ELSEVIER

Process development for the separation of copper(II), nickel(II) and zinc(II) from sulphate solutions by solvent extraction using LIX 84 I

B. Ramachandra Reddy *, D. Neela Priya

Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad 500 007, India

Abstract

Development of a solvent extraction flow sheet for the separation and recovery of Cu(II), Ni(II) and Zn(II) using LIX 84 I as an extractant from sulphate solutions was investigated. Extraction of the metals depends on the equilibrium pH of the aqueous phase and increases with rise in equilibrium pH. Based on the difference in their extraction behavior as a function of equilibrium pH of the aqueous phase, it was possible to separate and recover these metals. Their extraction behavior clearly demonstrates the application of LIX 84 I as the extractant for the selective separation of Cu(II), Ni(II) and Zn(II) in pure form. The copper extraction isotherm was obtained by contacting the metal solution and 0.05 M LIX 84 I at different aqueous to organic (A:O) phase ratios at an equilibrium pH of 4.0. The McCabe–Thiele plot suggested that quantitative copper extraction is achievable in two counter-current stages (C–C) at A:O phase ratio of five, which gave 99.4% copper extraction efficiency. The results of two-stage stripping simulation for 0.745 gpl of Cu-loaded organic (LO) carried out at O:A ratio of 1.5:1 with 2 M H_2SO_4 gave copper stripping efficiency of 99.94%. Copper in the strip solution was enriched by more than seven times. The extraction of nickel with the same concentration of LIX 84 I at an equilibrium pH of 7.50 at A:O phase ratio of 1:1.1 in two stages gave nickel extraction efficiency of 99.4%. A two-stage counter-current stripping simulation (CCSS) for nickel LO at A:O phase ratio at 1:1 gave nickel stripping efficiency of 99.93%. Further extraction of zinc with the same concentration of LIX 84 I at an equilibrium pH of 9.0 at A:O phase ratio of unity for two stages gave zinc extraction efficiency of 99.81%. A two-stage counter-current stripping simulation for zinc LO at A:O phase ratio of unity with 3 M H_2SO_4 gave zinc stripping efficiency of 99.7%. Based on the results, a complete solvent extraction flow sheet of the process was developed with extraction and stripping efficiencies >99.5%.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Solvent extraction separation; Copper; Nickel; Zinc; LIX 84 I

1. Introduction

Major sources for the production of copper, nickel and zinc appears to be from the raw material such as oxidic, silicate and sulphide ore concentrates namely chalcopyrite, pentaldite, scrap/spent catalyst or batteries/dust, etc. Hydrometallurgical methods of leaching/dissolution of such materials under atmospheric/pressure conditions employing chloride/sulphate systems result in leach liquors containing copper, nickel and zinc along with some impurities. Using classical methods such as precipitation, it is difficult to separate these metals. However, metals in pure form can be obtained by using SX.

In view of the industrial and economic importance of these metals, there is a great need to separate and recover them using cost effective commercial extractants. Literature survey reveals that, liquid–liquid extraction has been applied extensively for the separation of cobalt and nickel with alkyl phosphorous reagents viz., D2EHPA, PC 88A,Cyanex 272 or their equivalents [1]. Besides, many LIX reagents were also used earlier for the extraction, separation and recovery of copper, nickel and zinc mostly from ammoniacal sulphate solutions using LIX 87QN, LIX 54, LIX 973, LIX 984 and LIX 34, respectively [2–8]. Of LIX reagents, LIX 84 [9] was used commercially for extraction and also for selective removal of copper ions from aqueous solutions using modified silica beads impregnated with LIX84 I [10,11]. Also, it was used for the recovery of nickel and separation of nickel and

* Corresponding author. Tel.: +91 40 27160123; fax: +91 40 27160921.
E-mail address: brcreddy_iict@yahoo.com (B.R. Reddy).

copper from ammoniacal solutions through co-extraction and selective stripping [12,13].

In our recent studies on nickel(II) extraction from sulphate solutions using LIX 84 I, large differences in the percentage extraction behavior of Cu(II), Ni(II) and Zn(II) as a function of equilibrium pH of the aqueous phase was observed. The extraction of Cu(II) started at pH > 0.2 and reached quantitative at equilibrium pH ∼ 4. Under these conditions, extraction of Ni(II) and Zn(II) was nil [14]. In this paper, we report the solvent extraction separation of copper, nickel and zinc, from simulated synthetic sulphate solution using LIX 84 I as the extractant dissolved in Kerosene, with an objective to separate these metals by the single extractant. The parameters studied are: aqueous phase equilibrium pH, extraction isotherm, counter-current extraction and stripping simulations, effect of acidity on metal stripping from loaded organic. Development of flow sheet for the separation and recovery of copper, nickel and zinc from a typical synthetic sulphate solution using LIX 84 I was demonstrated.

2. Experimental

2.1. Apparatus

Perkin-Elmer Model A 300 atomic absorption spectrophotometer (AAS) and a digital Digisun (DI 707 model) pH meter with combined glass electrode were used.

2.2. Reagents

Stock solution of 0.1 M copper(II), nickel(II) and zinc(II) metal solutions were prepared by dissolving requisite quantity of analytical grade $CuSO_4$, $NiSO_4$ and $ZnSO_4$ in distilled water. The concentration of metals in these solutions was determined volumetrically by standard methods using EDTA as the reagent. Working standard solutions were prepared by suitable dilution of these stock solutions. LIX 84 I, a proprietary product of M/s. Cognis is 2-hydroxy-5-*t*-nonyl acetophenonoxime having a molecular weight ∼263 [10] and 97% purity was used. Distilled kerosene (bp, 160–200 °C) was used as the diluent. The aromatic and aliphatic contents (as determined by NMR) were 3.6 and 96.4%, respectively. All other chemical and reagents used were of analytical grade.

2.3. General extraction procedure

A suitable aliquot (10 ml) of the solution containing metal ions was equilibrated with an equal volume of LIX 84 I diluted in kerosene for 20 min in glass-stoppered bottles using a mechanical shaker. Initial experiments on the effect of time on metal extraction indicated that 15 min is sufficient to reach equilibrium reaction. Extraction experiments were carried out at the desired equilibrium pH values of the aqueous phase by adding dilute H_2SO_4 or NaOH. After phase disengagement, the aqueous phase was separated and metal
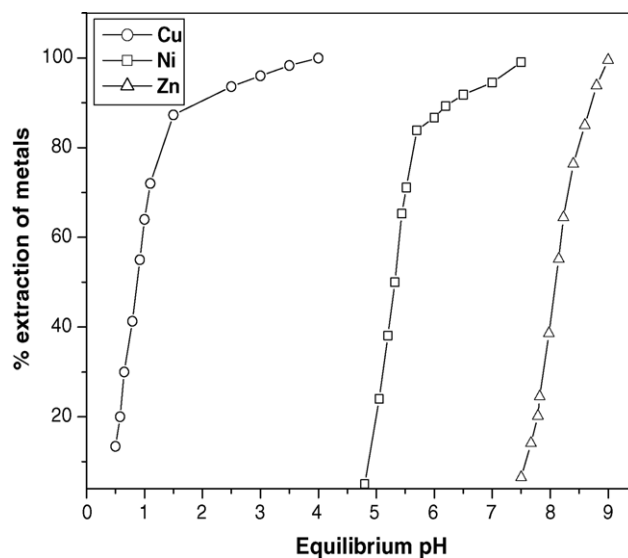

Fig. 1. Effect of equilibrium pH on the percentage extraction of metals using LIX 84 I. Cu(II), Ni(II) and Zn(II): 0.0025 M each; LIX 84 I: 0.005 M.

concentrations were analyzed by AAS. The distribution ratio, *D* was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. As and when required, the metal concentration in the organic phase was determined after filtration through a 1PS paper and stripping a suitable aliquot with 2 M H_2SO_4, followed by analysis. All the experiments were carried out at room temperature (30 ± 1 °C) and the general agreement with *D* values obtained was within ±5%.

3. Results and discussion

3.1. Influence of equilibrium pH

Extraction studies were carried with individual solutions containing 0.0025 M copper(II), nickel(II) and zinc(II), respectively. The extraction of these metals with 0.005 M LIX 84 I as a function of pH was studied in the pH range 0.5–9.0. It was observed from Fig. 1 that the percentage extraction of these metals depends mainly on the equilibrium pH of the aqueous phase. The extraction of copper(II) starts at pH values around 0.5 and reaches quantitative extraction at equilibrium pH 4.0. Under these conditions, the extraction of nickel and zinc was nil. Also, it was observed that the extraction of nickel starts after an equilibrium pH 4.80 and reaches more than 99% at an equilibrium pH 7.50, which is much below the zinc extraction starting pH. The extraction of zinc(II) starts at around 7.50 and reaches 99.5% at an equilibrium pH 9.0. The $pH_{1/2}$ values calculated from 50% extraction of copper, nickel and zinc are 0.9, 5.35 and 8.0, respectively, demonstrating the possible quantitative separation of copper(II), nickel(II) and zinc(II) from their mixtures. Based on the data of the extraction behavior of these metals, a synthetic solution containing copper(II), nickel(II) and