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Short communication

Application of hollow-fiber supported liquid membranes technique to the selective recovery of a low content of copper from a Chilean mine water

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Abstract

This communication describes the application of a hollow-fiber-type solid supported liquid membrane technique to the selective recovery and enrichment of copper from a Chilean mine water. The membrane extractor works by impregnating the porous structure of solid support with an organic film containing a selective salicylaldoximic extractant. Using a relatively low concentration of carrier extractant, a high degree of copper recovery was performed by the liquid membrane technique. The stripping flux of copper from membrane to receiving strip liquor was greatly influenced by the oximic carrier concentration and slightly by the sulfuric acid concentration utilized as stripping agent. No traces of all contaminant ions were detected in the resulting copper strip product solution. These results show the feasibility of separation and enrichment of copper using this liquid membrane technique. A bigger recovery of metal could be attained using a pilot-scale extractor whose design is the subject of current further work. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid membranes; Fiber membranes; Microporous and porous membranes; Copper; Solvent extraction

1. Introduction

In Chile, the biggest producer of copper in the world, mining will continue to be, by far, its most important economical activity. Although the grade of many ores has decreased dramatically in past years, which has increased its extraction and beneficiation costs, it is also remarkable for the introduction of new and more efficient technologies what have enabled an integral profit of their metal content.

Among these technological advances, special considerations have taken the development of solvent extraction in the hydrometallurgical copper recovery process from leach solutions, and whose final recovery of metal considers as alternatives electrowinning or copper sulfate crystallization steps.

The conventional solvent extraction (henceforth abbreviated as SX) is an effective method for separation of metal ions from aqueous solutions which is based in the right choice of a highly selective extractant molecule for desired metal. This technology is very attractive when rather dilute solutions are involved, since the treating ratio between the stripping

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phase and the feed phase can be very low, being possible to accomplish the metal concentration operation [1].

However, the current SX process in mixer–settlers present serious limitations, among them, huge inventories of expensive solvent, bigger reactor size, crud formation at interphase and phase entrainment difficulties [2]. Moreover, a great majority of natural mining waters or leach residual solutions contain less than 1.0 g/l Cu(II) being considered as very dilute solutions unsuited to be treated by conventional SX processes.

However, a novel membrane-based solvent extraction process was recently shown to be an effective alternative to current SX technology. Particularly, a liquid membrane process has sufficient ability of separating selectively metallic ions from aqueous solutions using a hollow fiber as solid support and a reduced quantity of organic solvent in a continuous process with higher extraction extent [3,4].

In recent years very substantial progress in the recovery of metals by solid supported liquid membranes have been made by many investigators [5–9].

We have reported results of extraction and stripping kinetics of copper with different extractants in a hollow-fiber membrane extractor from laboratory-prepared solutions and from natural mining waters. We found that the flux of metal and extraction extent are highly dependent on the carrier concentration in liquid membrane and moderately by acidity of feed phase. The permeability of the liquid membrane to copper was very much higher than the transport observed for other contaminant ions [10,11].

The steady-state experimental results have been explained by a heterogeneous interfacial adsorption of extractant at interface of both phases [12,13]. The effects of interfacial reaction and diffusional mass transfer of carrier and metal complex on the rate of extraction and stripping have been studied. The simulation diffusion model with interfacial reaction proposed in those works explained satisfactorily the experimentally observed data [14].

This communication describes a process of recovery and enrichment of Cu(II) from a Chilean mine water using a liquid membrane extractor which employs hollow fibers as solid support. The feed solution used in these experiments is the reject from the conventional SX plant in El Teniente Division of Copper Corporation of Chile (CODELCO), due to its low content of copper, which is economically inapplicable for the SX process.

The hollow-fibers-type solid supported liquid membrane extractor works by impregnating the pore structure of solid support with an organic solvent containing a selective salicylaldoximic extractant for copper(II).

The usefulness of this membrane-based SX process was confirmed by the improved efficiency to metal enrichment with a significant economy of solvent. Further experiments are being carried out in these days, which we shall hope to report extensively soon.

2. Experimental

The organic solution was prepared by dissolving 5-dodecylsalicylaldoxime (LIX-860) in Kermac 500-T (Triangle Refineries), an industrial diluent whose composition averages 91% of aliphatics compounds and 9% of aromatics. The salicylaldoximic extractant was used without further purification from the standpoint of industrial application, as the organic carrier of the liquid membrane. No phase modifier reagent was utilized during the extraction tests.

As feed cupric ion-donor solution was used a mine water of El Teniente Mine of Codelco-Chile which corresponds to a natural solution produced due to the chemical lixiviation and bioleaching processes by rainfall and snowsmelting of copper ores of that mineral deposit located at Andes Mountain. It is an acid solution whose pH averages 2.8–3.2 with a density of 1.05 g/ml at 20°C. Normally this solution contains around 0.8–1.4 g/l Cu(II), being fed to the mixer–settler SX plant, but when its metal concentration is lower than 1.0 g/l, it is discarded. The initial content of metals in the solution used in this work were 1.00 g/l Cu(II), 0.5 g/l Fe, 0.3 g/l Al(III) and minor quantities of As, Mo and other metals.

Concentrated sulfuric acid solutions were used as metal-acceptor stripping agents. All other chemicals were of analytical grade.

The hollow-fibers membrane module was formed by microporous polytetra-fluoroethylene fibers, kindly supplied by Japan Gore Tex, inserted in a glass shell. The characteristics of extractor were described in previous paper [15]. The inner and outer diameter of the fibers used were 0.80 and 1.80 mm, respectively. Effective length of the fiber: being 0.20 m; the maximum membrane pore size: 2.0 µm; porosity factor: 0.60. The inner diameter of the extractor glass tube: 10.0 mm.

Using a Masterflex microtube pump, the organic solution was circulated through the fibers. Because of the hydrophobic character of fibers, the porous structure of the membrane are filled rapidly with the solvent containing "carrier" extractant. After impregnation of fibers, the feed solution and acid strip aqueous phase were fed countercurrently along the outer and inner sides of the hollow fibers, respectively, during 2–3 h. The volumetric flow rates of feed and stripping aqueous solutions were 0.58×10^{-7} and 3.1×10^{-7} m^3/s, respectively. A variable number of fibers were inserted inside the glass shell of extractor during the experiments.

At the steady state, the concentrations of metals in effluent solutions were measured by atomic absorption spectrophotometry in a GBC-902 apparatus and by capillary ion analysis in a CIA-Waters Millipore equipment.

3. Results and discussion

As have been described in the previous papers [10,11] the mechanism of copper extraction in a membrane extractor using hollow fiber as solid support with salicylaldoximic-type extractants proceeds by diffusion of copper ions from bulk feed solution towards the outer wall of fiber, the phase boundary. As the pore structure of fiber is completely impregnated with the protonated carrier of solvent, the following reaction occurs:

$$Cu^{2+}_{(aq)} + 2HR_{(org)} = CuR_{2(org)} + 2H^{+}_{(aq)}, \qquad (1)$$

where HR is the acidic extractant, CuR_2 the metal complex extracted into the organic phase. The subscripts "aq" and "org" denote aqueous and organic solutions adjacent to the interface.

The extractant, which is now loaded with copper ions, then diffuses through the liquid membrane to the inner wall of fiber where the stripping reaction takes places with the carrier regenerated and copper ions collected in the strip liquor. Fig. 1 shows the scheme of metal permeation process into the solid supported liquid membrane.

Figs. 2 and 3 show the results of copper extraction obtained in an experiment performed under a recycling mode, allowing the feed and the strip liquor to flow continuously through the extractor, in order to measure the metal extraction extent. In Fig. 2 it is clearly observed that the decrease of copper content in raffinates depends on the concentration of carrier extractant in the organic solvent.

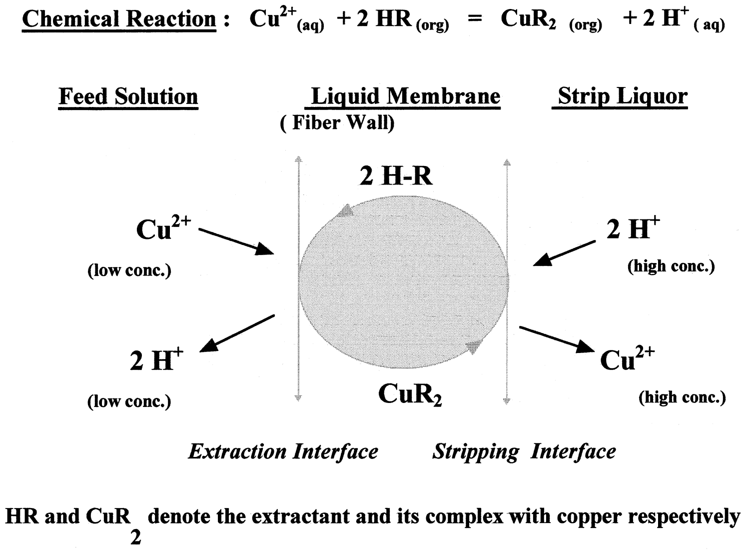

Fig. 1. Schematic representation of copper transport through hollow fiber membrane.

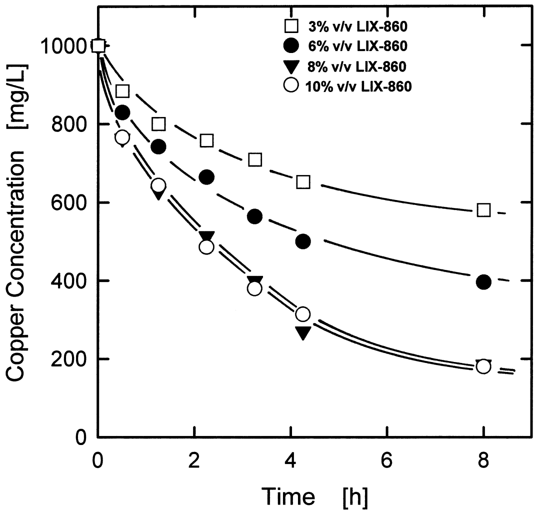

Fig. 2. Change of copper concentration at raffinates with time. Feed solution 1000 mg/l Cu(II), pH=2.8, volume 0.050 l, Q_{feed}: 0.58×10^{-7} m^3/s. Stripping solution 300 g/l H_2SO_4, volume 0.035 l, $Q_{\mathrm{Strip\ Liquor}}$ 3.10×10^{-7} m^3/s.

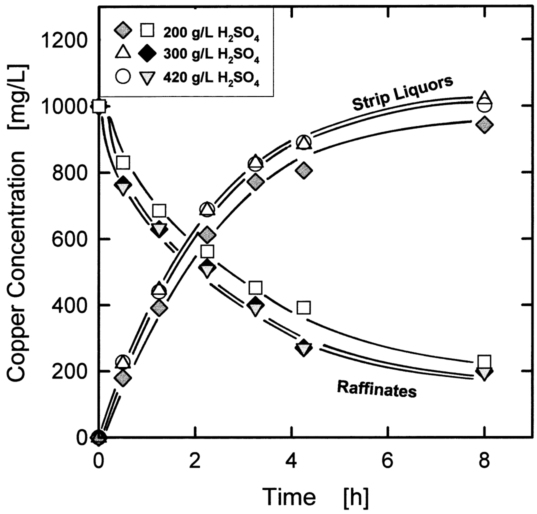

Fig. 4. The effect of sulfuric acid concentration in stripping solution on copper transport from feed to strip liquors. Feed solution 1000 mg/l Cu(II), pH=2.8, volume 0.050 l, Q_{feed} 0.58×10^{-7} m^3/s. Organic solvent 8% (v/v) LIX-860 in Kermac 500-T.

Fig. 3 shows the relation between the degree of metal transported to the strip liquor and the time of extraction, in the same experiments described in Fig. 2. In this experiment was used an extractor with six fibers inside, being circulated in a recycling mode samples of mine water and of sulfuric acid solution as feed solution and strip liquor, respectively, in order to check the feasibility to concentrate the metal. The pH of feed solution was continuously adjusted to a suitable value for metal recovery. The transport and concentration of copper ions from feed donor solution towards strip liquor is remarkable. However, a higher degree of copper recovery can be achieved, working in a continuous once-through mode, if a thinner membrane were used or if the total area of membrane were enhanced.

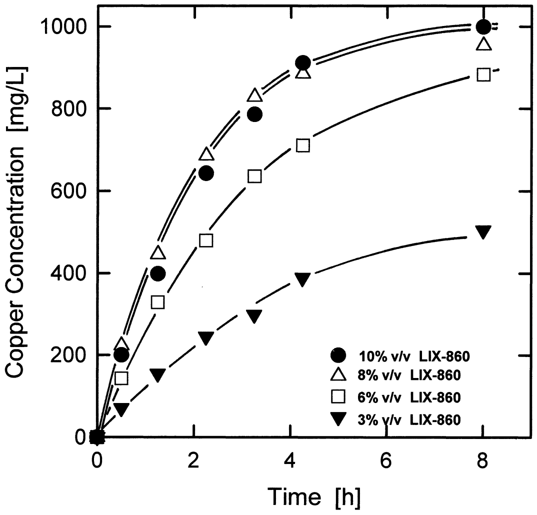

Fig. 3. Copper enrichment of strip liquor with time. Feed solution 1000 mg/l Cu(II), pH=2.8, volume 0.050 l, Q_{feed} 0.58×10^{-7} m^3/s. Stripping solution 300 g/l H_2SO_4, volume 0.035 l, $Q_{\mathrm{Strip\ Liquor}}$ 3.10×10^{-7} m^3/s.

In Fig. 4 is shown the effect of content of sulfuric acid in stripping solution on metal transport. It is appreciated that in the reviewed range there was only a slight negative effect for concentrations of acid below 300 g/l. The stability of membrane and the degradation of extractant were not affected during all the experiments, even when a maximum content of sulfuric acid (420 g/l) was utilized for preparing the stripping solution. Any reduction in metal flux was not observed either. However, it is not possible to raise over 450 g/l the acid concentration because a slow but continuous degradation of the oximic compound occurs with time in such excessive acid medium.

These results are much better than others obtained using a former extractor system made of two coupled modules (one for extraction and one for stripping) which works by recycling a big inventory of organic solvent between reactors. This extraction system which works by impregnating with the organic solution the pores of the solid support showed an improved efficiency to copper recovery saving a significant amount of solvent [15]. It could not be possible to improve the stripping stage results in the two coupled modules–extractor system. Probably, a much bigger membrane area in the back-extraction step compared to the extraction step is required.

In a further report we shall inform in detail a complete quantitative analysis of the results observed in this study in order to elucidate the mechanism of copper transport in this type of extractor. Such mathematical treatment of data uses a numerical method based on differential equations that describe the metal concentration drop along the fiber tube for certain boundary conditions. Extraction and back-extraction chemical equilibria-type considerations as well as eventual limitations to the extraction reaction rate necessarily must be taken into account to explain the overall transport of copper ions.

A minimum of solvent inventory was required in these experiments, just the necessary amount to impregnate the pore structure of fibers, because carrier is continuously regenerated since with a liquid membrane, extraction and stripping of metal occur on opposite sides of the membrane simultaneously.

In all the experiments, the feed and the stripping solutions were pumped at 0.58×10^{-7} and 3.1×10^{-7} m^3/s, respectively. These hydrodynamics conditions were chosen for the sake of maintenance of similar pressures at both sides of membrane in order to retain the organic solvent in the solid structure of membrane. Clean effluents of both aqueous phases were obtained during all the runs, free of entrainment of organic solution.

The polytetrafluoro-ethylene membrane employed in this study was found to be suitable as solid support material. Flux of metal values of 1×10^{-8} mol/s cm^2 normally obtained in these experiments could be enhanced if a thinner film as membrane wall were used.

No traces of Fe, Al, Mo and As were found in the resulting copper strip product solution. This fact indicates that these metals were not co-transported to strip liquor, which confirms that the selectivity of liquid membrane depends on the right choice of carrier for desired metal, like in a conventional SX process.

The results of this work demonstrate that liquid membrane process is a valuable alternative to current SX process for metal recovery from dilute solutions. A hollow-fiber supported liquid membrane has shown to enhance the performance of liquid–liquid separation by combining the extraction and stripping process in one step, just a small quantity of extractant to be used in the organic film being required.

The aim of this study was focused on the feasibility of selective copper recovery from a real mine water by solid supported liquid membrane. The next stage of this research is pointed out on the design of a pilot-scale extractor which shall be built up for treatment of substantial bigger flow of copper-containing mine water solution.

4. Conclusions

Using a salicylaldoximic extractant (LIX-860) as a carrier, the recovery and enrichment of Cu(II) from a real mine water was investigated using a hollow-fiber-type solid supported liquid membrane extractor.

A remarkable transport and concentration of copper ions from feed donor solution toward strip liquor was found. As was observed in a previous study, the transport of metal from feed solution to membrane is influenced by the extractant content at organic film. Furthermore, the stripping flux of copper from membrane to receiving phase depends slightly on concentration of sulfuric acid in back-extraction solution. The carrier presented a high affinity for Cu(II). Copper ions permeated selectively into the strip receiving phase against the concentration gradient. No co-extraction of all contaminant ions was observed.

The experimental results communicated in advance in this report show the feasibility of separation and enrichment of metals in an extractor using impregnated hollow-fibers-type liquid membranes.

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