A COMPUTATIONAL SIMULATION OF METAL EXTRACTION PROCESS USING POLYMERIC MEMBRANES THROUGH THE HYBRID SOLUTION OF THE SPECIES TRANSPORT EQUATIONS

Simone de Aviz Cardoso
Emanuel Negrão Macêdo
João Nazareno Nonato Quaresma
quaresma@ufpa.br
School of Chemical Engineering
Universidade Federal do Pará, UFPA
Campus Universitário do Guamá, Rua Augusto Corrêa, 01, 66075-110, Belém, PA, Brasil

Abstract. *The metal extraction process using polymeric membranes is analyzed by using the Generalized Integral Transform Technique (GITT) 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 gold 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, Gold extraction, GITT approach, Integral transforms.*

1. INTRODUCTION

Supported liquid membranes (SLM) have demonstrated to be promissory in the separation process of metals from aqueous solutions, therefore allowing the separation of metal species using a film of organic solution that is adhered in the pores of a polymeric support (Reyes-Aguilera et al., 2008). Currently, liquid membrane separation systems have shown to be an alternative extraction technique for metals in dilute solutions due to present advantages over the conventional process of solvent extraction, such as the employment of minimum solvent quantity and the low capital cost (Wang et al., 2000).

The computational simulation of mass transfer process in such membranes can be an alternative tool in order to determine mass transfer patterns in a reduced time scale, when compared to experimental procedures or as a complement task to the experiments by making use of inverse techniques for estimation of parameters of this process.

In this context, the Generalized Integral Transform Technique (GITT) may employ its hybrid analytical-numerical nature to determine concentration profiles in a membrane process. This hybrid technique is derived from the classical version (Mikhailov and Özisik, 1984), and was gradually expanded in its applicability and extensively employed in heat/mass transfer and fluid flow problems. For instance, a number of contributions have advanced this method towards the error controlled solution of internal flow and convective heat transfer problems (Cotta, 1993, 1994 and 1998; Santos et al., 2001; Cotta et al., 2005; Cotta and Mikhailov, 2006).

Therefore, the present work is aimed at developing a computational code capable of simulating the process of metal extraction using supported liquid membranes. The GITT approach is then employed to solve the equations of specie conservations related to metal extraction, particularly Au (III) from acid solutions. Numerical results are produced for the gold 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 of the membrane. Comparisons with previously reported experimental results in the literature by Argiropoulos et al. (1998) for typical situations are also performed.

2. MATHEMATICAL FORMULATION OF THE PHYSICAL PROBLEM

A typical process of polymeric membrane extraction is illustrated in Fig. 1, in which it is assumed that the first tank of the extraction cell presents a concentrated hydrochloric acid solution (HCl) that contains metallic gold, Au (III), with concentration C_{B1}; and in the second tank there is a diluted solution of HCl of concentration C_{B2}. The composition of the polymeric membrane consists of a mixture of Aliquat 336 and PVC, with concentration C_A of Aliquat 336. Also, C_{AB} indicates the concentration of the metallic complex in the membrane.

The mathematical modeling of this process is obtained through application of mass conservation for the chemical species in the extraction cell for a given temperature, T, volume, V, and agitation, Ω for each half-cell and membrane thickness, δ. 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 a uniform mixture:

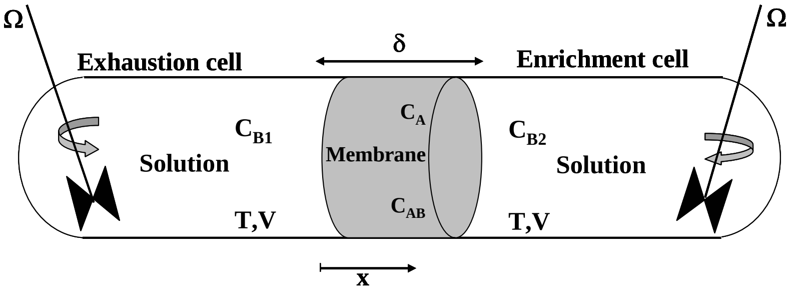

Figure 1. Schematic representation of a membrane cell extraction.

$$A_m + B_a \underset{K_{b1}}{\overset{K_{f1}}{\rightleftarrows}} AB_m; \qquad A_m + B_a \underset{K_{b2}}{\overset{K_{f2}}{\rightleftarrows}} AB_m \tag{1a,b}$$

Here, A_m represents the extractant Aliquat 336 inserted in the membrane, B_a represents the metal in solution and AB_m the complex metal in the membrane. In Eq. (1a), K_{f1} and K_{b1} are the forward and backward kinetic rate constants at position x=0 of the membrane, respectively. Similarly, Eq. (1b) brings the decomplexation reaction, where K_{f2} and K_{b2} are the forward and backward kinetic rate constants at the position x=δ of the membrane.

Since the concentration of metal in the feeding phase is higher than that in the stripping one, there is a metal concentration gradient between the two compartments of the extraction cell; 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=δ, which correspond to K_{b2} larger than K_{f2}, and consequently, the decomplexation of metal in stripping phase is dominant.

Similarly to the work of Cardoso et al. (2007) for the analysis of extraction of Cadmium, this physical problem is represented by equations of mass conservation for the chemical species, which in dimensionless form are written as:

$$\frac{\partial\theta_A(\eta,\tau)}{\partial\tau} = \frac{\partial^2\theta_A(\eta,\tau)}{\partial\eta^2}; \quad \frac{\partial\theta_{AB}(\eta,\tau)}{\partial\tau} = \xi\frac{\partial^2\theta_{AB}(\eta,\tau)}{\partial\eta^2}, \quad 0<\eta<1, \ \tau>0 \tag{2,3}$$

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

which are subjected to the following initial and boundary conditions:

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

$$\frac{\partial\theta_A(0,\tau)}{\partial\eta} - \beta_1\gamma_1\theta_{B1}(\tau)\theta_A(0,\tau) = -\gamma_1\theta_{AB}(0,\tau); \quad \frac{\partial\theta_{AB}(0,\tau)}{\partial\eta} - \frac{\gamma_1}{\xi}\theta_{AB}(0,\tau) = -\frac{\gamma_1}{\xi}\beta_1\theta_{B1}(\tau)\theta_A(0,\tau), \quad \tau>0 \tag{10a,b}$$

$$\frac{\partial\theta_A(1,\tau)}{\partial\eta} + \beta_2\gamma_2\theta_{B2}(\tau)\theta_A(1,\tau) = \gamma_2\theta_{AB}(1,\tau); \quad \frac{\partial\theta_{AB}(1,\tau)}{\partial\eta} + \frac{\gamma_2}{\xi}\theta_{AB}(1,\tau) = \frac{\gamma_2}{\xi}\beta_2\theta_{B2}(\tau)\theta_A(1,\tau), \quad \tau>0 \tag{11a,b}$$

The following dimensionless groups were employed in equations above:

$$\eta = \frac{x}{\delta}, \ \tau = \frac{D_A}{\delta^2}t, \ \theta_A = \frac{C_A}{C_{A0}}, \ \theta_{AB} = \frac{C_{AB}}{C_{A0}}, \ \theta_{B1} = \frac{C_{B1}}{C_{B0}}, \ \theta_{B2} = \frac{C_{B2}}{C_{B0}}, \ \alpha_1 = \frac{K_{b1}\delta^2 C_{A0}}{D_A.LC_{B0}}, \ \beta_1 = K_{ex1}C_{B0},$$

$$K_{ex1} = \frac{K_{f1}}{K_{b1}}, \ \gamma_1 = \frac{K_{b1}\delta}{D_A}, \ \xi = \frac{D_{AB}}{D_A}, \ \alpha_2 = \frac{K_{b_2}\delta^2 C_{A0}}{D_A.LC_{B0}}, \ \beta_2 = K_{ex2}C_{B0}, \ K_{ex2} = \frac{K_{f2}}{K_{b2}}, \ \gamma_2 = \frac{K_{b2}\delta}{D_A} \tag{12a-o}$$

where D_A are 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=δ. 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}).

Through a mass balance in the membrane for the species A_m and AB_m, and assuming that the diffusion coefficients D_A and D_{AB} are equals, and consequently ξ=1, it is found

$$\theta_{AB}(\eta,\tau) = 1 - \theta_A(\eta,\tau) \tag{13}$$

Introducing Eq. (13) into Eqs. (2) to (11), such equations are rewritten as

$$\frac{\partial\theta_A(\eta,\tau)}{\partial\tau}=\frac{\partial^2\theta_A(\eta,\tau)}{\partial\eta^2},\quad 0<\eta<1,\ \ \tau>0 \tag{14}$$

$$\theta_A(\eta,0)=1,\quad 0\le\eta\le 1 \tag{15}$$

$$\frac{\partial\theta_A(0,\tau)}{\partial\eta}-\gamma_1\left[1+\beta_1\theta_{B1}(\tau)\right]\theta_A(0,\tau)=-\gamma_1;\qquad \frac{\partial\theta_A(1,\tau)}{\partial\eta}+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\theta_A(1,\tau)=\gamma_2,\quad \tau>0 \tag{16,17}$$

$$\frac{d\theta_{B1}(\tau)}{d\tau}=-\alpha_1\left[1+\beta_1\theta_{B1}(\tau)\right]\theta_A(0,\tau)+\alpha_1,\quad \tau>0 \tag{18}$$

$$\theta_{B1}(0)=1 \tag{19}$$

$$\frac{d\theta_{B2}(\tau)}{d\tau}=-\alpha_2\left[1+\beta_2\theta_{B2}(\tau)\right]\theta_A(1,\tau)+\alpha_2,\quad \tau>0 \tag{20}$$

$$\theta_{B2}(0)=0 \tag{21}$$

Now, in order to improve the computational performance, it is convenient to make a split-up procedure for the potential $\theta_A(\eta,\tau)$ to homogenize the boundary conditions in the η direction, in the following form:

$$\theta_A(\eta,\tau)=\theta_{A,p}(\eta;\tau)+\theta_{A,h}(\eta,\tau) \tag{22}$$

In the particular potential $\theta_{A,p}(\eta;\tau)$, variable τ is only a parameter, therefore, introducing Eq. (22) into Eqs. (14), (16) and (17), the solution for this particular function is obtained from

$$\frac{\partial^2\theta_{A,p}(\eta;\tau)}{\partial\eta^2}=0,\quad 0<\eta<1 \tag{23}$$

$$\frac{\partial\theta_{A,p}(0;\tau)}{\partial\eta}-\gamma_1\left[1+\beta_1\theta_{B1}(\tau)\right]\theta_{A,p}(0;\tau)=-\gamma_1;\qquad \frac{\partial\theta_{A,p}(1;\tau)}{\partial\eta}+\gamma_2\left[1+\beta_2\theta_{B2}(\tau)\right]\theta_A(1;\tau)=\gamma_2 \tag{24,25}$$

The integration of Eq. (23) leads to the following solution for the particular potential $\theta_{A,p}(\eta;\tau)$:

$$\theta_{A,p}(\eta;\tau)=C_1(\tau)\eta+C_2(\tau) \tag{26}$$

and the coefficients $C_1(\tau)$ and $C_2(\tau)$ are obtained from the application of Eq. (26) into boundary conditions given by Eqs. (24) and (25), as

$$C_1(\tau)=\frac{\gamma_1\gamma_2[\beta_1\theta_{B1}(\tau)-\beta_2\theta_{B2}(\tau)]}{\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2} \tag{27a}$$

$$C_2(\tau)=\frac{\gamma_1+\gamma_2+\gamma_1\gamma_2+\beta_2\gamma_1\gamma_2\theta_{B2}(\tau)}{\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2} \tag{27b}$$

Finally, also from the introduction of Eq. (22) into Eqs. (14) to (21), the homogeneous problem becomes

$$\frac{\partial\theta_{A,h}(\eta,\tau)}{\partial\tau}=\frac{\partial^2\theta_{A,h}(\eta,\tau)}{\partial\eta^2}-\left[\frac{dC_1(\tau)}{d\tau}\eta+\frac{dC_2(\tau)}{d\tau}\right],\quad 0<\eta<1,\ \ \tau>0 \tag{28}$$

$$\theta_{A,h}(\eta,0)=1-\left[\frac{\gamma_1\gamma_2\beta_1\eta+\gamma_1+\gamma_2+\gamma_1\gamma_2}{\gamma_1\beta_1(1+\gamma_2)+\gamma_1+\gamma_2+\gamma_1\gamma_2}\right],\quad 0\le\eta\le 1 \tag{29}$$

$$\frac{\partial\theta_{A,h}(0,\tau)}{\partial\eta}-\gamma_1\left[1+\beta_1\theta_{B1}(\tau)\right]\theta_{A,h}(0,\tau)=0;\qquad \frac{\partial\theta_{A,h}(1,\tau)}{\partial\eta}+\gamma_2\left[1+\beta_2\theta_{B2}(\tau)\right]\theta_{A,h}(1,\tau)=0,\quad \tau>0 \tag{30,31}$$

$$\frac{d\theta_{B1}(\tau)}{d\tau}=-\alpha_1\left[1+\beta_1\theta_{B1}(\tau)\right]\left[C_2(\tau)+\theta_{A,h}(0,\tau)\right]+\alpha_1,\quad \tau>0 \tag{32}$$

$$\theta_{B1}(0)=1 \tag{33}$$

$$\frac{d\theta_{B2}(\tau)}{d\tau}=-\alpha_2\left[1+\beta_2\theta_{B2}(\tau)\right]\left[C_1(\tau)+C_2(\tau)+\theta_{A,h}(1,\tau)\right]+\alpha_2,\quad \tau>0 \tag{34}$$

$$\theta_{B2}(0)=0 \tag{35}$$

2.1. Solution methodology

The next step is to find a solution for the potential $\theta_{A,h}(\eta,\tau)$, and for this purpose, it is followed the ideas in the GITT approach (Cotta, 1993), so that it has to be selected an appropriate auxiliary eigenvalue problem, which shall provide the basis for the eigenfunction expansion. Therefore, the following eigenvalue problem is proposed:

$$\frac{d^2\Phi_i(\eta)}{d\eta^2}+\lambda_i^2\Phi_i(\eta)=0, \quad 0<\eta<1 \tag{36a}$$

$$\frac{d\Phi_i(0)}{d\eta}-\gamma_1(1+\beta_1)\Phi_i(0)=0; \quad \frac{d\Phi_i(1)}{d\eta}+\gamma_2\Phi_i(1)=0 \tag{36a,b}$$

Equations (36) can be analytically solved to yield, respectively, the eigenfunctions and eigenvalues as

$$\Phi_i(\eta)=\lambda_i\cos(\lambda_i\eta)+\gamma_1(1+\beta_1)\sin(\lambda_i\eta); \quad \tan(\lambda_i)=\frac{\lambda_i[\gamma_1(1+\beta_1)+\gamma_2]}{\lambda_i^2-\gamma_1\gamma_2(1+\beta_1)}, \quad i=1,2,3..... \tag{37a,b}$$

It can be shown that the eigenfunctions $\Phi_i(\eta)$ enjoy the following orthogonality property:

$$\int_0^1 \Phi_i(\eta)\Phi_j(\eta)d\eta=\begin{cases}0, & i\neq j\\ N_i, & i=j\end{cases} \tag{37c}$$

where N_i is the normalization integral, which together with the normalized eigenfunctions are, respectively, computed as

$$N_i=\frac{1}{2}\{[\lambda_i^2+\gamma_1^2(1+\beta_1)^2][1+\gamma_2/(\lambda_i^2+\gamma_2^2)]+\gamma_1(1+\beta_1)\}; \quad \widetilde{\Phi}_i(\eta)=\Phi_i(\eta)/N_i^{1/2} \tag{37d,e}$$

The auxiliary eigenvalue problem given by Eqs. (36) allows the definition of the following integral transform pair for the potentials $\theta_{A,h}(\eta,\tau)$ as:

$$\bar{\theta}_i(\tau)=\int_0^1 \widetilde{\Phi}_i(\eta)\theta_{A,h}(\eta,\tau)d\eta, \qquad \text{transform}; \quad \theta_{A,h}(\eta,\tau)=\sum_{i=1}^{\infty}\widetilde{\Phi}_i(\eta)\bar{\theta}_i(\tau), \qquad \text{inverse} \tag{38a,b}$$

The next step is thus to accomplish the integral transformation of the original partial differential system given by Eqs. (28) to (35). For this purpose, Eqs. (28) and the initial condition (29) are multiplied by the normalized eigenfunctions, integrated over the domain [0,1] in η, and the inverse formula given by Eq. (38b) is employed. After the appropriate manipulations, the following coupled ordinary differential system results, for the calculation of the transformed potentials $\bar{\theta}_i(\tau)$:

$$\frac{d\bar{\theta}_i(\tau)}{d\tau}+\sum_{j=1}^{\infty}A_{ij}(\tau)\bar{\theta}_j(\tau)=\bar{g}_i(\tau) \tag{39a}$$

$$\bar{\theta}_i(0)=f_i=\int_0^1 \widetilde{\Phi}_i(\eta)\left\{1-\left[\frac{\gamma_1\gamma_2\beta_1\eta+\gamma_1+\gamma_2+\gamma_1\gamma_2}{\gamma_1\beta_1(1+\gamma_2)+\gamma_1+\gamma_2+\gamma_1\gamma_2}\right]\right\}d\eta \tag{39b}$$

where the coefficients in Eq. (39a) are defined as follows:

$$\begin{aligned}A_{ij}(\tau)={}&\lambda_i^2\delta_{ij}-\beta_1\gamma_1[1-\theta_{B1}(\tau)]\widetilde{\Phi}_i(0)\widetilde{\Phi}_j(0)+\beta_2\gamma_2\theta_{B2}(\tau)\widetilde{\Phi}_i(1)\widetilde{\Phi}_j(1)\\&+\left[F_1(\tau)\int_0^1\eta\widetilde{\Phi}_i(\eta)d\eta+F_2(\tau)\int_0^1\widetilde{\Phi}_i(\eta)d\eta\right]\widetilde{\Phi}_j(0)+\left[F_3(\tau)\int_0^1\eta\widetilde{\Phi}_i(\eta)d\eta+F_4(\tau)\int_0^1\widetilde{\Phi}_i(\eta)d\eta\right]\widetilde{\Phi}_j(1)\end{aligned} \tag{39c}$$

$$\bar{g}_i(\tau)=F_5(\tau)\int_0^1\eta\widetilde{\Phi}_i(\eta)d\eta+F_6(\tau)\int_0^1\widetilde{\Phi}_i(\eta)d\eta \tag{39d}$$

$$F_1(\tau)=-\frac{\alpha_1\beta_1\gamma_1\gamma_2[1+\beta_1\theta_{B1}(\tau)][1+\beta_2\theta_{B2}(\tau)]\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2} \tag{39e}$$

$$F_2(\tau)=\frac{\alpha_1\beta_1\gamma_1[1+\beta_1\theta_{B1}(\tau)]\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2} \tag{39f}$$

$$F_3(\tau)=\frac{\alpha_2\beta_2\gamma_1\gamma_2[1+\beta_1\theta_{B1}(\tau)][1+\beta_2\theta_{B2}(\tau)]\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_1\theta_{B1}(\tau)]\}\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2} \tag{39g}$$

$$F_4(\tau)=\frac{\alpha_2\beta_2\gamma_2\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_1\theta_{B1}(\tau)]\}\}[1+\beta_2\theta_{B2}(\tau)]}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2} \tag{39h}$$

$$\begin{aligned}F_5(\tau)=&\frac{\alpha_2\beta_2\gamma_1\gamma_2[1+\beta_1\theta_{B1}(\tau)]\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_1\theta_{B1}(\tau)]\}\}\{1-[1+\beta_2\theta_{B2}(\tau)][C_1(\tau)+C_2(\tau)]\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2}-\\&\frac{\alpha_1\beta_1\gamma_1\gamma_2[1+\beta_2\theta_{B2}(\tau)]\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\}\{1-[1+\beta_1\theta_{B1}(\tau)]C_2(\tau)\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2}\end{aligned} \tag{39i}$$

$$\begin{aligned}F_6(\tau)=&\frac{\alpha_2\beta_2\gamma_2\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_1\theta_{B1}(\tau)]\}\}\{1-[1+\beta_2\theta_{B2}(\tau)][C_1(\tau)+C_2(\tau)]\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2}+\\&\frac{\alpha_1\beta_1\gamma_1\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\{\gamma_2+\gamma_1\{1+\gamma_2[1+\beta_2\theta_{B2}(\tau)]\}\}\{1-[1+\beta_1\theta_{B1}(\tau)]C_2(\tau)\}}{[\gamma_1\beta_1(1+\gamma_2)\theta_{B1}(\tau)+\beta_2\gamma_2(1+\gamma_1)\theta_{B2}(\tau)+\beta_1\beta_2\gamma_1\gamma_2\theta_{B1}(\tau)\theta_{B2}(\tau)+\gamma_1+\gamma_2+\gamma_1\gamma_2]^2}\end{aligned} \tag{39j}$$

Similarly, kinetic equations for the potentials θ_{B1} and θ_{B2}, Eqs (32) to (35), are integral transformed as

$$\frac{d\theta_{B1}(\tau)}{d\tau}=-\alpha_1\left[1+\beta_1\theta_{B1}(\tau)\right]\left[C_2(\tau)+\sum_{i=1}^{\infty}\tilde{\Phi}_i(0)\bar{\theta}_i(\tau)\right]+\alpha_1 \tag{40a}$$

$$\theta_{B1}(0)=1 \tag{40b}$$

$$\frac{d\theta_{B2}(\tau)}{d\tau}=-\alpha_2\left[1+\beta_2\theta_{B2}(\tau)\right]\left[C_1(\tau)+C_2(\tau)+\sum_{i=1}^{\infty}\tilde{\Phi}_i(1)\bar{\theta}_i(\tau)\right]+\alpha_2 \tag{41a}$$

$$\theta_{B2}(0)=0 \tag{41b}$$

In order to numerically handle the ODE system for the transformed potential given by Eqs. (39), together with the kinetic Eqs. (40) to (41) through the subroutine DIVPAG of the IMSL Library (1991), it is necessary to truncate the infinite series in a sufficiently high number of terms NT so as to guarantee the requested relative error in obtaining the original potentials. This subroutine solves initial value problems with stiff behavior, and provides the important feature of automatically controlling the relative error in the solution of the ordinary differential equations system, allowing the user to establish error targets for the transformed potentials. Therefore, such system is solved to compute the transformed potentials $\bar{\theta}_i(\tau)$, as well as the potentials $\theta_{B1}(\tau)$ and $\theta_{B2}(\tau)$.Once this system is solved for the transformed potential, the inverse formula, Eq. (38b), is recalled to provide the potential $\theta_{A,h}(\eta,\tau)$ and to furnish the complete concentration field.

3. RESULTS AND DISCUSSION

Numerical results for the Au (III) 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 an INTEL CORE (TM) 2 DUO 2.13 GHz computer. The routine DIVPAG from the IMSL Library (1991) was used to numerically handle the system of ordinary differential equations given by Eqs. (39) to (41), with a relative error target of 10^{-8} prescribed by the user. For the simulation of the membrane composition influence, the experimental results of Argiropoulos et al. (1998) 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 on the experimental data of Argiropoulos et al. (1998).

Table 1. Model parameters for the computational simulation of Au (III).

D_A (m^2/s)	D_{AB} (m^2/s)	K_{b1} (m/s)	K_{b2} (m/s)	K_{f1} (m^4/mol.s)	K_{f2} (m^4/mol.s)	δ (μm)	L (m)	C_{A0} (g/g)	C_{B0} (mg/l)
2.6×10^{-14}	$1\times D_A$	8.5×10^{-11}	$10\times K_{b1}$	6.35×10^{-9}	$0.95\times K_{f1}$	13	0.1	22%	130
8.5×10^{-14}	$1\times D_A$	2.7×10^{-10}	$6.4\times K_{b1}$	1.2×10^{-9}	$1\times K_{f1}$	14	0.1	30%	100
4.5×10^{-13}	$1\times D_A$	1.25×10^{-10}	$13\times K_{b1}$	1.1×10^{-9}	$1\times K_{f1}$	13.5	0.1	40%	100
2.5×10^{-10}	$1\times D_A$	4.6×10^{-10}	$13\times K_{b1}$	0.5×10^{-8}	$1\times K_{f1}$	16	0.1	50%	100

Table 2 shows the convergence behavior for the dimensionless concentrations of Aliquat 336, θ_A, as well as of metallic complex, θ_{AB}, in a membrane with 22% (w/w) of Aliquat 336. The analysis is done at different dimensionless positions and with times of 1.6, 80 and 160 h. As can be observed, a convergence of four digits is obtained for both concentrations with $NT \leq 300$. Also, it is verified an excellent behavior among the GITT results with those obtained with a Finite Difference Method (FDM) also here developed.

Table 2. Convergence behavior of the dimensionless concentrations θ_A and θ_{AB} for a membrane with 22% (w/w) of Aliquat 336.

Time=1.6 h										
NT	θ_A					θ_{AB}				
	η					η				
	0	**0.25**	**0.5**	**0.75**	**1**	**0**	**0.25**	**0.5**	**0.75**	**1**
25	0.8031	0.8387	0.8670	0.8878	0.9016	0.1969	0.1613	0.1330	0.1122	0.0984
50	0.8031	0.8387	0.8670	0.8878	0.9016	0.1969	0.1613	0.1330	0.1122	0.0984
100	0.8031	0.8387	0.8670	0.8878	0.9016	0.1969	0.1613	0.1330	0.1122	0.0984
200	0.8031	0.8387	0.8670	0.8878	0.9016	0.1969	0.1613	0.1330	0.1122	0.0984
300	0.8032	0.8387	0.8670	0.8878	0.9016	0.1968	0.1613	0.1330	0.1122	0.0984
400	0.8032	0.8387	0.8670	0.8878	0.9016	0.1968	0.1613	0.1330	0.1122	0.0984
500	0.8032	0.8387	0.8670	0.8878	0.9016	0.1968	0.1613	0.1330	0.1122	0.0984
FDM	0.8032	0.8387	0.8670	0.8878	0.9016	0.1968	0.1613	0.1330	0.1122	0.0984
Time=80 h										
NT	θ_A					θ_{AB}				
	η					η				
	0	**0.25**	**0.5**	**0.75**	**1**	**0**	**0.25**	**0.5**	**0.75**	**1**
25	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
50	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
100	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
200	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
300	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
400	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
500	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
FDM	0.6595	0.6738	0.6881	0.7024	0.7167	0.3405	0.3262	0.3119	0.2976	0.2833
Time=160 h										
NT	θ_A					θ_{AB}				
	η					η				
	0	**0.25**	**0.5**	**0.75**	**1**	**0**	**0.25**	**0.5**	**0.75**	**1**
25	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
50	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
100	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
200	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
300	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
400	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
500	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896
FDM	0.6827	0.6896	0.6965	0.7035	0.7104	0.3173	0.3104	0.3035	0.2965	0.2896

Figure 2 illustrates a comparison between the present GITT solution and that obtained with a Finite Difference Method (FDM). It can be noted an excellent agreement between the two methodologies, this way validating the numerical codes developed here.

Finally, Figure 3 shows the influence of the membrane composition for the Au (III) extraction. From this figure, it is observed that the extraction is more efficient when greater contents of Aliquat 336 are utilized. For the case of 50% of Aliquat in the membrane, more than 80% of Au (III) is extracted after 50 h of contact time. Also, this figure shows a comparison of the present GITT results with those experimental results of Argiropoulos et al. (1998) evidencing a good agreement. The behavior of Aliquat 336 content in the extraction process can be explained by the L'Chatelier principle, since from Eqs. (1) one may see that an increase in its content promotes the displacement of equilibrium for the formation of complex metal AB in the membrane.

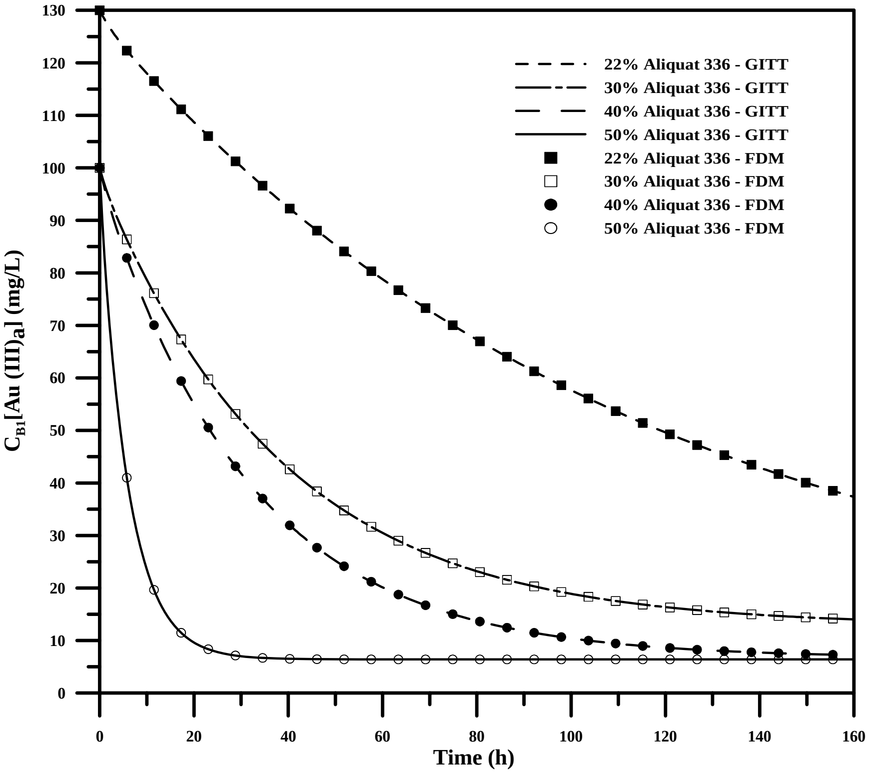

Figure 2. Comparison of the GITT and FDM approaches for the extraction of Au (III).

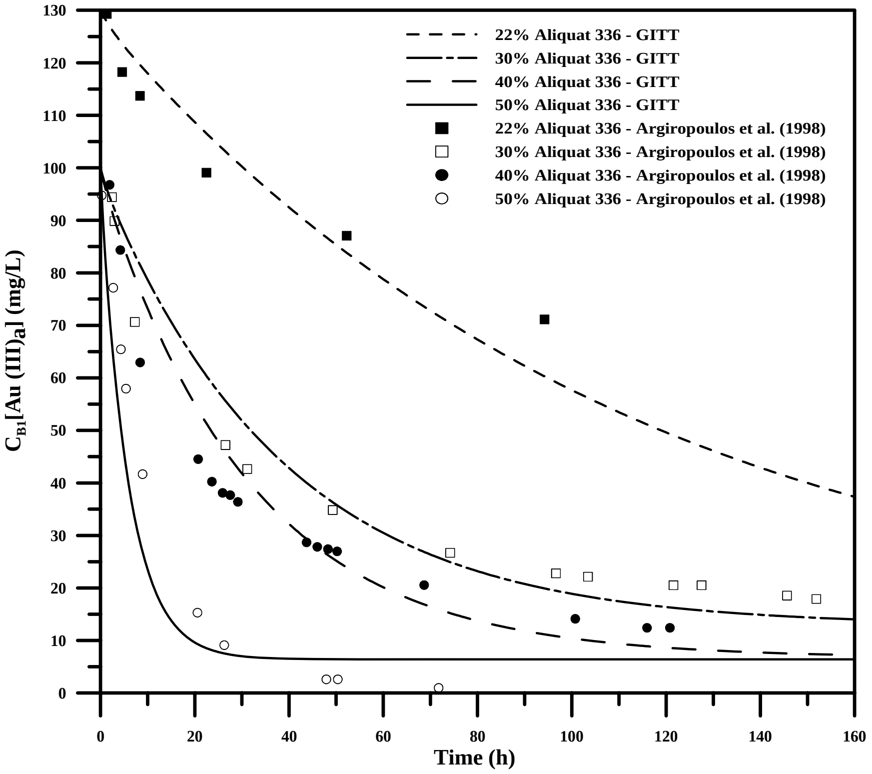

Figure 3. Influence of Aliquat 336 content in the membrane during the Au (III) extraction.

4. CONCLUSIONS

A study of membrane extraction process of gold Au (III) by using supported liquid membranes (SLM) 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 generalized integral transform technique (GITT), which provided reliable and cost effective simulations for the considered cases. Also, it was verified that the present GITT solution was in an excellent agreement with that developed with Finite Difference Method (FDM), this way offering a direct validation of the present results. The good agreement with the experimental results of Argiropoulos et al. (1998) demonstrated the consistency of this approach and adequacy for benchmarking such class of problems.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by the program of SEDECT (Secretaria Estadual de Desenvolvimento de Ciência e Tecnologia) a governmental support agency from the State of Pará in Brazil.

6. REFERENCES

Argiropoulos, G.A., Cattrall, R.W., Hamilton, I.C., Kolev, S.D. and Paimin, R., 1998, "The Study of a Membrane for Extracting Gold (III) from Hydrochloric Acid Solutions", J. Membr. Sci., Vol.138, pp. 279-285.

Cardoso, S.A., Quaresma, J.N.N., Macêdo, E.N. and Cotta, R.M., 2007, "Computational Simulation of Extraction Process of Gold Using Polymeric Membranes", Proceedings of the 19th Brazilian Congress of Mechanical Engineering, Vol.1, Brasília, Brazil, pp. 1-3.

Cotta, R.M., 1993, "Integral Transforms in Computational Heat and Fluid Flow", Boca Raton: CRC Press.

Cotta, R.M., 1994, "Benchmark Results in Computational Heat and Fluid Flow: - The Integral Transform Method", Int. J. Heat Mass Transfer (Invited Paper), Vol. 37 (Suppl. 1), pp. 381-393.

Cotta, R.M., 1998, "The Integral Transform Method in Thermal and Fluid Sciences and Engineering", Begell House, New York.

Cotta, R.M., Santos, C.A.C., Quaresma, J.N.N. and Perez-Guerrero, J.S., 2005, "Hybrid Integral Transforms in Convection-Diffusion: Recent Applications in Internal Flow Simulation", Invited Lecture, Proceedings of the 4th International Conference on Computational Heat and Mass Transfer, 4th ICCHMT, Vol. 1, Paris-Cachan, France, pp. 153-164.

Cotta, R.M. and Mikhailov, M.D., 2006, "Hybrid Methods and Symbolic Computations", in: Handbook of Numerical Heat Transfer, 2nd edition, Chapter 16, Eds. W. J. Minkowycz, E. M. Sparrow, and J. Y. Murthy, John Wiley, New York, pp. 493-522.

IMSL Library. MATH/LIB. Houston; 1991.

Mikhailov, M.D. and Özisik, M.N., 1984, "Unified Analysis and Solutions of Heat and Mass Diffusion", John Wiley, New York.

Reyes-Aguilera, J.A., Gonzalez, M.P., Navarro, R., Saucedo, T.I. and Avila-Rodriguez, M., 2008, "Supported Liquid Membranes (SLM) for Recovery of Bismuth from Aqueous Solutions", J. Membr. Sci., Vol. 310, pp. 13-19.

Santos, C.A.C., Quaresma, J.N.N. and Lima, J.A., 2001, "Benchmark Results for Convective Heat Transfer in Ducts: - The Integral Transform Approach", ABCM Mechanical Sciences Series, Editora E-Papers, Rio de Janeiro, Brazil.

Wang, L., Paimin, R., Cattral, R.W., Shen, W. and Kolev, S.D., 2000, "The Extraction of Cadmium (II) and Copper (II) from Hydrochloric Acid Solutions Using an Aliquat 336/PVC Membrane", J. Membr. Sci., Vol. 176, pp. 105-111.

7. RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.