

The Effects of Pore Constriction on the Behavior Of Electrochemical Fixed Bed Reactor: Mathematical Modeling And Computer Simulation

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-----ABSTRACT-----

A mathematical model of a flow-by packed bed electrochemical reactor consisting of copper particles and operating under constant current conditions is presented. The mathematical model describes the kinetic behavior of electrochemical reactor and its porosity field modification as a result of electrodeposition occurring in the reactor, when the reactor is used to remove copper ions from industrial effluents. A good computational method based on the context of orthogonal collocation coupled to a Newton-Raphson multivariable algorithm and a Dassl code is implemented to calculate the overpotential distribution, reaction rate, and the bed porosity time distribution in the reactor. The effect of constant current operation on the porosity field modification is addressed. The effects of other important design parameters such as the applied current and the bed width are analyzed. The results of the model here developed are in good agreement with experimental data.

INDEX TERMS: Electrochemical fixed bed reactor, Mathematical modeling, Pore Constriction, and Porosity

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I. INTRODUCTION

Electrochemical Engineering process offer alternative efficient mechanisms for the prevention, control and remedy of environmental pollution problems, particularly in the cleaning processes of industrial effluents and recovery of heavy metals present in the industrial reservoir or effluents. These effluents, though, in very low concentrations are highly toxic and present a lot of industrial and environmental or ecological hazards (especially aquatic life). Electrochemical engineering techniques offer several promising approaches in virtue of the fact that they constitute only one pass operation and a clean technology where the recovered metals are their pure and inert forms. Some of the major advantageous characteristics are versatility, energy efficiency and amenability to automation, environmental compatibility and cost effectiveness [1].

Electrochemical engineering techniques use reactors called electrochemical reactors for the process of cleaning and recovery of heavy metal from industrial wastewaters. These reactors are classified as two-dimensional when they constitute of two parallel plates and three-dimensional when they constitute of metallic conductive particles in the electrolyte solution. The particulate electrochemical reactors present a high specific area and a high rate of mass transfer which make them susceptible for the treatment of very dilute solutions that need very low current density [2]. The particulate reactors can be fixed on fluidized. When they are fixed, they are called fixed bed electrodes and when fluidized they are called fluidized bed electrodes. The fixed bed electrodes offer uniform effective conductivity in the particulate phase, high yields and a high current efficiency. The pressure drop in fixed bed electrode is high because of the pores blockages (agglomeration of the deposited metal) due to the metal deposition process occurring in the reactor when it is operated for a long time. This phenomenon shortens the operational life of the reactor.

The problem of agglomeration is solved by the use of a fluidized bed electrode because of the particles of the particles in the reactor. It is possible to remove and substitute grown particles on line thereby permitting a continuous operation of the reactor. From an engineering standpoint, this replacement of electrodes on line and the ease of construction are attractive. It has been shown that fluidized bed of conducting particles in a stream of electrolyte behaves as three-dimensional electrodes which are suitable for the design of a number of electrochemical reactors.

Apart from providing high rate of mass transfer, high rate of heat transfer through the bed and to cooling surfaces can be obtained [3]. The main restriction on the application of fluidized beds will be determined by their relative low electrical conductivity compared to that of porous electrode. Clearly, the value of this conductivity will determine the design of the electrode structures. Generally, three-dimensional electrodes fall into three categories, depending on whether the current flow is parallel or orthogonal to the flow of the electrolyte flow. The parallel configuration is called flow-through reactor while the perpendicular configuration is called flow-by reactor. The orthogonal configuration is usually preferred due to the fact that it offers a more residence time for the reactants and hence a high yield is achieved and also a uniform potential distribution in a reactor simultaneously [4]. Generally, mathematical model of electrochemical systems like electrolyzers, batteries and fuel cells is used for detailed analysis of the systems and the usual aim is to improve the productivity or save costs in investment and operation. To be able to perform such calculations a deep analysis is necessary, given a better understanding of the system behavior and performance.

Numerous publications have appeared in this area covering electrochemical rate equation governed by mixed kinetics: mass transport and electron transfer [5]. In electrochemical engineering the mathematical model equations, which describe the concentration and potential distributions in the reactor, are usually parabolic and elliptic equations with mixed boundary conditions, respectively. The set of nonlinear partial differential equations (PDEs) generally cannot be resolved analytically and thus require numerical methods. Several mathematical models to predict the behavior of porous and particulate bed electrodes have been reported [5-10] but there are only a few analyses based on the concept of orthogonal collocation. The method of orthogonal collocation has advantages of a shorter CPU time and less prior mathematical treatment before run time on a computer, although convergence may be difficult. This difficulty can be solved by coupling a Newton-Raphson multivariable algorithm or a finite difference model to the orthogonal collocation structure. Due to the electrodeposition on the processes occurring within the reactor, the mass transfer from the electrolytic solution to the bed particles can produce engineering phenomena of design interest. For example, if the reactor is a fixed bed one, the particles grow in sizes if the operating time is prolonged and the accumulated mass on the particle surface causes a local change in the value of the porosity. The overall effect is a total modification of the porosity field distribution within the reactor. No attempt has been made to describe the reactor behavior in relation to the porosity-time distribution. The objective of this paper is, therefore, to develop a mathematical model capable of describing the behavior of an electrochemical fixed bed reactor in which a variation of the local bed porosity, conduces the bed, after some operating time, to its complete inoperability.

II. DESCRIPTION OF THE STUDIED SYSTEM AND MATHEMATICAL MODEL

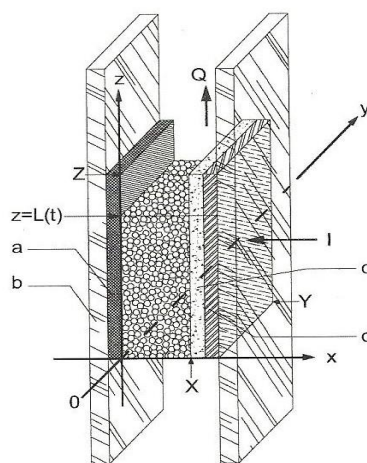


Fig. 1. Schematic view of the cell: a-metallic copper plate, b-cell wall, c-micro porous membrane, d-feeder plate.

The modeled system schematized in figure 1, is a fluidized electrochemical bed reactor with a rectangular geometry and a perpendicular configuration, whose thickness, width, and height are represented by X , Y , and Z , respectively. The bed is made of highly conducting copper particles whose specific surface area is a_m . The bed has a local porosity ϵ . When the electric current direction is the same as that of movement of positive charges, the current feeder can be said to be located at the surface $x = L$ and the counter current on the surface $x = 0$. A superficial velocity of the electrolyte solution v entering the reactor is uniform along the transversal area $A_b = XY$.

The reactor is operated under constant current and a constant flow rate. The electrochemical conductivities of the solid and liquid phases are denominated respectively, by σ_m and σ_s . The reactor is made of acrylic material for better visibility of the bed.

III. MATHEMATICAL MODEL

The formulation of the model is based on the transport equations proposed by Gubulin[11]. These equations are applied to a two-phase solid-liquid system resulting in the following charge and mass balances:

a) Solid phase

- Mass balance:

$$\frac{\partial}{\partial t} [(1 - \varepsilon)C_{k,m}] + \nabla \cdot [(1 - \varepsilon)C_{k,m}\vec{v}_{k,m}] = (1 - \varepsilon)R_{k,m} \quad (1)$$

$$C_{k,m}\vec{v}_{k,m} = C_{k,m}\vec{v}_m \quad (2)$$

- Charge balance

$$-\nabla \cdot [(1 - \varepsilon)\vec{i}_m] = (1 - \varepsilon)F \sum_k \frac{z_k}{M_k} R_{k,m} \quad (3)$$

$$-\vec{i}_m = -\sigma_m \nabla \phi_m \quad (4)$$

b) Liquid Phase

- Mass balance

$$\frac{\partial}{\partial t} [\varepsilon C_{k,s}] + \text{div}[\varepsilon C_{k,s} \vec{V}_{k,s}] = \varepsilon R_{k,s} \quad (5)$$

and

$$C_{k,s}\vec{v}_{k,s} = -D_{k,s}^{ef} \text{grad} C_{k,s} + C_{k,s}\vec{v}_s - z_k F C_{k,s} \mu_{k,s} \text{grad} \phi_s \quad (6)$$

- Charge balance

$$\text{div}[\varepsilon \vec{i}_s] = \varepsilon F \sum_k \frac{z_k}{M_k} R_{k,s} \quad (7)$$

and

$$i_s = - \sum_k F \frac{z_k}{M_k} D_{k,s}^{ef} \text{grad} C_{k,s} - \sigma_s \text{grad} \phi_s \quad (8)$$

By the principle of conservation of mass and charge, we have:

$$(1 - \varepsilon) \sum_{k=1}^m R_{k,m} = -\varepsilon \sum_{k=1}^m R_{k,s} \quad (9)$$

$$(1 - \varepsilon) \sum_{k=1}^m \frac{z_k}{M_k} R_{k,m} = -\varepsilon \sum_{k=1}^m \frac{z_k}{M_k} R_{k,s} \quad (10)$$

The rate of reaction of the chemical specie k, can be represented symbolically by:

$$R_{k,s} = a_m \frac{(1 - \varepsilon) i_{k,s}^*}{\varepsilon F \frac{z_k}{M_k}} \quad (11)$$

Where

$$i_{k,s}^* = i_{k,s}^* (\phi_s, \phi_m, C_{1,s}, C_{1,s}^*, \dots)$$

$R_{k,s}$ and $i_{k,s}^*$ are, respectively, the rate of reaction of the chemical specie k , per unit volume of the liquid phase and the rate of reaction for the chemical specie k , in terms of charge transferred per unit area of the liquid phase; z_k is the charge transferred, M_k is the molecular mass of the chemical specie, and F is the Faraday constant whose value is approximately 96500C/mol. The three-dimensional fluidized bed electrode used for this work is schematized in Fig. 1.

For the purpose of simplifying the transport equations, we make the following restrictions:

- i. Only component $k = 1$ reacts in the system;
- ii. There is no accumulation of the chemical species $k > 1$, in the liquid phase;
- iii. In the bulk of the solution, outside the diffusion layer, the effects of diffusion and dispersion are negligible compared to that of convection, which implies that $\vec{v}_{k,s} = \vec{v}_s$
- iv. The solid phase does not leave the system, or the average velocity of the solid phase is zero which implies that $\vec{v}_m = \mathbf{0}$; Then

$$\frac{\partial}{\partial t} [(1 - \varepsilon)C_{k,m}] + \text{div}[(1 - \varepsilon)C_{k,m}\vec{V}_m] = -\varepsilon R_{k,s}$$

(12)

$$\frac{\partial}{\partial t} [\varepsilon C_{k,s}] + \text{div}[\varepsilon C_{k,s}\vec{V}_s] = \varepsilon R_{k,s} \quad (13)$$

$$\text{div}[\varepsilon C_{k,s}\vec{V}_s] = 0, \quad k = 3, 4, \dots, m \quad (14)$$

$$\text{div}[(1 - \varepsilon)\vec{i}_m] = -\varepsilon F \frac{z_k}{M_k} R_{k,s} \quad (15)$$

$$\text{div}[\varepsilon \vec{i}_s] = \varepsilon F \frac{z_k}{M_k} R_{k,s} \quad (16)$$

$$\vec{i}_s = -\sigma_s \text{grad} \phi_s \quad (17)$$

$$\vec{i}_m = -\sigma_m \text{grad} \phi_m \quad (18)$$

Potential Distribution Equations in the Reactor

These equations are simplified and applied to a system of rectangular geometry and perpendicular configuration as shown in Fig. 1. The suppositions made for the simplification of the above equations are:

1. The potential and the current density are only functions of the variable x ,
2. The superficial velocity of the electrolytic solution is sufficiently high to ensure that concentration change through the through the bed height is insignificant,
3. The porosity and the specific area are kept uniform and do not vary with time during the operation.
4. The operation is isothermal.

With these conditions equations 15 through 18 reduce to

Potential in the solid phase

$$\frac{d^2 \phi_m}{dx^2} = \frac{1}{\sigma_m} \frac{\varepsilon}{(1 - \varepsilon)} F \frac{z_k}{M_k} R_{k,s} \quad (19)$$

Potential in the liquid phase

$$\frac{d^2 \phi_s}{dx^2} = -\frac{1}{\sigma_s} F \frac{z_k}{M_k} R_{k,s} \quad (20)$$

Boundary Conditions

The boundary conditions in the system in terms of the charge transfer are:

At the feeder, practically, all the current is carried by the liquid phase and at the receptor all the current is by the metallic phase. Therefore,

$$x = 0; \frac{d\phi_s}{dx} = 0 \text{ and } x = L, \frac{d\phi_m}{dx} = 0 \quad (21)$$

If the system operates under constant current, then

$$x=0; \frac{d\phi_m}{dx} = -\frac{I}{(1-\varepsilon)\sigma_m A} \quad (22)$$

$$x = L; \frac{d\phi_s}{dx} = -\frac{I}{\varepsilon A \sigma_s} \quad (23)$$

where I is the total current applied and $A = A_L = Y.L(t)$ is the lateral area of the bed.

Kinetic Consideration

At the solid-liquid interface, an intrinsic kinetic will always exist and can be represented by the Butler-Volmer equation given as:

$$i_{k,s}^* = i_0 \left\{ \exp \left[-\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (24)$$

Where

$$i_0 = n F k_0 C_{k,s}^* \quad (25)$$

In these equations, D_k is the diffusion coefficient of the chemical specie k participating in the reaction, n is the number of electrons involved in the reaction, i_0 is the exchange current density, $C_{k,s}$ and $C_{k,s}^*$ are the bulk and superficial concentrations, respectively, δ is the width of the boundary layer, α is the charge transfer coefficient, and η is the overpotential in the reactor defined by the relation:

$$\eta = \phi_m - \phi_s - \left[E_{eq} + \frac{RT}{nF} \ln(C_{k,s}^*) \right] \quad (26)$$

A combination with equation 7 results:

$$R_{k,s} = -a_m \frac{(1-\varepsilon) M_k}{\varepsilon F z_k} i_0 \left\{ \exp \left[-\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (27)$$

It is considered that the reaction is controlled by intrinsic reaction given by equation 24. When equation 27 is substituted in equations 19 and 20, the potential distribution in the solid and liquid phases can be calculated.

Since the bed is subject to a change in the local porosity with time, the specific surface area a_m turns to be time dependent. Consequently, if ε_0 and a_{m0} are, respectively, the initial porosity and the initial surface area of the bed, in time, we will have:

$$a_m = a_{m0} \left(\frac{1-\varepsilon_0}{1-\varepsilon} \right) \left(\frac{\varepsilon}{\varepsilon_0} \right)^{2/3} \quad (28)$$

It was here considered that there was no significant geometrical change in the structure of the pores during its constriction. However, for equilateral cylindrical particles of radius r_0 , used in this paper, we have that

$$a_{m0} = \frac{3}{r_0} \quad (29)$$

Overpotential in the Reactor

If equation 20 is subtracted from equation 19, the model for the distribution of the surtension in the reactor is obtained after substituting from equations 26 and 29:

$$\frac{d^2 \eta}{dx^2} = \left[\frac{1}{\sigma_m} + \frac{(1-\varepsilon)}{\varepsilon \sigma_s} \right] \left(\frac{3}{r_0} \right) \left(\frac{1-\varepsilon_0}{1-\varepsilon} \right) \left(\frac{\varepsilon}{\varepsilon_0} \right)^{2/3} \cdot i_0 \left\{ \exp \left[\frac{\alpha n F}{RT} \eta \right] - \exp \left[-\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (30)$$

The respective boundary conditions are

$$\left(\frac{d\eta}{dx} \right)_{x=0} = -\frac{1}{(1-\varepsilon)\sigma_m A} \quad (31)$$

$$\left(\frac{d\eta}{dx} \right)_{x=X} = \frac{1}{\varepsilon \sigma_s A} \quad (32)$$

Mathematical Model for the Closing of Pores

The relation that describes the variation of the local porosity with time is given by Equation 1.

$$\rho_m \frac{\partial \varepsilon}{\partial t} = \varepsilon R_{k,s} \quad ; \quad \rho_m = C_{k,m} \quad (33)$$

Substituting Equations 28, 29 and 30 in equation 34 yields:

$$\frac{d^2 \varepsilon}{dx^2} = \left(\frac{M_k}{F z_k} \right) \left(\frac{1-\varepsilon_0}{\rho_m} \right) \left(\frac{\varepsilon}{\varepsilon_0} \right)^{2/3} \cdot i_0 \left\{ \exp \left[\frac{\alpha n F}{RT} \eta \right] - \exp \left[-\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (34)$$

Whose initial condition is

$$t = 0, \varepsilon = \varepsilon_0 \quad (35)$$

Equations 30, 31, 32, 34 and 35 constitute the model equations for the porosity-time variation within the bed. If the electrochemical phenomena are more rapid than the dynamic constriction of the pores in the reactor, it is possible to consider the process pseudo-stationary. Therefore in time t, η(x,t) can be calculated using Equation 30. With these values, the function, ε(x,t), can be calculated in time t + Δt using Equation 34. Equation 30 was resolved numerically, with the boundary conditions 31 and 32 by applying the method of orthogonal collocation coupled to a Newton-Raphson algorithm. Equation 34 with the initial boundary condition given by Equation 35 was resolved numerically and analytically.

The analytically solution, considering a pseudo-stationary condition is given by:

$$\varepsilon(x, t + \Delta t) = \varepsilon_0 \left[\left(\frac{\varepsilon(x,t)}{\varepsilon_0} \right)^{1/3} + f(x, t) \Delta t \right]^3 \quad (36)$$

Where

$$f(x, t) = \frac{1}{\rho_m} \frac{M_k}{F z_k} \frac{(1-\varepsilon_0)}{\varepsilon_0} i_{k,s}^* (\eta(x, t)) \quad (37)$$

The result, for the values of ε, calculated by Equations 36, was precise with small values of Δt. It was verified in this work, that, the values of Δt = 100s did not introduce any significant errors (less that 1%) in the calculated values of ε. Apart from that, the computational time was reduced when Δt = 100s were adopted.

Table 1. Systems properties

z,n	2
σ _m (Ω ⁻¹ m ⁻¹)	600.0
σ _s (Ω ⁻¹ m ⁻¹)	60.0
α	0.8

X(m)	0.02, 0.029, and 0.039
C _{k,s} (M)	0.01, 0.05 and 0.1
i ₀ (A/m ²)	1.0, 5.0 and 10
A _L (m ²)	0.008

IV. RESULTS AND DISCUSSION

The simulations were based on three reactors R1, R2, and R3 with the following respective thicknesses: 0.019m, 0.029m and 0.039m. The other systems properties are shown on table 1. These systems properties were extracted from experimental results [12]. The simulation parameters are the applied current I, the bed thickness and the copper ions concentrations in the electrolyte C_{k,s}. Figures 2 and 3 show typical results for reactor R1. Reactors R2 and R3 have similar results. Figures 2 and 3 show, respectively, the distributions of the overpotentials and porosity across the bed thickness for two different current values of 2A and 3A, respectively. Comparing these figures, it can be observed that the influence of porosity modification on the overpotential distribution in the reactor is significant. It can also be verified, from these figures, that the major alterations for the overpotential as well as the porosity distributions occur at the region close to the current feeder.

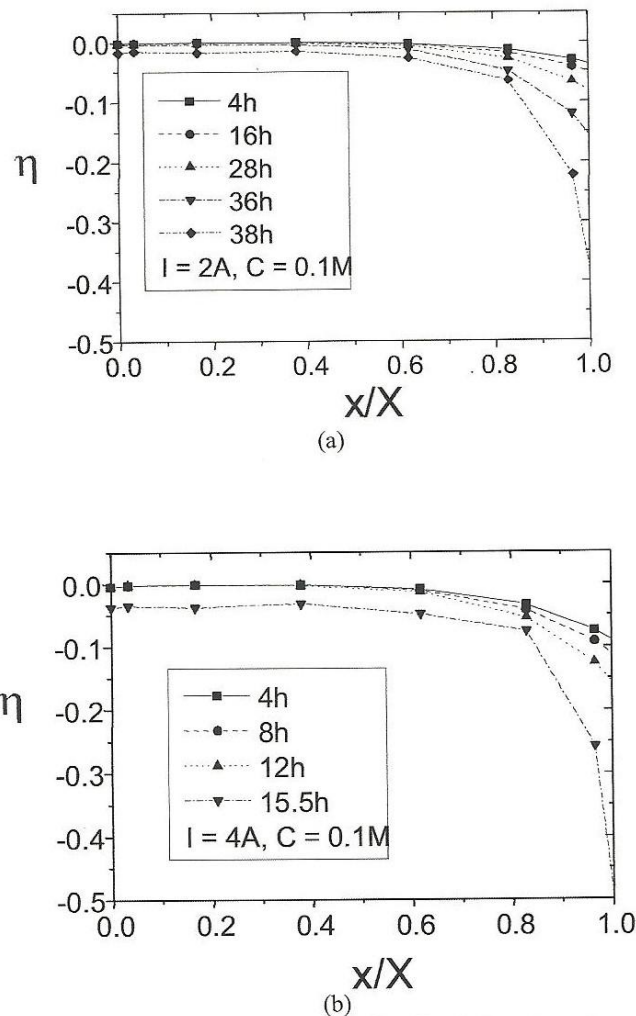


Fig. 2. Distribution of overpotential in the lateral direction in function of operating time: (a) $I = 2A$, $C_{k,s} = 0.1M$; (b) $I = 4A$, $C_{k,s} = 0.1M$

This observation shows that the electrochemical activities are confined to the regions close to the membrane as expected. Therefore, this region is said to be more favorable to the deposition reactions of the copper metal. A notable feature of the porosity distribution is that at the regions close to the membrane, the porosity decreases considerably. And this decrease is rapid with the increase in total applied current. The global effect of this phenomenon shortens the useful life of the reactor, since within a short operating time, the pores are completely blocked at the active regions. Consequently, only the pane $x/X = 0$ remains active and the bed loses its three

dimensional characteristics. It can also be observed that, although, the average reaction rate in the reactor remains constant, if there is no alteration in the value of the applied current throughout the operating time, the overpotential and porosity matrix change expressly in space as the operation time progresses.

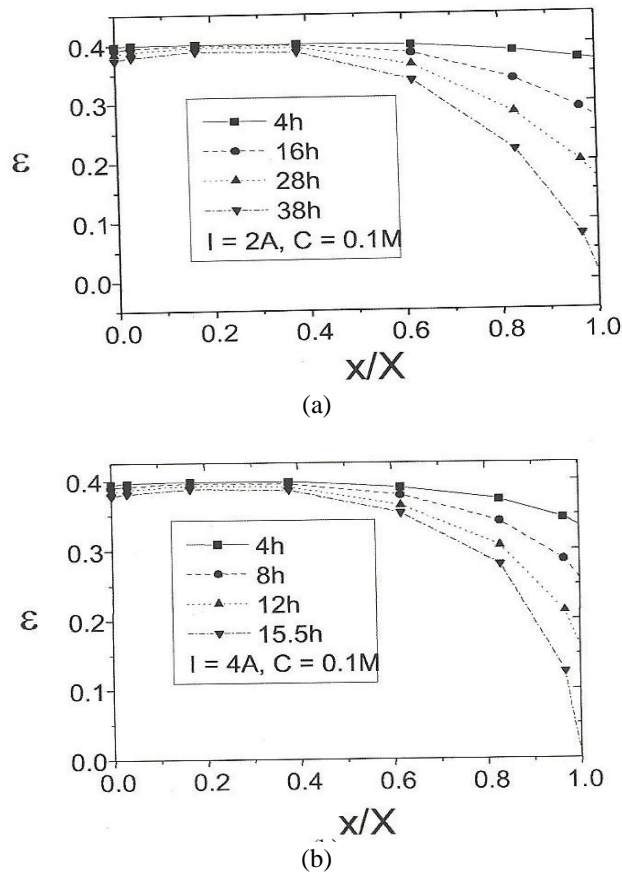
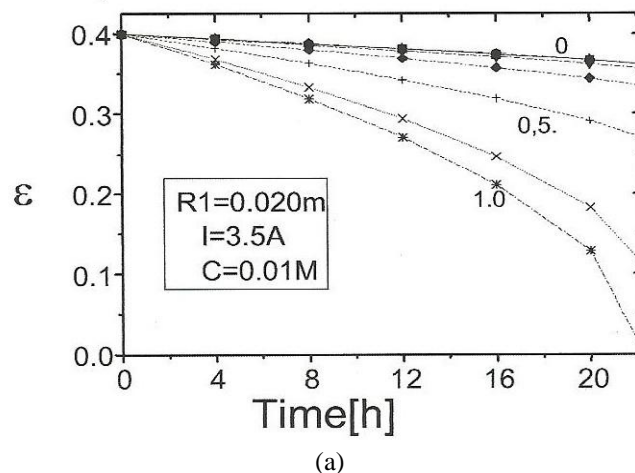


Fig. 3. Distribution of porosity in the lateral position of the bed in function of time. (a) $I = 2A$, $C_{k,s} = 0.1M$; (b) $I = 4A$, $C_{k,s} = 0.1M$

The cathodic increase of the overpotentials at the regions closer to the membrane can be explained probably due to the physical impedance or obstruction imposed by the membrane to the electrons and to the discharge at the metallic plate, thereby concentrating negative charges on the particles close to the membrane. This favors electrochemical reactions in this area. The local cathodic increase of the overpotential with time is due to the constriction of the pores occasioned by the mass transfer. The process of pore constriction results in the decrease of the local bed area but increase in the local current density. Figure 4 illustrates other important results of this paper. The influence of copper concentration for a reactor operating under the same conditions of applied current can be seen comparing figures (a) and (b). The effects of the bed thickness for the same applied current and copper concentration are shown in figures (a) and (c). It is important to note that, for a



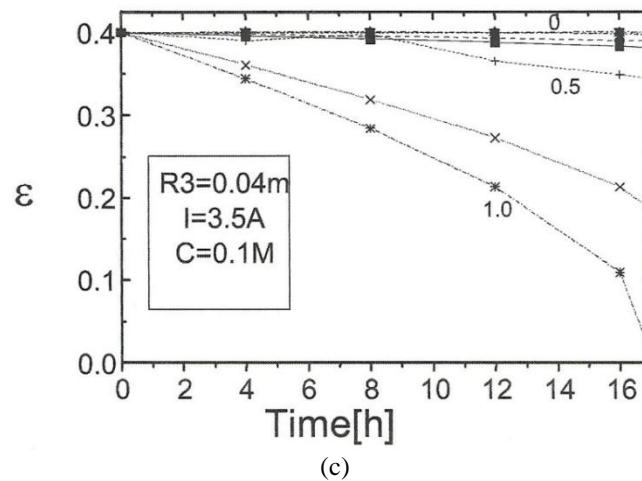
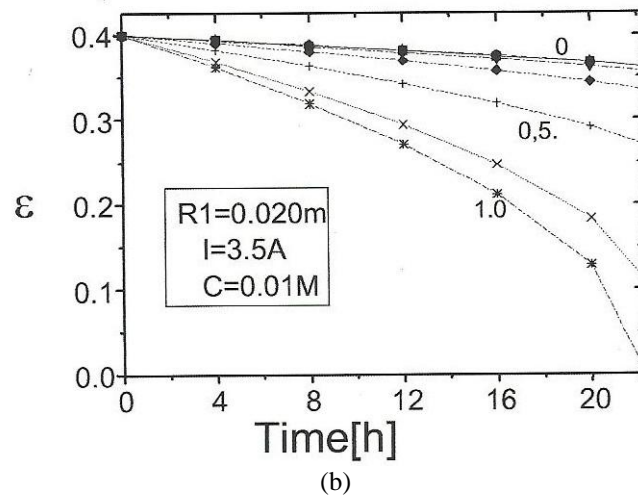


Fig. 4. Evolution of bed porosity with time for each lateral position.

given operating current, the reactor with a less concentrated copper solution takes a longer time or delays to close the pores or to reach a state of inactivity. The reason for this delay may be due to the fact that, the reaction rate is a function of copper concentration. In other words, lowering the concentration signifies a copper ions deficiency in the solution, available to react with the electrons. The final results provoke a reduction or decrease in the deposition kinetic. A very important result here is the effects of increase of the bed thickness on the porosity distribution. It can be clearly seen that at the same operating conditions, there was no significant change in the time of total closing of the pores at the feeder, $x/X = 1$, indicating clearly that the electrochemical active region is situated close to the current feeder.

V. CONCLUSION

The proposed model is capable of describing the behaviour of a fixed bed electrochemical reactor such as observed in the laboratory [12]. Apart from that, it can be easily extended to more complex systems such as those operating under mist kinetics (control for mass transfer and intrinsic reactions). The principal result of this work is that, in whichever be the operating condition, only about 30% of the bed is substantially active: that is to say that only the regions close to the current feeder possess important values of the overpotentials. This means that the electrochemical reactions (copper reduction) occur with great intensity at the regions close to the membranes as can be clearly observed in the figures. It is interesting to note that the reactor becomes operationally inactive at the feeder when the pores are completely closed. The results presented here, are of great importance for engineering calculations and scale-up for electrochemical systems whichever be the configuration and mode of operation.

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