Development and validation of a dynamic model for regeneration of passivating baths using membrane contactors

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A R T I C L E   I N F O
Article history:
Received 4 October 2010
Received in revised form 23 December 2010
Accepted 17 January 2011
Available online 25 January 2011

Keywords:
Passivating baths
Membrane contactors
Zinc separation
Emulsion pertraction technology
Facilitated transport

A B S T R A C T
This work aims at the development of a dynamic model for the mathematical description of facilitated transport separation processes carried out in membrane contactors where mass transport phenomena are coupled with chemical reactions. A general model that takes into account the description of all possible mass transport steps and interfacial chemical reactions is initially presented, allowing its application to a wide range of separation processes and operation conditions. The analysis of the specific system under study, regeneration of trivalent chromium spent passivating baths by removal of zinc using the emulsion pertraction technology, allowed to define several assumptions obtaining simplified models with minimum number of uncertain parameters and mathematical complexity. The final equations and parameters were validated with experimental data reported in a previous work (Urtiaga, Bringas, Mediavilla, & Ortiz, 2010).

1. Introduction
Membranes have gained an important place in separation technology and are used in a broad range of applications (Baker, 2004). In particular, the use of selective liquid membrane systems based on the principle of facilitated transport represents a promising alternative which excels the limitations of most conventional membrane-based separation processes since they have the capacity of combining extraction and concentration in a stripping solution into one single stage and thus have nonequilibrium mass-transfer characteristics and maximum driving force (Yang, Fane, & Soldenhoff, 2003). Hollow fiber membrane contactors have led to the integration of different configurations of liquid membranes creating new forms of separation processes such as the supported liquid membranes (SLM) (Urtiaga, Ortiz, Salazar, & Irabien, 1992), the non-dispersive solvent extraction (ND SX) (Samaniego, San Román, & Ortiz, 2007), the emulsion pertraction technology (EPT) (Bringas, San Román, & Ortiz, 2006; Ho & Poddar, 2001; Kl a s s e n & Jansen, 2001; Urtiaga, Bringas, Mediavilla, & Ortiz, 2010; Urtiaga, Gutiérrez, & Ortiz, 2009) and the hollow fiber renewal liquid membrane (HFRLM) (Ren, Zhang, Li, & Wei, 2009), which maximize the efficiency of the separation and concentration process as well as long-term stability (San Román, Bringas, Ibáñez, & Ortiz, 2010).

However, in spite of the known advantages and applications of liquid membrane separation processes in hollow fiber contactors, there are scarce examples of industrial application. The industrial implementation of a new technology requires a reliable mathematical model and parameters that serve for design, cost estimation and optimisation purposes allowing to accurately scale-up processes (de Gyves & Rodríguez de San Miguel, 1999). Therefore, the global aim of this work is to propose the methodology for the development of a dynamic model to describe the kinetics of facilitated transport based membrane separations. The proposed modelling strategy is illustrated by its application to a case of study that was experimentally analysed in a previous work (Urtiaga et al., 2010) dealing with the regeneration of trivalent chromium spent passivating baths by the EPT that combines the advantages of emulsion liquid membranes and supported liquid membranes.

2. Mathematical modelling of facilitated transport based membrane processes

Fig. 1 shows the flow diagram of the facilitated transport process named EPT that comprises three different units to be modelled: (i) a microporous hollow fiber membrane contactor (HFC) (Liqui-Cel® Extra-Flow 2.5 × 8, Membrana), (ii) the feed tank for homogenization and pH control of the passivating bath to be treated and (iii) the emulsion vessel that contains a pseudo-emulsion consisting of the organic phase formulated with a selective organic carrier and the stripping solution. The aqueous feed solution flowed through the inner side of the microporous hollow fiber membranes, and the emulsion flowed co-currently through the shell side of
the membrane contactor. The solute, exemplified by Zn\(^{2+}\) cation, is chemically transferred from the aqueous feed solution to the organic phase that is embedded in the pores of the hydrophobic hollow fibers. Next, it diffuses in the form of an organometallic complex ZnR\(_2\) to the inner side of the droplets where the stripping solution is situated. The solute is recovered from the internal aqueous phase after emulsion settling. Further details about the process can be found elsewhere (see Table 1) (Bringas et al., 2006; Urtiaga et al., 2010).

The mathematical description of the process shown in Fig. 1 requires the development of different submodels that are linked by the appropriate boundary conditions as shown in Fig. 2 (Bringas, San Román, Irabien, & Ortiz, 2009).

### 2.1. Submodel 1: membrane contactor

The following general assumptions are taken into account to mathematically describe the membrane contactor:

1. Pressure and temperature are assumed to be constant. Therefore the momentum and energy balances are not considered.
2. Aqueous solution is fed into the inner side of the fibers while the emulsion flows through the shell side of the contactor. As the hollow fibers are hydrophobic, the organic phase is embedded in the pores of the fibers which are considered free of aqueous droplets. The proper control of the pressures of the flowing phases guarantees the non-dispersive contact within the membrane contactor.
3. Each fiber is of identical specifications and can be modelled as a thin horizontal pipe of uniform diameter. Therefore, the mass balance equations in the membrane contactor are first derived from a small volume element and then integrated to cover the entire membrane length (Soni, Abildskov, Jonsson, & Gani, 2009).
4. Average and constant values of the membrane characteristics (pore size, porosity, thickness, interfacial area, etc.) are assumed.
5. The interfacial chemical reactions (extraction and back-extraction) are considered fast enough to reach equilibrium instantaneously.

The mathematical modelling of the membrane contactor consists of: (i) the characterization of the diffusive mass transport flux (submodel 1.1) and, (ii) the solute mass balances to the flowing phases (submodels 1.2 and 1.3).

#### 2.1.1. Submodel 1.1: diffusive mass transport flux

For the case study, Cyanex272 and sulphuric acid were used as selective extractant and stripping agent (Urtiaga et al., 2010). The extraction and back-extraction processes are described respectively by the following reversible reactions (Kanungo & Mohapatra, 1995):

\[
\begin{align*}
\text{Zn}^{2+}(a) + 2\text{RH}(o) & \rightleftharpoons k_{\text{EX}} \rightarrow \text{ZnR}_2(o) + 2\text{H}^+(a) \\
\text{ZnR}_2(o) + 2\text{H}^+(a) & \rightleftharpoons k_{\text{BEX}} \rightarrow \text{Zn}^{2+}(a) + 2\text{RH}(o)
\end{align*}
\]

where RH and ZnR\(_2\) are the free extractant and the organometallic complexes formed by reaction, respectively.

As shown in Fig. 3, several in-series steps are considered to describe the mass transfer of zinc ions from the spent bath to the stripping solution: (i) diffusion through the aqueous phase stagnant layer, (ii) interfacial extraction reaction (Eq. (1)), (iii) diffusion of the organic complex within the liquid membrane, (iv) diffusion through the organic phase stagnant layer and, (v) interfacial back-extraction reaction (Eq. (2)). On the other hand, free extractant and protons are counter–transported in a similar way.

The mass transport fluxes of zinc species through the feed phase stagnant layer, the liquid membrane and the organic phase stagnant layer are described according to Fick’s law as follows:

\[
\begin{align*}
J^{i}_{\text{Zn}^{2+}} &= k_{\text{f}}(i)(C_{\text{Zn}^{2+}} - C_{\text{Zn}^{2+}}) \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \\
J^{i}_{\text{m}} &= k_{\text{m}}(i)(C_{\text{Zn}^{2+}} - C_{\text{Zn}^{2+}}) \quad \forall i = \text{Zn} = \text{ZnR}_2, \text{RH} \\
J^{i}_{o} &= k_{\text{b}}(i)(C_{\text{Zn}^{2+}} - C_{\text{Zn}^{2+}}) \quad \forall i = \text{Zn}
\end{align*}
\]

where \(k_{\text{f}}, k_{\text{m}}\) and \(k_{\text{b}}\) are the individual mass transport coefficients. Assuming pseudo–steady state:

\[
\begin{align*}
|J^{i}_{\text{Zn}^{2+}}| &= \frac{1}{\alpha_{\text{EX}}^{i} \text{H}^+} |J^{m}_{\text{Zn}}| = \frac{1}{\alpha_{\text{EX}}^{i} \text{RH}} |J^{m}_{\text{Zn}}| = \frac{1}{\alpha_{\text{EX}}^{i} \text{Zn}} |J^{m}_{\text{Zn}}|
\end{align*}
\]

where \(\alpha_{\text{EX}}^{i}\) is the stoichiometric coefficient of species “i” in reaction “k”.

The interfacial chemical reactions are considered fast enough to reach equilibrium instantaneously (Ortiz, Galán, San Román, & Ibáñez, 2001). Thus, the species concentration at the organic–aqueous interfaces are obtained from the expressions of
Table 1

Values of the operation variables and model parameters used in the simulation runs.

<table>
<thead>
<tr>
<th>Operation variable</th>
<th>Model variable</th>
<th>Range of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influencing variables</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial pH of the spent passivation bath</td>
<td>pH</td>
<td>2-3</td>
</tr>
<tr>
<td>Initial [Zn] in the spent passivation bath</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial [Cyanex®272] in the organic solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial [H₂SO₄] in the stripping solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fixed variables</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flowrate of the aqueous feed solution</td>
<td>Fₚ</td>
<td>9 × 10⁻³ m³ h⁻¹</td>
</tr>
<tr>
<td>Flowrate of the organic phase</td>
<td>Fₚ</td>
<td>3.2 × 10⁻² m³ h⁻¹</td>
</tr>
<tr>
<td>Flowrate of the stripping solution</td>
<td>P</td>
<td>8 × 10⁻³ m³ h⁻¹</td>
</tr>
<tr>
<td>Initial [Zn] in the organic solution</td>
<td>Cₘ[Zn]</td>
<td>0</td>
</tr>
<tr>
<td>Initial [Zn] in the stripping solution</td>
<td>Cₘ[Zn]</td>
<td>0</td>
</tr>
<tr>
<td>Effective membrane area</td>
<td>A</td>
<td>1.24 m²</td>
</tr>
<tr>
<td>Effective length of the hollow fibers</td>
<td>L</td>
<td>0.15 m</td>
</tr>
<tr>
<td>Number of hollow fibers in the contactor</td>
<td>N</td>
<td>10,200</td>
</tr>
<tr>
<td>Membrane porosity</td>
<td>ε</td>
<td>0.4</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>δ</td>
<td>40 μm</td>
</tr>
<tr>
<td>Initial volume of feed solution in the tank</td>
<td>Vₚ</td>
<td>10⁻³ m³</td>
</tr>
<tr>
<td>Initial volume of emulsion in the tank</td>
<td>Vₑ[Emulsion]</td>
<td>10⁻³ m³</td>
</tr>
<tr>
<td>Effective volume of the fluid in the lumen side</td>
<td>Vₑ[Lumen]</td>
<td>6 × 10⁻⁵ m³</td>
</tr>
<tr>
<td>Effective volume of the fluid in the shell side</td>
<td>Vₑ[Shell]</td>
<td>2 × 10⁻⁴ m³</td>
</tr>
<tr>
<td>Emulsion volume ratio</td>
<td>Vₑ[Lumen]/Vₑ[Shell]</td>
<td>4/1</td>
</tr>
<tr>
<td>Time</td>
<td>t</td>
<td>3 h</td>
</tr>
<tr>
<td><strong>Model parameters (see Appendix A)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane mass transport coefficient of the organometallic complexes</td>
<td>kₚ[Zn]</td>
<td>2.95 × 10⁻⁴ m h⁻¹</td>
</tr>
<tr>
<td>Membrane mass transport coefficient of the selective extractant</td>
<td>kₑ[Zn]</td>
<td>4.46 × 10⁻⁴ m h⁻¹</td>
</tr>
<tr>
<td>Equilibrium parameter of the extraction reaction</td>
<td>kₑ[Zn]</td>
<td>2.79 × 10⁻⁴</td>
</tr>
<tr>
<td>Equilibrium parameter of the back-extraction reaction</td>
<td>kₑ[BEX]</td>
<td>3584</td>
</tr>
</tbody>
</table>

Fig. 1. Flow diagram of the EPT process.

Fig. 2. Model structure of EPT process.
Fig. 3. Model variables and detail of solute mass transport.
the equilibrium parameters of the extraction and back-extraction reactions described by a simple mass action law as follows:

\[ K_{eq}^j = \prod_i (C_i^{0})^{\theta_i} \quad \forall i = \text{Zn}^{2+}, \text{H}^+, \text{Zn}, \text{RH}; \]

\[ \forall j = o, s; \quad \forall k = \text{EX}, \text{BEX} \]  

(7)

2.1.2. Submodel 1.2: tube side flow model

The most accurate description of the tube side flow takes into account the axial and radial variation in the fluid properties by means of two-dimensional models (Alopeso & Pantelides, 1996). Nevertheless, the most extensive approach to the mathematical modelling of hollow fiber contactors is the assumption of ideal plug flow that neglects the concentration variations perpendicular to the bulk flow direction. As a result, only the concentration axial variation is taken into account obtaining a one-dimensional (1D) flow model (Bringas et al., 2009). Therefore, the solute mass balances in the aqueous feed solutions flowing through the tube side are as follows (see Fig. 3):

\[ \frac{\partial C_i}{\partial t} + \frac{F_o}{V_o} \frac{\partial C_i}{\partial z} = \mathcal{A}_i \mathcal{J}_{i, \text{m}} \quad \forall z; \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \]  

(8)

with boundary conditions

\[ C_i^0 (t = 0) = C_{i, \text{in}}^0 \quad \forall z; \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \]  

(9)

\[ C_i^0 (z = 0) = C_{i, \text{t,} \text{t}}^0 \quad \forall t; \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \]  

(10)

2.1.3. Submodel 1.3: shell side flow model

The emulsion flowing through the shell side consists of the organic and stripping phases. Therefore, the solute mass balances in both phases are expressed following the same hypothesis described above leading to the following equations (see Fig. 3):

\[ \frac{\partial C_i}{\partial t} + \frac{F_o}{V_o} \frac{\partial C_i}{\partial z} = \mathcal{A}_i \mathcal{J}_{i, \text{m}} - \mathcal{A}_i \mathcal{J}_{i, \text{m}}^{\text{m}} \quad \forall z; \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \]

(11)

\[ \frac{\partial C_i}{\partial t} + \frac{F_o}{V_o} \frac{\partial C_i}{\partial z} = \mathcal{A}_i \mathcal{J}_{i, \text{m}}^{\text{m}} \quad \forall z; \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \]

(12)

with boundary conditions

\[ C_i^0 (t = 0) = C_{i, \text{in}}^0 \quad \forall z; \quad \forall j = o, s; \quad \forall i = \text{Zn}^{2+}, \text{H}^+, \text{Zn}, \text{RH} \]  

(13)

\[ C_i^0 (z = 0) = C_{i, \text{t,} \text{t}}^0 \quad \forall t; \quad \forall j = o, s; \quad \forall i = \text{Zn}^{2+}, \text{H}^+, \text{Zn}, \text{RH} \]  

(14)

The first term on the left-hand side of Eqs. (8), (11) and (12) corresponds to solute accumulation while the second term, represents the convective transport along the tube length. The term on the right-hand side in Eqs. (8), (11) and (12) represents the diffusive transport of solute from the aqueous feed phase to the stripping solution through the liquid membrane.

2.2. Submodels 2 and 3: stirred tanks

The mass balances in the stirred tanks are developed under the assumption of ideal mixed flow (see Fig. 3).

2.2.1. Submodel 2: feed tank model

\[ \frac{d(V_o C_i^{\text{m}})}{dt} = F_o [C_i^{\text{Zn}^2+}(z = L) - C_i^{\text{Zn}^2+}] \quad \forall t \]

(15)

\[ C_i^{\text{Zn}^2+}(t = 0) = C_{i, \text{in}}^{\text{Zn}^2+} \]  

(16)

According to the extraction reaction (Eq. (1)), the extraction of zinc results in the release of protons into the feed solution affecting the extraction equilibrium and consequently the process kinetics. Therefore, the pH is kept constant in the feed tank by the controlled addition of a sodium hydroxide solution and thus, the proton concentration can be calculated as follows:

\[ C_i^{\text{H}^+} = 10^{-pH} \quad \forall t \]  

(17)

2.2.2. Submodel 3: emulsion tank model

Two fluid phases, the organic and the back-extraction are contained in the emulsion tank. Thus, the mass transfer process of zinc from the former to the latter phase is included in the following mass balances

\[ \frac{d(C_i^{\text{ex}})}{dt} = F_o [C_i^0(z = L) - C_i^{\text{ex}}] + \mathcal{A}_i^{\text{BEX}} k_{i, \text{T}, \text{ex}} A_{i, \text{t}, \text{e}} C_i^{\text{Zn}^2+} \quad \forall t; \quad j = o \Rightarrow i = \text{Zn}, \text{RH}, \quad j = s \Rightarrow i = \text{Zn}^{2+}, \text{H}^+ \]

(18)

\[ C_i^{\text{ex}}(t = 0) = C_{i, \text{in}}^{\text{ex}} \]  

where \( k_{i, \text{T}, \text{ex}} \) is the volumetric mass transfer coefficient defined to describe the solute mass transfer from the organic phase to the stripping solution in the emulsion tank, that differs from the equivalent parameter in the membrane contactor due to the differences in geometry and fluid dynamics (Carrera, Bringas, San Roman, & Ortiz, 2009).

In order to use the mathematical model the interfacial phenomenena need to be known. In this context, the chemical equilibrium parameters of the extraction (\( K_{\text{ex}} \)) and back-extraction (\( K_{\text{BEX}} \)) reactions, as well as the mass transport coefficients for the different species in the aqueous phase stagnant layer (\( k_i \)), the membrane (\( k_m \)), the organic phase boundary layer (\( k_o A_o \)) and in the emulsion tank (\( k_{i, o} A_{i, o} \)) should be determined.

2.3. Simplification procedure

According to the specific characteristics of the system under study, several simplifications can be made in order to reduce the number of parameters and mathematical complexity of the model:

1. The kinetic resistance corresponding to diffusion through the aqueous feed phase boundary layer was considered negligible due to the high zinc concentration (6–12 g L\(^{-1}\)) in the spent passivation baths. Consequently, \( k_i \) parameter and Eq. (3) are not considered.

2. Under the selected stirring conditions (8000–20,500 rpm) fully turbulent flow occurs in the emulsion tank with maximum values of the Reynolds number close to \( 4 \times 10^5 \) (Perry & Green, 2001). Therefore Eq. (5) and the second term on the right-hand side in Eq. (18) are neglected due to the minor contribution of the kinetic resistance corresponding to diffusion through the organic phase boundary layer.

Depending on the value of the equilibrium parameter of the back-extraction reaction (\( K_{\text{BEX}} \)) different simplified pathways are possible leading to two alternative models: (i) a three-parameter model (3-PM) valid for systems with finite values of \( K_{\text{BEX}} \) and, (ii) a two-parameter model (2-PM) applicable for systems with \( K_{\text{BEX}} \) tending to infinity (maximum driving force hypothesis).

2.3.1. Three-parameter model (3-PM)

Under the selected operation conditions the residence time of the stripping solution in the emulsion tank (72 s) is approximately four times higher than the corresponding value in the membrane contactor (18.5 s). Therefore, the stripping step is assumed to take place only in the emulsion tank. This assumption is described by
three different artificial units: two stirred tanks for the homogenization of the organic and stripping phases and an equilibration stage where the instantaneous back-extraction reaction takes place (Fig. 4).

As a result the solute mass balances to the stripping solution in the membrane contactor are omitted (Eq. (12) and the corresponding boundary conditions). On the other hand, the solute mass balances in the organic phase given by Eq. (11) are rewritten as follows:

\[
\frac{\partial C_0}{\partial t} + F \frac{\partial C_0}{\partial z} = \omega_i \frac{d_{EX}}{d_{m}} C_0 \forall z; \quad \forall i = Zn; \quad RH
\]

with boundary conditions given by Eqs. (13) and (14).

The equilibration stage is described by the back-extraction equilibrium expression given by Eq. (7) and the homogenization tanks are modelled by Eqs. (18) and (19) where the mass transfer terms are not taken into account. In conclusion, the simplified 2-PM mathematical model is constituted by Eqs. (4), (6)–(10), (13)–(19), (21) and (22) with \(K_{eq}^{EX}\) and \(k_m\) as model parameters.

2.3.2. Two-parameter model (2-PM)

The second simplification approach assumes that the equilibrium of the back-extraction reaction is completely shifted to the right. Then the concentrations of the organometallic species at the interface of the stripping droplets are equal to zero. Therefore the driving force for mass transfer through the organic-phase stagnant layer is maximized and thus, all the zinc cations extracted from the feed solution are totally back-extracted being \(K_{eq}^{BEX} = \infty\). According to this hypothesis, the solute mass balances in the membrane contactor in both the organic (Eq. (11)) and stripping (Eq. (12)) solutions are modified as follows:

\[
\frac{\partial C_0}{\partial t} + F \frac{\partial C_0}{\partial z} = 0 \quad \forall z; \quad \forall i = Zn, \quad RH
\]

with boundary conditions given by Eqs. (13) and (14). It should be noticed that 2-PM model is not able to predict the accumulation of zinc in the organic phase as was expected from Eq. (21) in contrast to 3-PM model that takes into account the non-steady behaviour of the organic liquid membrane.

As in the 3-PM model the solute mass balances in the emulsion tank are given by Eqs. (18) and (19) where the mass transfer terms are not taken into account. In conclusion, the simplified 2-PM model is constituted by Eqs. (4), (6)–(10), (13)–(19), (21) and (22) with \(K_{eq}^{EX}\) and \(k_m\) as model parameters.

3. Simulation analysis

In this section, 3-PM (Section 2.3.1) and 2-PM (Section 2.3.2) models are compared in terms of their performance and response to different values of the main operation variables affecting the process kinetics that were experimentally analysed in a previous work (Urtiaga et al., 2010). For this purpose the models were solved with the commercial software package ASPEN CUSTOM MODELER 2004.1 (ASPEN TECH). Table 1 shows the values of the operation variables and model parameters used in the simulation runs. The procedure employed for the calculation of the model parameters is collected in Appendix A.

Initially, simulated results obtained with both simplified models (3-PM and 2-PM) are compared under the same operation conditions (Table 1) as shown in Fig. 5 (curves (I) and (III)).

From these results it is concluded that both models describe the extraction kinetics (Fig. 5a) in a similar way, while faster back-extraction kinetics (Fig. 5b) are predicted by the model based on the maximum driving force hypothesis (curve (I)). Nevertheless, the uncertainty on the value of the equilibrium parameter...
of the back-extraction reaction employed in the 3-PM model supports the analysis of the parametric sensitivity of the mathematical model to different values of $K_{eq}^{BEX}$ in the range between 10 and 10,000, values that correspond to the inverse of the values of $K_{eq}^{EX}$ reported in the literature (Ali, Ahmad, & Daoud, 2006; Kanungo & Mohapatra, 1995; Mantuano, Dorella, Elias, & Mansur, 2006; Northcott, Kokusen, Komatsu, & Stevens, 2006; Salgado et al., 2003). Fig. 5 shows the influence of $K_{eq}^{EX}$ values on the extraction and back-extraction kinetics (curves (II)–(V)).

It is concluded that the influence of the equilibrium parameter in the range $100 \leq K_{eq}^{BEX} \leq 10,000$ (curves (II)–(V)) on the simulated kinetic curves obtained with model 3-PM can be considered negligible. On the other hand, a slight slowing down of the process kinetics is observed at values of $K_{eq}^{BEX} \leq 10$ (curve (V)). These results confirm the necessity for reliable values of the equilibrium parameter of the back-extraction reaction and the need for further research.

From the previous results it is concluded that the main difference between both simplified models comes from the mathematical description of the back-extraction elements of the EPT process. Therefore both 3-PM and 2-PM were compared in terms of their response to variations on the variables affecting the back-extraction equilibrium: (i) the concentration of Cyanex®272 in the organic solution and (ii) the concentration of sulphuric acid in the stripping solution. Figs. 6 and 7 show the results obtained in different simulation runs performed under the conditions depicted in Table 1.

The simulated curves plotted in Fig. 6, obtained after solving 3-PM and 2-PM models, exhibit faster kinetics at higher Cyanex®272 concentrations in good agreement with experimental runs (Urtiaga et al., 2010). At concentrations of Cyanex®272 higher than 200 mol m$^{-3}$ (stoichiometric concentration referred to the initial concentration of zinc in the passivation bath), the difference between the simulation results obtained with both modelling approaches is considered negligible. If the separation process is limited by the concentration of the selective extractant, the 2-PM model is able to predict faster extraction kinetics than the 3-PM model because the former approach assumes maximum driving force.

Concerning the concentration of acid in the stripping solution (Fig. 7), it can be observed that the simulated results obtained from the model based on the maximum driving force assumption (2-PM model) are not influenced by variations in this operation variable. On the other hand, the 3-PM model is able to describe the depletion of the stripping agent at low concentrations of acid and the consequent slowing down of the extraction kinetics.

### 4. Model validation

Due to the uncertainty on the back-extraction equilibrium parameter and the typical process operation using excess of the stripping agent, sulphuric acid, a 2-PM model based on the maximum driving force hypothesis will be considered as a valid and most useful approach to describe the kinetics of the EPT process applied to the regeneration of spent passivation baths. In this section the 2-PM model was validated using experimental data previously reported by Urtiaga et al. (2010). These experiments were performed under the same operation conditions used to carry out the simulation analysis (see Table 1) and following the experimental procedure described by the authors in a previous work. Figs. 8–10 show the comparison between experimental and simulated data.

All the experiments were performed with an emulsion containing fresh stripping acid and re-used organic solutions with initial concentrations of zinc different from zero. As a consequence, the first starting period of emulsion stabilization led to zinc concentration in the stripping solution different from zero.
Fig. 8. Extraction (a) and back-extraction (b) kinetics of zinc at different values of the initial pH of the spent passivation bath: pH 2 (■, experimental; —, simulated), pH 2.5 (▲, experimental; —, simulated) and pH 3 (○, experimental; ---, simulated). $C_{\text{t,2+}}^\text{f} = 107.2–112 \text{ mol m}^{-3}$; $C_{\text{t,H}^+}^\text{in} = 600 \text{ mol m}^{-3}$; $C_{\text{t,H}^+}^\text{out} = 2000 \text{ mol m}^{-3}$.

Fig. 9. Extraction (a) and back-extraction (b) kinetics of zinc at different values of the initial concentration of zinc spent passivation bath: $[\text{Zn}^{2+}] = 107.2 \text{ mol m}^{-3}$ (■, experimental; —, simulated), $[\text{Zn}^{2+}] = 37.3 \text{ mol m}^{-3}$ (▲, experimental; —, simulated). pH 2.5; $C_{\text{t,H}^+}^\text{in} = 600 \text{ mol m}^{-3}$; $C_{\text{t,H}^+}^\text{out} = 2000 \text{ mol m}^{-3}$.

Fig. 10. Extraction (a) and back-extraction (b) kinetics of zinc at different values of the initial concentration of the selective extractant in the organic solution: $[\text{Cyanex}^\text{®}272] = 200 \text{ mol m}^{-3}$ (■, experimental; —, simulated), $[\text{Cyanex}^\text{®}272] = 600 \text{ mol m}^{-3}$ (▲, experimental; —, simulated) and $[\text{Cyanex}^\text{®}272] = 1000 \text{ mol m}^{-3}$ (○, experimental; ---, simulated). pH 2.5; $C_{\text{t,H}^+}^\text{in} = 84.6–90.8 \text{ mol m}^{-3}$; $C_{\text{t,H}^+}^\text{out} = 2000 \text{ mol m}^{-3}$.

Fig. 11. Parity graphs. Comparison of experimental (EXP) and predicted (SIM) values of zinc concentration in the aqueous feed phase (a) and stripping solution (b).
Finally, the deviation between experimental and simulated data is quantified by the parity graphs (Fig. 11) and the “R-squared” parameter \( R^2 \) defined as follows:

\[
R^2 = 1 - \frac{\sum (C_{\text{EXP},i} - C_{\text{SIM},i})^2}{\sum (C_{\text{EXP},i} - \bar{C}_{\text{EXP}})^2}
\]  

It is concluded that 88% of simulated zinc concentrations in the spent passivation bath fall within the range \( C^T_{Zn^{2+},\text{EXP}} \pm 20\% C^T_{Zn^{2+},\text{EXP}} \), with values of \( R^2 \) in the range between 0.92 and 0.99. On the other hand, 91% of simulated data of the stripping phase fall within the range \( C^T_{Zn^{2+},\text{EXP}} \pm 20\% C^T_{Zn^{2+},\text{EXP}} \) with values of \( R^2 \) varying from 0.70 to 0.97. Considering the wide range of the operation conditions taken into account together with the complex nature of the spent passivation baths, it is thought that the 2-PM simplified model permits a satisfactory description of the separation and recovery of zinc from spent passivation baths using Cyanex®272 as selective extractant and sulphuric acid as the back-extraction agent. Furthermore, avoiding the use of \( K_{BEX}^\text{eq} \) parameter is considered the main advantage of the proposed model due to the uncertainty related to the characterization of the back-extraction step in EPT processes.

5. Conclusions

This work reports the mathematical modelling of facilitated transport based separations using membrane contactors. The proposed mathematical model, that considered all mass transport steps and interfacial chemical reactions, consisted of a system of partial differential equations corresponding to the solute mass balances in the phases flowing through the hollow fiber membrane contactor and in the homogenization tanks. The model developed was applied to describe the regeneration kinetics of trivalent chromium spent passivation baths by the selective removal and recovery of zinc using the EPT in hollow fiber membrane contactors. According to the specific system characteristics, two different simplification pathways that aimed at the minimum number of uncertain parameters and mathematical complexity were proposed leading to simplified models that differed mainly on the way the back-extraction process is described. A two-parameter model (membrane mass transport coefficient, \( k_m,\text{Zn} \), and equilibrium parameter of the extraction reaction \( K_{BEX}^\text{eq} = 2.79 \times 10^{-4} \)) that assumed maximum driving force through the liquid membrane was selected as the most suitable approach. Predicted values agreed satisfactorily well with experimental data reported in a previous work (Urtiaga et al., 2010).

Acknowledgments

Financial support from projects A542/2007/2-11.1 (MMA, Spain), CTQ2008-00690 (MCI, Spain), CTM2006-00317 (MCI, Spain) is gratefully acknowledged.

Appendix A. Determination of the model parameters

The membrane mass transport coefficients were calculated with the following equation (Prasad & Sirkar, 1988):

\[
k_{m,i} = \frac{D_{m,E}^i}{\varepsilon} \quad \forall i = \text{Zn, RH}
\]  

where \( \varepsilon = 0.4 \) and \( \delta = 40 \mu m \) are respectively the membrane porosity and the membrane thickness. The membrane tortuosity (\( \tau \)) is calculated using the following empirical correlation (Alves & Coelho, 2004):

\[
\tau = \left( 1 - \frac{\varepsilon}{\delta} \right)^2
\]  

The values of diffusivity of both the organometallic complexes (\( D_m^\text{Zn} \)) and the selective extractant (\( D_m^\text{RH} \)) are calculated using the Wilke–Chang equation (Perry & Green, 2001) considering the following properties: average molecular weight of the organic solution, \( M^\text{p} = 206 \) g mol\(^{-1} \), organic solution viscosity (experimentally measured), \( \mu^o = 11.2 \) cp, molar volume of the organometallic complexes and the selective extractant, \( V_m^\text{Zn} = 751 \) cm\(^3\) mol\(^{-1} \) and \( V_m^\text{RH} = 378 \) cm\(^3\) mol\(^{-1} \). The calculated diffusivities and membrane mass transport coefficients are as follows: \( D_m^\text{Zn} = 1.89 \times 10^{-7} \) m\(^2\) h\(^{-1} \), \( D_m^\text{RH} = 2.85 \times 10^{-7} \) m\(^2\) h\(^{-1} \), \( k_m,\text{Zn} = 2.95 \times 10^{-4} \) m h\(^{-1} \) and \( k_m,\text{RH} = 4.46 \times 10^{-4} \) m h\(^{-1} \).

The equilibrium parameter of the extraction reaction (Eq. (1)) given by Eq. (7) can be rearranged to yield:

\[
\log H_{\text{EX}}^\text{eq} = \log \left( \frac{K_{BEX}^\text{eq} (RH)^2}{Zn} \right)
\]  

where

\[
H_{\text{EX}}^\text{eq} = \frac{C_{\text{EXP},\text{Zn}}}{C_{\text{EXP},\text{RH}}}
\]  

To confirm the proposed extraction reaction and to obtain the value for \( K_{BEX}^\text{eq} \) several equilibrium experiments were performed following the experimental procedure detailed elsewhere (Brigas et al., 2006; Urtiaga et al., 2010) and then, the fitting of the experimental data to Eq. (A.3) was performed as it is shown in Fig. 12.

It can be observed that the slope of the straight line in Fig. 12, \( y = 2.108x - 3.999 \), is very close to the value of \( -2 \) expected from Eq. (A.3), providing further support to the proposed extraction mechanism. Once the mechanism has been checked the equilibrium parameter for the extraction reaction can be calculated from the value of the ordinate at the origin (\( -4.0 \)). Assuming a constant value of the selective extractant concentration (\( RH = 600 \) mol m\(^{-3} \)) the value of the equilibrium parameter is \( K_{BEX}^\text{eq} = 2.79 \times 10^{-4} \) which is in the range of values reported in the literature (Ali et al., 2006; Kanungo & Mohapatra, 1995; Mantuano et al., 2006; Northcott et al., 2006; Salgado et al., 2003). Finally, in spite of the different physicochemical characteristics of the spent bath and the stripping solution ideal conditions are assumed due to the lack of \( K_{BEX}^\text{eq} \) values in the literature and thus:

\[
K_{BEX}^\text{eq} = \frac{1}{K_{BEX}^\text{eq}} = 3584
\]
References


