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Heavy Metal removal by using liquid liquid extraction

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Abstract - ***Toxic metals are mostly present in the environment due to natural phenomenon and human activities as well. Exposure of these non-essential elements in the environment causes severe effects. They are known to cause problems in humans as well as in aquatic life [1]. Solvent extraction is recommended as a suitable method for the removal of heavy metals from the wastewaters of the chemical and electronic industries. Common extractent are organic compounds with molecular mass 200-450, almost insoluble in water (5-50 ppm), that selectively extract metals from aqueous solutions. On the basis of data from the literature, the extraction conditions are reviewed for the metals that cause problems in waste waters. The extraction conditions are understood to mean the type of extractent, anion present in the aqueous phase, and pH [2]. The extraction behaviours of Zn (II) and Cu (II) from perchlorate media have been investigated using bis-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester, (PC-88A) in toluene. The extraction of Zn (II) was found to be quantitative in the pH range 2.5 to 3.0 and 3.0 to 4.0 D2EHPA and PC-88A in toluene, respectively, while Cu (II) was extracted quantitatively in the pH range 6.0 to 8.0 and 5.5 to 7.0 D2EHPA and PC-88A in toluene, respectively. Zn (II) was stripped with HCl, while Cu (II) with H2SO4 and HNO3 from the organic phase containing D2EHPA and PC-88A, respectively [3].***

Keywords - Liquid-Liquid Extraction, Ion Recognition, Toxic Metals, D2EHPA, PC-88A, Extraction, Stripping, Separation

I. INTRODUCTION

The main objective of chemistry lies on research, discovery and exploitation of environmental appropriate methods. Today the new chemistry should aim at prevention; it must design and implement clean and safe processes, using less expensive raw materials and reducing the generation of wastes such as heavy metals. Liquid–liquid extraction has often been a good choice technique to separate heavy metals from industrial wastewater and in the development of separation process [4]. Metal finishing industries and the manufacturing process of printed circuit boards for electro less copper plating often discharge effluents containing heavy metals and strong chelating agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), and citrate. Such types of effluents are also encounter in washing remediation of metal-contaminated soils. The presence of chelating agents usually makes conventional chemical precipitation (e.g. OH and S) less efficient, even coupled with high levels of metals. Furthermore, the high buffer capacity provided by the chelating agents requires excessive amounts of chemicals to neutralize alkalinity. These problems warrant studies on the recovery/separation techniques [5]. Zinc and copper are essential elements in various biological and enzymatic reactions. Though they form desired constituents of various alloys and pharmaceutical preparations, their larger concentrations in the environment can severely affect aquatic as well as human life. In view of this, the separation and determination of zinc and copper are of great importance [3].

II. THEORY

Liquid–liquid extraction is an important separation process that is used in a wide range of industries such as petroleum refining, food industry, nuclear fuel processing, pharmaceuticals, biochemistry, metal extraction, waste management and other areas. Heavy metals are major pollutants in marine, ground and industrial wastewater. Among these heavy metals, copper, nickel and zinc ingestion beyond the permissible limits causes various chronic disorders in human beings. Therefore, a systematic study on the preconcentration and separation of copper, nickel and zinc ions from natural water is of considerable significance from an environmental point of view. Elimination of heavy metals from industrial wastes at the point of environmental aspects was always important. Furthermore there is an attitude toward the recovery of precious metals from low-grade or complex ores, secondary resources and industrial wastes because of the reduction of world’s high grade resources and metals high prices [6]. The separation procedure of a chemical species from a matrix is essentially based on the transportation of the solute between the two involved phases, generally an organic and an inorganic one. Specifically, solvent extraction uses the concept of unique solute distribution ratios between two immiscible solvents. However, there are several situations where solutes have been observed to completely move from the inorganic to the organic phase. Organic solvent extraction is the transport of solutes, e.g. heavy metal ions, from an inorganic (or aqueous) phase to an organic phase. Solvents used comprise of an extractant + diluents combination. The roles of each are as follows: 1) the extractant, as a specific metal ion extractant; 2) the diluent, as a solvent condition controller, i.e. hydrophobicity, which can affect the molecules extractability. Occasionally, a phase modifier can be added to solve the problem of emulsion formation, aside from improving the phase demarcation process in an aqueous organic system. Solvent extraction is widely applied to processes of metal ions recovery, ranging from aqueous solutions in hydrometallurgical treatment to environmental applications. It is also considered a useful technique to increase the initial concentration of the solute, commonly used in the separation processes of analytical applications [7]. In recent years, much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules. This attention results in part from environmental concerns, efforts to save energy and recycling at the industrial level. In this respect, the supramolecular chemistry has provided a much better solution to the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such away that they delineate a suitable binding site [1].

2.1 Effect of heavy metal

Industrialisation of chemical industries leads to discharging of huge amount of heavy metals such as zinc (Zn), lead (Pb), iron (Fe), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr) and mercury (Hg) along with the wastewater. These heavy metal ions have toxicity and can cause cancer. These heavy metals affect soil fertility, water resource and aquatic ecosystem. Heavy metals in wastewater come from metal complex dyes, pesticides, fertiliser, refining, fixing agents, mordant and bleaching agents. The main source of wastewater is electroplating industry, pigment, printing and textile industry. Lead has toxicity, which causes anaemia, gastrointestinal disease and elevates body blood pressure even at small concentration. Similarly, higher concentration of zinc causes irritation, stomach cramps, lung disorder and concentration should not increase more than 2 mg/L in the wastewater. Further, copper is present in two forms monovalent and divalent. Divalent copper is harmful when it is inhaled in a large amount and causes headache, vomiting, nausea, liver and kidney failure, respiratory problems and abdominal pain. Similarly, the major source of cadmium are corrosion of galvanised pipe, erosion of natural deposits, mining, refining of non-ferrous metal, pigment, printing and photographic industry. Cadmium is toxic and has negative effects on kidney and in oral route. However, source of chromium are leather tanning, nuclear power plant, electroplating and textile industries. Source of nickel are electroplating batteries, silver refineries, zinc base casting, landfill leachates. Mercury comes out mainly from chlor alkali industry and battery industries. A number of methods have been developed for the removal of heavy metals from wastewater. In this review article, various methods such as chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. has been discussed. Moreover advantages, disadvantages, limitations are also discussed in order to find out the best suitable method for heavy metal removal [8].

2.2 Materials and reagents

LIX984 was obtained from Dexing Copper Mine. The active components of LIX984 are 2-hydroxy-5 nonyl-acetonphenoneoxime and 2-hydroxy-5-dodecylsalicylaldoxime. D2EHPA was obtained from Shanghai. No. 260 kerosene, obtained from Suzhou Refinery, was used as diluent. Other reagents were analytically pure. The bioleaching solution was obtained from an experimental plant of heap leaching, which contained 0.54 g/L copper, 3.70 g/L zinc, 3.26 g/L iron and 0.40 g/L calcium. The solution pH value was 2. 27. For the oxidizing activities of bacteria *(Thiobacillus ferrooxidans)* , most of the iron in the solution existed as ferric ions [9].

2.3 Extraction reaction

I. Organic acid extractent (D2EHPA) [10]:

$$M_{aq}^{n+} + \text{xHR(org)} \xrightarrow{K_{eq}} \text{MRx (org)} + \text{x}H^{+} \text{ (aq)}$$

II. LIX 84 – I as a function of NH_3 [10]:

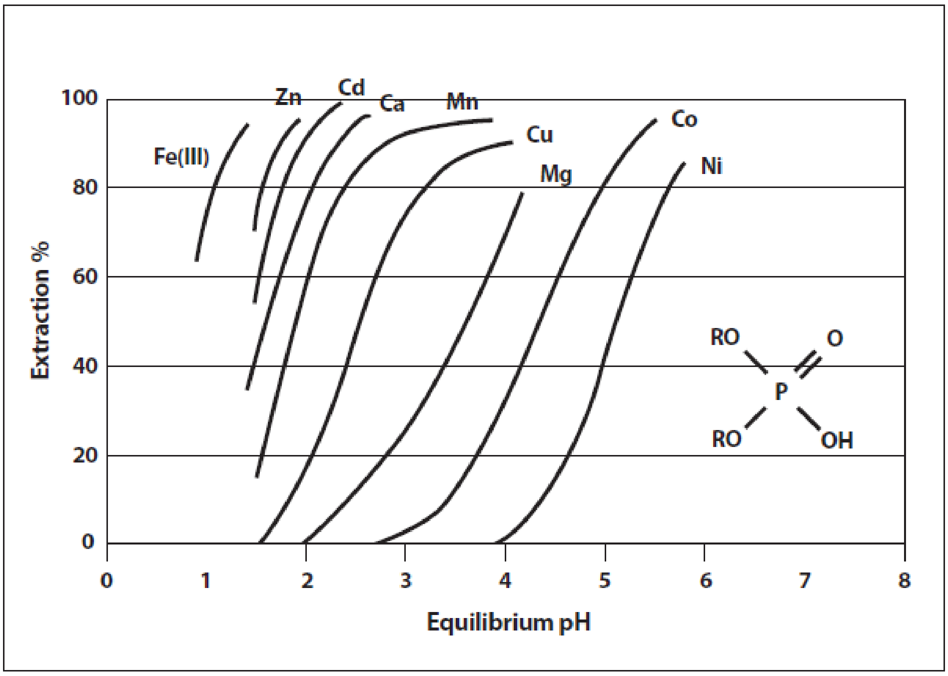
$$M_{aq}^{n+} + xHR_{(org)} \leftrightarrow MR_{x\,(org)} + xH^{+}_{(aq)}$$

2.4 Effect of pH

2.4.1 D2EHPA – Di-2-ethylhexyl phosphoric acid

The chemistry of this type of extractant has some characteristics which resemble chelating extractants and some which are similar to neutral or solvating extractants. D2EHPA molecules lose a proton much like a chelating extractant while two other D2EHPA molecules solvate the zinc similar to solvating type extractants. The pH extraction characteristics of D2EHPA with respect to several metals are shown in figure [10].

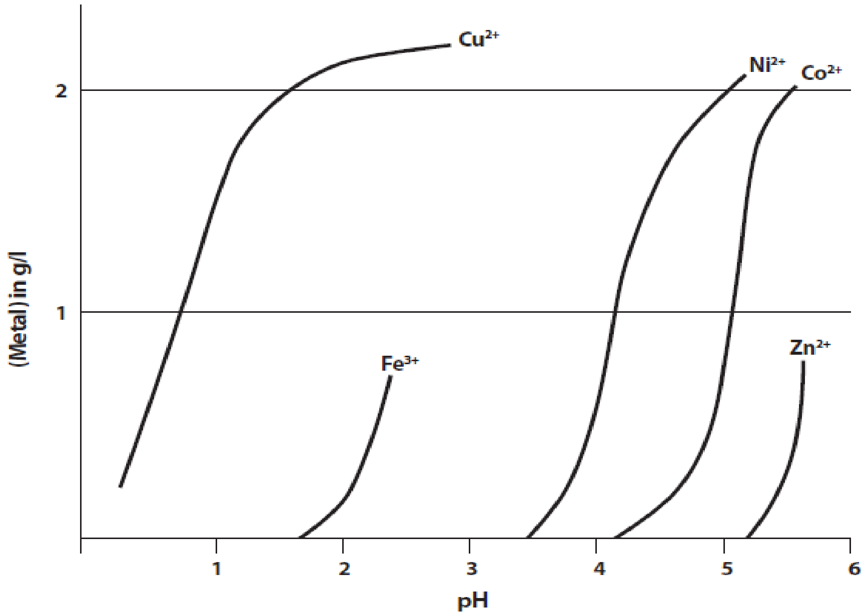
Figure 1. Metal extraction by D2EHPA as func. of pH



2.4.2 LIX-84

The extractant chemically bonds to the metal ion at two sites in a manner similar to holding an object between the ends of the thumb and the index finger. In many cases, upon bonding with the metal ion, the extractant releases a hydrogen ion into the aqueous solution from which the metal was extracted. One of the important parameters controlling the equilibrium position of this reaction is the acid content of the aqueous phase. A graphic representation of this behavior is referred to as a pH isotherm. These pH isotherms can be used to predict the extraction characteristics of the reagent with respect to the metals shown under a variety of conditions [10].

Figure 2. Metal extraction by LIX-84 as func. of pH



III. Conclusion

Liquid extraction of heavy metals is widely applied in many fields ranging from the environmental to the biomedical discipline. The pH plays important role in extraction of heavy metal, as conclude from graph of extraction of D2EHPA and LIX-84. The distribution coefficient and extraction percentage increased with growth of pH. Significant achievements have been made over the years in developing hosts for metal ions extraction. In order to understand the liquid-liquid extraction phenomenon of calixarene based ionospheres, two steps need to be considered. Firstly, designing of calixarene framework with sophisticated anchoring groups in a particular conformation. Secondly, the nature, size as well as the geometry of guest specie (ions or neutral molecules) are very important. The extractability of metal ions from medium with the extracting ligand, N- salicylideneaniline in biphasic system consisting of ionic liquid and an aqueous phase was studied using the liquid- liquid extraction process. This fact is particularly attractive because the green chemistry concept can be employed here. The use of chelate N- salicylideneaniline in two different middle ionic liquids and chloroform for the extraction of $Cu^{2+,}$ Co^{2+}, Ni^{2+} and Pb^{2+} gives a high extraction efficiency in the ionic liquid compared to chloroform.

IV. References

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