °C/min in an oxygen atmosphere on a Shimadzu thermal analyser (50 GA). EDX (Oxford Instruments) analysis was performed to detect the metals present in the precipitates formed. The morphology of the oxalate and oxide particles was determined using Field Emission Scanning Electron Microscopy (FESEM) (Zeiss Supra 40).

3. Results and discussion

Metal extraction in multi-solute systems depends on the physicochemical properties and the nature of the metal species present in the solution; these factors influence the selection of metal extractants and design of the processing scheme. The spent pickle liquor obtained from industrial sources had an initial pH value of 0.25 with a chloride content of 10.968 g/L, sulphate content 0.009 g/L and nitrate content less than 0.1 mg/L. The initial metal composition determined by ICP analysis is shown in Table 2.

3.1. Metal ions in chloride media

Extraction of metals from solutions containing chloride ions is complex. Most of the transition metals form chlorocomplexes with metal ions; the chlorocomplexes formed depends on the chloride concentration. The presence of chlorocomplexes increases the $pH_{0.5}$ and the equilibrium shifts towards higher chlorocomplexes as the chloride concentration increases [17]. Eq. (1) is the general expression for the formation of chlorocomplexes based on the chloride concentration in the aqueous phase [26].

$$M^{2+} + nCl^{-} \rightarrow MCl_n^{2-n} \tag{1}$$

The stability constant (β_n) of the chlorocomplex is given by Eq. (2)

$$\beta_n = \frac{[MCl_n^{2-n}]}{[M^{2+}][Cl^{-}]^n},\ n = 1 - 4 \tag{2}$$

Fig. 1 shows the chlorocomplexes of copper and zinc present in the pickle liquor. Theoretically it is possible to determine the percentage of species present in the aqueous solution based on the formation constants. The speciation of the pickle liquor having copper concentration 20 g/L (0.314 M) and zinc concentration 12.6 g/L (0.192 M) at varying chloride concentrations was evaluated using *Visual MINTEQ 3.1* operating platform. At initial chloride concentration of 10.968 g/L 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 $ZnCl_2$. The monovalent specie ($CuCl^{+}$) is the first chlorocomplex formed in solutions containing low chloride concentrations (~1 M) and is capable of cation exchange [37], higher chloride concentrations in solutions lead to formation of trivalent and higher chlorocomplexes of the metals. Zinc chlorocomplexes are more stable than copper as observed from their higher stability constants [26].

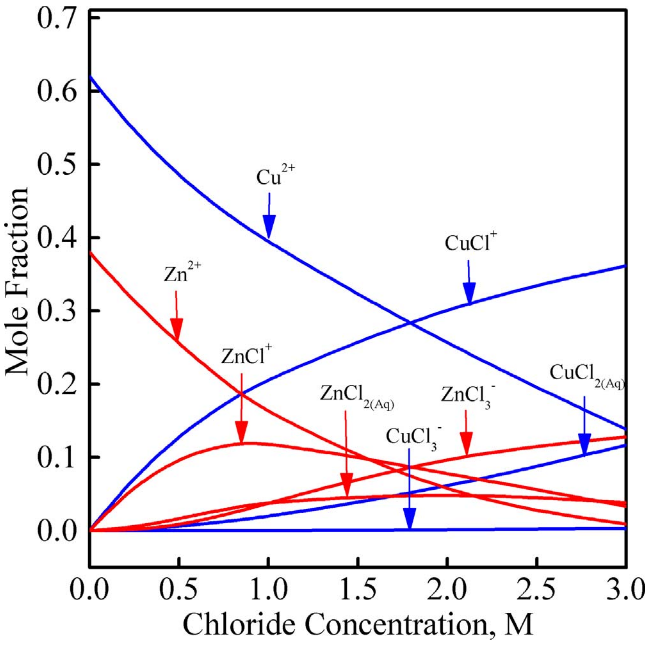

Fig. 1. Speciation diagram of copper and zinc in pickle liquor.

3.2. Extraction of copper using LIX 84 IC

LIX 84I a moderately strong chelating copper extractant selectively extracts copper over other metal ions with maximum extraction at pH 2-2.5 [38]. Extraction by chelation is an acid-base reaction wherein the oxime molecules donate protons in exchange for copper ions and the reaction takes place at the oil − water interface. The unpaired d orbital of copper is primarily responsible for complexation through electron pair of O and N atoms of the extractant molecules. The extraction of copper using hydroxyoximes is represented as

$$Cu^{2+} + 2RH \leftrightarrow CuR_2 + 2H^{+} \tag{3}$$

The formation of chlorocomplexes can affect the extraction of copper with hydroxyoximes in two ways; by reducing the concentration of the divalent Cu^{2+} cationic species and by the possibility of extracting the monovalent cationic complex, $CuCl^{+}$, or even the neutral $CuCl_2$ complex [20]. Zhou et al. [19] in their study on extraction of copper using LIX 65NHS explained the extraction of $CuCl^{+}$ by two possible mechanisms both leading to the formation of CuR_2 complex.

$$\text{Mechanism (1)}\qquad CuCl_i^{+} + RH_{ad} \leftrightarrow CuRCl_{ad} + H_i^{+} \tag{4}$$

$$CuRCl_{ad} + RH_i \leftrightarrow CuR_{2ad} + H_i^{+} + Cl_i^{-} \tag{5}$$

$$\text{Mechanism (2)}\qquad CuCl_i^{+} + RH_{ad} \leftrightarrow CuR_{ad}^{+} + H_i^{+} + Cl_i^{-} \tag{6}$$

$$CuR_{ad}^{+} + RH_i \leftrightarrow CuR_{2ad} + H_i^{+} \tag{7}$$

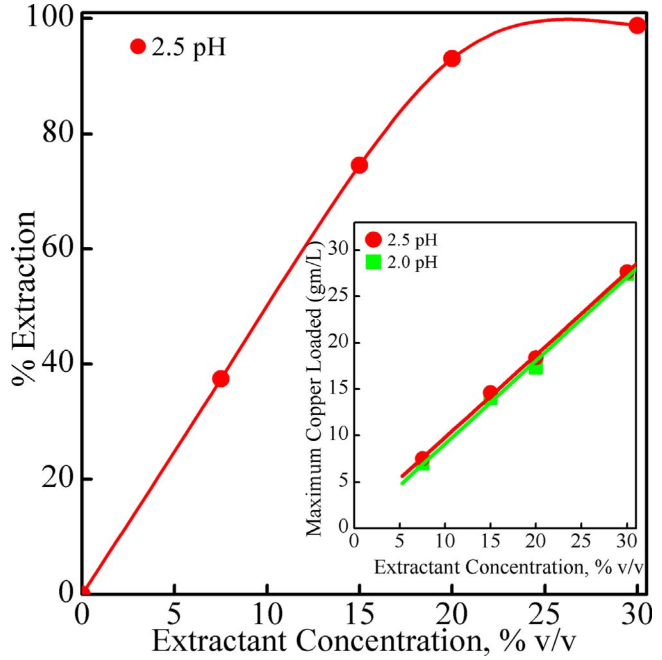

Fig. 2. Effect of LIX 84 IC concentration on copper extraction. (Inset: Maximum copper loading for LIX84IC in kerosene).

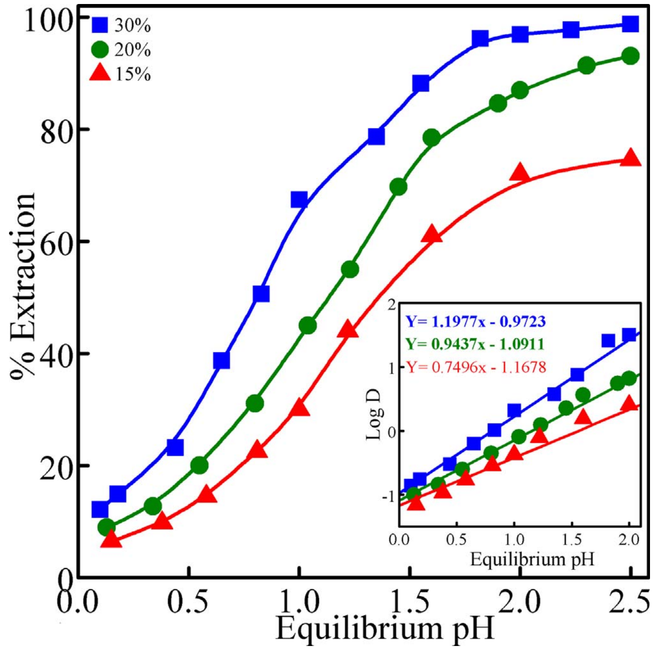

Fig. 3. Copper extraction using LIX84IC vs equilibrium pH at varying extractant concentrations. (Inset: Log D vs. equilibrium pH).

Most of the investigations on extraction of metals have been performed under experimental conditions that are deemed to be ideal, for single metal species at dilute concentration and extractant concentration in far excess than stoichiometric requirements. However, in reality situation is quite different. The extraction behaviour, the stoichiometric requirement and the presence of other metals all influence the extraction of metals. In the present study the industrial pickle liquor was used and metal extraction equilibria was determined under prevailing conditions.

Copper extraction was carried out using LIX 84IC 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 (Fig. 2) and at 30% v/v extractant concentration, 98.8% of initial copper present was extracted at an equilibrium pH of 2.5. The maximum loading capacity of LIX 84IC at an equilibrium pH value of 2 is found to be 0.9 g/L per 1% v/v of extractant as observed from the slope of the linear plot, maximum copper extracted vs extractant concentration (v/v), shown in Fig. 2 (inset). This is higher than the value of 0.7 reported for copper extraction from hydrochloride solutions at 2 pH using LIX 84IC [20] and 0.74 for copper removal from electroplating rinse bath solutions with high chloride concentrations in the equilibrium pH range of 1.7-2.1 using LIX 984NC [39].

The effect of pH on extraction for LIX84IC concentration from 15% v/v to 30%v/v is shown in Fig. 3. An increase in the extractant concentration, results in an increase in the percentage extraction and a decrease in $pH_{0.5}$ value. The plots of distribution coefficient vs equilibrium pH (Fig. 3, inset) is linear at all extractant concentrations, but the slope values are considerably lower than the theoretical value of 2, that is expected if the mechanism of extraction is exclusively by Eq. (3). Slope value of 2 in the plot of log D vs pH indicates binding of two oxime molecules with a single Cu^{2+} ion. Slope value of two is observed under ideal conditions when the concentration of extractant is in considerable excess to that of the metal ion [40]. Reduction in slope values could also occur due to the transfer of the monovalent ions ($CuCl^{+}$) along with the bivalent ions (Cu^{2+}). At low pH values $CuCl^{+}$ competes with Cu^{2+} whereas at higher pH values only Cu^{2+} is extracted [20].

Navarro and Ruiz [20] showed that LIX860NIC and to a lesser extent LIX84IC, extract $CuCl^{+}$. Earlier, LIX 63 was shown to transfer chlorocomplexes to organic phase [41]. Lakshmanan and Lawson [40] reported that LIX 64N and LIX 70 do not transfer $CuCl^{+}$ to the organic phase. The slope of log D vs pH obtained in this investigation points to the plausibility that the mechanism of extraction is perhaps not governed exclusively by Eq. (3), leaving scope for the transfer of $CuCl^{+}$ to the oil phase or being adsorbed at the interface after bonding as per Eq. (4) resulting in slope value markedly less than 2.

In such a situation less than two hydroxyoxime molecules bind with the copper ions, and consequently would lead to considerably greater extent of copper extraction. However, there is no convincing evidence to suggest that the decline in slope values is due to the transfer of $CuCl^{+}$ except that fairly large amount of copper was extracted. It is worthwhile noting that chloride uptake during extraction of metals has a deleterious effect during metal recovery by electrowinning, hence alternative recovery techniques must be considered for such cases.

Due to intermolecular hydrogen bonding hydroxyoximes have tendency to form dimers [42]. In the extraction environment hydroxyoxime molecules as well as their dimers could bind with copper. Hydroxyoxime dimerization can be ignored in solutions of aliphatic and aromatic hydrocarbons in hydroxyoxime concentration range of 0.01 and 0.1 mol/dm^{3} [42]. In the current investigation the hydroxyoxime concentration was much higher than this range.

Szymanowski [42] reported that in the IR spectra of 2- hydroxyl 5-alkylbenzaldehyde oxime the monomeric N—OH group manifests at 3580 cm^{-1} and the band at 3420 cm^{-1} is for the associated species and similar values were observed for other oximes. This finding was corroborated by Albrecht et al. [43] in their study on oximes and clusters by supersonic jet spectroscopy using IR direct absorption and Raman Scattering techniques and reported that for oxime the monomer peaks were at 3657 cm^{-1} and monomer/dimer peaks at 3364 cm^{-1}.

In the present investigation the infrared spectra for oxime in kerosene (organic phase), as well as the maximum copper loaded organic phase with extractant concentrations ranging from 7.5% to 30% v/v are shown in Fig. 4. The band due to N—OH monomeric group and the monomer/dimer were observed ~3593 cm^{-1} and ~3375 cm^{-1} respectively. The bands associated with stretching vibrations of the C—H bonds in CH_2 and CH_3 groups are in the range of 2960–2850 cm^{-1}. The absorption bands at 1585.53 cm^{-1} and 1620.25 cm^{-1} are assigned to C═N stretching vibrations and at 1494.8 and 1460.1 cm^{-1} assigned to —C═C— stretching vibrations. The absorption band of C—O—H

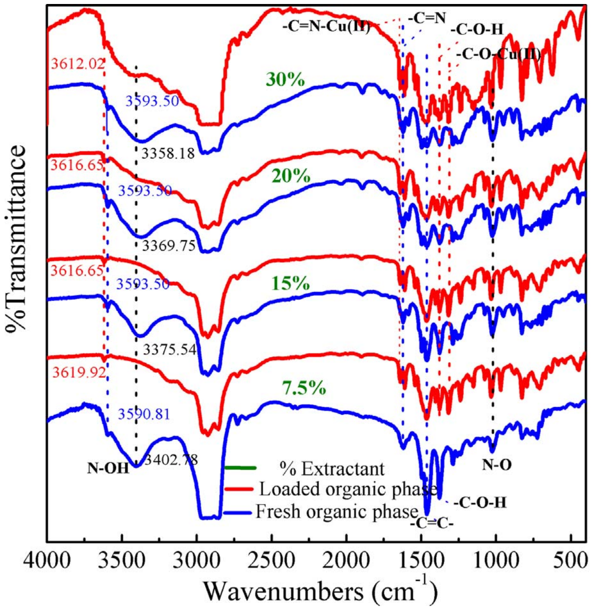

Fig. 4. FTIR spectra of fresh and copper loaded organic phase at varying LIX 84IC concentrations.

attached to the phenolic structure is at 1383 cm^{-1} and that assigned to nitrogen-oxygen stretching vibrations is observed at 1024 cm^{-1}. The IR spectrum of LIX84-IC loaded with copper shows absorption band at 1610.61 cm^{-1} assigned to C═N─Cu (II) stretching vibrations and at 1402.96 cm^{-1} assigned to the Cu(II) complex [44]. A shift in absorption band at 1377.2 cm^{-1} indicates C─O─H whereas stretching vibrations C─O─Cu (II) coordination bond is at 1317.42 cm^{-1}.The absorption band at 1030.02 cm^{-1} is assigned to N─O stretching vibrations.

The maximum copper loaded organic phase at all oxime concentrations studied, show absence of the monomer/dimer peak and peak shift from ∼3593 cm^{-1} to ∼3616 cm^{-1} corresponding to the monomeric group of the oxime, thereby indicating that both monomeric and dimeric groups are involved in the complexation process. This unfolds a very complex picture of molecular association and bonding in chloride media between hydroxyoxime and the copper ions with adsorbed complexes and the two ionic species of copper binding with monomeric, dimeric oximes.

3.3. Precipitation – stripping of copper 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. The acid dissociates into hydrogen ions and oxalate anions in the aqueous phase and acts both as a stripping and precipitating agent. Copper ion is released from the copper-oxime complex at the organic − aqueous interface by exchange with H$^+$ ions. The Cu^{2+} cation transfers to the aqueous phase where it undergoes a second reaction with the oxalate anion in the vicinity of the interface to form copper oxalate precipitate. Overall rate of stripping is controlled by the diffusion of the metal complex from the bulk of the organic to the liquid–liquid interface [45]. The driving force for mass transfer is high when the organic phase metal concentration is high. Stripping is much faster at high concentration of metal complex in organic phase. The faster rate at which metal ions are supplied to the aqueous solution combined with high stirring, results in production of finer oxalate particles. This is caused by the fast nucleation under the conditions where the aqueous phase copper concentration rises more rapidly to the threshold concentration at which nucleation can occur [29].

3.3.1. Theoretical aspects

The stripping and precipitation of copper with oxalic acid can be represented by Eq. (8)

$$CuR_2 + H_2C_2O_4 \rightarrow CuC_2O_4 + 2RH \tag{8}$$

Oxalic acid in solution dissociates into hydrogen ions and oxalate anions depending on the solution pH.

$$H_2C_2O_4 = H^+ + HC_2O_4{}^- \tag{9}$$

$$HC_2O_4 = H^+ + C_2O_4{}^{2-} \tag{10}$$

In a solution of oxalic acid, molecules of oxalic acid and its ions $HC_2O_4^-$ and $C_2O_4^{2-}$ co-exist in equilibrium. In strong acidic solutions pH < 2, $C_2O_4^{2-}$ concentration is negligible and the dominant species is $C_2O_4^-$. At pH values > 3 complete ionisation is there and both $C_2O_4^{2-}$and $HC_2O_4^-$ are formed. $C_2O_4^{2-}$ concentration is high in alkaline solutions and low in acidic solutions [46].

The equilibrium constant for Eqs. (9) and (10) are represented as K_1andK_2 respectively. The oxalate species can be expressed as

$$[C_2O_4{}^-] = \alpha_{C_2O_4} A_T \tag{11}$$

$$[C_2O_4{}^{2-}] = \left[1 + \frac{H^+}{K_1} + \frac{[H^+]^2}{K_1K_2}\right] A_T \tag{12}$$

Where, $A_T = H_2C_2O_4 + HC_2O_4 + C_2O_4{}^{2-}$ the total concentration of the oxalates and $\alpha_{C_2O_4}$ is the ionisation fraction of oxalate anion $C_2O_4{}^{2-}$. Introducing the equilibrium constants $K_1$and K_2 (Table 3) and total concentration $A_{T,}$ gives the concentration of oxalate species $(C_2O_4{}^{2-})$ at different pH values.

The solubility equilibrium for copper- oxalic acid system can be expressed as,

$$CuC_2O_{4(s)} = Cu^{2+} + C_2O_4{}^{2-} \tag{13}$$

Taking logarithm and rearranging gives

$$log\,[Cu^{2+}] = logK_{SP} - logC_2O_4{}^{2-} \tag{14}$$

Substituting the value of $C_2O_4{}^{2-}$ and K_{SP} results in Cu^{2+} concentration equilibrated with $CuC_2O_{4(s)}$ Fig. 5a shows the solubility curve, $CuC_2O_{4(S)}$ as a function of pH. Besides the solubility equilibrium, Cu^{2+} complexes with oxalate anion forming various soluble species $Cu(HC_2O_4)^+$, $CuC_2O_{4(aq)}$, $Cu(C_2O_4)_2^{2-}$. Since the domain in the current investigation is acidic the hydroxide species are neglected. Copper oxalate has appreciable solubility in the presence of excess oxalate ions due to the formation of increasing quantities of $Cu(C_2O_4)_2{}^{2-}$ [47].

Oxalate anion reacts with Cu^{2+} cation in aqueous solution to form successively two soluble complexes represented by the Eqs. (15) and (16). The complexes are characterized by their stability constants β_1 and β_2 respectively.

Table 3
Equilibrium constants of formation reactions of copper oxalate and zinc oxalate complexes.

Equilibrium reactions	Log of constant	Reference
$HC_2O_4 = H^+ + C_2O_4{}^-$	$K_1 = -4.266$	[48]
$H_2C_2O_4 = H^+ + HC_2O_4{}^-$	$K_2 = -1.252$	[48]
$CuC_2O_{4(s)} = Cu^{2+} + C_2O_4{}^{2-}$	$K_{SP} = -9.35$	[49]
$Cu^{2+} + C_2O_4{}^{2-} = CuC_2O_{4(aq)}$	$\beta_1 = 6.23$	[48]
$Cu^{2+} + 2C_2O_4{}^{2-} = Cu(C_2O_4)_2^{2-}$	$\beta_2 = 10.27$	[48]
$Cu^{2+} + HC_2O_4{}^{2-} = Cu(HC_2O_4)^+$	$\beta_3 = 7.32$	[48]
$ZnC_2O_{4(s)} = Zn^{2+} + C_2O_4{}^{2-}$	$K_{SP} = -8.86$	[49]
$Zn^{2+} + C_2O_4{}^{2-} = ZnC_2O_{4(aq)}$	$\beta_1 = 4.87$	[48]
$Zn^{2+} + 2C_2O_4{}^{2-} = Zn(C_2O_4)_2^{2-}$	$\beta_2 = 7.65$	[48]
$Zn^{2+} + HC_2O_4{}^{2-} = Zn(HC_2O_4)^+$	$\beta_3 = 6.44$	[48]
$Zn^{2+} + 2HC_2O_4{}^{2-} = Zn(HC_2O_4)_2$	$\beta_4 = 12.32$	[48]

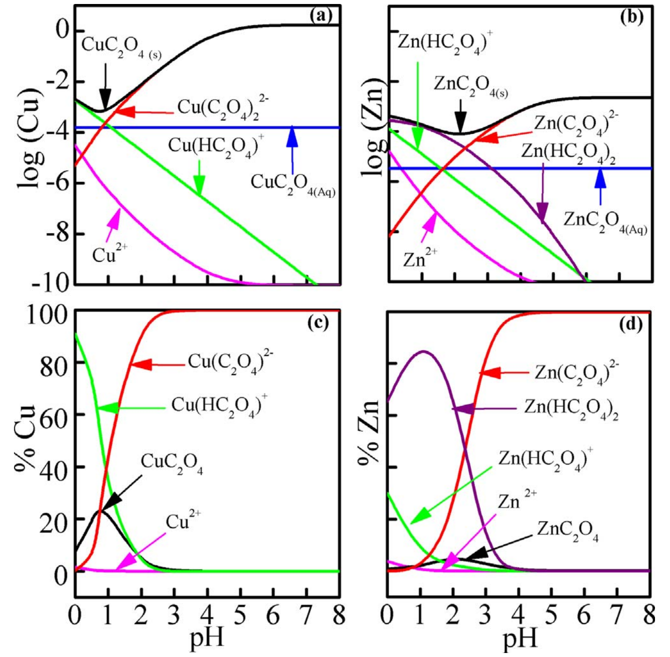

Fig. 5. Solubility diagram: (a) Copper-oxalic acid system, (b) Zinc-oxalic acid system. Soluble specie distribution curves: (c) Copper oxalate, (d) Zinc oxalate.

Table 4
Stage wise recovery of copper and zinc.

Stage No.	Copper loaded (19.76 gm)				Zinc loaded (12.38 gm)			
	S (gm)	P (gm)	% Yield		S (gm)	P (gm)	% Yield	
			E	T			E	T
1	13.26	13.17	99.32	99.68	9.78	9.72	99.38	99.83
2	4.15	4.06	97.83	98.96	2.59	2.55	98.45	99.82
3	2.31	2.25	97.4	98.14	–	–		
Total	19.72	19.48			12.37	12.27		

S: Stripped, P: Precipitated, E: Experimental, T: Theoretical.

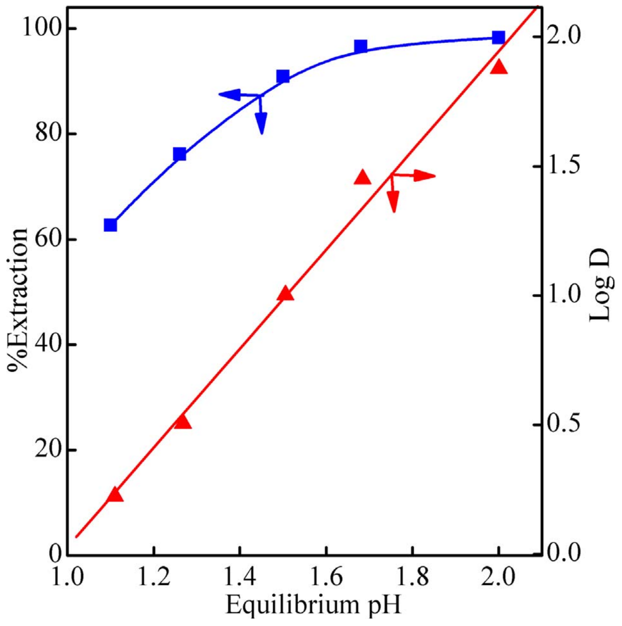

Fig. 6. Zinc extraction isotherm using D2EHPA. (Inset: log D vs. equilibrium pH).

$$Cu^{2+} + C_2O_4{}^{2-} = CuC_2O_{4(aq)} \tag{15}$$

$$Cu^{2+} + 2C_2O_4{}^{2-} = Cu(C_2O_4)_2^{2-} \tag{16}$$

$$\beta_1 = \frac{[CuC_2O_4\ ]}{[Cu^{2+}][C_2O_4{}^{2-}]} \quad \beta_2 = \frac{[Cu(C_2O_4)_2^{2-}]}{[Cu^{2+}][C_2O_4{}^{2-}]^2}$$

Rearranging and taking logarithm of Eqs. (15) and (16) results in

$$logCuC_2O_{4(aq)} = logCu^{2+} + \log\beta_1 + logC_2O_4{}^{2-} \tag{17}$$

$$logCu(C_2O_4)_2^{2-} = logCu^{2+} + \log\beta_2 + 2logC_2O_4{}^{2-} \tag{18}$$

Introducing the values of β_1 and β_2, the concentration of $CuC_2O_{4(aq)}$ and $Cu(C_2O_4)_2^{2-}$ species are obtained. In addition, the 1:1 oxalate complex can also be protonated to form $Cu(HC_2O_4)^+$ specie in acidic media. The resulting acid − base equilibrium is characterized by its ionisation constant $\beta_{3.}$

$$Cu^{2+} + HC_2O_4{}^- = Cu(HC_2O_4)^+ \tag{19}$$

Rearranging and taking logarithm of Eq. (19)

$$logCu(HC_2O_4)^+ = logCu^{2+} + log\beta_3 + logHC_2O_4{}^- \tag{20}$$

Where,

$$logHC_2O_4{}^- = logH^+ + \log C_2O_4{}^- \tag{21}$$

Introducing the values from Table 3 [48,49] enables the $logCuC_2O_{4(aq)}$ concentration equilibrated with solid $CuC_2O_{4(s)}$ to be plotted vs. pH (Fig. 5a). The solubility minima corresponding to the maximum precipitation of copper oxalate occurs in the pH range 0.6–0.7.

The solubility of oxalates of Cu, Ba, Ca, Bi etc. was investigated by Marta et al. [50] at varying oxalic acid concentrations ranging from 0.05M–1 M. They reported the optimum pH for copper oxalate precipitation to be 0.7–0.8, further except for Bi all other solubility curves showed a minima which was attributed to two opposing factors, protonation of the oxalate ions in strong acidic media and formation of complex oxalates at high pH values when the available oxalate concentration increases. Zielinski et al. [51] reported maximum precipitation of metal oxalates at oxalic acid pH < 1.

3.3.2. Experimental results

It is a common practice in extraction from chloride media to scrub the oil phase prior to stripping of metal values to remove chloride ions adsorbed at interface. When hydroxyoxime is used as a chelating agent, water can be used for scrubbing without any pH adjustment [28]. In this study the organic phase was scrubbed with distilled water to remove the adhering chloride ions. Precipitation-stripping was carried out using oxalic acid concentrations ranging from 0.3 to 1 M, at equal oil to aqueous volumes for three hours at 150 rpm and 30 °C. Increasing the concentration of oxalic acid resulted in an increase in amount of precipitates obtained. Oxalic acid strengths beyond 1 M were not attempted due to solubility constraints at the operating temperature. Stripping was performed using 1 M acid in three stages with fresh acid at each stage. The total copper stripped at each stage is the sum of copper present in the precipitate and the copper remaining dissolved in the oxalic acid solution.

Experimental data presented in Table 4 shows that of the 19.76 gm copper loaded in the organic phase, the amount of copper precipitated as oxalate was 13.17 gm in stage 1,4.06 gm and 2.25 gm in stage 2 and stage 3 respectively accounting for a cumulative yield of 98.6%. Copper remaining soluble in oxalic acid after precipitation in each stage was also determined experimentally. The solubility of copper oxalate at the precipitation pH value of 0.67 was determined from the solubility diagram Fig. 5(a). The experimental yield and the predicted yield considering dissolved copper obtained from solubility diagram are in close agreement as shown in Table 4.

Fig. 5(c) shows the distribution of soluble copper species present in

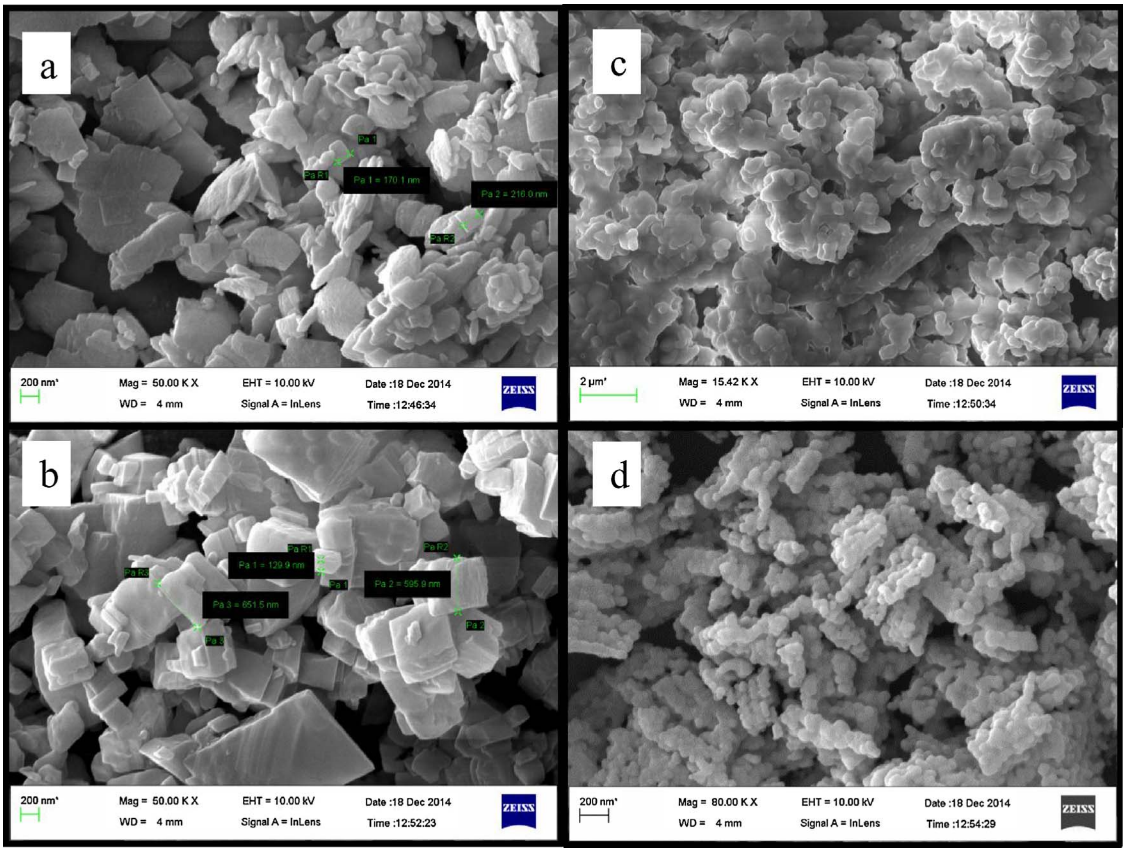

Fig. 7. FESEM (a) copper oxalate (b) zinc oxalate (c) copper oxide (d) zinc oxide.

the solution at pH 0.67 based on theoretical consideration. Analysis of the pickle liquor after copper extraction revealed that 77% of the 131 mg/L iron initially present was also extracted but none of the other metals present in the liquor were extracted under the operating conditions. It is well known that Fe^{3+} is moderately extracted by LIX 84IC at pH range 2 to 2.5 [38]. During stripping the ferric ions extracted were stripped as soluble ferric oxalate in the aqueous phase. Quantitative stripping of loaded iron was observed after three stages of stripping.

3.4. Extraction of zinc using D2EHPA

Selection of an extractant for zinc extraction from chloride media depends largely on the zinc specie formed in solution as well as the physicochemical properties of the solution. Below 1 M concentration the cationic specie Zn^{2+} is dominant which is extractable by LIX 84 and acidic extractants D2EHPA, and CYANEX 302. Above 1 M chloride concentration $ZnCl_4{}^{2-}$ and $ZnCl_3{}^{-}$ are formed that are extractable by secondary or tertiary amines [52]. The speciation diagram (Fig. 1) shows that dominant zinc specie present in the pickle liquor was Zn^{2+} and $ZnCl^{+}$. While LIX 84IC could be used for extraction but it would require pH balancing since Zn^{2+} is significantly extracted only above pH 5, moreover maintaining same extractant in the process has the possibility of impurity carryover from zinc to copper stream and vice-versa. Hence, it is prudent to use different extractants for copper and zinc recovery and keep both the streams separate. This strategy has been adopted by investigators for metal recovery from sulphate media (15).

Extraction of zinc with D2EHPA requires very little pH adjustment and a single stage zinc transfer can be achieved by using a high extractant concentration [52]. Increasing the extractant concentration can shift the extraction curves to lower pH values. Zinc extraction from chloride media using D2EHPA is well investigated by Li et al. [53]. They postulated the equilibria in the organic phase as follows:

$$2HR \leftrightarrow H_2R_2 \tag{22}$$

$$Zn^{2+} + (1 + x/2)H_2R_2 \leftrightarrow ZnR_2.\, xHR + 2H^{+} \tag{23}$$

D2EHPA has a strong tendency to form a dimer in organic solutions and subsequent reaction with zinc leads to the formation of Zn complex where x is the number of HR molecules complexed with ZnR_2, these investigators reported the value of x = 1. The effect of dimerization of D2EHPA is apparent only at low metal ion concentration, dimerization effects are eliminated at high metal concentration leading to formation of ZnR_2 as extractable species [54].

After copper removal, the pickle liquor was contacted with an oil phase containing 15% v/v D2EHPA at equal oil to aqueous ratio. Fig. 6 shows the extraction isotherm. It is observed that at pH 2 using 15% v/v D2EHPA almost 98.25% of the zinc present was extracted. The plot of Log D vs pH (Fig. 6) has a slope of 1.8 indicating two extractant molecules participating in the complexation process. The maximum loading capacity of zinc using 15% v/v D2EHPA at an equilibrium pH of 2 was 14.38 g/L.

3.4.1. Precipitation-stripping of zinc from oil phase

The metal loaded D2EHPA solution was stripped in two stages with 1 M oxalic acid at equal oil to aqueous ratio at 30 °C and 150 rpm. The solubility diagram developed theoretically for zinc-oxalic acid system, using appropriate values of constants (Table 3) is shown in Fig. 5(b). Zinc has one ionic species more than that observed for copper. The additional species $Zn(HC_2O_4)_2^{2-}$ forms due to protonation of $Zn(HC_2O_4)^{+}$ in acidic medium which is not observed in the case of copper because copper oxalate protonates to form the highly stable $(Cu(HC_2O_4)^{+})$ complex whereas when zinc oxalate gets protonated, it forms an unstable complex $(Zn(HC_2O_4)^{+})$ that has the capacity of getting protonated again to go to $[Ar]3d^{10}4s^{2}$ state to stabilize its energy level.

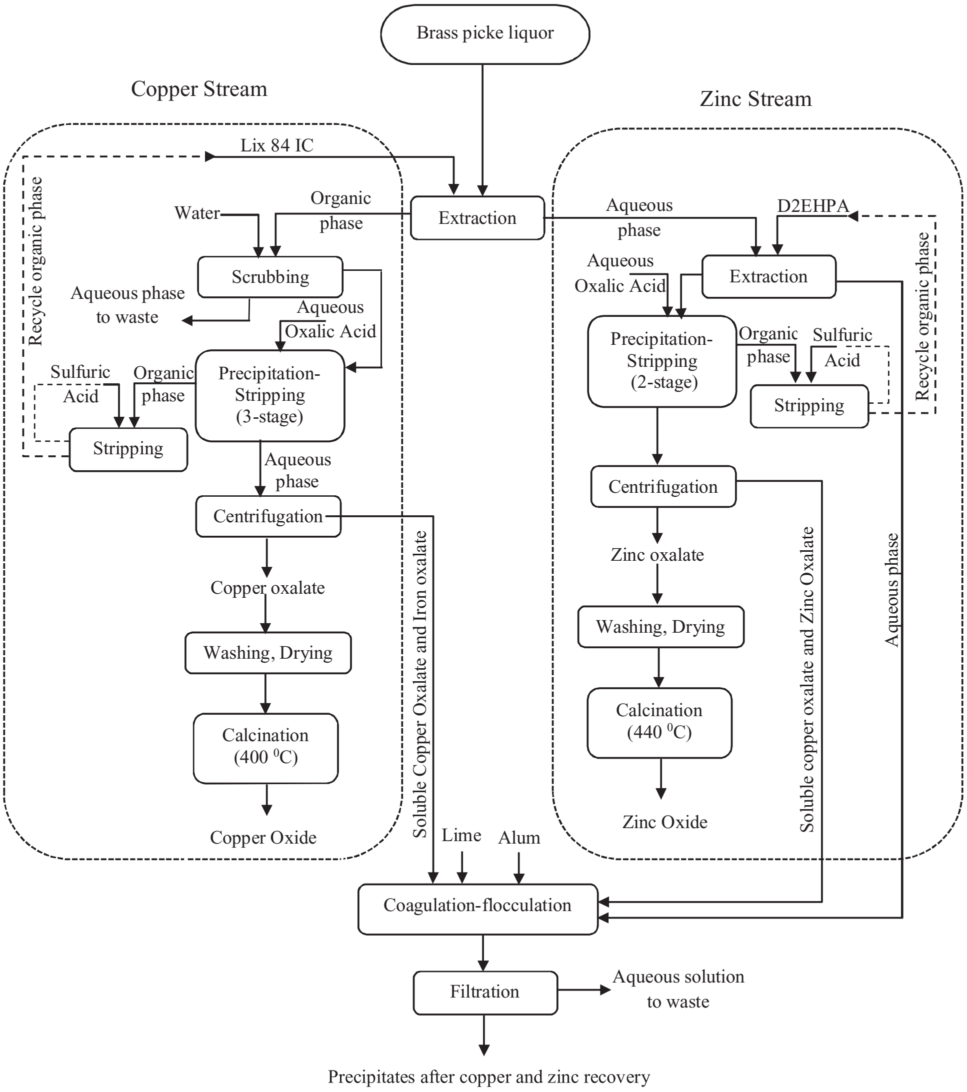

Fig. 8. Process flow diagram.

Fig. 5(d) shows the distribution of soluble Zn species in the strip solution. The solubility of zinc oxalate at the precipitation pH value of 0.97 was determined from solubility diagram Fig. 5(b). The percentage zinc stripped and precipitated in each stage is given in Table 4. The experimental and the predicted yield are in good agreement.

3.5. Recyclability of solvent

After precipitation-stripping process it was observed that the organic phase containing LIX84IC contained residual traces of copper while D2EHPA containing phase contained traces of zinc which were not stripped by oxalic acid. Both organic phases were treated separately with 1.5 M sulfuric acid to strip the residual copper and zinc prior to its reuse in the process. 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 by LIX84IC at pH 2.5 and 97.7% zinc was extracted by D2EHPA after 5 cycles at pH 2.

3.6. Characterization of copper oxalate and zinc oxalate

The precipitates of copper oxalate and zinc oxalate obtained were characterized by XRD, FTIR and their morphology was determined using FESEM analysis. The sharp diffraction peaks of copper oxalate were indexed as monoclinic phase and matched with standard data JCPDS 21-297 (Fig. S1) and that for zinc oxalate were indexed on the basis of monoclinic cell reported for zinc oxalate dihydrate (JCPDS 25-1029) (Fig. S1). The IR spectra (Fig. S2) showed a broad band at frequency 3462.06 cm^{-1} corresponding to the OH stretching vibration, peak at 1679.3 cm^{-1} is attributed to the main anti-symmetric carbonyl stretching band $\nu_{as}(C{=}O)$ specific to the oxalate family. Vibration band at 1362.7 cm^{-1} are attributed to $\sigma_s(C{-}O) + \sigma(C{-}C)$ while band at 1319.4 cm^{-1} corresponds to $\sigma_s(C{-}O) + \delta(O - C{=}O)$. Bands at 823.1 cm^{-1} and 504.89 cm^{-1} are due to $\delta(O - C{=}O)$ and σ(Cu-O) frequencies of the oxalate moiety. Similar peaks were also observed in the IR spectra for zinc oxalate (Fig. S2). FESEM image of the oxalates (Fig. 7a,b) show that zinc oxalate particles were more defined layered structures with sharp edges. In comparison, the copper oxalate particles were disc shaped, smaller in size and lacked sharp edges. In both cases highly agglomerated particles are observed.

3.7. Preparation and characterization of copper oxide and zinc oxide

Thermogravimetric analysis of copper oxalate and zinc oxalate samples was performed to determine the calcination temperature to convert the oxalates to their respective oxides. Copper oxalate was calcined at 400 °C and zinc oxalate at 440 °C for three hours to obtain their respective oxides. XRD of copper oxide and zinc oxide matched the standard data (JCPDS 5-611) and (JCPDS 36-1451) respectively (Fig. S1). No oxalate impurities were found in either sample. The IR spectra of both the oxides show a broad band ~3450 cm^{-1} indicating the presence of surface hydroxyl groups. The sharp peak observed in Fig. S1(c) at around at 531.75 cm^{-1} is due to Cu—O while the peak at 461 cm^{-1} in Fig. S1(d) is due to Zn—O lattice vibrations. FESEM images of the oxides (Fig. 7c,d) show that on calcination oxalates were transformed to their respective oxides without losing their ordered structure.

The EDX analysis of copper oxide (Fig. S3a) confirmed pure CuO phase with Cu and O in stoichiometric proportions. The chemical analysis of CuO also confirmed absence of impurity indicating formation of pure copper oxide. The EDX analysis of zinc oxide (Fig. S3b) reveals presence of Zn, O and Cu. After copper extraction, 240 mg/L of copper remained unextracted in the pickle liquor. This residual copper got extracted by D2EHPA during zinc extraction and was precipitated as copper oxalate along with zinc oxalate. Thus copper ends up as an impurity in zinc oxalate product. The chemical analysis showed that zinc oxide was 99.1% pure and contained 0.9% of copper oxide as impurity. However, this did not manifest in the XRD analysis of zinc oxide as copper oxide percentage was very low.

Post stripping the organic phase contained traces of copper (40 mg/L) in the copper stream and zinc (10 mg/L) in the zinc stream. Both the organic phases were stripped using 1.5 M sulphuric acid to recover the metals prior to recycle of the organic phase. Since the amount of the metal present was low the same acid could be reused. The aqueous phase after extraction of zinc contained the other metals present in the pickle liquor. This aqueous stream was mixed with the streams containing soluble oxalates. The combined stream was subjected to coagulation and flocculation to remove the metals present and filtered to separate the solids before disposal of the liquor.

EDX analysis (Fig. S3c) of the sludge generated after processing indicates the presence of the metals originally present in the pickle liquor after copper and zinc extraction. The additional peaks for sulphur in the EDX spectrum are due to the addition of alum during the coagulation and flocculation process. Fig. 8 shows the process flow diagram for the recovery of copper and zinc from pickle liquors.

4. Conclusions

Solvent extraction and precipitation-stripping was used to recover copper and zinc from spent chloride brass pickle liquors satisfying the dual goal of environmental sustainability and economic gain in terms of the reclaimed metals. Copper was selectively extracted from the pickle liquor using LIX 84IC as an extractant and subsequently zinc was extracted using D2EHPA. High copper loading in the organic phase was observed. The oxime extractant in organic phase was present both as a monomer and dimer at the extractant concentrations investigated and both were involved in the complexation process.

Precipitation-stripping of the loaded metal using oxalic acid resulted in formation of water insoluble metal oxalates. Solubility diagrams developed in this investigation could predict the yield of Cu and Zn precipitated as oxalates with high degree of accuracy. Calcination of the oxalates under controlled conditions converted the oxalates to corresponding oxides. 97.3% copper and zinc present in the pickle liquor were recovered as copper and zinc oxalate. Morphology of the precipitates reveal that zinc oxalate particles were layered structures with sharp edges while copper oxalate particles were disc shaped and lacked sharp edges. In both the cases highly agglomerated particles were observed. Calcinations did not induce any change in the ordered structure observed in oxalates. Pure copper oxide and zinc oxide of 99.1% purity were obtained as value added products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jece.2017.09.061.

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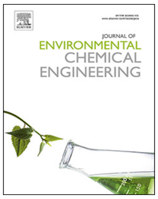

Reclamation of copper from spent ammoniacal Printed Circuit Board (PCB) etch solutions

Khyati Shah, Kamalesh Gupta, Bina Sengupta*

Chemical Engineering Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, India

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Precipitation-stripping

ABSTRACT

Ammoniacal spent etch liquors is a potential source for copper recovery. In the present investigation copper was extracted from spent ammoniacal PCB etch solutions using hydroxyoxime LIX 84I. Maximum extraction was observed at equilibrium pH of 8.9. Three counter-current stages were required for quantitative extraction of 51.8 g/L copper from the spent liquor using 50%v/v extractant at an O/A ratio of 1.5. It was also possible to achieve quantitative extraction with 20% v/v extractant concentration at an equilibrium pH of 8.9 and O/A ratio 4.5:1. Precipitation −stripping of the loaded organic phase using oxalic acid led to reclamation of copper as copper oxalate. Contacting the oil phase fully loaded with copper in 50% v/v extractant, with 1 M oxalic acid at equal O/A resulted in 77.4% copper getting stripped in first contact, quantitative stripping was achieved in the second contact with fresh acid. There was a close agreement between the experimental and predicted yields based on solubility plots developed for copper-oxalic acid system. Co-extracted ammonia to the organic phase was stripped as soluble ammonium oxalate offering an inherent advantage over the conventional stripping process where build-up of ammonium sulphate is observed during electrowinning process. Calcinations for three hours formed copper oxide, XRD and chemical analysis confirmed the formation of pure copper oxide. The copper present in waste etchant could thus be appropriately converted to value added product.

1. Introduction

Electronic devices encompass every aspect of human life and are built on the foundation of Printed Circuit Boards (PCBs), which carries the electronic architecture of the device with copper as the main conducting material. The copper concentration in PCB varies depending on the number of layers and the capacity of conductor current [1] and is usually about 15–35% by weight [2] of PCB. This copper content is far greater in comparison to the 3% copper in most of the newly mined ores [3]. According to Institute of Printed Circuits (IPC) the world PCB market reached an estimated $58.2 billion in 2016. The worldwide output of PCBs has increased by an average of 8.7% each year and will continue to increase [4] resulting in an increased use of copper. International Copper Study Group (ICSG) projections indicate a copper deficit of 150,000T for 2017 and 105,000T in 2018. Therefore, it is imperative to recover and recycle copper to the fullest extent from wastes and discards.

Production of PCB involves drilling, scrubbing, chemical cleaning, electroless deposition, photo imaging, pattern plating, resist stripping, and etching as the major steps [5]. Chemical etching process is used to develop the circuit pattern in PCB's by removing the excess portion of copper from the copper clad laminate. The copper dissolved away by etching process is about 50–70% of that originally present on the board [6]. PCB etching using acidic or alkaline cupric chloride is well established process. However, both function differently and have their own relative merits and demerits. Ammoniacal etching has the advantage that it does not remove the tin/lead solder that protects the portions of the copper circuit [7] but fine line etching is not achieved, which some products require. While acidic cupric chloride has a longer solution service life and can retain more copper in solution before it is spent and is used for boards with close traces.

Almost 1.5–3.5 L of waste etchant is generated per square meter of PCB produced [8]. This account's for one billion cubic meter of waste etchant being generated annually from the PCB industry with an increase in 15–18% [9]. The copper concentration in the spent ammoniacal etching solution depends on the composition of the bath. Maximum etching efficiency is obtained when the copper concentration is 50–70 g/L and decreases as the concentration increases. Copper build up in the etch solution is accompanied with corresponding depletion of the free ammonia content in the etch solution necessitating regeneration of the spent etch liquor. Ammoniacal etchant can be regenerated on site by recovering copper and recycling the etchant, simultaneously

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* Corresponding author.
E-mail address: bina.sengupta-chemengg@msubaroda.ac.in (B. Sengupta).

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Table 1
Processes for recovery of copper from ammoniacal and acidic PCB etch solutions.

Source	Recovery method	Composition of etchant	Operating Parameters	Reference
Synthetic spent copper (II) chloride etchant	Electrolytic	1.7 M $CuCl_2$, 0.1 M CuCl, 2 M HCl and 2 M NaCl	Voltage 1.63 V, Power 1.54 kWh/kg (on-site regeneration and recovery)	[11]
Ammonical spent copper etchant	Electrolytic	30.8 g/L Cu, 2.09 M NH_3, 38.5 g/L chloride	pH 8.5 to 9.5, Agitation rates 255 to 123 min^{-1}, Current density1100 Am^{-1}, Cu recovery 99.8–99.9%	[6]
Spent nitric etching solutions	Electrowinning	3.5 N HNO_3, 30 g/L Cu, 40 g/L Sn, 40 g/L Pb, 20 g/L Fe	pH 2.1, Current 3A, Depostion time 20 h, Cu recovery 98%	[12]
Spent etchant	Membrane electro-winning	Cu 167.8 g/L, Cl 158.6 g/L, carbonate 3.9 g/L, phosphate 5.3 g/L, thiourea 0.5 g/L	Temp. 40–50 °C,current density 500–1500 Am^{-1}, cell voltage 2–2.5 V, Cu recovery 90%	[13]
PCB spent etching solution	Ultrasonic	114.1 g/L Cu	Power 300W, Stirring rate 300 rpm, Cu recovery 93.76%	[14]
Acid Cu-PCB waste etchant	Liquid chemical reduction	95 g/L Cu	Time 12 h, pH 3, CuCl recovery 85%	[15]
Ammonical spent copper etchant	Cementation	135 g/L copper	Temp. 25 °C,Time 20 min, pH 2, Purity of Cu $>$ 99%	[16]
Synthetic ammonium chloride etchant	Solvent extraction	Cu 0.01 M, ammonium chloride 5 M	Extractant-Pyridineketoximes (0.01–0.2 M), pH 9 Stripping agent- water, Cu recovery 80–90%	[17]
Synthetic ammonium chloride etchant	Solvent extraction	Cu 112.98 g, 6 M NH_3	Extractant- 40% hindered β-diketone, O/A- 5:4, H_2SO_4 stripping O/A-1:2, Cu recovery 98.27%	[18]
PCB spent etchant	Solvent extraction	Cu 152.1 g/L	Extractant- 40% LIX54,O/A-5:1, H_2SO_4 stripping, O/A- 2.5:1, Cu recovery 54%	[19]

reducing the fresh etchant requirement as well as water discharge.

The MECER process uses solvent extraction and electrowinning to recover the etchant and reclaim high purity copper. After copper removal, the etchant is regenerated by adding makeup solvent and ammonia is directly recirculated to the process. Keskitalo et al. [10] have presented a comprehensive review on the different methods, electrowinning, cementation, solvent extraction, precipitation and membrane technology for the regeneration of acidic cupric chloride etchant waste along with their advantages and disadvantages. Table 1 lists the different processes available to recover copper from both acidic and ammoniacal PCB etch solutions.

Recovery of copper from ammoniacal solutions is important in various hydrometallurgical processes. Current status and the future perspective of recycling by hydrometallurgy are detailed by Xu et al. [20]. Solvent extraction is by far the most widely used method to recover copper from ammoniacal solutions due to its inherent advantages; ease of operation; low energy requirement and can handle a wide range of feed concentration [21]. β diketones and hydroxyoximes are the most widely used extractants to recover copper from ammoniacal solutions. Copper is extracted from ammoniacal solutions using β diketone, LIX 54 [22–24] sterically hindered β diketone [18], hydroxyoxime, LIX84I [25–27], LIX 84I, LIX 984N, LIX 54-100 [28], and aliphatic carboxylic acids [29].

The last decade has witnessed a number of research publications on recovery of copper and other precious metals from used PCBs using different techniques such as pyrometallurgy, hydrometallurgy, physical methods and their combinations [30]. Most of the research is focused on metal reclamation from discarded PCBs. There is considerable potential of copper recovery from spent etch solutions during the PCB fabrication process. In the present investigation copper is recovered from spent ammoniacal PCB etch solution using solvent extraction with LIX 84I as the extractant. Instead of attempting to strip the loaded copper from the extractant using a mineral acid followed by metal recovery by electrowinning, the loaded copper in the organic phase was stripped with oxalic acid to precipitate copper as an oxalate. The oxalate was subsequently converted to oxide by controlled calcinations.

2. Materials and methods

2.1. Materials

Spent printed circuit board etch solution was collected from a small scale PCB manufacturing industry in Vadodara, India. LIX 84I (BASF) was used as the copper extractant. Commercial kerosene (B.P-152–271 °C) used as the organic diluent was supplied by Indian Oil Corporation Limited. Other reagents, oxalic acid, sulfuric acid used were of AR grade.

2.2. Methods

The metal composition of the PCB etch solution was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 5300 DV) (Table 2). The ammoniacal nitrogen, chloride and the sulfate concentration in the etch solution was determined using the standard methods for analysis of water and waste water, APHA–4500N, APHA 4500-Cl-B and APHA 4500–SO_4-2E respectively [31].

Copper extraction was carried out in shake flasks at equal organic and aqueous volumes (100 mL each) on a rotary shaker (Remi-RS 24BL) at 150 rpm and 30 °C. The effect of equilibrium pH was studied using 20% v/v extractant for pH values ranging from 8.5 to 10. To study the effect of extractant concentration, the etch solution was contacted with organic phase containing 10%v/v to 50%v/v LIX 84I in kerosene. To determine the number of stages required for extraction, the etch solution was equilibrated with 20% v/v and 50% v/v of LIX 84I at varying organic to aqueous ratios keeping the total volume of organic and

Table 2
Composition of spent printed circuit board etchant.

Component[a]	Concentration (mg/L)
Copper	51800
Nickel	3.375
Lead	33.535
Zinc	14.05
Tin	1.856
Ammoniacal Nitrogen	48675
Chloride	53853
Sulphate	395
% of Ammonia	5.9%
pH	8.5
Specific gravity	1.307

[a] Composition of metals in spent PCB etchant determined by ICP analyses to get an idea of all trace metals present.

aqueous phase constant. The aqueous phase was analyzed for copper on an Atomic Absorption Spectrometer (AAS) (Chemito AA203) at 321 nm.

After extraction the organic phase was separated and scrubbed with water. Stripping was carried out by contacting the loaded organic phase with an equal volume of 1.0 M oxalic acid solution for time intervals ranging from 15 min to 3 h on a rotary shaker (Remi-RS 24BL) at 30 °C and 150 rpm. After the stipulated stripping time the aqueous and organic phase were separated. Copper oxalate precipitate in the aqueous phase was centrifugally separated, washed and dried. The oxalate precipitate was calcined in a tube furnace (Ants Ceramics) at 400 °C for 3 h to obtain copper oxide.

2.3. Analytical techniques

Precipitated copper oxalate and copper oxide were characterized by powder X-ray diffraction (XRD) on a PAN Analytical Xpert Pro diffractometer using Cu-Kα radiation at λ value of 1.54°A in Bragg-Brentano geometry. Thermogravimetric analysis was performed at a heating rate of 10 °C/min in air atmosphere on a Shimadzu TGA-50 analyser. The elemental composition was determined using EDX analysis (Oxford Instruments). Infrared spectroscopic analysis of copper oxalate and oxide was conducted over a frequency range of 400–4000 cm^{-1} with 32 scans using Thermo Scientific Nicolet iS5 spectrophotometer with iD1 transmission.

3. Results and discussion

3.1. Extraction of copper

The spent etchant collected from printed circuit board manufacturing unit had an initial pH value of 8.5. It contained 51.8 g/L copper with other metals present in trace amounts (Table 2). In ammoniacal solutions hydrated copper reacts with ammonia to form various copper ammine species. The coordination number of hydrated copper (II) species decreases when the coordinated water is replaced by ammonia. The geometry of the specie changes from octahedraon to distorted planar square when the water of hydrated copper is replaced by two or more ammonia molecules. Similarly, with an increase in the aqueous phase pH the copper (II) species changes from axially elongated octahedron to distorted planar square [32]. Copper extraction is sensitive to the presence of copper ammine species in the aqueous phase [21]. The speciation diagram of ammoniacal copper complexes for the spent etch solution at different pH values was plotted using *Visual MINTEQ 3.1* (Fig. 1). At a pH value of 8.5, copper was present predominantly as $Cu(NH_3)_4{}^{2+}$ Rosinda et al. [24] reported that Cu complex with four NH_3 is the dominant form present in ammoniacal solutions having excess of NH_3 to Cu. Such predominance of $Cu(NH_3)_4{}^{2+}$ species is expected due to its high formation equilibrium constant over other ammine complexes.

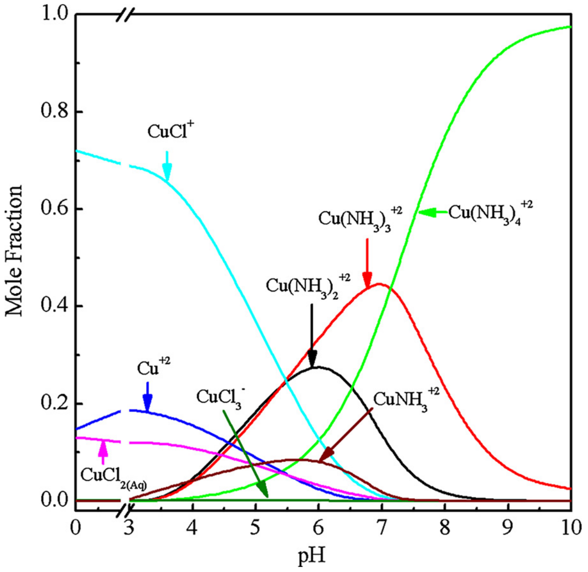

Fig. 1. Speciation diagram of copper in spent printed circuit board etchant as a function of pH.

The mechanism of copper extraction from ammoniacal solutions using β diketones and hydroxyoximes based on existence of $Cu(NH_3)_4{}^{2+}$ species in the feed can be described by Eq. (1) [22]

$$Cu(NH_3)_4^{2+} + 2HR \leftrightarrow CuR_2 + 2NH_4^+ + 2NH_3 \tag{1}$$

where *HR* represents the extractant and CuR_2 the copper-extractant complex. During extraction the ammonia ligands are pushed out and a chelate with hydroxyoxime is formed in the organic phase [28].

Copper extraction was carried out using hydroxyoxime extractant LIX 84 I at equilibrium pH values ranging from 8.5 to 10 using 20% v/v LIX84I at equal organic to aqueous (O/A) ratios. It was observed that percentage extraction increased from 20.66% at pH 8.5 to 22.01% at pH 8.9 and thereafter decreased to 20.27% at pH 10 (Fig. 2, inset). Eq. (1) shows that there is an increase in ammonia concentration due to release of ammonia leading to an increase in the pH. Nathsharma and Bhaskarsharma [33] reported that in actual practice there is no increase in pH, rather there is a small decrease due to uptake of ammonia in the

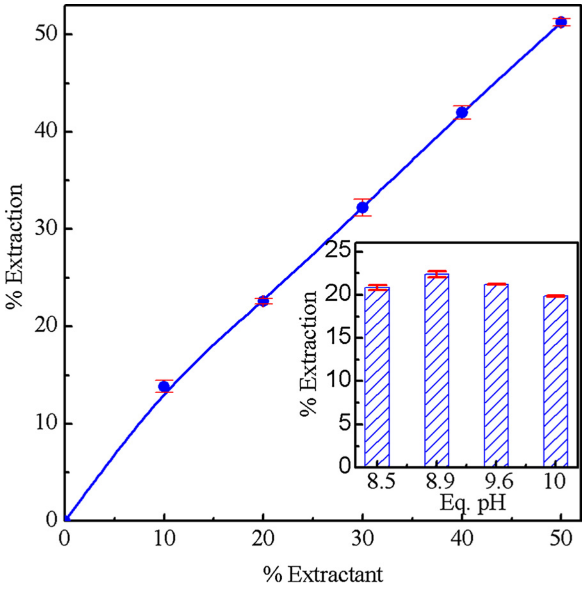

Fig. 2. Effect of LIX84I concentration on% extraction (pH-8.9, O/A = 1). Inset: Effect of Equilibrium pH on% extraction (20% (v/v) LIX84I, O/A = 1).

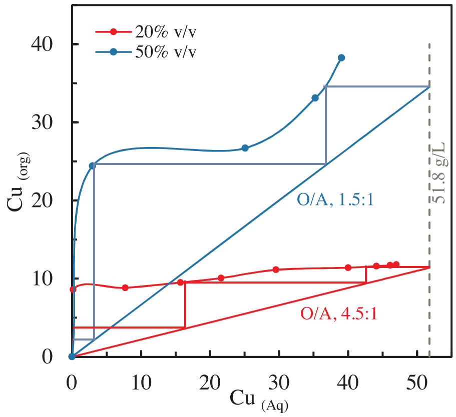

Fig. 3. McCabe −Thiele plot for the extraction of copper with 20% (v/v) LIX84I and 50% (v/v) LIX84I (pH-8.9).

organic phase. Though hydroxyoximes have a high affinity for copper they also have a tendency to co-extract ammonia. Hydroxyoximes transfer ammonia especially at higher pH (> 9) due to the presence of nonyl phenol in the extractant [22] resulting in decrease in the extraction. The increased stability of the ammine complexes also inhibits extraction. Copper extraction also decreases as the copper (II) species with distorted configuration increase due to an increase in pH [32].

3.2. Extraction isotherm and counter current simulation

The extractant concentration in the organic phase was varied from 10% v/v to 50%v/v at equal O/A ratio that led to an increase in percentage extraction in a single stage from 13.38% to 51.54% (Fig. 2). Maximum copper extracted for a given O/A ratio is obtained from the extraction isotherm. To determine the phase ratio and the number of stages required for extraction the spent solution was equilibrated using 20% v/v LIX84I at O/A phase ratio ranging from 1:6 to 6:1 and 50% v/v LIX 84I extractant concentration at O/A phase ratio ranging from 1:3 to 2:1. The extraction isotherms indicate that three stages are required for complete extraction of copper at a phase ratio of 4.5:1 using 20% v/v extractant and 1.5:1 at an extractant concentration of 50% v/v (Fig. 3). Based on the McCabe–Thiele plots, a three-stage counter-current simulation study was carried out at phase ratio (O/A) 4.5:1 for 20%v/v LIX 84I and at 1.5:1 for 50% v/v LIX 84I. The results indicate loading of 51.79 g/l copper in the organic phase corresponding to total copper extraction of 99.9% with 3 mg/L and 5 mg/L of copper in the raffinate from the third stage respectively (Fig. 4).

3.3. Precipitation-stripping of copper from loaded organic phase

Precipitation – stripping of copper from the loaded organic phase was carried out by contacting organic phase with aqueous oxalic acid solution (1 M). Oxalic acid dissociates into hydrogen ions and oxalate anions in the aqueous phase. An ion exchange reaction at the organic-aqueous interface between Cu^{2+} and H^{+} ions leads to the release of copper from the copper-oxime complex. The Cu^{2+} cation thus released in the aqueous phase undergoes a second reaction with the oxalate ion to form the copper oxalate precipitate and acts both as a stripping and precipitating agent (Eq. (2)).

$$CuR_2 + H_2C_2O_4 \rightarrow CuC_2O_4 \downarrow + 2RH \tag{2}$$

After copper extraction the organic phase was washed to remove the adhering ammonia. Stripping behavior was investigated at equal (O/A) ratios by contacting the loaded organic phase with 50% v/v of extractant with 1 M oxalic acid in a single stage contact. Previous studies on precipitation stripping from copper loaded solutions showed that 1 M oxalic acid was optimal for stripping [34]. Using higher concentrations of oxalic acid was not feasible due to limited solubility of oxalic acid in water at the stripping temperature. Fig. 5 shows the percent copper precipitated-stripped as copper oxalate with time. The percentage precipitation increased with an increase in contact time and after 1 h of stripping time 77.4% of the loaded copper was stripped as copper oxalate in the first contact. Stripping was performed using 1 M acid in two contacts using fresh acid each time. The total copper stripped after each contact is the sum of copper present in the precipitate and the copper remaining dissolved in the oxalic acid solution.

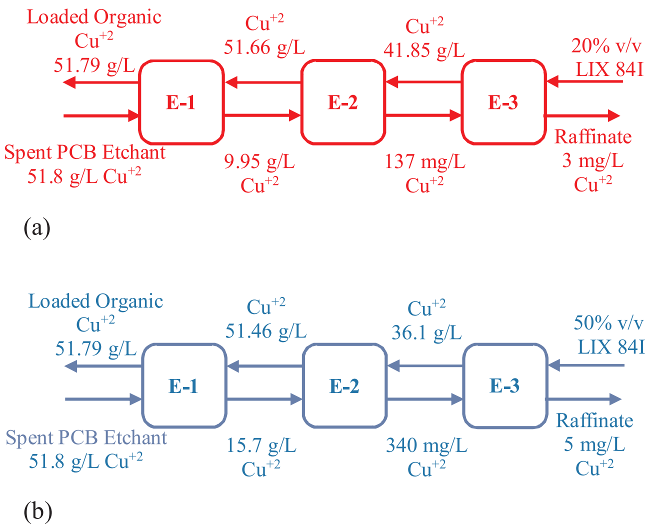

Fig. 4. Counter-current simulation for the extraction of copper (a) 20% (v/v) LIX84I, O/A = 4.5:1, (b) 50% (v/v) LIX84I, O/A = 1.5:1.

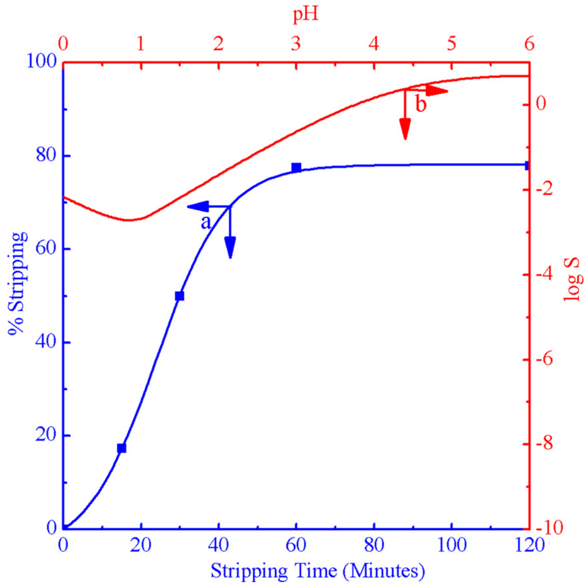

Fig. 5. (a) Effect of stripping time on% stripping. (b) Copper oxalate solubility curve.

Experimental data shows that out of the 26.7 g copper loaded in the organic phase, the amount of copper precipitated as oxalate was 20.55 g in first contact and 5.77 g in the second contact accounting for a cumulative yield of 98.57%. Copper remaining soluble in oxalic acid after precipitation was experimentally determined. The soluble copper after the first and second contact was 0.12 g and 0.07 g respectively. Thus, net copper stripped from organic phase in first contact is 20.67 g which accounts for 99.42% and 5.7 g in the second contact accounting for 98.8% of copper precipitated.

Soluble copper oxalato species were also determined based on theoretical considerations from the solubility diagram. Oxalic acid in solution dissociates into hydrogen ions and oxalate anions depending on the solution pH with equilibrium constants represented as K_1 and K_2 respectively [35].

$$H_2C_2O_4 = H^+ + HC_2O_4{}^-, \; logK_1 = -4.266 \tag{3}$$

$$HC_2O_4 = H^+ + C_2O_4{}^{2-}, \; logK_2 = -1.252 \tag{4}$$

Based on mass law, the oxalate species can be expressed as,

$$[C_2O_4{}^{2-}] = \alpha_{C_2O_4} A_T = [1 + \frac{H^+}{K_1} + \frac{[H^+]^2}{K_1 K_2}] A_T \tag{5}$$

Where, $A_T = H_2C_2O_4 + HC_2O_4 + C_2O_4{}^{2-}$, the total concentration of the oxalates and $\alpha_{C_2O_4}$the ionization fraction of oxalate anion $C_2O_4{}^{2-}$. Introducing the equilibrium constants K_1 and K_2 and total concentration A_T gives the concentration of oxalate species ($C_2O_4{}^{2-}$) at different pH values.

The solubility equilibrium for copper- oxalic acid system can be expressed by Eq. (6) [36].

$$CuC_2O_{4\,(s)} = Cu^{2+} + C_2O_4{}^{2-}, \;\; \log K_{SP} - 9.14 \tag{6}$$

Taking logarithm of Eq. (6) and substituting the value of $C_2O_4{}^{2-}$ and K_{SP} gives the soluble Cu^{2+} species.

Oxalate anions react with Cu^{2+} cations in aqueous solution to form successively two soluble complexes $CuC_2O_{4\,(aq)}$, $Cu(C_2O_4)_2^{2-}$, characterized by their stability constants β_1 and β_2 respectively. The 1:1 oxalate complex can also be protonated to form $Cu(HC_2O_4)^+$ specie in acidic media characterized by its ionization constant β_3 .The formation of oxalate complexes can be represented by Eqs. (7)–(9) [35]

$$Cu^{2+} + C_2O_4{}^{2-} = CuC_2O_{4\,(aq)}, \;\; \log\beta_1 = 6.1 \tag{7}$$

$$Cu^{2+} + 2C_2O_4{}^{2-} = Cu(C_2O_4)_2^{2-} \;\; \log\beta_2 = 10.23 \tag{8}$$

$$Cu^{2+} + HC_2O_4{}^- = Cu(HC_2O_4)^+, \;\; \log\beta_3 = 7.32 \tag{9}$$

Taking logarithm of Eqs. (7)–(9) and introducing the constant values β_1, β_2, β_3 enables to calculate soluble species $CuC_2O_{4\,(aq)}$, $Cu(C_2O_4)_2^{2-}$, $\mathrm{Cu}(HC_2O_4)^+$.

Summation of all the copper soluble complexes Cu^{2+}, $CuC_2O_{4\,(aq)}$, $Cu(C_2O_4)_2^{2-}$,$\mathrm{Cu}(HC_2O_4)^+$ Cu^{2+}, $CuC_2O_{4\,(aq)}$, $Cu(C_2O_4)_2^{2-}$,$\mathrm{Cu}(HC_2O_4)^+$ represented as $C uC_2O_{4\,(s)}$when plotted vs. pH results in the solubility diagram (Fig. 5). The solubility of copper oxalate at the precipitation pH value of 0.85 corresponding to minima in the solubility curve was determined from the solubility diagram. Based on theoretical considerations, copper solubilized in first and second contact turns out to be 0.075 g and 0.034 g respectively. Thus, theoretically copper precipitated in first contact was 99.64% and in the second contact it was 99.41%. These values are in close agreement with the experimental values indicating the robustness of the prediction method.

3.4. Ammonia transport to organic phase

It is well known that LIX84I when involved in copper extraction from ammoniacal media co-extracts ammonia in the oil phase. Lee and Chan [37] reported that only free ammonia is transported to the oil phase since ammonium ion is insoluble in the oil phase. The type of hydroxyoxime and its concentration, pH of the aqueous phase, diluent used and the metal content, all have a bearing on the transfer of ammonia [28]. With excess of copper in the feed phase, with an increase in LIX 84I concentration in the organic phase, the loading of copper in organic phase increases with a simultaneous decrease in the amount of ammonia co-extracted, indicating that the metal extracted replaces ammonia from the organic phase [28].

The co-extraction of ammonia was determined by contacting the spent etchant with an organic phase containing 20% v/v and 50% v/v LIX 84I at equal (O/A) ratios. The difference between the initial ammonia concentration in the aqueous phase and the final ammonia concentration after copper extraction gave a measure of ammonia transferred to the organic phase. The ammonia transferred in the organic phase containing 50% v/v extractant was 420 mg/L while with 20% v/v extractant it was 560 mg/L. At both the extractant concentrations investigated the system operates at maximum copper loading thereby restricting the transport of ammonia in organic phase. Maximum loading of copper minimizes the accumulation of ammonia in the organic phase, which reduces the need for ammonia scrubbing [38].

The ammonia transferred in the organic phase also reacts with oxalic acid forming ammonium oxalate. However, due to the high

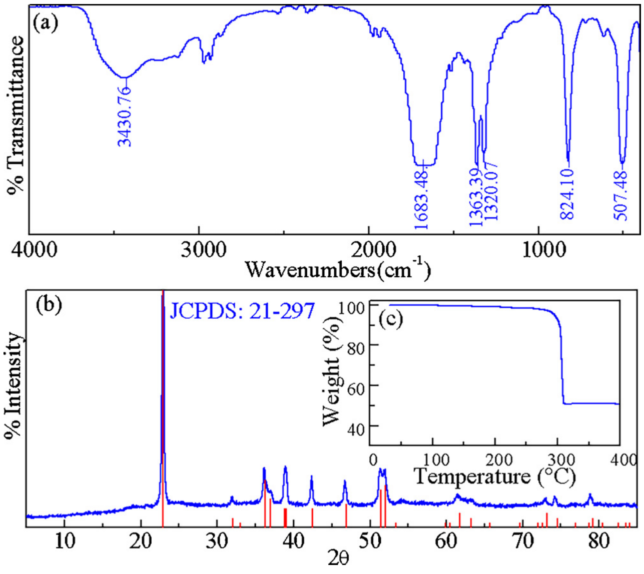

Fig. 6. Characterization of copper oxalate: (a) FTIR spectra (b) XRD pattern (c) TGA analysis.

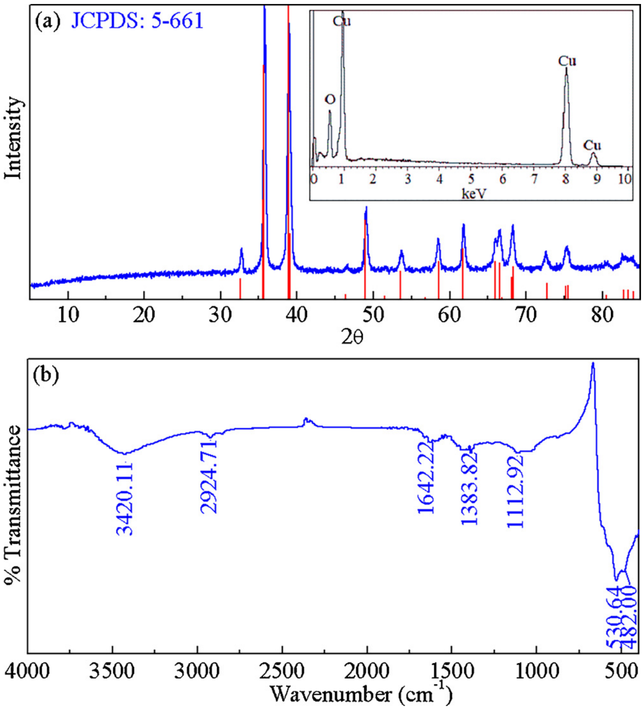

Fig. 7. Characterization of copper oxide (a) XRD pattern, Inset: EDX analysis (b) FTIR spectra.

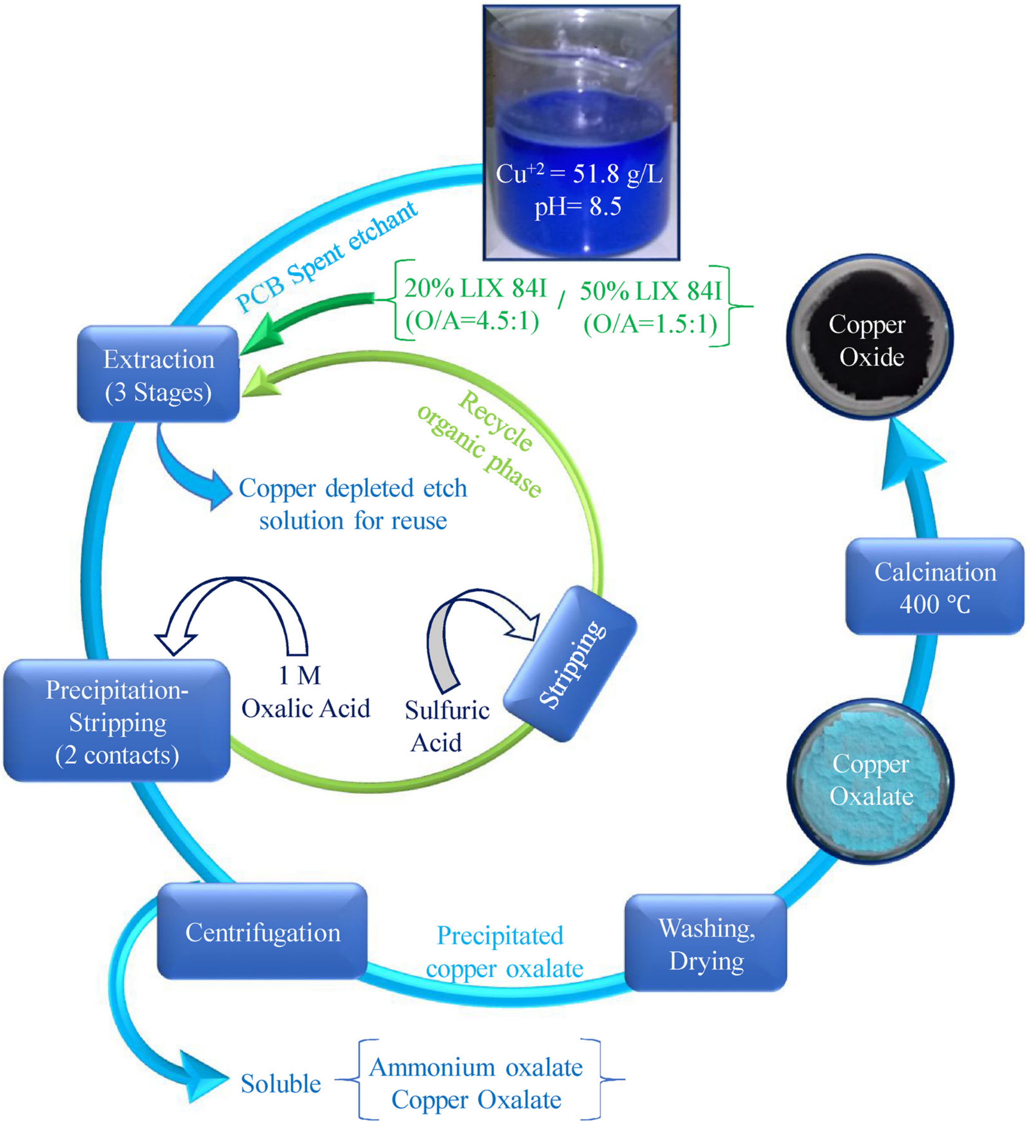

Fig. 8. Process scheme.

solubility of ammonium oxalate in water it dissolves in the aqueous phase.

3.5. Characterization of copper oxalate and oxide

IR spectra (Fig. 6a) of copper oxalate show a broad band at 3430.76 cm^{-1} corresponding to the OH stretching vibration and the hydrogen bonds between the water molecules and the carboxylate group. The band at 1683.48 cm^{-1} is attributed to the main antisymmetric carbonyl stretching band specific to the oxalate family. Bands at 1363.4 cm^{-1} and 1320.07 cm^{-1} correspond to $\sigma_s(C-O)+\sigma(C-C)$ and$\sigma_s(C-O)+\delta(O-C=O)$respectively. Bands at 824.1 cm^{-1} are due to $\delta(O-C=O)$ and 507.48 cm^{-1} are for the $\delta(Cu-O)$ for the oxalate moiety. Fig. 6b shows the XRD pattern of copper (II) oxalate. The diffraction peaks correspond to the orthorhombic phase of copper oxalate and matched with reported data JCPDS 021-0297.

TGA for copper oxalate in air is shown in Fig. 6c. The weight loss of 1.02% before 225 °C is attributed to the emission of surface water. The weight loss of 48% from 225 °C to 312 °C is due to the decomposition of the oxalate that matches closely with the theoretical value of 47.57%. Based on the information obtained from TGA analysis copper oxalate was calcined at 350 °C for three hours. However, XRD of the oxide formed revealed the presence of Cu_2O. Increasing the calcination temperature to 400 °C for the same time span resulted in the formation of only CuO. All the peaks in the XRD pattern could be indexed to monoclinic phase (JCPDS 5-661) for CuO (Fig. 7a). No other crystalline impurities were found in the sample indicating a high purity product obtained. The EDX analysis of copper oxide (Fig. 7a, inset) confirmed pure CuO phase with Cu and O in stoichiometric proportions. The weight compositions for copper (Cu) and oxygen (O) were 80.58% and 19.42%, respectively and no other metals were detected. The chemical analysis of CuO also confirmed absence of any impurity indicating formation of pure copper oxide. The IR spectra (Fig. 7b) for copper oxide showed a broad band at 3420.11 cm^{-1} indicating the presence of surface hydroxyl groups and peaks observed at 530.64 cm^{-1} and 482 cm^{-1} are assigned to Cu—O bonds. Broad band at ~1642 cm^{-1} corresponds to OH bending vibrations combined with copper atom. Band at ~1112 cm^{-1} is attributed to the OH bending vibrations of Cu—OH, band at 1383 cm^{-1} is due to CuO stretching, While the band at 2924 cm^{-1} is due to the asymmetrical CH_3 groups adsorbed on the surface of oxide particles.

Post stripping, the organic phase containing traces of copper was stripped using 1 M sulfuric acid to recover copper prior to recycle of the organic phase. The organic phase was tested to be used up to five cycles with 0.2% decline in the extraction ability. Since the amount of the metal present was low the same acid can be reused again. Fig. 8 shows the scheme for extraction/stripping and recovery of copper as copper oxide from the spent etchant. The etchant solution after copper recovery and ammonia make up can be recycled back and reused. Copper oxide finds wide application in various fields such as pigments, catalysts, antibacterial agents, sensors, semiconductors, magnetic storage media etc. hence, reclamation of copper as copper oxide from spent etch solutions is an attractive proposition [39,40].

4. Conclusions

Copper was extracted from spent ammoniacal PCB etch solutions using LIX 84I as the extractant. Effect of pH was investigated and a maximum in extraction was obtained at a pH value of 8.9. Increase in extraction concentration from 10% v/v to 50% v/v was a monotonically increasing function. Extraction using 20% and 50% were investigated at varying organic to aqueous ratios. In both the cases three equilibrium stages were required at O/A ratio of 4.5:1 and 1.5:1 as indicated by Mc Cabe Thiele plots. Stripping of the fully loaded organic phase with 50% extractant using 1 M oxalic acid was achieved in two contacts with fresh acid each time.

Copper extraction from ammoniacal solutions into hydroxyoximes is accompanied with ammonia transfer. However, maximum loading of copper minimizes the transfer of ammonia in the organic phase. In such a situation of extraction from ammoniacal solutions, precipitation stripping offers an inherent advantage during the reclamiation of copper where in conventional stripping process buildup of ammonium sulfate is observed after recycle of spent electrolyte over a period of time during electrowinning process. In precipitation stripping copper is reclaimed as copper oxalate and there is separation of the solid from the aqueous phase in which ammonium oxalate is soluble.

This work makes an attempt to recover copper from an potential waste stream of PCB etch liquors that is projected to grow significantly in the years to come in view of the great demand of PCBs for electronic devices. The reclaimed copper can be utilized effectively for various applications.

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