



Separation and recovery of copper from aqueous solutions using tri-*n*-butyl phosphate in benzene



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ABSTRACT

Purification of aqueous stream of sulphate containing copper ions (Cu^{2+}) has been studied by reactive extraction technique. Dissolved Cu^{2+} ions are removed from the aqueous solution with the help of tri-*n*-butyl phosphate (TBP) as a promising extractant with benzene used as a diluent to decrease the mass transfer resistances exists in the organic phase. The effect of parameters namely initial copper concentration (20 ppm, 60 ppm and 100 ppm), extractant composition (10 vol.% to 50 vol.%: 0.365 to $1.825 \text{ mol}\cdot\text{L}^{-1}$), organic/aqueous phase ratio (O/A ratio = 1:3 to 3:1), pH (2 to 11) and temperature (298 K to 333 K) are studied on the removal efficiency. 98% of copper is extracted at the conditions of $[\text{Cu}^{2+}]_{\text{in}} = 20 \text{ ppm}$, O/A ratio = 3:1, pH = 6, temperature = 298 K, and $[\text{TBP}] = 1.825 \text{ mol}\cdot\text{L}^{-1}$ or 50 vol.%. The organic phase is regenerated in a two stage stripping process using 4 N H_2SO_4 as the stripping agent and at 353 K. This regenerated organic phase is further used to remove copper from the aqueous solution. From the thermodynamic analysis it is inferred that the extraction process is exothermic, and favourable at low temperatures forming stable Cu-TBP complexes.

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1. Introduction

The discharge of large volumes of aqueous streams containing heavy metals globally is not only causing damage to the environment but also there is a loss of valuable resources. Therefore, efforts have been made to develop a suitable solvent extraction process for the extraction and separation of various heavy metals (copper, zinc, cadmium, nickel etc.) from their aqueous solutions [1]. Solvent extraction is one of the effective separation techniques to remove copper from aqueous solutions [2] among several methods such as chemical precipitation, coagulation-flocculation, flotation, ion exchange, electro-oxidation, membrane filtration [3] and biosorption [4,5]. In this process, transport of a solute molecule (say copper) takes place from the aqueous to the organic phase through a liquid interface [5]. The organic solvent phase is usually comprised of an extractant and a diluent [6,7]. The extractant is an active agent which extracts a specific metal ion, while the diluent facilitates easy mass transfer of solute in the extract phase [6–8].

Reactive extraction has come a long way since the 1970s and in the last decade there has been a tremendous development in the usability of reactive extraction to hydrometallurgy. There are more than 40 chemicals [Cyanex 921, Cyanex 272, Di-2-ethyl-hexyl phosphoric acid (D2EHPA), tri-*n*-butyl phosphate (TBP) etc.] that can be used as an extractant in order to remove metals from their aqueous streams [1,9].

In the reactive extraction, the extractant is used to remove the metals from the aqueous streams by making a complex with them. The extractant replaces, partially or fully the coordinated water molecules around the metal ions and form organically soluble species [10]. The extractant is expected to have high distribution coefficient, and dependency on pH of the system [11]. Futility of reactive extraction process lies in the reusability of the extractant after the extraction process is over. The organic phase comprising of metal-complexes are stripped with strong acids such as HCl, H_2SO_4 , HNO_3 etc. or strong bases like NaOH. Like extraction, the stripping process is also an ion-exchange phenomena, and pH dependent. The stripping agent breaks the metal-extractant complex in organic phase and frees the extractant molecule from the complex by rejecting the metal ion to the aqueous phase [12].

Copper is an important metal which is vital as well as toxic to the biological systems [13,14]. Many industries such as mining, metal processing and finishing, electroplating, printed circuit board manufacturing etc. produce effluents which contain copper. This untreated effluent can pose as a serious environmental risk [15,16]. Therefore, it is necessary to remove copper from aqueous stream generated from industrial effluents to prevent environmental pollution. In this study, tri-*n*-butyl phosphate (TBP), an extractant having organo-phosphorus group is used to separate copper from aqueous stream with benzene as an active diluent. TBP is readily soluble in organic solvents with small solubility in water. It can dissolve most nitrates, rare earth metals and transitional elements but not basic metals. TBP works well in extracting metallic elements of Ac and La families, and lots of heavy

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metals. It is chemically stable and has resistance to strong acids, strong bases and radiation. With a dipole moment of 3.07 debye and high capacity to supply electron, TBP is capable of forming complexes with metal ions easily [17].

2. Literature

Huang et al. [18] studied the use of di-2-ethylhexyl phosphoric acid (D2EHPA) as an extractant to remove zinc from sulphate medium. Kinetic study was performed using a constant facial area cell. Extraction and stripping rates were measured to develop the rate expressions and a probable mechanism for the process. Also, the extraction regimes and mechanism were proposed using the nature of the extractant for the formation of complexes of zinc. It was observed that the interfacial transport of metal was the limiting or controlling step in the extraction. They had also studied the total sulphate concentration on the extraction performance.

Woller et al. [19] used quinolines (LIX 26) and oximes (LIX84) as extractants to remove heavy metals namely, Cu, Cr, Cd, Ni, Zn and Pb in one step from the wastewater (e.g. leachate from landfills). They investigated the stoichiometry of the extracting reaction, selectivity of metals in extraction process, phase separation, and extraction/re-extraction experiments using a continuously operating mixer settler.

Devi et al. [20] used sodium salt of Cyanex 272 as the extractant for the extraction of zinc and manganese from their sulphate solutions. There was an increase in the metal extraction with increasing equilibrium pH and extractant concentration. In the extraction, $ZnA_2 \cdot 3HA$ and $MnA_2 \cdot 3HA$ species were formed. Loading capacity of Na-Cyanex 272 was found to be 0.1 M for zinc and manganese. The effect of NaCl, $NaNO_3$, Na_2SO_4 and NaSCN on the metal extraction was also studied. The presence of Na_2SO_4 in solution showed depressing effect on extraction systems, and it was observed that the separation factor was pH dependent.

Zhang et al. [21] developed a complete hydrometallurgical process for the recovery of metals (leach liquor composition in g/L: 23.4 Ni, 1.7 Co, 3.4 Fe, 0.72 Zn, 0.46 Al, 1.2 Mn, 4.2 La, 0.26 Ce, 0.82 Pr, 2.6 Nd, 0.074 Sm, and 50 Cl) from spent nickel-metal hydride (Ni-MH) secondary batteries. The effects of HCl concentration, temperature, reaction time and solid-to-liquid ratio on the leaching of metals were investigated. At optimum operating conditions (3 M HCl, temperature = 95 °C, leach time = 3 h, and pH = 1.2), up to 5.5 g of scrap in 50 ml of acid solution could be treated with recoveries of cobalt = 100%, nickel > 96% and rare earths = 99%. They used 25% D2EHPA in kerosene and 25% TOA in kerosene in the solvent extraction circuit to remove the metal ions in different steps. For the scrubbing of metals different amount of HCl was used with different O:A ratio of phases. The same group in 1999 [22] had studied the separation and recovery of metals (liquor composition in g/L: 10.6 Ni, 0.85 Co, 1.70 Fe, 0.36 Zn, 0.21 Al, 0.54 Mn, 1.73 La, 0.10 Ce, 0.33 Pr, 1.10 Nd and 0.032 Sm) by using 25% D2EHPA in kerosene and 20% bis(2,4,4-tri-methylpentyl) phosphinic acid (Cyanex 272) in kerosene at pH around 0.4. In their studies, they also proposed a total process flowsheet for the recovery of rare earths, cobalt and nickel from the spent Ni-MH batteries.

Reddy et al. [23] investigated a process for the removal of nickel using PC-88A in kerosene as the solvent-extractant system. With three stages of extraction, 99% of nickel was extracted with 1 M PC-88A neutralised to 50% and O/A of 2.2. In two counter-current stages, Nickel was stripped from loaded organic phase at O:A ratio of 5 with 82 kg/m³ of H_2SO_4 to obtain a strip solution containing about 55 kg/m³ nickel (pH ~ 3) with degree of stripping > 99.98%.

Juang et al. [24] studied the use of Aliquat 336 to extract Cu^{2+} -NTA chelated anions. The distribution ratios of Cu^{2+} were calculated. Effect of different parameters like pH, amine concentration and temperature were studied. With the increase in pH distribution ratios first increased and then decreased. Non-ideality of organic phase was discussed and enthalpy of extraction process was found out.

Kyuchokov and Szymanowski [25] used a mixture of two extractants (LIX 54 - a chelating agent, and Alamine 336 - a basic or solvating extractant) in the reactive extraction of copper (II) and zinc (II) from acidic solutions. They proposed series of step to recover Cu and Zn. Firstly, metal chloro-complex, solvates or ion-pairs were formed for the extraction from the chloride media. Secondly, chloride ions were scrubbed by an aqueous solution at appropriate pH with simultaneous transferring of metal ions to the chelate. Finally, the organic phase was stripped with sulphuric acid and the extractant was recovered.

Kyuchokov et al. [26] used alkyl-8-hydroxyquinoline (KELEX 100) as the reactive extractant to remove zinc and copper from the chloride solutions in three stages. Among these three steps, the stripping stage was found to be most efficient. An ammonical solution was used as a scrubbing agent to scrub chloride from the organic phase. The selective separation of Zn and Cu was carried out by using sulphuric acid of 0.25–0.8 M, and 3 M, respectively, with O/A ratio of 1.

Mhaske et al. [27] studied the extraction of palladium and rhodium received from spent catalyst using Cyanex 921 from aqueous HCl medium. Studies were performed in the presence and absence of Tin (II) chloride. Initially, extraction of individual elements were performed separately to see the effects of different variables namely HCl concentration, tin (II) chloride concentration, equilibrium time, stripping agents and initial concentration of elements. Also, extraction experiments were performed with a synthetic aqueous solution similar to the composition of leachate from spent catalyst.

Mansur et al. [28] proposed a modified equilibrium model for the reactive extraction of Zn (II) using D2EHPA + n-heptane, and validated by using statistical analysis. Two types of zinc complexes were formed by two simple consecutive reactions but their relative proportions changed as the conditions were changed from extraction to stripping. Newton's method was used to solve the model, and experimental data were fitted using the direct search method of Hooke and Jeeves to estimate all the parameters.

Kongolo et al. [29] used solvent extraction to remove Co and Zn from a synthetic solution (composition in g·L⁻¹: 2 Cu²⁺, 1 Co²⁺, 8.4 Fe²⁺ and 12.6 Zn²⁺). LIX 984 was used to extract copper, and H_2SO_4 was used as stripping agent. Subsequently, iron was precipitated with $CaCO_3$, and afterwards Co and Zn were extracted with D2EHPA and was stripped by H_2SO_4 . Removal percentage of more than 95%, 90% and 90% were observed for Cu, Co and Zn respectively.

Tsakiridis and Agatzini (2004) [30] used 20% Cyanex 301 diluted with Exxsol D-80 and modified by using 5% TBP to extract cobalt and nickel simultaneously from manganese and magnesium sulphate solutions. The organic solution could extract cobalt and nickel by 99.9% and 99.7%, respectively, at optimum condition of pH = 2, T = 50 °C, and A:O = 1:1 in one stage. After scrubbing with 1 M HCl at pH = 2, Mn^{2+} co-extraction in the loaded Cyanex 301 was obtained as 0.2%, whereas no Mg^{2+} extraction occurred in the pH range of 1–2. Then, Co and Ni were stripped by 5 M HCl with a stripping yield of 99.2% for Ni and 99.6% for Co at 50 °C and at O:A = 2. In another study by the same authors [31], the reactive extraction of Al in the presence of Co, Mg and Ni from sulphate solution was carried out with the same extractant mentioned. The removal percentage of Al was found to be 99.5% in a single step at pH of 3, temperature of 40 °C and O:A ratio of 1. Stripping of Co and Mg were done using 2 M H_2SO_4 and achieved a 99.6% stripping yield at a temperature of 40 °C with O/A ratio of 2:1.

Fang et al. [32] studied a liquid emulsion membrane process using 3,5-di-isopropyl salicylic acid (DIPSA) and tri-isobutyl phosphine sulphide (TIBPS) as carriers, and ammonium sulphide $(NH_4)_2S$ as precipitant. Sulphide ions have reactivity with cadmium ions in the aqueous solution which increases cadmium recovery significantly, and minimizes zinc impurities. This process was developed to enrich low concentrated cadmium from a solution of highly concentrated zinc ions. A single stage process gave a cadmium recovery of 98% at 99.6% cadmium sulphide content under optimum conditions.

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