

## **Copper recovery from ammoniacal media using hollow fibre contactors**

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### **Abstract**

This work aims to study the recovery of copper from ammoniacal aqueous solutions using hydrophobic propylene membrane contactors. The hydroxyoxime LIX 84-I and the  $\beta$ -diketone LIX 54 (both from Cognis) were used as extractants. The results obtained showed that practically all the copper content was removed from the ammoniacal feed solutions. The recovery of copper reached nearly 100% in several extraction-stripping experiments. The results were compared with the ones obtained by applying the emulsion liquid membranes (ELM) technique.

Keywords: copper extraction, LIX 54, LIX 84-I, hollow fibre, waste treatment

### **1. Introduction**

The ammoniacal leaching is an attractive approach to process concentrates, wastes, and by-products containing copper since this metal ion is easily solubilised through the formation of ammine complexes (Nathsarma and Sarma, 1993). For instance, the manufacture of printed circuit boards (PCB) involves an ammoniacal leaching step for removing the unmasked copper that covers the nonconductive board. The concentration of copper in a typical spent etching solution can attain a value as high as  $150\text{-}160\text{ kg m}^{-3}$  (Schwab and Kehl, 1997; Kyuchoukov et al., 1998; Yang et al., 2006). Besides this effluent, PCB industry also produces a more diluted copper (up to  $1\text{ kg m}^{-3}$ ) effluent as a result of rinse waters. Copper present in such leach solutions must be recovered due to economical and environmental reasons. It is worth mentioning that the environmental legislation imposes that copper content in the effluents to be discharged into soil or surface water must be reduced to values lower than 5 ppm.

The removal of copper from aqueous solutions can be carried out by solvent extraction. The recovery of copper from leach liquors by solvent extraction is already

a well-implemented process in several industrial plants (Cox, 1992; Sole, 2002). The extractants used in such processes are mainly hydroxyoximes (LIX 84, ACORGA M-5640) and  $\beta$ -diketones (LIX 54). Several relevant studies concerning the extraction of copper from ammoniacal solutions have been published in the literature (Szymanowski, 1993; Schwab and Kehl, 1997; Kyuchoukov et al., 1998; Hu and Wiencek, 2000; Yang et al., 2006). For instance, Schwab and Kehl (1997) described an integrated extraction-stripping process that allowed reducing the concentration of copper in an ammoniacal etching solution from 130-160 kg m<sup>-3</sup> to 20-30 g m<sup>-3</sup> using LIX 84 as extractant. These authors also referred the use of LIX 54 to reduce the copper content of the etchant in 30%. On the other hand, when the initial concentration of copper in leach solution is as low as 1 kg m<sup>-3</sup>, the recovery of copper drastically decreases and a large inventory of solvent is needed (Readett et al., 2003). This drawback can be overcome by using liquid membranes, such as non-dispersive solvent extraction (NDSX) using hollow fibres as contactors and emulsion liquid membranes (ELM).

NDSX using hollow fibres is simply liquid-liquid extraction in which aqueous and organic streams flow through the lumen and shell side of the fibres and come into contact at the pore mouth. One of the two phases wets the microporous fibre (membrane) and a slight overpressure should be applied to the other phase to stabilise the interface and to avoid the mixing of fluids. The hollow fibre contactors present several advantages such as a very large contact area without dispersion of phases, the capability of treating a large amount of dilute solutions, and the reduction in equipment volume and space (Juang and Huang, 2000). Such membrane-based dispersion-free extraction has been developed to avoid many of the problems associated with conventional liquid-liquid extraction including solvent losses, emulsion formation, phase separation, and the shortcomings due to flooding and loading in conventional contactors (e.g. columns and mixer-settlers).

ELM is a liquid membrane based process, where a primary emulsion is dispersed in the feed phase to be treated. During the contact between feed phase and emulsion, the solute is transported through the membrane into the internal phase droplets of stripping phase. After permeation, the emulsion is separated from the continuous phase and the splitting of the emulsion is usually performed by applying high voltage. ELM also exhibits a high interfacial area of mass transfer and the kinetics of stripping is particularly favoured due to the small size of the internal droplets of receiving phase. However, there are some deleterious phenomena such as the break-up of the emulsion and water transport, which decrease the efficiency of the process and their occurrence should be therefore minimised.

NDSX using membrane contactors and ELM have demonstrated a great potential in a wide variety of applications involving recovery and/or removal of many species from aqueous solutions. Concerning the extraction of copper from aqueous solutions, most of the studies have been focused on the treatment of acidic feed solutions (Valenzuela et al., 1999, 2005; Lin and Juang, 2001; Sengupta et al., 2006). Recently, Yang and Kocherginsky (2006, 2007) developed a hollow fibre supported liquid membrane system for recovering copper from spent ammoniacal etching solutions. In a previous

work (Gameiro et al., 2007a), the authors reported the extraction of copper from ammoniacal solutions by ELM using LIX 54 as carrier. Nevertheless, there is still a lack in the literature regarding the recovery of copper from ammoniacal media by using an integrated extraction-stripping process in two hollow fibres modules.

The aim of the present work was thus to study the recovery of copper from ammoniacal media by NDSX using hollow fibres. The  $\beta$ -diketone LIX 54 and the hydroxyoxime LIX 84-I were used as extractants in examining the extraction of copper. Simultaneous extraction and stripping experiments were carried out to check the possibility of solute concentration with high recovery. The results were then compared with the ones obtained by applying the ELM technique.

## **2. Experimental**

### *2.1. Reagents*

The organic phase consisted of an aliphatic diluent (Shellsol T, Shell Chemical Ltd.) and an extractant, the  $\beta$ -diketone LIX 54 or the ketoxime LIX 84-I. Both extractant reagents were kindly supplied by Cognis (Ireland). The concentration of extractant in the organic phase was in the range of 0.03-0.1 kmol m<sup>-3</sup>. In the ELM experiments, a non-ionic surfactant (polyamine ECA 4360J, Essochem Europe Inc.) was used to stabilise the emulsion. The organic reagents were used without further purification. The prepared organic solutions were washed with deionised water to remove the soluble impurities.

The aqueous feed phase was a 0.2 kmol m<sup>-3</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.32 kmol m<sup>-3</sup> NH<sub>3</sub> and 4.72×10<sup>-3</sup> kmol m<sup>-3</sup> CuSO<sub>4</sub> solution. The stripping phase was a 150-200 kg m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution. Analytical grade reagents were used to prepare the aqueous solutions.

### *2.2. NDSX experiments*

Non-dispersive solvent extraction (NDSX) was carried out using Liqui-Cel<sup>®</sup> Extra-Flow 2.5"×8" membrane contactors (Celgard, USA). Figure 1 shows a membrane contactor with flow of the aqueous phase through the lumens (tube side) of the hollow fibres and flow of the organic phase through the shell side of the fibres, as in the actual work. The overpressure on the tube side was in the range of 50-100 kPa to stabilise the interface in the pores and to prevent any leakage of the membrane phase. The characteristics of the modules are presented in Table 1.

The experimental apparatus is shown in Figure 2. The equipment consists of two membrane contactors (HF1 and HF2), three gear pumps (P1-P3) (DDS.38, Tuthill), three flow meters (F1-F3), six pressure gauges (PG1-PG6) and valves. The apparatus allows carrying out single experiments of extraction using HF1 or single experiments of stripping using HF2 and simultaneous extraction and stripping using HF1 and HF2.

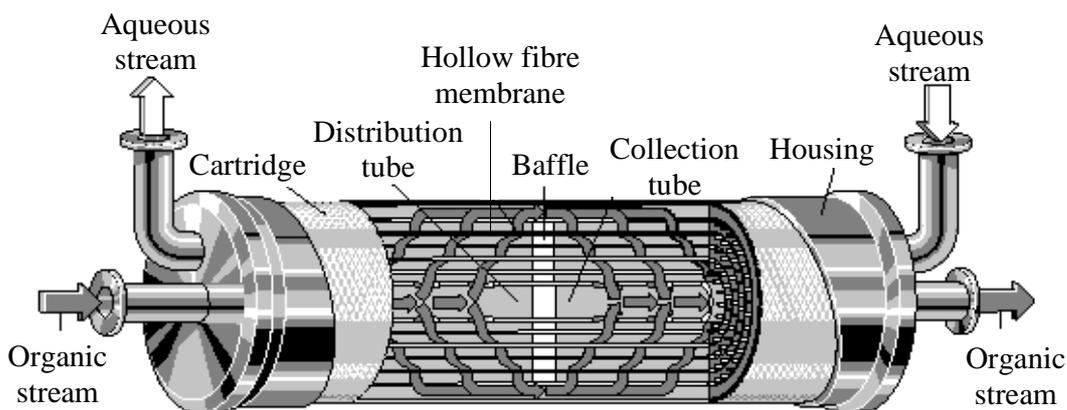


Figure 1: A Liqui-Cel® Extra-Flow membrane contactor with flow of the aqueous phase through the lumens (tube side) of the hollow fibres.

Table 1: Characteristics of hollow fibre modules

Type of module	G501 (contactor)
Module length (cm)	28
Module diameter (cm)	7.7
Case inner diameter (cm)	5.55
Centre tube diameter (cm)	2.22
Number of fibres	~10800
Fibre	X50 – polypropylene
Effective fibre length (m)	15.6
Inner diameter of the fibres ( $\mu\text{m}$ )	214
Outer diameter of the fibres ( $\mu\text{m}$ )	300
Pore size ( $\mu\text{m}$ )	0.03
Porosity (%)	40
Inner interfacial area ( $\text{m}^2$ )	1.13
Outer interfacial area ( $\text{m}^2$ )	1.58
Area per unit volume ( $\text{cm}^2/\text{cm}^3$ )	28

### 2.2.1. Single extraction experiments

To start the process, the organic phase was pumped directly to the hollow fibres module HF1 to fill the shell side of the contactor. Valves V11 and V13 were opened in the organic phase circuit of the apparatus setup, whereas valves V12 and V14 were closed. Next, the flow of the organic phase was stopped and deionised water was pumped through fibres tubes upstream (valves V6 and V7 were opened) to remove the organic phase from the tube side. After a few minutes (usually 2-3 L of water until the presence of organic phase was not observed), valves V6 and V7 were closed and

the actual feed phase was introduced into the respective reservoir. Valves V1 and V5 were opened and water was pushed out from the module HF1 and removed from the system. The feed phase started to be recycled after a volume of 0.5 L was expelled. The organic phase started to flow and the extraction process began. Samples (0.5-2 mL) of the aqueous phase were taken at appropriate intervals for measuring copper content. All the tests were carried out at 298 K.

### 2.2.2. Simultaneous extraction and stripping

The membrane phase was pumped through the hollow fibres to fill the shell side of the contactors HF1 and HF2 (valves V11, V12 and V14 were opened). Next, the flow of the organic phase was stopped and deionised water was pumped through fibres tubes (valves V6, V7, V9 and V10 were opened) to remove the organic phase from the tube side of the modules HF1 and HF2. Valves V6, V7, V9 and V10 were then closed and the actual feed and stripping phases were introduced into the respective reservoirs. Valves V3 and V8 were opened and water was pushed out from the module HF2 and removed from the system. The stripping phase started to be recycled after a volume of 0.5 L was expelled. Valves V1 and V5 were then opened and the feed phase was pumped through the tubes of the module HF1 as was already described. The organic phase started to flow and the extraction-stripping process began. Samples of the feed phase and stripping phase were taken at appropriate intervals for measuring the concentration of copper.

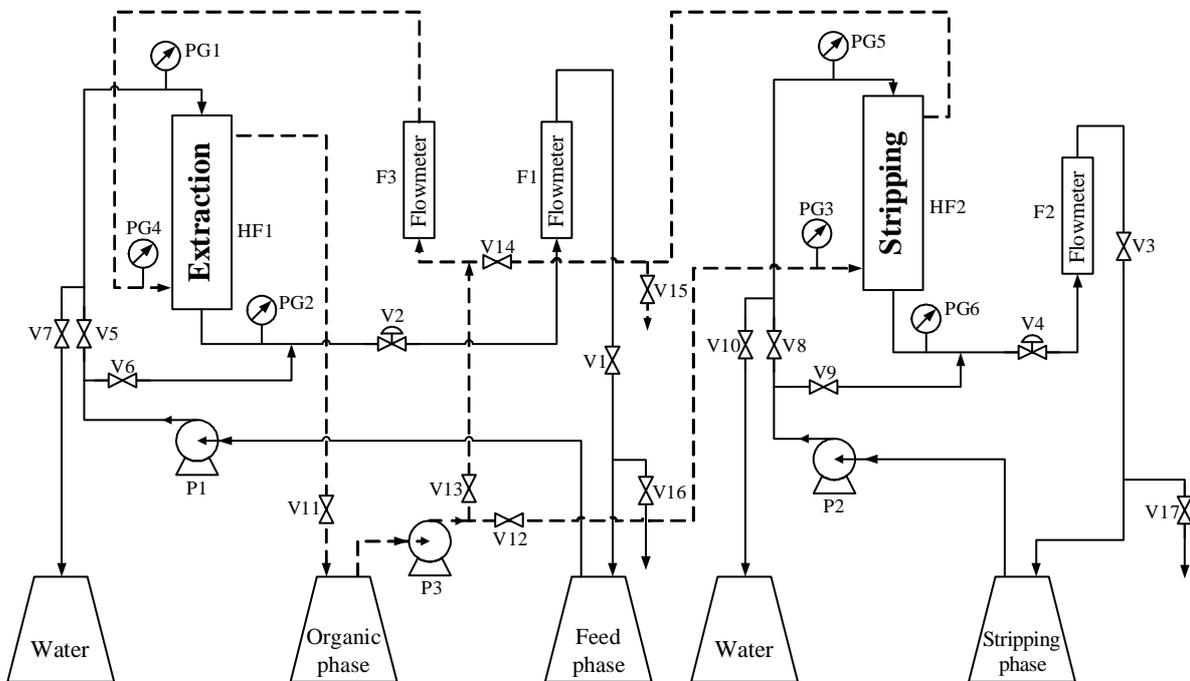


Figure 2: Schematic diagram of extraction-stripping apparatus.

### 2.3. ELM experiments

The emulsion was prepared by mixing the stripping aqueous solution with the organic membrane phase using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50) at 7000 rpm during 1200 s. The organic phase contained 2 wt.% of surfactant and  $0.06 \text{ kmol m}^{-3}$  of carrier. A predetermined volume ratio of 2:1 was maintained for organic phase to the internal stripping phase. The emulsion was dispersed in the external aqueous phase in a baffled glass reactor with 84 mm internal diameter and 20 cm height, immersed in a water bath with temperature control. The three-phase dispersion (1 L) was stirred at 298 K for 240 s with a stainless steel paddle (45×45×1 mm) at 300 rpm. During permeation, samples and photographs for drop size measuring were periodically taken. After permeation the phases were settled and the emulsion was broken in a coaxial electrocoalescer. Other details of the procedure of the ELM experiments are published elsewhere (Gameiro et al., 2007a).

### 2.4. Analyses

The concentration of copper, in both the feed and stripping phases, was measured with an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 200) at 324.75 nm.

## 3. Results and Discussion

### 3.1. Extraction using one hollow fibres module

Experiments were performed to assess the influence of the flow rates of both phases on the kinetics of copper extraction. The overall mass transfer coefficient was evaluated from the experimental data by solving the appropriate mass balance equations for the aqueous and organic phases. The mass balances for a steady state inside the tubes of the module fibres (aqueous phase) and on the shell side (organic phase) were used. The concentrations at the module inlet were obtained from the material balances applied to both reservoirs (Gameiro et al., 2007b). The equations were solved by using the simulation process software gPROMS<sup>®</sup> (Process Systems Enterprise Ltd., UK). It is worth mentioning that the extraction equilibrium of copper in ammoniacal medium with LIX 84-I was checked and only vestiges of copper were detected in the raffinates under the operating conditions studied. The solute concentration in the aqueous phase in equilibrium with the solute concentration in the organic phase was therefore neglected in the calculation of mass transfer coefficient.

Figure 3 shows the extraction rate of copper with LIX 84-I when the flow rates of phases varied in the range of 140-720  $\text{mL min}^{-1}$ . As observed, the increase in the aqueous flow rate from 140 to 300  $\text{mL min}^{-1}$ , while keeping constant the organic flow rate at 320  $\text{mL min}^{-1}$ , slightly increased the extraction rate of copper. Further augment in the aqueous flow rate had no significant influence on the kinetics of extraction. When the organic flow rate varied under the same range of values and the aqueous

flow rate was kept at  $300 \text{ mL min}^{-1}$ , the extraction rate was also practically constant. Similar effect of the flow rates on the kinetics was obtained using the  $\beta$ -diketone LIX 54 as copper extractant.

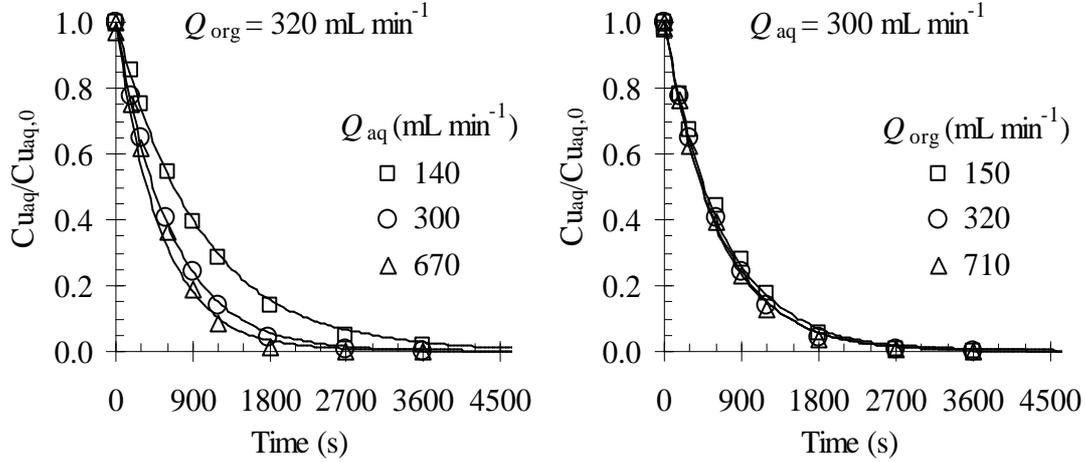


Figure 3: Influence of aqueous and organic flow rates on copper extraction kinetics with LIX 84-I ( $0.06 \text{ kmol m}^{-3}$ ). Initial aqueous phase:  $4.72 \times 10^{-3} \text{ kmol m}^{-3}$  of Cu ( $0.3 \text{ kg m}^{-3}$ ); pH 9.53.  $V_{\text{aq}}=2 \text{ L}$ ;  $V_{\text{org}}=0.9 \text{ L}$ . Solid lines represent calculated profiles ( $K_{\text{aq}}=4.0\text{-}4.4 \times 10^{-6} \text{ m s}^{-1}$ ).

Mass transfer in a hollow fibre contactor can be described using a conventional resistance in series model. Thus, the overall coefficient of mass transfer was also evaluated from this approach in order to make the comparison with the experimental values. Assuming that the chemical reaction between copper and extractant is fast and reaches equilibrium at the interface, the overall mass transfer coefficient based on the aqueous phase in the tube side ( $K_{\text{aq}}$ ) is related to the individual mass transfer resistances as follows:

$$\frac{1}{K_{\text{aq}}} = \frac{1}{k_t} + \frac{d_i}{mk_m d_{\text{lm}}} + \frac{d_i}{mk_s d_o} \quad (1)$$

where  $k_t$ ,  $k_m$  and  $k_s$  are the local mass transfer coefficients for the boundary layer resistance in the tube side, diffusion through the pores and boundary layer in the shell side.  $d_i$  and  $d_o$  are, respectively, the inner and the outer diameter of fibres, and  $d_{\text{lm}}$  is the logarithmic mean of diameters. Since the distribution ratio  $m$  is very large, the second and third terms of Eq. (1) can be neglected and the overall resistance to mass transfer is given as follows:

$$\frac{1}{K_{\text{aq}}} = \frac{1}{k_t} \quad (2)$$

The mass transfer coefficient in the aqueous phase flowing in the tube side was obtained from the L ev eque equation (Gabelman and Hwang, 1999):

$$Sh = 1.62 Gz^{1/3} \quad (3)$$

The Sherwood number  $Sh$  and the Graetz number  $Gz$  can be obtained from the following equations:

$$Sh = \frac{k_t d_i}{D_{Cu}} \quad (4) \quad Gz = \frac{d_i^2 v_t}{LD_{Cu}} \quad (5)$$

where  $D_{Cu}$  is the diffusivity of copper in the aqueous phase,  $v_t$  the flow velocity in the fibres and  $L$  the length of fibres. The diffusivity of solute in the aqueous phase was estimated to be  $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (Gameiro et al., 2007a).

Table 2 presents the theoretical values of the overall mass transfer coefficient calculated by Eq. (2) and the values obtained from the available experimental data. As listed, the latter values are rather lower than the former ones, mainly in the case of lower concentration of extractant. Therefore the difference between the values predicted by the conventional resistance in series model and the experimental values should be due to the additional contribution of resistance of chemical reaction to the overall resistance to mass transfer. In this case the overall mass transfer coefficient or the overall mass transfer resistance  $R_{aq}$  based on the aqueous phase is given as:

$$\frac{1}{K_{aq}} = \frac{1}{k_t} + \frac{1}{k_r} \quad (6) \quad R_{aq} = R_t + R_r \quad (7)$$

where  $k_r$  is the additional mass transfer coefficient for chemical reaction and  $R_t$  and  $R_r$  are, respectively, the mass transfer resistances due to diffusion inside the fibre tube and chemical reaction kinetics. The relative contribution of each resistance can be characterised by the fractional resistances  $\Delta_t$  and  $\Delta_r$  with respect to the total resistance. These values are also tabulated in Table 2. As is shown, the resistance due to chemical reaction is significant and cannot be neglected. Similar results were obtained

Table 2: Overall mass transfer coefficient of copper extraction,  $K_{aq}$ : experimental values and values predicted by the resistances in series model. Relative resistances to the overall mass transfer resistance

Flow rates	Extractant	Experimental	Tube side		From Eq. (2)	Chemical reaction	
$Q_{aq}/Q_{org}$ ( $\text{mL min}^{-1}$ )	$c_{LIX\ 84-I}$ ( $\text{kmol m}^{-3}$ )	$K_{aq}$ ( $\text{m s}^{-1}$ )	$k_t$ ( $\text{m s}^{-1}$ )	$\Delta_t$ (%)	$K_{aq}$ ( $\text{m s}^{-1}$ )	$k_r$ ( $\text{m s}^{-1}$ )	$\Delta_r$ (%)
140/320	0.06	$4.4 \times 10^{-6}$	$5.76 \times 10^{-6}$	76.4	$5.76 \times 10^{-6}$	$1.9 \times 10^{-5}$	23.6
300/320	0.06	$4.4 \times 10^{-6}$	$7.42 \times 10^{-6}$	59.3	$7.42 \times 10^{-6}$	$1.1 \times 10^{-5}$	40.7
670/320	0.06	$4.0 \times 10^{-6}$	$9.70 \times 10^{-6}$	41.3	$9.70 \times 10^{-6}$	$6.8 \times 10^{-6}$	58.7
300/150	0.06	$4.0 \times 10^{-6}$	$7.42 \times 10^{-6}$	53.9	$7.42 \times 10^{-6}$	$8.7 \times 10^{-6}$	46.1
300/710	0.06	$4.4 \times 10^{-6}$	$7.42 \times 10^{-6}$	59.3	$7.42 \times 10^{-6}$	$1.1 \times 10^{-5}$	40.7
300/320	0.03	$1.4 \times 10^{-6}$	$7.42 \times 10^{-6}$	18.9	$7.42 \times 10^{-6}$	$1.7 \times 10^{-6}$	81.1
300/320	0.1	$4.6 \times 10^{-6}$	$7.42 \times 10^{-6}$	62.0	$7.42 \times 10^{-6}$	$1.2 \times 10^{-5}$	38.0

by other authors. Hu and Wiencek (1998) reported the extraction of copper from acidic solutions using LIX 84 as extractant and the resistance due to chemical reaction was found dominant in most cases. In addition, Lin and Juang (2001) showed that the extraction of copper in acidic medium with LIX 64N was governed by the aqueous-layer diffusion or chemical reaction depending on the concentration of carrier. Concerning the removal of copper from ammoniacal wastewater using the  $\beta$ -diketone LIX 54 as carrier, Yang and Kocherginsky (2007) concluded that the resistance due to chemical reaction was also significant.

### 3.2. Extraction-stripping using two hollow fibres modules

In an integrated extraction-stripping process, the solute is extracted from the feed phase to the organic phase and is simultaneously transferred to the stripping solution, using two hollow fibres modules. The membrane phase is thereby continuously regenerated, which allows attaining a low content of solute in the raffinate. If the volume ratio of feed phase to stripping phase is properly adjusted, a high content of solute may be reached in the stripping solution. From the results obtained using a single module, it was decided to carry out the extraction-stripping experiments keeping the flow rates of aqueous feed and organic phases at  $300 \text{ mL min}^{-1}$ . The flow rate of the stripping phase was also kept at the same value.

Several experiments were then carried out to assess the influence of the extractant on copper recovery. The effect of volume ratio of feed phase to stripping phase and the concentration of sulphuric acid in the stripping phase were also examined. Figure 4 shows representative concentration profiles in the aqueous feed phase and stripping phase. As depicted, the stripping step was slower than the extraction step thus controlling the overall rate of the process for both the extractants, LIX 54 and LIX 84-I. Nevertheless, this effect was rather pronounced when the membrane contained LIX

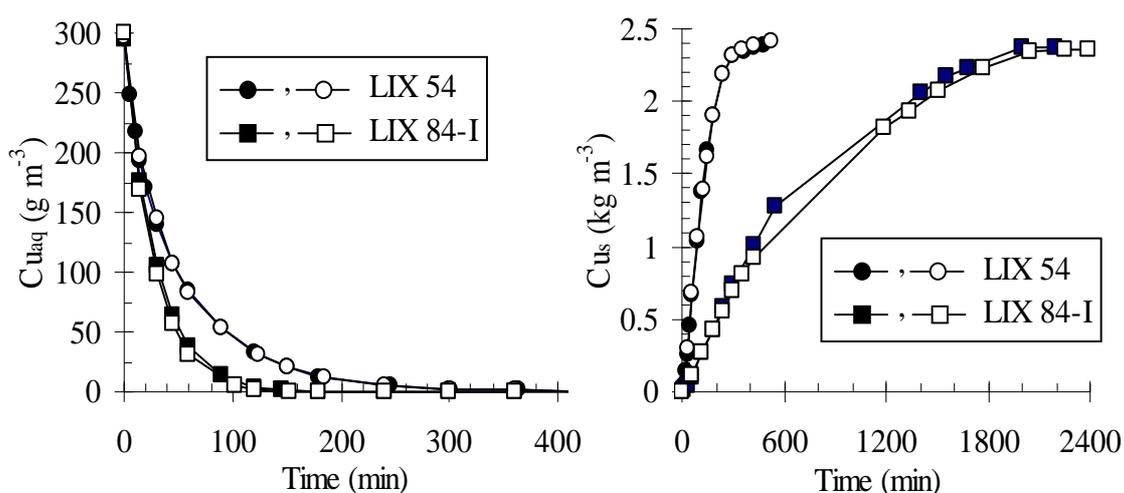


Figure 4: Copper concentration profiles in the aqueous phases during extraction-stripping experiments. Stripping phase:  $150 \text{ kg m}^{-3} \text{ H}_2\text{SO}_4$  (●, ■),  $200 \text{ kg m}^{-3} \text{ H}_2\text{SO}_4$  (○, □). Initial aqueous phase:  $4.72 \times 10^{-3} \text{ kmol m}^{-3}$  of Cu ( $0.3 \text{ kg m}^{-3}$ ); pH 9.53.  $V_s=0.5 \text{ L}$ ;  $V_{\text{org}}=0.9 \text{ L}$ ;  $V_{\text{aq}}/V_s=8$ .

84-I. Thus, the extractant LIX 54 was confirmed to be more advantageous than LIX 84-I for recovering copper from ammoniacal medium in terms of transfer kinetics. The increase in the concentration of sulphuric acid in the receiving phase from 150 to 200 kg m<sup>-3</sup> did not practically affect the kinetics of extraction and stripping. The results also showed that the recovery of solute was complete for both the extractants by using 150-200 kg m<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub> in the stripping phase.

Table 3 summarises the values of copper recovery and concentrations reached in the raffinate and receiving phases in several experiments with hollow fibres. The results obtained by using the ELM technique are also tabulated for comparing the performance of liquid membranes with different configurations. As observed, NDSX allowed removing practically all the copper from the feed solution and 100% of recovery could be attained. On the other hand, the recovery was slightly lower in the ELM experiments. These results can be attributed to the occurrence of non-idealities such as the leakage of the internal stripping phase to the external feed phase and water transport. These deleterious phenomena decreased the efficiency of the process. It is worth noting that the final content of copper in the raffinate phase was found slightly higher in the case of ELM system. The increase in the concentration of sulphuric acid from 150 to 200 kg m<sup>-3</sup> was also found disadvantageous because it increased the difference of ionic strength between the two aqueous phases, which enhanced the non-ideal phenomena and decreased the recovery of copper by ELM. It is worth mentioning that the ELM technique was found advantageous in terms of the kinetics of copper transfer. For instance, the recovery obtained in the ELM experiments is referred to 4 min of permeation time and a feed volume of 0.73 L for a volume ratio  $V_{aq}/V_s=8$ . In the case of NDSX experiments, a few hours were necessary to achieve a similar recovery in processing 4 L of feed phase. It should be emphasized that ELM exhibit a very high specific interfacial area for mass transfer due to the small size of the internal droplets of receiving phase, which favours the stripping step.

Table 3: NDSX versus ELM – Copper recovery and concentrations reached in the raffinate and stripping phases

Technique	$V_{aq}/V_s$	Extractant	H <sub>2</sub> SO <sub>4</sub> (kg m <sup>-3</sup> )	Cu <sub>aq</sub> (g m <sup>-3</sup> )	Cu <sub>s</sub> (kg m <sup>-3</sup> )	Recovery (%)
NDSX	8	LIX 54	150	0.03	2.4	100
		LIX 84-I	150	0.01	2.4	100
		LIX 54	200	0.00	2.4	100
		LIX 84-I	200	0.01	2.4	100
	20	LIX 54	150	0.36	5.8	99
		LIX 84-I	150	0.01	5.5	91
ELM	8	LIX 54	150	0.60	2.3	96
		LIX 84-I	150	0.33	2.7	92
		LIX 54	200	0.19	2.2	92
		LIX 84-I	200	0.12	2.1	88
	20	LIX 54	150	2.10	5.6	92
		LIX 84-I	150	0.27	6.1	92

Initial feed phase: Cu<sub>aq</sub> = 0.3 kg m<sup>-3</sup>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/NH<sub>3</sub>, pH 9.53; 0.06 kmol m<sup>-3</sup> of extractant; V<sub>s</sub> (NDSX)=0.5 L; V<sub>org</sub>/V<sub>s</sub>=2; Stripping phase: 150 or 200 kg m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

## **Conclusions**

Non-dispersive solvent extraction using hollow fibres showed to be adequate for the extraction of copper from ammoniacal media. Integrated extraction-stripping process with two hollow fibre modules allowed removing practically all the copper content from the ammoniacal feed solutions using LIX 54 and LIX 84-I as carriers. Copper was totally recovered by using 150-200 kg m<sup>-3</sup> of sulphuric acid in the stripping phase. In terms of the kinetics of solute transfer, LIX 54 was found to be more adequate than LIX 84-I because the stripping step was particularly faster. The results were then compared with the ones obtained by applying the emulsion liquid membranes. The removal and the recovery of copper were slightly lower in the case of the ELM system because of the occurrence of non-ideal phenomena.

## **Acknowledgement**

Financial support for this study by “Fundação para a Ciência e a Tecnologia” (FCT, Portugal) and the European Community, through the project POCTI/EQU/39342/2001, is gratefully acknowledged.

## **Nomenclature**

$D_{Cu}$	diffusivity of copper in the aqueous phase (m <sup>2</sup> s <sup>-1</sup> )
$d_i$	fibre inner diameter (m)
$d_o$	fibre outer diameter (m)
$Gz$	Graetz number
$K_{aq}$	overall mass transfer coefficient of extraction (m s <sup>-1</sup> )
$k$	local mass transfer coefficient (m s <sup>-1</sup> )
$L$	length of hollow fibre (m)
$m$	distribution ratio
$Q$	volumetric flow rate (m <sup>3</sup> s <sup>-1</sup> )
$R_{aq}$	overall mass transfer resistance of extraction (s m <sup>-1</sup> )
$Sh$	Sherwood number
$V$	volume (m <sup>3</sup> )
$\Delta$	fractional resistance

## *Subscripts*

aq	aqueous feed phase
org	organic phase
r	chemical reaction of extraction
s	aqueous stripping phase
t	tube
0	initial value

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