

# COPPER SEPARATION FROM AQUEOUS EFFLUENTS BY LIQUID MEMBRANE PERTRACTION

**A. Onjia<sup>1</sup>, S. Stevanović<sup>1</sup>, Ya. I. Korenman<sup>2</sup>,  
Lj. Rajaković<sup>1</sup>, and M. Mitrović<sup>1</sup>**

<sup>1</sup>Faculty of Technology and Metallurgy, University of Belgrade,  
Karnegijeva 4, 11001 Belgrade, Yugoslavia

<sup>2</sup>Faculty of Ecology and Chemical Technology, State Technological academy  
of Voronezh, Prospect Revolution 19, 394000 Voronezh, Russia

## Abstract

In this paper the feasibility of applying liquid membrane pertraction to the copper recovery from aqueous effluents has been examined. A continuous laboratory-scale hollow fiber-in-fiber type membrane pertractor was constructed to solve a variety of problems encountered in the conventional solvent extraction equipment. Copper-ions present in the feed solution were transferred through an organic liquid containing 2-hydroxy-5-nonylacetophenone oxim in kerosene and concentrated in an acid solution on the strip side. The operational factors such as flow rates of the three liquid streams were considered. The overall mass transfer rate is greatly influenced by the resistances in the aqueous film boundary layer on the feed side, and by the rate of interfacial reaction taking place at organic-strip interface.

## Key words

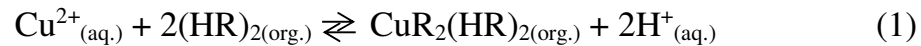
Membrane pertraction, copper, flux, flow rate, LIX 84, hollow fiber.

## 1. Introduction

In the past two decades, membrane science and technology has undergone a dramatic development. Especially, the possibility of chemical species separation and concentration in one device has attracted much attention. For this purpose, extensive research has led to the development of liquid membrane pertraction technique. Liquid pertraction combines the loading and stripping step of solvent extraction into a single unit operation, allowing the continuous removal and concentration of a given species. Various pertraction techniques were considered for copper separation: emulsion liquid membrane (ELM) [1-4], supported liquid membrane (SLM) [5-12], and some bulk liquid membrane (BLM) [13-18]. The objective of this work is to explore a new hollow fiber-in-fiber membrane configuration of a module for its capability of simultaneous removal and concentration of copper from simulated high strength waste water.

## 2. Transport mechanism

Transport of the copper ion through a three-phase system is accomplished by the formation of carrier-metal complex:



where HR denotes 2-hydroxy-5-nonylaceto-phenone oxim. By complexing with the extractant, the copper cation is able to enter the organic phase in which it is otherwise insoluble. Concentration gradients within the organic phase cause the Cu-HR complex to diffuse to the opposite side where it is decomposed and copper ion is released. The mechanism and concentration profiles for copper

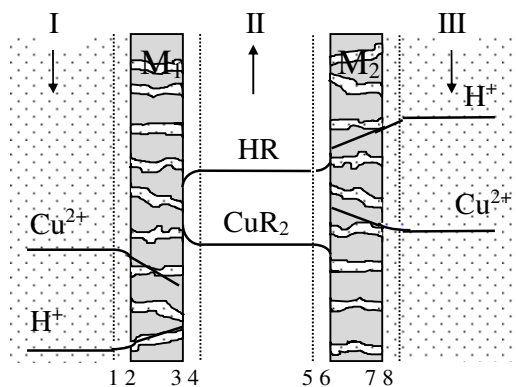


Fig. 1. Concentration profiles in a membrane pertractor

transport were shown in Fig. 1. According to this scheme copper ions are transported from aqueous feed through an organic into the aqueous strip phase by coupled-counter transport. Permeation rate is expected to be determined by extraction equilibrium constants, individual mass transfer resistances, and by chemical species concentrations. There are many papers dealing with the effects of the compositions of the three-phase system on permeation kinetics of copper [1-18]. In this paper, the attention will be paid on the effects of hydrodynamic conditions on permeation rate in a new configuration of hollow fiber module.

## 3. Experimental

Aqueous solutions of copper ions were prepared by dissolving copper sulfate pentahydrate salts in de-ionized water. The pH was adjusted by sulfuric acid or sodium hydroxide and the total sulfate concentration was adjusted by adding sodium sulfate:  $[\text{SO}_4^{2-}]_{\text{T}} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{CuSO}_4]$ . The organic solutions were prepared by dissolving LIX 84 (Henkel Co.) containing 2-hydroxy-5-nonylaceto-phenone oxim as a chelating agent in kerosene. Strip solution was prepared by dissolving sulfuric acid in de-ionized water. Prior to chemical analysis copper in the organic phase was stripped with 3 mol/dm<sup>3</sup> nitric acid. The copper concentration was determined by atomic absorption spectrophotometry (PYE Unicam SP 9) and pH was controlled by pH-meter (Iscra MA 5725). The permeation experiments were performed in a module with microporous hollow fibers in which each fiber is placed into one larger fiber. The aqueous feed and strip are fed separately (phase I and III) and co-currently.

An organic extracting solution (phase II) is fed counter-currently into the annular space.

#### 4. Results and discussion

In order to establish the effects of hydrodynamics on the copper ion transfer, the experiments were carried out at various volumetric flow rates of all three streams. Fig. 2. illustrate the copper fluxes vs. feed flow rate variation. It

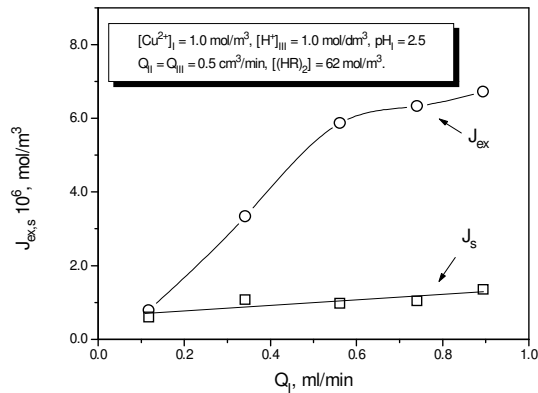


Fig. 2. The effect of feed flow rate on the copper fluxes through pertractor.

is obvious from Fig. 2. That in the extraction step mass transfer rate increase with increasing feed flow rates.  $J_{ex}$  do not increase indefinitely as the feed velocity is raised, but level up to limiting value. Since, this level corresponds to the maximum fluxes that can be achieved, a further increase in feed velocity will accomplish nothing other than to diminish the efficiency of the process. The flux of the stripping step,  $J_s$ , was affected only slightly. At the same time,

an increase in the feed velocity causes a rise in the copper concentration in the outlet of the stream, presumably due to less time for loading. It is desirable to

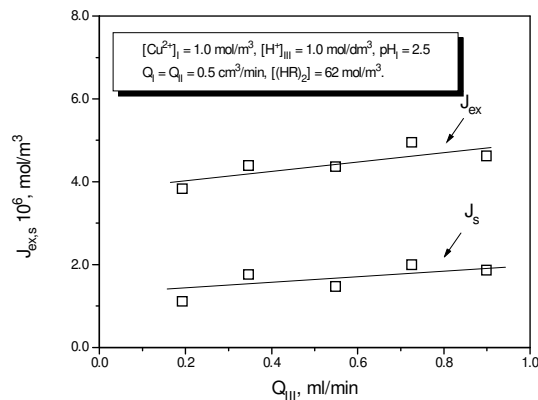


Fig. 3. The effect of strip flow rate on the copper fluxes through pertractor

use a larger membrane surface area at the organic-strip interface to reduce the effect of slow decomposition of copper-complex in stripping step on overall permeation rate. The effect of the strip velocity on the  $J_{ex,s}$  can be seen in Fig. 3. Over the experimental condition, the results show that both fluxes are almost independent on the strip velocity (Fig. 3.). It should be mentioned that the level of copper strip outlet concentration dramatically shrinks as the strip flow rate is raised,

because the residence time of this stream is decreasing. The residence time decreasing has a great influence at organic flow rate is growing. Furthermore, it diminishes the stripping efficiency. There is no strongly effect of organic

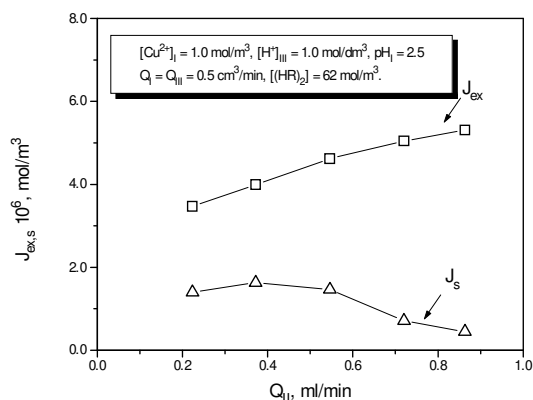


Fig. 4. The effect of organic flow rate on the copper fluxes through pertractor

velocity on  $J_{ex}$ , but  $J_s$  is abated by reducing the residence and loading time (Fig. 4.). It can be established that under the experimental conditions, the extraction flux is dependent on feed flow rate that means that film resistance is significant. However, at stripping interfacial reaction seems to be restricting step.

## 5. Conclusion

A liquid membrane pertraction process of copper recovery from aqueous solutions using a hollow fiber-in-fiber type membrane contactor and LIX 84 as carrier was studied. It was concluded that under the experimental conditions by changing the flow rates, mass transfer resistances in the extraction step could be diminished. However, the copper stripping rate depends primarily on copper complex decomposition rate. The overall mass transfer rate is greatly influenced by the resistances in the aqueous film boundary layer on the feed side, and by the rate of interfacial reaction taking place at organic-strip interface.

## References

- [1] W. Völkel, W. Halwaks, K. Schiügerl, *J. Membr. Sci.*, 6 (1980) 19.
- [2] N. N. Li, R. P. Cahn, D. Naden, R. W. Lai, *Hydrometallurgy*, 9 (1983) 277.
- [3] J. W. Frankelfield, R. P. Cahn, N. N. Lee, *Sep. Sci. Technol.*, 6 (1984) 385.
- [4] J. Draxler, R. J. Marr, *Chem. Ing. Process.*, 20 (1986) 319.
- [5] T. Kataoka, T. Nishiki, K. Ueyama, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1306.
- [6] M. Teramoto, H. Tanimoto, *Sep. Sci. Technol.*, 18 (1983) 871.
- [7] I. Komasaawa, T. Otake, T. Yamashita, *Ind. Eng. Chem. Fundam.*, 22 (1983) 127.
- [8] P. R. Danesi, *Sep. Sci. Technol.*, 19 (1984-5) 857.
- [9] K. Takahashi, H. Takeuchi, *J. Chem. Eng. Jpn.*, 18 (1985) 205.
- [10] P. A. O'Hara, M. P. Bohrer, *J. Membr. Sci.*, 44 (1989) 273.
- [11] A. B. deHaan, P. V. Bartels, J. deGraaw, *J. Membr. Sci.*, 45 (1989) 281.
- [12] J. Yi, L. L. Tavlarides, *AIChE J.*, 38 (1992) 1957.
- [13] L. Boyadzhiev, Z. Lazarova, *Chem. Eng. Sci.*, 42 (1987) 1131.
- [14] Y. Sato, K. Kondo, F. Nakashio, *J. Chem. Eng. Jpn.*, 23 (1990) 23.
- [15] L. Boyadzhiev, Z. Lazarova, T. Sapundzhiev, *Sep. Sci. Technol.*, 27 (1992) 493.
- [16] A. K. Guha, C. H. Yun, R. Basu, K. K. Sirkar, *AIChE J.*, 40 (1994) 1223.
- [17] L. Boyadzhiev, S. Alexandrova, *Hydrometallurgy*, 35 (1994) 109.
- [18] A. Onjia, S. Simonović, S. Stevanović, M. Mitrović, *Tehnika (RGM)*, 6 (1995) 11.