

# THE COUPLED INTEGRAL EQUATIONS APPROACH IN THE MODELING AND SIMULATION OF THE MEMBRANE SEPARATION PROCESS OF METALS

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**Abstract.** *A mixed lumped-differential mathematical model is proposed to analyze the extraction of metallic palladium Pd (II) present in a hydrochloric acid medium by using a polymeric liquid membrane with the extractant Aliquat 336 immobilized in a PVC matrix. The Coupled Integral Equations Approach (CIEA) is employed in order to simplify the associated equations of species conservation and obtain improved lumped formulations. This technique is aimed at reducing the number of space variables involved in the mathematical formulation of the original problem through an averaging procedure on the coordinate(s) selected to be eliminated from the reformulated problem, employing Hermite's approximations for integrals. In the present model, it was considered that a second-order chemical reaction occurs at the membrane interfaces. From the constructed model, the behavior of the metal 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. Also, the proposed model results are verified against the fully differential formulation, previously solved through integral transforms, and compared with other models reported in the literature to demonstrate its consistency.*

**Keywords:** *Lumped analysis, Mass transfer, Aliquat 336/PVC membrane, Palladium extraction, Coupled integral equations approach.*

## 1. INTRODUCTION

In supported liquid membranes the liquid barrier material is selectively stabilized as a thin film with the aid of a support material, such as in membranes using Aliquat 336 as extractant immobilized in PVC, which is used as support material. The extractant Aliquat 336, also known as methyl tri-octyl-ammonium chloride, is a quaternary ammonium salt that is insoluble in water and made by methylation of the mixture tri(octyl-decyl) amine, which is capable of forming oil soluble salts of anionic species and neutral pH slightly alkaline. This extractant is widely used in the preparation of liquid membranes. In this case comprises a variety of anionic complex associations, employing it as a quaternary ammonium ion. It is also useful as an analytical tool in organic and biochemical activities (Cardoso, 2007).

Argiropoulos *et al.* (1998), Kolev *et al.* (2000) and Wang *et al.* (2000) have studied the extraction efficiency of Pd (II), Cu (II), Cd (II) and Au (III) in hydrochloric acid solution using polymeric liquid membranes. Argiropoulos *et al.* (1998) conducted an experimental study for the extraction of Au (III) in supported liquid membrane consisting of Aliquat 336 in order to investigate the efficiency of membrane extraction of metal gold (III) and to investigate the influence of membrane composition in Aliquat 336, as well as of other metals present in the hydrochloric acid solution, indicating that the membrane is able to extract Au (III). The work of Kolev *et al.* (2000) emphasizes the study of an extraction model of palladium in hydrochloric acid solution using a supported polymer membrane Aliquat 336/PVC. The authors adjusted their model to extraction experimental data in order to obtain the values of the constant physical and chemical properties (diffusion coefficient and kinetic constants). Wang *et al.* (2000) were concerned with describing the influence of a given polymeric membrane extraction process for copper and cadmium, and applied a model in which the extraction mechanism was governed by chemical kinetics at the membrane interfaces and by diffusion within the membrane. The results were adjusted to the experimental values to provide values of the diffusion coefficients and kinetic constants of the complexation reaction between the extractant species (Aliquat 336) and the metal to be extracted.

Cardoso (2007) and Macêdo *et al.* (2007) conducted research on modeling and simulation of metals extraction, namely, cadmium, gold and palladium in supported liquid membranes with Aliquat 336/PVC. In this study, the

extraction problem was modeled from the equations of species conservation and was solved using the Method of Lines. The model was verified by comparison with the experimental results of Argiropoulos *et al.* (1998), Kolev *et al.* (2000) and Wang *et al.* (2000). It was assumed that there is no symmetry condition across the membrane thickness because the membrane walls are separated by acidic aqueous solutions with different concentrations in relation to the metal of interest in the study. More recently, Cardoso (2010) has conducted a similar study employing the same model proposed by Cardoso (2007), but employing the Generalized Integral Transform Technique (GITT) for solving the involved nonlinear partial differential equations of the model, and verifying the previous obtained numerical solution.

It is of interest in engineering practice, to propose simpler formulations of such partial differential systems, through a reduction of the number of space variables, since the local variation of concentrations is not of fundamental concern, by integration (averaging) of the full partial differential equations in one or more space variables, but retaining some information in the direction integrated out, provided by the related boundary conditions. Different levels of approximation in such mixed lumped differential formulations can be used, starting from the plain and classical lumped system analysis, towards improved formulations, obtained through Hermite-type approximations for integrals (Hermite, 1878; Mennig *et al.*, 1983). Such an approach known as the Coupled Integral Equations Approach, CIEA (Cotta and Mikhailov, 1997) has been already exploited in different heat transfer problems, including phase change problems, extended surfaces, heat exchangers analysis and drying problems (Aparecido and Cotta, 1989; Cotta *et al.*, 1990; Scofano Neto and Cotta, 1993; Cheroto *et al.*, 1997).

In this context, the present study aims at employing the Coupled Integral Equations Approach (CIEA) (Cotta and Mikhailov, 1997) to obtain improved lumped-differential formulations for the analysis of palladium Pd (II) extraction from a hydrochloric acid solution using a supported polymer membrane Aliquat 336/PVC. The CIEA technique allows the reduction on the number of independent variables, this way, markedly reducing the complexity in the simulation process. The resulting system of reformulated ordinary differential equations is then solved through the subroutine DIVPAG from the IMSL Library (1991) and critical comparisons with experimental data and theoretical results are performed in order to assess the adequacy of the present approach.

## 2. MATHEMATICAL FORMULATION

A typical process with polymeric membrane is illustrated in Figure 1 below, in which it is assumed that the first compartment of the extraction cell has an acidic solution concentrated in metals of interest, such as palladium Pd (II) in hydrochloric acid (HCl),  $C_{B1}$ , in the second compartment there is a dilute solution in the metals of interest, in the presence of HCl with concentration  $C_{B2}$ .

The composition of the polymer membrane consists of a mixture of Aliquat 336 and PVC. In the present model, we have assumed the following hypotheses:

- Elementary reversible reaction of order 2 for the metal palladium, Pd (II), and the extractant Aliquat 336 occurs at the membrane interfaces (complexation in the exhaustion cell and decomplexation in the enrichment cell);
- The ion metal rate of extraction is influenced by the kinetics of chemical reaction that occurs on the membrane surface;
- The diffusion in the aqueous phase is neglected because the mass transport at this phase is fast and occurs by mechanical agitation;
- One-dimensional transient diffusion through the membrane by the complex species (Aliquat-metal) formed on the membrane interface.

Mathematical modeling of this process is obtained via the equations of mass conservation for the chemical species in the extraction cell at a given temperature  $T$ , volume  $V$  and stirring angular velocity  $\Omega$  in each half-cell, considering the extraction kinetics as a reversible elementary reaction of order 2:



Here,  $A_{(me)}$  represents the extractant in the membrane, Aliquat 336,  $B_{(aq)}$  represents the metal in solution,  $[A_2B]_{(me)}$  the metal that was inserted into the membrane and will be referenced for  $AB_{(me)}$ , and  $K_{f1}$  and  $K_{b1}$  are the forward and the backward kinetic rate constants, respectively, at the position  $x = 0$  of the membrane. Similarly,



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

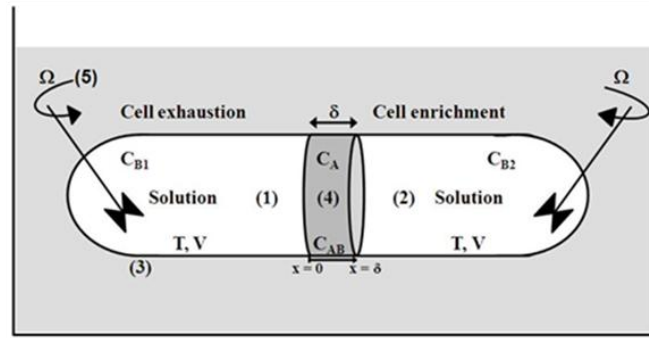


Figure 1. Schematic representation of the extraction cell: (1) Phase feed; (2) Phase of data collection; (3) Thermostatic bath; (4) Membrane and (5) Stirrer.

The membrane diffusion occurs through a thin film as shown in Figure 2. On each side of the film there is a well-mixed solution. Both solutions are diluted, and the solute diffuses through the membrane from the more concentrated solution, located at  $x = 0$ , to the lower concentration, located at  $x = \delta$ .

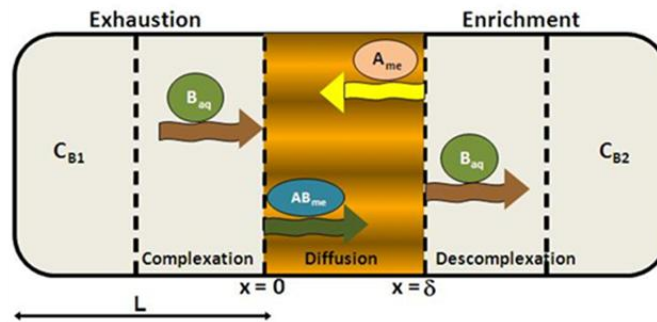


Figure 2. Extraction mechanism in the cell.

In each compartment of the extraction cell occurs the same elementary reversible reaction of order 2, but with different physico-chemical parameters. At the position  $x = 0$ , there is the consumption of metal  $B_{(aq)}$  through the reaction with kinetic constants  $K_{f1}$  and  $K_{b1}$ . After the metal is consumed, it is transformed in a complex species, which is formed by the reaction of metal  $B_{(aq)}$  in solution with the extractant Aliquat 336 present in the membrane at a given concentration. Then, this new species moves by diffusion to the other membrane edge,  $x = \delta$ . At this surface, the metallic species is then consumed for the regeneration of the metal in the second compartment of the extraction cell with kinetic rate constants  $K_{f2}$  and  $K_{b2}$ . This is due to the concentration gradient in the extraction cell, which favors the transport of the species  $AB_{(me)}$  in the membrane, thus providing in this way different kinetic rate constants at each membrane edge.

According to Cardoso (2007), the nonlinear partial differential model in dimensionless form for the transient diffusion of species  $A_{(me)}$  and  $AB_{(me)}$  in the membrane, with their respective initial and boundary conditions, are given by:

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

$$\theta_A(\eta, 0) = 1; \quad \theta_{AB}(\eta, 0) = 0 \quad (2.c,d)$$

$$\frac{\partial \theta_A(0, \tau)}{\partial \eta} = f_1(0, \tau); \quad \frac{\partial \theta_{AB}(0, \tau)}{\partial \eta} = f_2(0, \tau); \quad \frac{\partial \theta_A(1, \tau)}{\partial \eta} = f_3(1, \tau); \quad \frac{\partial \theta_{AB}(1, \tau)}{\partial \eta} = f_4(1, \tau) \quad (3.a-d)$$

where,  $f_1(0, \tau)$ ,  $f_2(0, \tau)$ ,  $f_3(0, \tau)$  and  $f_4(0, \tau)$  are defined as:

$$f_1(0, \tau) = \gamma_1 \beta_1 \theta_{B1}(\tau) [\theta_A(0, \tau)]^2 - \gamma_1 \theta_{AB}(0, \tau); \quad f_2(0, \tau) = \left\{ \gamma_1 \theta_{AB}(0, \tau) - \gamma_1 \beta_1 \theta_{B1}(\tau) [\theta_A(0, \tau)]^2 \right\} / \xi \quad (4.a,b)$$

$$f_3(1, \tau) = \gamma_2 \theta_{AB}(1, \tau) - \gamma_2 \beta_2 \theta_{B2}(\tau) [\theta_A(1, \tau)]^2; \quad f_4(1, \tau) = \left\{ \gamma_2 \beta_2 \theta_{B2}(\tau) [\theta_A(1, \tau)]^2 - \gamma_2 \theta_{AB}(1, \tau) \right\} / \xi \quad (4.c,d)$$

The following dimensionless groups were used in Eqs. (2) to (4) above:

$$\eta = \frac{x}{\delta}; \quad \tau = \frac{D_A t}{\delta^2}; \quad \theta_A = \frac{C_A}{C_A^0}; \quad \theta_{AB} = \frac{C_{AB}}{C_A^0}; \quad \theta_{B1} = \frac{C_{B1}}{C_{B1}^0}; \quad \theta_{B2} = \frac{C_{B2}}{C_{B1}^0}; \quad \xi = \frac{D_{AB}}{D_A}; \quad \alpha_1 = \frac{K_{b1} \delta^2 C_A^0}{D_A L C_{B1}^0}; \quad \gamma_1 = \frac{K_{b1} \delta}{D_A} \quad (5.a-i)$$

$$\alpha_2 = \frac{K_{b2} \delta^2 C_A^0}{D_A L C_{B1}^0}; \quad \gamma_2 = \frac{K_{b2} \delta}{D_A}; \quad \beta_1 = K_{ex1} C_{B1}^0 C_A^0; \quad \beta_2 = K_{ex2} C_{B1}^0 C_A^0; \quad K_{ex1} = \frac{K_{f1}}{K_{b1}}; \quad K_{ex2} = \frac{K_{f2}}{K_{b2}} \quad (5.j-o)$$

where,  $K_{ex1}$  and  $K_{ex2}$ , are parameters with units  $m^6/mol^2$ .

In addition, the following dimensionless kinetic equations in the exhaustion and enrichment cells are obtained for the metal  $B_{(aq)}$  (Cardoso, 2007):

$$\frac{d\theta_{B1}(\tau)}{d\tau} = -\alpha_1 \beta_1 \theta_{B1}(\tau) [\theta_A(0, \tau)]^2 + \alpha_1 \theta_{AB}(0, \tau); \quad \theta_{B1}(0) = 1, \quad \text{at } \eta=0 \text{ (exhaustion surface)} \quad (6.a,b)$$

$$\frac{d\theta_{B2}(\tau)}{d\tau} = -\alpha_2 \beta_2 \theta_{B2}(\tau) [\theta_A(1, \tau)]^2 + \alpha_2 \theta_{AB}(1, \tau); \quad \theta_{B2}(0) = 0, \quad \text{at } \eta=1 \text{ (enrichment surface)} \quad (7.a,b)$$

To obtain the potentials  $\theta_{B1}(\tau)$  and  $\theta_{B2}(\tau)$  through the solution of Eqs. (6) and (7), it will also be necessary to calculate the potentials  $\theta_A(\eta, \tau)$  and  $\theta_{AB}(\eta, \tau)$  that will be obtained by the solution of Eqs. (2) and (3). For this purpose, we shall here employ the Coupled Integral Equations Approach (CIEA) in order to reduce the number of independent variables, and as a consequence the computational cost of the simulation, by lumping the system with respect to the space variable.

### 3. SOLUTION METHODOLOGY

In order to obtain improved lumped-differential formulations for the system given by Eqs. (2) to (7), we shall employ Hermite-type approximations for integrals in evaluating the spatially averaged quantities. Hermite(1878) developed a way of approximating an integral, based on the values of the integrand and its derivatives at the integration limits, in the form:

$$\int_{x_{i-1}}^{x_i} y(x) dx \cong \sum_{v=0}^{\alpha} C_v y_{i-1}^{(v)} + \sum_{v=0}^{\beta} D_v y_i^{(v)} \quad (8.a)$$

where  $y(x)$  and its derivatives  $y^{(v)}(x)$  are defined for all  $x \in (x_{i-1}, x_i)$ . Furthermore, it is assumed that the numerical values of  $y^{(v)}(x_{i-1}) \equiv y_{i-1}^{(v)}$  for  $v=0, 1, 2, \dots, \alpha$  and  $y^{(v)}(x_i) \equiv y_i^{(v)}$  for  $v=0, 1, 2, \dots, \beta$ , are available at the end points of the interval. In such a manner, the integral of  $y(x)$  is expressed as a linear combination of  $y(x_{i-1})$ ,  $y(x_i) \equiv y_{i-1}^{(v)}$  and their derivatives,  $y^{(v)}(x_{i-1})$  up to order  $v=\alpha$ , and  $y^{(v)}(x_i)$  up to order  $v=\beta$ . This is called the  $H_{\alpha, \beta}$  - approximation (Cotta and Mikhailov, 1997). The resulting expression for the  $H_{\alpha, \beta}$  - approximation is given by:

$$\int_{x_{i-1}}^{x_i} y(x) dx \cong \sum_{v=0}^{\alpha} C_v(\alpha, \beta) h_i^{v+1} y_{i-1}^{(v)} + \sum_{v=0}^{\beta} C_v(\beta, \alpha) (-1)^v h_i^{v+1} y_i^{(v)} + O(h_i^{\alpha+\beta+3}) \quad (8.b)$$

where,

$$h_i = x_i - x_{i-1}, \quad C_v(\alpha, \beta) = \frac{(\alpha+1)! (\alpha+\beta+1-v)!}{(v+1)! (\alpha-v)! (\alpha+\beta+2)!} \quad (8.c,d)$$

Three Hermite integration formulae were here selected for analysis, including the classical trapezoidal and corrected trapezoidal expressions, i.e.:

$$H_{0,0} \rightarrow \int_0^h f(x) dx \cong \frac{h}{2} (f(0) + f(h)); \quad H_{1,1} \rightarrow \int_0^h f(x) dx \cong \frac{h}{2} (f(0) + f(h)) + \frac{h^2}{12} (f'(0) - f'(h)) \quad (8.e,f)$$

(Trapezoidal Rule) (Corrected Trapezoidal Rule)

$$H_{0,1} \rightarrow \int_0^h f(x) dx \cong \frac{h}{3} (f(0) + 2f(h)) - \frac{h^2}{6} f'(h) \quad (8.g)$$

We now seek a simplified formulation for the partial differential system, through elimination of the spatial dependence, i.e., by integrating out the independent variable  $\eta$  over the domain  $0 \leq \eta \leq 1$ , in Eqs. (2) to (7), so that a system of ordinary differential equations is obtained for the average and surface concentrations. Therefore, the definition of the average potentials for the species  $\theta_A(\eta, \tau)$  and  $\theta_{AB}(\eta, \tau)$  is taken as:

$$\bar{\theta}_A(\tau) = \int_0^1 \theta_A(\eta, \tau) d\eta; \quad \bar{\theta}_{AB}(\tau) = \int_0^1 \theta_{AB}(\eta, \tau) d\eta \quad (9.a,b)$$

The above definition above for the average potentials is employed in defining the integral operator to average the partial differential equations, Eqs. (2) and (3). For this purpose, such equations are integrated on the spatial variable  $\eta$ , over the domain  $[0,1]$ , and the following simpler notation for the boundary potentials is adopted:

$$\theta_A(0, \tau) \equiv \theta_{A0}(\tau); \quad \theta_{AB}(0, \tau) \equiv \theta_{AB0}(\tau); \quad \theta_A(1, \tau) \equiv \theta_{A1}(\tau); \quad \theta_{AB}(1, \tau) \equiv \theta_{AB1}(\tau) \quad (10a-d)$$

Then, after the averaging process, it follows that:

$$\frac{d\bar{\theta}_A(\tau)}{d\tau} = \bar{f}_3(\tau) - \bar{f}_1(\tau); \quad \frac{d\bar{\theta}_{AB}(\tau)}{d\tau} = \bar{f}_4(\tau) - \bar{f}_2(\tau); \quad \bar{f}_i(\tau) = f_i(0, \tau); \quad \bar{f}_{i+2}(\tau) = f_{i+2}(1, \tau), \quad i=1,2 \quad (11.a-f)$$

$$\frac{d\theta_{B1}(\tau)}{d\tau} = -\alpha_1 \beta_1 [\theta_{A0}(\tau)]^2 \theta_{B1}(\tau) + \alpha_1 \theta_{AB0}(\tau); \quad \frac{d\theta_{B2}(\tau)}{d\tau} = -\alpha_2 \beta_2 [\theta_{A1}(\tau)]^2 \theta_{B2}(\tau) + \alpha_2 \theta_{AB1}(\tau) \quad (11.g,h)$$

$$\bar{\theta}_A(0) = 1; \quad \bar{\theta}_{AB}(0) = 0; \quad \theta_{B1}(0) = 1; \quad \theta_{B2}(0) = 0 \quad (12.a-d)$$

To find the desired lumped formulation from Eqs. (11) and (12), it is necessary to find relationships among the boundary potentials  $\theta_{A0}(\tau)$ ,  $\theta_{AB0}(\tau)$ ,  $\theta_{A1}(\tau)$  and  $\theta_{AB1}(\tau)$ , and the average potentials, to be obtained through approximation of the integrals that define the averaged potentials and fluxes, such as those given by Eqs. (8).

### 3.1. Improved lumped-differential formulations

A few different formulations were here considered by employing different approximation formulae for the averaged dimensionless concentrations, while keeping the trapezoidal rule ( $H_{0,0}$  approximation) for the average dimensionless mass fluxes. We now briefly describe each of these approximation options.

#### Classical lumped analysis/ $H_{0,0}$ approximation

One of the simplest possible approximations is the classical lumped analysis, assuming that the concentrations of Aliquat 336 and of the complex species do not vary significantly along the membrane thickness, due to be order of micrometers, thus allowing for the following approximations:

$$\theta_{A0}(\tau) \cong \bar{\theta}_A(\tau); \quad \theta_{AB1}(\tau) = \bar{\theta}_{AB}(\tau) \quad (13.a,b)$$

#### $H_{0,0}/H_{0,0}$ approximation

In this case, the trapezoidal rule ( $H_{0,0}$  approximation) is employed to approximate the average concentrations:

$$\bar{\theta}_A(\tau) = \int_0^1 \theta_A(\eta, \tau) d\eta \cong [\theta_A(0, \tau) + \theta_A(1, \tau)] / 2 = [\theta_{A0}(\tau) + \theta_{A1}(\tau)] / 2; \quad (14.a,b)$$

$$\bar{\theta}_{AB}(\tau) = \int_0^1 \theta_{AB}(\eta, \tau) d\eta \cong [\theta_{AB}(0, \tau) + \theta_{AB}(1, \tau)] / 2 = [\theta_{AB0}(\tau) + \theta_{AB1}(\tau)] / 2$$

#### $H_{0,1}/H_{0,0}$ approximation

In this model, Equations (9) are approximated by Eq. (8.c), to yield:

$$6\bar{\theta}_A(\tau) = 2[\theta_{A0}(\tau) + 2\theta_{A1}(\tau)] - \bar{f}_3(\tau); \quad 6\bar{\theta}_{AB}(\tau) = 2[\theta_{AB0}(\tau) + 2\theta_{AB1}(\tau)] - \bar{f}_4(\tau) \quad (15.a,b)$$

#### $H_{1,1}/H_{0,0}$ approximation

Equations (9) are approximated by Eq. (8.b), the corrected trapezoidal rule, resulting in:

$$12\bar{\theta}_A(\tau) = 6[\theta_{A0}(\tau) + \theta_{A1}(\tau)] + [\bar{f}_1(\tau) - \bar{f}_3(\tau)]; \quad 12\bar{\theta}_{AB}(\tau) = 6[\theta_{AB0}(\tau) + \theta_{AB1}(\tau)] + [\bar{f}_2(\tau) - \bar{f}_4(\tau)] \quad (16.a,b)$$

In all the above propositions, the average mass fluxes are approximated considering the trapezoidal rule, the  $H_{0,0}$ -approximation for the derivatives of the potentials  $\theta_A(\eta, \tau)$  and  $\theta_{AB}(\eta, \tau)$ . Then, one finds the following approximate relations, respectively:

$$\int_0^1 \frac{\partial \theta_A(\eta, \tau)}{\partial \eta} d\eta = \theta_A(1, \tau) - \theta_A(0, \tau) \cong \frac{1}{2} \left[ \frac{\partial \theta_A(0, \tau)}{\partial \eta} + \frac{\partial \theta_A(1, \tau)}{\partial \eta} \right] \quad (17.a)$$

$$\int_0^1 \frac{\partial \theta_{AB}(\eta, \tau)}{\partial \eta} d\eta = \theta_{AB}(1, \tau) - \theta_{AB}(0, \tau) \cong \frac{1}{2} \left[ \frac{\partial \theta_{AB}(0, \tau)}{\partial \eta} + \frac{\partial \theta_{AB}(1, \tau)}{\partial \eta} \right] \quad (17.b)$$

Making use of the boundary conditions, Eqs. (3), and after substituting in Eq. (9), we obtain:

$$2[\theta_{A1}(\tau) - \theta_{A0}(\tau)] = [\bar{f}_1(\tau) + \bar{f}_3(\tau)]; \quad 2[\theta_{AB1}(\tau) - \theta_{AB0}(\tau)] = [\bar{f}_2(\tau) + \bar{f}_4(\tau)] \quad (18.a,b)$$

After choosing one of the approximations described by Eqs. (13) to (16), combined with Eqs. (18), one reaches an algebraic system to determine the quantities  $\theta_{A0}(\tau)$ ,  $\theta_{AB0}(\tau)$ ,  $\theta_{A1}(\tau)$  and  $\theta_{AB1}(\tau)$ , as functions of  $\bar{\theta}_A(\tau)$ ,  $\bar{\theta}_{AB}(\tau)$ ,  $\theta_{B1}(\tau)$  and  $\theta_{B2}(\tau)$ . Once these boundary quantities have been determined, they are substituted into Eqs. (11) and (12) to complete the system of ordinary differential equations to be solved for  $\bar{\theta}_A(\tau)$ ,  $\bar{\theta}_{AB}(\tau)$ ,  $\theta_{B1}(\tau)$  and  $\theta_{B2}(\tau)$ .

#### 4. RESULTS AND DISCUSSION

A computational code was developed in the FORTRAN 95/2003 programming language and implemented on a Intel (R) Core (TM) 2 Duo 2.2 GHz micro-computer from the Laboratory of Processes Simulation of the School of Chemical Engineering at the Universidade Federal do Pará (LSP/FEQ/UFPA). The subroutine DIVPAG for initial value problems, with a relative error target of  $10^{-8}$ , was used together with the subroutine DNEQNF, both from the IMSL Library (1991), for the solution of the ordinary differential equations system, Eqs. (11) and (12), in conjunction with one of Eqs. (13) to (16), resulting from the classical,  $H_{0,0}$ ,  $H_{0,1}$  and  $H_{1,1}$  approximations for the average concentrations in the physical model of metals separation. Computations were then performed to calculate the potentials  $\bar{\theta}_A(\tau)$ ,  $\bar{\theta}_{AB}(\tau)$ ,  $\theta_{B1}(\tau)$  and  $\theta_{B2}(\tau)$ .

Numerical results for the concentration distributions were obtained as a function of time and at the interface positions, for the case of a second order kinetics reaction, such as in the analysis of palladium Pd (II). Table 1 shows the diffusion coefficients and kinetic parameters used in the analysis of the composition influence and of Aliquat 336 concentration (Kolev *et al.*, 2000).

Table 1. Model parameters for the computational simulation of palladium Pd (II) extraction.

m (g)	$D_A$ (m <sup>2</sup> /s)	$D_{AB}$ (m <sup>2</sup> /s)	$K_{b1}$ (m/s)	$K_{b2}$ (m/s)	$K_{f1}$ (m <sup>4</sup> /mol.s)	$K_{f2}$ (m <sup>7</sup> /mol <sup>2</sup> .s)	$\delta$ (μm)	L (m)	$C_{A0}$ (g/g)	$C_{B0}$ (mg/l)
0.3876	$2.995 \times 10^{-11}$	$1 \times D_A$	$9.99 \times 10^{-9}$	$1 \times K_{b1}$	$1.80 \times 10^{-9}$	$0.075 \times K_{f1}$	15	0.1	50%	80.4
0.6134	$5.30 \times 10^{-11}$	$1 \times D_A$	$21.8 \times 10^{-9}$	$1 \times K_{b1}$	$1.95 \times 10^{-9}$	$0.048 \times K_{f1}$	15	0.1	50%	78.8
0.5628	$2.10 \times 10^{-11}$	$1 \times D_A$	$19.5 \times 10^{-9}$	$1 \times K_{b1}$	$0.77 \times 10^{-9}$	$0.073 \times K_{f1}$	15	0.1	50%	39.5
0.5596	$0.45 \times 10^{-12}$	$1 \times D_A$	$1.10 \times 10^{-9}$	$39 \times K_{b1}$	$0.75 \times 10^{-10}$	$7.565 \times K_{f1}$	18	0.1	30%	41.3
0.5440	$0.70 \times 10^{-11}$	$1 \times D_A$	$7.50 \times 10^{-9}$	$12 \times K_{b1}$	$0.93 \times 10^{-10}$	$0.850 \times K_{f1}$	18	0.1	40%	41.3

Figures 3 first of all provide a comparative analysis between the present CIEA results for the concentration evolution at the exhaustion, against those obtained with the Generalized Integral Transform Technique, GITT (Cotta, 1993), as applied to the fully differential model of the membrane separation process, Cardoso (2010), for a truncation order of  $NT = 70$  in the eigenfunction expansions. An excellent agreement could be observed, for all four examined approximation paths, in Figs.3.a-d. Figures 3 also show the influence of membrane mass at the same concentration of Aliquat 336 (50%), and membrane of 15 μm. It is observed in these figures that the higher extraction of Pd (II) occurs with membranes of larger mass (membrane with 0.6134g). This leads to a larger amount of extractant in 50% of Aliquat 336. These theoretical results obtained by the CIEA approach, employing combinations of Hermite approximations (Classical Approach/ $H_{0,0}$ ,  $H_{0,0}/H_{0,0}$ ,  $H_{0,1}/H_{0,0}$  and  $H_{1,1}/H_{0,0}$ ) are then shown to agree also quite well with those experimentally obtained by Kolev *et al.* (2000).

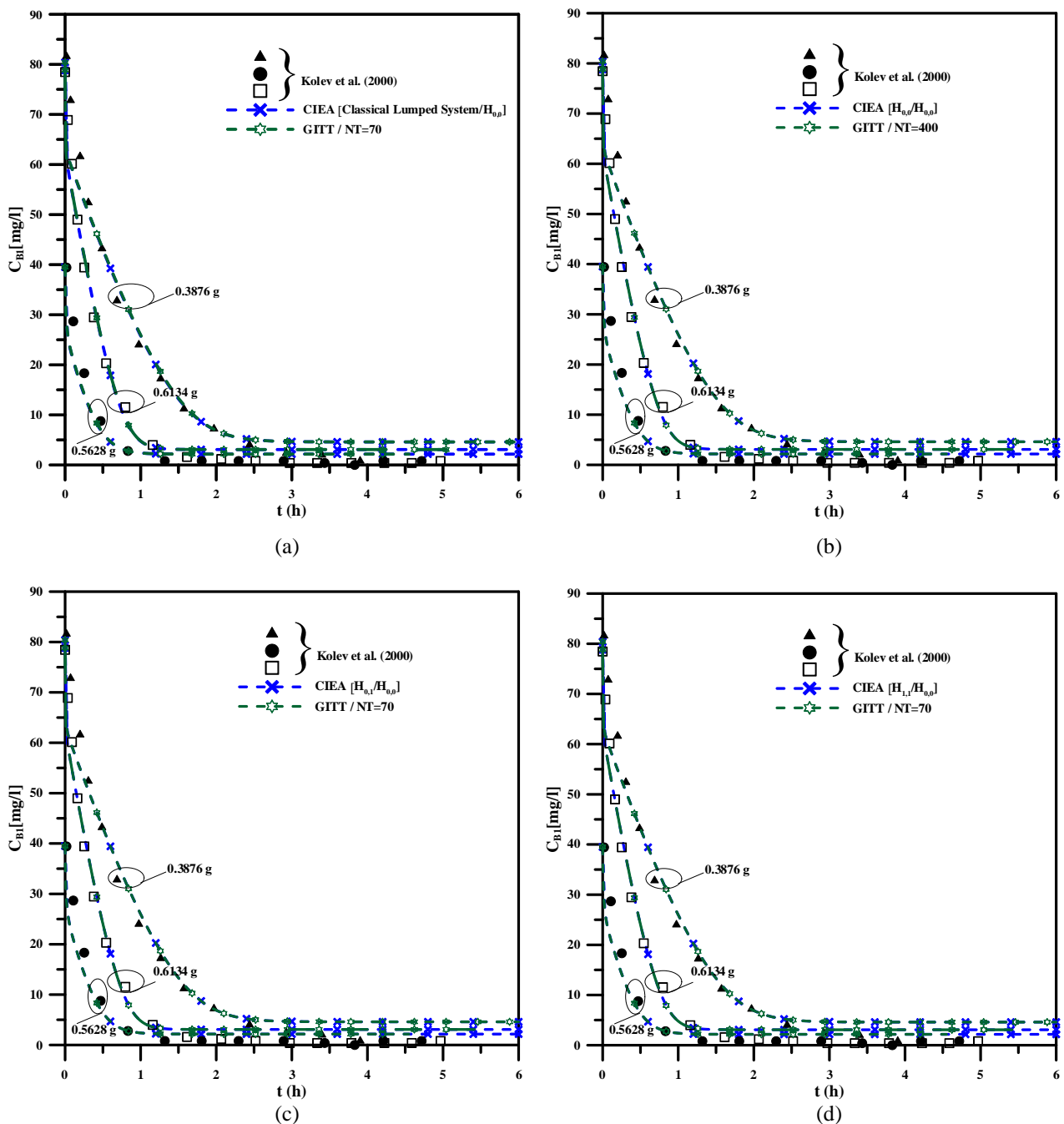
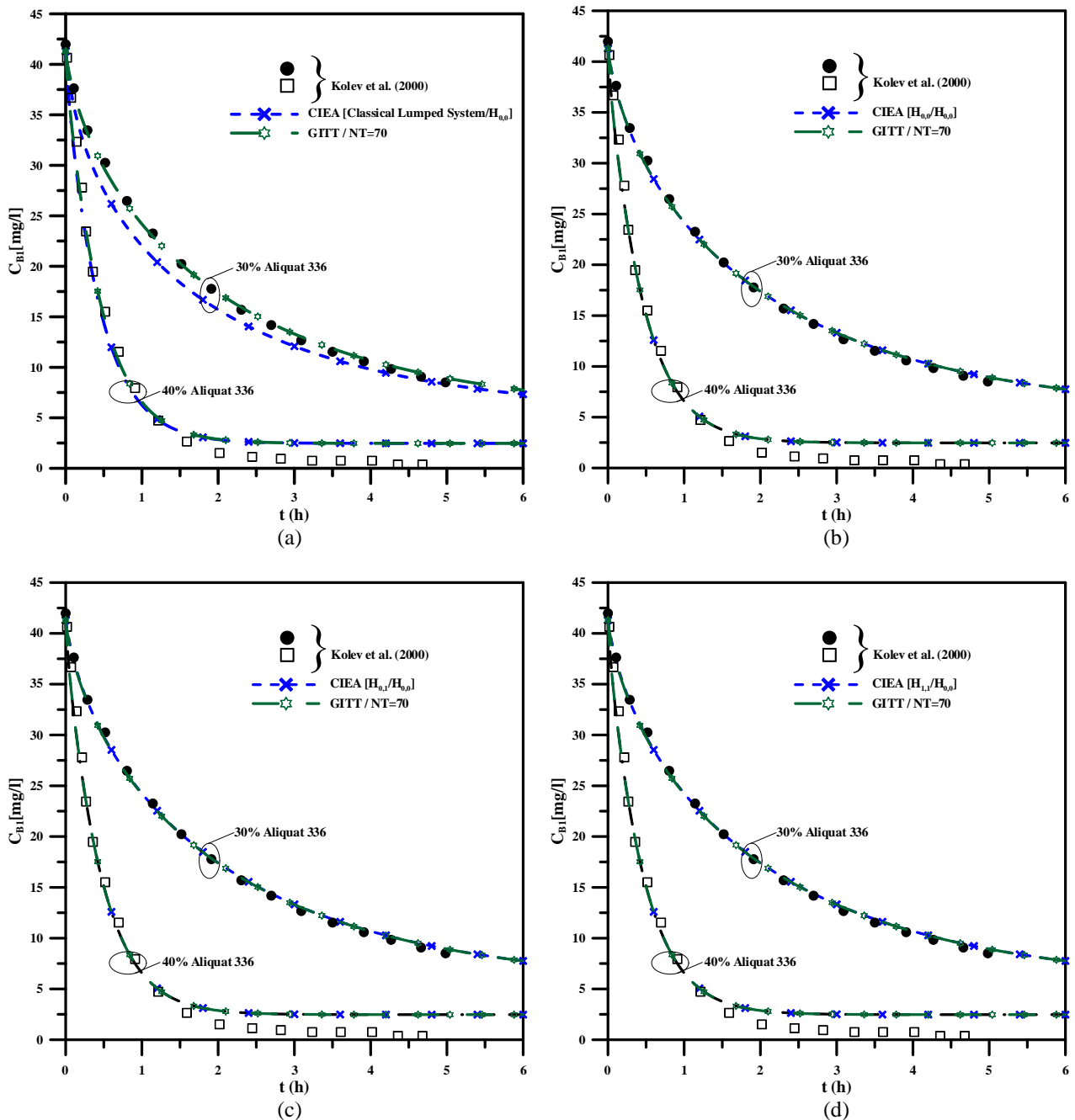


Figure 3. Comparison of exhaustion concentration evolutions obtained with the CIEA (lumped-differential model) and the GITT (fully differential model) approaches and the experimental data of Kolev *et al.* (2000) for the influence of the mass of Aliquat 336: (a) Classical Approach/ $H_{0,0}$ ; (b)  $H_{0,0}/H_{0,0}$ ; (c)  $H_{0,1}/H_{0,0}$ ; (d)  $H_{1,1}/H_{0,0}$ .

The analysis of the membrane concentration influence on the extraction of Pd (II) was performed with concentrations of 30% and 40% m/m of Aliquat 336, in Figures 4. It is observed that the extraction of Pd (II) is more efficient at higher concentrations of Aliquat 336 (40%). This behavior is due to the higher amount of extractant present in higher concentrations of Aliquat 336. However, in this situation, the theoretical results obtained by the CIEA with the classical approach/ $H_{0,0}$ , for the analysis of the membrane with 30% of Aliquat 336, does not seem to agree quite well with those obtained experimentally by Kolev *et al.* (2000) as well as with those from the partial differential model solved by the GITT approach. Clearly in this case the assumption of a practically uniform concentration distribution is not the most adequate. The other combinations  $H_{0,0}/H_{0,0}$ ,  $H_{0,1}/H_{0,0}$  and  $H_{1,1}/H_{0,0}$  led to excellent results for the case of extraction of Pd (II) under the influence of the concentration of Aliquat 336 in membrane content of 30% Aliquat 336.



Figures 4. Comparison of exhaustion concentrations evolution obtained with the CIEA (lumped-differential model) and the GITT (fully differential model) approaches and the experimental data of Kolev *et al.* (2000) for the influence of the concentration of Aliquat 336: (a) Classical Approach/ $H_{0,0}$ ; (b)  $H_{0,0}/H_{0,0}$ ; (c)  $H_{0,1}/H_{0,0}$ ; (d)  $H_{1,1}/H_{0,0}$ .

Table 2 presents a more direct comparison between the exhaustion concentration results obtained in the present study from the improved lumped formulations with those obtained by solving the full partial differential model with the GITT, as detailed in Cardoso (2010). For the cases analyzed in the extraction of Pd (II), it has been observed that all combinations of Hermite approximations used to obtain the solution led to excellent agreement with those obtained by GITT in the cases with 50% of Aliquat 336, with deviations below 2%, while in the cases for 40% and 30% of Aliquat 336, more significant deviations in the predicted concentrations in the extraction of Pd (II) were encountered. The results for the classical approach were those of larger deviations, reaching almost 10% in the case of 40% of Aliquat 336. The results obtained by the higher order approximation  $H_{1,1}/H_{0,0}$  were those that led to the smallest deviations for all cases analyzed. Nevertheless, the resulting formulation for this higher order approximation is as straightforward as the previous ones considered.



Table 2. Comparison of the present results of the exhaustion concentration with those obtained by GITT approach for  $\eta=0$  (exhaustion surface) and different times for the extraction of Pd (II).

Membrane composition	t (h)	$\theta_{B1}(\tau)$								
		Classical Approach / $H_{0,0}$	$\varepsilon$ (%)	$H_{0,0}/H_{0,0}$	$\varepsilon$ (%)	$H_{0,1}/H_{0,0}$	$\varepsilon$ (%)	$H_{1,1}/H_{0,0}$	$\varepsilon$ (%)	GITT
50% Aliquat 336 0.3876 g $\alpha_1 = 0.001244$	0.06	0.75171	0.18	0.75307	0.00	0.75316	0.01	0.75316	0.01	0.75307
	0.30	0.63040	0.26	0.63211	0.01	0.63215	0.02	0.63215	0.02	0.63204
	0.60	0.48831	0.42	0.49045	0.02	0.49049	0.03	0.49049	0.03	0.49036
	3.00	0.05803	0.03	0.05805	0.01	0.05805	0.01	0.05805	0.01	0.058047
	6.00	0.05715	0.00	0.05715	0.00	0.05715	0.00	0.05715	0.00	0.057146
50% Aliquat 336 0.6134 g $\alpha_1 = 0.001566$	0.06	0.72598	0.21	0.72756	0.00	0.72761	0.01	0.72761	0.01	0.72753
	0.30	0.48072	0.52	0.48330	0.02	0.48333	0.02	0.48333	0.02	0.48322
	0.60	0.22706	1.16	0.22983	0.04	0.22985	0.05	0.22985	0.05	0.22973
	3.00	0.03908	0.00	0.03908	0.00	0.03908	0.00	0.03908	0.00	0.03908
	6.00	0.03908	0.00	0.03908	0.00	0.39081	0.00	0.03908	0.00	0.03908
50% Aliquat 336 0.5628 g $\alpha_1 = 0.007199$	0.06	0.59919	0.80	0.60372	0.05	0.60415	0.02	0.60415	0.02	0.60402
	0.30	0.30690	1.41	0.31139	0.03	0.31141	0.04	0.31141	0.04	0.31130
	0.60	0.11647	1.69	0.11852	0.04	0.11852	0.04	0.11852	0.04	0.11847
	3.00	0.05482	0.00	0.05482	0.00	0.05482	0.00	0.05482	0.00	0.05482
	6.00	0.05482	0.00	0.05482	0.00	0.05482	0.00	0.05482	0.00	0.05482
40% Aliquat 336 0.5596 g $\alpha_1 = 0.017172$	0.06	0.91455	2.23	0.93557	0.01	0.93995	0.48	0.93995	0.48	0.93546
	0.30	0.74750	6.25	0.79719	0.01	0.80022	0.36	0.80022	0.36	0.79731
	0.60	0.63411	7.93	0.68868	0.01	0.69081	0.30	0.69081	0.30	0.68876
	3.00	0.29255	9.16	0.32202	0.00	0.32260	0.17	0.32260	0.17	0.32204
	6.00	0.17737	5.49	0.18769	0.00	0.18786	0.10	0.18786	0.10	0.18768
30% Aliquat 336 0.5440 g $\alpha_1 = 0.009460$	0.06	0.84778	0.85	0.85479	0.03	0.85525	0.02	0.85525	0.02	0.85508
	0.30	0.51546	3.38	0.53353	0.01	0.53359	0.02	0.53359	0.02	0.53347
	0.60	0.29009	4.81	0.30479	0.01	0.30482	0.02	0.30482	0.02	0.30475
	3.00	0.06069	0.13	0.06077	0.00	0.06077	0.00	0.06077	0.00	0.06077
	6.00	0.05981	0.00	0.05981	0.00	0.05981	0.00	0.05981	0.00	0.05981

$$\varepsilon = \frac{\theta_{\text{approach Hermite}} - \theta_{\text{GITT}}}{\theta_{\text{GITT}}} \times 100\%$$

## 5. CONCLUSIONS

A study of the palladium extraction process using supported liquid membranes (PLMs) was undertaken in this work. Equations of mass conservation of the involved chemical species were reformulated with the Coupled Integral Equations Approach, CIEA, that promoted a significant simplification of the problem formulation, yielding improved lumped models and low-cost computational simulations for all the cases considered. The present CIEA results were compared with the experimental results obtained by Kolev *et al.* (2000) and also with the fully differential model solution (Cardoso, 2010) as obtained by the Generalized Integral Transform Technique, GITT, demonstrating the consistency of the achieved results for the palladium extraction. The CIEA has been shown to be a recommendable alternative to solving problems based on nonlinear formulations for mass diffusion in polymeric membranes for the extraction of metals, markedly simplifying the derivation and simulation efforts.

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## 7. REFERENCES

- Aparecido, J.B., and Cotta, R.M., 1989, "Improved one-dimensional fin solutions", *Heat Transfer Engineering*, Vol. 11, pp.49-59.
- Argiropoulos, G. A., Cattrall, R. W., Hamilton, I. C., Kolev, S. D., Paimin, R., 1998, "The study of a membrane for extracting gold (III) from hydrochloric acid solutions", *Journal of Membrane Science*, Vol. 138, pp.279-285.
- Cardoso, S. A., 2007, "Modelagem e Simulação de Processo de Separação de Metais por Membrana Difusiva Polimérica". Dissertação de Mestrado (Programa de Pós-Graduação em Engenharia Química – PPEQ) – Universidade Federal do Pará, Belém.
- Cardoso, S. A., 2010, "A Técnica da Transformada Integral na Modelagem e Simulação de Processos de Separação de Metais por Membrana Difusivas Poliméricas". Tese de Doutorado (Programa de Pós-Graduação em Engenharia de Recursos Naturais da Amazônia – PRODERNA) – Universidade Federal do Pará, Belém.
- Cheroto, S., Guigon, S. M. S., Ribeiro, J. W., Cotta, R. M., Mikhailov, M. D., 1997, "Lumped-differential formulations for drying in capillary porous media". *Drying Technology*, Vol. 15, pp. 811-835.
- Cotta, R. M., Ozisik, M. N., and Mennig, J., 1990, "Coupled Integral Equation Approach for Phase-Change Problem in Two-Region Finite Slab", *J. Franklin Institute*, Vol. 327, pp.225-234.
- Cotta, R. M., 1993, "Integral Transforms in Computational Heat and Fluid Flow", Boca Raton, CRC Press.
- Cotta, R. M.; Mikhailov, M. D., 1997, "Heat Conduction: Lumped Analysis, Integral Transform, Symbolic Computation", John Wiley & Sons.
- Hermite, M. Ch., 1878, "Sur la Formule d'Interpolation de Lagrange", *J. Crelle*, v. 84.
- IMSL Library, 1991, MATH/LIB. Houston.
- Kolev, S. D., Sakai, Y., Cattrall, R. W.; Paimim, R., Potter, I. D., 2000, "Theoretical and experimental study of palladium (II) extraction from hydrochloric acid solutions into aliquat 336/PVC membranes", *Analytica Chimica Acta*, Vol. 413, pp. 241-246.
- Macêdo, E. N., Quaresma, J. N. N., Cotta, R. M., and Cardoso, S. A., 2007, "Computational simulation of metal extraction process using polymeric membranes", *International Conference of the Brazilian Society of Mechanical Sciences, COBEM-2007, Brasilia, DF, Brazil, November*.
- Mennig, J., Auerbach, T. and Hälg, W., 1983, "Two point Hermite approximation for the solution of linear initial value and boundary value problems", *Comp. Meth. Appl. Mech. Eng.*, Vol. 39, pp.199-224.
- Scofano Neto, F., and Cotta, R. M., 1993, "Improved hybrid lumped-differential formulation for double-pipe heat exchangers analysis", *J. Heat Transfer*, Vol. 115, pp.921-927.
- Wang, L; Paimin, R.; Cattral, R. W.; Shen, W.; Kolev, S. D., 2000, "The extraction of cadmium (II) and copper (II) from hydrochloric acid solutions using an aliquat 336/PVC membrane", *Journal of Membrane Science*, Vol. 176, pp.105-111.

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