

# COMPARATIVE STUDY OF COPPER (II) REMOVAL/RECOVERY FROM AQUEOUS SOLUTIONS BY BULK LIQUID MEMBRANES CONTAINING SIX DIFFERENT CARRIERS

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The removal/recovery of metals from secondary sources is an interesting research field from both economic and environmental view points. In this paper we study the removal/recovery of copper(II) from aqueous solutions by bulk liquid membranes through a carrier mediated transport mechanism using six different carriers. The efficiency of the different carriers is analyzed bases on the values of different transport parameters (flux and permeability through feed/membrane and membrane/product interfaces) and on the percentages of copper (II) removed from the feed phase, recovered in the product phase and accumulated in the membrane phase.

*Key words:* copper, removal/recovery, bulk liquid membranes, counter-transport, co-transport

## INTRODUCTION

Copper is among the most prevalent and valuable metals used by industry. Considered as an energy critical element due to its conductive properties, it is a scarce mineral, with only sixty year of expected availability at current production levels [1]. Copper is also one of the most toxic metals, regarded as being of most immediate concern by the World Health Organization [2] and classified as a priority pollutant by US EPA [3].

Therefore, the removal/recovery of copper from raw materials and secondary sources is an interesting field in hydrometallurgical investigations from both economic and environmental view points.

Several methods has been described for copper (II) removal/recovery from wastewater during last years, including cementation [4], chemical precipitation [5], adsorption [6], ion exchange [7], chelation [8] electrocoagulation [9], electrodialysis [10], pressure driven membrane processes [11] and liquid membranes [12,13].

Liquid membranes have shown great potential as for use in removal/recovery processes, since they combine the extraction and stripping processes into a single unit operation [14]. In a liquid membrane, two miscible liquids (feed and product phases) are separated by a third immiscible liquid, which constitutes the membrane phase.

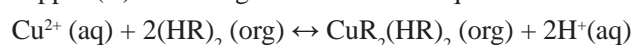
In order to improve the effectiveness of the separation process, facilitated transport mechanisms, which maximize both the extraction velocity and the reception capacity of the diffusing specie into the product phase, have been described [15]. In carrier facilitated transport, the transport of the diffusing specie is facilitated by an ion exchange reagent, which is incorporated in

the membrane phase to carry the diffusing specie from the feed to the product phase across the membrane phase, a process that is usually accompanied by the transport of other chemical specie (coupled transport), either from the feed to the product phase (carrier facilitated co-transport) or from the product to the feed phase (carrier facilitated counter-transport).

This paper represents a comparative study of copper (II) removal/recovery from aqueous solutions through bulk liquid membranes containing six different carriers, bis-2-ethylhexyl phosphoric acid (DP8R)), bis-2,2,4-trimethyl pentyl phosphinic acid (CYANEX 272), mixture (50 %) of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenoneoxime (LIX 984N), benzoyl acetone (BA), 8-hydroxy quinoline (8-OHQ) and tri-n-octyl amine (TOA).

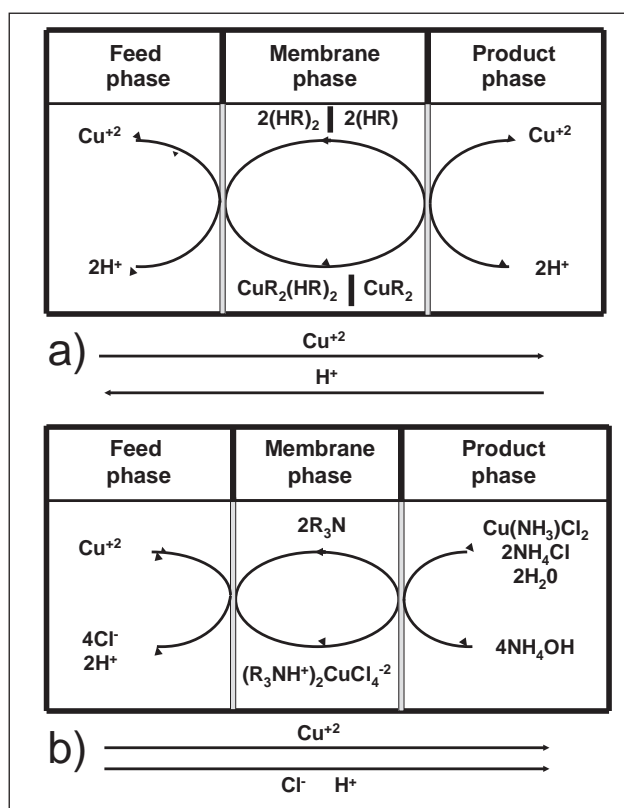
Two types of carrier facilitated transport mechanisms are involved, a counter-transport mechanism, which uses DP8R, CYANEX 272, LIX 984N, BA or 8OHQ as carriers and protons ( $H_2SO_4$ ) as counter-ions (Figure 1a), and a co-transport mechanism, that uses TOA as carrier and chloride and protons as co-ions (Figure 1b).

In the counter-transport mechanism (Figure 1a), the carrier diffuses from the bulk membrane phase to the feed/membrane interface where it reacts with copper (II). Two types of reactions can be considered according to the carrier used. When an organophosphorous carrier is used (DP8R or CYANEX 272), due to their high interfacial reactivity, two dimerized molecules of carrier  $(HR)_2$  [16], undergo acid dissociation and react with copper (II) according to the chemical equation:

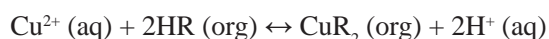


When LIX 984N, BA or 8OHQ are used as carrier, two molecules of carrier (HR) react with copper (II), according to the chemical equation:

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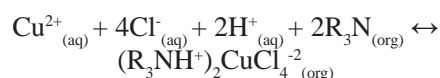


**Figure 1** Carrier facilitated transport of Cu (II). a) Counter-transport and b) Co-transport

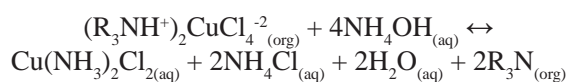


In both cases, the copper(II)-carrier complex formed ( $\text{CuR}_2(\text{HR})_2$  or  $\text{CuR}_2$ ) diffuses through the membrane to the membrane/product interface where, by reversing the above reactions, protons are exchanged for copper (II) ions, which are released into the product phase. Carrier is regenerated, thus initiating a new separation cycle.

In the co-transport mechanism (Figure 1b), the carrier diffuses from the bulk membrane phase to the feed membrane interface, where it reacts with copper (II) (copper chloride) (which in HCl media is forming  $\text{CuCl}_4^{2-}$ ), according to the chemical equation:



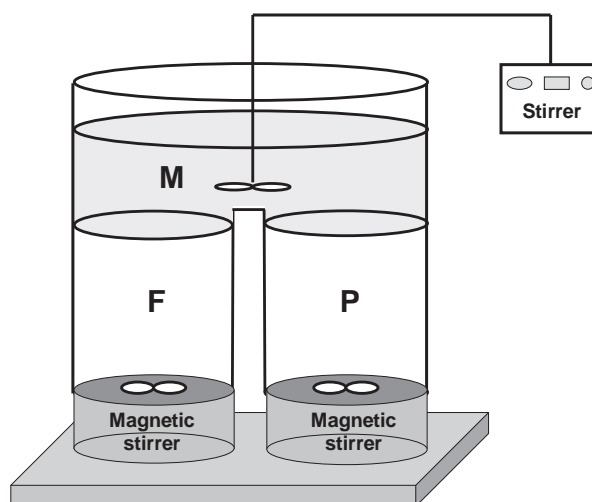
The complex formed ( $(\text{R}_3\text{NH}^+)_2\text{CuCl}_4^{2-}$ ) diffuses through the membrane to the membrane/product interface where, the  $\text{NH}_4\text{OH}$  present in the product phase, breaks up the complex, leading to the stripping of Cu (II) according to the chemical equation:



## EXPERIMENTAL

Transport experiments were performed in a stirred transfer Lewis type cell with the liquid membrane layered over the feed and product phases (Figure 2).

In the experiments involving carrier facilitated co-transport (TOA as carrier), a 0,025 M copper (II) chlo-



**Figure 2** Schematic representation of the experimental cell (F, feed phase; M, membrane phase; P, product phase)

ride solution in 0,5 M HCl was used as feed phase. The membrane phase comprised a 3 % solution of TOA in kerosene, while a 0,5 M aqueous  $\text{NH}_4\text{OH}$  solution was used as product phase. In the carrier facilitated counter-transport experiments (the rest of the carriers), 0,025 M copper (II) chloride solutions in formic acid/sodium formate buffer (pH 4,0), were used as feed phase. Three percent (3 %) solutions of each different carrier in kerosene were used as membrane phase and 1M solution of sulphuric acid was used as product phase.

The volumes of feed, membrane and product phases were 25 ml and the areas of the feed/ membrane and membrane/product interfaces were both 3,2 cm<sup>2</sup>. Three phases were stirred at 200 rpm and 25 °C for 12 hours.

At the end of the experiments, copper (II) ion concentrations in both feed and product phases were determined by atomic absorption spectrometry, using a Shimadzu AA-6200 instrument at a wavelength of 324,8 nm. The copper (II) concentration in the membrane phase was established from the material balance.

Feed/membrane and membrane/product interfaces fluxes were obtained by monitoring copper (II) concentrations in the feed and product phases as a function of time, based on the following equations [17]

$$J_{f/m} = -\frac{V}{A} \frac{dC_{ft}}{dt} \quad (1)$$

$$J_{m/p} = \frac{V}{A} \frac{dC_{pt}}{dt} \quad (2)$$

where  $C_{ft}$  and  $C_{pt}$  are copper (II) concentrations in the feed and product phases, respectively, at a time  $t$ ,  $C_{fo}$  is the initial concentration of copper (II) in the feed phase,  $V$  is the volume of feed, product and membrane phases and  $A$  is the area of the feed/membrane and membrane/product interfaces.

In the same way, the permeability through the feed/membrane and membrane/product interfaces was obtained, respectively, from the expressions [18]:

$$\ln \frac{C_{ft}}{C_{fo}} = -\frac{A}{V} P_{f/m} t \quad (3)$$

$$\ln \frac{C_{fo} - C_{pt}}{C_{fo}} = -\frac{A}{V} P_{m/p} t \quad (4)$$

The percentages of copper (II) removed from the feed phase (RmF) and copper (II) recovered in the product phase (RcP) were determined by the equations:

$$RmF = 100 \cdot \frac{C_{fo} - C_{ft}}{C_{fo}} \quad (5)$$

$$RcP = 100 \cdot \frac{C_{pt}}{C_{fo}} \quad (6)$$

Copper accumulated in the organic membrane phase (AcM) was calculated through a material balance.

## RESULTS AND DISCUSSION

The values of Cu (II) flux and permeability through both feed/membrane and membrane/product interfaces using the six different studied carriers are shown in Figure 3a, while Figure 3b shows percentages of copper (II) removed from the feed phase (RmF), recovered in the product phase (RcP) and accumulated in the membrane phase (AcM) for the same six carriers.

In all cases, flux and permeability through the feed/membrane interface was higher than that through the membrane/product interface, which led to some copper being accumulated in the membrane phase, due to the

higher percentage of copper removed from the feed phase than copper recovered in the product phase. The copper accumulated in the membrane phase was very similar for all the carriers used in the study, which means that similar flux and permeability differences, through the feed/membrane and the membrane/product interfaces, existed for all the studied carriers.

Figure 3 shows that the highest Cu (II) flux and permeability values, through both the feed/membrane and the membrane/product interfaces, were obtained in the carrier facilitated counter-transport of Cu (II) using benzoyl acetone as carrier. This led to the highest degree of Cu (II) removal from the feed phase and to the highest degree of Cu (II) recovery in the product phase, while the lowest Cu (II) accumulation percentage in the membrane phase was observed.

In contrast, the carrier facilitated co-transport of Cu (II) using tri-n-octylamine as carrier led to the lowest degree of Cu (II) transport, as can be seen from the lowest values of Cu (II) flux and permeability through both interfaces. This produced the lowest Cu (II) removal percentage from the feed phase and recovery in the product phase, while the highest value of Cu (II) accumulation in the membrane phase was observed. LIX 984N was the second best carrier for the removal of Cu (II) from the feed phase and its recovery in the product phase. It showed better transport parameters than CYANEX 272, DP8R and 8-hydroxy quinoline in that order.

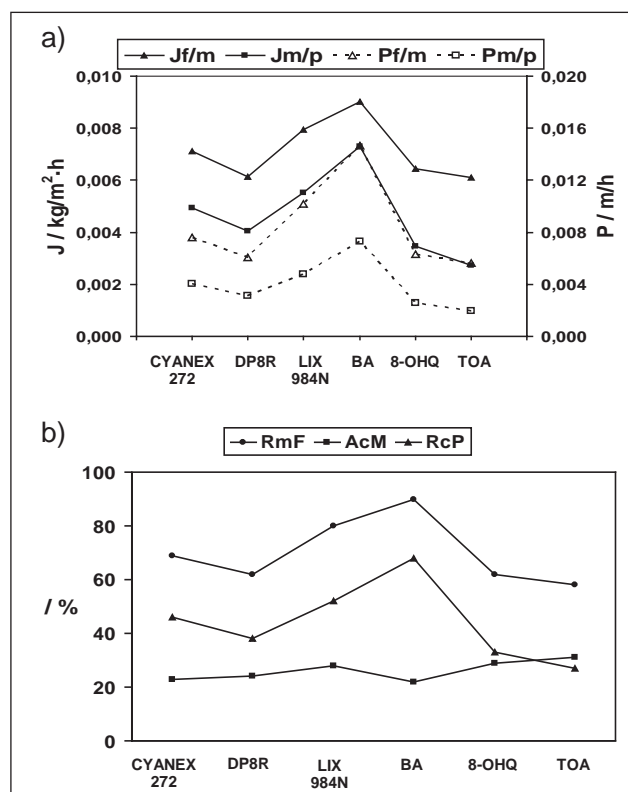
## CONCLUSIONS

The compared removal/recovery of copper(II) from aqueous solutions by bulk liquid membranes using six different carriers was studied in this paper. Fluxes and permeabilities through the feed/membrane interface were in all cases higher than those through the membrane/product interface, leading to higher copper removal from the feed phase than copper recovery in the product phase, and hence, to copper accumulation in the membrane phase.

The highest Cu (II) flux and permeability, through both interfaces, were obtained using benzoyl acetone (BA) as carrier, which led to the highest degree of Cu (II) removal from the feed phase (80 %), the highest level of Cu (II) recovery in the product phase (65 %) and the lowest degree of Cu (II) accumulation in membrane phase (19 %).

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**Figure 3** Values of studied parameters of copper (II) removal/recovery from aqueous solutions through bulk liquid membranes using different carriers

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**Note:** The responsible translator for English language is Mr. Philip Thomas (Thomas Language Services), Spain