

COMPUTATIONAL SIMULATION OF METAL EXTRACTION PROCESS USING POLYMERIC MEMBRANES

Simone de Aviz Cardoso

Emanuel Negrão Macêdo

João Nazareno Nonato Quaresma

School of Chemical Engineering, ITEC, Universidade Federal do Pará, UFPA
Campus Universitário do Guamá, 66075-110, Belém, PA, Brazil; quaresma@ufpa.br.

Renato Machado Cotta

Mechanical Engineering Department – POLI/COPPE, Universidade Federal do Rio de Janeiro, UFRJ
Cx. Postal 68503 – Cidade Universitária, 21945-970, Rio de Janeiro, RJ, Brazil; cotta@mecanica.coppe.ufrj.br.

Abstract. *The metal extraction process using polymeric membranes is analyzed by using the Finite Difference Method in conjunction with the Gear's Approach for the hybrid solution of the related equations of species conservations. The mathematical modeling of the physical problem considers the diffusion process through polymeric membranes in order to extract metals, such as Cd (II) from acid solutions. Therefore, the behavior of the metals concentration profiles to be extracted from the feeding phase is discussed in light of the influence of relevant parameters in the extraction process, such as, composition and thickness of the membrane, diffusion coefficient and extraction constant. Comparisons with previously reported experimental results in the literature for typical situations are also performed.*

Keywords: *Aliquat 336/PVC membrane, cadmium, metal extraction, finite difference and Gear's methodologies.*

1. INTRODUCTION

In recent years, membrane process extraction has been showing to have some important advantages over traditional solvent extraction, due to the non-formation of emulsions and flog, which represent a direct risk to the health, as well as the economy related to the employment of minimum amount of solvent, with a consequent lower capital cost. Since the early 70's, when liquid membranes were introduced by Li and Shrier (1972), the recovery and separation of metals by this alternative technique have been investigated by several researchers with a great variety of substances as carrier species incorporated in the membrane (Valenzuela *et al.*, 2002).

Liquid membrane systems consist of a liquid barrier between the feeding and the stripping phases. The most important types of liquid membranes are: bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs), supported liquid membranes (SLMs), gelled supported liquid membranes (GSLMs) and polymeric liquid membranes (PLMs). Polymeric or supported liquid membranes are self-supported and contain carrier species that generally are commercial extractants, which act as a plasticizer for the polymer, and as a result a homogeneous membrane is obtained (Argiropoulos *et al.*, 1998; Breembroek *et al.*, 1998; Kolev and Sakai, 2000; Wang *et al.*, 2000).

A membrane that is being utilized with success by chemical researchers is based on polyvinyl chloride (PVC). This type of membrane has the capacity of presenting selectivity to ions transport depending on its composition. Similar membranes are frequently referred as interlaced membranes, since they are a homogeneous mixture of reagents, plasticizer and PVC. These PVC membranes are easily prepared and show excellent mechanical properties (Kolev *et al.*, 1997).

In this context, the present work is aimed at developing a computational code capable of simulating the membrane process of metal extraction using supported liquid membranes. The Finite Difference Method (FDM) in conjunction with the Gear's Approach is then employed to solve the equations of specie conservations related to metal extraction, particularly Cd (II) from acid solutions. Numerical results are produced for the cadmium concentration distribution to be extracted from the feeding phase, which are discussed in the light of the influence of relevant parameters in the extraction process, such as, composition and thickness of the membrane, diffusion coefficient and extraction constant. Comparisons with previously reported experimental results in the literature (Wang *et al.*, 2000) for typical situations are also performed.

2. ANALYSIS

A typical process of polymeric membrane extraction is illustrated in Fig. 1, in which is assumed that the first tank of the extraction cell presents a concentrated hydrochloric acid solution (HCl) 3 M with heavy metals; and in the second tank there is a diluted solution of HCl 0.1 M. The membrane composition consists of a mixture of Aliquat 336 and PVC.

The mathematical modeling of this process is obtained through application of mass conservation for the chemical species in the extraction cell according to Fig. 2. The extraction kinetic is considered to be a pseudo-first order chemical reaction, due to the presence of chloride ions in excess in the extraction cell, which is stirred constantly to warrant an uniform mixture:

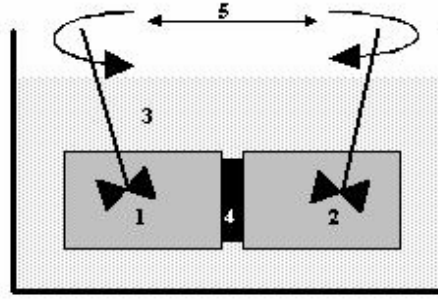


Figure 1. Schematic representation of a membrane extraction cell. (1) Feeding phase, (2) stripping phase, (3) thermostatic bath, (4) membrane and (5) stirrers.



where A_m represents the Aliquat 336 in the membrane, B_a represents the metal in solution and AB_m the metal inserted in the membrane and K_{f1} e K_{b1} are the forward and backward kinetic rate constants at $x = 0$ of the membrane, respectively. Similarly,



where, K_{f2} e K_{b2} are the forward and backward kinetic rate constants in $x = \delta$ of the membrane.

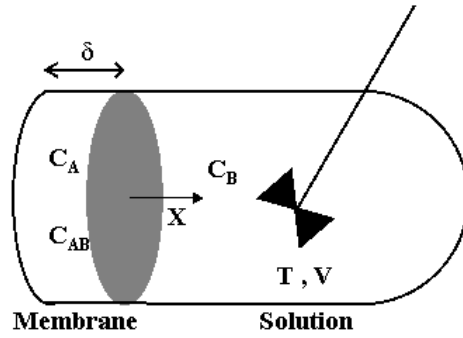


Figure 2. Schematic representation of a half membrane cell extraction.

Because exist a metal concentration gradient between the two compartments of the extraction cell, due to the concentration of metal in the feeding phase to be higher than in stripping one, therefore the kinetic constant K_{f1} is larger than k_{b1} , this way favoring the formation of AB_m that by diffusion is transported to the stripping phase. On the other hand, a reverse behavior is encountered at $x = \delta$, which correspond to K_{b2} larger than K_{f2} , and consequently, the dissociation of metal in stripping phase is dominant.

This physical problem is represented by equations of mass conservation for the chemical species, which in dimensionless form are written as:

$$\frac{\partial \theta_A}{\partial \tau} = \frac{\partial^2 \theta_A}{\partial \eta^2}; \quad \frac{\partial \theta_{AB}}{\partial \tau} = \lambda \frac{\partial^2 \theta_{AB}}{\partial \eta^2} \quad (2,3)$$

$$\frac{d\theta_{B1}(\tau)}{d\tau} = -\alpha_1 \beta_1 \theta_A(0, \tau) \theta_{B1}(\tau) + \alpha_1 \theta_{AB}(0, \tau); \quad \frac{d\theta_{B2}(\tau)}{d\tau} = \alpha_2 \theta_{AB}(1, \tau) - \alpha_2 \beta_2 \theta_A(1, \tau) \theta_{B2}(\tau) \quad (4,5)$$

which are subjected to the following initial and boundary conditions:

$$\theta_A(\eta, 0) = 1; \quad \theta_{AB}(\eta, 0) = 0; \quad \theta_{B1}(0) = 1; \quad \theta_{B2}(0) = 0 \quad (6-9)$$

$$\frac{\partial \theta_A}{\partial \eta} - \beta_1 \gamma_1 \theta_{B1} \theta_A = -\gamma_1 \theta_{AB}; \quad \frac{\partial \theta_{AB}}{\partial \eta} - \frac{\gamma_1}{\lambda} \theta_{AB} = -\frac{\gamma_1}{\lambda} \beta_1 \theta_{B1} \theta_A, \quad \text{at } \eta = 0 \quad (10a,b)$$

$$\frac{\partial \theta_A}{\partial \eta} + \beta_2 \gamma_2 \theta_{B2} \theta_A = \gamma_2 \theta_{AB}; \quad \frac{\partial \theta_{AB}}{\partial \eta} + \frac{\gamma_2}{\lambda} \theta_{AB} = \frac{\gamma_2}{\lambda} \beta_2 \theta_{B2} \theta_A, \quad \text{at } \eta = 1 \quad (11a,b)$$

The following dimensionless groups were employed in equations above:

$$\eta = \frac{x}{\delta}, \tau = \frac{D_A}{\delta^2} t, \theta_A = \frac{C_A}{C_A^0}, \theta_{AB} = \frac{C_{AB}}{C_A^0}, \theta_{B1} = \frac{C_{B1}}{C_{B1}^0}, \theta_{B2} = \frac{C_{B2}}{C_{B1}^0}, \alpha_1 = \frac{K_{b1} \cdot \delta^2 C_A^0}{D_A \cdot L C_{B1}^0}, \beta_1 = K_{ex1} \cdot C_{B1}^0,$$

$$K_{ex1} = \frac{K_{f1}}{K_{b1}}, \gamma_1 = \frac{K_{b1} \cdot \delta}{D_A}, \lambda = \frac{D_{AB}}{D_A}, \alpha_2 = \frac{K_{b2} \cdot \delta^2 C_A^0}{D_A \cdot L C_{B1}^0}, \beta_2 = K_{ex2} \cdot C_{B1}^0, K_{ex2} = \frac{K_{f2}}{K_{b2}}, \gamma_2 = \frac{K_{b2} \cdot \delta}{D_A} \quad (12a-o)$$

where D_A and D_{AB} are the diffusion coefficients, L is the length of the extraction cell, which is defined as being the ratio of the cell volume to the membrane area surface exposed to the HCl solution; C_A is the membrane concentration and C_{AB} is the metal concentration in the membrane, δ is the membrane thickness, C_{B1} is the metal concentration at $x = 0$ and C_{B2} is the metal concentration at $x = \delta$. Also, it is assumed that the diffusion coefficient for the Aliquat chloride (D_A) is equal to the diffusion coefficient of the complex metal-Aliquat (D_{AB}).

2.1. Solution methodology

For the solution of the system of differential equations given by (2) to (11), the Finite Difference Method (FDM) is then employed for the discretization of the spatial variable through approximations in terms of truncated Taylor series in M intervals (see Fig. 3) (Özsisik, 1994). Therefore, after performed such discretizations the following system of ODE equations for the potentials θ_A and θ_{AB} is found:

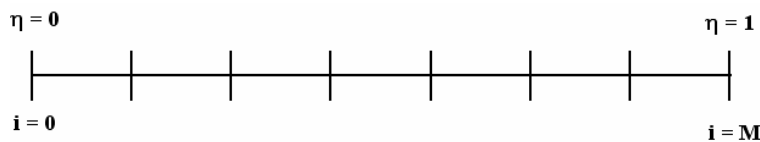


Figure 3. Mesh scheme for the domain discretization in the spatial variable.

$$\frac{d\theta_{Ai}}{d\tau} = \delta_{Ai}; \quad \delta_{Ai} = (\theta_{Ai+1} - 2\theta_{Ai} + \theta_{Ai-1}) / \Delta\eta^2; \quad \theta_{Ai}(0) = 1, \quad \text{for } 1 \leq i \leq M-1 \quad (13a-c)$$

$$\frac{d\theta_{ABi}}{d\tau} = \delta_{ABi}; \quad \delta_{ABi} = (\theta_{ABi+1} - 2\theta_{ABi} + \theta_{ABi-1}) / \Delta\eta^2; \quad \theta_{ABi}(0) = 0, \quad \text{for } 1 \leq i \leq M-1 \quad (14a-c)$$

- For the node $i = 0$:

$$\theta_{A0} = \frac{\Delta_1}{\Delta}; \quad \theta_{AB0} = \frac{\Delta_2}{\Delta}; \quad \Delta = C_1 C_4 - C_2 C_3; \quad \Delta_1 = d_1 C_4 - d_2 C_2; \quad \Delta_2 = d_2 C_1 - d_1 C_3 \quad (15a-e)$$

$$C_1 = -(3 + 2\beta_1 \gamma_1 \Delta \eta \theta_{B1}); \quad C_2 = 2\gamma_1 \Delta \eta; \quad C_3 = \frac{2\beta_1 \gamma_1 \Delta \eta \theta_{B1}}{\lambda}; \quad C_4 = -\left(3 + \frac{2\gamma_1 \Delta \eta}{\lambda}\right) \quad (15f-i)$$

$$d_1 = \theta_{A2} - 4\theta_{A1}; \quad d_2 = \theta_{AB2} - 4\theta_{AB1} \quad (15j,k)$$

- For the node $i = M$:

$$\theta_{AM} = \frac{\Delta'_1}{\Delta}; \quad \theta_{ABM} = \frac{\Delta'_2}{\Delta}; \quad \Delta' = C'_1 C'_4 - C'_2 C'_3; \quad \Delta'_1 = d'_1 C'_4 - d'_2 C'_2; \quad \Delta'_2 = d'_2 C'_1 - d'_1 C'_3 \quad (16a-e)$$

$$C'_1 = (3 + 2\beta_2 \gamma_2 \Delta \eta \theta_{B2}); \quad C'_2 = 2\gamma_2 \Delta \eta; \quad C'_3 = -\frac{2\beta_2 \gamma_2 \Delta \eta \theta_{B2}}{\lambda}; \quad C'_4 = \left(3 + \frac{2\gamma_2 \Delta \eta}{\lambda}\right) \quad (16f-i)$$

$$d'_1 = 4\theta_{AM-1} - \theta_{AM-2}; \quad d'_2 = 4\theta_{ABM-1} - \theta_{ABM-2} \quad (16j,k)$$

Equations (13) to (16) above form a set of coupled first order ODEs, which must be solved in conjunction with the kinetic equations give by (4) and (5) subjected to the initial conditions (8) and (9). The ODE system of $2M+1$ equations is computationally solved with the use of the subroutine DIVPAG from the IMSL Library (1991). The routine DIVPAG solves a system of first-order ordinary differential equations of the form $y' = f(t,y)$ or $Ay' = f(t,y)$ with initial conditions, where A is a square nonsingular matrix of order $2M+1$. Two classes of implicit linear multistep methods are available. The first is the implicit Adams-Moulton method; the second uses the backward differentiation formulas BDF. The implicit linear multistep method used in present work was BDF method, often called Gear's stiff method. The ODE solver was employed with a required tolerance of 10^{-8} .

3. RESULTS AND DISCUSSION

Numerical results for the Cd (II) concentration distribution were obtained along the time evolution. For this purpose, a computational code was developed in FORTRAN 90/95 programming language and implemented on a PENTIUM-IV 1.7 GHz computer. The routine DIVPAG from IMSL Library (1991) was used to numerically handle the system of ordinary differential equations given by Eqs. (13) to (16) and the kinetic equations (4) and (5) subjected to the initial conditions (8) and (9), with a relative error target of 10^{-8} prescribed by the user. For the simulation of the membrane composition influence, as well as of the membrane thickness, diffusion coefficient and kinetic parameters, the experimental results of Wang *et al.* (2000) were fitted, which are shown in Tab. 1. Also, the length of the extraction cell was taken as $L = 0.1$ m. In addition, the computation of the membrane composition was based in the experimental data of Argiropoulos *et al.* (1998).

Table 1. Cd (II) model parameters for the computational simulation.

D_A (m^2/s)	D_{AB} (m^2/s)	K_{f1} ($m^4/mol.s$)	K_{f2} ($m^4/mol.s$)	K_{b1} (m/s)	K_{b2} (m/s)	δ (μm)	L (m)	C_{A0} (g/g)	C_{B0} (mg/l)
2.00×10^{-15}	$1 \times D_A$	7.000×10^{-8}	7.00000×10^{-9}	2.4799×10^{-9}	9.9196×10^{-8}	81.7	0.1	30%	120
3.30×10^{-15}	$1 \times D_A$	6.999×10^{-8}	6.64905×10^{-8}	2.4799×10^{-9}	9.9196×10^{-8}	279	0.1	30%	100
8.20×10^{-13}	$1 \times D_A$	2.300×10^{-7}	2.30000×10^{-8}	5.0000×10^{-7}	5.0000×10^{-11}	138	0.1	40%	100
3.85×10^{-12}	$1 \times D_A$	1.000×10^{-8}	1.00000×10^{-8}	1.5000×10^{-7}	1.5000×10^{-7}	133	0.1	50%	100

Figure 4 shows the influence of the membrane composition for the Cd (II) extraction. From this figure, it is observed that the extraction is more efficient when lower contents of Aliquat 336 are utilized. For the case of 50% of Aliquat in the membrane, more than 50% of Cd (II) is extracted after 20 h of contact time. The present results show a good agreement with the experimental results of Wang *et al.* (2000). The behavior of Aliquat 336 content in the extraction process can be explained by the L'Chatelier principle as occurs in the membrane system, once by Eqs. (1) an increase in this content promotes the displacement of equilibrium for the formation of complex metal AB in the membrane.

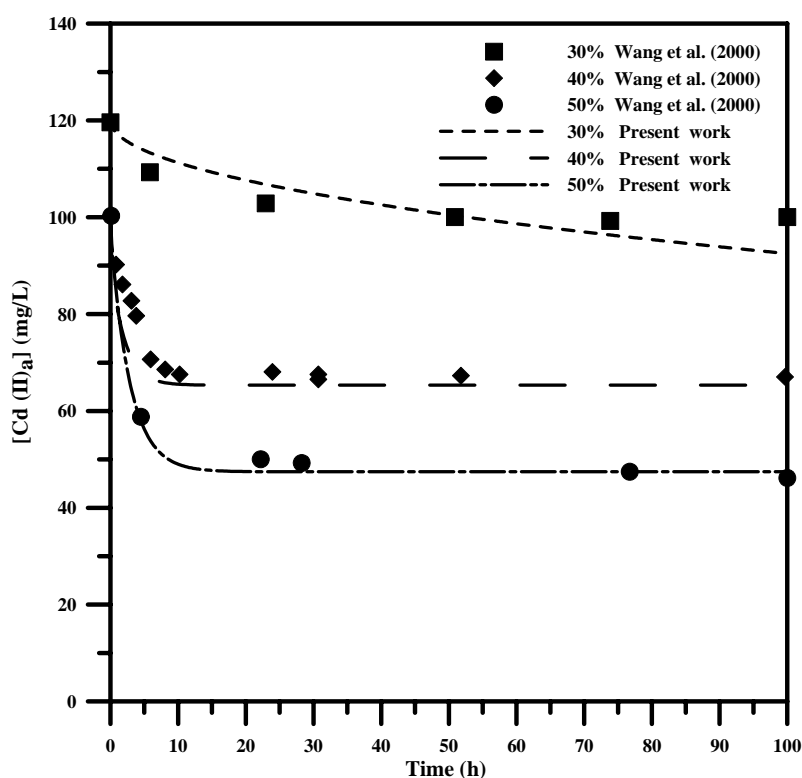


Figure 4. Influence of Aliquat 336 content in the membrane during the Cd (II) extraction.

Figure 5 presents the behavior of cadmium extraction with the influence of the membrane thickness. The present results were simulated using 40% of Aliquat 336 in the membrane composition and thickness of 81.7 and 279 μm . It is observed a more efficient extraction for the case of thickness 279 μm . This behavior is in agreement with the literature (Wang *et al.*, 2000), because the thickness of the organic phase (membrane), in which is occurring the diffusion of ionic pairs, will influence the transfer speed of the metal-complex ion formed by the reversible reaction of ionic exchange, for the feeding and stripping phases, in accordance with Eqs. (4) and (5). Once again, it is observed a good agreement among the present results and those of Wang *et al.* (2000).

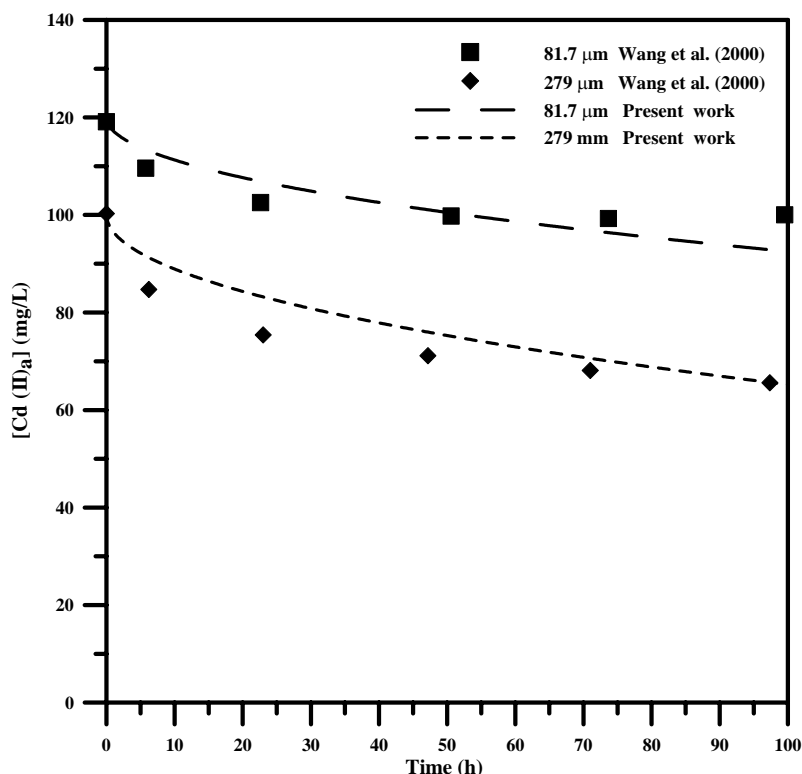


Figure 5. Influence of membrane thickness during the Cd (II) extraction.

In order to make a parametric analysis of the most important dimensionless governing parameters on the extraction process, Table 2 brings the set of values for the groups α_1 and β_1 , as defined by Eqs. (12), which determine the relative influence of the diffusion and of the chemical kinetics at the position $x = 0$ of the membrane. Such groups are also used as an indication if the extraction process is under either diffusive or kinetic controlled.

Table 2. Parameters used in the parametric analysis during the Cd (II) extraction.

D_A (m^2/s)	D_{AB} (m^2/s)	K_{f1} ($\text{m}^4/\text{mol}\cdot\text{s}$)	K_{f2} ($\text{m}^4/\text{mol}\cdot\text{s}$)	K_{b1} (m/s)	K_{b2} (m/s)	δ (μm)	L (m)	C_{A0} (g/g)	C_{B0} (mg/l)
3.3×10^{-13}	$1 \times D_A$	6.999×10^{-8}	6.64905×10^{-8}	2.4799×10^{-9}	9.9196×10^{-8}	279	0.1	30%	100

Figure 6 shows the evolution of θ_{B1} with time for different values of K_{b1} for $\beta_1 = 5$, while the diffusivity D_A is maintained constant. From this figure, it is noted that the extraction behavior is influenced by the kinetic constant K_{b1} , since for increasing values of this parameter better extraction efficiency is obtained.

Figure 7 illustrates the effect of K_{b1} and α_1 with different times and constant D_A . It is verified that for the time interval between 1 and 5 hours, the variation of θ_{B1} is less sensitive to the variation of K_{b1} , i.e., the extraction reaction in this period has less sensibility to the kinetic reaction changes.

Figure 8 brings the influence of β_1 (D_A fixed and varying K_{b1}) in order to verify the extraction of Cd (II). As observed, an increase of β_1 increases the extraction efficiency, as a result of an increase in K_{b1} .

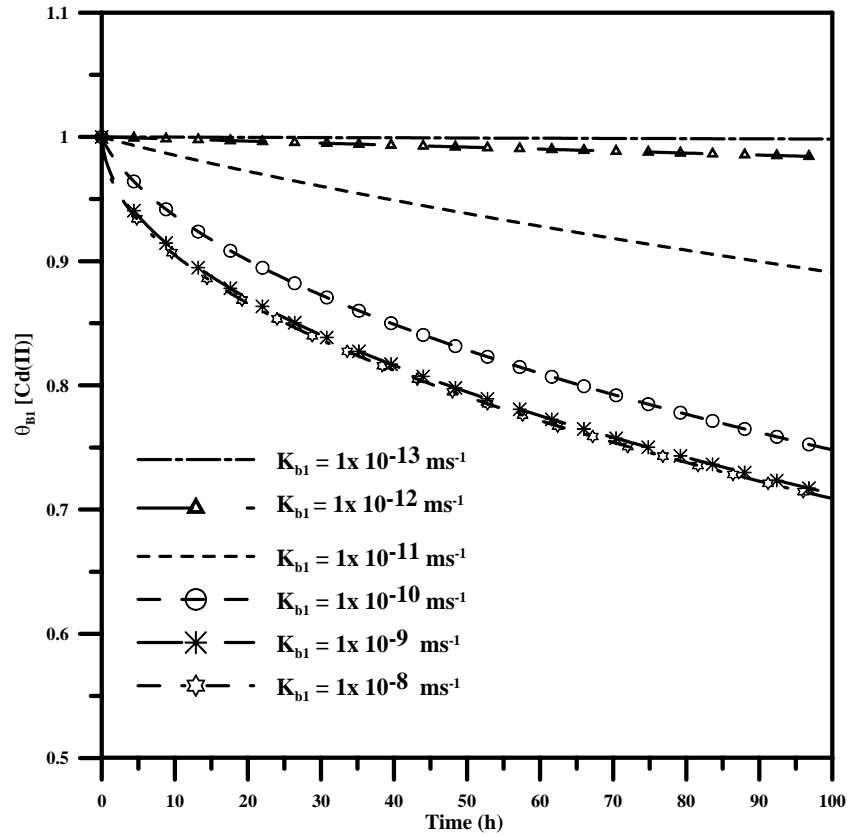


Figure 6. Dimensionless cadmium concentration as function of time with different values of K_{b1} and $\beta_1 = 5$.

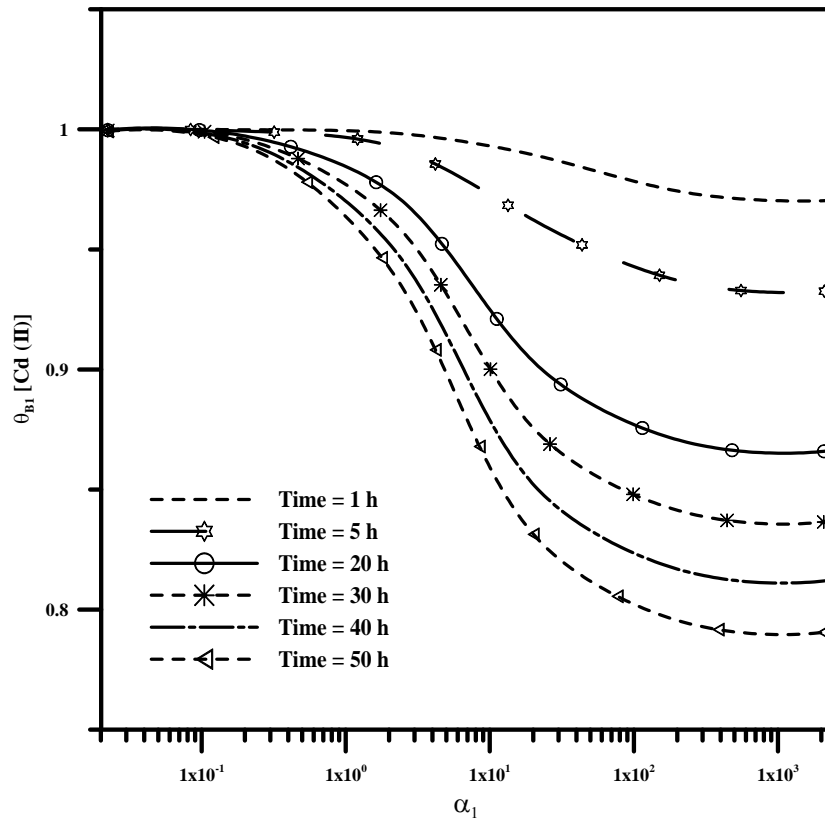


Figure 7. Dimensionless cadmium concentration as function of the parameter α_1 with different extraction times and $\beta_1 = 5$ (D_A fixed and K_{b1} varying).

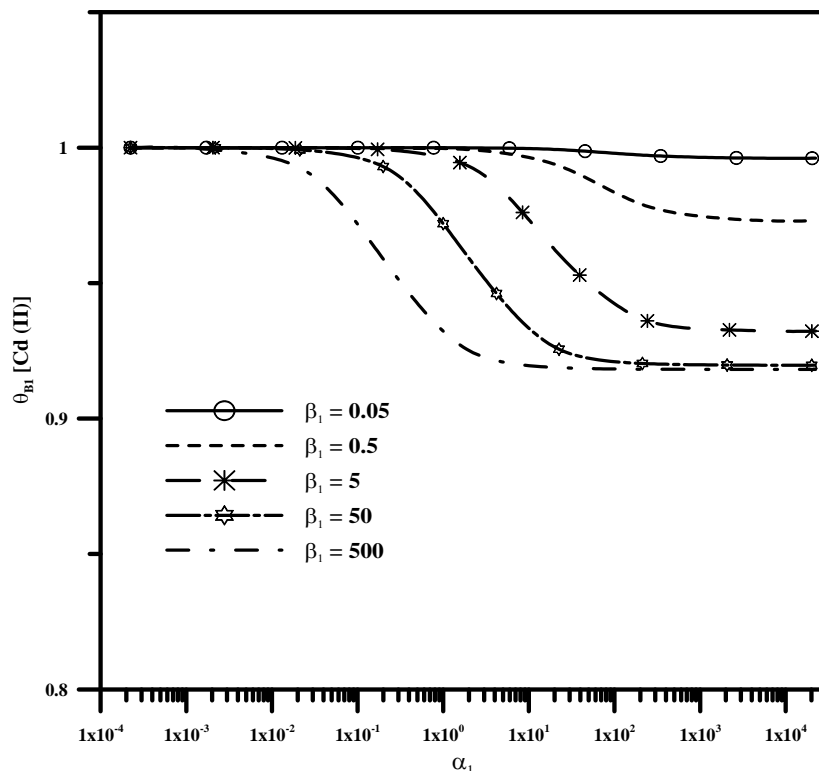


Figure 8. Dimensionless cadmium concentration as function of the parameter α_1 with different values of β_1 and $t = 5$ h.

From Fig. 9 it is verified that the Cd (II) extraction suffers a strong influence of D_A . As this parameter increases occurs a sensible decrease of B concentration in the feeding phase and consequently an increase of B concentration in the stripping phase, i.e., higher diffusivities promote better extraction rates due to a more affinity of the content of Aliquat 336 in the membrane with the ion complex.

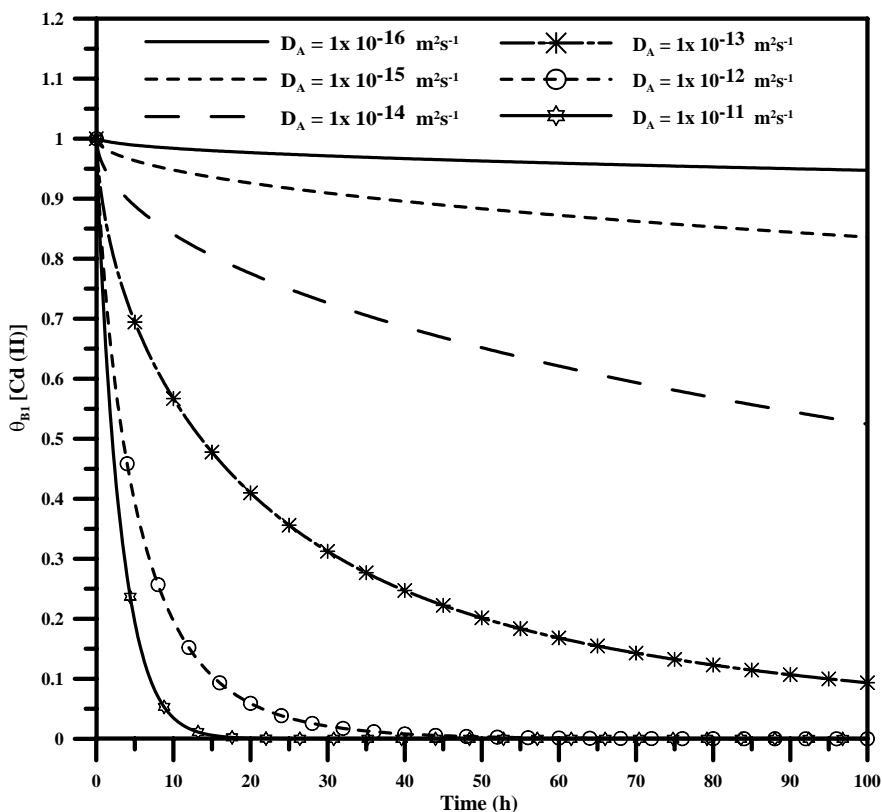


Figure 9. Dimensionless cadmium concentration as function of time with different values of D_A and $\beta_1 = 5$.

Figure 10 presents the behavior of cadmium extraction under influence of the diffusivity D_A with constant K_{b1} for different times. As it is observed, an increase of metal extraction time significantly increases in the extraction efficiency until to be reached the equilibrium, which is characterized by higher time intervals, i.e., $t = 50$ h for the present analysis.

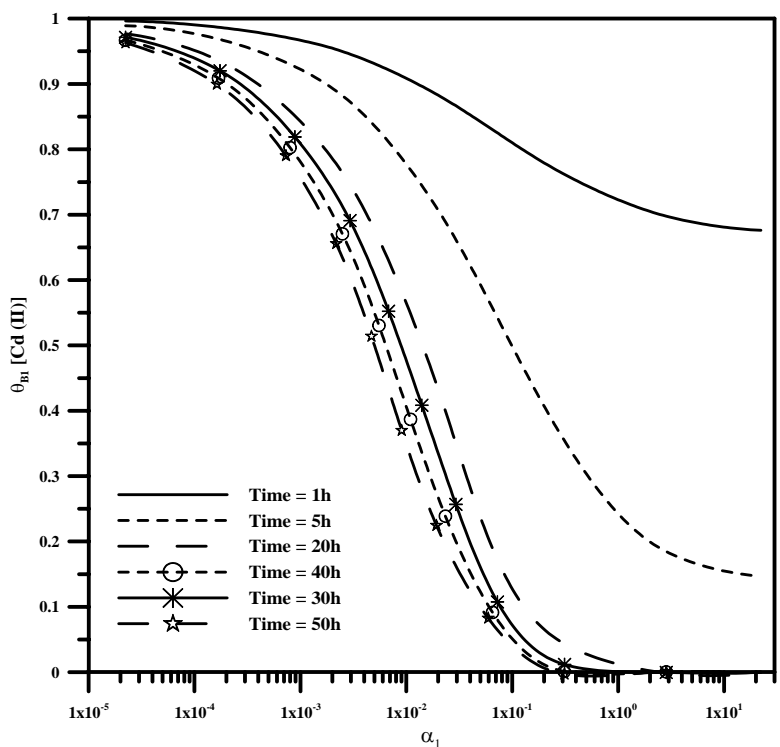


Figure 10. Dimensionless cadmium concentration as function of the parameter α_1 with different extraction times and $\beta_1 = 5$ (D_A varying and K_{b1} fixed).

It is presented in Fig.11 the behavior of Cd (II) extraction under influence of the diffusivity D_A with constant K_{b1} for different values of β_1 for a extraction time $t = 5$ h. From this figure, one can see that for higher β_1 more efficient becomes the extraction process, since the kinetic constant K_{f1} is the responsible for this gain in the extraction.

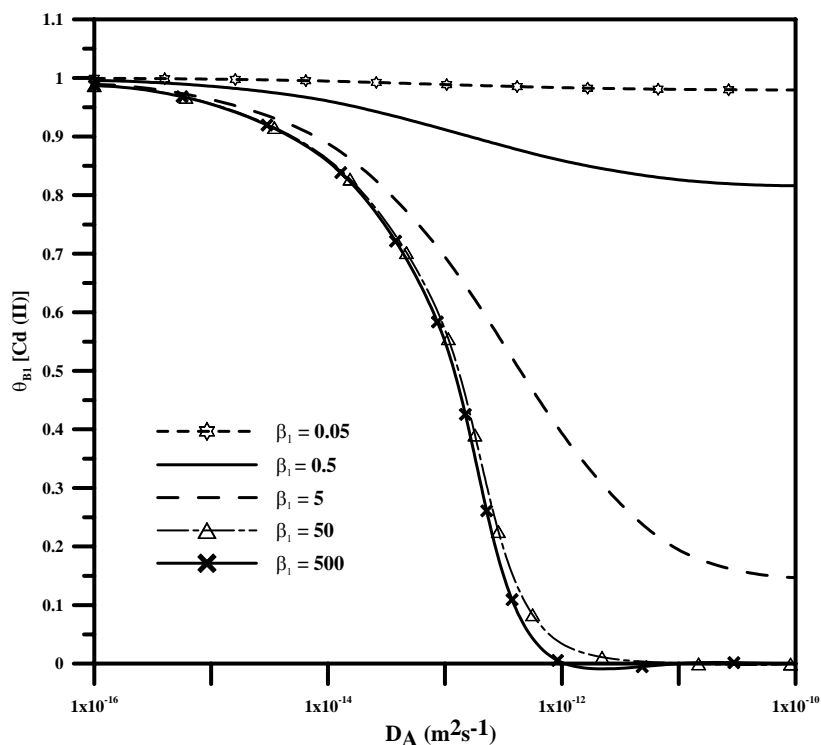


Figure 11. Dimensionless cadmium concentration as function of the diffusivity D_A with different values of β_1 and $t = 5$ h.

4. CONCLUSIONS

A study of membrane extraction process of cadmium Cd (II) by using polymeric liquid membranes (PLMs) was developed in the present work. The mathematical modeling of physical problem was done through the equations of mass conservation of chemical species, which were solved through the finite difference method (FDM) in conjunction with the Gear's Approach, which provided reliable and cost effective simulations for the considered cases. The behavior of the concentration distribution was analyzed under the governing parameters, such as membrane composition, membrane thickness, diffusion coefficient and kinetic parameters.

It was noticed that the liquid membrane with Aliquat 336/PVC can be successfully used to extract Cd (II) from acid hydrochloric solutions. Also, one can see that the mathematical model was well indicated to fit experimental data from the literature (Wang *et al.*, 2000). Also, the parametric analysis has shown the strong influence of the governing parameters in the extraction process.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by CNPq.

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