



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

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### ABSTRACT

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 (Urutiaga, Bringas, Mediavilla, & Ortiz, 2010).

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### 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) (Urutiaga, Ortiz, Salazar, & Irabien, 1992), the non-dispersive solvent extraction (NDSX) (Samaniego, San Román, & Ortiz, 2007), the emulsion pertraction technology (EPT) (Bringas, San Román, & Ortiz, 2006; Ho & Poddar, 2001; Klaassen & Jansen, 2001; Urutiaga, Bringas, Mediavilla, & Ortiz, 2010; Urutiaga, 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 (Urutiaga 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

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**Nomenclature**

$A$	effective membrane area ( $\text{m}^2$ )
$A_v$	specific area of the stripping phase droplets ( $\text{m}^2 \text{m}^{-3}$ )
$C$	solute concentration ( $\text{mol m}^{-3}$ )
$D$	diffusion coefficient ( $\text{m}^2 \text{h}^{-1}$ )
$F$	volumetric flowrate ( $\text{m}^3 \text{h}^{-1}$ )
$H$	distribution coefficient
$J$	diffusive mass transport flux ( $\text{mol h}^{-1} \text{m}^{-2}$ )
$K_{\text{eq}}$	equilibrium parameter of interfacial reactions
$k_l$	mass transport coefficient through the aqueous phase stagnant layer ( $\text{m h}^{-1}$ )
$k_m$	membrane mass transport coefficient ( $\text{m h}^{-1}$ )
$k_o$	mass transport coefficient through the organic phase stagnant layer ( $\text{m h}^{-1}$ )
$L$	effective fiber length (m)
$V$	effective volume of the fluid phases in the process units ( $\text{m}^3$ )
$t$	time (h)
$z$	axial dimension of the fiber (m)

*Greek letters*

$\alpha$	stoichiometric coefficient
$\delta$	membrane thickness (m)
$\varepsilon$	membrane porosity
$\tau$	membrane tortuosity

*Superscripts*

$i_n$	inlet concentration
$j$	fluid phases (a: aqueous feed solution; o: organic phase; s: stripping solution)
$k$	interfacial reactions (EX: extraction; BEX: back-extraction)
*	interface between feed solution and organic liquid membrane
**	interface between organic liquid membrane and stripping droplets

*Subscripts*

$i$	solutes ( $\text{Zn}^{2+}$ , $\text{H}^+$ , $\overline{\text{Zn}}$ , $\overline{\text{RH}}$ )
$m$	membrane contactor
$T$	homogenization tank

the membrane contactor. The solute, exemplified by  $\text{Zn}^{2+}$  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  $\text{ZnR}_2$  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; Urriaga 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**

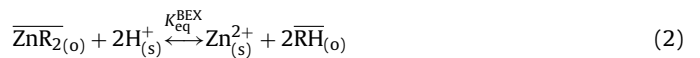
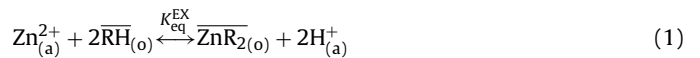
The following general assumptions are taken into account to mathematically describe the membrane contactor:

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, Cyanex®272 and sulphuric acid were used as selective extractant and stripping agent (Urriaga et al., 2010). The extraction and back-extraction processes are described respectively by the following reversible reactions (Kanungo & Mohapatra, 1995):



where  $\overline{\text{RH}}$  and  $\overline{\text{ZnR}}_2$  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 I-Fick's law as follows:

$$J_i^a = k_{l,i}(C_i^a - C_i^{a*}) \quad \forall i = \text{Zn}^{2+}, \text{H}^+ \quad (3)$$

$$J_i^m = k_{m,i}[\pm(C_i^{o*} - C_i^o)] \quad \forall i = \overline{\text{Zn}} = \overline{\text{ZnR}}_2, \overline{\text{RH}} \quad (4)$$

$$J_i^o = k_{o,i}(C_i^o - C_i^{o**}) \quad \forall i = \overline{\text{Zn}} \quad (5)$$

where  $k_l$ ,  $k_m$  and  $k_o$  are the individual mass transport coefficients. Assuming pseudo-steady state:

$$|J_{\text{Zn}^{2+}}^a| = \left| \frac{1}{\alpha_{\text{H}^+}^{\text{EX}}} J_{\text{H}^+}^a \right| = |J_{\overline{\text{Zn}}}^m| = \left| \frac{1}{\alpha_{\overline{\text{RH}}}^{\text{EX}}} J_{\overline{\text{RH}}}^m \right| = |J_{\overline{\text{Zn}}}^o| \quad (6)$$

where  $\alpha_i^k$  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

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