N,*N*-Dihexyl-*N’*-Hydoxypyridine-2-Carboximidamide as Promising Extractant of Cu(II) and Ni(II) from Sulfate Media

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This paper presents studies on the extraction of Cu(II), Zn(II) and Ni(II) from model sulfate solutions using novel reagent: *N*,*N*-dihexyl-*N'*-hydroxypyridine-2-carboxyimidamide (DH2PIA). The effect of different variables influencing the extraction of the metals ions such as the effect of contact time and the pH of the aqueous phase has been investigated. The studies also covered the determination of selectivity of the extraction of copper(II) over nickel(II) and zinc(II) and further determination of the optimum stripping process condition

1. Introduction

Metals are produced from primary and secondary deposits, and both sources can be treated pyrometallurgically or hydrometallurgically. Nowadays, it can be seen a growing role of solvent extraction in mineral ores processing [1,2]. Leaching is the first chemical step in the hydrometallurgical ore processing. Hydrometallurgical processes generally consist of different steps of pre-treatment, in order to improve metal dissolution rates in the aqueous phase, followed by leaching, purification and finally recovery of different metals from the leach solution. It involves dissolving the metal from ore in leaching reagent. In the leaching step either an acid or a base can be used depending on the material being treated, but still the most frequently used solutions for this purpose are sulfuric acid solutions and an oxidizing agent (e.g.,: $Fe_2(SO_4)_3$, hydrogen peroxide) or bacteria. The effectiveness of the oxidative leaching of sulphide concentrates in sulphuric acid solution is very high [2-5]. Solvent extraction technique is most common used to separate required metal ions from multimetal aqueous solution. In solvent extraction procedure, the solution containing the metal of interest is mixed with an organic solution containing an extractant [6].

Several extractants have been investigated to extract Cu(II) from Ni(II) and Zn(II): organophosphorous_extractant (Cyanex 272 [7,8], Cyanex 301 [9], Cyanex 923 [10] and D2EHPA [8]) and LIX84I [10-12]. However, the selective extraction of the metals is still an unsolved problem [9]. Therefore, the present work was to study the extraction of copper(II), zinc(II) and nickel(II) from sulfate solution by novel reagent having extracting properties - *N*,*N*-dihexyl-*N'*-hydroxy-pyridine-2-carboximidamide (DH2PIA).

2. Experimental

2.1 Reagents

N,*N*-dihexyl-*N'*-hydroxypyridine-2-carboxyimidamide (DH2PIA, Figure 1) was synthesized according to a three-step method described in the previous paper [13]. Purity was determined by thin layer chromatography method (TLC) and quality by FT-IR and NMR (^{1}H and ^{13}C) spectroscopy. Heptane (POCH) was used as diluent to make 0.1M extractant concentration solution. Zinc(II) sulfate heptahydrate (Sigma Aldrich), nickel(II) sulfate monohydrate (Sigma Aldrich), copper(II) sulfate pentahydrate (POCH), sodium sulfate (CHEMPUR), sodium hydroxide (CHEMPUR) and sulfuric(VI) acid (CHEMPUR) was used to make aqueous feed solutions. Aqueous feed solutions had constant concentration of metal ions (0.01M) and sulfate ions (0.01M). pH of the aqueous solution was regulated by an addition of appropriate amounts of sodium hydroxide or sulfuric acid(VI). All used reagents were of analytical-grade.

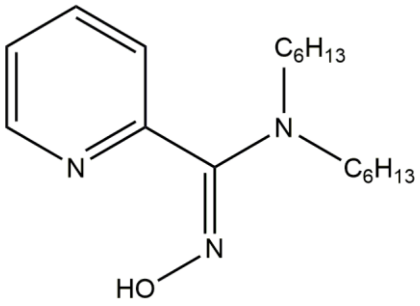

Figure 1. Structure of studied reagent.

2.2 Extraction procedure

The extractant was used at equal volumes of aqueous and organic phases (5 mL) were shaken at room temperature for 5 minutes. After separation of the phases, metal ions concentration and pH of the raffinate were determined.

Concentrations of Cu(II), Ni(II) and Zn(II) ions were determined by Atomic Absorption Spectroscopy using Avanta PM spectrometer (GBC Scientific Equipment) and pH was regulated using T50 titrator (Mettler Toledo) equipped with a DG111-SC combined glass electrode. The content of the metal in the organic phase was calculated from the difference in starting concentrations and concentrations in the raffinate.

Aqueous sulfuric acid solutions were used as reagent enabling a back extraction of metal to the aqueous phase.

3. Results and Discussion

3.1 pH dependency

Figure 2 (A) shows the effect of equilibrium pH on extraction of Cu(II), Zn(II) and Ni(II) from a single metal solution. It has been shown that in the case of Cu(II) the extraction increases with the increase of pH and the maximum is achieved above pH of 3(~ 100%).

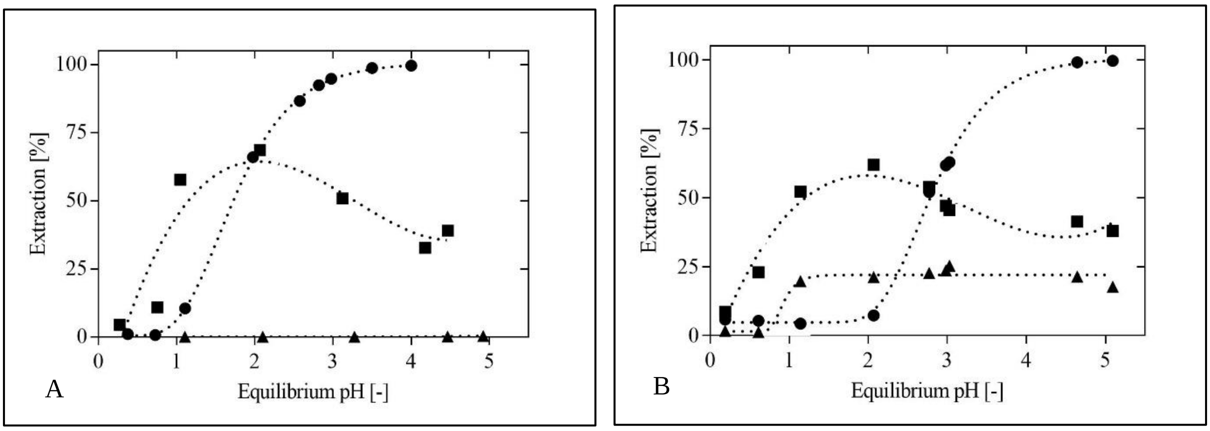

Figure 2. **A**-Effect of equilibrium pH on extraction of Cu(II) - ●, Ni(II) - ■ and Zn(II) - ▲ from single model solutions. **B**- Effect of equilibrium pH on extraction of Cu(II) - ●, Ni(II) - ■ and Zn(II) - ▲ from mixture of metals ions. Dotted line represents approximations.

The different correlation can be observed for Ni(II), when initially the extraction yield increases from 58 to 69% (pH 1-2) and after that decreases up to 39% for pH 5. The Zn(II) extraction is insignificant and observed only at pH of 5. At more acidic conditions all of zinc(II) ions remain in the aqueous phase.

Different results were obtained using mixture of the metals. As it can be observed in Figure 2 (B), the increasing pH also increases Cu(II) extraction, but the most effective removal is observed at pH above 4. It is also observed that Ni(II) is extracted comparably to that obtained for the single metal solutions, but Zn(II) is transported in 20-24%.

3.2 Time dependency

Study of shaking time influence on the extraction was carried out at constant pH equal to 4 for Cu(II) and Zn(II), at pH of 2 for Ni(II), and at a constant concentration of metal ions equal to 0.01 mol/L. The experiment was investigated in the time range of 1-60 minutes.

Figure 3 compares results obtained for Cu(II), Ni(II) and Zn(II), which indicated that equilibrium of the extraction is reached within first 2 minutes and further prolongation of shaking time does not affect the process significantly.

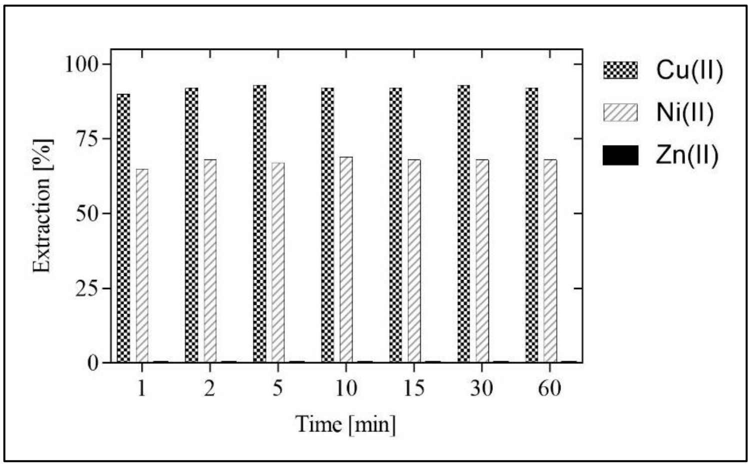

Figure 3. Effect of time on Cu(II), Ni(II) and Zn(II) extraction using DH2PIA as extractant.

3.3 Stripping study

The stripping of Cu(II) and Ni(II) from loaded organic phase was investigated. As a stripping agents water and sulfuric acid solutions were used. It was observed that the co-extracted zinc(II) can be washed out by water, while Cu(II) and Ni(II) require sulfuric acid solution as stripping agent. The optimum concentration of H_2SO_4 for Cu(II) is 3 %, but for the Ni(II) recovery minimum 20% solution allows for the back-extraction of the metal. Moreover, Cu(II) and Ni(II) can be separated conducting extraction at pH 2, and after that the co-extracted copper(II) can be stripped using diluted sulfuric acid.

4. Conclusion

The obtained results indicated the usefulness of the novel reagent DH2PIA as the selective extractant of copper(II) and nickel(II) from acidic sulfate solutions containing also zinc(II). The studied reagent formed complexes according to chelate mechanism, and the complexation was very fast. The selectivity of Ni(II) over Cu(II) depended on the equilibrium pH of the aqueous phase, but co-extracted metal can be washed out by water (Zn(II)) or stripped after shaking with 3% H_2SO_4 (Cu(II)).

Acknowledgement

This study was funded by National Science Center Poland research grant funds according to decision No. DEC-2015/17/N/ST8/00285. This study was also supported by the Polish Grant: 03/32/DSMK/0720.

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