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A semi-analytical solution of amperometric enzymatic reactions based on Green's functions and fixed point iterative schemes

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ABSTRACT

In this paper, a constructed Green's function coupled with a fixed point iteration scheme will be employed to solve nonlinear dynamical problems that arise in electroanalytical chemistry. More precisely, the method will be used to mathematically model and solve the kinetics of the amperometric enzyme. A main property that makes the proposed method superior to other iterative methods is the way it handles boundary value problems, where both endpoints are taken into consideration while other iterative methods only make account of the initial point and as a result, the approximate solution may deteriorate for values that are far away from the initial point and closer to the other endpoint. Through tests on some known amperometric enzyme kinetics, the proposed method gave more accurate results than many numerical schemes that were employed for this purpose. The method is found to be easily implemented, fast, and computationally economical and attractive.

1. Introduction

The development of biosensors has received great deal of attention in recent years. In principle, biosensors are analytical devices composed of biological recognition element and an optical or electronic transducer [1]. The biological element is usually an enzyme that recognizes a specific analyte whereas the transducer translates the biorecognition event into an electrical signal [2]. The advantages of biosensors include their high sensitivity, their high selectiveness of their biological recognition and their relatively low cost. Most recently amperometric enzyme electrodes have been more emphasized for the development of a wide spectrum of biosensors [2–4].

The diffusion and reaction boundary value problems that arise in amperometric enzyme kinetics have received great attention in the past three decades. One of the early studies was carried out by Bartlett and Whitaker [5], where an approximate analytical treatment of the response of an amperometric enzyme electrode was derived for the case where immobilisation of redox enzymes at electrode surfaces was done by electrochemical polymerisation. Relevant to this research, a mathematical model based on diffusion equations related to Michaelis-Menten kinetics of the enzymatic reaction was proposed by Baronas et al. [6]. The variation iteration method (VIM) developed by J. He [7], which proved to be effective in finding approximate-analytic solution for a wide spectrum of nonlinear dynamical models [8–11] has also been intensively used to give approximate and analytic solutions of amperometric enzymatic reactions. For example, the VIM was implemented to give approximate and analytical solutions of nonlinear reaction diffusion equations containing a nonlinear term related to Michaelis-Menten kinetic of the enzymatic reaction [12,13]. Malvandi and Ganji used the variational iteration method coupled with Padé approximation to find a reliable expression for amperometric enzyme kinetics based on the rational functions [14]. The homotopy perturbation method (HPM), proposed by J.H. He [15], has been received with great enthusiasm by researchers who seek approximate-analytic solutions of nonlinear dynamical systems. Shanmugarajan et al. employed the HPM to obtain analytical solution of amperometric enzymatic reactions [16]. Commenting on the use of the HPM in article [16], He and Mo showed how the HPM can be made more accessible to non-mathematicians by suitable construction of a homotopy equation [17]. Also, Chebyshev wavelets based method was introduced by Mahalakshmi and Hariharan [18] for finding approximate solution of this kind of enzymatic reactions.

In this paper, we employ an iterative method that combine the classical Green's function, with the latest results of fixed point theory. The method proposed by S.A. Khuri et al. [19] proved to be more effective in solving dynamical systems especially of the boundary value types. The effectiveness of the method resides in the fact that both endpoints of the domain are accounted for in constructing the iterative formula, whereas most methods consider only one endpoint

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of the domain making the possibility of poor approximations grows larger as we approach the other endpoint. Of other desirable features of the proposed method is its simple implementation and fast convergence where sometimes a highly accurate solution is obtained by very few iterations. The proposed method also puts no restrictions on the nonlinear terms and requires no finite domain to maintain convergence and stability.

2. The mathematical model

In biochemical systems, the enzyme kinetics in n-dimensional medium, Ω, is modeled by the reaction-diffusion equation [20]

$$\frac{\partial S}{\partial t} = D_S \nabla.(\nabla S) - \upsilon(t,X), \quad x \in \Omega, \tag{1}$$

where D_S is the substrate diffusion coefficient, υ is the initial reaction velocity. Using Michaelis-Menton hypothesis, the velocity υ for a simple reaction process without competitive inhibition is given by [20,21]

$$\upsilon(t,X) = \frac{KS}{1 + S/K_M}, \tag{2}$$

where $K = k_2 E_0/K_M$ represents a pseudo first order, in which k_2 is the unimolecular rate constant, E_0 is the total amount of enzyme, and K_M is the Michaelis constant. The one-dimensional form of Eq. (1) is given by

$$\frac{\partial S}{\partial t} = D_S \frac{\partial^2 S}{\partial X^2} - \frac{KS}{1 + S/K_M}, \quad x \in \Omega, \tag{3}$$

with initial condition given by

$$S(0,X) = S_0(X). \tag{4}$$

By introducing the parameters

$$s = \frac{S}{KS^{\infty}}, \quad x = \frac{X}{L}, \quad \tau = \frac{D_S}{L^2}, \quad K = \frac{kL^2}{D_S} = \phi^2, \quad \alpha = \frac{kS^{\infty}}{K_M}, \tag{5}$$

we obtain the steady state nonlinear reaction-diffusion equation

$$\frac{\partial^2 s}{\partial x^2} - \frac{Ks}{1 + \alpha s} = 0, \quad 0 < s \leq 1, \tag{6}$$

where S^{∞} is the substrate concentration in bulk solution (mol dm^{-3}), ϕ^2 is the Thiele module. In this paper, we will present an approximate profile for the concentration $s(x)$ by solving the governing steady-state Eq. (6) subject to the boundary conditions

$$\begin{aligned} &s'(0) = 0, \\ &As(0) + Bs(l) = C, \end{aligned} \tag{7}$$

where A, B, and C are constants. The cases of utmost interest, which will be emphasized on this paper are:

1. The enzyme substrate reaction diffusion process ($B = 0$), and
2. The amperometric enzymatic reaction ($A = 0$).

3. Green's function iteration method

Letting $L[s] = \frac{\partial^2 s}{\partial x^2}$ and $F(\alpha, K, s) = \frac{Ks}{1+\alpha s}$, then the enzyme substrate reaction equation takes the form

$$L[s] = F(\alpha, K, s), \tag{8}$$

subject to the initial conditions

$$s(0) = a, \quad \frac{\partial s(0)}{\partial t} = 0, \tag{9}$$

where a is constant. On the other hand, the amperometric enzymatic reaction is given by Eq. (8) together with the boundary conditions

$$\frac{\partial s(0)}{\partial t} = 0, \quad s(l) = b, \tag{10}$$

where b is constant.

The Green's function $G(x,\xi)$ for the differential operator is defined as a solution to

$$L\left[G(x,\xi)\right] = \delta(x - \xi), \tag{11}$$

subject to the corresponding homogeneous initial conditions

$$\begin{aligned} &G(x,\xi)|_{x=0} = 0, \\ &\frac{d}{dx} G(x,\xi)|_{x=0} = 0. \end{aligned} \tag{12}$$

The particular solution, $s_p(x)$, of Eq. (8) is given by

$$s_p(x) = \int_0^1 G(x,\xi) F(\alpha, K, \xi) d\xi. \tag{13}$$

Clearly the solution to the homogeneous equation $L[s] = 0$ is given by

$$s_h = C_1 x + C_2. \tag{14}$$

So we construct $G(x,\xi)$ in the form

$$G(x,\xi) = \begin{cases} C_1 x + C_2, & 0 < x < \xi \\ C_3 x + C_4, & \xi < x < 1 \end{cases}. \tag{15}$$

The constants $C_i, i = 1,2,3,4$ will be determined by using the following properties of Green's function:

First, $G(x,\xi)$ satisfies the homogeneous initial conditions (Eq. (12)). This implies that

$$C_1 = C_2 = 0. \tag{16}$$

Second, $G(x,\xi)$ is continuous at $x = \xi$, that is

$$G(x,\xi)|_{x \to \xi^+} = G(x,\xi)|_{x \to \xi^-}, \tag{17}$$

which implies that

$$C_3 \xi + C_4 = C_1 \xi + C_2. \tag{18}$$