Research Article

Analytical Expressions Pertaining to the Concentration of Substrates and Product in Phenol-Polyphenol Oxidase System Immobilized in Laponite Hydrogels: A Reciprocal Competitive Inhibition Process

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Theoretical analysis corresponding to the diffusion and kinetics of substrate and product in an amperometric biosensor is developed and reported in this paper. The nonlinear coupled system of diffusion equations was analytically solved by Homotopy perturbation method. Herein, we report the approximate analytical expressions pertaining to substrate concentration, product concentration, and current response for all possible values of diffusion and kinetic parameters. The numerical solution of this problem is also reported using Scilab/Matlab program. Also, we found excellent agreement between the analytical results and numerical results upon comparison.

1. Introduction

Theoretical modeling of biosensors usually provides some important insight into understanding the functioning of a biosensor. Usually, with the aid of an analytical device, it is not possible to measure the concentration of substrates inside the enzyme membranes. As a result, theoretical model in biosensors has been developed and employed as an important tool to study the analytical characteristics of biosensors. Initially, Goldman et al. [1] reported the theoretical modeling on biosensor. In that report [1], they have published an extensive theoretical treatment corresponding to substrate and product distribution in membranes containing enzymes. Later, Sundaram and Laidler [2] reported equations that describe the kinetics of reaction in an enzyme membrane immersed in a substrate solution. Kasche and coworkers [3] presented a model and equations that describe steady-state catalysis by an enzyme immobilized in spherical gel particles. Furthermore, they have demonstrated that the catalysis by a bounded enzyme at low substrate concentrations differs from the catalysis brought about by an unbound enzyme.

Blaedel et al. [4] derived equations for steady-state fluxes of substrates and product through a membrane in simple systems.

Catalytic biosensors are sensors that use enzymes which catalyse a specific conversion of analyte [5]. The analysis of the action of the biosensors containing one and two enzymes was performed under internal diffusion limitation in [6]. Gough et al. [7] have simulated the performance of a cylindrical biosensor employed for glucose monitoring at steady state. Jobst et al. [8] reported a finite difference scheme for the discretization of the model equation. Bacha et al. [9, 10] have developed a model that takes into account a variety of configuration designs to describe the behaviour of an amperometric biosensor for glucose monitoring. Recently, Baronas et al. [11–14] have developed a theoretical model to examine the dynamic response of amperometric biosensors under stirred and nonstirred solutions. Coche-Guerente et al. [15] analyzed the amperometric response of PPO-based rotating disk bioelectrodes based on the kinetic model by considering the internal and external mass transport effects and a CEC' electroenzymatic mechanism.

Amperometric biosensors are rapid, sensitive, and highly stable candidates for environmental, clinical, and industrial applications. The general features of amperometric biosensors have been studied and analyzed extensively in the literature [16, 17]. However, due to the limited calculation possibilities and lack of model, the calculations were restricted by two critical concentrations of substrate (when enzyme acted at the first- and zero-order reaction conditions). Later, there are few reports that reported steady-state and nonstationary kinetics of amperometric biosensor response [17–21]. Baronas et al. [22] developed the model based on nonstationary diffusion equations containing a nonlinear term related to the enzymatic reaction. Ames [23] performed the digital simulation of the biosensor response with the implicit difference scheme.

Recently, Coche-Guerente et al. [24, 25] presented a theoretical analysis of the transport and kinetics of substrate and product in an immobilized enzyme layer involving an electrochemical substrate-recycling scheme. Baronas et al. [26] developed the mathematical model of the biosensor action to investigate the dynamics of the response of biosensors utilizing a triggered enzymatic reaction followed by the electrochemical and enzymatic product cyclic conversion scheme (CEC scheme). To the best of our knowledge, there are no analytical expressions corresponding to the steady-state substrate, product concentrations, and current for all values of parameters μ_1, μ_2, α_1 , and α_2 at the rotating disk electrode for reciprocal competitive inhibition process [15]. These parameters are explained below (8). The purpose of this communication is to derive an analytical expression of steady-state concentration and current at electrodes for all values of parameters μ_1, μ_2, α_1 , and α_2 .

2. Mathematical Formulation of the Problem and Analysis

The complete mathematical formulation of this problem is described in Coche-Guerente et al. [15]. Figure 1 shows the schematic representation of a rotating disk electrode modified by a PPO enzymatic layer of thickness L [15]. The enzymatic reaction of substrates S_1, S_2 and the product P_2 follows reciprocal competitive inhibition process. Therefore, enzymatic rate of formation of *o*-quinone from phenol and catechol substrates, V_1 and V_2 can be expressed as follows:

$$V_1 = \frac{k_1[E_T][S_1]}{[S_1] + K_1(1 + [S_2]/K_2)}, \quad (1)$$

$$V_2 = \frac{k_2[E_T][S_2]}{[S_2] + K_2(1 + [S_1]/K_1)},$$

where $[E_T]$ represent the total concentration of active enzyme. K_1, K_2, k_1 , and k_2 are the kinetic parameters. The nonlinear differential equations corresponding to the reciprocal competitive inhibition process with concentrations

S_1, S_2 and P_2 within the enzymatic layer [15, 26] at steady state condition can be written as follows:

$$\begin{aligned} \frac{\partial^2[S_1]}{\partial X^2} - \frac{[S_1]}{\Lambda_1^2(1 + [S_1]/K_1 + [S_2]/K_2)} &= 0, \\ \frac{\partial^2[S_2]}{\partial X^2} - \frac{[S_2]}{\Lambda_2^2(1 + [S_1]/K_1 + [S_2]/K_2)} &= 0, \\ \frac{\partial^2[P_2]}{\partial X^2} + \frac{[S_1]}{\Lambda_1^2(1 + [S_1]/K_1 + [S_2]/K_2)} &+ \frac{[S_2]}{\Lambda_2^2(1 + [S_1]/K_1 + [S_2]/K_2)} = 0, \end{aligned} \quad (2)$$

where X represents the distance from the electrode surface, Λ_1 and Λ_2 are the reaction lengths related to phenol substrate S_1 , and catechol substrate S_2 . Further, $\Lambda_1 = (D_f K_1/k_1[E_T])^{1/2}$, $\Lambda_2 = (D_f K_2/k_2[E_T])^{1/2}$, where D_f is the diffusion coefficient in the enzymatic layer. These equations are solved for the following initial and boundary conditions as described in the literature [15]:

$$\begin{aligned} \frac{\partial[S_1]}{\partial X} &= 0, \quad [S_1] + [S_2] = [S_1]_\infty, \quad [P_2] = 0 \quad \text{when } X = 0, \\ [S_1] &= [S_1]_\infty, \quad [S_2] = 0, \quad [P_2] = 0 \quad \text{when } X = L + \delta. \end{aligned} \quad (3)$$

In addition, the mass conservation implies that $[S_1] + [S_2] + [P_2] = [S_1]_\infty$ when $X \geq L^+$, where L is the thickness of the enzymatic layer and δ is the thickness of the diffusion convection. At $X = L$, the fluxes J_{S_1}, J_{S_2} , and J_{P_1} of S_1, S_2 , and P_2 on each side of the interface are equal [15]. Next, we introduce the following set of dimensionless variables:

$$u = \frac{[S_1]}{[S_1]_\infty}, \quad v = \frac{[S_2]}{[S_1]_\infty}, \quad w = \frac{[P_2]}{[S_1]_\infty}, \quad x = \frac{X}{L}, \quad (4)$$

where u, v , and w represent dimensionless concentration and x is the distance parameter. The dimensionless nonlinear equations for rotating disk electrode are as follows:

$$\frac{\partial^2 u}{\partial x^2} - \frac{\mu_1 u}{1 + \alpha_1 u + \alpha_2 v} = 0, \quad (5)$$

$$\frac{\partial^2 v}{\partial x^2} - \frac{\mu_2 v}{1 + \alpha_1 u + \alpha_2 v} = 0, \quad (6)$$

$$\frac{\partial^2 w}{\partial x^2} + \frac{\mu_1 u}{1 + \alpha_1 u + \alpha_2 v} + \frac{\mu_2 v}{1 + \alpha_1 u + \alpha_2 v} = 0, \quad (7)$$

where

$$\mu_1 = \frac{L^2}{\Lambda_1^2}, \quad \mu_2 = \frac{L^2}{\Lambda_2^2}, \quad \alpha_1 = \frac{[S_1]_\infty}{K_1}, \quad \alpha_2 = \frac{[S_1]_\infty}{K_2}, \quad (8)$$

where μ_1 is the ratio of the square of the thickness L and the reaction length Λ_1 ; μ_2 is the ratio of the square of the thickness L and the reaction length Λ_2 ; α_1 is the ratio of $[S_1]_\infty$ and the kinetic parameter K_1 ; α_2 is the ratio of $[S_1]_\infty$ and the kinetic parameter K_2 . Now the initial and boundary conditions are given by the following equation:

$$\begin{aligned} \frac{\partial u}{\partial x} &= 0, \quad u + v = 1, \quad w = 0 \quad \text{when } x = 0, \\ u &= 1, \quad v = 0, \quad w = 0 \quad \text{when } x = 1 + \frac{\delta}{L} = m. \end{aligned} \quad (9)$$

The dimensionless current is given by [15]

$$I = \frac{j_f}{2F} = -\left(\frac{\partial v}{\partial x}\right)_{x=0}, \quad (10)$$

where F is the Faraday constant.

3. Solution of Boundary Value Problem Using the Homotopy Perturbation Method

The HPM [27] uses the embedded parameter p as small, and only a few iterations are essential for an asymptotic solution. Using this method (see Appendix A), the solutions to (5)–(7) can be deduced as follows:

$$\begin{aligned} u(x) = & a \cosh(\sqrt{\mu_1}x) \\ & + \alpha_2 A_0 \left[2a \cosh(\sqrt{\mu_2}m) (\mu_2 - 2\mu_1) \sqrt{\mu_2} \right. \\ & \times \sinh(\sqrt{\mu_1}(m-x)) \\ & + 4a\mu_1 \sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \cosh(\sqrt{\mu_1}x) \\ & - (\mu_2 + 2\sqrt{\mu_1\mu_2}) \sqrt{\mu_1} \sinh(\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \\ & - (\mu_2 - 2\sqrt{\mu_1\mu_2}) \sqrt{\mu_1} \\ & \left. \times \sinh(-\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \right] \\ & + \frac{\alpha_1 a^2}{6} \left[a \cosh(\sqrt{\mu_1}x) \cosh(2\sqrt{\mu_1}m - 3) \right. \\ & \left. - \cosh(2\sqrt{\mu_1}x + 3) \right], \end{aligned} \quad (11)$$

$$\begin{aligned} v(x) = & (1-a)b \sinh(\sqrt{\mu_2}(m-x)) - \alpha_2 A_0 \sinh(\sqrt{\mu_2}(m-x)) \\ & \times (2ab\sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \\ & \times (\cosh(\sqrt{\mu_2}m) (\mu_2 - 2\mu_1) + 2\mu_1) - 2\sqrt{\mu_1\mu_2}) \\ & + A_1 \left[2\mu_1 \sinh(\sqrt{\mu_2}(m-x)) + 4b\sqrt{\mu_1}\sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \right. \\ & \times \sinh(\sqrt{\mu_2}x) - (\mu_1 + 2\sqrt{\mu_1}\sqrt{\mu_2}) \\ & \times \sinh(\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \\ & \left. - (\mu_1 - 2\sqrt{\mu_1}\sqrt{\mu_2}) \sinh(-\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \right] \\ & - \alpha_1 a^2 b \sinh(\sqrt{\mu_2}(m-x)) \\ & \times \left(\frac{a(\cosh(2\sqrt{\mu_1}m) - 3)}{6} + \frac{1}{3} \right) \\ & + A_2 \left[(\cosh(2\sqrt{\mu_2}m) + 3) \sinh(\sqrt{\mu_2}(m-x)) \right. \end{aligned}$$

$$\begin{aligned} & + 4 \sinh(\sqrt{\mu_2}x) - \sinh(\sqrt{\mu_2}m) \\ & \times (\cosh(2\sqrt{\mu_2}(m-x)) + 3) \Big], \end{aligned} \quad (12)$$

where $a = 1/(\cosh(\sqrt{\mu_1}m))$; $b = 1/(\sinh(\sqrt{\mu_2}m))$; $A_0 = (a(1-a)b\sqrt{\mu_1})/(2(\mu_2^2 - 4\mu_1\mu_2))$; $A_1 = (\alpha_1\mu_2ab(1-a))/(2(\mu_1^2 - 4\mu_1\mu_2))$; $A_2 = (\alpha_2(1-a)^2b^3)/6$. Adding (5) and (6) using the boundary conditions (9), we can obtain

$$w(x) = 1 - u(x) - v(x). \quad (13)$$

Equations (11)–(13) are the analytical expressions corresponding to the dimensionless concentrations as a function of dimensionless distance x . These equations satisfy the boundary conditions (9). When α_1 and $\alpha_2 \rightarrow 0$ (K_1 and $K_2 \rightarrow \infty$), the concentrations u , v , and w become

$$\begin{aligned} u(x) &= a \cosh(\sqrt{\mu_1}x), \\ v(x) &= (1-a)b \sinh(\sqrt{\mu_2}(m-x)), \\ w(x) &= 1 - u(x) - v(x). \end{aligned} \quad (14)$$

Using (10) the current density is

$$\begin{aligned} I = & (1-a)b\sqrt{\mu_2} \cosh(\sqrt{\mu_2}m) - \alpha_2 A_0 \sqrt{\mu_2} \cosh(\sqrt{\mu_2}m) \\ & \times (2ab\sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \\ & \times (\cosh(\sqrt{\mu_2}m) (\mu_2 - 2\mu_1) + 2\mu_1) - 2\sqrt{\mu_1\mu_2}) \\ & + A_1 \left[2\mu_1 \sqrt{\mu_2} \cosh(\sqrt{\mu_2}m) - 4b\sqrt{\mu_1}\mu_2 \sinh(\sqrt{\mu_1}m) \right. \\ & + (\mu_1 + 2\sqrt{\mu_1}\sqrt{\mu_2}) \cosh(\sqrt{\mu_2}m) (\sqrt{\mu_1} - \sqrt{\mu_2}) \\ & \left. - (\mu_1 - 2\sqrt{\mu_1}\sqrt{\mu_2}) \cosh(\sqrt{\mu_2}m) (\sqrt{\mu_1} + \sqrt{\mu_2}) \right] \\ & - \alpha_1 a^2 b \sqrt{\mu_2} \cosh(\sqrt{\mu_2}m) \\ & \times \left(\frac{a(\cosh(2\sqrt{\mu_1}m) - 3)}{6} + \frac{1}{3} \right) \\ & + A_2 \left[(\cosh(2\sqrt{\mu_2}m) + 3) \sqrt{\mu_2} \cosh(\sqrt{\mu_2}m) - 4\sqrt{\mu_2} \right. \\ & \left. - 2\sqrt{\mu_2} \sinh(\sqrt{\mu_2}m) \sinh(2\sqrt{\mu_2}m) \right]. \end{aligned} \quad (15)$$

Equation (15) represents the dimensionless current as a function of dimensionless parameters μ_1 , μ_2 , α_1 , α_2 , and m .

4. Numerical Simulation

The system of steady-state nonlinear differential equations (5)–(7) are also solved in numerical methods. The function `pdx4` in Scilab/Matlab software which is a function of solving partial differential equations is used to solve these equations. Its numerical solution is compared with the analytical solution obtained by HPM. Satisfactory agreement is noted. The Scilab/Matlab program is also given in Appendix B.

5. Results and Discussion

5.1. Concentration Profiles. Equations (11)–(13) are the new and simple analytical expressions of concentrations of phenol (substrate $u(\mu_1, \mu_2, \alpha_1, \alpha_2, \delta/L)$), catechol (substrate $v(\mu_1, \mu_2, \alpha_1, \alpha_2, \delta/L)$), and *o*-quinone (product $w(\mu_1, \mu_2, \alpha_1, \alpha_2, \delta/L)$), respectively. All substrate molecules are enzymatically oxidized within the enzymatic layer before reaching the electrode surface. Thus, the high sensitivity observed with a PPO bioelectrode working at a cathodic potential can be explained by an efficient electrochemical recycling of substrate which can enter a new enzymatic step in the proximity of the enzymatic layer interface. This interpretation agrees well with the substrates and product concentration profiles in the enzymatic layer calculated on the basis of (11)–(13) and reproduced in Figures 2–4. In these figures, the profiles of substrates (phenol and catechol) as well as product (*o*-quinone) concentration in the enzyme layer are presented for biosensor acting in CEC mechanism. The thickness of the enzymatic layer constitutes an important parameter that governs the biosensor sensitivity. The normalized concentration of phenol substrate u is represented in Figures 2(a)–2(c). From this figure, it is evident that the value of phenol substrate concentration u decreases when the thickness of the enzymatic layer increases and enzyme activity increases (μ_1, μ_2 increase) for all values of α_1 and δ/L . The concentration of phenol substrate u is equal to 1 when $\mu_1 \leq 0.1$ and u becomes zero when $\mu_1 \geq 30$ for all values α_1 and μ_2 . Figures 3(a)–3(c) stand for the normalized concentration profile of catechol v . It is clear that the catechol concentration v increases when the thickness of the enzymatic layer increases. The concentration of catechol substrate v becomes zero when $\mu_1 \leq 0.1$ for all values of parameters. Figures 4(a)–4(c) represent the normalized *o*-quinone concentration w . It is clear that the concentration of *o*-quinone w increases when the thickness of the enzymatic layer increases. The concentration of *o*-quinone product w reaches the maximum value when $x = 0.3$ and then decreases to the minimum value zero when the diffusion-convection layer is equal to zero.

5.2. Current Response. The analytical expression of steady-state current $I(\mu_1, \mu_2, \alpha_1, \alpha_2, \delta/L)$ is given in (15). The steady-state current of membrane biosensors significantly depends on the thickness of the enzymatic layer. Figures 5(a) and 5(b) show the dimensionless current I for all values of parameters μ_1, μ_2, α_1 and α_2 . From these figures it is inferred that the current increases gradually when μ_1 and μ_2 increase. When $\mu_2 \rightarrow 0$ at any $\mu_1 > 0$ current $I \rightarrow 0$ (refer to Figure 5(b)). Figures 5(c) and 5(d) represent the dimensionless current I for all values of kinetic parameters. From these figures it is evident that the current decreases when α_1 and α_2 increase. The current I is monotonously increasing function of both arguments μ_1 and μ_2 . In the case of CEC mode an application of an active enzyme [E_T] ($\mu_2 > 0$) stimulates an increase of the biosensor current. The steady-state current of membrane biosensor significantly depends on the thickness of the enzyme layer (L). In view

FIGURE 1: Schematic representation of rotating disk electrode modified by a PPO enzymatic layer and principle of the bioelectrode functioning in the presence of phenol substrates S_1, S_2 and product P_2 [15].

of biosensor optimizations, it can be seen that the current I (refer to Figure 5(e)) is higher for low electrode rotation rate and small thickness of enzymatic layer.

6. Conclusions

This paper reports a mathematical treatment for analyzing amperometric enzymatic reactions. In this paper, we have evaluated a theoretical model for a rotating disk electrode based on an immobilized enzyme layer. The novelty of this paper is an application of approximate method to the second-order nonlinear partial differential equations. The approximate analytical expressions for the steady state substrate concentrations and product concentration profiles for all values of μ_1, μ_2, α_1 and α_2 at the rotating disk electrode were obtained using Homotopy perturbation method. Furthermore, an analytical expression corresponding to the steady state current response is also presented. A satisfactory agreement with the existing limiting cases results is noted. The results presented in the paper extend to many applications related to biosensors modeling.

FIGURE 2: The profile of the normalized concentration of phenol substrate u versus the normalized distance x . The concentrations were computed using (11) when the parameters $\mu_2 = 1, \alpha_1 = 0.1, \alpha_2 = 0.1$ and for various values of μ_1 and δ/L . The key to the graph (stacked line) represents (11) and (dotted line) represents the numerical solution. (a) $\delta/L = 0$, (b) $\delta/L = 0.5$, (c) $\delta/L = 1$, (d) $\mu_1 = 0.1$.

Appendices

A. Solution of (5)–(7) Using Homotopy Perturbation Method

In this appendix, we indicate how (11)–(13) in this paper are deduced. In order to obtain the solution of (5)–(7), we first construct a Homotopy as follows:

$$(1-p) \left[\frac{\partial^2 u}{\partial x^2} - \mu_1 u \right] + p \left[\frac{\partial^2 u}{\partial x^2} - \mu_1 u + \alpha_1 u \frac{\partial^2 u}{\partial x^2} + \alpha_2 v \frac{\partial^2 u}{\partial x^2} \right] = 0,$$

$$(1-p) \left[\frac{\partial^2 v}{\partial x^2} - \mu_2 v \right] + p \left[\frac{\partial^2 v}{\partial x^2} - \mu_2 v + \alpha_1 u \frac{\partial^2 v}{\partial x^2} + \alpha_2 v \frac{\partial^2 v}{\partial x^2} \right] = 0. \quad (\text{A.1})$$

The approximate solutions of (A.1) are

$$\begin{aligned} u &= u_0 + p u_1 + p^2 u_2 + p^3 u_3 + \dots, \\ v &= v_0 + p v_1 + p^2 v_2 + p^3 v_3 + \dots. \end{aligned} \quad (\text{A.2})$$

FIGURE 3: The profile of the normalized concentration of catechol substrate v versus the normalized distance x . The concentrations were computed using (12) when the parameters $\mu_2 = 10$, $\alpha_1 = 0.1$, $\alpha_2 = 0.1$ and for various values of μ_1 and δ/L . The key to the graph (stacked line) represents (12) and (dotted line) represents the numerical solution. (a) $\delta/L = 0$, (b) $\delta/L = 0.5$, (c) $\delta/L = 1$, (d) $\mu_1 = 0.1$.

Substituting (A.2) into (A.1) and comparing the coefficients of like powers of p

$$\begin{aligned}
 p^0 : \frac{\partial^2 u_0}{\partial x^2} - \mu_1 u_0 &= 0, \\
 p^1 : \frac{\partial^2 u_1}{\partial x^2} - \mu_1 u_1 + \alpha_1 u_0 \frac{\partial^2 u_0}{\partial x^2} + \alpha_2 v_0 \frac{\partial^2 u_0}{\partial x^2} &= 0, \\
 p^0 : \frac{\partial^2 v_0}{\partial x^2} - \mu_2 v_0 &= 0, \\
 p^1 : \frac{\partial^2 v_1}{\partial x^2} - \mu_2 v_1 + \alpha_1 u_0 \frac{\partial^2 v_0}{\partial x^2} + \alpha_2 v_0 \frac{\partial^2 v_0}{\partial x^2} &= 0.
 \end{aligned} \tag{A.3}$$

The boundary conditions are

$$\begin{aligned}
 \frac{\partial u_0}{\partial x} &= 0, \quad u_0 + v_0 = 1 \quad \text{when } x = 0, \\
 u_0 &= 1, \quad v_0 = 0 \quad \text{when } x = 1 + \frac{\delta}{L} = m, \\
 \frac{\partial u_1}{\partial x} &= 0, \quad u_1 + v_1 = 0 \quad \text{when } x = 0, \\
 u_1 &= 0, \quad v_1 = 0 \quad \text{when } x = 1 + \frac{\delta}{L} = m.
 \end{aligned} \tag{A.4}$$

FIGURE 4: The profile of the normalized concentration of *o*-quinone product w versus the normalized distance x . The concentrations were computed using (13) when the parameters $\mu_2 = 10$, $\alpha_1 = 0.1$, $\alpha_2 = 0.1$ and for various values of μ_1 and δ/L . The key to the graph (stacked line) represents (13) and (dotted line) represents the numerical solution. (a) $\delta/L = 0$, (b) $\delta/L = 0.5$, (c) $\delta/L = 1$, (d) $\mu_1 = 0.1$.

Solving (A.3) using the boundary conditions (A.4), we can obtain

$$u_0 = a \cosh(\sqrt{\mu_1}x),$$

$$u_1 = \alpha_2 A_0 \left[2a \cosh(\sqrt{\mu_2}m) (\mu_2 - 2\mu_1) \right. \\ \times \sqrt{\mu_2} \sinh(\sqrt{\mu_1}(m-x)) \\ + 4a\mu_1 \sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \cosh(\sqrt{\mu_1}x) \\ - (\mu_2 + 2\sqrt{\mu_1\mu_2}) \sqrt{\mu_1} \sinh(\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \\ - (\mu_2 - 2\sqrt{\mu_1\mu_2}) \sqrt{\mu_1} \\ \left. \times \sinh(-\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \right]$$

$$+ \frac{\alpha_1 a^2}{6} \left[a \cosh(\sqrt{\mu_1}x) \cosh(2\sqrt{\mu_1}m - 3) \right. \\ \left. - \cosh(2\sqrt{\mu_1}x) + 3 \right], \quad (\text{A.5})$$

$$v_0 = (1-a)b \sinh(\sqrt{\mu_2}(m-x)),$$

$$v_1 = -\alpha_2 A_0 \sinh(\sqrt{\mu_2}(m-x)) \\ \times (2ab\sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \\ \times (\cosh(\sqrt{\mu_2}m) (\mu_2 - 2\mu_1) + 2\mu_1) \\ - 2\sqrt{\mu_1\mu_2})$$

$$\begin{aligned}
& + A_1 \left[2\mu_1 \sinh(\sqrt{\mu_2}(m-x)) \right. \\
& \quad + 4b\sqrt{\mu_1}\sqrt{\mu_2} \sinh(\sqrt{\mu_1}m) \sinh(\sqrt{\mu_2}x) \\
& \quad - (\mu_1 + 2\sqrt{\mu_1}\sqrt{\mu_2}) \sinh(\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \\
& \quad \left. - (\mu_1 - 2\sqrt{\mu_1}\sqrt{\mu_2}) \sinh(-\sqrt{\mu_1}x + \sqrt{\mu_2}(m-x)) \right] \\
& - \alpha_1 a^2 b \sinh(\sqrt{\mu_2}(m-x)) \\
& \times \left(\frac{a(\cosh(2\sqrt{\mu_1}m) - 3)}{6} + \frac{1}{3} \right) \\
& + A_2 \left[(\cosh(2\sqrt{\mu_2}m) + 3) \sinh(\sqrt{\mu_2}(m-x)) \right. \\
& \quad + 4 \sinh(\sqrt{\mu_2}x) - \sinh(\sqrt{\mu_2}m) \\
& \quad \left. \times (\cosh(2\sqrt{\mu_2}(m-x)) + 3) \right].
\end{aligned} \tag{A.6}$$

According to the HPM, we can conclude that

$$u = \lim_{p \rightarrow 1} u(x) \approx u_0 + u_1, \tag{A.7}$$

$$v = \lim_{p \rightarrow 1} v(x) \approx v_0 + v_1. \tag{A.8}$$

After putting (A.5) into (A.7) and (A.6) into (A.8), the final results can be described in (11) and (12) in the text.

B. Scilab/Matlab Program to Find the Numerical Solutions for (5), (6), and (7)

function pdex4

```

m = 0;
x = linspace(0,1);
t = linspace(0,100000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,1);
u2 = sol(:,2);
u3 = sol(:,3);
figure
plot(x,u1(end,:))
title("u1(x,t)")
xlabel("Distance x")
ylabel("u1(x,2)")
figure
plot(x,u2(end,:))
title("u2(x,t)")
xlabel("Distance x")
ylabel("u2(x,2)")

```

figure

```
plot(x,u3(end,:))
```

```
title("u3(x,t)")
```

```
xlabel("Distance x")
```

```
ylabel("u3(x,2)")
```

```
function [c,f,s] = pdex4pde(x,t,u,DuDx)
```

```
c = [1; 1; 1];
```

```
f = [1; 1; 1].* DuDx;
```

```
M = 100;
```

```
N = 0.1;
```

```
P = 1;
```

```
Q = 0.1;
```

```
F = -M*u(1)/(1 + N*u(1) + Q*u(2));
```

```
F1 = -P*u(2)/(1 + N*u(1) + Q*u(2));
```

```
F2 = -F - F1;
```

```
s = [F; F1; F2];
```

```
function u0 = pdex4ic(x);
```

```
u0 = [0; 1; 0];
```

```
function [pl,ql,pr,qr] = pdex4bc(xl,ul,xr,ur,t)
```

```
pl = [0; ul(2) - 1 + ul(1); ul(3)];
```

```
ql = [1; 0; 0];
```

```
pr = [ur(1) - 1; ur(2); ur(3)];
```

```
qr = [0; 0; 0].
```

Nomenclature and Units

$[S_1]$:	Concentration of the phenol substrate (mole cm^{-3})
$[S_2]$:	Concentration of the catechol substrate (mole cm^{-3})
$[P_2]$:	Concentration of the <i>o</i> -quinone product (mole cm^{-3})
$[S_1]_\infty$:	Bulk concentration of the phenol substrate (mole cm^{-3})
$[S_2]_\infty$:	Bulk concentration of the catechol substrate (mole cm^{-3})
$[P_2]_\infty$:	Bulk concentration of the <i>o</i> -quinone product (mole cm^{-3})
$[E_T]$:	Enzyme concentration (mole cm^{-3})
L :	Thickness of the enzymatic layer (cm)

FIGURE 5: The steady state-current I versus dimensionless parameters. The current is computed using (15). (a) $\alpha_1 = 0.1, \alpha_2 = 0.1, \delta/L = 1$, (b) $\alpha_1 = 0.1, \alpha_2 = 0.1, \delta/L = 1$, (c) $\mu_1 = 100, \mu_2 = 0.01, \delta/L = 0$, (d) $\mu_1 = 100, \mu_2 = 0.01, \delta/L = 0$, (e) $\mu_1 = 0.1, \alpha_1 = 0.1, \alpha_2 = 0.1$.

δ :	Thickness of the diffusion-convection layer (cm)
D_f :	Diffusion coefficient in the enzymatic layer ($\text{cm}^2 \text{s}^{-1}$)
D_e :	Diffusion coefficient in the diffusion convection layer ($\text{cm}^2 \text{s}^{-1}$)
Λ_1, Λ_2 :	Reaction lengths (cm)
K_1, K_2 :	Kinetic parameters (mole cm^{-3})
k_1, k_2 :	Kinetic parameters (s^{-1})
μ_1 :	Ratio of the square of thickness of the enzymatic layer and the reaction length (None)
μ_2 :	Ratio of the square of thickness of the enzymatic layer and the reaction length (None)
α_1 :	Dimensionless parameter (None)
α_2 :	Dimensionless parameter (None)
δ/L :	Ratio of the thickness of the enzymatic layer and the thickness of the diffusion-convection layer (None)
F :	Faraday constant (None)
u :	Normalized concentration of the phenol substrate (None)
v :	Normalized concentration of the catechol substrate (None)
w :	Normalized concentration of the <i>o</i> -quinone product (None)
I :	Dimensionless current (None).

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