SYNOPSIS OF

THE THESIS ENTITLED

EXTRACTION OF HEAVY METALS FROM AQUEOUS STREAMS AND THEIR RECOVERY AS FINE PARTICLES

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Chapter 1: Introduction:

The term “heavy metal” refers to any metallic element that has a relatively high density, five times or more than water. Many of the heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in aqueous streams include zinc, copper, nickel, cobalt, cadmium, lead and chromium since they are non-biodegradable and tend to accumulate in living organisms (Sharma, 2015). Heavy metals directly or indirectly discharged into aqueous streams are increasing day by day, especially in developing countries. Heavy 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, 2010), battery manufacturing units (Zewail, 2010; Salam et al., 2011), spent catalyst units (Liang, 2004), rayon manufacturing units (Jha et al., 2008), tannery units (Apaydin et al., 2009; Fu et al., 2011) etc. These metals enter into the aquatic ecosystem where they bio-accumulate and bio-magnify and find their way in the food chain and become toxic for living organisms at higher tropic levels in nature.

Precipitation, ion exchange, adsorption, membrane separations and solvent extraction are the most commonly used techniques to recover heavy metals from aqueous streams. In the last few decades, number of articles and review papers (Peter et al., 1985; Chen, 2004; Barakat, 2011; Fu et al., 2011; Peng et al., 2011; Nassef et al., 2015) have been published detailing the source of heavy metals, their concentrations, removal techniques along with their inherent advantages and limitations. Selection of a suitable method for removal depends on the type of metal, its concentration, the cost incurred and the environmental impact (Kurniawan et al., 2006). Recovery of these metals is not only important from the point of view of pollution abatement but also for recyclability of the metal values.

Solvent extraction, the most important process in hydrometallurgy 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). Post solvent extraction of metal values from aqueous streams the reclamation of metals can be achieved by two methods:- The classical method involves liquid extraction of the metal ions using a suitable extractant and stripping the same with mineral acid solutions of considerable concentration followed by electrowinning to recover the metal. The other option would be to use systems where stripping is combined with precipitation in the same stage. This results in the formation of sparingly soluble precipitates of metal salts such as oxalates.

Number of systems capable of precipitating metals in acidic environments is limited, the sulfide anions and oxalate anions. The sulfide system suffers from the inherent disadvantage of its inability to precipitate some metals at low pH values, whereas the oxalate system is more suitable at low pH values (Zielinski et al., 1998). Hence, the extracted metal can be stripped using a weak acid such as oxalic acid precipitating the metal as a water insoluble metal oxalate. This method has been widely used for preparation of rare earth oxalates (Innocenzi et al., 2015; Smith, 2007). The sparingly soluble oxalates are used as precursors in the synthesis of nanomaterials and high temperature superconductive ceramic materials.

Electrowinning is preferred for large scale applications when facilities are available, in the absence of electrowinning facilities recovery of metals in metallic form involves processes incurring large costs and generation of large amount of wastes. Therefore, the second method, involving precipitation of metals as insoluble salts during stripping could become a versatile alternative to conventional methods for reclamation of the metal values particularly in small scale operations.

The objective of the work was to explore the possibility and feasibility of stripping-precipitation option for recovery of metals as fine particles during the stripping process and use the resulting particles as catalysts for industrial processes. In order to pursue these objectives three industrial aqueous steams were used to recover metal.

1. Acidic wash liquors from brass processing industries primarily containing copper and zinc.
2. Printed circuit board ammonical etching liquors primarily containing copper.
3. Plating industry liquors containing nickel.

The thesis is presented in five Chapters. Chapter 1, introduces the overall scope of the study and lists its objectives.

Chapter 2, *Literature survey,* presents an overview on heavy metals in aqueous solutions, their sources, different techniques for their removal with their advantages and limitations. Fundamentals of solvent extraction, types of extractants, diluents, mechanism of extraction along with details on stripping as in the conventional process and precipitation during stripping to yield fine particles is also included in Chapter 2.

Chapter 3, *Materials and Methods,* lists the different materials and chemicals used in this work. The extraction and stripping procedure is discussed in detail. The various analytical techniques used for characterization of the fine particles are highlighted.

Chapter 4, *Results and Discussion,* reports the results obtained by extraction and stripping-precipitation of metals present in the three industrial waste streams. The extraction patterns of metal values in different extractant solutions was evaluated, subsequently the stripping patterns in oxalic acid solutions were also evaluated. The yield of precipitates was determined. The metal oxalate precipitate was characterized and converted to its oxide by calcinations. The metal oxide was also characterized using XRD, EDX, FTIR and the size and size distribution of the particles was determined using FESEM and particle size analysis. The oxide particles were used as catalysts and their behavior was compared with standard samples from Sigma Aldrich. Discussion and inferences drawn from the results obtained are presented.

Chapter 5: *Summary and Conclusions*, summarizes the results obtained and draws significant conclusions pertaining to, recovery, of metal values from the waste streams as metal oxides and their application as catalysts for important reactions.

Chapter 2: Literature Survey

This Chapter presents an overview on heavy metals in aqueous solutions, their sources, different techniques for their removal, fundamentals of solvent extraction; types of extractants, diluents, and mechanism of extraction along with details on stripping. Literature on precipitation during stripping to yield fine particles and their applications are highlighted. A brief review on the simultaneous extraction and stripping/precipitation is also included.

Heavy metals

Over the past few decades due to industrialization the amount of heavy metals in the waste waters is increasing. These metals find their way into aqueous streams from various industries viz. Fertilizer, electronics, mining, electroplating, paints and pigments, tannery, rayon industries etc. Electroplating plants are by far the biggest and most frequent contaminators of waste waters with heavy metals, followed by the battery manufacturers. Recently, the electronics industry is also in a big way contributing to heavy metal pollution predominantly the waste waters containing copper from printed circuit board manufacturing units.

Since heavy metals are non-biodegradable they tend to accumulate and pass to the food chain. Though some of the metals are essential in trace amounts but when present in concentrations beyond the permissible limits they effect the functioning of living organisms. Due to the stringent regulations heavy metal pollution is a cause of serious concern. Technologies for the removal of metals from waste water have been studied using chemical, physical and biological processes (Wang and Ren, 2014).

Solvent extraction of metals

Solvent extraction of metals is an important technology in hydrometallurgical industry, analytical separations, and liquid waste treatment. It is by far the most widely used technique which can recover the metal in pure and reusable form. Solvent extraction for recovery of metals from aqueous solutions serves the following three purposes:

i) Pre-concentration of trace elements
ii) Elimination of matrix interference
iii) Differentiation of chemical species

It is an environmental friendly process with no air, water or soil pollution. Due to this advantage solvent extraction can replace many conventional processes.

Principle of Solvent extraction:

Solvent extraction of metals is a selective separation procedure for isolating and concentrating metals from aqueous solutions with the aid of an immiscible organic solvent. Since, this process is energetically highly inefficient a metal extractant is added to the oil phase for extraction. Since metals don't have any significant solubility in organic solvents, metal extractant compounds are added to the solvent to enhance the solubility.

Properties of Extractants:

To show the appropriate strength and selectivity of extraction any extractant should have following properties.

- Extractant should have low solubility in aqueous phase, but interact with metal ions and obtain high solubility in organic phase complex. (Kislik, 2012)
- Direct interaction or adduct formation between the extractant and the diluent.
- Facilitate fast metal transfer between the two liquid phases in both loading and stripping and rapid phase disengagement, otherwise the throughput of metal in the overall process will be low.
- Show high chemical stability under the conditions of operation to reduce make-up costs and minimize the transfer of degradation products to other parts of the circuit or to the environment.
- Suitable physical properties of low density, low viscosity, low flash point, non toxic and nonvolatile.

Types of extractants:

According to the mechanism of extraction, organic extractants can be calssified into (1) Metal cationinc extraction, (2) Metal anionic extraction and (3) solavting extraction

Metal cationic Extraction:

In this type of extraction the extractant (L) transfers metal cations, Mn^+, from the aqueous phase by an exchange process in which the metal cation usually substitutes ionizable protons on the extractant, as shown in Equation 2.1

$$nLH_{org} + Mn^{+} \quad \leftrightarrow \quad [MLn]_{org} + nH^{+} \text{ ………2.1}$$

Cation exchange reagents most frequently operate in pH dependent equilibria in which the extractants are organic acids. A ''strong'' extractant is one which has a low $pH_{1/2}$ value (the pH at which 50% of the extractant is loaded with metal). The cation exchange process can be divided into two subgroups chelate and acid extraction. The most widely used acidic chelating extractants are the LIX reagents used to extract copper from acidic and ammonical solutions. Equation 2.2 shows the reaction carried out for the copper extraction from copper sulfate solution

$$CuSO_4 + 2LH_{(org)} \quad \leftrightarrow \quad [Cu(L)_2]_{(org)} + H_2SO_4 \qquad \text{(Extraction) …..2.2}$$

Some of the commercially available basic extractants include phenolic oximes eg. .Acorga, LIX 84, LIX 860), β diketones, Dialkylphosphonic acids eg. PC88A, Ionquest 801, Dialkylphosphoric acids eg. D2EHPA, versatic acid, Kelex 100, Dialkylphosphinic acids eg. CYANEX 272, 302 (Wilson, 2014).

Metal anion Extraction:

The liquid anion exchangers also known as basic extractants function by ion exchange mechanism. It requires the formation of neutral assemblies (often referred to as ‘‘ion pairs’’) in the water immiscible phase as shown in Equation 2.3.

$$nH^+ \quad + \quad nL_{org} + MX_y{}^{n-} \quad \leftrightarrow \quad [(LH)_nMX_y]_{org} \text{ …….2.3}$$

Two types of processes are most commonly involved in which the load/strip processes are controlled by either pH or anion-swing mechanisms. In pH-swing processes, protonation is required to generate the cationic extractant and the loading and stripping can be controlled by varying pH.

This type of extractant extracts metals selectively and yield highly pure solutions. Long-chain alkylamines are the most important group of basic extractants.

The extractant used in anionic extraction are of three types: primary amines, secondary amines and tertiary amines. Some of the commercially exploited basic extractants include the primary, secondary tertiary and quarternary amines.

Metal salt extraction:

The use of a water-immiscible reagent (L) is used to extract a metal salt. In this process ion-pairing interaction between the anion and a positively charged metal in the anion receptor is used to enhance the strength and selectivity of binding which can be shown by equation 2.4

$$nL_{org} + MX_y \quad \leftrightarrow \quad [L_nMX_y]_{org} \text{ …………..2.4}$$

A number of organic reagents like alcohols, ethers, ketones, alkyl phosphates with an O-atom as an electron donor can solvate the metal ions and thus find application as solvating extractants. Some of the commonly used solvating extractant are Acorga CLX50, Acorga ZNX50, TBP, TOPO, Cyanex 471, Cyanex 921 and MIBK.

Polytopic solvent extractants are used to bind both cations and anions as a metal salt. These reagents are targeted to recover alkali metal salts, incorporating a strong and selective binding site for the metal cation.

Diluent/oil phase:

Diluent is a liquid or homogeneous mixture of liquids in which extractant and possible modifier are dissolved to form the solvent phase. The diluent by itself does not extract the main (extractable) solute appreciably. Diluents can be classified according to their physical properties and preferable according to their ability to form ordered networks (Lofstrom, 2010).

Paraffinic diluents are better than aromatic ones. Khorfan and Koudsi (1995) gave general order to describe the efficiency of diluent in the following order: Paraffinic kerosene > cyclohexane > carbon tetrachloride > toluene > benzene > chloroform > alcohols.

Stripping

In solvent extraction metal, ions are extracted from their respective solutions in an oil phase. Subsequent to extraction, the metal ions are then stripped from the organic phase to regenerate the oil phase. Commonly, stripping is accomplished with mineral acid solutions of considerable concentration, as required for the high efficiency of the operation. Stripping-precipitation is a process combining the stripping and precipitation stages in a conventional solvent extraction process instead of the traditional acid stripping to reduce the aqueous waste generated by an industrial facility.

Stripping is accomplished with a mixture of acidic strip solution and a reagent which precipitates the heavy metal ions in the form of sparingly soluble precipitates. By selectively selecting the strippant one can precipitate a metal salt in the aqueous phase due to its low solubility in the aqueous phase. Apart from material savings, due to elimination of the need for neutralization of acid, the benefit is the possibility of recycling of the strip solution, after adjusting its composition. Also, by appropriate selection of conditions of operation of extraction and stripping, particular metals may be precipitated selectively, which greatly simplifies further recovery (Zielinski et al., 1998).

The extraction of divalent metal ions from aqueous solutions is given by Equation 2.5

$$M^{2+}{}_{(A)} + 2(RH)_{(O)} \rightleftharpoons (MR_2)_{(O)} + 2H^+{}_{(A)} \quad \ldots\ldots\ldots..2.5$$

Where, RH is the ligand used and (A) and (O) represent aqueous and organic phases respectively.

In stripping- precipitation process, the loaded metal organic phase is contacted with weak acids like oxalic acid and precipitated as insoluble powders of oxalates. Oxalic acid dissociates into hydrogen ions and oxalate anions in the aqueous phase, acts as both a stripping agent and a precipitating agent, the metal in the organic phase is stripped with the hydrogen ions and subsequently precipitated by oxalate anions. Ammonium oxalate and sodium oxalate can also be used as the stripping agents. When oxalic acid is to be used to precipitate the metal oxalate, the reaction will be given by Equation 2.6

$$(MR_2)_{(O)} + (COOH)_{2(A)} \rightleftharpoons MC_2O_{4(A)} + 2(RH)_{(O)} \quad \ldots\ldots\ldots..2.6$$

Metal oxalates produced during the stripping-precipitation technique then can be calcined to get their metal oxides respectively. This technique has mostly been used to prepare rare earth oxalates (Zielinski et al., 1991; Zielinski and Szczepanik, 1993; Konishi et al.,1993; Combes, 1997; Smith 2007). Zielinski et al. (1998) examined the stripping-precipitation process for heavy metals like zinc, lead, copper, cadmium and nickel.

Combined extraction-stripping/precipitation

Combined extraction-stripping/precipitation can be carried out in an emulsion liquid membrane (ELM) system. An ELM system involves the preparation of a W/O emulsion and dispersing the same as tiny globules of 0.5 – 3 mm in diameter, in a feed solution from which a solute has to be removed. The oil phase of the emulsion is the membrane phase that separates two aqueous phases, the aqueous feed phase in which the emulsion is dispersed and the internal aqueous phase where the solute is entrapped or concentrated. When metal ions have to be removed from the aqueous feed phase a suitable extractant is added to the membrane phase. The metal ions present in the feed phase react with the extractant ($HR_{org.}$) at the interface between the emulsion globule and the feed. The chemical reaction that takes place at the interface can be described by equation 2.7

$$2HR_{org} + M^{2+}_{aq} \leftrightarrows MR_{2org} + 2H^{+}_{aq.} \quad \ldots\ldots 2.7$$

The resulting metal complex (MR_{2org}) diffuses through the oil membrane phase of the emulsion and on contact with the internal stripping phase of the emulsion the metal gets stripped from the extractant as per the following chemical reaction:

$$2H^{+}_{inner} + R_2M \leftrightarrows M^{2+}_{inner} + 2RH_{org} \quad \ldots\ldots\ldots 2.8$$

The stripped ion is effectively encapsulated within the emulsion globules while the extractant stripped of metal shuttles back to scavenge more metal ions from the feed phase to deposit in the internal stripping phase of the emulsion.

Commonly used stripping agents are mineral acids. The metal salts formed by the stripping reaction are highly soluble in the acidic environment prevalent within the internal emulsion droplets hence, these salts remain dissolved. When an organic acid such as oxalic acid is used as the stripping phase the resulting metal oxalates formed are only sparingly soluble in the weakly acidic environment within the internal phase droplets resulting in the precipitation of the metal oxalates in the form of fine particles.

This technique offers a distinct advantage for the production of fine particles having diameters less than 10 μm in the liquid phase, Moreover, the reaction leading to oxalate formation takes place in the aqueous internal droplets of the ELM that are of restricted size hence, the size and morphology of the particles can also be controlled (Hirai et al., 1999). Thus the synthesis of particles in an ELM system also has the advantage of obtaining a narrow particle size distribution. Such particles can be conveniently used in applications involving thermal or plasma spray of particles due to the uniform melting behavior.

Submicron sized particles of Nickel oxalate (Sengupta et al., 2011) copper oxalate (Hirai et al.,1996) as well as rare earth oxalates of Ce, Pr, Nd and Gd La, Dy and Y (Hirai et al., 1998) particles have been synthesized in ELM systems

Catalytic properties of metal oxides:

Metal oxides were widely used as a catalyst for many organic reactions, such as oxidation, dehydration, dehydrogenation and isomerization. They provide either as active phases or as supports. Metal oxides are utilized both for their acid–base and redox properties and constitute the largest family of catalysts in heterogeneous catalysis. Among the metal oxide catalysts, those of transition metals occupy a predominant place owing to their low cost of production, easy regeneration and selective action. The major application of metal oxides are in pharmaceutical industry, organic synthesis, synthesis of fine chemicals, industry and green chemistry (Gawande et.al., 2012) 50% of the metal oxides synthesized are used as catalysts.

The performance of metal-oxide catalysts depends on their nature, size, shape, and surface area. According to synthetic approaches to metal oxide catalysts, their activity can be changed and thermal treatments can cause the morphological changes of metal oxide catalysts. (Lee et al., 2014)

Copper oxide is one of the most active catalysts and has been considered as a potential substitute for noble metal-based emission control catalysts. Copper oxide is used for the oxidation of ammonia to Nitrogen (Lu Gang, 2000). Nickel oxide shows very good activity for photo degradation of dyes (Farzaneh and Haghshenas, 2012), oxidation of peroxidase substrate (Ray et al., 2014), and ethyl benzene(Peng et al., 2014). Cadmium oxide used for hydrolysis, esterification, and transesterification of fatty acids. (Alves et al., 2014)

Chapter 3: Materials and Methods

This Chapter highlights various reagents and chemicals used and the experimental methodology for recovery of heavy metals from three industrial samples as metal oxide fine particles. The different techniques used for the characterization of the particles obtained are also detailed. The application of the metal oxide as catalysts for industrially important reactions is also discussed.

Materials used:

Industrial waste samples

Printed circuit board etchant was supplied by a printed circuit board manufacturing unit in Vadodara, Gujarat. Electroplating industry waste water was obtained from an optical frame plating industry, Mumbai. Acidic wash liquor from brass artefact manufacturing industry was collected from a cottage industry in Rajkot, Gujarat.

Extractants

LIX 84I, a water insoluble 2-hydroxy-5nonylacetophenoneoxime in a mixture with a high flash point hydrocarbon diluent, a brown colored, viscous and odorless liquid with density around 0.9 $g.cm^{-3}$ supplied by Cognis Inc. Ireland was used as the extractant for copper and nickel.

D2EHPA, a clear almost colorless medium viscosity and highly acidic liquid with slightly sweetish odor, having a boiling point 48^0C at 12 mm Hg, density 0.97 $g.cm^{-3}$ and a flash point 137^0C, obtained from Merck Specialties Private Limited, Germany was the extractant for nickel and zinc.

Miscellaneous chemicals

- Sulfuric acid of AR grade with assay 98% was supplied by Merck Specialties Private Limited.
- Oxalic Acid of AR grade with assay 99.8% was supplied by S.D fine Chemical limited.
- Kerosene (B.P. 152-271°C) was supplied by Indian Oil Corporation Limited, Vadodara, Gujarat, India.
- Buffer tablets: Buffer tablets of pH, 4.0, 7.0 and 9.0 supplied by Fischer Scientific Manufactured by Qualigens Fine Chemicals were used to prepare buffer solutions used to calibrate digital pH meter.

- Metal standards: Certified AAS standard of SRL make were used to generate standard curves for metals at various concentration.
- Nitrobenzene of AR grade with assay 99% was supplied by Spectrochem Pvt. Ltd. Mumbai.
- Aniline and Methanol of AR grade with assay 99% was supplied by S.D.fine Chemical limited.

Analysis of wastes

Prior to extraction studies, inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was carried out to determine the different metals present in all the three waste samples. The pH of the waste samples along with the chloride, sulfate, nitrate and the ammonical content was also determined to select the appropriate extractant for metal recovery.

Extraction of metals

The Printed circuit board etchant contained a high level of copper and small amount of other metal ions in ammonical media. The pH of the waste sample was 8.7. Extraction experiments were performed using equal volumes of oil phase (50% LIX84 and 50% kerosene) and waste sample in shake flasks on a rotary shaker (Remi-RS 24BL) at 150 rpm and 30^0C. Ammonia was added for pH adjustment and the extraction was carried out at an equilibrium pH of 8.7. The total number of stages required for extraction was determined. The concentration of the metal in the aqueous phase was determined using atomic absorption spectrometer (Chemito AA203) and that extracted in the oil phase containing extractant was determined by mass balance.

Stripping – Precipitation

After extraction the oil phase was washed with water several times and then subjected to stripping-precipitation on a rotary shaker (Remi-RS 24BL) at 150 rpm and 30^0C using oxalic acid at equal volumes of both the phases to recover the metals as their oxalates. The number of stages required for stripping was determined. Effect of concentration of the acid and time of contact on stripping and precipitation was investigated,

The stripped oil phase was separated from the aqueous phase containing the oxalate particles. The aqueous phase was centrifuged at 7000 rpm to separate the copper oxalate particles. The aqueous phase after stripping was also analyzed for the metal content to determine the amount of dissolved metal oxalate present in the aqueous phase. The precipitated metal oxalate particles were further washed several times and dried. The oxalate particles were then calcined in a tube furnace to obtain the metal oxides.

The oil phase containing the metal extractant was further stripped with 1.5M sulfuric acid to remove traces of metal present. To determine the efficacy of extraction cycle the oil phase was recycled and contacted with fresh waste samples for a number of times.

The same procedure was used for obtaining metal oxalate and oxide with other two waste samples Depending on the pH values and the metals present the extractants were selected accordingly. Figure 3.1 shows the schematic of the process.

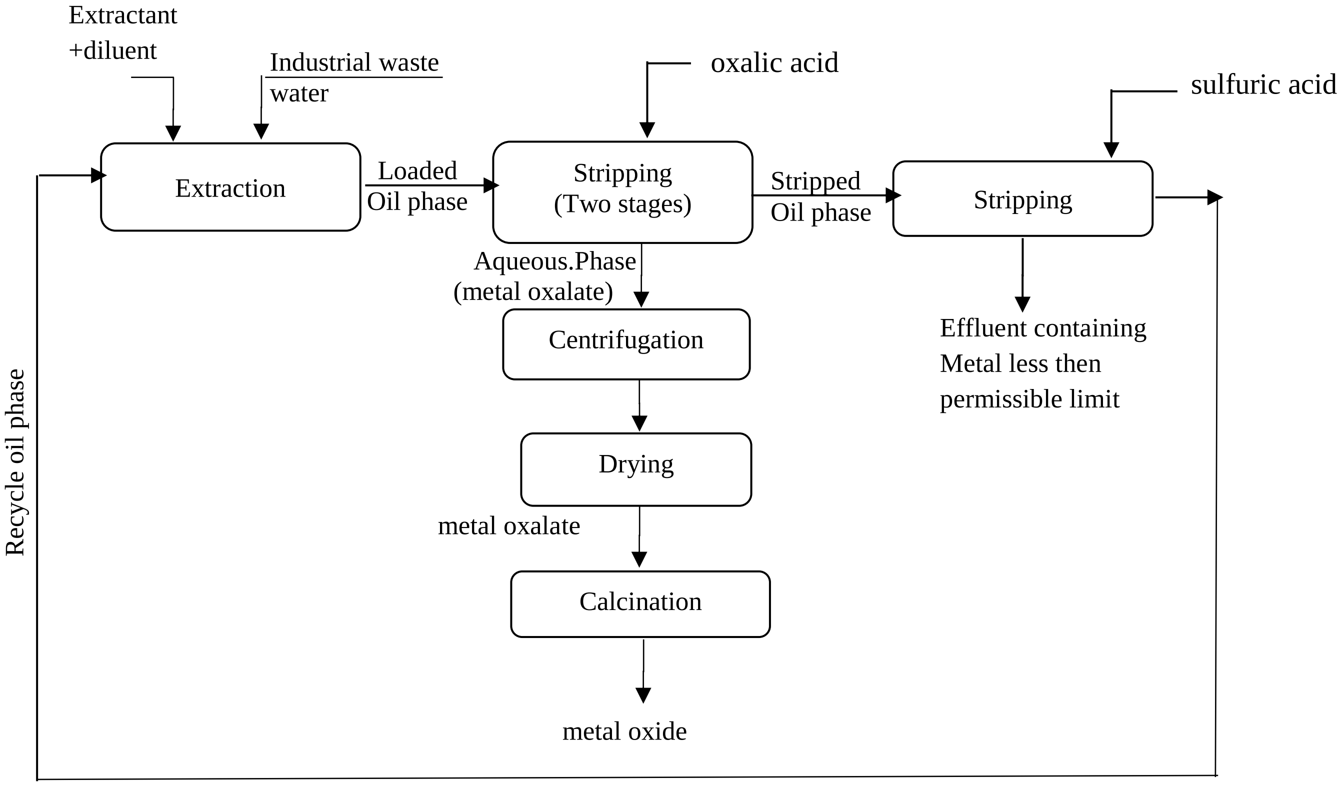

Figure 3.1: Schematic of metal recovery from waste.

Combined extraction and Stripping-precipitation

Copper oxalate particles were also prepared by carrying out simultaneous extraction and stripping-precipitation in a W/O emulsion using the emulsion liquid membrane route. Wherein

W/O emulsions were prepared by mixing kerosene (oil phase), carrier LIX 84I, (10% v/v of the membrane phase) and emulsifier Span 80 (5 % wt/wt of oil phase) with an aqueous solution of oxalic acid using a high-speed blender at 12,000 rpm. The volume fraction of the internal phase of the emulsion was 0.5 except when the internal phase volume fraction was varied the resulting emulsion was contacted with synthetic solutions of copper sulphate (500 mg/L) at treat ratios of 1:5.

Extraction of copper was carried out at 30^0C ± 1 in a four baffled batch extractor 0.105 m in diameter equipped with a six bladed disk turbine agitator having disk diameter 0.038 m. The emulsion was dispersed in the copper sulfate solution by stirring the contents at 160 rpm. The pH was maintained at 4. The oxalic acid concentration was varied so as to obtain a mole ratio of copper to oxalic acid (M) of 0.5 and 1. The volume of emulsion to copper sulfate solution (external aqueous phase) ratio was maintained at 1:5. On completion of the extraction/precipitation the emulsion was separated from the external aqueous washed with water and subsequently demulsified using acetone. The particles synthesized in the internal phase of the W/O emulsion were separated by centrifugation, washed with acetone and dried prior to their characterization.

Analytical Techniques

- Systronics make – 335 pH meter was used for pH measurement.
- The metal content in the industrial waste samples was analyzed by Inductively coupled plasma optical emission spectrometry (ICP-OES). Perkin Elmer Optima 5300 DV was used for analysis.
- Metal concentrations in aqueous solutions were measured using atomic absorption spectrophotometer ‘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 metal standards within the available concentration range and then the samples were analyzed after required dilution.
- Metal oxalate and oxides were analysed using XRD which is primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. Bruker D2 diffractometer using Cu-Kα radiation at λ value of 1.54A° was used for characterization.

- Fourier transform infrared spectroscopy (FTIR) was used to obtain an infrared spectrum of absorption or emission of metal oxalate and metal oxides which simultaneously collects high spectral resolution data over a wide spectral range to identify chemical compounds. Analysis was carried out over a frequency range of 400–4000 cm^{-1} with 32 scans using Thermo Scientific Nicolet iS5 spectrometer with iD1 transmission.
- Field Emission Scanning Electron Microscopy (FESEM) was used to determine the morphology of the particles. High-resolution images were taken on a Ziess Supra 40 FESEM.
- Size and size distribution of the oxalate particles were determined on a Particle size analyser (Malvern Mastersizer 2000MU)
- Thermo gravimetric analysis (TGA) of the metal oxalates was carried out on a Perkin Elmer thermal analyzer (TAC7/DX) at a heating rate of 20^0C/min, in an oxygen atmosphere.
- The elemental composition was determined using Energy-dispersive X-ray spectroscopy (EDX) on Oxford instrument.
- Surface area of the particles was determined on a BET analyser of Micromeritics.
- Thin layer chromatography (TLC): TLC method was used to identify the compound present after the reaction and also monitor the progress of a reaction when using the metal oxide as catalysts.
- Gas chromatography (GC) technique was carried out on Shimadzu (GC-17A) used to quantitatively or qualitatively test the purity of the different products formed while performing the reactions using metal oxides.

Catalytic activity

Hydrogenation of *p*-nitrophenol (PNP) to *p*-aminophenol (PAP) using $NaBH_4$ as a reducing agent was studied as a test reaction for determining the catalytic activity of the metal oxides. The reaction was carried out at room temperature, with water as a solvent. UV-vis spectroscopy was used to monitor the conversion.

Copper oxide particles were used as catalyst for the conversion of nitrobenzene to aniline. The effect of reaction time, temperature and catalyst loading was investigated. The reusability of the catalyst was also studied.

In a similar manner the applicability of the other metal oxide particles as catalysts for different reactions was also studied.

Chapter 4: Result and Discussion

The results obtained for the extraction of heavy metals using different extractants are listed in Chapter 4 for the three wastes. The recovery of the metals as their corresponding oxalates using stripping-precipitation is also included. The characterization of the metal oxalate and oxide particles are also detailed.

Recovery of heavy metal from the printed circuit board etchant:

The printed circuit board industry commonly uses ammonical alkaline copper etchant to remove unwanted copper from printed circuit boards as part of the fabrication process. Ammonical alkaline copper etchant is a mixture of copper ammonium chloride, ammonium chloride, ammonium hydroxide, ammonium carbonate, and small amounts of other materials. Copper ammonium chloride itself is the active etchant when the copper is in the cupric (+2) state. Cupric ammonium chloride attacks and dissolves metallic copper, forming cuprous (+1) ammonium chloride. The cuprous salt is inactive as an etchant material. Cuprous salts are reoxidized to the active etchant or cupric form by atmospheric oxygen. This etchant is widely used in printed circuit board production industries. The etch rate is very fast and the etch solution can hold large amounts of copper. After etching, the normal maximum loading of copper is l05—l88 grams of copper per liter. The solution, once loaded with copper, is either discarded or is recycled and processed to remove the excess copper to yield fresh etchant and metallic copper.

Copper extraction from PCB waste

The PCB waste having initial pH of the waste was 8.75 was analyzed for its metal content by ICP. Table4.1 shows the metal composition in the PCB waste.

Table 4.1: Metals present in PCB waste

Metal	Cu	Fe	Cd	Pb	Ni	Se	Zn	Sn
Concentration(mg/L)	42925	ND	ND	33.53	3.37	ND	14.05	1.85

Hydroxyoximes are widely used copper extractants, LIX 84 I a ketoxime, is a moderately strong copper extractant of the hydroxyoxime family suitable for copper removal above 1.6-1.8 in acidic media. LIX 84 I has also been used as an extractant for copper removal from ammoniacal media (Hua et al., 2013; Ochromowicz et al., 2014; Panigrahi et al., 2009).

Extraction of copper was carried out by equilibrating equal volumes of waste with kerosene containing 50% LIX 84I. Copper extraction was as per Equation 4.1. Pilot experiments revealed that 5 minutes was sufficient for equilibrium to be attained. To ensure attainment of equilibrium, the oil and aqueous phases were contacted for a period of 15 minutes. The phases were separated and the equilibrium pH value was noted. After extraction there was an increase in the pH this was due to release of ammonia in the aqueous phase (Equation 4.1). Ammonia with its lone pair of electrons on nitrogen atom competes with the extractant for the metal ion.

$$[\mathrm{Cu(NH_3)_4}]^{2+}_{\mathrm{aq}} + 2\mathrm{RH_{org}} \leftrightarrow \mathrm{CuR_2} + 2\mathrm{NH_4^+} + 2\mathrm{NH_3} \ldots\ldots\ldots \qquad 4.1$$

It was found that 52% of copper was extracted in the first stage and all of the nickel and zinc was also extracted. The other metals present were not extracted under the operating conditions. The waste was further contacted with fresh extractant in the second stage to recover the remaining copper in the waste. 99% of the copper was removed in the second stage. Around 22 mg/L of copper remained in the aqueous phase along with lead, and tin. The oil phase was washed several times to remove the free ammonia that was transported to the oil phase since $\mathrm{NH_4^+}$ is not soluble in the oil phase.

Synthesis of particles using stripping-precipitation:

Post extraction the copper loaded oil phase was contacted with 1M oxalic acid to precipitate copper as an insoluble oxalate thereby, combining the stripping and precipitation stages in a single stage in comparison to the conventional solvent extraction process.

Stripping was carried for varying time intervals (15 minutes - 3 hours), copper stripped from the oil phase and was converted to copper oxalate according to Equation 4.2, thereby releasing the extractant in the oil phase for reuse. Table 4.2 shows the percentage stripped at varying time intervals.

$$\mathrm{CuR_{2(O)}} + \mathrm{(COOH)_{2(A)}} \longrightarrow \mathrm{CuC_2O_{4(A)}} + 2\mathrm{(RH)_{(O)}} \ldots\ldots\ldots \qquad 4.2$$

Table 4.2: Percentage stripping with time

Stripping time (Min)	% stripping
0	0
15	36.97
30	67.22
60	73.42
120	77.70
180	79.37
240	80.85

Hence, the synthesis of particles of metal oxalate was a two-step process involving loading of a metal into an organic phase and subsequent stripping in the form metal oxalate using appropriate stripping agent. Recyclability and reuse potential of the stripped oil phase was evaluated by contacting the oil phase with the waste under the desired set of conditions and thereafter, was stripped again in the second cycle. This process was continued for multiple cycles. Figure 4.2 shows the reusability of the extractant for multiple cycles. The performance of the extractant system was sufficiently stable even after the 10th cycle of extraction for both the stages.

The oxalate particles obtained were calcined in a tube furnace at 400°C for three hours to obtain the metal oxide.

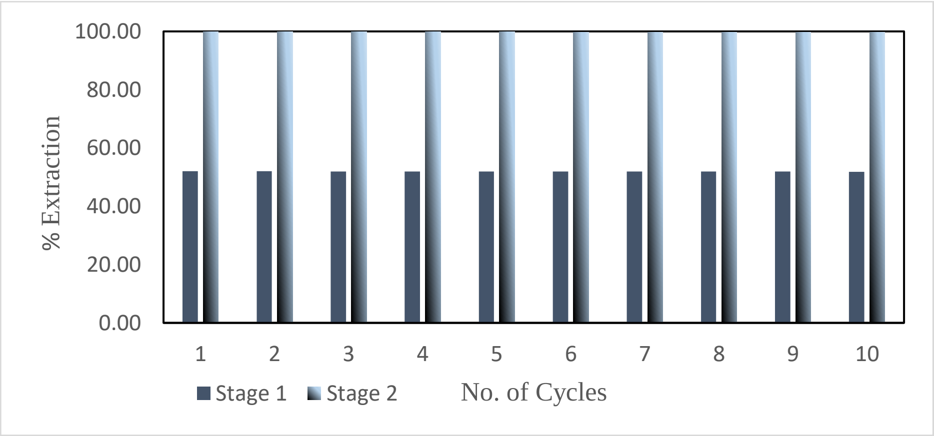

Fig: 4.2: Reusability of extractant

Characterization

The X-ray diffraction patterns of the metal oxalate and oxide samples prepared is shown in the Figure 4.4. All the peaks in the XRD patterns are consistent with JCPDS (021-0297) for copper oxalate and JCPDS (48-1548) for copper oxide with a monoclinic phase. No characteristic peaks of other metal impurities are observed, indicating the formation of a pure phase of copper oxalate and copper oxide. The crystallite size was found using the Scherrer's equation to be 31.45 nm. SEM images of the Copper oxalate and copper oxide are also shown in Figure 4.5. It can be seen that the material has become porous after calcinations.

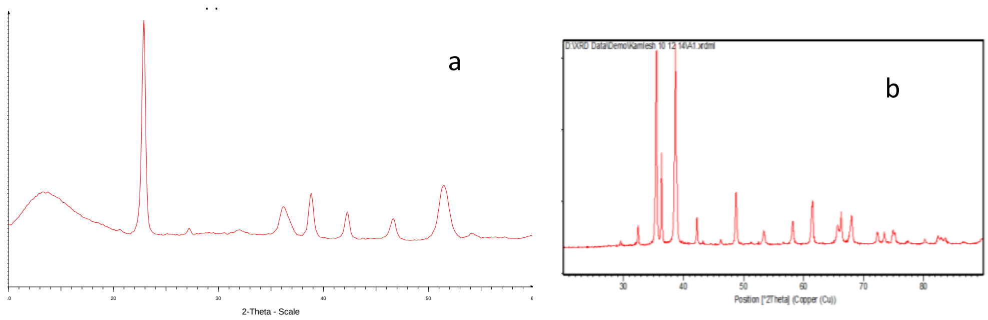

Figure 4.4: XRD of (a) copper oxalate and (b)copper oxide

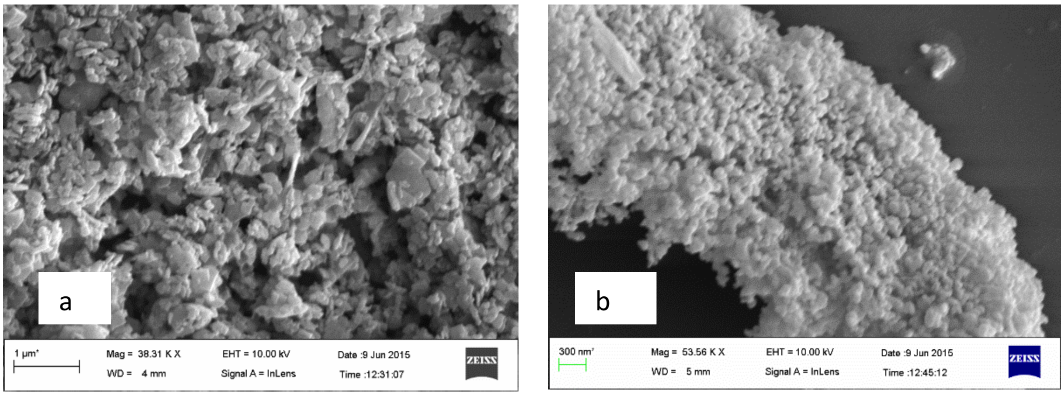

Fig.4.5: FESEM images of (a) copper oxalate and (b)copper oxide

Combined extraction and stripping-precipitation

Copper oxalate particles were also prepared by carrying out simultaneous extraction and stripping-precipitation in a W/O emulsion using the emulsion liquid membrane route. The particles were synthesized in the confined internal phase of water in oil emulsions. The internal phase droplet sizes of the emulsion where precipitation took place were ~3.2 µm in size.

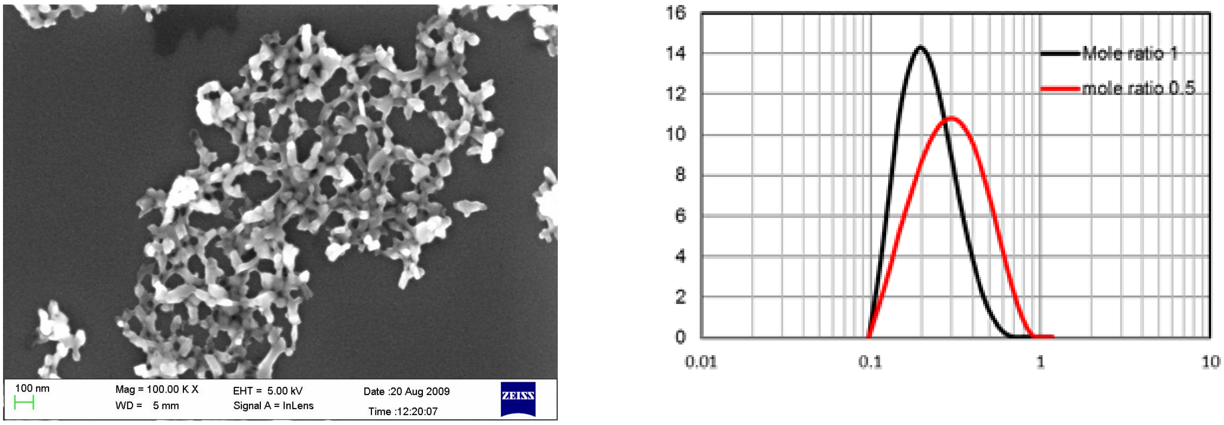

Fig: 4.6: (a) FESEM image of Copper oxalate and (b) Particle size distribution for particles prepared in W/O emulsions

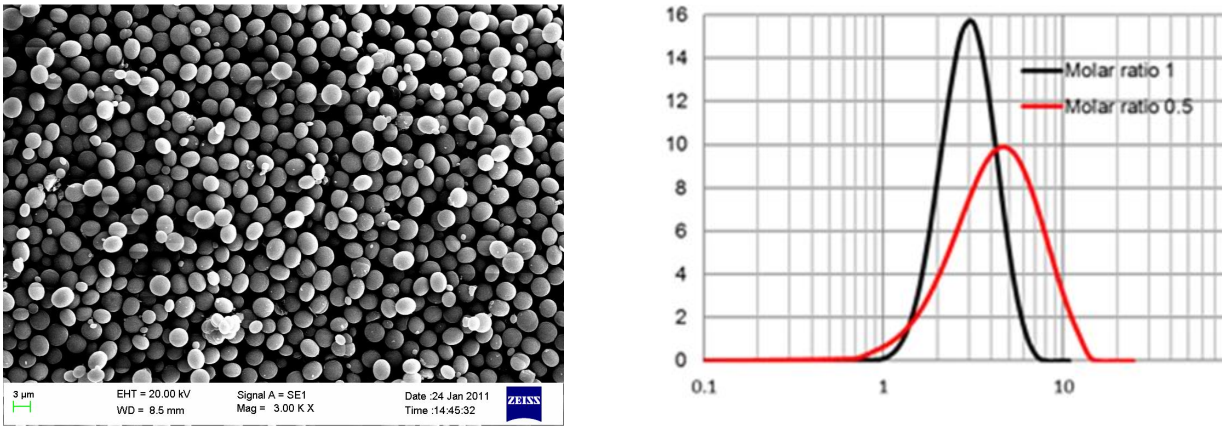

Fig: 4.6: (a) FESEM image of Copper oxalate and (b) Particle size distribution for particles prepared in homogeneous solutions

It was observed that the particle size of the oxalates ranged between 0.1 to 1 µm and rectangular shaped particles (Figure 4.6). Copper oxalate particles when synthesized under the same conditions in a homogeneous system had sizes ranging between 1 to 10 µm and exhibited a spherical morphology with the spheres formed by the aggregation of nanoparticles (Figure 4.7).

Application of metal oxide as catalysts

The synthesized copper oxide particles were used for the Reduction of Nitro Aryl Compounds. A mixture of nitrobenzene, synthesized copper oxide and solvent methanol were added to a three-necked flask, and sodium borohydride then added drop wise to the above solution under the continuous stirring. The mixture was stirred and monitored by TLC. After the completion of the reaction, the mixture was cooled to room temperature and then filtered. The filtrate was washed with methylene chloride, the organic layer was washed successively with brine and water, it was then dried with anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The residue was purified by chromatography on silica gel to give desired product (Aniline). The product was analyzed using gas chromatograph. The catalyst was reused up to 4 cycles and there was no significant change in its activity as observed by consistent result of its conversion of the reactant. Before reuse the catalyst was washed with distilled water and then dried.

Chapter 5: Conclusions

Recovery of metals from waste streams is not only important from the point of view of pollution abatement but also for economic gain as these metals can be recycled. Conventional technique of chemical precipitation of metals using hydroxide and sulphide though relatively simple and inexpensive results in the formation of large amount of sludge and its disposal is a big issue and moreover the metals cannot be conveniently reused again.

An attempt has been made in this investigation to use three industrial waste streams containing heavy metals and recover the heavy metals for reuse as catalysts in industrially important reactions. Solvent extraction and stripping-precipitation was used to recover the metals as their oxides. Results indicate that this technique will hold a promise to recover metals where electrowinning is not possible or for small scale applications. A simple solvent extraction strategy in combination with stripping-precipitation can be used to reclaim the metals from secondary sources for reuse, satisfying the dual goal of environmental sustainability and economic gain in terms of the reclaimed heavy metal.

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