CHAPTER 3

Materials and Methods

This Chapter lists the sources of the metal containing aqueous streams collected from industrial sectors for metal recovery. The general methodology for extraction and stripping of metals from such metal bearing streams to prepare fine particles is discussed. Different instrumental techniques used for the characterization of particles and the instrument details for the same are also listed.

3.1 Materials and reagents

3.1.1 Metal bearing aqueous streams as resources

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

Brass when exposed to atmosphere undergoes surface discoloration, called tarnish, due to the formation of a thin oxide layer. Pickling is done to remove tarnish from brass artefacts and components using pickle liquors that are either sulfuric acid or hydrochloric acid solutions. Usually the pickling bath is used till the acid concentration declines to so low a value that the time required for tarnish removal becomes too large and uneconomical for operation and this eventually leads to substantial metal build up in the pickle liquor. In many cases the metal loaded pickle liquor and rinse waters are discharged to sewers without any treatment. In the present investigation such a metal loaded pickle liquor (Figure 3.1a) was collected from a brass component manufacturing industry in Rajkot, Gujarat.

Printed circuit board (PCB) production involves a number of steps including, chemical etching, a process used to develop circuit pattern by removing the excess portion of copper from the copper clad laminate. Large amount of waste etchant loaded with copper is generated during the etching process from which copper can be recovered and reused. An ammoniacal spent etching solution (Figure 3.1b) was collected from a printed circuit board manufacturing unit in Vadodara, Gujarat.

Post pickling operation, the brass artefacts and components are removed from the pickle solution and put in a rinse bath. The rinse solution is also acidic in nature in view of the adhering acid on the brass components and artefacts. A rinse solution was also collected from brass manufacturers and was used as a source for recovery of metals (Figure 3.1c).

(a) Brass pickle liquor (b) Printed circuit board etch solution (c) Brass rinse liquor

Fig.3.1: Metal bearing aqueous streams

3.1.2 Extractants

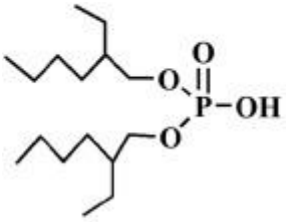
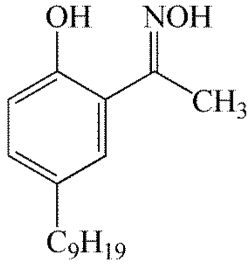
Metal extraction in multi-solute systems depends on the physicochemical properties and the nature of the metal species present in the solution; these factors influence the selection of metal extractants. Organophosphorous acids and hydroxyoxime extractants were used to recover the heavy metals from the metal bearing streams.

LIX 84-I®: LIX 84-I a water insoluble ketoxime (2-hydroxy-5nonylacetophenone oxime) was supplied by BASF in a mixture with a high flash point hydrocarbon diluent. It is a commercial extractant widely used for selective copper extraction. It is a brown colored, viscous and odorless liquid with density 0.9 – 0.92 g/cm^3 at 25^{0}C and a maximum copper loading capacity of 4.7-5 gm/L. LIX 84-IC a concentrated form of LIX84-I with a higher molar concentration of the active ingredient was supplied by Cognis Inc. Ireland. LIX 84-I and LIX 84-IC were used to extract copper from printed circuit board etch solutions and spent brass pickle and rinse liquors respectively.

D2EHPA: Di (2-ethylhexyl) phosphoric acid ($C_{16}H_{35}O_4P$), 95% minimum assay with mono ethylhexyl) phosphoric acid less than 2% was obtained from Merck Specialties Private Limited, Germany. D2EHPA is an acidic extractant and extracts a wide range of metals but has a poor selectivity. In order to achieve selectivity a careful pH control is desired during extraction. D2EHPA was used to extract zinc from spent brass pickle liquors and rinse solutions.

The extractants were used directly as supplied by the vendors. Table 3.1 shows the general structure and properties of the extractants used.

Table 3.1: Extractant properties

Name	**D2EHPA**	**LIX 84-I/LIX 84-IC**
	Di(2-ethylhexyl) phosphoric acid	2-hydroxy-5-nonylacetophenone oxime
Structure	$C_{16}H_{35}O_4P$ 	
Molecular weight	322.4	265
Flash point, °C	206	> 71
Specific Gravity (25°/25°C)	~ 0.97	0.89 – 0.91
Viscosity, mPa s	40	2.44
Extractant appearance	Colorless to yellow liquid	Amber colored liquid
Supplier	Merck Specialties Private Limited, Germany	BASF Corporation. COGNIS, Ireland

3.1.3 Diluent

Kerosene, having boiling range 152–271^{0}C with viscosity of 1.6 cP and specific gravity of 0.80 at 30^{0}C supplied by Indian Oil Corporation, Gujarat Refinery, Vadodara was used as a diluent for all the extraction experiments.

3.1.4 Strippant

Oxalic acid of AR grade with assay 99.8% supplied by S.D. Fine Chemicals Limited was used as a stripping and precipitating agent. Sulfuric acid of AR grade with assay 98%, supplied by Merck Specialties Private Limited was used to strip the residual copper/zinc and after precipitation-stripping (PS) before recycle of the organic phase.

3.1.5 Miscellaneous chemicals

- Ethanol: Rectified spirit supplied by Shree Chalthan Vibhag Khand Udyog Sahakari Mandali Limited Chalthan, via Government of Gujarat was used for washing of metal oxalate particles and as a solvent for precipitation using ethanolic-oxalic acid system.

- Sodium hydroxide: Sodium hydroxide pellets of AR grade with minimum assay of 98% supplied by Merck Specialities Private limited was used to control the pH during extraction.

- Buffer tablets: Buffer tablets of pH 4.0, 7.0 and 9.2, Qualigens make were used to prepare buffer solutions to calibrate the digital pH meter.

- Metal standards: Certified AAS standards of SRL make were used to generate standard curves for metal analysis.

- Potassium bromide: Potassium bromide (KBr) from Spectrochem with a minimum assay of 99.6% was used for FTIR analysis.

- Copper Oxide: Copper(II) oxide (<50 nm particle size) from Sigma-Aldrich was used to compare the catalytic activity with recovered copper oxide.

Other chemicals specific to requirements are listed in the individual Chapters.

3.2 Analytical procedures:

3.2.1 Metal analysis:

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 5300 DV) 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) (Chemito AA–203) equipped with Photon make hollow cathode lamps. The instrument was fully computer controlled. Ratio method was used for curve fitting. The instrument was first calibrated with the standards of the metal within the available concentration range. Samples were analyzed after adequate dilution with distilled water. The metal concentrations measured are reported in mg/L. The parameters used for measurement are listed in a Table 3.2.

Table 3.2: Optimized parameters for AAS analysis of metals

Parameter	**Copper**	**Zinc**	**Iron**
Wave length (nm)	324.8	212.5	248.26
Current (mA)	5.0	5.0	9.0
Slit width	0.5	1.0	0.3
Pmt (V)	274.7	333	472
Burner height(mm)	1.0	1.0	1.0
Fuel rate (liter / min)	3.5	3.5	3.5
Working Range (ppm)	2-8	0-2	2-8

3.2.2 pH measurement

Extraction of metals from aqueous solutions is pH sensitive and continuous monitoring of pH is essential. pH measurements were made using a Systronics make digital pH meter that was calibrated at pH values of 4 and 7 for extraction of metal solutes from acidic media and pH of 9.2 for extraction of metal solutes from ammoniacal media using standard buffer solutions.

3.3 General experimental procedure

3.3.1 Chloride, sulfate, nitrate and ammoniacal nitrogen determination

The chloride, sulphate, 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.

- Chloride concentration: Argentometric method was used for chloride determination [APHA: (4500 Cl^- B), APHA 22nd Edition].
- Sulfate concentration: Turbidimetric method was used for sulfate determination [APHA: (4500 SO_4^{2-} E), APHA 22nd Edition].
- Nitrate concentration: Chromotropic acid method was used for nitrate determination [APHA: (418-D), APHA 16th Edition].

- Ammonical Nitrogen: Macro-Kjeldahl method was used for the determination of ammonical nitrogen. [GBNC macro APHA-4500 N, APHA 22nd Edition]

3.3.2 Extraction

Metal extraction was carried out in shake flasks at equal organic and aqueous volume on a rotary shaker (Remi-RS 24BL) at 150 rpm and $30 \pm 2\ ^0C$. 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. pH adjustments 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.

3.3.3 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 (Remi-RS 24BL) at $30 \pm 2\ ^0C$. Effect of parametric variation 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 on a REMI make (R-24) research centrifuge. 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 (Ants Ceramics) 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 3.2 shows the sequence of steps used to recover the metal from aqueous streams as particles.

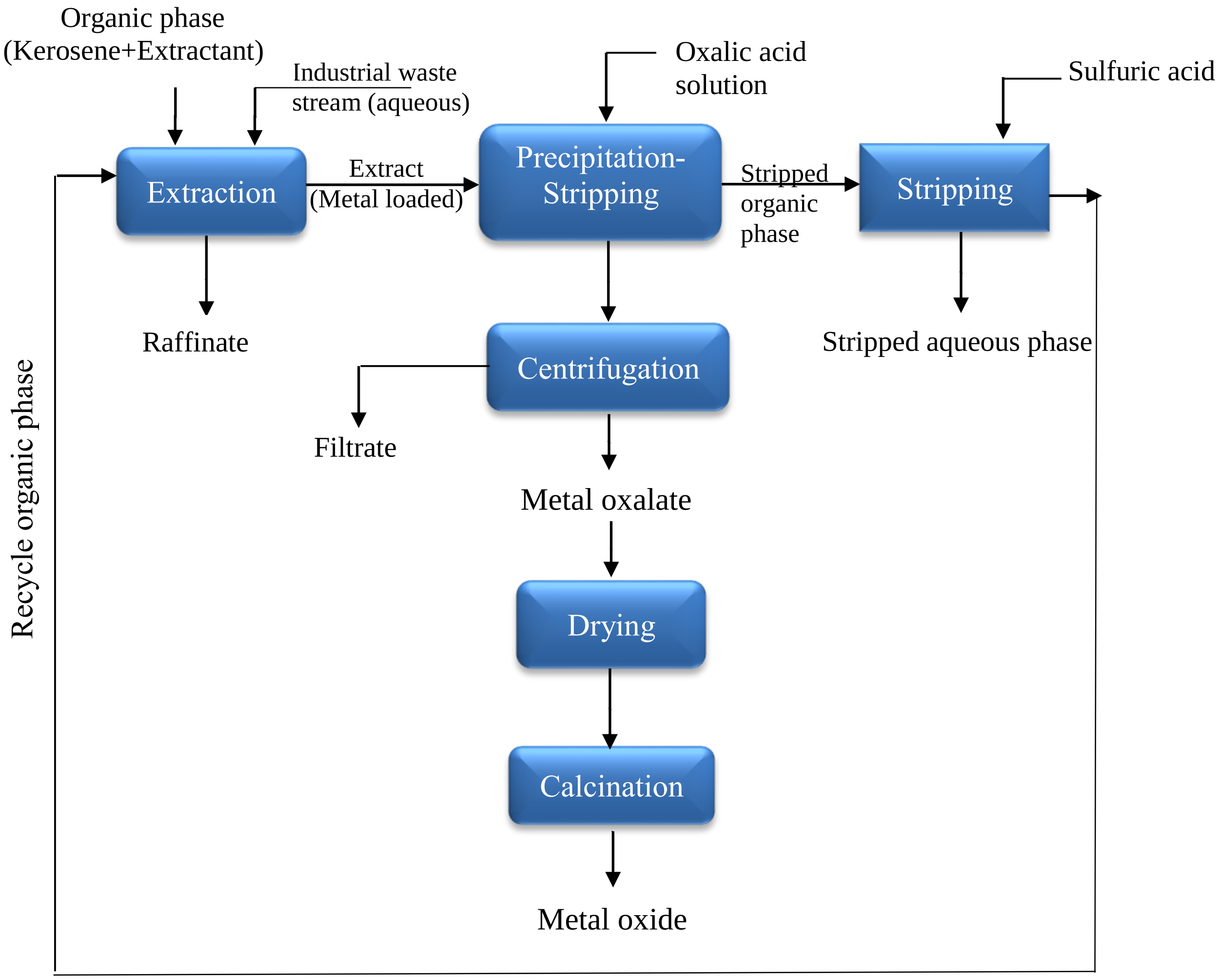


Fig: 3.2: Processing steps for metal recovery

3.4 Characterization of particles

Material characterization of the particles obtained was carried out to analyze purity, crystallinity and crystal size, functional groups present, thermal decomposition data, surface area, elements present etc. Table 3.3 presents the compilation of characterization techniques used.

- Thermogravimetric Analysis: Thermogravimetric analysis of the oxalates was performed at a heating rate of 10^0C/min in an air atmosphere on a Shimadzu Thermal Analyser (50 GA).
- Powder X-Ray Diffraction (XRD) patterns of the metal oxalate and oxide particles were recorded on Bruker, D2 Phaser X-Ray Diffraction meter with CuKα radiation at 1.54 Å wavelength in the 2θ range from 10 to 80 degrees.

- Fourier transform infrared spectroscopy (FTIR) of metal oxalate and oxides were recorded on a Thermo Scientific Nicolet iS5 spectrometer with iD1 transmission over a frequency range of 400–4000 cm^{-1}. All measurements consisted of 32 scans. The samples were ground with dried KBr and pelletized. Infrared spectra of the organic phase before and after extraction were also recorded in order to determine the association of extractant molecules in the formation of metal complexes.
- The morphology of the particles was examined by Field Emission Scanning Electron Microscopy (FESEM). High-resolution images were taken on a Ziess Supra 40 FESEM. The particles were dispersed in ethanol and sonicated. A drop of the liquid was placed on a slide which was cut to size 1cm x1cm. The slide was gold coated before examination.
- Size distribution of the oxalate particles were determined on a laser diffraction particle size analyser (Malvern Mastersizer 2000MU). The particles were sonicated in water in a sonicating bath prior to size measurements. Water was used as a dispersant. The refractive index of the dispersant was 1.33 and for the oxalates particles copper oxalate was 1.77 and zinc oxalate was 1.33.
- The Brunauer-Emmet-Teller (BET) analysis to determine the specific surface area of the oxide particles was carried out on Tristar II 3020 Micrometrics Instrument.
- Energy-dispersive X-ray spectroscopy (EDX) was performed on Oxford instrument. to detect the metals present in the precipitates formed
- Gas chromatography (GC) was carried out on Shimadzu (GC-17A) for determination of purity, identification of samples, and monitoring of organic reactions using metal oxides.
- X-ray spectrometry (XRF) used to determine chemical compositions of the elements using EDX-800 at 200 live seconds.
- Surface tension and Interfacial tension was measured using a K9 (Kruss) tensiometer.
- Measurement of surface charges in term of zeta potential was measured on BIC 90 plus (Brookhaven instrument)

Table 3.3: Compilation of characterization techniques

Analytical Techniques	Purpose	Instrument
ICP	Identification and detection of trace metals content	Perkin Elmer Optima 5300 DV
AAS	Assess the concentration elements	Chemito model AA–203
XRD	Phase identification of a crystalline material	Bruker D2 diffractometer
FTIR	Identifies chemical bonds in a molecule	Thermo Scientific Nicolet iS5 spectrometer
TGA	Observe the thermal behavior for weight change as a function of temperature	Shimadzu thermal analyser (50 GA)
FESEM	Morphology of the particles	Ziess Supra 40
Particle size analyser	Size and size distribution	Malvern Mastersizer 2000MU
BET	Specific surface area	Tristar II 3020 version 3.02
EDX	Elemental composition	Oxford Instruments
GC analyser	Determination of purity, identification of samples and monitoring of organic reactions	Shimadzu (GC-17A)
XRF	Material analysis	EDX-800 at 200 live seconds
Zeta analyser	Measurement of surface charges	BIC 90 plus (Brookhaven)
Tensiometer	Determine Interfacial and Surface tension	Tensiometer K9 (Kruss)

The experimental methods and techniques highlighted above were adopted throughout this investigation, but with modifications to suit the specific requirements of the systems involved. These aspects are detailed in individual Chapters.

References

- 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.