Synergistic extraction of copper Cu(II) using di(2-ethyl hexyl) phosphoric acid (D2EHPA) and tri-n-octyl phosphine oxide (TOPO)

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Abstract: This work consists of a water purification technique that involves $Cu2^+$, H_3O^+ and_ Cl^- ions. It is well known that extraction of Cu2+ from chlorhydric acid is quite difficult regarding to the presence of many Cu (II) species in the aqueous media. The copper is enquired to form different aqueous species such as hydroxyl: Cu OH^+, $Cu(OH)_2$ (aq), $Cu(OH)_3{}^-$ and $Cu(OH)_4{}^{-2}$ further the formation of aqueous complexes having chloride bonds. In this study we considered various forms of Cu(II) present in the chlorhydric acid solution: $CuCl^+$, $CuCl_2$; $CuCl_3^-$ $CuCl_4^{-2}$ in the aqueous phase were taken into account in the analysis of the extractions.
The optimum synergetic parameter giving the ions extraction efficiency was determined for diluted copper solutions.
The chemical parameters have allowed us to obtain the variables giving the optimum synergistic extraction efficiency for diluted solutions of copper.
The fundamental parameters influencing the extraction synergism by mixing of two extractants, di(2-ethyl hexyl) phosphoric acid and tri-n-octyl phosphine oxid of copper(II) from chlorhydric acid solutions have been examined.
The synergistic extraction by the mixture: Extractant cation exchanger (D2EHPA)/ Extractant solvating (TOPO) dissolved in kerosene were investigated.

Key words: Synergistic, extraction, copper, treatment, environment.

1. Introduction

Heavy metals are toxic to human beings and organisms[1-2]. The metal concentration was determinate by atomic absorption spectroscopy (AAS) [Pinta M. (1971)].

For strong acidities, taking into account the predominance of the copper species, an exchange like the mechanism proposed by F. Sadi *et al.*[5] presented as follows:

In order to design and optimize a synergistic extraction of copper Cu (II) using di(2-ethyl
hexyl) phosphoric acid (D2EHPA) and Tri-n-octyl phosphine oxide (TOPO)
Synergistic process for industrial application, the effect of transport conditions has been studied. The study the influence of different parameters such as: the acidity, nature and concentration of the carriers, effect of ratio HDEHP/TOPO.

2. Experimental

2.1.Principle of the extraction by solvent

The liquid - liquid extraction is a method of separation that permits to isolate present substances in a solution by selective transfer in another non miscible solution, it is a technique very used in analytic chemistry and in organic chemistry. In hydrometallurgy it permits the purification and the concentration of the solutions obtained of the l leaching of ores.
Its setting illustrated by the figure1.

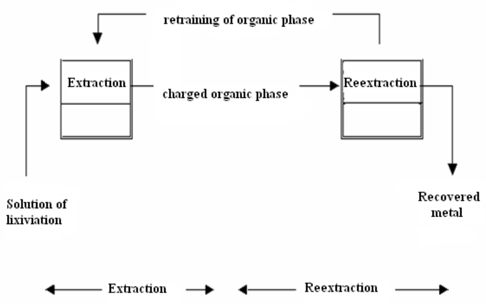


Figure 1. Principle of the extraction by solvent

2.2.Extraction procedure

The initial concentration of the copper (II) was 100 ppm in all experiments. Copper (II) extraction was carried out using a synthetic aqueous solution of constant concentration of copper (100 ppm) and a variable concentration of hydrochloric acid, with organic solutions containing two extractants TOPO and D2EHPA or HDEHP of concentration 0.01M dissolved in kerosene.

The experiments were carried out using 10 ml volumes of aqueous and organic phases. The samples were shaken mechanically for 20 min, which was sufficient to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined by atomic absorption spectroscopy (AAS) [Pinta M. (1971)].

3. Results and discussion

3..1. Effect of the concentration of chlorhydric acid on the extraction efficiency

The Extraction of copper (II) in chlorydric acid medium has been examined by testing liquid membranes made of TOPO, D2EHPA or HDEHP and TOPO/HDEHP.

The results obtained are shown in the figure below

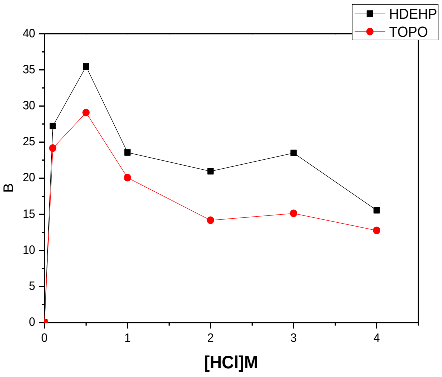


Figure 2. Variation of efficiency extraction the Cu(II) from chlorhydric acid medium with TOPO and HDEHP

[HDEHP]= [TOPO]= 10^{-2}M, $[Cu^{2+}]_0$ = 100 ppm.

The copper(II) extracted by tri-n-octyl phosphine oxide showed a significant extraction in the order of 80%. for HCl 0,5M.

The extraction of copper by the di (2-ethyl hexyl) acid (HDEHP) , showed that for the weak concentrations in chlorhydric acid, the outputs of extraction are important, of the order of 82% for HCl 0,5M.

3.2. Mechanism extraction

3.2.1. Solvatation mechanism by TOPO:

We propose the mechanism by solvatation [Marcus Y .(1969)] as follows:

** To the weak acidities*

$$Cu^{2+} + H^+, Cl^- + 2\overline{TOPO} \leftrightarrow \overline{CuCl2, 2TOPO} \quad (1)$$

**To the strong acidities* the following mechanism is in competition:

$$H3O^+, Cl^- + \overline{TOPO} \leftrightarrow \overline{H3O^+, Cl^-, TOPO}$$

3.2.2. Cationic exchanger mechanism by D2EHPA

We propose the ion-exchange mechanism [Ritcey G.M.and Ashbrook A. W, (1984)] as follows:

** To the weak acidities*

Extraction of copper by D2EHPA noted : HX

$$Cu^{2+} + \frac{3}{2}\overline{(HX)2} \leftrightarrow \overline{X2\,Cu, HX} + 2H^+ \quad (3)$$

** To the strong acidities*, while taking into account the predominance of the copper species , an exchange like mechanism [Hassaine-Sadi,F. . (2013), following:

$$Cu\,Cl2 + \frac{1}{2}\overline{(HX)2} \leftrightarrow \overline{Cu\,Cl2, HX} \quad (4)$$

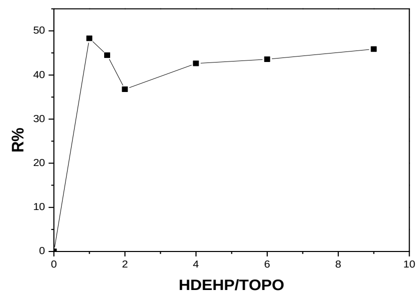
An elevation of the acidity increases the extracted quantities, with the latter ones being limited however by the capacity solvate of the HDEHP.

3.3.Cation exchanger extractant / Solvating extractant

Study of the synergistic effect of the HDEHP - TOPO mixture.

3.3.1. Effect of ratio HDEHP/TOPO

The results obtained are shown in the figure below:



Figur 3: Variation in copper extraction yield on function of the ratio HDEHP /TOPO

[HDEHP]= [TOPO]= 10^{-2}M, [HCl] =0.5M, $[Cu^{2+}]_0$= 100 ppm.

A synergistic effect is observed when the HDEHP-TOPO mixture is used, a high copper extraction efficiency of the order of 48.29% for a ratio [HDEHP] / [TOPO] = 1,

and a hydrochloric acid concentrate on 0.5 M.

3.3.2. Transport of Cu(II) by synergism [Taube M. (1961).]

We achieved the transport of copper (II) through the membrane by using a mixture of extractants, HDEHP – TOPO, diluted in kerosene. The copper ion is extracted according to the reaction:

$Cu^{2+} + H^+, Cl^- + x/2\ (HX)_2, nTOPO$
$\leftrightarrow \quad CuCl_2, nTOPO, (1-x)HX + 2H^+ \quad (5)$

Conclusions

In the present work we proposed a new process to the treatment of diluted solutions from heavy metals. Synergistic extraction of copper Cu(II) using di(2-ethyl hexyl) phosphoric acid (D2EHPA) and tri-n-octyl phosphine oxide (TOPO) has been successfully achieved by extracting Cu(II) from HDEHP-TOPO mixture using kerosene as solvent. The process purification by extraction synergism would be particularly judicious in the case of the treatments of the industrial wastes containing heavy metals. It is very sparing out of water and raw materials (recycling of the reagents and organic phase). This also allows an effective protection of the environment while being profitable.

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