CHAPTER 2

Heavy Metals in Aqueous Solutions: Sources, Effects and Reclamation

2.1 Introduction

In common parlance the term “heavy metal” refers to any metallic element that has a relatively high density, five times or more than water. Heavy metals are those metals in the periodic table with an atomic number greater than 20, excluding the alkali metals. These metals have similarity in their chemical properties and environmental behavior. The metal industry is a key sector in the Indian economy as it meets the requirements of a wide range of important industries such as engineering, electrical and electronics, infrastructure, automobile and automobile components, packaging etc. Metals, which include aluminum, copper, zinc, lead, nickel and tin, are used to make alloys, castings, forgings, extrusions, wires, cables, pipes, etc., and find their application in a number of sectors such as agriculture, infrastructure facilities like power plants, automobiles, railways, telecommunications, building and construction and in engineering and chemical plants. (Metals market and opportunities, 2007)

Metals play an important part in modern societies and have historically been linked with industrial development and improved living standards. During the past few decades, Indian industries have registered a quantum jump, which has contributed to high economic growth but simultaneously it has also given rise to severe environmental pollution (Lokhande *et al.*, 2011). In aqueous streams heavy metals of particular concern include zinc, copper, nickel, cobalt, cadmium, lead and chromium since, they are non-biodegradable and tend to accumulate in living organisms (Gautam, 2015). Many of the heavy metal ions are known to be toxic or carcinogenic even in very low concentrations (Tchounwou *et al*., 2012). Increased industrial activities has increased the incidence of percolation of toxic metal ions to the soil and water bodies and presently their presence in ecosystem, have reached to an alarming level that environmentalists are finding it difficult to enforce control measures. (Kulshrestha *et al.*, 2013).

As human populations and economies have increased, simultaneously, the use of metals and industrial minerals has also increased. This dramatic growth in metals and minerals use has serious implications for both the availability of future resources and the health of the environment, which is affected by the outputs associated with their use (Rogich and Matos, 2008). 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. Society is now attempting to remediate, control and minimize such pollution wherever possible due to their toxic effect.

2.2 Sources of heavy metals in wastes and the need for recycle

Sources of heavy metals in waste waters and aqueous streams are diverse, but metal related industries are the largest contributors. Metals find their way into aqueous streams from the effluents of metal plating industries (Bode, 1998; Benito *et al.*, 2002; Barakat, 2011), hydrometallurgical applications (Elejalde *et al.*, 1991; Zewail and El-Garf, 2010), battery manufacturing units (Zewail and El-Garf, 2010; Salam *et al.*, 2011), spent catalyst units (Liang, 2004), rayon manufacturing units (Jha *et al.*, 2007) and tannery units (Apaydin *et al.*, 2009; Fu *et al.*, 2011). Other sources are the discharge from basic steel works, aircraft plating industries, paper and pulp industries, petroleum refining and printed circuit board industries (Kadirvelu and Goel, 2007). Table 2.1 lists the industrial sources of heavy metals.

Table 2.1: Industrial sources of heavy metals

Industries	Metals	References
Fertilizers	Cd, Cr, Mo, Pb, U,V, Zn	Otero *et al.*, 2005; Ajmal *et al.*, 2001
Batteries	Cd, Ni, Hg	Jadhav *et al.*, 2012
Electronics and Electricals	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn, Ag ,Au, Co, Sn, Zn	Veglio *et al.*, 2003
Sewage sludge	Zn, Cu, Ni, Pb, Cd, Cr, As, Hg	Nicholson *et al.*, 2003
Alloys and steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Rule *et al.*, 2006; Cheng, 2003; Ajmal *et al*., 2001
Electroplating	Cd, Cr, Ni, Zn, Cu, Fe	Castelblanque *et al*., 2004; Jordao *et al*., 2002; Ajmal *et al.*, 2001
Paints & Pigments	Pb, Cr, As, Ti, Ba, Zn, Fe, Ni	Monken, 2000
Petroleum spent catalyst	Ni,Co,Mo	Jadhav *et al.*, 2012
Paper mill	Cu, Zn	Lokhande *et.al.* 2011
Textile and dye	Zn	Lokhande *et.al.* 2011
Metal finishing industrial waste	Cr, Ni, Cu, Zn, Au, Ag, Cd	Jadhav *et al.*, 2012; Ajmal *et al.*, 2001
MSW fly ash	Cu, Zn, Ni, Al, Cr, Pb	Jadhav *et al.*, 2012

Metal industry comprises of primary and secondary segments. Primary producers are those who process the mined ore into primary metal, which is commercially available in the form of rods, ingots, cathodes, wires etc. Secondary producers are those who manufacture value added products like foils, extrusions, dry batteries, castings etc. either by procuring the metal from the primary producers or from scrap (Metal, IBEF report 2006).

In recent years the average ore grade has gone down by 25% in just ten years whilst the energy consumption per ton of production has increased by around 12 % due to the disappearance of high quality natural resources. Pressures on demand, coupled with a growth in commodities prices and increasing costs of primary production, create the perfect conditions to drive an increase in recycling rates (Johnson, 2017). Therefore, there is a clear need within the industry for further increase in recycling of all valuable base metals from secondary sources in order to reduce the pressure on primary supply.

The most significant solid waste materials contain nonferrous metals such as gold, silver, nickel, molybdenum, copper, zinc, chromium and others, as potential heavy metals. Therefore, these residues would be considered secondary resources or artificial resources. Non-ferrous metals, including aluminum, copper, lead, nickel, tin, zinc and others, are among the few materials that do not degrade and do not lose their chemical or physical properties during the recycling process. Consequently, nonferrous metals and precious metals have the capacity to be recycled for infinite number of times. (Canda *et al.*,2016).

As the demand of metal increases, recycling plays a very important role. For example, in 1970 the global consumption of copper was 8 million tons per annum, out of this 5 million tons was obtained from primary mining and 3 million from recycling. In 2008 copper consumption was about 24 million tonnes per annum, from which 8 million came from recycling and remaining from primary production. For most metals recycling currently provides 10 to 15 percent of demand (Bloodworth, 2012). Out of about 19,909 thousand tons per year of copper production globally, about 40 % of copper is produced from secondary sources. World copper mine production to increase 2.5% on an annual basis in 2018 to 20.3 million tonnes of copper content. (ASIA copper week, 2017)

The success of secondary metals markets depends on cost of retrieving and processing metals embedded in used materials. The higher the concentration, the easier is to recycle.

The choice of whether to use primary or secondary sources is determined primarily by the type and capacity of existing capital equipment, quality of the feed, metal prices, and relative supply (Wernick and Themelis, 1998). As per Cole and Sole (2002), increasing awareness of secondary zinc materials as a valuable resource, stricter environmental legislation restricting dumping of these hazardous materials has led to an interest in recycling. Approximately 30% of global zinc production arises from recycled zinc.

Wernick and Themelis (1998) have listed the benefits of recovering and reclaiming metals from secondary sources such as:

- Reduction in energy needed to produce a ton of metal (e.g. Copper from ore requires five to seven times more energy than that required for processing recycled metal).
- Requires considerably less energy than mining and processing ore.
- Avoids mine, concentrator, leach and smelter wastes.
- Reduces mining and beneficiation activities that disturb ecosystems.
- Decreases environmental impacts associated with mining and release of toxic wastes into the environment.

During the treatment of wastes, the objective is to remove the metals so as to produce a liquid waste stream capable of reuse, or dispose the liquid meeting the environmental discharge limits. Energy savings is the major benefit of recycling. Table 2.2 shows significant benefits and energy savings by using recycled materials in place of virgin materials (Awasthi, 2017).

Table 2.2: Benefits of recycling

Benefits	Percentage
Savings in energy	74
Savings in virgin materials use	90
Reduction in air pollution	86
Reduction in water pollution	76
Reduction in mining wastes	97
Reduction in water use	40
Reduction in consumer wastes generated	105

Market research report 2004 shows that until 1990's Indian market was mainly depending on primary resources but the increasing demand can be fulfilled only through recovery, recycle and reuse.

2.3 Toxic effect of heavy metals on human body

Heavy metals interact with living organisms in number of ways. Copper, zinc, nickel, iron, vanadium are necessary micronutrients and essential part of metalloenzymes. (Bontidean *et al.,* 2002) These metals are present naturally in water at low concentration levels, but in industrial waste water the concentration level is very high, which is toxic for the environment, aquatic life as well as human health.

The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human. Lead, cadmium, chromium, nickel, and copper etc. are the most hazardous pollutants of freshwater reserves (Zhao *et al.,* 2016). These metals have the potential to contaminate crops. As heavy metals are non-degradable, long biological half-lives, high potential to accumulate in living parts, they heavy a marked effect on the aquatic flora and fauna which through bio-magnification enter the food chain and ultimately affect the human beings as well (Lokhande *et al.,*2011).

The sources and toxicological effects of heavy metals on human health with their maximum permissible limits are presented in Table 2.3 (Ravindra *et al.,* 2015; Status of Trace and Toxic Metals in Indian Rivers, May 2014)

2.4 Heavy metal removal from aqueous streams (techniques)

Most of the heavy metal salts are soluble in water and form aqueous solutions. Consequently, they cannot be separated by ordinary physical separation. This aspect is much more pronounced `when the concentration of heavy metals in aqueous solution is very low, of the order of 1-100 mg/L (Leissner and Wegen, 2005). Faced with ever stringent regulations, heavy metals are now environmental priority pollutants which, need to be removed from wastewaters to protect the human ecosphere.

A diverse range of treatment techniques (Figure 2.1) such as chemical precipitation, membrane filtration, adsorption, ion exchange, electrochemical, cementation, solvent extraction have been employed for the removal of heavy metals from wastewater. While all these techniques can be employed for the treatment of heavy metal laden wastewater but the

Table 2.3: Sources of heavy metal in industrial waste and their side effects

Heavy metal	Major industrial sources	Effect	Requirement in drinking water (Acceptable Limit) mg/lit	Permissible limit by WHO
Copper	Mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries.	Liver damage, Wilson disease, insomnia, defects in pigmentation, bone formation.	0.05	1.5
Chromium	Steel and textile industry, metallurgical and chemical industry, cement and asbestos units	Ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema.	0.05	No relaxation
Nickel	Effluents of silver refineries, electroplating, zinc base casting and storage battery industries, burning of coal and oil	Respiratory disorder, cancer of lungs, abnormalities in fertility, dermatitis, nausea, chronic asthma, coughing	0.02	No relaxation
Zinc	Washing of the electroplating tanks, galvanizing processes, brass manufacturer, metal plating	Corrosive effects on skin and cause irritation, damage mucous membrane, depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst	5	15
Lead	Lead-based paint and possibly water pipes in older homes, lead smelter, burning of coal and oil,	Adsorbs through gastrointestinal and respiratory track and deposits in mucous membrane, causes liver and kidney damage, abnormality in fertility and pregnancy.	0.01	No relaxation
Mercury	Coal-burning power plants, laboratories using mercury	Toxic effect to protoplasm, methyl mercury is highly toxic and may damage the central nervous system and brain	0.001	No relaxation
Cadmium	Plating industry, pigments, manufacture of plastic material, batteries and alloys	Salivation, difficulty in breathing, nausea, vomiting, pain, anemia, kidney failure, and diarrhea.	0.003	No relaxation

selection of the most suitable treatment technique depends on many factors such as; the initial metal concentration, the composition of the wastewater, capital investment and operational cost, plant flexibility, reliability and environmental impact (Stuart and Greenberg, 1999). Over the years numerous approaches have been investigated for the development of more effective and cheaper technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent (Rajasulochana and Preethy, 2015, Li *et al.*, 2014).

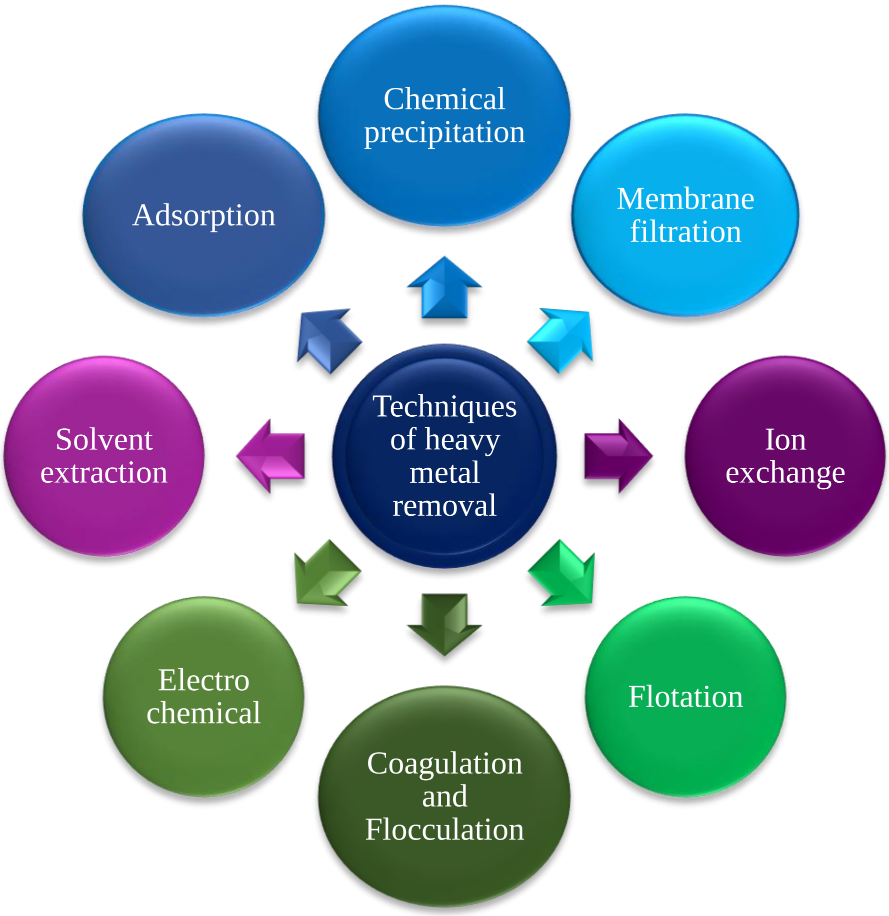


Fig. 2.1: Treatment techniques for heavy metal recovery

Numerous investigators have presented comprehensive review papers on wastewater treatment techniques (Carolin *et al.*, 2017; Fu and Wang, 2011; Barakat, 2011).

2.4.1 Chemical precipitation

This technique is widely used for removal of heavy metals from waste waters since, it is the cheapest method of all and also relatively simple to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. This results in the production of relatively low density sludge, and both the metals and acid resource cannot be efficiently recovered for recycle (Yan *et al.,* 2017). Precipitates can be separated by sedimentation or filtration and the treated water can be decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation, sulfide precipitation and heavy metal chelating precipitation (Matlock *et al.,* 2002). Chemical precipitation is also used in conjunction with other treatment methods (Gonzalez-Munoz *et al.*, 2006).

2.4.2 Adsorption

Adsorption is a well-developed unit operation for the treatment of aqueous waste waters. Adsorption process offers flexibility in design and operation and can produce high-quality treated effluent. Since, adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process (Fu *et al.,* 2011). The three main steps involved in pollutant sorption onto solid sorbent include (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle (Barakat, 2011). Commonly used adsorbents include activated carbon, carbon nanotubes, and bioadsorbents (Burakov *et al.,* 2018) nanometal oxides (Hua, 2012). Low cost adsorbants from plant wastes are also been widely used (Wan Ngah and Hanafiah, 2008; Aeisyah *et al.,* 2013; Cheng *et al.,* 2018). Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluents (Barakat, 2011).

2.4.3 Electrochemical

Electrochemical methods include electrocoagulation, electroflotation, and electrodeposition Chen (2004) has discussed in detail the application of electrochemical technologies in waste water treatment.

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes (Fu et al., 2011). The metal ion generation takes place at the anode, and hydrogen gas which is released from the cathode helps in flocculation. In recent years number of review papers on the use of electrochemical methods for waste water treatreat (Hakizimana et al., 2017, Zailini and Jin 2018), its potentials and challenges (Moussa *et al.*, 2017), emerging uses, (An *et al.*, 2017), advanced electrocoagulation processes and its association with other technologies (Garcia-Segura *et al.*, 2017) are reported.

Electro flotation separates pollutants by floating ions or solid particles, suspended or dissolved in a liquid phase, by the adhesion on tiny bubbles of hydrogen and oxygen formed on cathode and anode and moves upward in the flotation cell (Oliveira da Mota *et al.*, 2015). The overall reaction in the cell is electrolysis of water that releases oxygen and hydrogen into the solution (Azimi, 2017). The floatability of chemical species is the hydrophobicity and the ratio of collector to metal ion. Kyzas and Matis (2016) have presented a review on the literature published in the last five years on the applications of electro flotation to treat waste waters, heavy metals, biological wastes etc.

Electrodeposition process is based on reduction and oxidation of heavy metal ions in a cell consisting of an anode, a cathode, an electrolyte cell, and a current source. The heavy metals are reduced and electroplated onto the cathode. This transforms dissolved metal ions into solid particles by deposition on ionic conductors (cathode and anode) (Chen and Lim, 2005) to protect them from corrosion (Jayakrishnan, 2012).

2.4.4 Coagulation and flocculation

Coagulation and flocculation is also employed to treat wastewater laden with heavy metals. The coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (Alexander *et al.*, 2012). To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (Kurniawan *et al.,* 2006). Conventional coagulation–flocculation process can be modified by adding a trapping agent (Li *et al.*, 2003). The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment (Shammas, 2004). This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment. To overcome this problem, electro-coagulation process is used (Shafaei *et al.*, 2010). Teh *et al.* (2016) have presented a comprehensive review on the recent advancements on coagulation-flocculation and its application in wastewater treatment.

2.4.5 Floatation

Flotation is employed to separate finely dispersed solids and dissolved ions from a liquid phase using bubble attachment (Shammas, 2004). The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) vacuum air flotation, (iv) electroflotation, and (v) biological flotation, of which DAF is most widely used in treating metal laden waste water (Kurniawan *et al.*, 2006). Overview of flotation as a waste water treatment technique is reported by Rubio *et al.* (2002).

2.4.6 Ion Exchange

In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs**,** where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin (Kurniawan *et al.,* 2006). After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents. Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Synthetic resins are commonly preferred since they are effective to nearly remove the heavy metals from the solution (Alyuz and Veli, 2009).

2.4.7 Membrane Filtration

Membrane filtration a pressure driven process separates the particles based on its size, solution concentration, pH and applied pressure (Bruggen *et al.,* 2003). Membranes show great promise for heavy metal removal due to their high efficiency, easy operation and space saving (*Wang et al.,* 2017). Membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis. These processes are pressure driven but have major differences in use of membrane types (pore structure, pore size, pore size distribution, and porosity), membrane permeability, and applied operating pressures. Membranes for membrane adsorption (MA) with a dual function of membrane filtration and adsorption to remove trace amounts of pollutants such as cationic heavy metals, anionic phosphates and nitrates are also reviewed (Khulbe and Matsuura, 2018).

Solvent extraction (SX) of metals is an important technology in hydrometallurgical industry, analytical separations, and liquid waste treatment and has special emphasis in this study hence, it is treated as a separate section.

Table 2.4 lists the treatments techniques for recovery of heavy metals and their advantages and disadvantages.

Table 2.4: Treatment techniques for recovery of heavy metals

Treatment	Advantages	Disadvantages	Reference
Precipitation	• Removes metal upto ppm level • Low capital cost • Simple operation • Non- metal selective	• Highly pH sensitive • Generates large volumes of relatively low density sludge • Extra operational cost for sludge disposal • Large space required • Presence of complexing agents may have an adverse effect on metal removal	Peters et al., 1985; Barakat 2011; Yan et al., 2017; Abdel-Raouf and Abdul-Raheim 2017
Coagulation/ Floculation	• High removal rate • Can remove secondary contaminants	• Chemical consumption and increased sludge volume generation • Cannot treat heavy metal wastewater completely. • Must be followed by other treatment techniques. • May create by-products like flocks which are secondary pollutants	Fu and Wang 2011; Kang and yang 2011; Carolin *et al*., 2017
Ion exchange	• Avoids generation of sludge • High removal efficiency, fast kinetic, versatile process • ppb level clean up • Convenience for fieldwork since the required equipment is portable • Resins also have certain ligands that can selectively • Bond with certain metal cations, making ion exchange • Easy to use and less time-consuming	• Expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration • Cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids, • Nonselective and highly sensitive to the pH, Ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution • Appropriate pre-treatment systems for secondary effluent such as the removal of suspended solids from wastewater are required • Suitable ion exchange resins are not available for all heavy metals	Peters *et al.*, 1985 Ahluwalia and Goyal, 2005; Kurniawan *et al.*, 2006; Kang *et al.*, 2004.

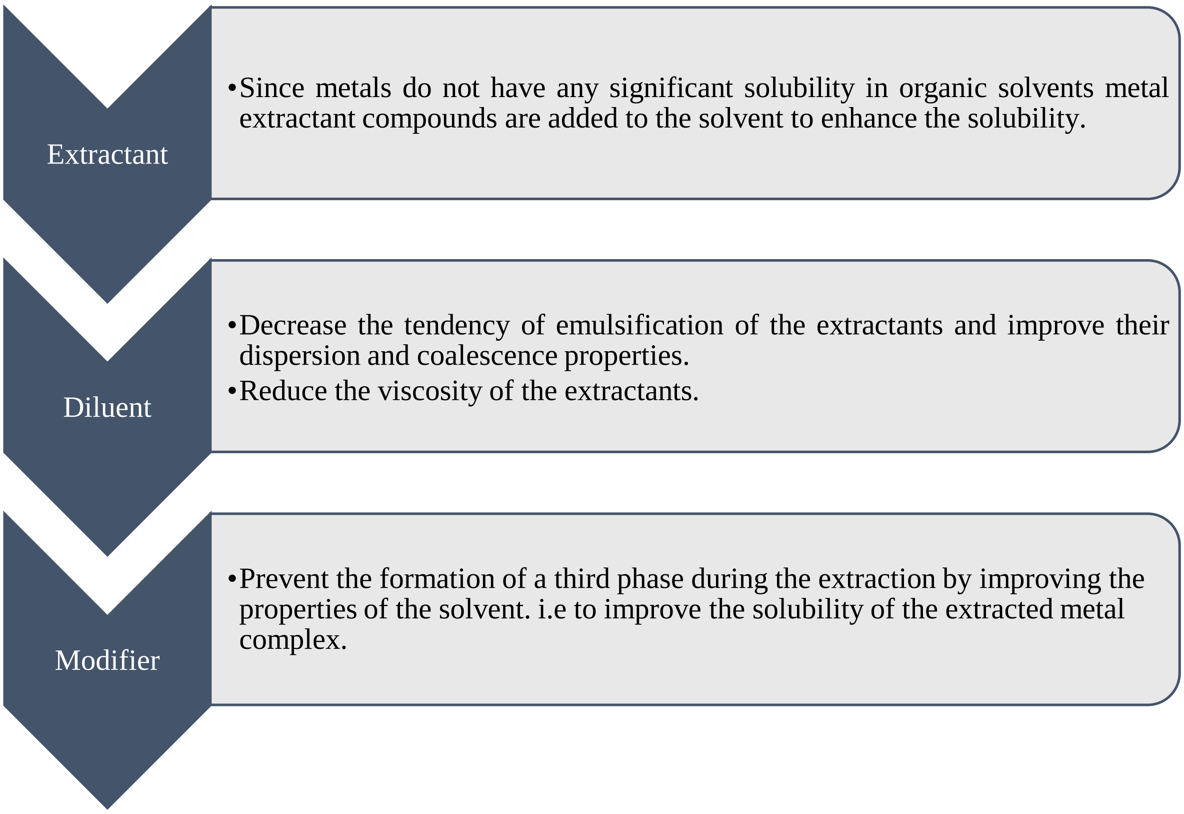
Electrochemical	• Rapid and well-controlled • Provide good reduction yield • Produces less sludge so eco-friendly	• Electrodes would frequently have to be replaced due to corrosion • High initial capital investment and the expensive electricity supply	Peters *et.al.*, 1985; Lin, 1994; Chen, 2004; Abdel-Raouf and Abdul-Raheim, 2017
Adsorption	• Low-cost • Easy operating conditions • Having wide ph range • High metal-binding capacities • Produce high quality treated effluent. • Fast kinetics • Selectivity depends on type of adsorbent	• Performance depends on type of adsorbent • Low selectivity • Production of waste products • Frequently needs desorption of adsorbent to improve efficiency	Peters *et.al.*, 1985; Barakat, 2011
Membrane separation	• Low solid waste generation, low chemical consumption • High selectivity for a specific metal • Simplicity of operation • High chemical and physical stabilities. Small space requirement • High efficiency	• Membrane fouling • Low permeate flux • Limited life of the membranes • Dissolution of the membrane by strong oxidizing agents, solvents, and other organic compounds • Ph sensitive and cannot use for high temp. ($>50^{0}C$)	Peters *et.al.*, 1985; Barakat, 2011; Fu and Wang 2011; Abdel-Raouf and Abdul-Raheim 2017
Floatation	• Better removal of small particles • High metal selectivity shorter hydraulic retention times	• High initial capital cost • High maintenance and operation costs	Rubio *et al.* 2002.
Solvent extraction	• Provide the selectivity • Necessary to create valuable product streams suitable for recycle or reuse	• Conventional solvent extraction methods are not frequently used because of high operating costs when compared to the value of the materials recovered	Yan *et. al.*, 2017

2.5 Solvent Extraction:

Solvent extraction has been applied to separate almost every element in the periodic table (Ritcey, 2006). 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 (Alfassi and Wai, 1991):

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

Solvent extraction is a selective separation procedure based on the distribution of a solute between two immiscible liquid phases that are in contact with each other. It is used for isolating and concentrating metals from aqueous solutions with the aid of an immiscible organic solvent and a suitable extractant which selectively loads the metal ions. The organic phase of the solvent extraction mixture consists of an extractant, a diluent and optionally a modifier may also be added to prevent the formation of third phase during extraction (Figure 2.2)



Extractant
- Since metals do not have any significant solubility in organic solvents metal extractant compounds are added to the solvent to enhance the solubility.

Diluent
- Decrease the tendency of emulsification of the extractants and improve their dispersion and coalescence properties.
- Reduce the viscosity of the extractants.

Modifier
- Prevent the formation of a third phase during the extraction by improving the properties of the solvent. i.e to improve the solubility of the extracted metal complex.

Fig. 2.2: Constituents of organic phase

Most of the metal salts are ionic in character and readily dissolve in water due to its high value of dielectric constant. These metal ions are not transferred to the organic solvents, which are non-polar with low values of dielectirc constant. It order to transfer a metal bearing anion or cation to the organic solvent, the bonds with water molecules are to be broken and charge be neutralised. This is achieved either by forming an organic soluble netural complex between cations and anions in the aqueous phase or by direct reaction between the metal ions and a suitable organic compounds to form a neutral species soluble in the organic phase (Gupta and Mukherjee, 1990)

For extraction to occur metal ions (M) and extractant ligand (L) must react as depicted in Figure 2.3. The reaction steps which characterize the overall reaction mechanism, either occurring in bulk phases (homogeneous reactions) or at the liquid-liquid interface (heterogeneous reactions), can in principle be slow enough to determine the rate of solvent extraction. In addition, since the chemical species are transferred from one phase to another, the transport of material from the bulk of the phases to the interface vice versa is another very important factor to be taken into consideration (Ritcy and Ashbrook, 1979).

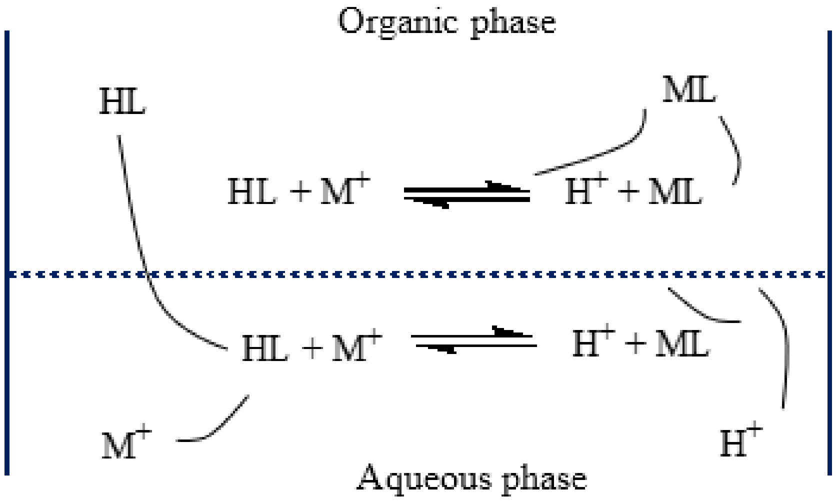


Fig. 2.3: Metal extraction mechanism

The distribution ratio D is a thermodynamic measure for the distribution of the solute between the two phases and is defined as the ratio of the concentration of the solute in the organic phase C_{org} and the concentration in the aqueous phase C_{aq} at equilibrium. (Morrison and Freiser, 1966).

2.5.1 Metal extractants and their classification

Metals in aqueous solutions exist as hydrated ions before they are extracted into the non-polar organic phase, wherein the water molecules have to be replaced or any ionic charge be reduced or removed (Cox, 2008). Metal extraction can be achieved using extractants which are classified considering both the extraction mechanism and the physico-chemical properties of the extractant. Extractants are classified on the basis of the functional group as acidic, basic and neutral (Gu et al, (1988); Wilson *et al.,* (2014) have divided the metal extractants into three categories 1) according to whether the metal is extracted as a metal cation M^{n+} by a cation exchanger, also called acidic extractant, 2) as a metalate anion $MX_x{}^{n-}$ by an anion exchanger, also called basic extractant, or 3) as a neutral metal salt MX_n by a solvating extractant. A comprehensive survey of metal extractant systems are detailed by Morrison and Freiser 1966; Danesi *et al.,* 1980; Gupta and Mukherjee, 1990; Cox, 2004; Ritcey, 2006; Chapman, 2009.

2.5.2 Cationic /Acidic extractants

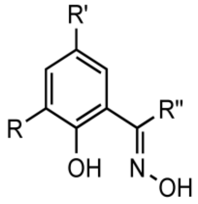
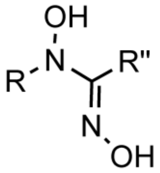
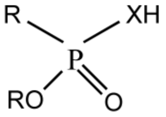
Cationic extractants have an acid function in their structure wherein there is an exchange of proton between the aqueous and organic phase. An extractable neutral complex is formed by replacement of one proton for every positive charge on the metal. These extractants are grouped in two classes, chelating and acidic. Chelating extractants include the oximes, β diketones, oximes etc. whereas alkyl carboxylic, phosphoric and sulfonic acids belong to the acidic group (Table 2.5)

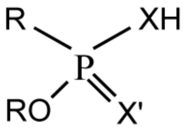
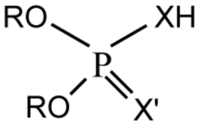
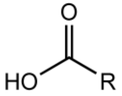
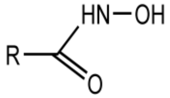
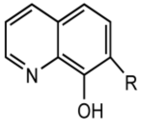
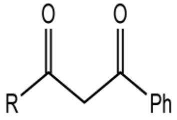
With chelating extractants the transfer of metal ion takes place due to the formation of electrically neutral chelate which satisfies both the valance and coordination number of the metal ion. For extractants containing both acidic and basic functions, the extractant combines with the metal ion to form a chelate salt. Equation 2.1 shows the mechanism of extraction by chelation

$$M^{n+} + nHA \leftrightarrow MA_n + nH^+ \qquad (2.1)$$

Since there is an increase in the H^+ ions in the solution, increasing the pH of solution increases extraction and decreasing pH. Stripping is achieved by changing the acidity of the system. Extractant which will extract the metal at low pH values will require a high acid strength for stripping.

Table 2.5: Metal cationic extractants

	Extractant	Substituent			Commercial name	Manufacturer	Applications
		R	R’	R’’			
Metal Cationic Extractants	Phenolic oximes 	H	C_9H_{19}	H	Acorga P50	Acorga Ltd. Cognis Inc, BASF, sherex chemicals	Cu extraction, Cu, Ni ,Co from ammonical solution
		H	C_9H_{19}	Me	Acorga K2000 LIX 84-I, SME 529		
		H	C_9H_{19}	Phenyl	LIX 65N		
		H	$C_{12}H_{25}$	Phenyl	LIX 64		
		C_l	C_9H_{19}	Phenyl	LIX 70		
		H	$C_{12}H_{25}$	H	LIX 860, LIX 622		
	α-Hydroxyoximes 	R=R’=n-$C_4H_9(C_2H_5)CHCH_2$			LIX 63	Cognis Inc,	Extraction of Cu, Zn from ammonical solution
	Dialkylphosphonic acids 	R= n-$C_4C_9(C_2H_5)CHCH_2$			PC 88A	Daihachi Chemical Industry Co.	Rare earth extraction, Co, Ni separation
					P507	Tianjin Beichen	
					Ionquest 801	Wilson Americas	
	Dialkylphosphinic acids and derivatives	R= t-$C_4H_9CH_2(CH_3)CHCH_2$ X=X’=O			Cyanex 272	Cytec Inc.	Separation of Co from Ni
		R= t-$C_4H_9CH_2(CH_3)CHCH_2$			Cyanex 302		

Metal Cationic Extractants		X=O, X'=S			
		R= t-$C_4H_9CH_2(CH_3)CHCH_2$ X=X'=S	Cyanex 301		
	Dialkylphosphoric acids and derivatives 	R= n-$C_4H_9CH_2(C_2H_5)CHCH_2$ X=X'=O	D2EHPA	Daihachi Chemical Industry Co.	Co, Ni separation, Rare earth separation, Zn extraction
		R= n-$C_4H_9CH_2(C_2H_5)CHCH_2$ X=O, X'=S	Hoe F 3787	Hoechst A.G	
		R= n-$C_4H_9CH_2(C_2H_5)CHCH_2$ X=X'=S	DEHTPA	Albright and Wilson Ltd.	
		Branched aliphatic groups (C_9H_{19})	Versatic acid 10	Shell chemicals	Cu, Ni Separation
		Branched aliphatic groups	LIX 1104	Cognis Inc.	Extraction of Fe, Co, Ni, Cu, Zn and Cd
		R= i-$C_{11}H_{23}$	Kelex 100	Sherex Chemicals Co. Inc.	Cu extraction
	B-Diketones 	R= i-C_7H_{15}	LIX 54	Cogniz Inc,	Extraction of copper and ammonia from $Cu^{2+}NH_3Cl^{-}.H_2O$ solution

The extraction mechanism of the other class is more complex (Equation 2.2) as organophosphorous and carboxylic acids form dimers or n-mers in the organic phase due to hydrogen bonding and effect their extraction properties (Ritcey, 2006).

$$M^{n+} + {}^{m}/_{2}\ (H_2A_2)_{org} \quad \leftrightarrow \quad [MA_n\ (m-n)HA]_{org} \ + \ nH^+_{aq} \tag{2.2}$$

Where, H_2A_2 is the dimer and m is the number of extractant molecules in the extracted species.

Extraction increases as the metal ions become more basic, charge on the metal ion also affects extractability. An increase in charge increases extractability, for metal ions with same charge extraction varies inversely with their ionic radii.

For some extractants, Kelex 100, the extraction is kinetic rather than thermodynamic, which is in contrast with extraction by hydroxyoximes. Similarly, organic acid extractant such as D2EHPA has some characteristics which resemble chelating extractants and some which are similar to neutral or solvating extractants.

2.5.3 Anionic/Basic extractants

Basic extractants or anionic extractants are similar to ion exchange resins where the metal ions can be extracted both as negatively charged complexes and neutral complexes. These extractants require the presence of stable anionic metal complexes to form the extractable ion pair complexes, so that only metals that produce these species can be extracted. Since only a limited number of metals can from anionic complexes, provided certain conditions are maintained, liquid anion exchangers extract metals selectivity and yield highly pure solutions.

Anionic extractants include primary, secondary, tertiary amines. Quaternary ammonium compounds are also used as extractants (Table 2.6). The order of extraction follows $R_4N^+ > R_3NH^+ > R_3NH_2^+ > RNH_3$ with the alkyl group (R) between 8 to 10 carbon atoms. Trialkyl ammonium compounds are widely used inspite of their poor extracting properties since they are cheaper than the quaternary compounds. The extraction is by ion pair formation according to Equation 2.3.

$$(R_3N)_{org} + H^+ + A^- \rightleftarrows (R_3NH^+A^-)_{org} \tag{2.3}$$

Table 2.6: Metal anionic extractants

	Extractant	Substituent R	Commercial name	Manufacturere	Uses
Metal Anion Extractants	Primary amines (H_2NR)	$C_{16–22}H_{34–46}$ (mixture of isomers)	Primene JM-T	Dow Chemical	Extraction of iron from sulfate solution
		$C_{12–14}H_{26–30}$ (mixture of isomers)	Primene 81-R		
	Secondary amines (HNRR’)	$C_{12–14}H_{25–29}$	Amberlite LA-2	Dow Chemical	Extraction of U from sulfate solution, Extration of Co from chloride solution
		$C_{13}H_{27}$	Ditridecylamine,	Sherex chemicals Co.	
		C_8H_{17} (mixture of isomers)	Adogen 283		
		$C_{12}H_{25}$	HOE 2652	Hoechst A.G.	
	Tertiary amines (NR_3)	C_8H_{17}	TOA, Alamine 300	Cognis Inc.	Extraction of U,V, Mo from sulfate solution, Extraction of Co, Cu from chloride solution
		C_8H_{17} and $C_{10}H_{21}$ (2 : 1)	Alamine 336		
		C_8H_{17} (mixture of isomers)	Alamine 308		
		$C_{10}H_{21}$ (mixture of isomers)	Alamine 310		
		$C_{12}H_{25}$	Alamine 304		
	Quaternary amines ($NR_3R’X$)	C_8H_{17} and $C_{10}H_{21}$ (2 : 1) R’= CH_3 X= countrion Cl^-	Aliquat 336	Cognis Inc.	Separation of V, Cr and Cu. Separation of rare earth

2.5.4 Solvating Extractants

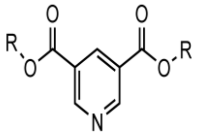
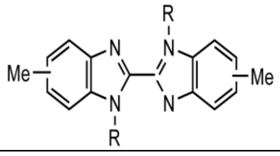
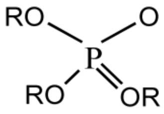
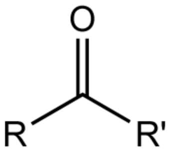
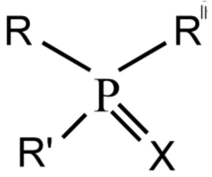
Solvating extractants are oxygen containing organic extractants which solvate inorganic molecules or complexes. The solubility of the inorganic species in organic phase is greatly increased by solvation. Solvating extractants facilitate extraction by coordinating with the metal with simultaneous displacement of water molecules and formation of a neutral complex through ion association. The extraction reaction is according to Equation 2.4:

$$MA(H_2O)_m + n\,S \rightleftarrows MA(H_2O)_{m-n}\,S_n + n\,H_2O \tag{2.4}$$

Where MA is metal ion pair and S is solvent.

Extractants in these groups are those wherein oxygen is bonded to carbon viz. ethers, alcohols, ketones and oxygen bonded to phosphorous in alkyl phosphate esters. Those reagents possessing a carbon bound oxygen tend to extract water with the metal salt whereas the phosphorus based reagents do not. Selectivity in extraction by solvating agents depends primarily on the change in solvation energy that takes place on replacement of water of hydration by the solvent. Since the bonds formed in solvation extraction reactions are not highly specific, the stoichiometric coefficient n as well as the amount of co-extracted water, vary with extraction conditions. Stripping here is achieved by breakdown of the anionic metal complex with water or by increasing the temperature of the system. Some of the commonly used solvating extractants are given in Table 2.7.

Table 2.7: Solvating extractants

	Extractant	Substituent R	Commercial name	Manufacturerere	Uses
Solvating Extractant		$C_{10}H_{21}$	Acorga CLX50	Acorga Ltd.	Zinc from chloride leach solutions,
		$COOC_{13}H_{27}$	Acorga ZNX50		
		n-C_4H_9	TBP	Union Carbide	Extraction of Fe from chlie solution. Purifiaction of U for nuclear application. Rear earth separtion
		R=Me, R'= i-C_4H_9 R=R'= i-C_4H_9	MIBK DIBK	Various	Separtion of Hf from Zr. Sepration of Au from chloride solution
	Phosphine  R=R'=R''	R= i-C_4H_9 X=S	Cyanex 471	Cytec Inc.	Separation of Co and Ni Recovery of Metals from Electroplating Waste
		R= $CH_3(CH_2)_7$ X=O	Cyanex 921, TOPO		
		R= i- $CH_3(CH_2)_7$ X=O	Cyanex 925		
		$CH_3(CH_2)_5$ and $CH_3(CH_2)_7$ X=O	Cyanex 923		

2.5.5 Properties of Extractants:

For appropriate strength and selectivity of extraction an extractant should have following properties (Kislik, 2012):

- Low solubility in aqueous phase, but interact with metal ions and obtain high solubility in organic phase complex.
- 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.

- High chemical stability under the conditions of operation to reduce make-up costs and minimize the transfer of degradation products.

2.5.6 Selection of extractant

Choice of extractant depends on (Ramachandra Rao, 2007; Gupta and Mukherjee, 1990):

- Easy availability at reasonable cost.
- Ability to extract the metal at the required pH.
- High solubility in the organic diluent and low aqueous solubility.
- Ease of formation of complex with the metal of interest and high solubility of metal organic species in the organic phase.
- Ease of recovery of the metal from the organic phase and easy regenration of extracntat for recycling.
- Resonable selecivity for the extraction of desired metal.
- Suitable physical properties of low density, low viscosity, low flash point, non toxic and nonvolatile.
- Acceptable rates of extraction, scrubbing and stripping.

2.5.7 Diluent

Diluent is a liquid or homogeneous mixture of liquids in which extractant and possible modifier dissolve to form the solvent/organic phase. Diluents can be classified according to their physical properties and preferable according to their ability to form ordered networks (Rydberg *et al.*, 2004).

Class 1: Liquids capable of forming three dimensional networks of strong hydrogen bonds. e.g. water, poly- and amino-alcohols, hydroxyl-acids.

Class 2: Liquids that have the capacity to form hydrogen bonds, but form chain like oligomers. e.g. primary alcohols, carboxylic acids etc.

Class 3: Liquids composed of molecules containing donor atoms, but no active hydrogen atoms. e.g. ethers, ketones, aldehydes, ester

Class 4: Liquids composed of molecules containing active hydrogen atoms but no donor atoms, e.g. chloroform and aliphatic halides.

Class 5: Liquids with no hydrogen bond forming capability and no donor atoms e.g. hydrocarbons, carbon disulfide, carbon tetrachloride etc.

Diluents, dilute the extractant, decrease its viscosity and provide a better contact between the extractant and aqueous phase. Diluents should be cheap, readily available and immiscible with water. They should not reduce the extraction coefficient of the solvent and separate well at the temperature of separation as an organic phase. Paraffinic diluents are better than aromatic ones. Since kerosene is cheap, available and not very volatile at the temperature of extraction hence, it is most commonly used as a dilutent. However, kerosene used should be treated to reduce the aromatic content to a minimum. (Khorfan and Koudsi, 1995)

2.5.8 Overview of recent literature

Solvent extraction, the most important process in hydrometallurgy is an established technique for recovery of heavy metals from low grade, mixed metal, ores and has been widely used as a potential technique for the recovery of metal values from secondary sources (Wilson et al., 2014). It is mostly useful in large and medium scale operations when solute concentrations are high. However, when the metal concentration in the waste stream is low SX has it limitation by the need of high aqueous to organic phase ratios (Kentish and Stevans, 2001). 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).

In the last decade, a number of research articles have been published focusing of removal of various metal species from aqueous solutions viz. nickel from nickel plating baths (Tanaka *et al.*, 2008; Sulaimana and Othman, 2018) and laterite leach solutions (Cheng *et al*., 2010; Preez and Kotze, 2013), copper from plating waste waters (Liqing *et al.*, 2011; Li *et al.*, 2014) and bleed solutions (Agrawal *et al.*, 2008, 2012, 2014), Cu, Mo, V, and U from leach solutions of copper ore and flotation tailings (Smolinski *et al.*, 2017), copper and zinc from pickling solutions (Sahu *et al.*, 2011; Sinha, 2012), copper, zinc, nickel, and cadmium from concentrated smelting wastewaters (Sun *et al.*, 2018), zinc recovery from hot-dip galvanizing spent pickling liquor (Lum *et al.*,2014), Cr from electroplating wastes (Sahu *et al.*, 2008) and Zn-Co electroplating rinse waters (Sze *et al.*, 2001)

However, it is worthwhile to mention that all these investigations were performed using feeds that were simulated to match the specification of the targeted component in the waste streams. There has been a small volume of work where actual industrial feeds were used to recover metals from various waters. Table 2.8. lists the use of real life wastes for metal removal using solvent extraction.

Table 2.8: Recovery of heavy metals from industrial waste water using solvent extraction

Waste	Metal	Extractant	Diluents	Stripping agent	Optimum Parameter	Recovery	Reference
PCB spent etchant Elek and Eltek Company Ltd.	Copper	LIX 54	Escaid 110	Sulfuric acid	40% LIX 54, O/A=5	54%	Sze and Wong, 1994
Tannery (pickling and chrome) effluent, Uttar Pradesh (India)	Chromium from copper and iron	Cyanex 923	Toluene	Hydro chloric acid / Sulfuric acid	pH=6 to 7.	Cr=99.9% pure	Gupta *et al.*, 2002
Rayon waste effluent M/s Baroda Rayon Co., Gujarat, India	Zinc from Calcium	Cyanex 272 + 1% isodecanol	Kerosene	Sulfuric acid	5% Cyanex 302 , pH 3.32, O/A=1/3	97.7%	Jha *et al.*, 2007
Electroplating rinse bath solution	Copper	LIX 984N-C	Kerosene	Sulfuric acid	30 % LIX 984N-C O/A: 1/8 , pH: 2	100%	Kul and Cetinkaya (a), 2009
	Zinc	LIX 984N-C	Kerosene	Sulfuric acid	10 % LIX 984N-C, O/A :1/4 , pH 8.00	98.41%	Kul and Cetinkaya (b), 2009

Continued...

Continued...

Electroplating rinse bath solution	Nickel	DEHPA	Kerosene	Sulfuric acid	0.5M DEHPA pH 5.25	98%	Kul and Cetinkaya, 2010
Electroplating and tannery units Tamil Nadu, India	Chromium	Tribenzylamine	Toluene	Ascorbic acid	pH 1–3, extractant= 0.1-0.2M	98%	Kalidhasan *et al*,. 2010
Pickle liquor, Tata.	Iron	Cyanex 923	Kerosene	Sulfuric acid	40% Cyanex 923 O/A=1 , pH 1.13	49.6%	Agrawal *et al.*, 2011
Copper bleed solution	Copper from nickel.	Cyanex 272 saponified with NaOH	Kerosene	Sulfuric acid	O:A = 1, pH 5.48 shaking time 5 min	Cu^{2+} = 98.5%	Agrawal *et al.*, 2012
Brass pickle liquor, Jharkhand, India	Copper and Zinc	LIX 984N	Kerosene	Sulfuric acid	30% LIX 984N Cu: O/A = 2/1, pH 2.5 Zn: O/A = 2/1 pH 5.5	Cu=99.9% Zn=99%	Sinha *et al.*, 2016
Brass pickle liquor, India	Copper and Zinc	LIX 84-IC, D2EHPA	kerosene	Oxalic acid	Cu : pH 2.5, 30% LIX 84-IC, Zn: pH=2 15% D2EHPA	Cu=98.8% Zn=98.25%	Shah *et al.*, 2017
PCB spent etchant, India	Copper	LIX 84-I	Kerosene	Oxalic acid	50% LIX 84-I, O/A=1.5, pH 8.9	99.9%	Shah *et al.*, 2018

2.6 Conclusions

The work on reclamation of metal values from real life wastes is limited. However, there are a number of publications where investigators have attempted to simulate the waste liquor and extract/reclaim the metal from it. Working with the actual waste samples involves a number of challenges

1. There will be inconsistency in the composition of the waste collected from time to time.
2. There could be additional trace impurities present in the actual waste samples that do not manifest in simulated wastes.
3. Often industries are very reluctant to share their liquid effluents without a secrecy clause with any research agency / University.
4. Publications of real life data is inhibited by the industry generating the waste.

On the other hand, a simulated waste does not reveal the true picture nor does it bring out all the effect of various interactions in a complex matrix and at best remains only a pointer towards development of a recovery process.

After a thorough literature survey it is observed that in spite of a huge amount of published work on solvent extraction of metals from aqueous streams there is dearth of literature on real life systems encountered by industry as well as environmental agencies. Most of the work published addresses single solutes extraction, prepared synthetically and existing in a condition different from that which it is encountered in real practice. This study is an attempt to work with real life waste streams that was received, ‘without any strings attached’ on brass pickling liquors, PCB etch solutions and brass rinse liquors which are detailed in subsequent chapters. Further, this work explores Precipitation-Stripping (PS) a lesser known metal reclamation technique that recovers the metal values as its oxalates and oxides.

References:

- Abdel Salam OE, Reiad NA, ElShafei MM. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *J Adv Res.* 2011; 2(4): 297-303.
- Abdul-Raouf MS, Abdul-Raheim ARM. Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review. *J Pollut Eff Control*. 2017; 5(1): 1-13.

- Aeisyah A, Ismail MHS, Lias K, Izhar S. Adsorption process of heavy metals by low-cost adsorbent: A review. *World Appl Sci J.* 2013; 28 (11): 1518-1530.
- Agrawal A, Kumari S, Bagchi D, Kumar V, Pandey BD. Recovery of copper powder from copper bleed electrolyte of an Indian copper smelter by electrolysis. *Miner Eng.* 2007; 20: 95-97.
- Agrawal A, Kumari S, Parveen M, Sahu KK. Exploitation of copper bleed stream for the extraction and recovery of Copper and Nickel by bis (2, 4, 4- trimethylpentyl) phosphinic Acid. *Mineral Processing & Extractive Metall. Rev*. 2012; 33: 339-351.
- Agrawal A, Kumari S, Sahu KK. Iron and Copper recovery / removal from industrial wastes : A review. *Ind Engg Chem Res.* 2009: 48(13) 6145-6161.
- Agrawal A, Kumari S, Sahu KK. Studies on solvent extraction of iron (III) as a step for conversion of a waste effluent to a value added product. *J Environ Manage*. 2011; 92(12): 3105-3111.
- Agrawal A, Manoj MK, Kumari S, Bagchi D, Kumar V, Pandey BD. Extractive separation of copper and nickel from copper bleed stream by solvent extraction route. *Miner Eng*. 2008; 21(15): 1126-1130.
- Ahluwalia SS, Goyal D. Removal of heavy metals by waste tea leaves from aqueous solution. *Eng life Sci.* 2005; 5: 158-162.
- Ajmal M, Rao RAK, Ahmad R, Ahmad J, Rao LAK. Removal and recovery of heavy metals from electroplating waste water by using Kyanite as an adsorbent. *J Hazard Mater*. 2001; 87: 127-137.
- Alexander JT, HaiFI, Al-aboud TM. Chemical Coagulation based processes for trace organic contaminant removal: Current state and future potential. *J Environ Manage.* 2012; 111: 195-207.
- Alyuz B, Veli S, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. *J Hazard Mater.* 2009; 167: 482–488.
- An C, Huang G, Yao Y, Zhao S. Emerging usage of electrocoagulation technology for oil removal from wastewater: A review. *Sci Total Environ*. 2017; 579: 537-556.
- Apaydin O, Kurt U, Gonullu MT. An investigation on the treatment of tannery wastewater by electrocoagulation. *Water.* 2009; 11(4): 546-555.
- Awasthi AK, Zlamparet GI, Zeng X. Evaluating waste printed circuit boards recycling : Opportunities and challenges, a mini review. *Waste Manag. Res*. 2017; 35: 346-356.

- Azimi A, Azari A, Rezakazemi M, Ansarpour M. Removal of heavy metals from industrial wastewaters: A review. *ChemBioEng Rev.* 2017; 4 (1): 37-59.
- Barakat MA. New trends in removing heavy metals from industrial wastewater. *Arab J Chem.* 2011; 4: 361–377.
- Benito Y, Ruiz ML. Reverse osmosis applied to metal finishing wastewater. *Desalination.* 2002; 142: 229–234.
- Bloodworth A. Track flows to manage technology-metal supply. *Nature.* 2014; 505: 9-10
- Bode H. Control of heavy metal emission from metal plating industry in a German river basin. *Water Sci Technol.* 1998; 38: 4-5, 121-129.
- Bontidean I, Csoregi E, Corbisier P,Lloyd JR, Brown NL. Bacterial metal-responsive elemements and their use in biosnsonrs for meonitoring of heavy metal. In: *Heavy Metals in the Environment*. 2002; Sarkar B. (eds.), Marcel Dekker Inc. New York.
- Bruggen B Van Der, Vandecasteele C, Gestel T Van, Doyenb W, Leysenb R. Review of pressure-driven membrane processes. *Environ Prog.* 2003; 22 (1): 46-56.
- Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicol Environ Saf*. 2018; 148: 702-712.
- Canda L, Heput T, Ardelean E. Methods for recovering precious metals from industrial waste. *IOP Conf Ser Mater Sci Eng*. 2016; 106(1): 1-9.
- Carolin CF, Kumar PS, Saravanan A, Joshiba GJ, Naushad M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J Environ Chem Eng.* 2017; 5 (3): 2782-2799.
- Castelblanque J, Salimbeni F. NF and RO membranes for the recovery and reuse of water and concentrated metallic salts from waste water produced in the electroplating process. *Desalination.* 2004; 167: 65–73.
- Chelouaou S, Graiche M, Boudaa A. Treatment and valorization of heavy metals from wastewater by solvent extraction using DI-2-ethylhexylphosphoric acid (D2EHPA). In: *Env Sci Technl.* 2013; 1-6.
- Chen G. Electrochemical technologies in wastewater treatment. *Sep Purif Technol*. 2004; 38(1): 11-41.

- Chen Hsiu-Liang, Tseng Yun-Sheng, Hsu Kung-Chung. Spent FCC catalyst as a pozzolanic material for high-performance mortars. *Cem Concr Composites.* 2004; 26: 657–664.
- Chen JP, Lim LL. Recovery of precious metals by an electrochemical deposition method. *Chemosphere*. 2005; 60: 1384-1392.
- Cheng CY, Boddy G, Zhang W, et al. Hydrometallurgy recovery of nickel and cobalt from laterite leach solutions using direct solvent extraction : Part 1- Selection of a synergistic SX system. *Hydrometallurgy*. 2010; 104(1): 45-52.
- Cheng CY. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. *Hydrometallurgy*. 2000; 56: 369-386.
- Cheng S, Liu J, Hu W, Liu C, Zhang L, Xia H, Penga J, Lin G, Jiang X. Removal of organic dyes from aqueous solution using waste catalyst-derived adsorbent: Isotherm modeling and kinetic studies. *Mater Res Express.* 2018; 5: 065603
- Cheng SP. Heavy metal pollution in China: Origin, pattern and control. *Environ Sci Pollut Res.*2003; 10: 192-198.
- Cox M. The use of solvent extraction in the recovery of waste. In: *Solvent extraction principles and practices*. 2004.609-649. Rydberg J, Cox M, Musikas C, Choppin G. (eds.) CRC Press.
- Danesi PR, Chiarizia R, Coleman CF. The kinetics of metal solvent extraction. In: *Critical Reviews in Analytical Chemistry*. 1980; 10(1): 1-126. CRC Press.
- Datta MC, Saha CR, Sen D. Studies on the reduction of nitrobenzene to aniline catalyzed by bis(acetylacetonato) palladium(II)-pyridine system. *J Appl Chem Biotechnol.* 1978; 28(11): 709-711.
- De Oliveira Da Mota I, De Castro JA, De Goes Casqueira R, De Oliveira Junior AG. Study of electroflotation method for treatment of wastewater from washing soil contaminated by heavy metals. *J Mater Res Technol*. 2015; 4 (2): 109-113.
- Du Preez, A.C., Kotze, M.K. (2013) Evaluation of a Versatic 10 acid/Nicksyn™ synergistic system for the recovery of nickel and cobalt from a typical laterite leach liquor. In: *Base Metals Conference.* 2014; 114(5): 192-208. The Southern African Institute of Mining and Metallurgy.
- Elejalde C, Romero F,Diaz JM. Separation and recovery of heavy metals from hydrometallurgical effluents by solvent extraction. *Fresenius J Anal Chem.* 1991; 340: 182-185.

- F.J. Hurst, Recovery of uranium from wet process phosphoric acid, *Ind Eng Chem Process Development*. 1972; 11(1): 122-128
- Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. *J Environ Manage*. 2011; 92: 407-418.
- Garcia-Segura S, Eiband MMSG, de Melo JV, Martinez-Huitle CA. Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies. *J Electroanal Chem.* 2017; 801: 267-299.
- Gautam RK, Sharma SK, Chattopadhyaya MC. Functionalized magnetic nanoparticles for heavy metals removal from aqueous solutions. In: Heavy Metals in Water: Presence, Removal and Safety. Sharma SK (Eds.), RSC, 2015.
- Goes MF, Sinhoreti MA, Consani S, Silva MA. Morphological effect of the type, concentration and etching time of acid solutions on enamel and dentin surfaces. *Braz Dent J*. 1998; 9(1): 3-10.
- Gonzalez-Munoz MJ, Rodriguez MA, Luquea S, Alvareza JR. Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. *Desalination.* 2006; 200: 742-744.
- Gupta B, Deep A, Tandon SN. Recovery of Chromium and Nickel from Industrial Waste. *Ind Eng Chem Research.* 2002; 41(12): 2948-2952.
- Gupta CK, Mukherjee TK. Hydrometallurgy in Extraction Processes. 1990; 2. CRC press.
- Hakizimana JN, Gourich B, Chafi M, Stiriba Y, Vial C, Drogui P, Naja J. Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination.* 2017; 404: 1-21.
- Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *J Hazard Mater.* 2012; 211-212: 317-331.
- Jadhav UU, Hocheng H. A review of recovery of metals from industrial waste. *J Achieve Mat Manuf Eng*. 2012; 54(2): 159-167.
- Jayakrishnan DS. Electrodeposition: The versatile technique for nenomaterials. In: *Corrosion Protection and Control Using Nanomaterials.* 2012; 86–125. Saji VS, Cook R. (eds.). Woodhead Publishing, Cambridge.

- Jha MK, Kumar V, Bagchi D, Singh RJ, Lee J chun. Processing of rayon waste effluent for the recovery of zinc and separation of calcium using thiophosphinic extractant. *J Hazard Mater.* 2007; 145(1-2): 221-226.
- Jordao CP, Pereira Mde G, Einloft R, Santana MB, Bellato CR, De Mello JW. Removal of Cu, Cr, Ni, Zn, and Cd from electroplating wastes and synthetic solutions by vermicompost of cattle manure. *J Environ Sci Health A Tox Hazard Subst Environ Eng.* 2002; 37(5): 875-92.
- Kadirvelu K, Goel J. Eco-friendly technology for removal of hazardous heavy metal from water and industrial wastewater. In: *Hazardous Materials and Wastewater:* Treatment, Removal and Analysis. Lewinsky AL. (ed.) Nova Publishers, New York.
- Kalidhasan S, Sricharan S, Ganesh M, Rajesh N. Liquid - liquid extraction of chromium (VI) with tricaprylmethylammonium chloride using isoamylalcohol as the diluent and its application to industrial effluents. *J Chem Eng Data* 2010; 55: 5627–5633.
- Kang SY, Lee JU, Moon SH, Kim KW. Competitive adsorption characteristics of Co^{+2}, Ni^{+2}, and Cr^{+3} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere.* 2004; 56: 141-147.
- Kang X, Yang Y. An experimental study on removal of copper ions from industrial wastewater by magnetic flocculation. *Ind Water Wastewater*. 2011; 42: 24-27.
- Kentish SE, Stevens GW. Innovations in separations technology for the recycling and re-use of liquid waste streams. *Chem Engeneering J*. 2001; 84: 149-159.
- Keypour H, Noroozi M, Rashidi A, Shariati Rad M. Application of response surface methodology for catalytic hydrogenation of nitrobenzene to aniline using ruthenium supported fullerene nanocatalyst. *Iran J Chem Eng English Ed*. 2015; 34(1): 21-32.
- Khorfan S, Koudsi Y. Effect of organic diluents on the extraction of uranium from phosphoric acid. *J RadioanaNuclChem, Letters.*1995; 199(5): 339-345.
- Khulbe KC, Matsuura T. Removal of heavy metals and pollutants by membrane adsorption techniques. *Appl Water Sci.* 2018; 8(1):19.
- Kislik V. Competetive complexation/solvation theory of solvent extraction. II. Solvent extraction of metals by acidic extractants. *Sep Sci Technol.* 2002; 37(11): 2623-2657.
- Kislik VS. Chemistry of Metal Solvent Extraction. In: *Solvent Extraction, Classical and Novel Approaches.* 2012; 113–156. Elsevier Science.
- Kul M, Cetinkaya U. Recovery of copper by LIX 984 N-C from electroplating rinse bath solution. *Hydrometallurgy.* 2009(a); 98: 86-91.

- Kul M, Cetinkaya U. Recovery of nickel by solvent extraction from electroplating rinse bath solution. *Solvent Extr Ion Exch.* 2010; 28(2): 225-243.
- Kul M, Cetinkaya U. Recovery of zinc by LIX 984N-C from electroplating rinse bath solution. *Solvent Extr Ion Exch.* 2009(b); 27(4): 536-550.
- Kul M, Oskay KO. Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction. *Hydrometallurgy.* 2015; 155: 153-160.
- Kulshrestha S, Awasthi A, Dabral SK. Assessment of heavy metals in the industrial effluents, tube-wells and municipal supplied water of Dehradun, India. *J Environ Sci Eng.* 2013; 55(3):290-300.
- Kumar V, Pandey BD, Delhi N, Kumari S. Value addition in the processing of copper bleed solution by value addition in the processing of copper bleed. 2016.
- Kurniawan TA, Chan GYS, Lo WH, Babel S. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chem Eng J*. 2006; 118 (1-2): 83-98.
- Kyzas GZ, Matis KA. Electroflotation process: A review. *J Mol Liq.* 2016; 220: 657-664.
- Leissner C, Wegen E. Industrial wastewater treatment at PCETP, India - A primary investigation of the heavy metals content. 2005; 28. Sweden.
- Li L, Tan Y, Yang L. Using Lix984 to recover Cu^{2+} from plating wastewater containing chloride. *AdvMat Res*. 2014; 883: 529-532.
- Li WW, Yu HQ, He Z. Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. *Energy Environ Sci*. 2014; 7(3): 911-924.
- Li Y, Yang L, Xu Z, Sun Q. Separation and recovery of heavy metals from waste water using synergistic solvent extraction. In: *Materials Science and Engineering.*2017; 167:1-5.
- Li Y, Zeng X, Liu Y, Yan S, Hu Z, Ni Y. Study on the treatment of copper-electroplating wastewater by chemical trapping and flocculation. *Sep Purif Technol.* 2003; 31: 91–95.
- Lin SH, Peng CF. Treatment of textile waste-water by electrochemical method, *Water Res.*1994; 28(2): 277– 282.
- Liqing LI, Hong Z, Zhanfang CAO, Lu Y. Recovery of Copper (II) and Nickel (II) from Plating Wastewater by Solvent Extraction. *Chin J Chem Eng.* 2011; 19(6): 926-930.
- Lokhande RS, Singare PU, Pimple DS. Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja industrial estate of Mumbai, India. *Resour Environ.* 2011; 1(1): 13-19.

- Lum KH, Stevens GW, Kentish SE. Development of a process for the recovery of zinc sulfate from hot-dip galvanizing spent pickling liquor via two solvent extraction steps. *Hydrometallurgy*. 2014; 142: 108–115.
- M.K. Sinha, S.K. Sahu, P. Meshram, B.D. Pandey, V. Kumar. Solvent extraction and separation of copper and zinc from a pickling solution. *Int J Metall Eng*. 2012; 1(2): 28–34.
- Matlock MM, Henke KR, Atwood DA. Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs. *J Hazard Mater*. 2002; 92: 129-142.
- Monken A. Water pollution control for paint booths. *Met Finish*. 2000; 98: 464–471.
- Moussa DT, El-Naas MH, Nasser M, Al-Marri MJ. A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. *J Environ Manage.* 2017; 186: 24-41.
- Mubeena K, Muthuraman G. Solvent extraction technique for removal and recovery of nickel from effluent by Trimethyl amine as a carrier. *IJSETR*. 2015; 4(1):128-137.
- Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers BJ. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci Total Environ.* 2003; 311(1-3): 205-219.
- Otero N, Vitoria L, Soler A, Canals A. Fertiliser characterisation: Major, trace and rare earth elements. *Appl Geochemistry*. 2005; 20(8): 1473-1488.
- Peters R, Ku Y, Bhattacharyya D. Evaluation of recent treatment techniques for removal of heavy metals from industrial wastewaters. In: *AICHE Symp Ser.* 1985; 81: 165-203.
- Preconcentration techniques for trace elements. 1991. Alfassi Z, Wai CM.(eds.) CRC Press,
- Radmehr V, Koleini SMJ, Khalesi MR, Tavakoli MR. Ammonia leaching in the copper industry : A review. In: *XXVI Int Miner Process Congr.* 2012; 487: 2512-2523.
- Rajasulochana P, Preethy V. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. *Resour Technol*. 2016; 2(4): 175-184.
- Ramachandra Rao S. Resource Recovery and Recycling from Metallurgical Wastes. 2007; 7: 71-108. Elsevier Science.

- Ravindra KG, Sharma SK, Mahiya S, Chattopadhyaya CM. Contamination of heavy metals in aquatic media: Transport, toxicity and technologies for remediation. In: *Heavy Metals in Water:* Presence, Removal and Safety. 2015; Sharma SK. (Ed.) RSC.
- Ritcey GM. Solvent extraction in hydrometallurgy: Present and future. *Tsinghua Sci Technol.* 2006; 11(2): 137-152.
- Ritcey GM, Ashbrook AW. Solvent Extraction: Principles and applications to process metallurgy. 1979. Elsevier Scientific Pub Co., Amsterdam, New York.
- Rogich GD, Matos RG. The Global Flows of Metals and Minerals. U.S. Geological Survey, Reston, Virginia: 2008. OFR 2008–1355.
- Chapman TW. Extraction-Metal processing. In: Handbook of Separation Process Technology. Rousseau RW. (ed.) 2009; 467-499. John Wiley & Sons.
- Rubio J, Smith RW. Overview of flotation as a wastewater treatment technique. *Miner Eng*. 2002; 15(15): 139–155.
- Rule KL, Comber SDW, Ross D, Thornton A, Makropoulus CK, Rautiu R. Diffuse sources of heavy metals entering an urban wastewater catchment. *Chemosphere*. 2006; 63: 64-72.
- Rydberg J, Cox M, Musikas C, Choppin G. Solvent extraction principles and practice. Revised and Expanded. 2004. CRC press.
- Saha A, Ranu B. Highly chemoselective reduction of aromatic nitro compounds by copper nanoparticles. *J OrgChem.*2008; 73(17): 6867-6870.
- Sahu SK, Sinha MK, Meshram P, Pandey BD, Kumar V. Solvent extraction of copper and zinc from a pickling solution using Versatic 10 Acid, Cyanex 272 and LIX 984N. In: *Proceedings of Non-ferrous metals -2011*. Pashkov G, Polyakov P. (eds.) 2011. Russia.
- Sahu SK, Verma VK, Bagchi D, Kumar V, Pandey BD. Recovery of chromium(VI) from electroplating effluent by solvent extraction with tri-n-butyl phosphate. *Indian J Chem Technol.* 2008; 15(4): 397-402.
- Senthilnathan J, Mohan S, Palanivelu K. Recovery of chromium from electroplating wastewater using di 2-(ethylhexyl) phosphoric acid. *Sep Sci Technol.* 2005; 40(10): 2125-2137.
- Shafaei A, Rezayee M, Arami M, Nikazar M. Removal of Mn^{2+} ions from synthetic wastewater by electrocoagulation process. *Desalination*. 2010; 260: 23-28.

- Shammas NK. Coagulation and flocculation. In: *Physicochemical Treatment Processes.* 2004; 103-139. Wang LK, Hung YT, Shammas NK. (eds.); Humana Press, New Jersey.
- Silva JE, Paiva AP, Soares D, Labrincha A, Castro F. Solvent extraction applied to the recovery of heavy metals from galvanic sludge. *J Hazard Mater.* 2005; 120(1-3): 113-118.
- Smolinski T, Wawszczak D, Deptula A. Solvent extraction of Cu, Mo, V, and U from leach solutions of copper ore and flotation tailings. *J Radioanal Nucl Chem*. 2017; 314(1): 69–75.
- Soares LC. Precipiatation and transformation of nanostructured copper oxalate and copper/cobalt composite precursor synthesis. 2004; 3083. Thesis
- Sole KC, Cole PM. Solvent extraction in the primary and secondary processing of zinc. 2002; 2: 17-21. In: *Proceedings of International Solvent Extraction Conference* (ISEC'2002); Sole KC, Cole PM, Preston JS, Robison DJ. (eds.), Chris van Rensburg Publications Ltd., SouthAfrica.
- Solvent Extraction in Analytical Chemistry. 1966. Morrison GH, Freiser H. (eds.), John Wiley and Sons, Inc. New York.
- Status of trace and toxic metals in Indian rivers. River data directorate planning & development organization, Government of India, Ministry of water resources, Central Water Commission, 2014. New Delhi.
- Stuart LG, Greenberg LA. Optimized wastewater treatment for a printed circuit board facility.1999; 1-10.
- Sulaimana RNR, Othman N. Solvent extraction of nickel ions from electroless nickel plating wastewater using synergistic green binary mixture of D2EHPA-Octanol system. *J Environ Chem Eng.* 2018; 6(2): 1814-1820.
- Sun Q, Wang W, Yang L, Huang S, Xu Z, Ji Z. Separation and recovery of heavy metals from concentrated smelting wastewater by synergistic solvent extraction using a mixture of 2-hydroxy-5-trimethylpentyl-phosphinic acid. *Solvent Extr Ion Exch.* 2018; 36(2): 175-190.
- Sze YK, Wong JC. A study of a solvent extraction method for the regeneration of ammoniacal etching solutions of copper. *Environ Technol.* 1994; 15(8): 785-794.
- Sze YKP, Xue LZ, Lee MY. Treatment of Alloy-Electroplating wastewater by an automated solvent extraction technique. *Environ Technol.* 2001: 22: 979-990

- Tanaka M, Huang Y, Yahagi T, Hossain MK, Sato Y, Narita H. Solvent extraction recovery of nickel from spent electroless nickel plating baths by a mixer-settler extractor. *Sep and purification technol.* 2008; 62: 97-102.
- Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Molecular, Clinical and Environmental Toxicology. *EXS.* 2012; 101: 133–164.
- Teh CY, Budiman PM, Shak KPY, Wu TY. Recent advancement of coagulation-flocculation and its application in wastewater treatment. *Ind Eng Chem Res.* 2016; 55 (16): 4363-4389.
- Teh CY, Budiman PM, Shak KPY, Wu TY. Recent advancement of coagulation-flocculation and its application in wastewater treatment. *Ind Eng Chem Res.* 2016; 55(16): 4363-4389.
- Veglio F, Quaresima R, Fornari P, Ubaldini S. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. *Waste Management.* 2003; 23: 245-252.
- Verma AK, Dash RR, Bhunia P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *J Environ Manage.* 2012; 93(1): 154-168.
- Wan Ngah WS, Hanafiah MAKM. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour Technol.* 2008; 99 (10): 3935-3948
- Wang X, Zhou K, Ma Z, Lu X, Wang L, Wang Z, Gao X. Preparation and characterization of novel polyvinylidene fluoride/2-aminobenzothiazole modified ultrafiltration membrane for the removal of Cr(VI) in wastewater. *Polymers*. 2017; 10(1): 1-10.
- Wernick I, Themelis NJ. Recycling metals for the environment. *Annu Rev. Energy Environ.* 1998. 23: 465-497.
- Wilson AM, Bailey PJ, Tasker PA, Turkington JR, Grant RA, Love JB. Solvent extraction: The coordination chemistry behind extractive metallurgy. *Chem Soc Rev.* 2014; 43(1): 123-134.
- Yan L, Yang L, Xu Z, Sun Q. Separation and recovery of heavy metals from waste water using synergistic solvent extraction. *Materials Science and Engineering* 2017; 167: 1-5.
- Zailani LWM, Zin NSM. Application of electrocoagulation in various wastewater and leachate treatment-A review. In: *Earth and EnvScience.* 2018; 140: 1-9.

- Zewail TM, El-Garf SAM. Preparation of agriculture residue based adsorbents for heavy metal removal. *Desalin Water Treat.* 2010; 22: 363-370.
- Zewail TM, Yousef NS. Chromium ions (Cr^{6+} and Cr^{3+}) removal from synthetic wastewater by electrocoagulation using vertical expanded Fe anode. *J Electroanal. Chem. 2014;* 735: 123–128.
- Zhao M, Xu Y, Zhang C, Rong H, Zeng G. New trends in removing heavy metals from wastewater. *Appl Microbiol Biotechnol*. 2016; 100 (15): 6509-6518.

Web Reference

- METALS: A report by KPMG for India Brand Equity Foundation (IBEF), Confederation of Indian Industry, Kolkata, India 2006. Retrieved on 11june 2011, <https://www.ibef.org/download/Metal.pdf>
- Market research report 2004. Retrieved on 11 November 2012, <indiabefore91.in/1991-economic-reforms>
- ASIA COPPER WEEK 2017. Retrieved on 20 July 2018. <https://www.metalbulletin.com/Article/3770720/ASIA-COPPER-WEEK-2017-ICSG-estimates-2018-global-copper-production-to-increase-25.html>
- Johnson Electric Holdings Limited Annual Report 2017. Retrieved on 12 December 2017,<https://www.johnsonelectric.com/-/media/files/annual-and-interim-reports-pdf/en/e_20170601_annual-report.ashx?v=3b295eae405040a3bfa9832eb6fadb48>