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Application of a mathematical model for copper permeation from a Chilean mine water through a hollow fiber-type supported liquid membrane

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Abstract

The application of a mathematical model for copper permeation through a hollow fiber-type supported liquid membrane containing a salicylaldoxime (LIX-860) as the carrier was studied at 30 °C. The liquid membrane (the carrier in n-hexane) permitted an adequate copper diffusion when the pH of mine water was adjusted around a value of 2.0.

A quantitative analysis of the experimentally observed results is given. A discrete formulation was obtained through the application of the Crank–Nicholson method to a set of dimensionless differential equations, used to model the metal concentration drop along the fiber tube under certain boundary conditions. The model developed in this study considers a chemical reaction between the metal and the oximic carrier at the aqueous feed/membrane interphase. The application of a numerical model to evaluate the permeation of metal along the hollow fiber membrane is presented. In the model, the kinetic equations for extraction and stripping steps deduced in previous studies were introduced.

A fairly close agreement was obtained between the dimensionless average concentration of metal along the dimensionless axial distance of the fiber, calculated according to the model and the experimentally observed values. This fact was appreciated in runs carried out using an extractor with a variable number of fibers inside. It was found that the metal concentration drops in a similar way in all experiments. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper permeation; Liquid membrane; Mathematical model

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1. Introduction

Solvent extraction is a well known hydrometallurgical process for metal recovery from aqueous solutions, being highly selective and an effective enrichment method based on the right choice of an appropriate extractant molecule for the desired metal. In these days it is widely employed in the mining industry. However, and specifically from an operational point of view, this technique is far from being satisfactorily resolved and many difficulties are normally observed when conventional mixer-settler extractors are utilized.

Among others, the current solvent extraction process in mixer-settlers presents serious disadvantages. In particular, they require a big inventory of expensive solvents, considerable reactor size and rather long processing times [1,2].

Since the end of 1960s when liquid membranes were introduced by Li and Shrier [3], the recovery and separation of metals by this alternative technique has been investigated by a number of researchers, with a

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Nomenclature

$C_{\mathrm{H^+}}$	hydrogen ion concentration (mol/cm^3)
C_{HR}	carrier extractant concentration (mol/cm^3)
C_{MR}	metal complex concentration in the membrane (mol/cm^3)
$C_{\mathrm{MR_0}}$	metal ion concentration at the beginning of the tube in the membrane (mol/cm^3)
$C_{\mathrm{M}}^{\mathrm{F}}$	metal ion concentration of the metal ion (mol/cm^3)
$C_{\mathrm{M_0}}^{\mathrm{F}}$	metal ion concentration at the beginning the tube in the feed phase (mol/cm^3)
D_{E}	external diameter of fiber
D_{I}	internal diameter of fiber
D_{M}	diffussion coefficient of the metal ion in the feed phase (cm^2/s)
D_{MR}	diffussion coefficient of the metal complex in the membrane phase (cm^2/s)
f	dimensionless concentration in the feed phase ($C_{\mathrm{M}}^{\mathrm{F}}/C_{\mathrm{M_0}}^{\mathrm{F}}$)
f_{a}	average dimensionless concentration
g	dimensionless metal chelating agent concentration in the membrane $C_{\mathrm{MR}}/C_{\mathrm{M_0}}^{\mathrm{F}}$
h_1	radial size corresponding to the feed phase $\tilde{\lambda}/n_1$
h_2	radial size corresponding to the membrane phase $(1-\tilde{\lambda})/n_2$
$J_{\mathrm{M}}^{\mathrm{F}}$	molar flux of metal at the extraction stage (mol cm^2/s)
$J_{\mathrm{M}}^{\mathrm{S}}$	molar flux of metal in the stripping step (mol/cm^2 s)
k	axial size
$k_{\mathrm{Cu}R_2}$	(cm/s)
k_f	kinetic coefficient (cm^2/mol s)
k_r	inverse kinetic coefficient (cm^4/mol s)
K_1	equilibrium constant of metal-extractant complex formation
K_{HR}	adsorption equilibrium constant
L	length of the membrane housing shell (cm)
m	number of sub-intervals in which $[0, y_0]$ is divided
n_1	radial size corresponding to the feed phase
n_2	radial size corresponding to the membrane phase
N	number of fibers inside reactor
Q_{F}	volumetric velocity at the feed phase
r	radial distance from center tube (cm)
R	inner radius (cm)
S_{HR}	interphasal area ocuppied by mol HR (cm^2/mol)
u	dimensionless radius $r/\kappa R$
u_i	$i+1$-esime point determined by the division of radial interval $[0, \tilde{\lambda}]$ in n_1 subinterval ih_1
v_0	average radial velocity
v_{F}	aqueous volume
v_{R}	volume ocuppied by organic solvent inside the membrane wall
v_{S}	acid strip solution volume
$v^{\mathrm{F}}(r)$	flow velocity expression at the feed phase (cm/s)
$v^{\mathrm{S}}(r)$	flow velocity expression at the stripping phase
w_i	$i+1$-esime point determined by the division of radial interval $[\lambda, 1]$ in n_2 subinterval $\tilde{\lambda}+ih_2$
y	dimensionless axial distance along the tubular module
y_j	$j+1$-esime point determined by the division of axial interval $[0, Y_0]$ in m subinterval kj
Y_0	maximal length
z	axial distance along tubular module L

Greek letters

ϵ	porosity
κ	rate between the outside radius of the tubular membrane and the glass shell radius
κR	outside radius of tubular membrane (cm)
λ	rate between the inside radius of the tubular membrane and the glass shell radius
$\tilde{\lambda}$	rate between the inside radius and the outside radius of the tubular membrane λ/κ
λR	inside radius of tubular membrane (cm)

wide variety of carrier compounds incorporated into the membrane [4–10].

Particularly, the application of a membrane extractor made of hollow fibers as microporous solid support has been specially and succesfully employed for recovery of metallic ions from dilute aqueous solutions and for removal of pollutants from wastewater. These facts let us predict that this technique will be fully competitive with other conventional separation processes such as ion exchange and liquid–liquid extraction using current mixer-settler reactors [11–14].

As part of a continuing study for applying liquid membranes for recovery and concentration of metal ions from dilute mine waters, we have been interested in studying the transport of copper through hollow fiber-type solid supported liquid membranes.

A number of mathematical models have been proposed in order to explain the mechanism of metal permeation through liquid membranes [15–27]. Among them, particularly important due to its contribution to the comprehension of metal permeation through liquid membranes, the work of Kim and Stroeve stands out. This relate to mass transfer in separation reactors based on hollow fibers and facilitated transport of metals in heterogeneous media [15,16], the studies of Way et al. and Noble on facilitated transport membranes including analysis of shape factors and two-dimensional permeate, and lastly a solution given for a fluid flowing in plug flow through a reactive tube [17–19]. Danesi et al. have studied the permeation of metal ions through a hollow fiber supported liquid membrane using different extractor module arrangements. Danesi has also presented a simplified model for the coupled transport of metal ions through a hollow fiber-type supported liquid membrane given a simple model from a fluid flowing under a plug flow [20,21]. Many of these models consider analytical solutions under ideal steady-state conditions, assuming that contributions due to interfacial chemical reaction and aqueous film diffusion are negligible. Other groups of experimental data treatment analysis are concerned with the determination of facilitated or coupled transport parameters. The right modeling of metal transport in the membrane is the necessary tool for designing and scaling-up an industrial application of a membrane-based process.

In former reports we have attempted to elucidate the metal permeation mechanism, using an heterogeneous interfacial reaction model which considers interfacial adsorption of an extractant at the interface between the phases [28,29]. In another work we have attempted to give an explanation of the experimental results of copper extraction by a diffusion model which predicts that the extraction chemical reaction would occur at the interface of the liquid membrane [30,31]. Undoubtedly, the right selection of extractant and stripping agent was found to be the key factor in determining an effective system for the recovery of metals.

In previous papers we communicated the application of a hollow fiber-type solid supported liquid membrane process to the selective recovery and enrichment of copper from a Chilean mine water [32]. Using a relatively low concentration of the carrier (LIX-860, a commercial salicylaldoximic extractant) it was observed as a remarkable transport and concentration of copper ions from the feed donor solution toward the strip liquor. The transport of metal from the feed solution to the membrane was influenced predominantly by the extractant content of the organic film. On the other hand, the stripping flux of copper from the membrane to the receiving solution depended slightly on the concentration of sulfuric acid in the back-extraction solution. In spite of the content of feed solution, no traces of Fe, Al, Mo and As were detected in the resulting copper strip product solution which indicates the feasibility of separation and selective enrichment of metals using a membrane-based extractor. In another paper we have reported the effective separation of Cu(II) and Mo(VI) from a waste mine water using this membrane extraction system [33].

In this paper, we present in detail a quantitative analysis of the experimental results observed in those studies. The application of a numerical model to evaluate the permeation of metal along the hollow fiber membrane is presented. This model has been derived from other analogue models found in the literature. However, we have modified it by introducing the correspondent kinetic equations for extraction and stripping steps deduced in our former studies [28,29]. The discrete formulation of a mathematical model was obtained through the application of the Crank–Nicholson method, to the set of dimensionless differential equations that model the metal concentration drop along the fiber tube, under certain boundary conditions [34]. Extraction and back-extraction chemical equilibria-type considerations as well as eventual limitations to the extraction reaction rate are taken into account to explain the overall transport of copper ions.

The observed experimental results were compared with previously determined values according to a mathematical model for a simple extractor. Under steady-state conditions, mass balance equations are established for feed, membrane and receiving phases for very precise boundary conditions. Close agreement was obtained between the calculated and the experimentally observed values.

The final purpose of this contribution on the modeling of a chemically active liquid membrane is to study the applicability of the numerical solution proposed to solve the mathematical model, which is concerned with the copper transport in a hollow fiber-type solid supported liquid membrane.

2. Experimental procedure

2.1. Reagents and membrane

The hydrophobic organic phase forming the liquid membrane was immobilized within the pores of a poly-tetrafluoroethylene hollow fiber, kindly supplied by Japan Gore-Tex, inserted in a glass shell. In Table 1 some characteristics of the fibers are shown. The technical specifications of the extractor have been described in previous papers [31,32]. LIX-860 (5-dodecylsalicylaldoxime) was used as a carrier extractant dissolved in *n*-hexane of commercial GR grade as a diluent. The metal donor solution was a cupric mine water of El Teniente Mine, Codelco, Chile, naturally generated by lixiviation and bioleaching of copper ores from the Andes Mountains. It is an acid solution whose pH average is 3.0 and normally contains around 1 g/l Cu(II), 0.5 g/l Fe, 0.3 g/l Al(III), minor quantities of As, Mo and other metals. Concentrated sulfuric acid solutions were used as metal-acceptor stripping agents.

Table 1
Characteristics of hollow fiber

Porosity (%)	60
Maximum pore size (μm)	2.0
Inner diameter (mm)	0.8
Outer diameter (mm)	1.8
Wall thickness (mm)	0.5

2.2. Permeation measurements

Masterflex peristaltic microtube pumps were used to make the phases circulate through the fibers. First of all, the organic solution was pumped to the extractor in order to impregnate the pore structure of the fibers which was rapidly achieved due to the hydrophobic character of the fibers. After impregnation of the hollow fibers, the feed solution and acid strip aqueous phase were fed countercurrently along the inner and outer sides of the hollow fibers, respectively, for 3 h. The volumetric flow rates of feed and stripping aqueous solution were indicated in a former paper [29]. The concentration of metal ions was determined by atomic absorption spectrophotometry in a GBC-902 apparatus and by capillary ion analysis in CIA-Waters Millipore equipment, once equilibrium was attained.

2.3. Mathematical modeling

Assuming fully developed laminar flow, the Newtonian fluid of the feed and strip solution streams contact the reactive membrane part. The active chelation agent is constrained within the pores of the porous membrane by capillary forces. As the fluids flow along the reactive section of the membrane, metal ions diffuse through the boundary and react with the chelation acid at the interface between the aqueous and organic membrane phase. The chelate complex formed by the reaction, diffuses defined through the membrane phase and the stripping reaction occurs at the interface on the other side of the membrane. In Fig. 1 a longitudinal profile of metal permeation system is shown.

2.4. Continuous problem

The mass conservation equations for steady state and the associated conditions using cylindric coordinates give us the following equations.

(i) Feed phase: $0 \leq r \leq \lambda R$, $0 \leq z \leq L$.

$$v^{\mathrm{F}}(r)\left(\frac{\partial C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial z}\right) = D_{\mathrm{M}}\left[\left(\frac{\partial^2 C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial r^2}\right) + \frac{1}{r}\left(\frac{\partial C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial r}\right)\right], \quad (1)$$

where $C_{\mathrm{M}}^{\mathrm{F}}(r,z)$ is the metal ion concentration, D_{M} the diffusion coefficient of the metal ion in

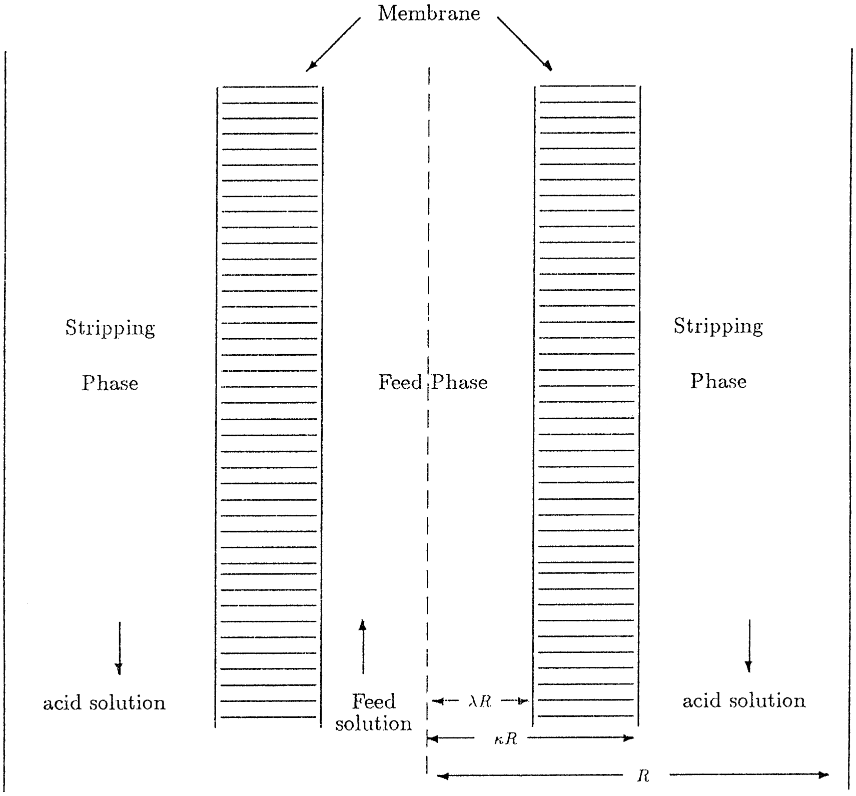

Fig. 1. Longitudinal profile of extraction system.

the feed phase, λR the inside radius of the tubular membrane, R the inner radius, L the length of the membrane housing shell and $v^F(r)$ is the flow velocity expression. The fluid velocity expression, for a Newtonian fluid flowing inside the tube, can be written as

$$v^F(r) = 2v_0\left(1 - \frac{r^2}{(\lambda R)^2}\right) \tag{2}$$

where v_0 is the average radial velocity. In this phase, axial diffusion is assumed to be negligible compared to axial convection in the feed solution streams. This assumption is valid when the Peclet number is greater than 100 [35].

(ii) Membrane phase: $\lambda R \leq r \leq \kappa R$.

$$D_{MR}\left[\left(\frac{\partial^2 C_{MR}(r,z)}{\partial r^2}\right) + \frac{1}{r}\left(\frac{\partial C_{MR}(r,z)}{\partial r}\right)\right] = 0, \tag{3}$$

where $C_{MR}(r, z)$ is metal complex concentration in the membrane, D_{MR} the diffusion coefficient of the metal complex in the membrane phase and κR is the outside radius of the tubular membrane. Here, there is no axial convection and the axial diffusion is negligible.

(iii) Stripping phase: $\kappa R \leq r \leq R$, $0 \leq z \leq L$.

$$v^S(r)\left(\frac{\partial C_M^S(r,z)}{\partial z}\right) = D_M^S\left[\left(\frac{\partial^2 C_M^S(r,z)}{\partial r^2}\right) + \frac{1}{r}\left(\frac{\partial C_M^S(r,z)}{\partial r}\right)\right], \tag{4}$$

where $C_M^S(r, z)$ is the metal ion concentration, D_M^S the diffusion coefficient of the metal ion in the stripping phase, κR the outside radius of the tubular membrane, R the inner radius, L the length of the membrane housing shell and $v^{\mathrm{S}}(r)$ is the flow velocity expression.

The analysis of this phase can be neglected due to the low transport of metal to the strip liquor. Then Eq. (4) was not considered.

(iv) Boundary conditions

- The boundary conditions for the feed phase are

$$\left(\frac{\partial C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial r}\right)|_{r=0}=0, \tag{5}$$

and

$$-D_{\mathrm{M}}\left(\frac{\partial C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial r}\right)|_{r=\lambda R}=J_{\mathrm{M}}^{\mathrm{F}}(C_{\mathrm{M}}^{\mathrm{F}})|r=\lambda R, \tag{6}$$

where the molar flux is the following function of $C_{\mathrm{M}}^{\mathrm{F}}$

$$J_{\mathrm{M}}^{\mathrm{F}}(C_{\mathrm{M}}^{\mathrm{F}})=\frac{a_1C_{\mathrm{M}}^{\mathrm{F}}}{(1+a_2+a_3C_{\mathrm{M}}^{\mathrm{F}})^2} \tag{7}$$

where the constants a_1, a_2, a_3 are given by [28,36] as follows:

$$a_1=k_fK_{\mathrm{HR}}^2K_1C_{\mathrm{HR}}^2C_{\mathrm{H}^+}^{-1} \tag{8}$$

$$a_2=K_{\mathrm{HR}}S_{\mathrm{HR}}C_{\mathrm{HR}} \tag{9}$$

$$a_3=K_{\mathrm{HR}}S_{\mathrm{HR}}K_1C_{\mathrm{HR}}C_{\mathrm{H}^+}^{-1} \tag{10}$$

- The boundary conditions for the membrane phase are the continuity of the flux at λR

$$-D_{\mathrm{MR}}\frac{\partial C_{\mathrm{MR}}(r,z)}{\partial r}|_{r=\lambda R}=-D_{\mathrm{M}}\frac{\partial C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{\partial r}|_{r=\lambda R} \tag{11}$$

On the outer edge $r=\kappa R$, we have the following condition on the molar flux

$$-D_{\mathrm{MR}}\left(\frac{\partial C_{\mathrm{MR}}(r,z)}{\partial r}\right)|_{r=\kappa R}=J_{\mathrm{M}}^{\mathrm{S}}(C_{\mathrm{MR}})|_{r=\kappa R} \tag{12}$$

where the molar flux is the following function of C_{MR}:

$$J_{\mathrm{M}}^{\mathrm{S}}(C_{\mathrm{MR}})=b_1C_{\mathrm{MR}} \tag{13}$$

where b_1 is defined by [36].

$$b_1=\frac{k_rk_{\mathrm{Cu}R_2}C_{\mathrm{H}^+}}{k_{\mathrm{Cu}R_2}+k_rC_{\mathrm{H}^+}} \tag{14}$$

Finally at $z=0$, we have

$$C_{\mathrm{M}}^{\mathrm{F}}(r,z)|_{z=0}=C_{\mathrm{M}_0}^{\mathrm{F}},\quad 0\le r\le \lambda R \tag{15}$$

In order to simplify the discussion and the analysis of the solution, it is convenient to use the dimensionless groups defined by Kim and Stroeve [16].

$$f=\frac{C_{\mathrm{M}}^{\mathrm{F}}(r,z)}{C_{\mathrm{M}_0}^{\mathrm{F}}} \tag{16}$$

$$u=\frac{r}{\kappa R} \tag{17}$$

$$y_0=\frac{LD_{\mathrm{M}}}{2v_0(\kappa R)^2} \tag{18}$$

$$y=\frac{zD_{\mathrm{M}}}{2v_0(\kappa R)^2} \tag{19}$$

$$g=\frac{C_{\mathrm{MR}}(r,z)}{C_{\mathrm{M}_0}^{\mathrm{F}}} \tag{20}$$

$$\tilde{\lambda}=\frac{\lambda}{\kappa} \tag{21}$$

where f is the dimensionless concentration, u the dimensionless radius, y the dimensionless axial distance along the tubular module, $0\le y\le y_0$ and g is the dimensionless metal chelating agent concentration in the membrane. In accordance with this, the differential Eqs. (1) and (3) may be written as follows:

$$\left(1-\left(\frac{u}{\tilde{\lambda}}\right)^2\right)\frac{\partial f}{\partial y}=\frac{1}{u}\frac{\partial f}{\partial u}+\frac{\partial^2 f}{\partial u^2} \tag{22}$$

$$\frac{1}{u}\frac{\partial g}{\partial u}+\frac{\partial^2 g}{\partial u^2}=0, \tag{23}$$

being the boundary conditions

$$\frac{\partial f}{\partial u}|_{u=0}=0 \tag{24}$$

$$-\frac{\partial f}{\partial u}|_{u=\tilde{\lambda}}=\frac{\Phi_1 f}{(1+\Phi_2+\Phi_3 f)^2} \tag{25}$$

$$-\frac{\partial g}{\partial u}|_{u=\tilde{\lambda}}=\frac{\Phi_1 f}{(1+\Phi_2+\Phi_3 f)^2} \tag{26}$$

$$-\frac{\partial g}{\partial u}|_{u=1} = \Phi_4 g \tag{27}$$

$$f|_{(0,u)} = 1 \tag{28}$$

$$g|_{(0,u)} = \frac{C_{\mathrm{MR}_0}}{C^{\mathrm{F}}_{\mathrm{M}_0}} \tag{29}$$

where Φ_1, Φ_2, Φ_3 and Φ_4 were explained in a previous paper and defined as follows:

$$\Phi_1 = k_f K^2_{\mathrm{HR}} K_1 C^2_{\mathrm{HR}} C^{-1}_{\mathrm{H}^+} \left(\frac{R}{D_{\mathrm{M}}}\right) \tag{30}$$

$$\Phi_2 = K_{\mathrm{HR}} S_{\mathrm{HR}} C_{\mathrm{HR}} \tag{31}$$

$$\Phi_3 = K_{\mathrm{HR}} S_{\mathrm{HR}} K_1 C_{\mathrm{HR}} C^{-1}_{\mathrm{H}^+} C^{\mathrm{F}}_{\mathrm{M}_0} \tag{32}$$

$$\Phi_4 = \frac{k_r k_{\mathrm{Cu}R_2} C_{\mathrm{H}^+}(R/D_{\mathrm{MR}})}{k_{\mathrm{Cu}R_2} + k_r C_{\mathrm{H}^+}} \tag{33}$$

2.5. The discrete problem

To find a numerical solution for the dimensionless partial differential equations and their boundary conditions, we chose the Crank–Nicholson method which is an appropriate method since it is unconditionally stable. In this sense, a grid on the plane *YU* was constructed. For this, we chose two numbers n_1 and n_2, for the adimentional radial axe U which define two different radial sizes h_1 and h_2, corresponding to the feed phase and to the membrane phase respectively,

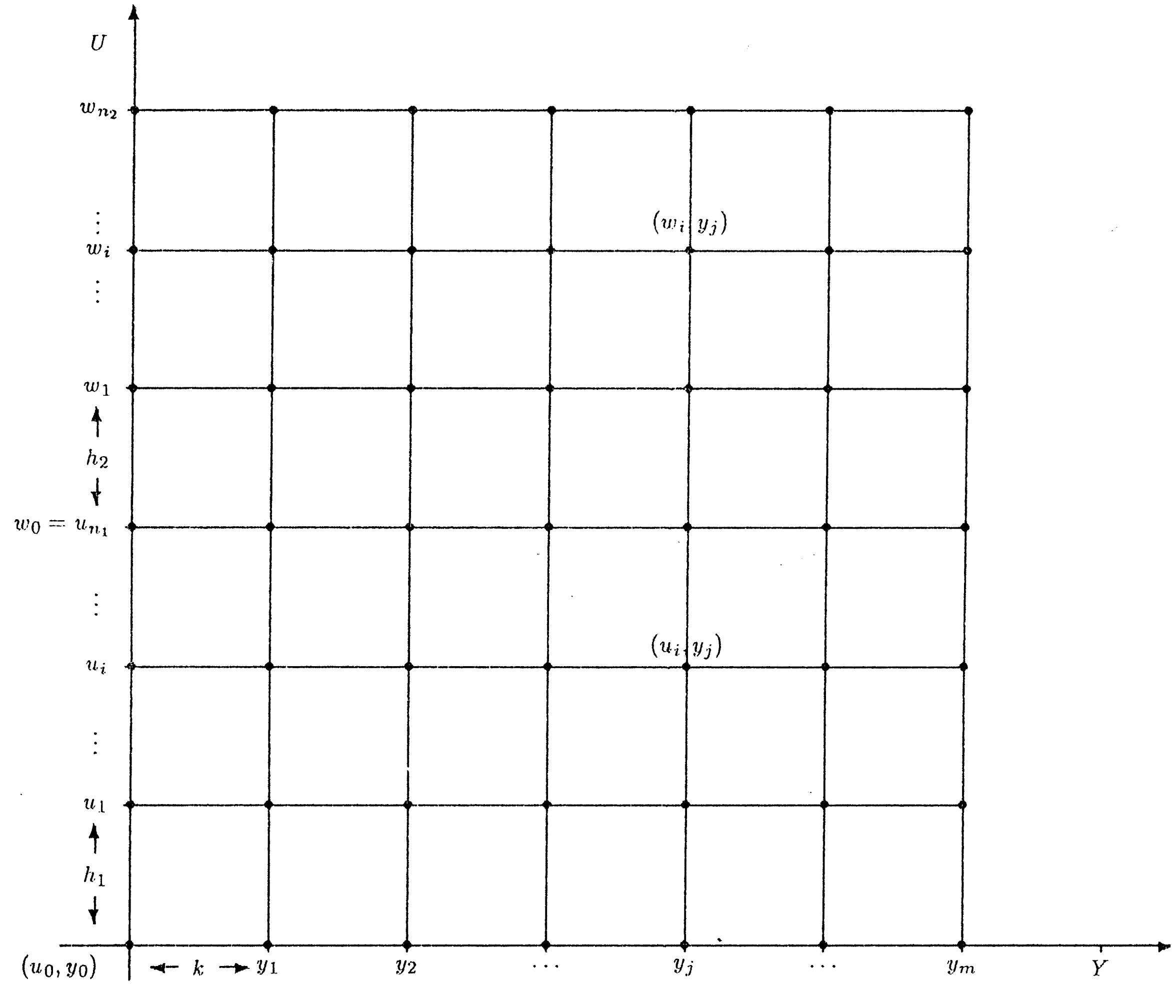

Fig. 2. Grids of points of discrete domain of function.

as follows:

$$h_1 = \frac{\tilde{\lambda}}{n_1}, \qquad h_2 = \frac{1-\tilde{\lambda}}{n_2}.$$

Also we chose a number m for the dimensionless axial axis Y, which defines the axial size k as follows:

$$k = \frac{Y_0}{m}$$

In this way, a net with $(n_1 + n_2 + 2) \times (m + 1)$ nodes was generated, such that

$$(u_i, y_j), \quad \text{where}\, u_i = ih_1, \quad i = 0, 1, \ldots, n_1 \quad \text{and} \quad y_j = jk, \quad j = 0, 1, \ldots, m.$$

$$(w_i, y_j), \quad \text{where}\, w_i = ih_2, \quad i = 0, 1, \ldots, n_2 \quad \text{and} \quad y_j = jk, \quad j = 0, 1, \ldots, m.$$

The grid is shown in Fig. 2. In each node, the partial derivatives were approximated according to the finite difference method and in each axial step the system of equations was solved using gaussian elimination.

Experimentally, the concentration of metal at the inlet and outlet of the extractor was measured. In this way, it is more appropriate to define the dimensionless radial average concentration of a flowing system given by:

$$f_\mathrm{a} = \frac{\int_0^{\tilde{\lambda}} v^\mathrm{F}(u) f(u, y) u \, \mathrm{d}u}{\int_0^{\tilde{\lambda}} v^\mathrm{F}(u) u \, \mathrm{d}u} \tag{34}$$

$$f_\mathrm{a} = \frac{4}{\tilde{\lambda}^2} \int_0^{\tilde{\lambda}} f(u, y) \left(1 - \left(\frac{u}{\tilde{\lambda}}\right)^2\right) u \, \mathrm{d}u. \tag{35}$$

3. Results and discussion

In order to obtain a numerical solution for the model, it is first necessary to define the corresponding expressions for the molar flux density at the extraction and the stripping interphases J_M^F and J_M^S, respectively, only the concentration of copper being kept as variable. The values of the constants were determined in a previous work [29]. Therefore, in order to define J_M^F and J_M^S, we only need to define the pH of the feed phase F, the concentration of the free oximic extractant [HR], the metal complex $[\mathrm{Cu}R_2]$ in the membrane phase and the corresponding sulfuric acid content at stripping phase.

In the experiments, at the stripping phase, a 300 g/l of free $\mathrm{H_2SO_4}$ solution was utilized. It can be considered that in the feed solution a pH value of 2.8 is kept constant because of the short residence time of this solution inside the fibers. [HR] was estimated from a mass balance and from the steochoimetry of the extraction reaction. Then, $[\mathrm{HR}]_\mathrm{free} = [\mathrm{HR}]_\mathrm{initial} - 2[\mathrm{Cu}R_2]$, where $[\mathrm{Cu}R_2]$ represents the complexed copper which is calculated from the initial content of this metal at feed and its concentration on raffinate and strip liquor at the time of measurement.

For instance, after 30 min of operation, enough to reach equilibrium conditions at steady-state, the following expression can be used:

$$[\mathrm{HR}]_\mathrm{free} = \frac{[\mathrm{HR}]_\mathrm{i} V_\mathrm{R} - 2([\mathrm{Cu}]_{\mathrm{F_i}} V_\mathrm{F} - ([\mathrm{Cu}]_{\mathrm{F}_{t=30}} V_\mathrm{F} + [\mathrm{Cu}]_{\mathrm{S}_{t=30}} V_\mathrm{S}))}{V_\mathrm{R}}$$

The subindex i denotes the initial states, whereas the subindex $t = 30$ denotes the state after 30 min of running the experiment. On the other side, V_F corresponds to the aqueous volume (50 ml in these experiments) being V_S the acid strip solution volume (35 ml) and V_R the volume occupied by the organic solvent inside the membrane wall (porous solid support). This volume

Table 2
Variation of concentration of species on content of extractant in impregnation solution

Oxime/*n*-hexane (% v/v)	$[\mathrm{HR}]_\mathrm{i}$ (mol/l)	$[\mathrm{Cu}]_{\mathrm{F}_{t=30}}$ (ppm)	$[\mathrm{Cu}]_{\mathrm{S}_{t=30}}$ (ppm)	$[\mathrm{HR}]_\mathrm{free}$ (mol/l)	$[\mathrm{Cu}R_2]$ (mol/l)
3	0.0868	884	71	0.0009	0.0859
6	0.1736	820	138	0.0655	0.1081
8	0.2314	761	223	0.1239	0.1075
10	0.2893	764	197	0.1621	0.1272

Table 3
Values of molar flux density constants and diffusivities [28–31,36]

k_f (cm^2/mol s)	5.93×10^{10}
K_f (cm^2/mol s)	0.664
K_{HR} (cm)	6.726×10^{-7}
S_{HR} (cm^2/mol)	6.3×10^{8}
k_r (cm^4/mol s)	0.0635
$K_{\mathrm{Cu}R_2}$ (cm/s)	7.93×10^{-5}
D_{M} (cm^2/s)	5×10^{-5}
D_{MR} (cm^2/s)	3×10^{-5}

can be calculated according to the next equation:

$$V_{\mathrm{R}} = \frac{\pi}{4}(D_{\mathrm{E}}^2 - D_{\mathrm{I}}^2)L\epsilon N, \qquad (36)$$

where L corresponds to the length of fibers, N the number of fibers inside the reactor, D_{E} and D_{I} the external and internal diameters of a fiber, respectively, and ϵ is the porosity factor.

In Table 2 a summary of experimentally observed values is presented, while the concentration of the extractant employed to impregnate the porous structure of fiber was changed. In these runs an extractor whose length was 230 mm was utilized, composed of six fibers and with a shell diameter of 10 mm, resulting in this case a $V_{\mathrm{R}} = 1.2139$ ml. The program for modeling was run using all the values taken from Tables 2 and 3 with a maximum dimensionless length Y of 0.155. Partitions of 100 radial steps by 100 axial steps (50 for feed phase and 50 for membrane) were used.

The values calculated according to the model were compared with the experimentally observed values, in different experiments using a diverse number of fibers inside reactors and under distinct concentrations of the extractant employed to impregnate the porous structure of fibers. These results are presented in Tables 4–6. The y values indicated in tables were calculated as follows:

$$y = \frac{ZD_{\mathrm{M}}}{2v_0(\kappa R)^2}, \qquad (37)$$

where v_0 is the average velocity inside each fiber, calculated from the volumetric velocity Q_{F} and from the number of fibers, N, is given as

$$v_0 = \frac{Q_{\mathrm{F}}}{\pi(D_{\mathrm{I}}/2)^2 N} \qquad (38)$$

where Z denotes the length of the fiber and all the values used in these experiments are found in Table 7.

The results are the values of the dimensionless concentration f_{a} with respect to a dimensionless length Y according to the function:

$$f_{\mathrm{a}}(y) = \mathrm{e}^{\alpha y}. \qquad (39)$$

These type of solutions correspond to the family of curves that describe the heat and mass transfer in our geometry. Fig. 3 shows the change of the dimensionless average concentration of metal f_{a} with the dimensionless axial distance along the tubular reactor module Y, calculated from the mathematical model proposed in this study. It can be observed that the drop of metal concentration is similar in all cases, no matter the number of fibers (membrane area). From this fact it can be concluded that although the perfomances of these extractors are similar, the greater the number of fibers inside the module, the shorter the extractor can be built, which means a simpler and cheaper module.

In the following figures we show the influence of changing the concentration of LIX-860—the salicylaldoximic carrier extractant—used to prepare the liquid membrane, on the drop of the average dimensionless metal concentration. Fig. 4 presents this effect when an extractor with six fibers is assumed in the model. In Figs. 5 and 6 the same effect can be appreciated when

Table 4
Experimental results observed for a 6% v/v oxime/n-hexane impregnation

Q_{F}	R4		R6		R10		R16	
	y	f_{a}	y	f_{a}	y	f_{a}	y	f_{a}
0.62	0.07	0.843	0.105	0.756	0.182	–	0.195	–
1.45	0.03	0.86	0.045	0.859	0.078	0.746	0.083	0.856
2.15	0.02	0.885	0.03	0.91	0.053	0.803	0.056	0.893
2.75	0.016	0.91	0.024	0.954	0.041	0.866	0.044	0.916
3.45	0.013	–	0.019	0.976	0.033	0.905	0.035	0.931

Table 5
Experimental results observed for a 8% v/v oxime/*n*-hexane impregnation

Q_F	$R4$		$R6$		$R10$		$R16$	
	y	f_a	y	f_a	y	f_a	y	f_a
0.62	0.07	0.797	0.105	0.721	0.182	–	0.195	–
1.45	0.03	0.844	0.045	0.852	0.078	0.727	0.083	0.796
2.15	0.02	0.860	0.03	0.881	0.053	0.778	0.056	0.859
2.75	0.016	0.891	0.024	0.931	0.041	0.808	0.044	0.882
3.45	0.013	–	0.019	0.953	0.033	0.860	0.035	0.929

Table 6
Experimental results observed for a 10% v/v oxime/*n*-hexane impregnation

Q_F	$R4$		$R6$		$R10$		$R16$	
	y	f_a	y	f_a	y	f_a	y	f_a
0.62	0.07	0.760	0.105	0.715	0.182	–	0.195	–
1.45	0.03	0.801	0.045	0.807	0.078	0.712	0.083	0.791
2.15	0.02	0.8760	0.03	0.833	0.053	0.756	0.056	0.842
2.75	0.016	0.892	0.024	0.886	0.041	0.823	0.044	0.880
3.45	0.013	–	0.019	0.945	0.033	0.837	0.035	0.899

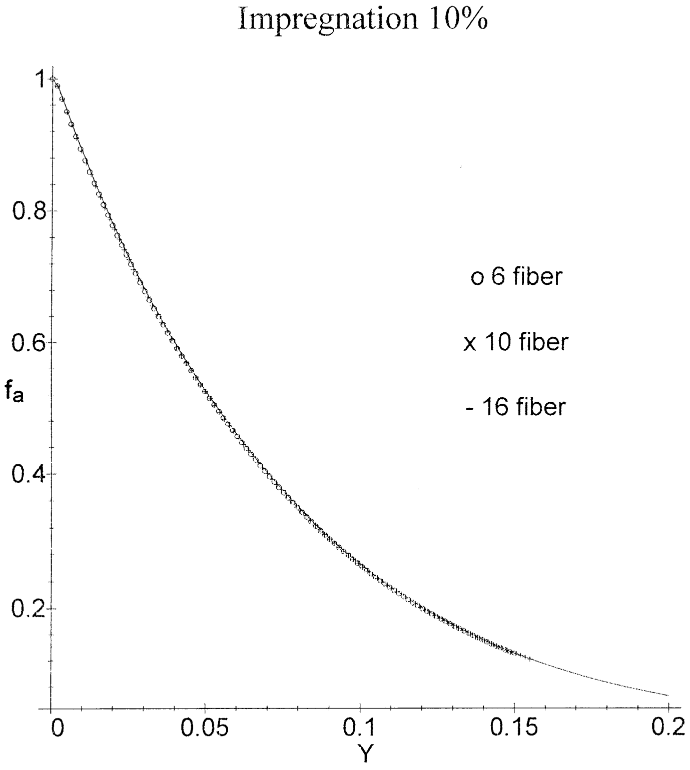

Fig. 3. Change of dimensionless average concentration of metal with the dimensionless axial distance of reactor. Impregnation 10% LIX-860/*n*-hexane for 6, 10 and 16 fibers.

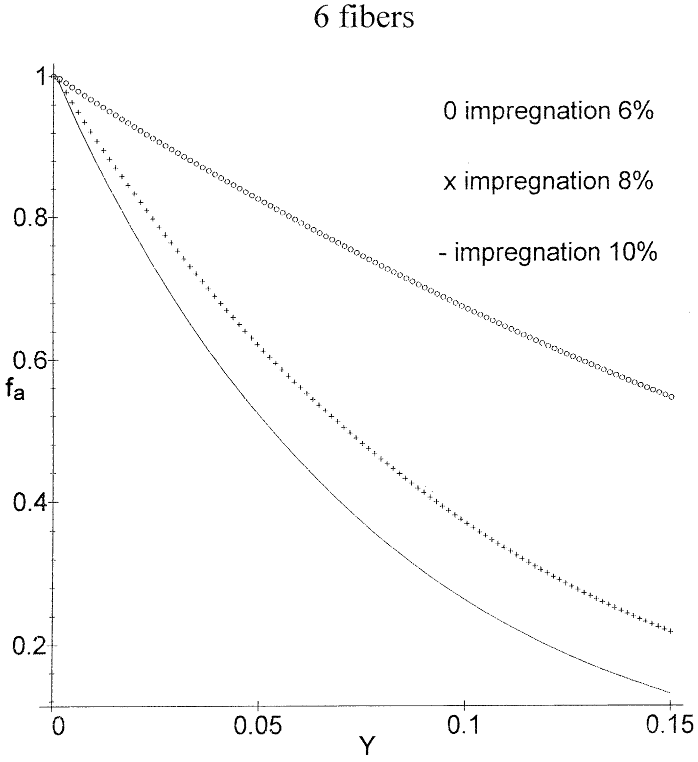

Fig. 4. Influence of carrier concentration in liquid membrane on the drop of average dimensionless metal concentration in a reactor with six fibers.

two different extractors were considered, the former with 10 fibers and the latter one including 16 fibers in modules.

These figures clearly show the positive effect of increasing the content of carrier extractant in the preparation of liquid membrane on the metal transfer. A higher metal concentration drop was determined when a higher concentration of extractant was used to impregnate the porous structure of hollow fibers, which also implies that in this case a shorter extractor can be employed for the same metal transport. This fact had been experimentally demonstrated before and was reported in previous papers [28–33]. These figures also show that a good prediction of the metal concentration drop can be achieved no matter the number of fibers used to build the extractor.

Figs. 7–9 show the comparison between the values of the average dimensionless metal concentration drop calculated by the model and the observed experimental value. In the three cases a same 10% v/v content of LIX-860 in n-hexane was used to impregnate the pores of fibers employed as solid support. A fairly good agreement is observed between the calculated values and the experimentally measured ones using these kind of extractors, which validates the model proposed in this study.

The discrete formulation obtained through the application of the Crank–Nicholson method to the set of dimensionless differential equations has modeled the metal concentration drop along the fiber tubes. As was assumed, the main drop of metal occurs in the first fraction of the extractor length, which means that a

Table 7
Specifications of reactors employed in this study

Reactor	Length L (cm)	Number of fibers N
$R4$	23	4
$R6$	23	6
$R10$	24	10
$R16$	14	16

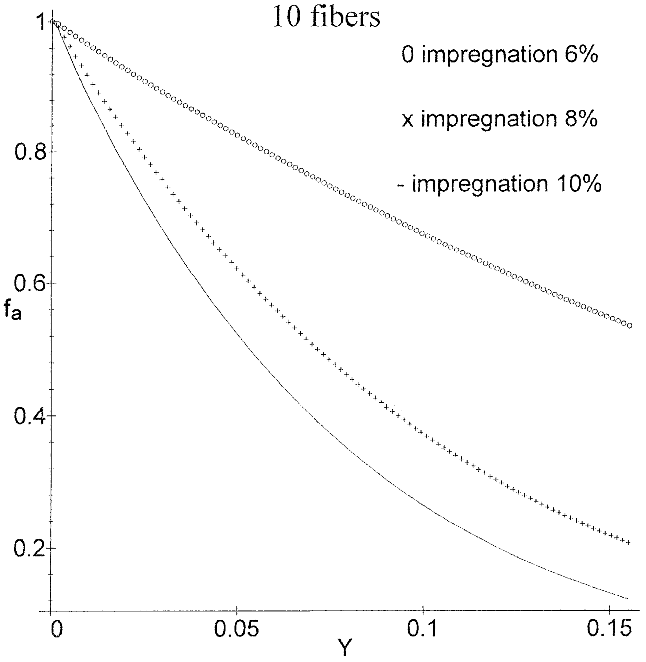

Fig. 5. Influence of carrier concentration in liquid membrane on the drop of average dimensionless metal concentration in a reactor with 10 fibers.

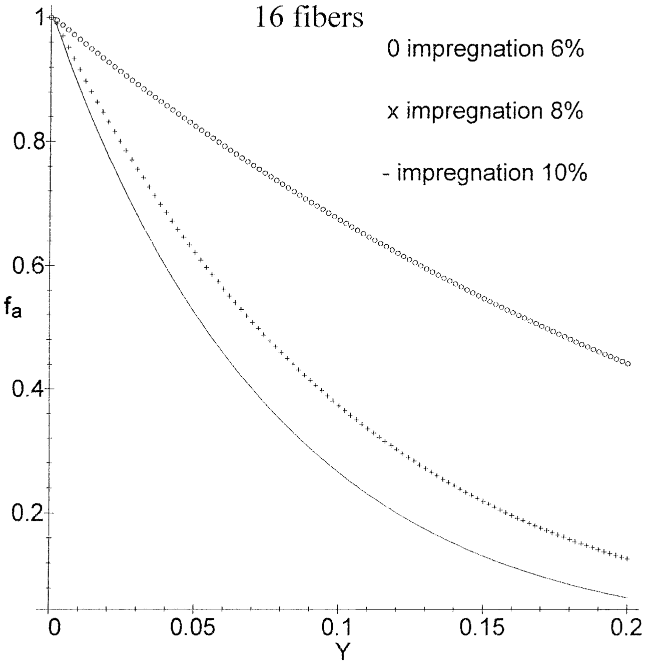

Fig. 6. Influence of carrier concentration in liquid membrane on the drop of average dimensionless metal concentration in a reactor with 16 fibers.

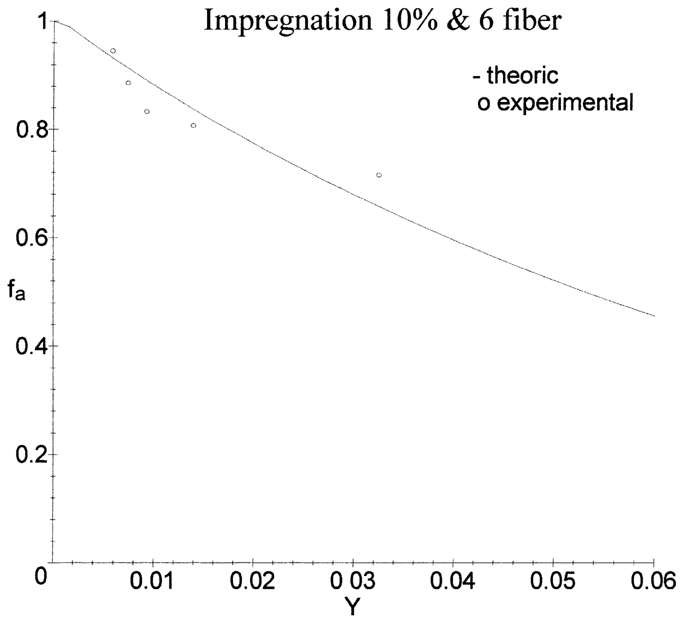

Fig. 7. Comparison of average dimensionless metal concentration drop calculated by the model and the experimentally observed. Reactor with six fibers impregnated with 10% v/v LIX-860/*n*-hexane.

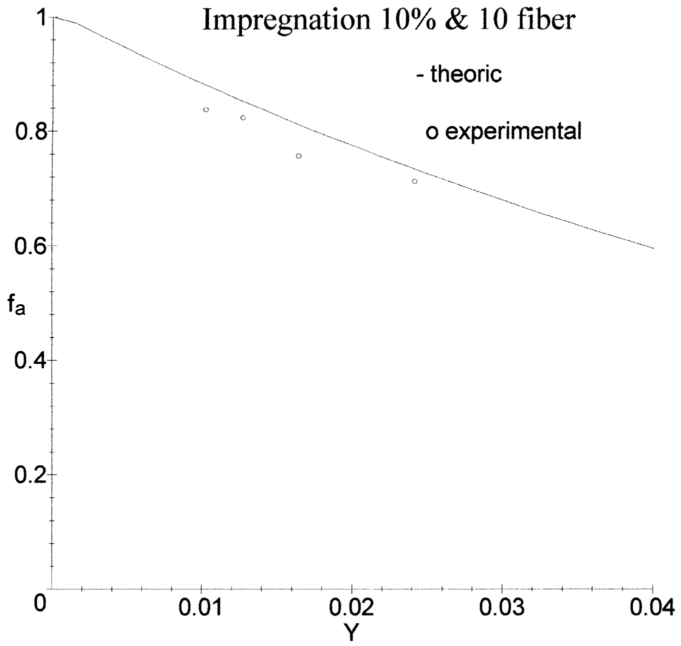

Fig. 8. Comparison of average dimensionless metal concentration drop calculated by the model and the experimentally observed. Reactor with 10 fibers impregnated with 10% v/v LIX-860/*n*-hexane.

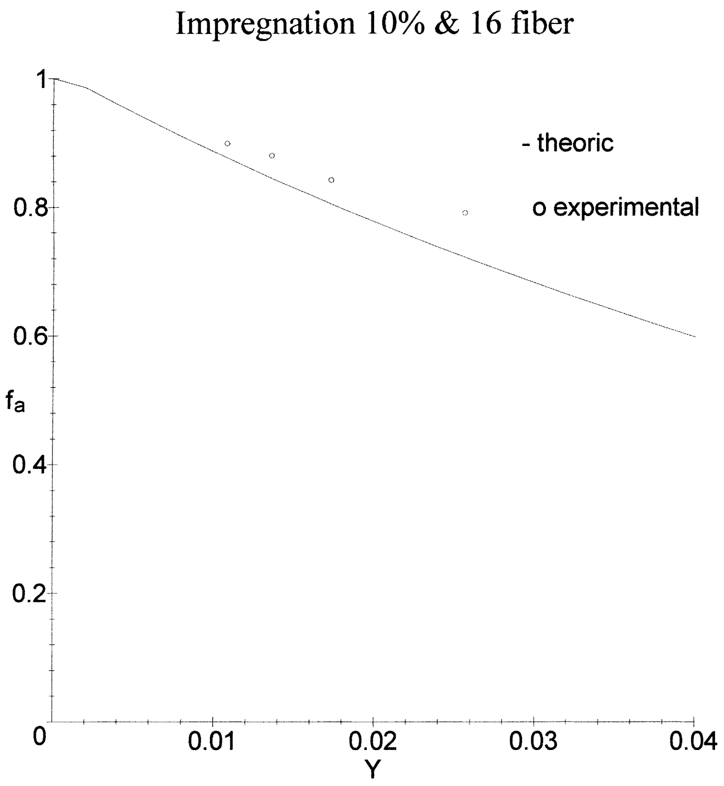

Fig. 9. Comparison of average dimensionless metal concentration drop calculated by the model and the experimentally observed. Reactor with 16 fibers impregnated with 10% v/v LIX-860/*n*-hexane.

most efficient extractor should be constructed with an important number of fibers inside a shorter shell. The analysis reported in this study includes the reaction at the aqueous feed phase/membrane interface which assumes a later diffusion of complexed metal species towards the stripping interface. In a further report we will analyse in detail the metal transport with chemical reaction that would occur in the back-extraction boundary.

However, for a given hollow fiber extraction module, the key for an efficient transport of metal is the right choice of the carrier extractant and the stripping solution.

4. Conclusions

The application of a mathematical model derived from other analogue models found in the literature, for copper permeation through a hollow fiber-type supported liquid membrane, containing a salicylaldoxime (LIX-860) as the carrier was studied at 30 °C.

The liquid membrane (LIX-860/*n*-hexane) used in these experiments permitted an adequate copper diffusion through the membrane when the pH of the feed solution was adjusted around a value of 2.0.

A quantitative analysis of the experimentally observed results is given. A discrete formulation was obtained through the application of the Crank–Nicholson method to a set of dimensionless differential equations used to model the metal concentration drop along the fiber tube, under certain boundary conditions.

The model developed in this study considers the chemical reaction between the metal and the carrier (the oximic extractant) at the aqueous/membrane interface. The application of a numerical model to evaluate the permeation of metal along the hollow fiber membrane is presented. This model has been derived from other analogue models found in literature. However, we have modified it by introducing the corresponding kinetic equations for the extraction and stripping steps deduced in our former studies.

A fairly close agreement was obtained between the dimensionless average concentration of metal along the dimensionless axial distance of the fiber, calculated according to the model proposed in this study and the experimentally observed value. This fact was observed in different experiments carried out using an extractor with a variable number of fibers inside it, finding that the metal concentration drops in a similar way in all runs.

The positive effect of increasing the content of carrier extractant to prepare the liquid membrane on the metal permeation extent was clearly verified. Both values, with the first one calculated according to the model and the experimentally observed numbers, show that a bigger metal concentration drop occurs when a higher concentration of carrier is employed to impregnate the porous structure of hollow fibers, which implies that a shorter extractor can be used for a similar metal transport.

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