



Copper extraction from ammoniacal medium in a pulsed sieve-plate column with LIX 84-I

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ABSTRACT

This article reports on a study of copper removal from ammoniacal aqueous solution (1.0 kg m^{-3} Cu, pH 9.5) by liquid–liquid extraction using a pulsed sieve-plate column. The extractant tested was the hydroxoxime LIX 84-I (2-hydroxy-5-nonylaceto-phenone oxime) in the aliphatic diluent Shellsol D-70. The results of the pilot plant experiments demonstrated the feasibility of operating the extraction process in this type of column, with efficiencies of copper removal in the range of 90.5–99.5%. Several effects on the column performance were examined, namely the aqueous and organic flow rates and the pulse velocity. The axial dispersion model was applied to simulate the concentration profiles, which reasonably predicted the experimental data. The overall mass transfer coefficient was evaluated from the experimental data and was found to be between 9×10^{-6} and $1.2 \times 10^{-5} \text{ m s}^{-1}$. These data were compared with the ones obtained from the resistances in series model, which indicated that the resistance due to chemical reaction was 84–91% of the overall resistance to mass transfer. The extraction using a hollow fiber contactor was also carried out to compare the membrane process performance with the one of conventional process.

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1. Introduction

The ammoniacal leaching of ores, concentrates, wastes, by-products and scrap, containing copper, is a process of notable interest, since this metal ion is easily solubilized through the formation of ammine complexes. Therefore, the range of copper materials that can be efficiently processed via hydrometallurgy is extended [1,2]. For instance, the etching of copper from printed circuit boards (PCB), using ammonium chloride and ammonium sulfate, is practiced for years [3]. However, in recent years, this industry evolved rapidly due to the development of modern electronic equipments, namely television sets, refrigerators, air conditioners, personal computers, mobile phones, etc.

The copper present in the effluents must be recovered on account of economical and environmental reasons. In fact, there is a crescent concern about minimizing the discharge of liquid effluents containing heavy metals. The Portuguese environmental legislation defines emission limit values, ELV, for the waste waters discharge which for total copper is 1.0 mg L^{-1} [4].

With the increasing demand for non-ferrous metals owing to population growth and improvements in the standard of living

in the world, under the constraint of limited availability of natural resources, it is indispensable to consider, in the near future, the sustainable development of more efficient metals production processes taking environmental concerns into account [5]. Gerst and Graedel [6] research compares several features of the 1994 and 2000 copper cycles, demonstrating that the use of copper by consumers, on a global level, increased significantly, by about 32%, while the corresponding global population increased by only 8%. Thus, copper recovery, recycling and reuse – the 3 R's concept – are extremely important and therefore it is evident that ammoniacal leaching will assume a huge relevancy in coming years [3,7].

If, as referred previously, the development of modern electronic equipments gave rise to a rapid evolution of the printed circuit boards industry, it also brought on tremendous increase in electrical and electronic scrap [8]. Most of these wastes – which contain a large amount of copper – are still deposited in landfills. For example, a mobile phone contains 17.2% of copper, a tape recorder 8.2% and a video camera 6.9% [9].

Copper may be recovered from electronic scrap via pyrometallurgical processes [9]. However, copper smelters are generally located away from the urban areas that generate the electronic scrap, which raises the energy consumption and cost of transportation [10]. The hydrometallurgical processes have reduced process costs, for example lower power consumption [11], and can

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Nomenclature

| | |
|-------------------|---|
| a | specific interfacial area, m^{-1} |
| A | pulse amplitude, m |
| c | concentration, kmol m^{-3} or kg m^{-3} |
| D | molecular diffusivity, $\text{m}^2 \text{s}^{-1}$ |
| d_{32} | Sauter mean diameter of the dispersed phase drops, m |
| d_{col} | column diameter, m |
| d_o | hole diameter, m |
| d_p | pitch of holes on plate, m |
| E_0 | continuous phase axial mixing coefficient at zero flow rate, $\text{m}^2 \text{s}^{-1}$ |
| E | axial mixing coefficient, $\text{m}^2 \text{s}^{-1}$ |
| f | pulse frequency, Hz |
| g | acceleration due to gravity (9.8), m s^{-2} |
| h | plate spacing, m |
| HR | extractant generic designation |
| HTU_c | overall height of transfer unit based on the continuous phase, m |
| K_{aq} | overall mass transfer coefficient based on the aqueous phase, m s^{-1} |
| K_c | overall mass transfer coefficient based on the continuous phase, m s^{-1} |
| k | local mass transfer coefficient, m s^{-1} |
| L | column length, m |
| m | distribution ratio |
| Q | volumetric flow rate, $\text{m}^3 \text{s}^{-1}$ |
| R | resistance to mass transfer, $\text{m}^{-1} \text{s}$ |
| S | cross-sectional column area, m^2 |
| v | superficial velocity ($v = Q/S$), m s^{-1} |
| v_{slip} | slip velocity, m s^{-1} |
| z | axial distance, m |

Greek letters

| | |
|-----------------|---|
| α | fractional plate free area |
| Δ | fractional resistance (relatively to the total resistance), % |
| $\Delta\rho$ | density difference between phases, kg m^{-3} |
| ε_D | mechanical power dissipation per unit mass, $\text{m}^2 \text{s}^{-3}$ |
| ϕ | dispersed phase hold-up |
| κ | viscosity ratio |
| μ | viscosity, $\text{kg m}^{-1} \text{s}^{-1}$ |
| ρ | density, kg m^{-3} |
| σ | interfacial tension between the organic and the aqueous phases, N m^{-1} |

Subscripts

| | |
|------|------------------------------|
| 0 | initial value |
| aq | aqueous phase |
| c | continuous phase |
| calc | calculated value |
| d | dispersed phase |
| eq | equilibrium |
| exp | experimental value |
| f | final |
| org | organic phase |
| r | extraction chemical reaction |
| tr | transition |

Dimensionless numbers

| | |
|------|--------------------------------|
| Pe | dv/D (Péclet number) |
| Re | $dv\rho/\mu$ (Reynolds number) |
| Sc | $\mu/\rho D$ (Schmidt number) |

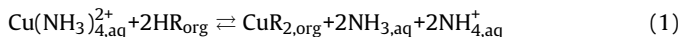
| | |
|--------|---|
| Sh_c | $kd_{32}/D_{\text{Cu}(\text{NH}_3)_4^{2+}}$ (Sherwood number for continuous phase) |
| Sh_d | $k_d d_{32}/D_{\text{CuR}_2}$ (dispersed phase Sherwood number for droplet dispersions) |

be economically operated even on a small scale. These advantages enable the construction of an on-site plant for economical recycling without transportation costs [8,10].

Some references have been found in the literature about the application of new hydrometallurgical copper recycling processes for electronic scrap [12,13]. Some authors developed a process with the potential to produce high purity copper with a low power consumption, where copper in the PCB, proceeding from end-of-life electronic equipment, was leached into an ammonia/ammonium sulfate solution of pH 10.5 [10,14]. Han and Fuerstenau [15] studied the factors affecting the dissolution behaviour of metals from Au/Cu and Ag/Cu alloy systems, existent in scrap, in several lixiviants such as ammonia. Sano et al. [16] examined the copper removal from steel scrap, coming from the automobile industry, in a variety of solutions, such as ammonia, concluding that this solution can selectively dissolve the copper with the greatest stability and at a relatively high rate.

After the ammoniacal leaching, copper can be removed from the aqueous solutions by several techniques, like precipitation, adsorption and solvent extraction [17]. Solvent extraction is the most efficient method since it offers multiple advantages, such as the absence of sludge formation, greater ease and flexibility of operations, ability to handle a wide range of feed concentrations, choice of solvents to control selectivity of separation, etc. [3].

In the solvent extraction process, well-established copper extractants like hydroxyoximes or β -diketones are used [18]. These are marketed as LIX, from Cognis or ACORGA, from Avecia. The use of such extractants in copper recovery is well-documented elsewhere [18–21]. The equilibrium of copper extraction from ammoniacal solutions, with β -diketones or oximes, may be described by the following equation [22]:



The results described by Flett and Melling [23], Szymanowski [18], Schwab and Kehl [19], Kyuchoukov et al. [20] and Bermejo et al. [24] demonstrated that the β -diketone LIX 54 has some advantages, when compared with the hydroxyoxime LIX 84-I, for copper recovery from ammoniacal medium. In fact, LIX 54 provides low ammonia loading, ease of stripping and fast transfer kinetics. In a previous study, the present authors corroborated that the kinetics of the extraction-stripping process in hollow fibers was faster using LIX 54 [25]. Also, the recovery of copper from ammoniacal medium using emulsion liquid membranes was examined [25,26]. LIX 84-I exhibited a very high extraction rate but the accumulation of solute in the membrane was higher than in the case of LIX 54.

The most common type of solvent extraction equipment used in the hydrometallurgical industry is the mixer-settler arrangement. However, more recently, pulsed columns have been considered as a possible alternative to the existing technology [27,28].

The main advantages of pulsed columns over mixer-settlers are higher throughput and separation efficiency, lower organic entrainment and therefore lower organic loss, reduced solvent inventory and crud formation, less environmental pollution due to a closed system, less maintenance need, lower floor space requirement and reduced operating and maintenance costs [29–32].

Pulsed columns are contactors in which the mass transfer rate is enhanced by hydraulic or pneumatic pulsation of the liquids. The periodic pulsing of both phases up and down the column, in the presence of internals such as sieve plates, causes the required dispersed phase droplets break-up and coalescence [28]. For constant phase flow rates there are three stable (mixer-settler, dispersion and emulsion) and one unstable regime of operation and two flooding types depending on the pulse frequency and amplitude [33].

In the literature there are several references to the application of pulsed columns to the chemical, biochemical, nuclear, petroleum and metallurgical industries, for the extraction of uranium, cobalt, nickel, zinc and copper [28,32–35]. For instance, Buchalter et al. [34] tested the extraction and stripping of copper using Bateman pulsed columns as part of a pilot plant at a processing facility of a copper producer. They achieved a copper recovery of 90–95% and metal concentrations in the raffinate between 0.1 and 0.15 g L⁻¹. The organic entrainment in the raffinate was 55–80% lower than at the mixer-settler pilot plant, which represented significant savings. Crud was removable without shutting down. In spite of all the published studies, the pulsed columns complexity requires the development of further research about each system hydrodynamics and mass transfer.

Thus, the aim of this work was the extraction of copper from ammoniacal medium in a pulsed sieve-plate column. To the best of our knowledge, there is no data published in the literature regarding this topic. The hydroxyoxime LIX 84-I was used as an extractant, despite the LIX 54 advantages mentioned before. In fact, it was not possible to purchase this reagent from Cognis, because its production has been ceased. The performance of the selected column was studied for this extraction process. The effects of the aqueous and organic flow rates and of the pulse velocity on the mass transfer were examined. This study can provide fundamental data to the design of pulsed sieve-plate columns to be used in the processing of ammoniacal waste waters.

2. Theory

There are two main groups of mathematical models for liquid–liquid extraction in columns [36,37]. One of them is based on the concept of axial mixing and the other one is the well known drop population balance model (DPBM). In the first group, the axial dispersion model is the most frequently used. In this model, all the hydrodynamic non-idealities are quantified through the axial dispersion coefficient [38]. Although this model does not properly describe the real hydrodynamic behaviour in the column [39], it conjugates the relative ease of implementation with the achievement of relatively accurate mass transfer results [40].

The DPBM considers that the dispersed phase is discontinuous and takes into account the complex dispersed phase interactions, like coalescence, break-up, droplet rise and backmixing. So, these models predict within a good accuracy the drop size distribution, the dispersed phase hold-up and the concentration profiles in the extraction columns [38,39]. However, such models have the disadvantage of being complicated in terms of mathematical formulation [41–43] and are of limited usefulness for control system design [44].

Besides the aforementioned approaches, it is important to refer the Computational Fluid Dynamics (CFD) [27,45]. This is the most accurate approach to model extraction columns. It applies rigorous mathematical models that take into consideration the hydrodynamics and/or mass transfer. However, due to the enormous complexity of the problem, the development is rather slow. And, as for now, there is no program that solves the three-dimensional flow in a column for both hydrodynamics and mass transfer simultaneously [46]. Thus, the axial dispersion model was selected for simulating the mass transfer in the present study.

2.1. Axial dispersion mathematical model

The equations of the axial dispersion model for continuous and dispersed phases can be written as [47]:

$$E_c \frac{d^2 c_c}{dz^2} - \frac{Q_c}{S} \frac{dc_c}{dz} - aK_c (c_c - c_{c,eq}) = 0 \quad (2)$$

$$E_d \frac{d^2 c_d}{dz^2} + \frac{Q_d}{S} \frac{dc_d}{dz} + aK_c (c_c - c_{c,eq}) = 0 \quad (3)$$

In these equations, E_c and E_d represent the continuous and dispersed phases axial mixing coefficients, respectively, c_c and c_d are the copper concentrations in the aqueous and organic phases, $c_{c,eq}$ is the aqueous phase solute concentration in equilibrium with the organic phase, Q_c and Q_d are the aqueous and organic phases volumetric flow rates, S is the cross-sectional column area, a is the specific interfacial area obtained by Eq. (4) and K_c is the overall mass transfer coefficient of extraction based on the continuous phase.

$$a = \frac{6\phi}{d_{32}} \quad (4)$$

In this expression, ϕ represents the dispersed phase hold-up, and d_{32} denotes the Sauter mean diameter of the dispersed phase drops.

The convention that the aqueous phase flows from $z=0$ (aqueous phase entry) to $z=L$ (organic phase entry) was adopted. The boundary conditions at the bottom and top of the column were expressed by:

$$z = 0, \quad -E_c \frac{dc_c}{dz} + \frac{Q_c}{S} c_c = \frac{Q_c}{S} c_{c,0}, \quad \frac{dc_d}{dz} = 0 \quad (5)$$

$$z = L, \quad \frac{dc_c}{dz} = 0, \quad -E_d \frac{dc_d}{dz} + \frac{Q_d}{S} c_d = \frac{Q_d}{S} c_{d,0} \quad (6)$$

where the subscript '0' denotes the initial condition.

The system of differential equations was solved by the processes modelling system gPROMS[®], from Process Systems Enterprise Ltd., UK. The value of K_c was obtained by optimization through gOPT, minimizing an objective function F which was the error square sum, defined as:

$$F = \sum (c_{c,calc} - c_{c,exp})^2 \quad (7)$$

To apply the presented model, in order to simulate the concentration profiles in the pulsed column, several parameters are necessary. These parameters were obtained by experimental measurements or estimated from literature correlations.

The dispersed phase drops diameters to calculate d_{32} were measured by a photographic technique. The equilibrium copper concentration, $c_{c,eq}$, was obtained through laboratory experiments. The experimental details are presented in Section 3.

The continuous phase axial mixing coefficient was estimated by the correlation obtained by Ingham et al. [48] developed from axial mixing studies in pulsed sieve-plate extraction columns, using the stationary phase tracer technique:

$$E_c = E_0 \left(1 + \frac{v_c}{2Af} \right) \quad (8)$$

This technique involves operating the column with zero flow of continuous phase. Thus, in this expression, E_0 represents the continuous phase axial mixing coefficient at zero flow rate:

$$E_0 = a_1 \left(\frac{\rho_c d_o Af}{\mu_c} \right)^{-0.3} \frac{(Af)(1 - \alpha^2) d_{col}^{1.33}}{(h\alpha^2 C_p^2)^{0.33}} + a_2 \left(\frac{A^2 f}{\alpha^2} \right) \left(\frac{h}{a_1} \right)^{0.45} \quad (9)$$

The correlation describes the effects of column diameter, d_{col} , for diameters from 40 to 152 mm, pulse amplitude, A , and frequency, f , fractional plate free area, α , plate spacing, h , hole diameter, d_o ,

and continuous phase viscosity, μ_c , considering wide ranges of these values. ρ_c is the continuous phase density. a_1 , a_2 and C_D are coefficients which assume the values of 0.0290, 0.0088 and 0.6, respectively. α is calculated by Eq. (10) [29], where d_p is the pitch of holes on plate:

$$\alpha = \frac{\pi d_o^2}{\sqrt{12} d_p^2} \quad (10)$$

The dispersed phase axial mixing coefficient was estimated by the Miyachi and Oya [49] correlation developed from axial mixing studies in pulsed sieve-plate columns:

$$E_d = \frac{d_o A f h^{2/3}}{\alpha d_{col}^{2/3}} \left(1 + \frac{v_d}{2A f \phi}\right) \phi \quad (11)$$

2.2. Conventional resistances in series model

To identify the limiting step on the extraction process, it was decided to compare the experimental values of the overall mass transfer coefficient for copper extraction from an aqueous to an organic phase, K_c , with the ones calculated by the conventional resistances in series model, which is supported by the two-film theory [50]. This model assumes that the process is only diffusion controlled. Therefore, K_c can be calculated as follows:

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{1}{m k_d} \quad (12)$$

where m represents the copper distribution ratio between the aqueous and the organic phases at the equilibrium, obtained by the following equation:

$$m = \frac{c_d}{c_c} \quad (13)$$

k_c and k_d denote, respectively, the local mass transfer coefficients in the continuous phase aqueous film and in the dispersed phase organic film, determined from the Kumar and Hartland [51] correlations, for pulsed sieve-plate columns:

$$\frac{Sh_c / (1 - \phi) - Sh_{c,rigid}}{Sh_{c,\infty} - Sh_c / (1 - \phi)} = 5.26 \times 10^{-2} Re^{1/3} + 6.59 \times 10^{-2} Re^{1/4} \times Sc_c^{1/3} \left(\frac{v_{slip} \mu_c}{\sigma}\right)^{1/3} \times \frac{1}{1 + \kappa^{1.1}} \left[1 + C_1 \left\{\frac{\varepsilon_D}{g} \left(\frac{\rho_c}{g\sigma}\right)^{1/4}\right\}^{n_1}\right] \quad (14)$$

$$Sh_d = 17.7 + \frac{3.19 \times 10^{-3} (Re Sc_d^{1/3})^{1.7}}{1 + 1.43 \times 10^{-2} (Re Sc_d^{1/3})^{0.7}} \left(\frac{\rho_d}{\rho_c}\right)^{2/3} \frac{1}{1 + \kappa^{2/3}} \times \left[1 + C_2 \left\{\frac{\varepsilon_D}{g} \left(\frac{\rho_c}{g\sigma}\right)^{1/4}\right\}^{n_2}\right] \quad (15)$$

In these expressions, Sh_c and Sh_d represent the continuous and the dispersed phases Sherwood numbers, respectively, obtained by the following equations:

$$Sh_c = \frac{k_c d_{32}}{D_c} \quad (16)$$

$$Sh_d = \frac{k_d d_{32}}{D_d} \quad (17)$$

where D_c and D_d represent the copper diffusivities in the continuous and in the dispersed phases. D_c denotes the diffusivity of the cupric tetrammine complex in the aqueous phase, which

was estimated to be about $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [52]. D_d is the diffusivity of CuR_2 complex in the organic phase and was estimated to be $3.96 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ by the Wilke–Chang equation [53]. The molar volume of such complex was determined by using the Le Bas method [54] and assumes the value of $701 \text{ cm}^3 \text{ mol}^{-1}$.

$Sh_{c,rigid}$ is the continuous phase Sherwood number for rigid drop conditions, obtained by:

$$Sh_{c,rigid} = 2.43 + 0.775 Re^{1/2} Sc_c^{1/3} + 0.0103 Re Sc_c^{1/3} \quad (18)$$

where Re is the Reynolds number and Sc_c is the continuous phase Schmidt number:

$$Re = \frac{d_{32} v_{slip} \rho_c}{\mu_c} \quad (19)$$

$$Sc_c = \frac{\mu_c}{\rho_c D_c} \quad (20)$$

v_{slip} is the slip velocity, determined by:

$$v_{slip} = \frac{v_d}{\phi} + \frac{v_c}{1 - \phi} \quad (21)$$

$Sh_{c,\infty}$ corresponds to the upper limiting value of Sh_c , only for $Re \rightarrow \infty$, in order to cover the data for oscillating drops, and was obtained from:

$$Sh_{c,\infty} = C_3 + \frac{2}{\sqrt{\pi}} (Pe_c)^{1/2} \quad (22)$$

where C_3 is a constant which assumes the value of 50 and Pe_c represents the continuous phase Péclet number, calculated by:

$$Pe_c = \frac{d_{32} v_{slip}}{D_c} \quad (23)$$

And finally in Eq. (14), σ is the interfacial tension, g is the acceleration due to gravity, C_1 and n_1 are constants with values fixed at 4.33, for pulsed columns, and 1/3, respectively, κ is the viscosity ratio determined by Eq. (24) and ε_D is the power dissipation per unit mass obtained from Eq. (25) [55].

$$\kappa = \frac{\mu_d}{\mu_c} \quad (24)$$

$$\varepsilon_D = \frac{2\pi^2 (1 - \alpha^2)}{3h C_0^2 \alpha^2} (Af)^3 \quad (25)$$

μ_d represents the dispersed phase viscosity. The value of the coefficient C_0 is assumed to be 0.6.

In Eq. (15), Sc_d is the dispersed phase Schmidt number, calculated through Eq. (26), ρ_d is the dispersed phase density and C_2 and n_2 are constants which assume, respectively, the values of 4.33, for pulsed columns, and 1/3.

$$Sc_d = \frac{\mu_d}{\rho_d D_d} \quad (26)$$

3. Experimental

3.1. Reagents

The feed phase was a 0.2 kmol m^{-3} $(\text{NH}_4)_2\text{SO}_4$, 0.32 kmol m^{-3} NH_3 (pH 9.5) and $\approx 1.0 \text{ kg m}^{-3}$ copper aqueous solution. The aqueous phases were prepared using commercial grade reagents – $(\text{NH}_4)_2\text{SO}_4$, with 20.5% nitrogen, from Quimepec, NH_3 in solution at 25%, from Sameca, Produtos Químicos, S.A. and CuSO_4 (97% of purity) from Sociedade Magalhães & Magalhães, Lda. – and tap water – ionic conductivity of $6.5 \mu\text{S cm}^{-1}$, measured with a conductivity meter mod. DPM/03 Auto from ORM Instruments.

The organic phase contained 0.09 kmol m^{-3} of the extractant and the diluent Shellsol D-70, from Drogas Vigo (Portugal). The

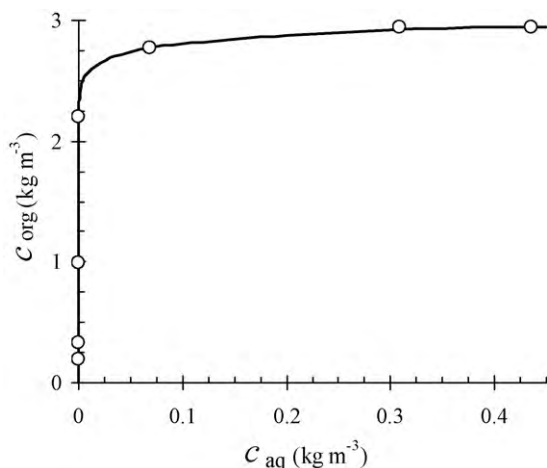


Fig. 1. Equilibrium partition data of copper extraction in the system $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{NH}_3/\text{LIX 84-I}$, at 20 °C. Initial aqueous phase: $\approx 1.0 \text{ kg m}^{-3}$ Cu, pH 9.5. Initial organic phase: 0.09 kmol m^{-3} LIX 84-I in Shellsol D-70.

extractant tested was the hydroxyoxime LIX 84-I, 2-hydroxy-5-nonylaceto-phenone oxime, which was supplied by Cognis (Ireland). The extractant and the diluent were used as received without any purification. After the first extraction experiments, the organic phase was continuously stripped using 150 kg m^{-3} H_2SO_4 and washed with tap water in a Kühni column (diameter = 15 cm; height = 6 m) and reused in the subsequent extraction runs. The concentration of copper in the organic phase after stripping was in the range of $0.36\text{--}0.59 \text{ kg m}^{-3}$.

3.2. Equilibrium experiments

To determine the copper concentration in the aqueous phase in equilibrium with the organic phase ($c_{c,eq}$ in Eqs. (2) and (3)), copper extraction equilibrium experiments were carried out in the $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{NH}_3/\text{LIX 84-I}$ system, with the same aqueous and organic phases used in the pulsed column extraction experiments.

The aqueous and the organic phases, with several volume ratios, were put into contact in an orbital shaker (Aralab Agitorb 160E) with temperature control during at least 4 h. After the two phases had settled, they were separated. All the experiments were carried out in duplicate. As a result of these equilibrium studies, the extraction isotherm shown in Fig. 1 was represented. As observed, the equilibrium of extraction was very favourable. The distribution ratio, which is defined as the ratio of the concentration of solute in the organic phase to the concentration of solute in the aqueous phase, was higher than 10^4 for the aqueous to organic phases volume ratios, in the range of 0.2–2. For these conditions, only vestiges of copper were detected in the raffinate (i.e., $0\text{--}3 \text{ mg m}^{-3}$ Cu). When the amount of copper in the organic phase was higher than 2.2 kg m^{-3} , the distribution ratio started to decrease and attained the value 6.7 under the loading conditions of the solvent (i.e., 2.94 kg m^{-3} Cu).

3.3. Pulsed sieve-plate column extraction experiments

The extraction experiments were performed at room temperature, between 18 and 20 °C, in a pilot plant using a pulsed sieve-plate column (PC75) in continuous operation. The arrangement of column and auxiliary equipment is shown diagrammatically in Fig. 2.

The effective height of the column was 6.15 m. The main column section comprised a 75 mm internal diameter glass tube, divided in

11 fragments of different heights, enclosing 118 perforated stainless steel plates of 73.4 mm in diameter and 2 mm in thickness. These plates, each drilled with 194 holes of 2.9 mm in diameter on a 5 mm triangular pitch, giving a nominal free area fraction of 0.305, were assembled in a stack, spaced 50 mm apart by means of three 6 mm diameter rods located on a 50 mm triangular pitch.

For each extraction run the column was first filled with the continuous aqueous phase. Then, the dispersed organic phase was introduced. The phases flowed countercurrently, the aqueous phase in descending direction and the organic phase in ascending direction. The column's phases inlet was made using the two stainless steel lobule pumps P1 and P2 (Tuthill Pump Group). The organic phase was introduced through a stainless steel distributor with 13 holes of 3 mm in diameter. The phases flow rates were set through the calibrated flowmeters F1 and F2 (GEC-Elliott 2000, Process Instruments, Ltd.).

Pulsation was applied using compressed air and a system composed of a temporizer and a pneumatic control valve steered by a solenoid valve (SV1) installed in the top of the column. This set allows generating rectangular wave pulses with independent control of the positive and the negative semiwaves. The extraction experiments were performed using symmetrical waves at pulsation frequencies between 1.0 and 1.7 Hz and pulse amplitudes between 2.3 and 2.5 cm. The horizontal cylindrical tank T2 allows damping the oscillations in the compressed air system.

When the steady-state conditions were reached, samples of the aqueous and organic phases and hold-up were collected from taps distributed along the column. Those conditions were attained after about 2–3 h, when the concentration of copper in the samples collected 47 cm above the organic phase distributor was constant. During the last 30 min of each experiment, photographs were also taken to measure the size of the organic phase drops.

To photograph the drops, plain surface perspex boxes were placed on three column zones: bottom ($z = 4.2 \text{ m}$), center ($z = 1.7 \text{ m}$) and top ($z = 0.3 \text{ m}$). These boxes were filled with water to remove the effects of the column wall curvature and of the difference between the media refractive indexes. The photographs were taken through the boxes by a Nikon F90X camera attached to a Nikon PB-6 bellows and a 60 mm Micro Nikkor objective lens. The illumination of the column section to be photographed was obtained by two 40 W lamps and a Nikon SB-26 flash with power manual adjustment. 24 photographs were taken (200–350 drops, on average), in every experiment, at each one of the referred three points. In addition, a 10 cm scale photograph was taken, in the same focusing conditions, for later calibration. The negatives were developed and subsequently scanned in an EPSON FilmScan200 device. The images were then treated using the KS100 image analysis software, from KONTRON Imaging System. On average, a 500–1000 drops measurement set was obtained in each experiment. Considering all the experiments, typical values of the drops diameters between 450 and $2700 \mu\text{m}$ have been found.

3.4. Extraction in a hollow fiber contactor

Non-dispersive solvent extraction was carried out using a Liqui-Cel® Extra-Flow 2.5" × 8" membrane contactor (Celgard, USA). The aqueous phase flowed through the lumens of the hollow fibers and the organic phase flowed through the shell side of the fibers. The membrane contactor was operated in batch mode, both phases being totally recycled. The aqueous and organic flow rates were kept at 18.1 and 19.6 L h^{-1} , respectively. The extraction was carried out in duplicate, at 20 °C. The characteristics of the hollow fibers and the details of the experimental procedure are published elsewhere [52].

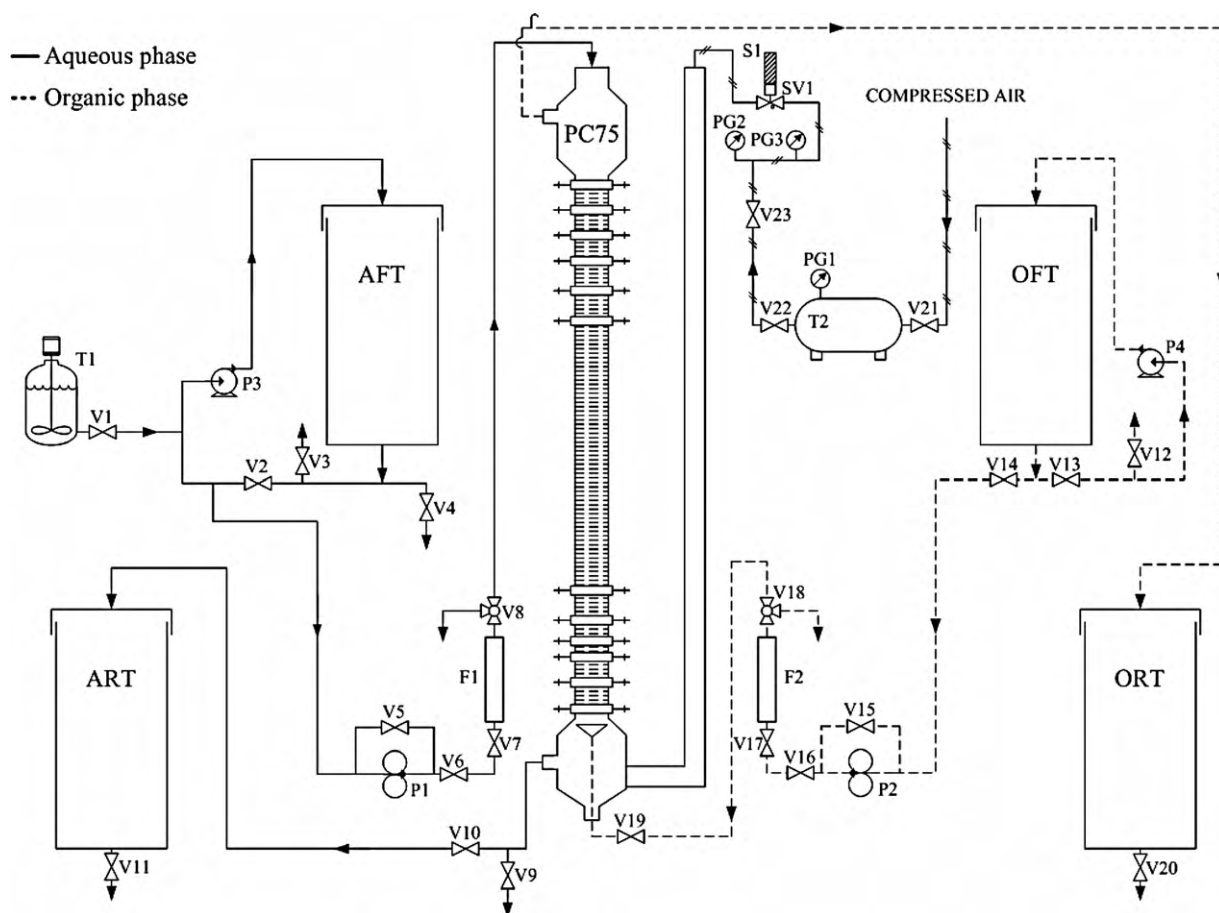


Fig. 2. Schematic flow diagram of the extraction pilot plant using a pulsed sieve-plate column. AFT – tank of the aqueous feed phase, ART – tank of the aqueous receiving phase, OFT – tank of the organic feed phase, ORT – tank of the organic receiving phase.

Table 1
Physical properties of the phases used in the system, at 20 °C.

| | ρ (kg m ⁻³) | μ ($\times 10^3$ kg m ⁻¹ s ⁻¹) | σ ($\times 10^3$ N m ⁻¹) |
|---------------|------------------------------|--|--|
| Aqueous phase | 1017 | 1.08 | 19.2 |
| Organic phase | 795 | 1.89 | – |

3.5. Chemical analysis and phases properties determination

The concentration of copper in both phases was determined by atomic absorption spectroscopy (Perkin Elmer, AAnalyst 200 and 1100 models for the aqueous and the organic phases, respectively) at 324.75 nm.

The pH value of the aqueous phase was measured on a Metrohm pH meter with a combined electrode, reference 6.0232.100 (pH 0–14; 0–80 °C; 3 M KCl).

The density of the aqueous and the organic phases was determined by the pycnometer method. The viscosity of both phases was measured with an Ubbelohde viscometer. Interfacial tension data were obtained with a Krüss tensiometer, model DSA10HS-Mk2. Table 1 lists the physical properties of the different phases.

4. Results and discussion

4.1. Extraction in a pulsed sieve-plate column

As previously mentioned, for constant phase flow rates there are three stable regimes of pulsed sieve-plate columns operation, depending on the pulse frequency and amplitude: mixer-settler, dispersion and emulsion [33]. The mixer-settler regime corre-

sponds to a pulse velocity, Af , smaller than 0.015 m s⁻¹. The dispersion regime is associated with a value of Af between 0.015 and 0.04 m s⁻¹ and for the emulsion regime Af is greater than 0.04 m s⁻¹ [56]. Nevertheless, there are several correlations for predicting regime transition in pulsed sieve-plate columns [33]. In the present work, the Kumar and Hartland [57] correlation has been tested:

$$(Af)_{tr} = 9.69 \times 10^{-3} \left(\frac{\sigma \Delta \rho^{1/4} \alpha}{\mu_d^{3/4}} \right)^{0.33} \quad (27)$$

where $\Delta \rho$ is the density difference between the two phases.

The column operates under the mixer-settler or the dispersion regimes when $Af < (Af)_{tr}$ and $Af \geq (Af)_{tr}$, respectively. The calculated $(Af)_{tr}$ was then found to be 0.013 m s⁻¹. Therefore, higher operating Af values were chosen to carry out the column tests.

Exploratory tests were carried out to examine the hydrodynamics and flooding conditions, varying the aqueous and organic phases flow rates and the pulse frequency and amplitude. For instance, the characteristics of one of the flooding points were: aqueous and organic flow rates of 60.9 and 28.1 L h⁻¹, respectively, and pulse velocity of 0.074 m s⁻¹.

The hold-up data obtained for different flow rates were used to calculate the slip velocity (Eq. (21)), which was related to the drop characteristic velocity concept, v_0 , through the Thornton equation [58]:

$$v_{slip} = v_0(1 - \phi) \quad (28)$$

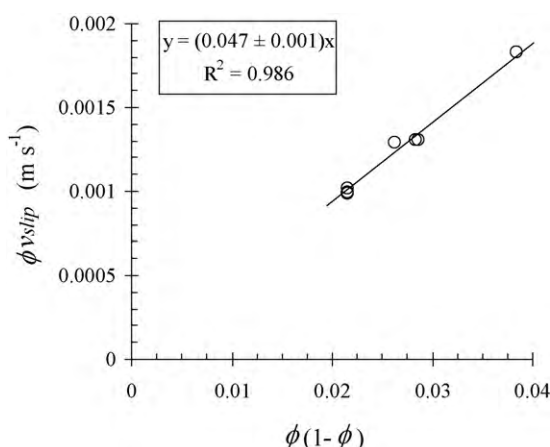


Fig. 3. Characteristic velocity plot for the system $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{NH}_3/\text{LIX 84-1}$. Initial aqueous phase: $\approx 1.0 \text{ kg m}^{-3}$ Cu, pH 9.5. Initial organic phase: 0.09 kmol m^{-3} LIX 84-1 in Shellsol D-70. Pulse velocity: 0.025 m s^{-1} .

Fig. 3 illustrates the plot of the results in this form for the present system using the pulse velocity of 0.025 m s^{-1} . As shown, there is a linear plot through the origin between the slip velocity and $(1 - \phi)$, thus demonstrating the validity of the Thornton expression. The characteristic velocity v_0 was determined to be 0.047 m s^{-1} from the slope of the straight line (Fig. 3). It is worth mentioning that the characteristic velocity is a very useful parameter to determine flooding velocities in the pulsed sieve-plate columns [33].

The operating conditions of the mass transfer experiments carried out for modelling are listed in Table 2. The efficiency of copper extraction for each run is also presented in Table 2.

The objective of the axial dispersion model application was to simulate the system concentration profiles, corresponding to the influence of the experimental conditions mentioned before on the solute extraction along the column. The values of the parameters used in the modelling are presented in Table 3. Regarding the parameter d_{32} , the correlation of Kumar and Hartland [59] was also applied for predicting the drop size, but the calculated values were considerably lower than the experimental ones, the standard mean deviation being 40%.

Figs. 4–6 illustrate the concentration profiles for the aqueous phase (a) and organic phase (b) and show the comparison between the experimental data and the simulated concentration profiles through the axial dispersion model. The agreement between the calculated and the experimental values was considered to be satisfactory. The percentage of extraction was predicted with a standard mean deviation of 3%.

In Fig. 4, the influence of the aqueous flow rate on the copper extraction was analysed, considering the E4 and E5 experiments, where the organic flow rate was maintained between 19.7 and 20.1 L h^{-1} for constant pulse velocity. Thus, the aqueous flow rate reduction from 29.5 to 21.4 L h^{-1} , that is, the decrease in the aqueous/organic phase volumetric ratio from 1.5 to 1.1 corresponded to an increase in the extraction efficiency. This may be expected, as the operating line moves far from the equilibrium line. Besides, as

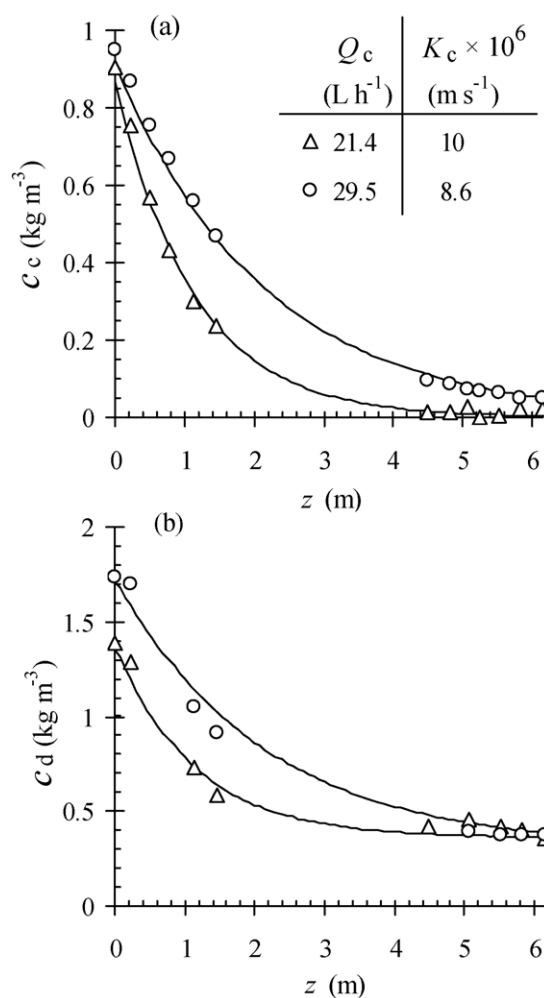


Fig. 4. Effect of aqueous flow rate on copper extraction with LIX 84-1: (a) aqueous profile and (b) organic profile; $Q_d = 19.7\text{--}20.1 \text{ L h}^{-1}$. Initial aqueous phase: $\approx 1.0 \text{ kg m}^{-3}$ Cu, pH 9.5. $Af = 0.035 \text{ m s}^{-1}$. Solid lines represent calculated profiles.

shown in Table 3, the dispersed phase drops diameter was lower in E5 experiment (smaller aqueous flow rate), which is equivalent to a superior specific interfacial area, since the variation of the dispersed phase hold-up was not significant (i.e., 0.027–0.029). The column performance was then increased with decreasing aqueous flow rate, the overall height of transfer unit $HTU_c (= v_c/(K_c \times a))$ being 2.06 and 1.00 m for Q_c equal to 29.5 and 21.4 L h^{-1} , respectively. The values of the overall mass transfer coefficient were found similar: $8.6\text{--}10 \times 10^{-6} \text{ m s}^{-1}$.

The copper concentration profiles using different organic flow rates are presented in Fig. 5, corresponding to the E1, E2 and E3 experiments. When the flow rate increased from 15.7 to 28.2 L h^{-1} , that is, the aqueous/organic phase volumetric ratio decreased from 1.4 to 0.7, the extraction was favoured. It was found that practically all the copper in the aqueous feed phase was removed, the extrac-

Table 2
Operating conditions of the column experiments and % extraction of copper.

| Run | $Q_c (\text{L h}^{-1})$ | $Q_d (\text{L h}^{-1})$ | Q_c/Q_d | $Af (\text{m s}^{-1})$ | $c_{c,0} (\text{kg m}^{-3})$ | $c_{c,f} (\text{kg m}^{-3})$ | $c_{d,0} (\text{kg m}^{-3})$ | $c_{d,f} (\text{kg m}^{-3})$ | Extraction (%) |
|-----|-------------------------|-------------------------|-----------|------------------------|------------------------------|------------------------------|------------------------------|------------------------------|----------------|
| E1 | 21.3 | 15.7 | 1.4 | 0.024 | 0.95 | 0.090 | 0.59 | 1.72 | 90.5 |
| E2 | 20.9 | 28.2 | 0.7 | 0.025 | 0.98 | 0.005 | 0.59 | 1.35 | 99.5 |
| E3 | 21.4 | 20.1 | 1.1 | 0.026 | 0.98 | 0.005 | 0.59 | 1.67 | 99.5 |
| E4 | 29.5 | 19.7 | 1.5 | 0.035 | 0.95 | 0.052 | 0.38 | 1.73 | 94.6 |
| E5 | 21.4 | 20.1 | 1.1 | 0.035 | 0.96 | 0.005 | 0.36 | 1.39 | 99.5 |
| E6 | 30.2 | 15.1 | 2.0 | 0.026 | 0.95 | 0.047 | 0.54 | 2.35 | 95.1 |

Table 3
Model parameters for each experiment.

| Run | Q_c (L h ⁻¹) | Q_d (L h ⁻¹) | Hold-up, ϕ | d_{32} ($\times 10^3$ m) | E_c ($\times 10^4$ m ² s ⁻¹) | E_d ($\times 10^6$ m ² s ⁻¹) |
|-----|----------------------------|----------------------------|-----------------|-----------------------------|--|--|
| E1 | 21.3 | 15.7 | 0.020 | 1.70 | 1.17 | 6.69 |
| E2 | 20.9 | 28.2 | 0.040 | 1.70 | 1.25 | 12.6 |
| E3 | 21.4 | 20.1 | 0.029 | 1.79 | 1.31 | 10.0 |
| E4 | 29.5 | 19.7 | 0.027 | 1.53 | 1.65 | 11.4 |
| E5 | 21.4 | 20.1 | 0.029 | 1.32 | 1.64 | 12.1 |
| E6 | 30.2 | 15.1 | 0.022 | 1.84 | 1.32 | 7.66 |

tion efficiency being 99.5% for 20.1–28.2 L h⁻¹ of organic flow rate (see Table 2). The column performance increased with the organic flow rate, given that the overall height of transfer unit was reduced from 2.23 to 1.44 and 0.93 m, when Q_d augmented from 15.7 to 20.1 and 28.2 L h⁻¹, respectively. In fact, this augment in the organic flow rate led to the increase in the specific interfacial area through the increase in the dispersed phase hold-up (i.e., it increased from 2.0% to 2.9% and 4.0%). Regarding the overall mass transfer coefficient, it practically did not change with organic flow rate keeping in the range of $(8.5\text{--}10) \times 10^{-6}$ m s⁻¹.

In Fig. 6, the effect of pulse velocity on the mass transfer performance is examined, considering the E3 and E5 experiments. Thus, for an aqueous/organic phase volumetric ratio of 1.1, the increase in the pulse frequency from 1.0 to 1.5 Hz maintaining the amplitude between 2.3 and 2.5 cm increased the extraction rate. In fact,

smaller drops are created for higher pulse frequencies and, consequently, the interfacial area is bigger. According to Table 3, the Sauter mean diameter of drops decreased 26%, when the pulse frequency increased from 1.0 to 1.5 Hz, and the dispersed phase hold-up did not change. Actually, the overall height of transfer unit was found to be reduced about 30% (i.e., from 1.44 to 1.00 m) under these agitation conditions. The overall mass transfer coefficient was practically constant, assuming values between 9.5 and 10×10^{-6} m s⁻¹.

4.2. Conventional resistances in series model

As stated before, having as the main objective the identification of the limiting step of extraction, it was decided to compare the experimental values of K_c with the ones predicted by the conven-

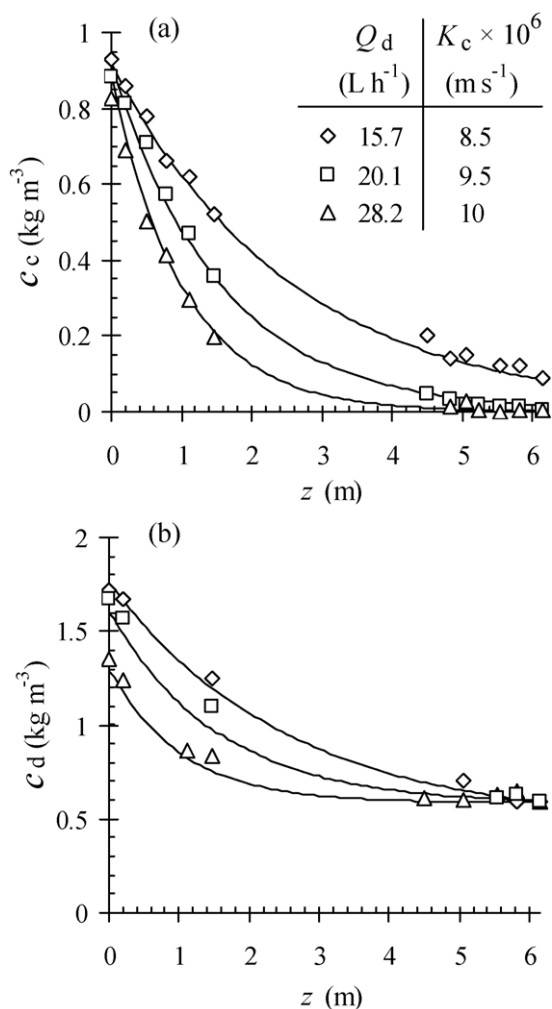


Fig. 5. Effect of organic flow rate on copper extraction with LIX 84-I: (a) aqueous profile and (b) organic profile; $Q_c = 20.9\text{--}21.4$ L h⁻¹. Initial aqueous phase: ≈ 1.0 kg m⁻³ Cu, pH 9.5. $Af = 0.024\text{--}0.026$ m s⁻¹. Solid lines represent calculated profiles.

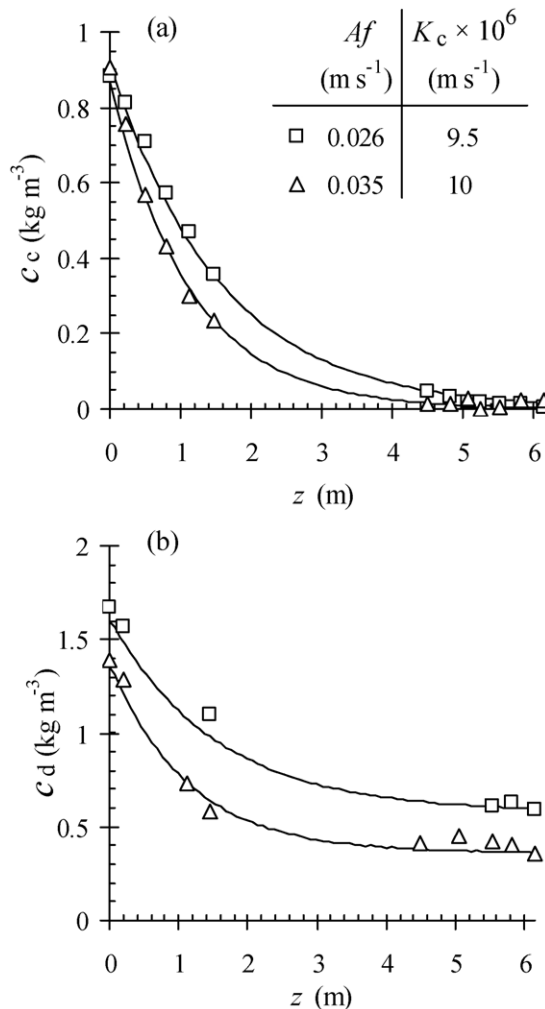


Fig. 6. Effect of pulse velocity on copper extraction with LIX 84-I: (a) aqueous profile and (b) organic profile. $Q_c = 21.4$ L h⁻¹; $Q_d = 20.1$ L h⁻¹. Initial aqueous phase: ≈ 1.0 kg m⁻³ Cu, pH 9.5. Solid lines represent calculated profiles. $f = 1.0$ and 1.5 Hz.

Table 4Overall mass transfer coefficient of copper extraction, K_c : experimental values and values calculated by the resistances in series model.

| Run | Experimental | | Continuous | Calculated | Chemical Reaction | Resistances (%) | | |
|-----|-------------------------------|-------------|---|---|---|---|-----------------------|------------------------------|
| | Q_c/Q_d (Lh ⁻¹) | HTU_c (m) | K_c ($\times 10^6$ m s ⁻¹) | k_c ($\times 10^5$ m s ⁻¹) | K_c ($\times 10^5$ m s ⁻¹) | k_r ($\times 10^5$ m s ⁻¹) | Continuous Δ_c | Chemical reaction Δ_r |
| E1 | 21.3/15.7 | 2.23 | 8.5 | 8.5 | 8.5 | 0.94 | 10.0 | 90.0 |
| E2 | 20.9/28.2 | 0.93 | 10 | 7.8 | 7.8 | 1.2 | 12.9 | 87.1 |
| E3 | 21.4/20.1 | 1.44 | 9.5 | 7.6 | 7.6 | 1.1 | 12.5 | 87.5 |
| E4 | 29.5/19.7 | 2.06 | 8.6 | 9.2 | 9.2 | 0.95 | 9.4 | 90.6 |
| E5 | 21.4/20.1 | 1.00 | 10 | 8.9 | 8.9 | 1.1 | 11.3 | 88.7 |
| E6 | 30.2/15.1 | 2.20 | 12 | 7.7 | 7.7 | 1.4 | 15.6 | 84.4 |

tional resistances in series model (Eq. (12)). Hence, the local mass transfer coefficients, k_c and k_d , for all the copper extraction experiments were evaluated by applying Eqs. (14) and (15) and the values were in the ranges of $(7.6\text{--}9.2) \times 10^{-5}$ and $(4.6\text{--}6.0) \times 10^{-5}$ m s⁻¹, respectively. Since the distribution ratio m was very large, being higher than 2×10^3 for the highest content of solute achieved in the solvent, the resistance due to the diffusion in the boundary organic layer was negligible (<0.1%). Thus, the value of K_c was determined from the local mass transfer coefficient k_c .

The experimental values of the overall mass transfer coefficient K_c and the calculated values of the local mass transfer coefficient k_c for all the copper extraction experiments are presented in Table 4. The experimental overall resistance to mass transfer was found to be higher than the one obtained by the conventional resistances in series model. This difference was determined and assigned to the chemical reaction contribution ($R_r = 1/k_r$) to the overall resistance to mass transfer. The relative contribution of each resistance to the global one, also indicated in Table 4, was obtained from the following expression:

$$\Delta_i = \frac{R_i}{R_c + R_r} \times 100, \quad i = c, r \quad (29)$$

The results presented in Table 4 indicate that the copper extraction from ammoniacal medium with LIX 84-I, in a pulsed sieve-plate column, was governed by a mixed regime, the resistance due to chemical reaction being predominant. The kinetic parameter k_r was found to be approximately constant (i.e., $\sim 1 \times 10^{-5}$ m s⁻¹). The contribution of chemical kinetics to the overall resistance to mass transfer was found to be in the range of 84–91%, whereas the resistance due to the diffusion in the boundary aqueous layer was then between 9.4% and 16%. The results also showed that the relative resistances were not significantly affected by the operating conditions, since the level of extractant/copper in the solvent did not vary in a great extension.

In an earlier study on copper extraction from an acidic solution with ACORGA M5640 to be published elsewhere, similar results regarding the importance of the chemical kinetics on the overall process of mass transfer were obtained. The pilot tests carried out in a pulsed sieve-plate column revealed that the resistance due to chemical reaction was in the range of 85–96%.

4.3. Extraction in a hollow fiber contactor

Non-dispersive solvent extraction was also carried out using a hollow fiber contactor to examine its performance and compare the results with the ones obtained with the pulsed sieve-plate column. Fig. 7 depicts the kinetics of copper extraction in the membrane process.

The overall mass transfer coefficient, K_{aq} , was evaluated from the experimental data by solving the appropriate mass balance equations for the aqueous and organic phases, as described with detail in a previous study [52]. As in the case of column tests, the

equilibrium data presented in Fig. 1 were considered for evaluating the overall mass transfer coefficient of the process.

As shown, the concentration of solute attained in the raffinate, after 2 h, was very low (i.e., 1.3 g m⁻³), the approach to equilibrium being 99.9%. The overall mass transfer coefficient, which was calculated on the basis of the total internal area of the fibers (i.e., 1.13 m²), was found to be 1.2×10^{-6} m s⁻¹. As the area per unit volume of contactor is 2.8×10^3 m⁻¹, the overall volume coefficient $K_{aq}a$ was evaluated to be 3.4×10^{-3} s⁻¹.

The relative resistances to mass transfer in the membrane process were also determined according to the same approach described in previous studies [25,52]. The contribution of chemical reaction to the overall resistance of mass transfer was found to be around 80%, which is in agreement with the results obtained with column tests.

Regarding the values of the specific interfacial area using the column, they were in the range of $70\text{--}140$ m⁻¹. The overall volume coefficient $K_c a$ was then found to be between 6.0×10^{-4} and 1.4×10^{-3} s⁻¹. The higher column performances were attained in runs E2 and E5, where Q_c/Q_d was $1/1.35$ and $1/0.93$ and A_f was 0.025 and 0.035 m s⁻¹, respectively. For these operating conditions, the overall height of transfer unit was $0.93\text{--}1.00$ m and the overall volume coefficient was $1.3\text{--}1.4 \times 10^{-3}$ s⁻¹.

Despite the relatively lower volume coefficient of mass transfer exhibited in the process carried out in the column, the results were very satisfactory. In fact, if the membrane process was operated at continuous level, a large ratio of feed flow rate to volume of equipment would be allowed, but also several hollow fiber modules in series would be necessary to attain a similar efficiency of extraction as the one achieved in column experiments E2 and E5.

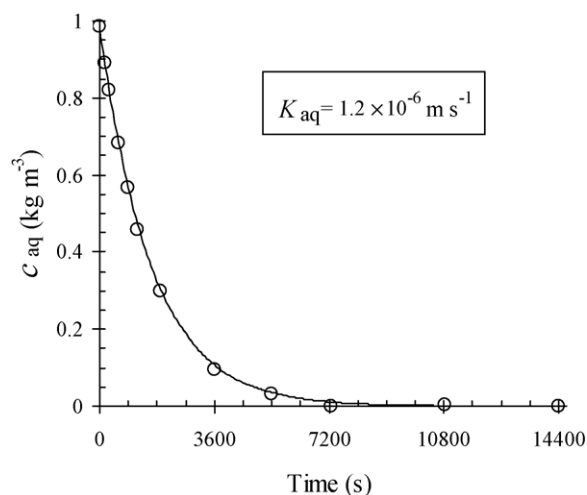


Fig. 7. Kinetics of copper extraction with LIX 84-I using a hollow fiber contactor. Aqueous phase volume: 2.0 L, organic phase volume: 0.85 L. Initial aqueous phase: 1.0 kg m⁻³ Cu, pH 9.5. Solid line represents calculated profile.

5. Conclusions

The results of copper extraction from ammoniacal medium (1.0 kg m^{-3} Cu, pH 9.5) with LIX 84-I, in a conventional pilot plant using a pulsed sieve-plate column, showed the technical viability of the operation, with efficiencies of removal between 90.5% and 99.5%.

The axial dispersion model allowed a very satisfactory prediction of the mass transfer in the column. The influence of several operating conditions on the efficiency of mass transfer was examined. The column performance was found to decrease with increasing aqueous flow rate and to increase with increasing organic flow rate and pulse velocity. The overall height of transfer unit based on the aqueous phase was determined to be in the range of 0.93–2.2 m. The overall mass transfer coefficient did not vary significantly under the conditions tested being between 9×10^{-6} and $1.2 \times 10^{-5} \text{ m s}^{-1}$.

The experimental values of the overall mass transfer coefficient were found to be lower than the ones obtained by the conventional resistances in series model. In the operating conditions tested, the extraction was governed by the chemical reaction and also by the diffusion in the boundary aqueous layer. The relative contribution of chemical kinetics to the overall resistance to mass transfer was found to be between 84% and 91%.

The extraction process was also carried out using a hollow fiber contactor. The overall volume coefficient of mass transfer was found to be slightly higher than the one obtained in the column tests.

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