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Approximate analytical solution for non-linear reaction diffusion equations in a mono-enzymatic biosensor involving Michaelis–Menten kinetics

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ABSTRACT

Here we consider the case where the enzyme reacts with an electroinactive substrate to produce an electroactive product which is quickly oxidized or reduced at the electrode/film interface. This model is based on the system of non-linear reaction diffusion equations containing a nonlinear term related to the Michaelis Menten kinetic of the enzymatic reaction. In this paper the powerful analytical method, called the recent approach of Homotopy analysis method is applied to solve the non-linear reaction diffusion equations in amperometric biosensors. A simple and closed-form of analytical expression for concentrations of substrate, product and corresponding current response in the case of an enzyme immobilized into a planar film onto an electrode have been derived. The effect of various parameters on current density is discussed. Numerical simulation (Matlab) for the concentration profile for non-steady state condition was carried out and compared with the analytical results. A satisfactory agreement is noted. A graphical procedure for estimating the kinetic parameters and sensitivity analysis of the parameters from current density is suggested.

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1. Introduction

The electrochemical biosensors can be classified based on the measured electrical parameters as conductometric, amperometric, and potentiometric. An amperometric biosensor is a type of biosensor which measures the change in the current of a working indicator electrode by direct electrochemical oxidation or reduction of the products of a biochemical reaction. The enzyme catalyzed electrochemical oxidation (or reduction) of the substrate to yield catalytic currents is called bioelectrocatalysis. This is the principle of the current response of mediated amperometric biosensors and many research papers have appeared dealing with this type of biosensor, where enzymes immobilized on electrodes catalyze the electrolytic oxidations or reductions of the substrates by using redox compounds as electron transfer mediators. Significance of bioelectrocatalysis is not limited to biosensor application. It is also applied to the constructions of other energy devices such as bioreactors and biofuel cells [1,2]. These are known to be reliable, cheap and highly sensitive for environment, clinical and industrial purposes. Hence mathematical modeling of the same is highly desirable.

Enzymes are large complex protein molecules, which act as a catalyst to speed up chemical reactions in living organisms. In biochemistry, Michaelis–Menten kinetics is one of the simplest and important models to enzyme kinetics. In this model the rate of enzymatic reactions is a nonlinear function of concentration of a substrate. Also these reactions are important in biochemistry because the most of cell processes require enzymes to obtain a significant rate [3,4].

Rajendran and Anitha [5] solved the nonlinear mass balance equation for amperometric enzymatic reaction for steady state condition using Homotopy perturbation method. Rajendran et al. [6] obtained the analytical approximate solution of steady state current for amperometric polymer molecular electrodes for the first-order and zero-order kinetics using Danckwert's expression. Eswari et al. [7,8] derived the steady state concentration and current occurring at microdisk and the microcylinder enzyme electrode for amperometric biosensor using Homotopy perturbation method. The complete review of mathematical modeling of biosensor is given in [9].

Some numerical solutions were presented for the amperometric and potentiometric cases, where the nonlinear chemical homogeneous terms were approximated by linearized forms. The

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Nomenclature

$a = \mu/(1+k)$	dimensionless parameter (none)
D_s,D_p	diffusion coefficients of substrate and product (cm^2/s)
d	thickness of the layer (cm)
F	Faraday constant ($C\ mol^{-1}$)
G	dimensionless current density (none)
h	non zero auxiliary parameter (none)
j	current density (A/cm^2)
K_m	Michaelis–Menten constant (mol/cm^3)
k	dimensionless Michaelis–Menten constant (none)
m	dimensionless parameter (none)
P	concentration of product (mol/cm^3)
p	embedding parameter (none)
r	ratio of diffusion coefficients (none)
S	concentration of substrate (mol/cm^3)
S_0	initial substrate concentration (mol/cm^3)
t	dimensionless time (none)
T	time (s)
u	dimensionless concentration of substrate (none)
v	dimensionless concentration of product (none)
V_m	maximal rate of the enzymatic reaction ($mol\ s^{-1}/cm^3$)
x	dimensionless distance (none)
X	distance (cm)
μ	dimensionless enzyme reaction rate (none)

mathematical modeling is useful to understand and optimize the behavior of enzyme electrodes. Electrodes for biosensors have significant overlap with enzymatic electrodes for fuel cell application but this aspect is already covered by the detailed review by Bartlett et al. [10].

Achi et al. [11] developed the mathematical model of an amperometric biosensor response for substrate and inhibitor detection. The numerical simulation of an amperometric biosensor response was carried out using the implicit finite difference technique. By changing input parameters, Aseris et al. [12] analyzed the action of biosensor with a special emphasis to the influence of the catalytic activity and the geometry of the biosensor on its response and sensitivity.

Recently the mathematical model based on the enzymatic conversion of the substrate and the diffusion of the substrate was created [13]. Morf and co-workers developed an analytical and numerical simulation of potentiometric and amperometric enzyme electrodes and of enzyme reactors for steady state [14] and non-steady state conditions [15]. Mehala et al. [16] discussed the mathematical model of potentiometric enzyme electrodes for non-steady state conditions.

Britz et al. [17] describes the algorithms for the simulation of chronoamperometry at a thin enzyme layer on an electrode. However there are no clear guidelines for the design of electrochemical biosensors, or biofuel cell or bioreactor employing immobilized enzymes that will produce a targeted linear range, limit of detection and sensitivity. Such guidelines can be provided using theoretical results that assess sensor feasibility prior to experimental studies.

To our knowledge no rigorous analytical solutions for non-steady-state concentration and current density in amperometric biosensor have been reported. In general, an analytical result is more stimulating and beneficial than the results of numerical simulations as they are amenable to various kinds of manipulation, optimization of parameter and data analysis. In this paper, we have derived an approximate (or leading order) analytical expressions of concentration and current density in order to describe and evaluate the performances energy devices using a new approach of Homotopy analysis method [18–23]. This method is a well-established method; it is among the pioneer techniques to approach various types of nonlinear problems in chemical sciences. The new simple and closed-form of our approximate analytical expressions of non-steady state concentration of substrate and product gives satisfactory agreement with the numerical results when $(\mu/k) \leqslant 1$. The result of the Eqs. ((2) and (3)) in amperometric biosensor is relevant because its solution describes important applications such as bioreactors and biofuel cells, among others.

2. Mathematical formulation of the problem

The chemical reactions in the layer are

$$E + S \leftrightarrow ES \rightarrow E + P \tag{1}$$

where E refers to the enzyme, S is the substrate, ES is an enzyme substrate complex assumed to be at a steady concentration, and P is the product. The schematic diagram of the system modeled in this study is shown in Fig. 1(a). An aqueous drop containing substrate (S) is placed on the electrode with an immobilized enzyme layer. As the substrate diffuses through the enzyme layer it reacts with the enzyme to form product (P). The product then diffuses through the layer, and if it is electroactive, is oxidized or reduced at the electrode. When modeling this system, we used the Michaelis–Menten equation to describe the kinetics within the enzyme layer.

The mass balance equations to describe the diffusion of the substrate S and product P for one dimensional in mono-enzymatic biosensor are given below [17].

$$\frac{\partial S(X,T)}{\partial T} = D_s \frac{\partial^2 S(X,T)}{\partial X^2} - V_m \frac{S(X,T)}{K_m + S(X,T)}, \tag{2}$$

$$\frac{\partial P(X,T)}{\partial T} = D_p \frac{\partial^2 P(X,T)}{\partial X^2} + V_m \frac{S(X,T)}{K_m + S(X,T)}, \quad T > 0,\ 0 < X < d \tag{3}$$

where D_s and D_p are the diffusion coefficients, V_m is the maximal rate of the enzymatic reaction and K_m is the Michaelis–Menten constant. The initial and boundary conditions are:

$$\begin{aligned} &T = 0,\ 0 \leqslant X < d: \quad S = 0,\ P = 0 \\ &T > 0,\ X = 0: \quad \tfrac{\partial S}{\partial X} = 0,\ P = 0 \\ &T \geqslant 0,\ X = d: \quad S = S_0,\ P = 0 \end{aligned} \tag{4}$$

Current density j (A/cm^2) occurring at the electrode due to reduction or oxidation of P is given by [17]

$$j = n_e F D_p \left(\frac{\partial P(X,T)}{\partial X} \right)_{X=0} \tag{5}$$

The boundary conditions at $X = d$ hold only, if the electrolyte outside the enzyme layer is well stirred. The initial boundary value problem (Eqs. (2) and (3)) which has to be solved in this case can be written in dimensionless forms as follows:

$$\frac{\partial u(x,t)}{\partial t} = \frac{\partial^2 u(x,t)}{\partial x^2} - \frac{\mu u(x,t)}{k + u(x,t)} \tag{6}$$

$$\frac{\partial v(x,t)}{\partial t} = r \frac{\partial^2 v(x,t)}{\partial x^2} + \frac{\mu u(x,t)}{k + u(x,t)} \qquad 0 < x < 1,\ t > 0 \tag{7}$$

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