

# Recovery of Cu(II) from diluted aqueous solutions by non-dispersive solvent extraction<sup>(\*)</sup>

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**Abstract** The removal of copper from diluted aqueous solutions with ACORGA M5640 extractant using non-dispersive solvent extraction technology was studied. It was possible to remove Cu(II) below the international standards from solutions having initially as low concentration as 0.01 g/l under various experimental conditions, i.e. aqueous pH  $4.0 \pm 0.1$ , 10 % v/v ACORGA M5640 in Exxsol D100, an organic flow of 100 ml/min, and an aqueous flow 50 ml/min. Since the removal occurs by chelating ion exchange between copper from solution and protons from the extractant, the former was stripped by using a 180 g/l sulphuric acid solution which flowed (50 ml/min) through the tube side and organic was passed (400 ml/min) through the shell side of the fibers of the module.

**Keywords** Non-dispersive solvent extraction. ACORGA M5640. Copper(II). Hollow fiber module.

## Recuperación de Cu(II) de disoluciones acuosas diluidas mediante extracción con disolventes no dispersiva

**Resumen** Se estudia la eliminación del cobre presente en disoluciones acuosas diluidas empleando el agente de extracción ACORGA M5640 y la tecnología de extracción con disolventes no dispersiva. Bajo las condiciones experimentales estudiadas, pH de la fase acuosa  $4,0 \pm 0,1$ , 10 % v/v ACORGA M5640 en Exxsol D100, flujo de la fase orgánica 100 ml/min, flujo de la fase acuosa 50 ml/min, es posible eliminar el Cu(II), por debajo de los límites marcados internacionalmente, en disoluciones con un contenido tan bajo como 0,01 g/l del metal. Debido a que la extracción transcurre mediante un intercambio catiónico (y formación de un compuesto tipo quelato) entre el cobre presente en el medio acuoso y los protones del agente de extracción, el metal se puede reextraer mediante la utilización de una disolución de 180 g/l de ácido sulfúrico que fluye (50 ml/min) a través de la parte interior de las fibras del módulo, mientras que la fase orgánica fluye (400 ml/min) por la parte exterior de las mismas fibras.

**Palabras clave** Extracción con disolventes no dispersiva. ACORGA M5640. Cobre(II). Módulo de fibra hueca.

## 1. INTRODUCTION

The effluents generated by the modern industries have generally a complex composition including metals (ions or complexes), suspended solids and other components. According to the more stringent environmental laws, these effluents must be decontaminated because of their hazardous character for human life, animals and plants. For copper can be found in human brain, skin, myocardium, etc.<sup>[1]</sup>

Regarding the removal of inorganic (i.e. metals) pollutants, several techniques have been proposed

for their processing, e.g. precipitation, flotation, ion exchange, solvent extraction, etc.<sup>[2-9]</sup>

Because of some drawbacks (lack of selectivity, slow kinetics, etc) encountered in the above mentioned techniques, alternative technologies for the treatment of liquid effluents having heavy metals are needed and among them non-dispersive solvent extraction (NDSX) has emerged as an effective tool due to its versatility and the fact that it overcomes problems found in conventional solvent extraction. The nature of the NDSX technology is described elsewhere<sup>[10]</sup>, broadly

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speaking, it is characterized by the stabilization of the aqueous-organic interface at a (normally) hydrophobic porous material, eliminating the dispersion of the two immiscible phases (organic and aqueous) and thus avoiding phase entrainment and emulsion formation.<sup>[11-16]</sup>

In the last decade, and with the aim of improving the utilization of NDSX, most of the research work published deals with the study of several parameters covering aspects of hydrodynamics and chemical applications. These had been recently reviewed<sup>[17]</sup>. Case studies included laboratory and pilot-scale approach. Though the NDSX technique has been used for some years, in various fields, e.g., bioseparation, its application in hydrometallurgy is rare. Thus, in order to obtain further information about the applicability of this technique in the removal/recovery of toxic elements from liquid effluents, the present investigation reports on the performance of the NDSX technology in the recovery of copper from diluted aqueous sulphate solutions by using ACORGA M5640 extractant (a reagent with little, if any, uses in this field).

## 2. EXPERIMENTAL

Stock metal solutions were prepared from the corresponding salts (AR grade). The organic diluent used in NDSX studies was Exxsol D100 (ExxonMobil Chem. Iberia) having the following characteristics: boiling range 239-265 °C, flash point 102 °C, density (15 °C) 0.819 g/cm<sup>3</sup>, aromatic content 0.2 %. ACORGA M5640 (Avecia), belonging to the fourth group of oximes extractants also forms the second generation of hydroxyoxime derivatives. The active substance of the reagent is 2-hydroxy-5-nonyl-benzaldehyde oxime to which a fatty ester had been added as modifier to improve some of the extraction-stripping properties of the extractant.<sup>[18]</sup> Both ACORGA M5640 and Exxsol D100 were used as received. All other chemicals were AR grade.

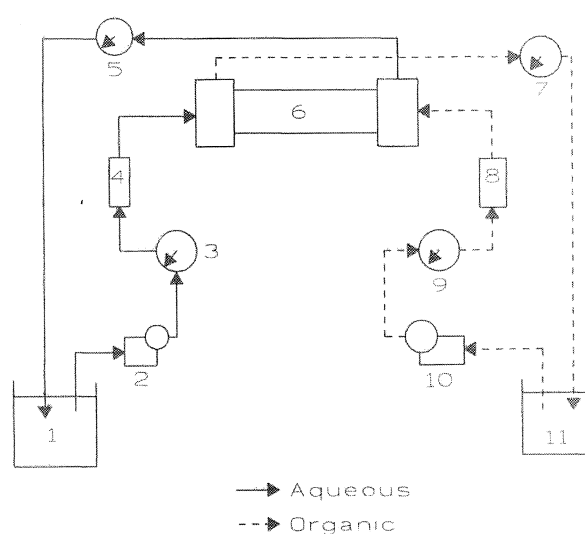
The hollow fiber module was manufactured by Celgard Celanese Corp. (5PCS-1002 Liqui-Cel laboratory unit and 5PCG-259 contactor). The characteristics of the contactor are given in table I.

A schematic view of the NDSX process for Cu(II) using a hollow fiber contactor in recirculation mode is shown in figure 1. Both aqueous and organic phases were contacted in counter-current, unless otherwise stated, for

**Table I.** Characteristics of the hollow fiber module

*Tabla I. Características del modulo de fibra hueca*

Module diameter (cm)	8
Module length (cm)	28
Active interfacial area (m <sup>2</sup> )	1.4
Fiber internal diameter (cm)	24·10 <sup>-3</sup>
Fiber outer diameter (cm)	30·10 <sup>-3</sup>
Fiber length (cm)	15
Porosity (%)	40
Pore size (μm)	0.03
Polymeric material	Polypropylene



**Figure 1.** A schematic view of the non-dispersive solvent extraction set-up in the countercurrent configuration. 1 and 11 aqueous and organic reservoir tanks (stirred). 2 and 10 pumps. 3, 5, 7 and 9 inlet and outlet pressure gauges. 4 and 8 flow meters. 6 hollow fiber module.

*Figura 1. Esquema del sistema de extracción con disolventes no dispersiva en su configuración en contracorriente. 1 y 11 tanques (agitados) de fases acuosa y orgánica. 2 y 10 bombas. 3, 5, 7 y 9 manómetros. 4 y 8 caudalímetros. 6 modulo de fibra hueca.*

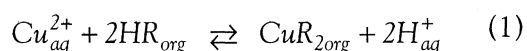
extraction runs under recirculation mode. In the contactor, the feeded aqueous phase flowed (50 ml/min) through the tube side of the fibers, while the organic phase circulated (25-100 ml/min) through the shell side, wetting the wall of the hydrophobic fibers. The pressure of the aqueous phase was held at 2-3 psi higher than the pressure in the organic phase; while these conditions are maintained the appearance of the organic phase on the other side of the membrane can be prevented if an immobilized phase is maintained on this side at

a pressure equal to or greater than that of the organic phase<sup>[19]</sup>. In the stripping run, loaded organic phase (ACORGA M5640 with copper complex) flowed through the shell side of the module (200-400 ml/min), whereas H<sub>2</sub>SO<sub>4</sub> flowed through the tube side (50 ml/min) countercurrently and in recirculation mode.

Small aliquots of the corresponding phases were taken at different times for analysis of metal concentration by atomic absorption spectrophotometry.

### 3. RESULTS AND DISCUSSION

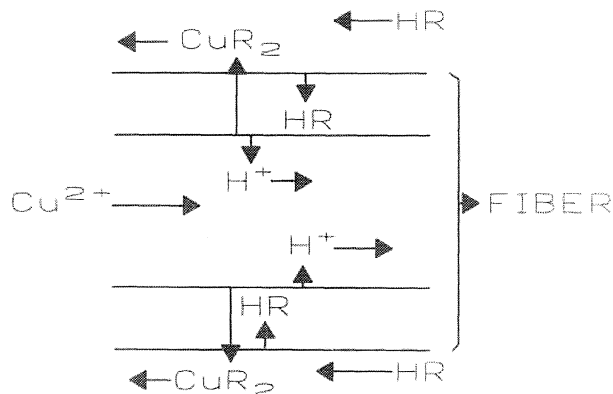
The extraction mechanism for copper with ACORGA M5640 is based in a chelation-ion exchange reaction type. The extraction of Cu(II) from the process stream (further referred as the removal of Cu(II) from the feed phase) takes place at the interface between the feed and the membrane. Cu(II) ions in acidic media form a complex with the extractant ACORGA M5640 (salicylaldoxime, HR), in accordance with the reaction:



Copper stripping is carried out by shifting the equilibrium to the left using a relatively concentrated acid solution.

The extraction mechanism of copper with ACORGA M5640 in the hollow fiber contactor is shown in figure 2. The system consists of an aqueous phase containing Cu<sup>2+</sup> flowing in the tube side of the microporous hollow fiber membranes, being the pores filled with the organic phase, which flows co or countercurrently in the shell side. The reaction takes place at the inside wall of the membrane where the interface is located. There are various steps in the extraction process:<sup>[20]</sup>

- I. Copper ion contained in the aqueous phase (tube side) diffuses from the bulk of the aqueous-organic interface (inside wall of fiber) through the boundary layer.
- II. In the aqueous-organic interface, Cu<sup>2+</sup> reacts in the membrane pore with ACORGA M5640 contained in the organic phase to form the CuR<sub>2</sub> complex. Protons are released into the aqueous phase boundary layer diffusing to the bulk of the feed phase.



**Figure 2.** Extraction mechanism of Cu<sup>2+</sup> with ACORGA M5640 in hollow fiber module.

*Figura 2.* Extracción de Cu<sup>2+</sup> con ACORGA M5640 en el modulo de fibra hueca.

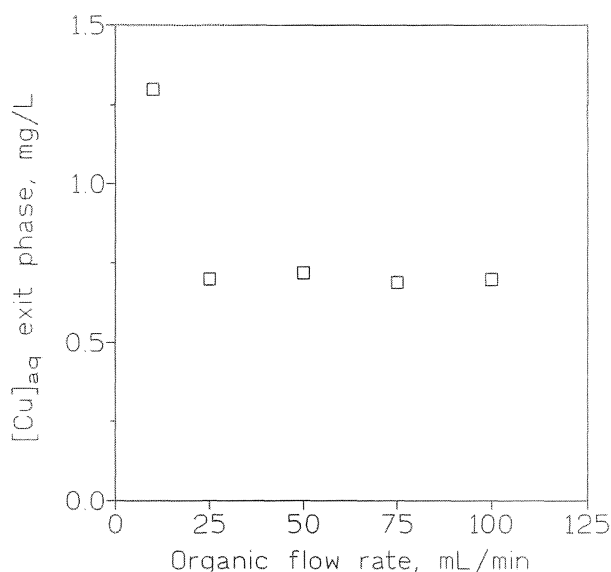
- III. CuR<sub>2</sub> complex diffuses from the aqueous-organic interface to the outside wall of fiber through the organic filled membrane pore, and free ACORGA M5640 extractant solution diffuses in the opposite direction from the shell side into the pore.
- IV. CuR<sub>2</sub> complex diffuses from the outside fiber wall to the organic phase bulk (shell side) flowing co or countercurrently to the aqueous feed phase.

Thus, the expression for the overall mass transfer coefficient K<sub>Cu,E</sub> can be written as:<sup>[21]</sup>

$$\frac{1}{K_{\text{Cu,E}}} = \frac{[\text{H}^+]_{\text{aq}}^2}{[\text{HR}]_{\text{org}}^2} \frac{1}{k_e} + \frac{1}{k_f} + \frac{r_i}{\eta_m} \frac{[\text{H}^+]_{\text{aq}}^2}{[\text{HR}]_{\text{org}}^2} \frac{1}{K_{\text{ext}} k_m} + \frac{r_o}{r_i} \frac{[\text{H}^+]_{\text{aq}}^2}{[\text{HR}]_{\text{org}}^2} \frac{1}{K_{\text{ext}} k_s} \quad (2)$$

where 1/K<sub>Cu,E</sub> represents the total resistance and the terms on the right side of eq. (2) represent the reaction resistance (first term), tube-side resistance (second), membrane resistance (third) and shell side resistance (fourth).

Figure 3 shows the effect of changing the shell side organic phase flow rate keeping the aqueous flow rate constant for 5 % v/v ACORGA M5640 in Exxsol D100. It appears that beyond an organic flow rate of 25 ml/min there was hardly any effect, but the module extraction efficiency decreased below 25 ml/min of organic flow rate. This implies that most Cu<sup>2+</sup> can be easily transferred into the



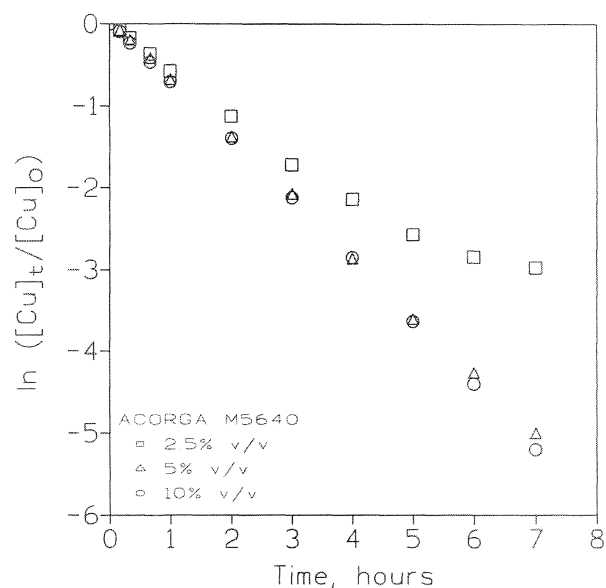
**Figure 3.** Exit concentration of the aqueous phase with copper from the hollow fiber module as a function of the organic phase flow rate. Organic phase (400 ml): 5 % v/v ACORGA M5640 in Exxsol D100. Aqueous phase (4 l): 0.05 g/l Cu<sup>2+</sup> at pH 4.0±0.1. Aqueous flow rate: 50 ml/min. Time: 6 h.

Figura 3. Concentración de cobre a la salida de la fase acuosa del modulo de fibra hueca en función del flujo de la fase orgánica. Fase orgánica (400 ml): 5 % v/v ACORGA M5640 en Exxsol D100. Fase acuosa (4 l): 0,05 g/l Cu<sup>2+</sup> a pH 4,0±0,1. Flujo de la fase acuosa: 50 ml/min. Tiempo: 6 h.

organic phase by the interfacial reaction when the concentration of the oxime is in excess due to an increase in the organic phase flow rate. Therefore, the shell side resistance (eq. (2)) is negligible beyond an organic flow rate of 25 ml/min. It should be mentioned that the concentration of copper in the aqueous phase was under the international limit (2 mg/l) set for this heavy metal<sup>[22]</sup> and also under the limit established by the Spanish law<sup>[23]</sup>.

Figure 4 shows the influence of changing the concentration of ACORGA M5640 contained in the organic phase on the Cu<sup>2+</sup> extraction kinetics. No change in the relative concentration decay was observed when 5 and 10 % v/v extractant concentrations were used, whereas the extraction process seems to slow down when the lower reagent concentration was used. The targeted copper exit concentration was reached after 4.5 h using 5 or 10 % v/v ACORGA M5640 in Exxsol D100 and probably after 7 h using 2.5 % v/v of the extractant.

The effect of the aqueous feed phase pH is showed in figure 5. This variable influenced the removal of Cu(II) from the feed phase, being this



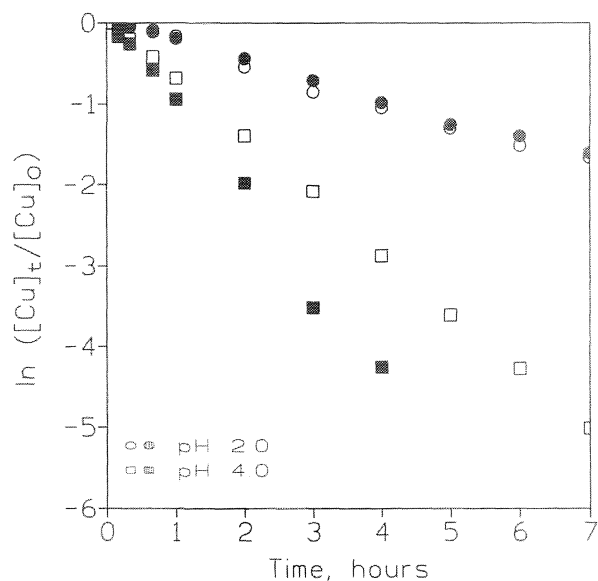
**Figure 4.** Removal of Cu(II) from the feed phase at various extractants concentrations. Organic phase (400 ml): ACORGA M5640 in Exxsol D100. Aqueous phase (4 l): 0.05 g/l Cu<sup>2+</sup> at pH 4.0±0.1. Organic flow rate: 100 ml/min. Aqueous flow rate: 50 ml/min.

Figura 4. Eliminación de Cu(II) de la corriente de alimentación a varias concentraciones del agente de extracción. Fase orgánica (400 ml): ACORGA M5640 en Exxsol D100. Fase acuosa (4 l): 0,05 g/l Cu<sup>2+</sup> a pH 4,0±0,1. Flujo de la fase orgánica: 100 ml/min. Flujo de la fase acuosa: 50 ml/min.

enhanced at pH values of 4.0, though the international limit for copper content in the effluent was also reached at pH 2.0 when the initial concentration of 0.01 g/l Cu(II) in the aqueous feed was used.

The influence of the initial metal concentration on the removal of Cu(II) from the feed phase is presented in table II. The time required to reach the limiting exit concentration for copper was dependent on the initial metal concentration: shorter times at lower copper concentrations in the feed phase.

It was also found that the Cu(II) removal from the feed phase was not particularly influenced by the module configuration used: co or countercurrent. In this set of experiments the aqueous phase (4 l) contained 0.05 g/l Cu(II) at pH 4.0±0.1, whereas the organic phase (400 ml) contained 5 % v/v ACORGA M5640 in Exxsol D100; flow rates were of 50 ml/min and 100 ml/min for the aqueous and organic phases, respectively. The target value of 2 mg/l for copper exit concentration was reached for both module configurations after roughly 4.5 h.



**Figure 5.** Removal of Cu(II) from the feed aqueous phase at different pH. Organic phase (400 ml): 5 % v/v ACORGA M5640 in Exxsol D100. Aqueous phase (4 l): 0.01 g/l Cu<sup>2+</sup> (■ and ●) or 0.05 g/l Cu<sup>2+</sup> (□ and ○). Organic flow rate: 100 ml/min. Aqueous flow rate: 50 ml/min.

Figura 5. Eliminación de Cu(II) de la alimentación acuosa a distintos valores del pH. Fase orgánica (400 ml): 5 % v/v ACORGA M5640 en Exxsol D100. Fase acuosa (4 l): 0,01 g/l Cu<sup>2+</sup> (■ y ●) o 0,05 g/l Cu<sup>2+</sup> (□ y ○). Flujo de fase orgánica: 100 ml/min. Flujo de fase acuosa: 50 ml/min.

**Table II.** Influence of initial metal concentration on the removal of Cu(II)

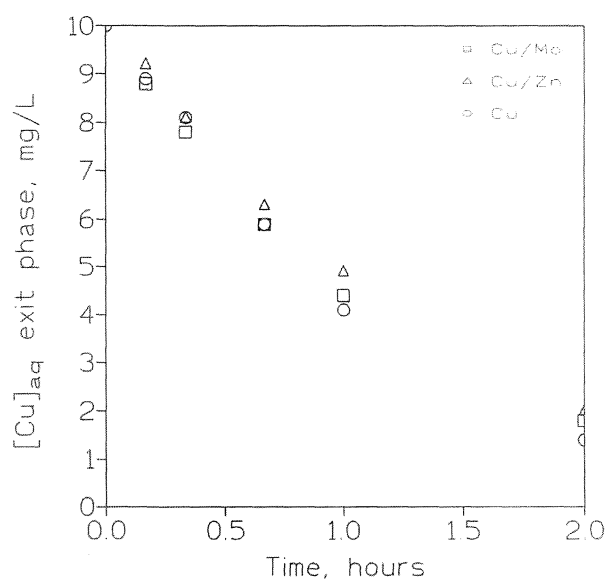
Tabla II. Influencia de la concentración inicial del metal en la eliminación de Cu(II)

Initial Cu(II) concentration g/l	pH	Time for [Cu <sup>2+</sup> ] <sub>aq</sub> <2 mg/l
0.01 <sup>a</sup>	4.0±0.1	1.8 h
0.05 <sup>a</sup>	4.0±0.1	4.5 h
0.01 <sup>a</sup>	2.0±0.1	7.1 h
0.05 <sup>a</sup>	2.0±0.1	not reached after 9.0 h
0.05 <sup>b</sup>	2.0±0.1	9.0 h

<sup>a</sup> Organic phase: 5 % v/v ACORGA M5640 in EXXSOL D100. Aqueous flow rate: 50 ml/min. Organic flow rate: 100 ml/min.

<sup>b</sup> Organic phase: 10 % v/v ACORGA M5640 in Exxsol D100. Aqueous and organic flow rates as above.

To evaluate the effect of co-ions on the removal of copper, several experiments were performed using mixed solutions of copper/zinc and copper/molybdenum. Figure 6 shows the results obtained from these experiments. The presence of



**Figure 6.** Exit copper concentration of the aqueous phase from the hollow fiber module in the presence of zinc(II) or molybdenum(VI). Organic phase (400 ml): 5 % v/v ACORGA M5640 in Exxsol D100. Aqueous phase (4 l): 0.01 g/l Cu<sup>2+</sup> and 0.0025 g/l Zn<sup>2+</sup> or 0.01 g/l Cu<sup>2+</sup> and 0.1 g/l Mo(VI) at pH 4.0(0.1). Organic flow rate: 100 ml/min. Aqueous flow rate: 50 ml/min.

Figura 6. Concentración de cobre a la salida de la fase acuosa del modulo de fibra hueca en presencia de cinc(II) o molibdeno(VI). Fase orgánica (400 ml): 5 % v/v ACORGA M5640 en Exxsol D100. Fase acuosa (4 l): 0,01 g/l Cu<sup>2+</sup> y 0,0025 g/l Zn<sup>2+</sup> o 0,01 g/l Cu<sup>2+</sup> y 0,1 g/l Mo(VI) a pH 4,0(0,1). Flujo de fase orgánica: 100 ml/min. Flujo de fase acuosa: 50 ml/min.

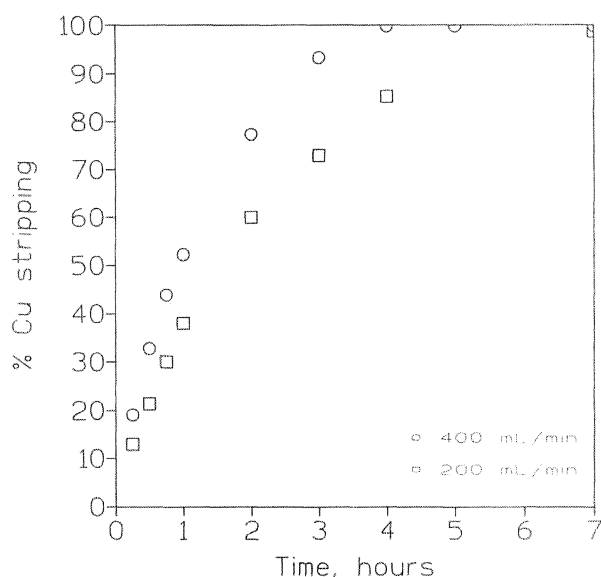
these co-ions had little effect on copper removal from the feed phase, the targeted concentration value being attained at near the same contact times.

It should also be noted that neither zinc(II) nor molybdenum(VI) were co-extracted with copper. In the case of Mo(VI) this is also probable due to the presence of anionic-molybdenum complexes in the aqueous phase at the present experimental conditions, since Mo(VI) can be extracted by oximes at more acidic pH values.<sup>[24]</sup> Under the present experimental conditions, the concentration of zinc in all the effluent was under the international limit set for this heavy metal, this limit varies between 3 and 5 mg/l depending on the type of process originating the waste solution and the treatment used<sup>[25]</sup>.

Copper stripping was performed separately in a single module (same characteristics as shown in table I) by flowing loaded organic solution (ACORGA M5640 with metal complex) on the shell side and H<sub>2</sub>SO<sub>4</sub> solution (180 g/l acid) on the

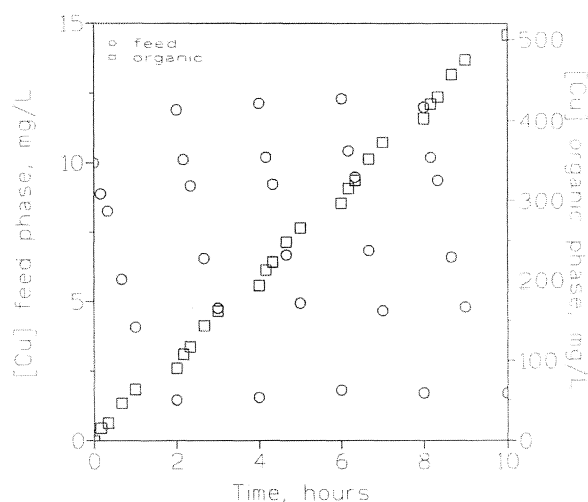
tube side. Figure 7 shows a typical plot of the percentage of copper stripping versus time when the organic flow rate was changed. It can be seen that by increasing the flow rate, the time required to reach near quantitative copper stripping was reduced to near a half.

A last series of kinetic experiments were performed using an aqueous feed with an initial concentration of copper of near 0.01 g/l and pH 4.0. In order to increase the concentration of copper in the organic solution (and later in the stripping solution), this set of experiments were carried out replacing the aqueous feed solution by a fresh one after two hours running, whereas the organic phase was maintained the same. In figure 8 it can be seen that copper concentration in the organic phase increased with time. The loaded organic phase was then stripped with 180 g/l sulphuric acid as described above. According with the results obtained, it is possible to pass from a large volume of feed solution (20 l) with extremely low content of copper (0.01 g/l) to a new and more attractive acidic solution with a small volume (250 ml) and therefore a higher content of copper (1 g/l).



**Figure 7.** Copper stripping at two different organic flow rates. Organic phase (500 ml): 5 % v/v ACORGA M5640 in Exxsol D100 loaded with 0.32 g/l Cu(II). Aqueous phase (250 ml): 180 g/l H<sub>2</sub>SO<sub>4</sub>. Aqueous flow rate: 50 ml/min.

*Figura 7. Reextracción de cobre bajo dos flujos diferentes de fase orgánica. Fase orgánica (500 ml): 5 % v/v ACORGA M5640 en Exxsol D100 cargada con 0,32 g/l Cu(II). Fase acuosa (250 ml): 180 g/l H<sub>2</sub>SO<sub>4</sub>. Flujo de la fase acuosa: 50 ml/min.*



**Figure 8.** Evolution of copper concentration in feed and organic solutions. Organic phase (400 ml): 5 % v/v ACORGA M5640 in Exxsol D100. Organic flow rate: 100 ml/min. Aqueous flow rate: 50 ml/min.

*Figura 8. Variación de la concentración de cobre en las fases orgánica y de alimentación. Flujo de fase orgánica: 100 ml/min. Flujo de fase acuosa: 50 ml/min.*

#### 4. CONCLUSIONS

Based on the results obtained, it is possible to conclude about the viability of the application of the non-dispersive solvent extraction technique for the removal of copper(II) from acidic solutions by using ACORGA M5640 extractant in Exxsol D100; the procedure offers a technological alternative to the reduction of copper from initial diluted solutions (0.01 g/l) to values below the permitted international standards. The use of a sulphuric acid solution allowed the complete recovery of copper in a small solution volume (and thus with a higher concentration in the metal). A good selectivity of copper(II) against other accompanying metals was found. A first analysis showed that within of the experimental conditions the non-dispersive solvent extraction of copper was controlled by interfacial kinetics.

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## Nomenclature

$[Cu]_{aq}$	copper concentration in the feed solution at an elapsed time
$[Cu]_t$	
$[Cu]_o$	initial copper concentration in the feed solution
$[H^+]_{aq}$	proton concentration in the aqueous phase
$[HR]_{org}$	oxime concentration in the organic phase
$K_{Cu,E}$	overall mass transfer coefficient for extraction
$K_{ext}$	equilibrium concentration constant for eq.(1)
$k_e$	forward reaction rate constant for eq. (1)
$k_f$	mass transfer coefficient of aqueous feed
$k_m$	membrane mass transfer coefficient
$k_s$	organic mass transfer coefficient
$r_i$	hollow fiber radius (inner)
$r_{lm}$	logarithmic mean radius of a hollow fiber
$r_o$	hollow fiber radius (outer)

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