

## Research Article

# Analytical Expressions of Concentrations of Substrate and Hydroquinone in an Amperometric Glucose Biosensor

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The theoretical model for an amperometric glucose biosensor is discussed. In this model glucose oxidase enzyme is immobilized in conducting polypyrrole. This model contains a nonlinear term related to enzyme reaction kinetics. The homotopy perturbation method is used to find the approximate analytical solutions of coupled non-linear reaction diffusion equations. A closed-form expression of substrate and mediator concentration under non-steady-state conditions is obtained. A comparison of the analytical approximation and numerical simulation is also presented. An agreement between analytical expressions and numerical results is observed.

## 1. Introduction

Since the second half of the last century, numerous efforts have been devoted to the development of insoluble immobilized enzymes for a variety of applications [1]. These applications can clearly benefit from use of the immobilized enzymes rather than the soluble counterparts, for instance as reusable heterogeneous biocatalysts, with the aim of reducing production costs by efficient recycling and control of the process [2], as stable and reusable devices for analytical and medical applications [3–9], as selective adsorbents for purification of proteins and enzymes [10], as fundamental tools for solid-phase protein chemistry [11, 12], and as effective microdevices for controlled release of protein drugs [13].

Immobilized enzymes are becoming increasingly popular as reusable, selective analytical chemical reagents in solid-phase flow-through reactors, as membranes in sensors, and as films in dry reagent kits. The attractions of immobilized enzymes from an analytical standpoint are primarily their reusability, and hence cost saving, and the greater efficiency and control of their catalytic activity [14] (e.g., potentially longer half-lives, predictable decay rates and more efficient multistep reactions).

The immobilization of enzymes in conducting polymer [15] during electro-polymerization step has proved to be well suited to the preparation of biosensors [16–19]. This method is simple and easy to control. Another important advantage of this immobilization technique is the possibility of entrapping the mediator in the polymer as a dopant anion [20–23] or by covalent fixation on the pyrrole monomer [24]. Bartlett and Whitaker [25] have already presented a theoretical model for an amperometric polypyrrole + glucose oxidase (PPY + GOD) electrode. In their model PPY was considered as an insulating polymer, and the reduced mediator  $H_2O_2$  was oxidized at the metallic surface after diffusion in the polymer. Marchesiello and Geniès [26] obtained the analytical expressions of concentrations of substrate and benzoquinone for low substrate and high benzoquinone concentration compared with respective Michaelis constants.

To my knowledge no rigorous analytical expressions of concentrations of substrate and mediator of amperometric glucose under non-steady-state conditions for all values parameters  $\alpha$ ,  $\alpha'$  and  $M$  have been reported. These parameters are defined in (6). The purpose of this communication is to derive approximate analytical expressions for the

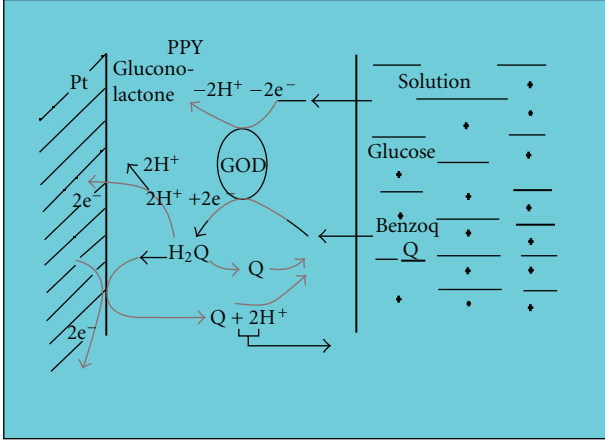
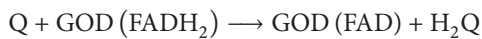
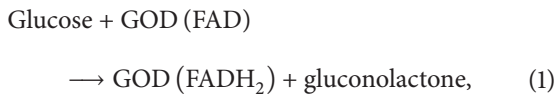


FIGURE 1: Schematic diagram of the electrocatalytic oxidation of glucose at a GOD + PPY electrode in the presence of benzoquinone (Q).

non-steady-state concentrations and current using Homotopy perturbation method.

## 2. Mathematical Formulation and Analysis of the Problems

**2.1. Mathematical Formulation.** Building upon earlier work, Marchesiello and Geniès [26] presented a concise discussion and derivation of mass transport nonlinear equations in glucose biosensor, which is summarized briefly below. Figure 1 is a schematic representation of the PPY + GOD electrode working as a glucose sensor. The different steps which lead to the electrocatalytic current are as follows. (i) Glucose and benzoquinone diffusion from bulk of the solution to the electrode, (ii) glucose and benzoquinone diffusion into the conducting polymer, and (iii) the enzymatic reaction between glucose and benzoquinone:



(iv) The oxidation of hydroquinone:  $\text{H}_2\text{Q} \rightarrow \text{Q} + 2\text{H}^+ + 2\text{e}^-$ .

As shown in Figure 1, this reaction occurs on the surface of the platinum electrode after diffusion in the polymer and in the conducting polymer itself. The rate of the enzymatic reaction between glucose and benzoquinone follows a ping-pong type mechanism [27]  $v = k_{\text{cat}}[E]/[1 + K_Q/[Q] + K_S/[S]]$  where  $k_{\text{cat}}/\text{s}^{-1}$  is the turnover number for GOD,  $K_S$  and  $K_Q$  are the Michaelis constants for glucose and benzoquinone, respectively, and  $[E]$ ,  $[Q]$ , and  $[S]$  are the enzyme, benzoquinone, and glucose concentrations in the film. The third term is the  $\text{H}_2\text{Q}$  oxidation term. The rate of the electrochemical reaction in the conducting polymer can be written as  $v = K\Sigma[\text{H}_2\text{Q}]$ , where  $K/\text{ms}^{-1}$  is the charge-transfer constant for the oxidation of  $\text{H}_2\text{Q}$  in the conducting

polymer. It depends on the electrode potential.  $\Sigma$  is the PPY specific surface and it was estimated to be in the range  $5\text{--}50 \text{ m}^2 \text{ m}^{-3}$  for a PPY electrode deposited film [28]. The differential equations describing the concentrations of  $S$  and  $\text{H}_2\text{Q}$  at steady state are as follows [26]:

$$\begin{aligned} D_S \frac{d^2[S]}{dx^2} - \frac{k_{\text{cat}}[E]}{1 + K_Q/[Q] + K_S/[S]} &= 0, \\ D_{\text{H}_2\text{Q}} \frac{d^2[\text{H}_2\text{Q}]}{dx^2} + \frac{k_{\text{cat}}[E]}{1 + K_Q/[Q] + K_S/[S]} &= K\Sigma[\text{H}_2\text{Q}]. \end{aligned} \quad (2)$$

These nonlinear reaction/diffusion equations are solved for the following boundary conditions. The boundary conditions are as follows [27]:

$$\begin{aligned} [S] &= [S]_0, \quad [\text{H}_2\text{Q}] = 0, \\ \text{at } x &= L \text{ (polymer/solution interface),} \\ \frac{d[S]}{dx} &= 0, \quad [\text{H}_2\text{Q}] = 0, \\ \text{at } x &= 0 \text{ (platinum/polymer interface).} \end{aligned} \quad (3)$$

The total electrocatalytic current  $I_T$  is the sum of two currents. The current

$$I_S = 2FAD_{\text{H}_2\text{Q}} \left( \frac{d[\text{H}_2\text{Q}]}{dx} \right)_{x=0}. \quad (4)$$

For  $\text{H}_2\text{Q}$  oxidation on the platinum electrode, and

$$I_P = \int_0^L dI = \int_0^L 2FAK\Sigma[\text{H}_2\text{Q}] dx, \quad (5)$$

where  $L$  is the film thickness of the reaction layer. We assume that there is no concentration polarization of  $S$  and  $\text{H}_2\text{Q}$  in the solution and that the partition coefficients are equal to unity.  $[S_0]$  is the concentration of glucose in the bulk of the solution.

**2.2. Normalized Form.** By introducing the following set of nondimensional variables,

$$\begin{aligned} X &= x/L, \quad U = [S]/[S]_0, \quad V = [\text{H}_2\text{Q}]/[S]_0, \\ \alpha &= L/\Lambda, \quad \alpha' = L/\Lambda', \\ \Lambda &= \left( \frac{D_S K_S}{K_{\text{cat}}[E]} \right)^{1/2}, \quad \Lambda' = \left( \frac{D_{\text{H}_2\text{Q}}}{K\Sigma} \right)^{1/2}, \end{aligned} \quad (6)$$

$$M = \frac{[S]_0}{K_S} + \frac{[S]_0 K_Q}{K_S [Q]}.$$

The dimensionless parameters  $\alpha$  compares the enzymatic reaction rate with the substrate diffusion in the polymer. The dimensionless parameter  $\alpha'$  compares the  $\text{H}_2\text{Q}$  oxidation rate in the conducting polymer with  $\text{H}_2\text{Q}$  diffusion in the polymer. For electrochemically inert polymer,  $\alpha'$  has low value and for electrochemically active polymer,  $\alpha'$  has high value. The parameter  $M$  is a dimensionless constant.

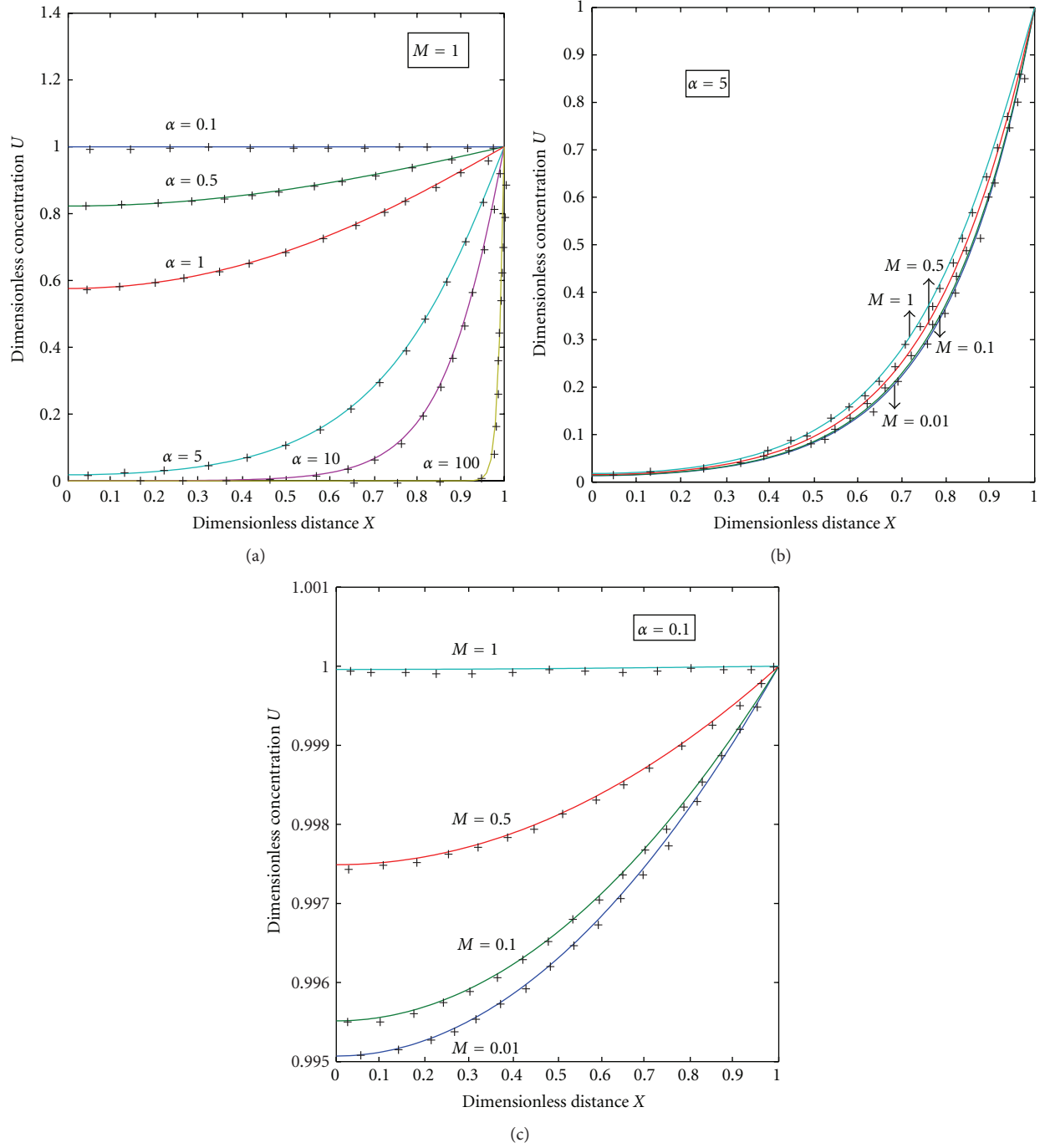


FIGURE 2: Profile of the normalized concentrations of the glucose. The concentrations were computed for various values of  $\alpha$  and  $M$ . The curves are plotted using (10).

The coupled reaction/diffusion equations (2) take the following normalized form:

$$\begin{aligned} \frac{d^2 U}{dX^2} - \frac{\alpha^2 U}{MU + 1} &= 0, \\ \frac{d^2 V}{dX^2} + \frac{\alpha^2 U}{MU + 1} &= \alpha'^2 V, \end{aligned} \quad (7)$$

where  $U$  and  $V$  are the dimensionless concentration of S and  $H_2Q$ .

The transformed boundary conditions are

$$\begin{aligned} \frac{dU}{dX} &= 0, \quad V = 0, \quad \text{when } X = 0, \\ U &= 1, \quad V = 0, \quad \text{when } X = 1. \end{aligned} \quad (8)$$

The dimensionless form of the current is given by

$$\begin{aligned}\psi_S &= \frac{I_S}{2FAD_{H_2Q}} = \left[ \frac{d[V]}{dX} \right]_{X=0}, \\ \psi_P &= \frac{I_P}{2FAK\Sigma} = \int_0^1 V dX.\end{aligned}\quad (9)$$

**2.3. Analytical Expressions of Concentrations of Substrate and the Mediator under Steady-State Condition.** In recent days, Homotopy perturbation method (HPM) is often employed to solve several analytical problems. In addition, several groups demonstrated the efficiency and suitability of the HPM for solving nonlinear equations and other electrochemical problems [29–32]. Mousa and Ragab [33] used HPM to solve the Lighthill equation, the Duffing equation [34], and the Blasius equation [35]. HPM has also been used to solve nonlinear boundary value problems [33], integral equation [36–38], Emden-Flower type equations [39], and several other problems. Detailed derivation of the concentrations using Homotopy perturbation method is described in Appendix 5. As a result, we can obtain the dimensionless concentrations of substrate and mediator as follows:

$$\begin{aligned}U(X, \alpha) &= \frac{\cosh(\alpha X)}{\cosh(\alpha)} + \frac{M \cosh(\alpha X) [\cosh(2\alpha) - 3]}{6\cosh^3(\alpha)} \\ &\quad - \frac{M [\cosh(2\alpha X) - 3]}{6\cosh^2(\alpha)},\end{aligned}\quad (10)$$

$$V(X, \alpha, M) = \frac{\alpha^2}{\alpha'^2(M+1)} \left[ 1 - \frac{e^{\alpha'X} + e^{\alpha'(1-X)}}{(e^{\alpha'} + 1)} \right]. \quad (11)$$

The dimensionless current  $\psi_S$  and  $\psi_P$  are obtained using (9) and (11):

$$\psi_S(\alpha, \alpha', M) = \frac{\alpha^2 (e^{\alpha'} - 1)}{\alpha'(M+1)(e^{\alpha'} + 1)}, \quad (12)$$

$$\begin{aligned}\psi_P(\alpha, \alpha', M) &= \frac{\alpha^2 (\alpha' e^{\alpha'} - e^{\alpha'} + \alpha' + 1)}{\alpha'^3 (M+1)(e^{\alpha'} + 1)} \\ &\quad - \frac{\alpha^2 (e^{\alpha'} - 1)}{\alpha'^3 (M+1)(e^{\alpha'} + 1)}.\end{aligned}\quad (13)$$

The electrocatalytic current  $\psi_T$  is the sum of two currents  $\psi_S$  and  $\psi_P$

$$\begin{aligned}\psi_T(\alpha, \alpha', M) &= \frac{\alpha^2 (e^{\alpha'} - 1)}{\alpha'^3 (M+1)(e^{\alpha'} + 1)} \\ &\quad \times [e^{\alpha'} (\alpha' - 1) + \alpha' (\alpha' + 1)].\end{aligned}\quad (14)$$

**2.4. First-Order Catalytic Kinetics.** In this case,  $MU < 1$  or  $1 + K_Q/[Q] \ll K_S/[S]$ . Now (7) reduces to the following forms:

$$\begin{aligned}\frac{d^2 U}{dX^2} - U\alpha^2 &= 0, \\ \frac{d^2 V}{dX^2} + U\alpha^2 &= \alpha'^2 V.\end{aligned}\quad (15)$$

The solutions of (15) are given as follows:

$$U(X, \alpha) = \frac{\cosh(\alpha X)}{\cosh(\alpha)}, \quad (16)$$

$$\begin{aligned}V(X, \alpha, \alpha') &= \frac{\alpha^2}{(\alpha^2 - \alpha'^2)} \left[ \frac{e^{\alpha'X}}{\cosh(\alpha)} - \frac{\cosh(\alpha X)}{\cosh(\alpha)} \right. \\ &\quad \left. - \frac{\sinh(\alpha'X)}{\sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right],\end{aligned}\quad (17)$$

$$\begin{aligned}\psi_S(\alpha, \alpha') &= \frac{\alpha'^2 \alpha^2}{(\alpha^2 - \alpha'^2)} \\ &\quad \times \left[ \frac{1}{\cosh(\alpha)} - \frac{1}{\sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right],\end{aligned}\quad (18)$$

$$\begin{aligned}\psi_P(\alpha, \alpha') &= \frac{\alpha^2}{(\alpha^2 - \alpha'^2)} \\ &\quad \times \left[ \left( \frac{1}{\cosh(\alpha)} \right. \right. \\ &\quad \left. \left. - \frac{1}{2 \sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right) \right. \\ &\quad \left. \times \left( \frac{1}{\alpha'} (e^{\alpha'} - 1) \right) \right. \\ &\quad \left. + \frac{(e^{-\alpha'} - 1)}{2\alpha' \sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right. \\ &\quad \left. - \left( \frac{\sinh(\alpha)}{\alpha^2 \cosh(\alpha)} \right) \right],\end{aligned}\quad (19)$$

$$\psi_T = \psi_S + \psi_P. \quad (20)$$

**2.5. Zero-Order Catalytic Kinetics.** In this case,  $MU > 1$  or  $1 + K_Q/[Q] \gg K_S/[S]$ . Now (7) reduce to the following forms:

$$\begin{aligned}\frac{d^2 U}{dX^2} - \frac{\alpha^2}{M} &= 0, \\ \frac{d^2 V}{dX^2} + \frac{\alpha^2}{M} &= \alpha'^2 V.\end{aligned}\quad (21)$$

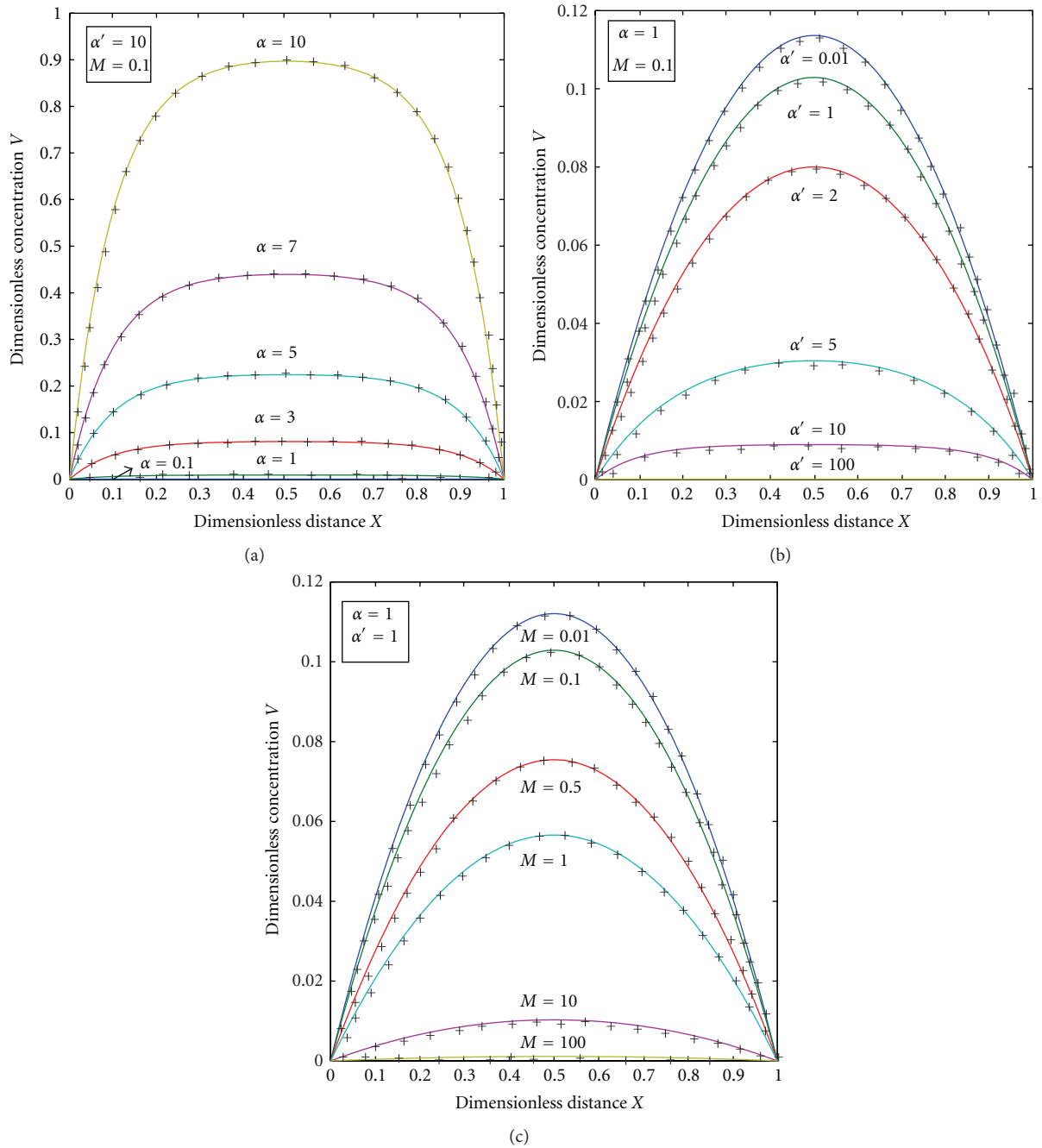


FIGURE 3: Profile of the normalized concentration of the mediator. The concentrations were computed for various values of  $\alpha$ ,  $\alpha'$ , and  $M$ . The curves are plotted using (11).

The solution of (21) is given as follows:

$$U(X, \alpha, M) = 1 - \frac{\alpha^2}{2M} (1 + X^2), \quad (22)$$

$$V(X, \alpha, \alpha', M) = \frac{\alpha^2}{M\alpha'^2} \left[ 1 - \frac{Me^{\alpha'X} + e^{\alpha'(1-X)}}{M(e^{\alpha'} + 1)} \right]. \quad (23)$$

The current is given by

$$\psi_S(\alpha, \alpha', M) = \frac{\alpha^2}{M\alpha'^2(e^{\alpha'} + 1)} \left( \frac{e^{\alpha'}}{(e^{\alpha'} + 1)} - \alpha' \right), \quad (24)$$

$$\psi_P(\alpha, \alpha', M) = -\frac{2\alpha^2(1 - e^{\alpha'})}{M\alpha'^3(1 + e^{\alpha'})}, \quad (25)$$

$$\psi_T = \psi_S + \psi_P. \quad (26)$$

### 3. Numerical Simulation

The nonlinear differential equations (7) are also solved numerically. The function pdepe in Matlab/Scilab software

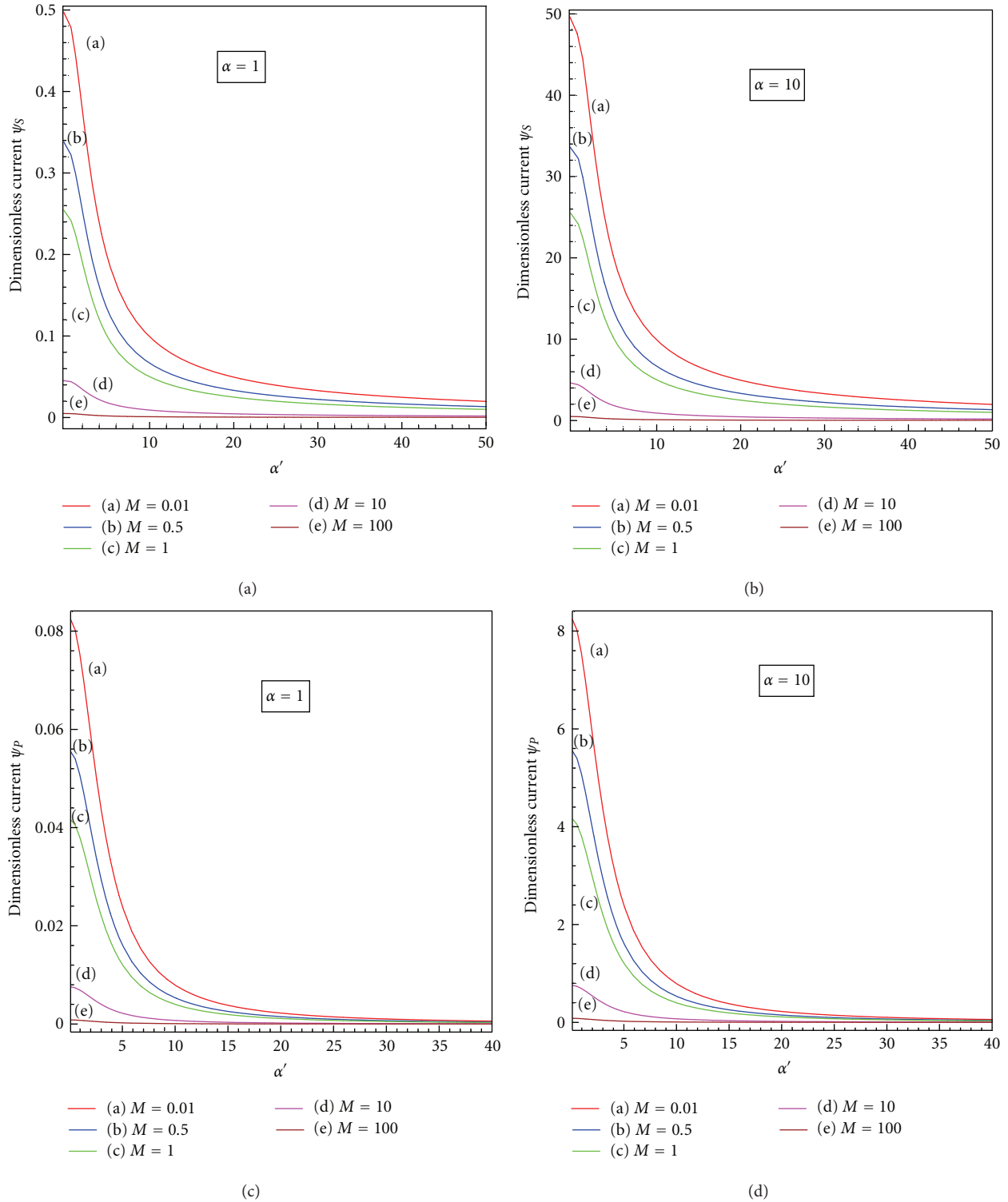


FIGURE 4: Profile of the normalized current. The current curves were computed for various values of  $\alpha$ ,  $\alpha'$ , and  $M$ . The curves are plotted using (12) and (13).

is used to solve boundary value problems (BVPs) for partial differential equations. The numerical solution is compared with our analytical results. The Matlab/Scilab program is also given in Table 1. Upon comparison it is evident that both results gives satisfactory agreement.

#### 4. Discussion

Figures 2(a)–2(c) represents the normalized non-steady state concentration of substrate  $U$  versus dimensionless distance  $X$ , for different values of dimensionless reaction diffusion

TABLE 1: Summary of analytical expressions of concentrations and currents.

Limiting case	Concentration and current	Eqn. no	Figures	Parameter values
All Values of $M$	$U(X, \alpha, M) = \frac{\cosh(\alpha X)}{\cosh(\alpha)} + \frac{M \cosh(\alpha X) (\cosh(2\alpha) - 3)}{6 \cosh^3(\alpha)} - \frac{M (\cosh(2\alpha X) - 3)}{6 \cosh^2(\alpha)}$	(see (10))	Figure 2	$\alpha = (0.1, \dots, 100)$ and $M = (0.001, \dots, 1)$
	$V(X, \alpha, M) = \frac{\alpha^2}{\alpha'^2 (M + 1)} \left[ 1 - \frac{e^{\alpha' X} + e^{\alpha' (1-X)}}{(e^{\alpha'} + 1)} \right]$	(see (11))	Figure 3	$\alpha = (0.1, \dots, 10), \alpha' = (0.01, \dots, 100)$ , and $M = (0.01, \dots, 100)$
	$\psi_S(\alpha, \alpha', M) = \frac{\alpha^2 (e^{\alpha'} - 1)}{\alpha' (M + 1) (e^{\alpha'} + 1)}$	(see (12))	Figures 4(a) and 4(b)	$\alpha = 1, 10$ and $M = (0.01, \dots, 100)$
	$\psi_P(\alpha, \alpha', M) = \frac{\alpha^2 (\alpha' e^{\alpha'} - e^{\alpha'} + \alpha' + 1)}{\alpha'^3 (M + 1) (e^{\alpha'} + 1)} - \frac{\alpha^2 (e^{\alpha'} - 1)}{\alpha'^3 (M + 1) (e^{\alpha'} + 1)}$	(see (13))	Figures 4(c) and 4(d)	$\alpha = 1, 10$ and $M = (0.01, \dots, 100)$
	$\psi_T = \psi_S + \psi_P$ $U(\alpha, X) = \frac{\cosh(\alpha X)}{\cosh(\alpha)}$	(see (14)) (see (16))	Figures 5(a) and 5(b)	$\alpha = 1, 10$ and $M = (0.01, \dots, 100)$
First-order catalytic	$V(X, \alpha, \alpha') = \frac{\alpha^2}{(\alpha^2 - \alpha'^2)} \left[ \frac{e^{\alpha' X}}{\cosh(\alpha)} - \frac{\cosh(\alpha X)}{\cosh(\alpha)} - \frac{\sinh(\alpha' X)}{\sinh(\alpha')} \right]$	(see (17))		
	$\psi_S(\alpha, \alpha') = \frac{\alpha' \alpha^2}{(\alpha^2 - \alpha'^2)} \left[ \frac{1}{\cosh(\alpha)} - \frac{1}{\sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right]$	(see (18))	Figure 6(a)	$\alpha = 10, 50, 100$
Kinetics $MU < 1$	$\psi_P(\alpha, \alpha') = \frac{\alpha^2}{(\alpha^2 - \alpha'^2)} \left[ \left( \frac{1}{\cosh(\alpha)} - \frac{1}{2 \sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) \right) \left( \frac{1}{\alpha'} (e^{\alpha'} - 1) \right) + \frac{(e^{-\alpha'} - 1)}{2 \alpha' \sinh(\alpha')} \left( \frac{e^{\alpha'}}{\cosh(\alpha)} - 1 \right) - \left( \frac{\sinh(\alpha)}{\alpha^2 \cosh(\alpha)} \right) \right]$	(see (19))	Figure 6(b)	$\alpha = 0.5, \dots, 100$
	$\psi_T = \psi_S + \psi_P$ $U(X, \alpha, M) = 1 - \frac{\alpha^2}{2M} (1 + X^2)$	(see (20)) (see (22))	Figure 6(c)	$\alpha = 0.5, \dots, 100$
	$V(X, \alpha, \alpha', M) = \frac{\alpha^2}{M \alpha'^2} \left[ 1 - \frac{M e^{\alpha' X} + e^{\alpha' (1-X)}}{M (e^{\alpha'} + 1)} \right]$	(see (23))		

TABLE 1: Continued.

Limiting case	Concentration and current	Eqn. no	Figures	Parameter values
Zero-order catalytic	$\psi_S(\alpha, \alpha', M) = \frac{\alpha^2}{M\alpha'^2(e^{\alpha'} + 1)} \left( \frac{e^{\alpha'}}{(e^{\alpha'} + 1)} - \alpha' \right)$	(see (24))	Figure 7(a)	$M = 0.01, \dots, 100$ and $\alpha = 1$
Kinetics $MU > 1$	$\psi_P(\alpha, \alpha', M) = \frac{2\alpha^2(1 - e^{\alpha'})}{M\alpha'^3(1 + e^{\alpha'})}$	(see (25))	Figure 7(b)	$M = 0.01, \dots, 100$ and $\alpha = 1$
	$\psi_T = \psi_S + \psi_P$	(see (26))	Figure 7(c)	$M = 0.01, \dots, 100$ and $\alpha = 1$



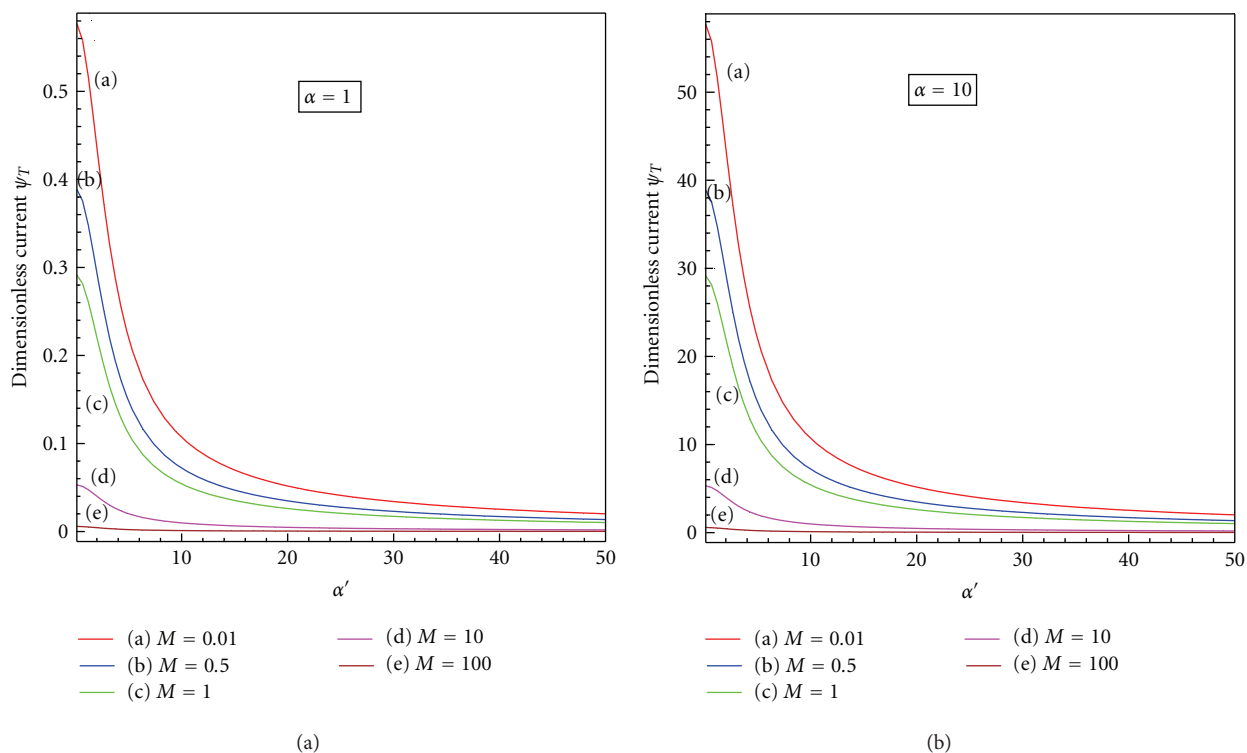


FIGURE 5: Profile of the normalized current. The current curves were computed for various values of  $\alpha$ ,  $\alpha'$ , and  $M$ . The curves are plotted using (14).

parameter  $\alpha = 0.1, \dots, 100$  and  $M = 0.001, \dots, 1$ . From this figure, it is evident that the concentration of substrate increases when  $\alpha$  decreases and  $M$  increases. From this Figures 1(a)–1(c), it is evident that the value of concentration is uniform when  $\alpha \geq 0.5$ .

Figures 3(a)–3(c) shows the concentration of mediator  $V$  versus dimensionless distance  $X$ , for various values of dimensionless diffusion parameter  $\alpha$  ( $= 0.1, \dots, 10$ ),  $\alpha'$  ( $= 0.01, \dots, 100$ ) and  $M$  ( $= 0.01, \dots, 100$ ). From this figure, it is inferred that the value of the concentration of mediator decreases abruptly when  $\alpha$  decreases and  $M$  and  $\alpha'$  increases. Also the concentration of mediator reaches the maximum value at the middle of membrane ( $x = 0.5$ ) for all values of  $\alpha$ ,  $\alpha'$ , and  $M$ .

The normalized steady state current  $\psi_s(\alpha, \alpha', M)$  and  $\psi_p(\alpha, \alpha', M)$  as the function of the dimensionless parameter  $\alpha'$  is given in Figures 4(a)–4(d). From this figures, it is obvious that the values of the current decreases slowly and reaches constant value when  $\alpha' \geq 40$ . Also values of the current decreases when  $M$  increases.

In Figures 5(a)–5(b), profile of the normalized current  $\psi_T$  is shown. The current were computed for various values of  $\alpha$ ,  $\alpha'$ , and  $M$ . The curves are plotted using (12). The value of the current increases when  $\alpha$  increases. The normalized non-steady-state current for diverse values of dimensionless diffusion parameter  $\alpha$  is plotted in Figures 6(a)–6(c).

## 5. Conclusions

The steady state nonlinear reaction/diffusion equations in an amperometric glucose sensor have been solved analytically.

An approximate analytical expression for the concentrations and current for an amperometric glucose sensor are obtained by using the Homotopy perturbation method. The primary result of this work is simple approximate calculation of concentration profiles and current for all values of fundamental parameters  $\alpha$  and  $\alpha'$ . The analytical results obtained can be used for the optimization of the design of glucose sensor.

## Appendix

### Approximate Analytical Expression of the Normalized Concentration of Substrate and $H_2Q$

Using Homotopy perturbation method, we construct a homotopy for (7) as follows:

$$(1-p) \left( \frac{d^2 U}{dX^2} \right) + p \left[ \frac{d^2 U}{dX^2} - \frac{\alpha^2 U}{MU+1} \right] = 0, \quad (A.1)$$

$$(1-p) \left( \frac{d^2 V}{dX^2} - \alpha'^2 V \right) + p \left[ \frac{d^2 V}{dX^2} - \alpha'^2 V + \frac{\alpha^2 U}{MU+1} \right] = 0. \quad (A.2)$$

The approximate solution of (A.1) is given by

$$U = U_0 + pU_1 + p^2U_2 + p^3U_3 + \dots \quad (A.3)$$

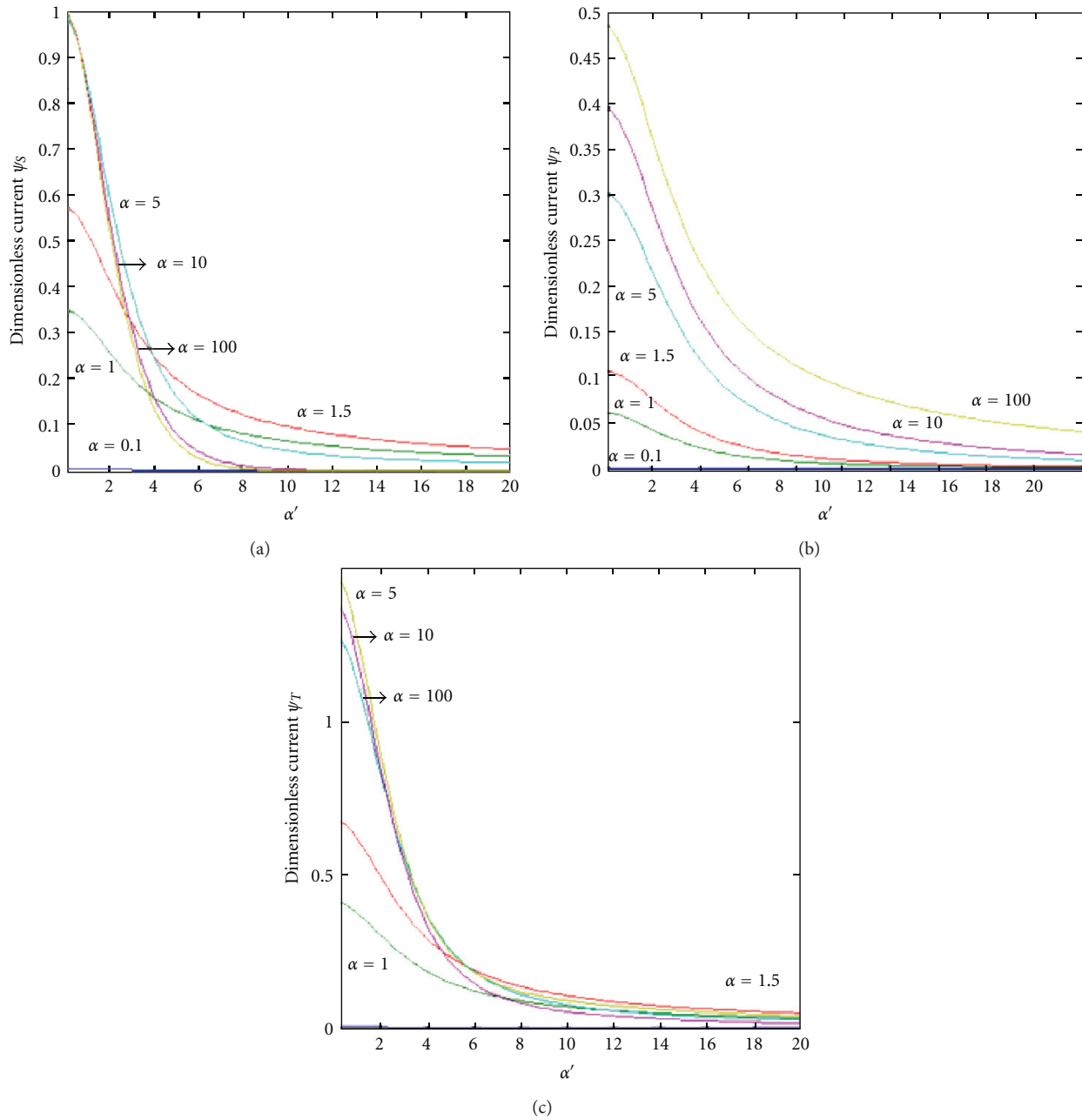


FIGURE 6: Profile of the normalized current for first-order kinetics. The current curves were computed for various values of  $\alpha$ ,  $\alpha'$ , and  $M$ . The curves are plotted using (18)–(20).

Substituting (A.3) into (A.1) and comparing the coefficients of like powers of  $p$ :

$$\begin{aligned} p^0: \frac{d^2 U_0}{dX^2} - \alpha^2 U_0 &= 0, \\ p^1: \frac{d^2 U_1}{dX^2} - \alpha^2 U_1 + M U_0 \frac{d^2 U_0}{dX^2} &= 0. \end{aligned} \quad (\text{A.4})$$

The boundary conditions for the above equations are

$$\begin{aligned} \frac{dU_0}{dX} &= 0 \quad \text{at } X = 0, & U_0 &= 1, \quad \text{at } X = 1, \\ \frac{dU_1}{dX} &= 0 \quad \text{at } X = 0, & U_1 &= 0, \quad \text{at } X = 1. \end{aligned} \quad (\text{A.5})$$

Using this boundary conditions the solution of (A.4) becomes as follows:

$$\begin{aligned} U_0 &= \frac{\cosh(\alpha X)}{\cosh(\alpha)}, \\ U_1 &= \frac{M \cosh(\alpha X) (\cosh(2\alpha) - 3)}{6 \cosh^3(\alpha)} \\ &\quad - \frac{M (\cosh(2\alpha X) - 3)}{6 \cosh^2(\alpha)}. \end{aligned} \quad (\text{A.6})$$

Adding (A.6) we get (10) in the text

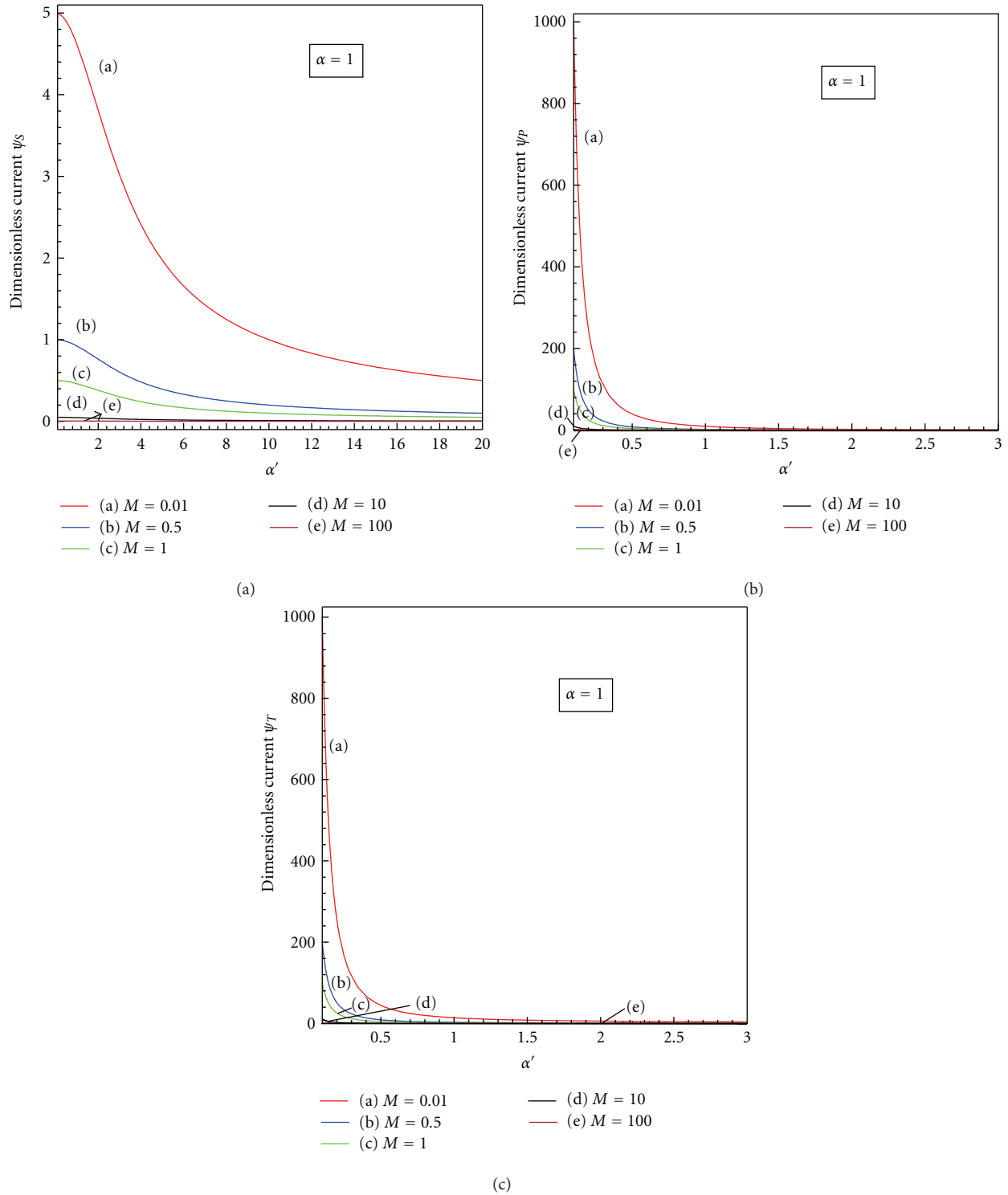


FIGURE 7: Variation of normalized non-steady-state current response for zero-order kinetics. The current curves were computed for various values of  $\alpha$ ,  $\alpha'$  and  $M$ . The curves are plotted using (24)–(26).

The approximate solution of (A.2) is given by

$$V = V_0 + pV_1 + p^2V_2 + p^3V_3 + \dots \quad (\text{A.7})$$

Substituting (A.3) and (A.2) and arranging the coefficients of like powers of  $p$ , we have

$$p^0: \frac{d^2V_0}{dX^2} - \alpha'^2V_0 = 0, \quad (\text{A.8})$$

$$p^1: \frac{d^2V_1}{dX^2} - \alpha'^2V_1 + \frac{\alpha^2U_0}{MU_0 + 1} = 0. \quad (\text{A.9})$$

The boundary conditions for the above equations are as follows

$$\begin{aligned} V_0 = 0, \quad V_1 = 0, \quad & \text{when } X = 0, \\ V_0 = 0, \quad V_1 = 0, \quad & \text{when } X = 1. \end{aligned} \quad (\text{A.10})$$

Upon solving (A.7) and (A.8), and using this boundary condition, we get

$$V_0(X) = 0,$$

$$V_1(X) = \frac{\alpha^2}{\alpha'^2(M+1)} \left[ 1 - \frac{e^{\alpha'X} + e^{\alpha'(1-X)}}{(e^{\alpha'} + 1)} \right]. \quad (\text{A.11})$$

Adding (A.11) we get, (11) in the text.

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