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ORIGINAL PAPER

Analytical expression of the steady-state catalytic current of mediated bioelectrocatalysis and the application of He's Homotopy perturbation method

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Abstract A mathematical model of mediated bioelectrocatalysis is restudied in this paper. Here He's Homotopy perturbation method is implemented to give approximate and analytical solutions of steady-state non-linear reaction diffusion equation containing a non-linear term related to Michaelis–Menten kinetics of the enzymatic reaction. Approximate analytical expressions for mediator concentration and current have been derived for all values of saturation parameter α and reaction diffusion parameter k for the various types of boundary conditions. The Homotopy perturbation method which produces the solutions in terms of convergent series, requiring no linearization or small perturbation. These analytical results are compared with numerical results (Matlab program) and are found to be in good agreement.

Keywords Reaction/diffusion equation · Michaelis–Menten kinetics · Homotopy perturbation method · Mediated bioelectrocatalysis · Numerical simulation

1 Introduction

Several oxidoreductase reactions such as quinones and ferrocenes consist of electrode reactions which allow conjugating between redox enzyme reactions and electrode reactions. The redox compound-mediated and enzyme-catalyzed electrode process is called mediated bioelectrocatalysis [1,2]. It is utilized for biosensors, bioreactors, and biofuel cells. Ohgaru et al. [3] have reported the analysis of mediated bioelectroanalysis mediator diffusion, Michaelis–Menten rate equation. The steady-state concentration and current have been obtained analytically for the case of very low concentrations of the mediator compared with its Michaelis constant [4–6]. Recently Rajendran et al. [7]

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derived the steady-state analytical solution of concentration for the substrate at polymer modified electrode for all values α and K using Variational iteration method.

Ohgaru et al. [3] have calculated the steady-state current for the limiting cases. However, to the best of our knowledge, till date there was no analytical results corresponding to the steady-state mediator concentration and current for all values of saturation parameter α and reaction diffusion parameter k have been reported. The purpose of this communication is to derive an analytical expression for the steady-state mediator concentration and the current of mediated bioelectrocatalysis based on "Homotopy perturbation method" for various boundary conditions.

2 Mathematical formulation of the boundary value problem and analysis

The two-substrate redox enzyme reaction for the oxidation of the substrate (S) to the product (P) in solution is given by

$$S + M_{ox} \overset{K_M}{\rightleftharpoons} SM_{0x} \overset{K_{cat}}{\rightarrow} P + M_{red} \tag{1}$$

where M_{ox} is the concentration of the soluble acceptor (or the oxidized form of the mediator or enzyme or second substrate), M_{red} is the reduced form of M_{ox} (or reduced mediator) and K_{cat} is the catalytic constant. In this case, the steady-state kinetic constant of the redox enzyme reaction v_E is given by the Michaelis–Menten equation

$$v_E = \frac{K_{cat}[E]}{1 + K_M/[M_{ox}]} \tag{2}$$

where $[E]$ is the concentration of the soluble enzyme, and K_M and $[M_{ox}]$ are the Michaelis constant and the concentration of M_{ox} respectively. Note that M_{red} is oxidized at the electrode surface to generate M_{ox}, which takes part in the enzyme reaction in Eq (1).

$$M_{red} \rightarrow M_{\text{ox}} + ne^- \tag{3}$$

where n is the number of electrons. The steady-state diffusion of the mediator with the enzyme reaction results as [3]

$$D_M \frac{d^2[M_{ox}]}{dX^2} - \frac{K_{cat}[E]}{1 + K_M/[M_{ox}]} = 0 \tag{4}$$

Now the boundary conditions become [3]

$$[M_{ox}]_{X=0} = [M_{red}]^* \tag{5a}$$

$$[M_{ox}]_{X=\delta} = 0 \tag{5b}$$

$$\left.\frac{dM_{0x}}{dX}\right|_{X=\delta} = 0 \tag{5c}$$

where $[M_{red}]^*$ is the bulk concentration of M_{red} and assumed to be equal to $[M_{ox}]_{X=0}$. Eq. (5a) is a valid assumption only if the D values for the two species are identical and there are no chemical complications. M_{red} is also assumed to be constant through the reaction zone. The thickness of steady-state diffusion layer δ is given by the following expression

$$\delta = \sqrt{\frac{2D_M[M_{red}]^*}{k_{cat}[E]}} \tag{6}$$

The current is given by [3]

$$\frac{i}{nFA} = -D_M \left(\frac{d[M_{ox}]}{dX}\right)_{X=0} \tag{7}$$

Introducing a rate constant

$$K = \frac{K_{cat}[E]}{K_M} \tag{8}$$

We can write the Eq. (4) as

$$D_M \frac{d^2[M_{ox}]}{dX^2} - \frac{K[M_{ox}]}{1 + [M_{ox}]/K_M} = 0 \tag{9}$$

We can make the non-linear differential equation dimensionless by defining the following parameters:

$$u = \frac{[M_{ox}]}{[M_{red}]^*}; \;\; x = \frac{X}{\delta}; \;\; k = \frac{K\delta^2}{D_M}; \;\; \alpha = \frac{[M_{red}]^*}{K_M} \tag{10}$$

where u and x represent dimensionless concentration and distance respectively. Here α denotes a saturation parameter and k denotes reaction diffusion parameter. Now the Eq. (9) reduces to the following dimensionless form:

$$\frac{d^2u}{dx^2} - \frac{ku}{1 + \alpha u} = 0 \tag{11}$$

Now the boundary condition reduces to

$$x = 0, \;\; u = 1 \tag{12a}$$

$$x = 1, \;\; u = 0 \tag{12b}$$

The current Eq. (7) in dimensionless form is as follows:

$$\psi = \frac{i\delta}{nFAD_M[M_{red}]^*} = -\left(\frac{du}{dx}\right)_{x=0} \tag{13}$$

3 Analytical solution of the concentration and current using Homotopy perturbation method

Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [10–13]. This method is a combination of homotopy in topology and classical perturbation techniques. Ji-Huan He used the HPM to solve the Lighthill equation [14], the Duffing equation [15] and the Blasius equation [16]. The idea has been used to solve non-linear boundary value problems [17–19], integral equations [20–22], Klein–Gordon and Sine–Gordon equations [23], Emden–Flower type equations [24] and many other problems. This wide variety of applications shows the power of the HPM to solve functional equations. The HPM is unique in its applicability, accuracy and efficiency. The HPM [25] uses the imbedding parameter p as a small parameter, and only a few iterations are needed to search for an asymptotic solution. Using homotopy perturbation method (refer Appendix "A"), the concentration of the mediator is

$$u = e^{\sqrt{k}x} - e^{\sqrt{k}}\left[\frac{\sinh\left(\sqrt{k}x\right)}{\sinh\left(\sqrt{k}\right)}\right] - \frac{\alpha e^{2\sqrt{k}x}\left[e^{-4\sqrt{k}(x-1)} + 1 + 6e^{-2\sqrt{k}(x-1)}\right]}{3\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)} + Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x} \tag{14}$$

The normalized current is

$$\psi = (A - B + 1)\sqrt{k} - \frac{e^{\sqrt{k}}}{\sinh\left(\sqrt{k}\right)} + \frac{2\alpha\left(e^{4\sqrt{k}} - 1\right)\sqrt{k}}{3\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)} \tag{15}$$

where

$$A = -\frac{\alpha\left[e^{3\sqrt{k}} - 7e^{2\sqrt{k}} - e^{\sqrt{k}} - 1\right]}{3\left(e^{\sqrt{k}} + 1\right)\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)} \quad \text{and} \quad B = \frac{\alpha}{3}\left[\frac{e^{4\sqrt{k}} + 6e^{2\sqrt{k}} + 1}{e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1}\right] - A \tag{16}$$

Substitution of the appropriate expression for δ (Eq. 6) and k (Eq. 8) in the expression $k = K\delta^2/D_M$,we obtain $k = 2\alpha$. If this value of $k(= 2\alpha)$ is substituted in the above Eq. (15) we obtain the current for small value of α as

$$\psi = 1 + \frac{1}{\sqrt{2\alpha}} - \frac{2\alpha}{3} + \frac{2\sqrt{2\alpha}}{3} - \frac{5\sqrt{2}}{9}\alpha^{3/2} - \frac{1}{9\sqrt{2}}\alpha^{5/2} \tag{17}$$

Eq. (14) represents the most general new approximate analytical expression for the dimensionless mediator concentration profile for all values of the parameter α and k.

Equation (15) represents the normalized steady-state current response ψ. In dimension form, the expression of the mediator concentration and current becomes the following.

$$[M_{0x}] = [M_{red}]^* e^{\sqrt{\beta}X} - [M_{red}]^* e^{\sqrt{\beta}\delta}\left[\frac{\sinh\left(\sqrt{\beta}X\right)}{\sinh\left(\sqrt{\beta}\delta\right)}\right]$$
$$-\frac{([M_{red}]^*)^2\, e^{2\sqrt{\beta}X}\left[e^{-4\sqrt{\beta}(X-\delta)} + 1 + 6e^{-2\sqrt{k}(X-\delta)}\right]}{K_M\left(e^{4\sqrt{\beta}\delta} - 2e^{2\sqrt{\beta}\delta} + 1\right)}$$
$$+Ae^{\sqrt{\beta}X} + Be^{-\sqrt{\beta}X} \tag{18}$$

$$\frac{i\delta}{nFAD_M[M_{red}]^*} = (A-B)\sqrt{\beta} + [M_{red}]^*\sqrt{\beta} - [M_{red}]^*\frac{e^{\sqrt{\beta}\delta}}{\sinh\left(\sqrt{\beta}\delta\right)}$$
$$+\frac{2\left([M_{red}]^*\right)^2\left(e^{4\sqrt{\beta}\delta} - 1\right)\sqrt{\beta}}{3K_M\left(e^{4\sqrt{\beta}\delta} - 2e^{2\sqrt{\beta}\delta} + 1\right)} \tag{19}$$

$$\text{where } \beta = \frac{K_{cat}[E]}{K_M D_M},\ \ \delta = \sqrt{\frac{2D_M[M_{red}]^*}{k_{cat}[E]}} \tag{20}$$

$$A = -\frac{([M_{red}]^*)^2\left[e^{3\sqrt{\beta}\delta} - 7e^{2\sqrt{\beta}\delta} - e^{\sqrt{\beta}\delta} - 1\right]}{3K_M\left(e^{\sqrt{\beta}\delta} - 1\right)^2\left(e^{\sqrt{\beta}\delta} + 1\right)^3} \tag{21}$$

and

$$B = \frac{([M_{red}]^*)^2\left(e^{\sqrt{\beta}\delta}\right)^2\left[e^{3\sqrt{\beta}\delta} + 7e^{2\sqrt{\beta}\delta} + e^{2\sqrt{\beta}\delta} - 1\right]}{3K_M\left(e^{\sqrt{\beta}\delta} - 1\right)^2\left(e^{\sqrt{\beta}\delta} + 1\right)^3} \tag{22}$$

4 Theoretical model of Ohgaru and coworkers

Recently Ohgaru and coworkers have obtained the analytical expression of current for the limiting cases using the following boundary conditions

$$x = 0,\ \ u = 1 \tag{23}$$

$$x = 1,\ \ \frac{du}{dx} = 0 \tag{24}$$

We can obtain the expression of concentration for all values of parameters α and k using Homotopy perturbation method

$$u = e^{\sqrt{k}x} + \frac{\alpha\left(e^{\sqrt{k}x} - e^{2\sqrt{k}x}\right)}{3} - \frac{e^{\sqrt{k}}}{3\cosh\left(\sqrt{k}\right)}\left[3\sinh\left(\sqrt{k}x\right) + 4\alpha e^{\sqrt{k}x} - \alpha e^{2\sqrt{k}x} - 3\alpha\right]$$
$$+ \frac{\alpha e^{2\sqrt{k}}}{6\cosh\left(\sqrt{k}\right)^2}\left[4e^{\sqrt{k}x} - \cosh\left(2\sqrt{k}x\right) - 3\right] - 2G\alpha\sinh\left(\sqrt{k}x\right) \tag{25}$$

where

$$G = \frac{\left(e^{\sqrt{k}} - 2e^{2\sqrt{k}}\right)}{6\cosh\left(\sqrt{k}\right)} - \frac{\left(2e^{2\sqrt{k}} - e^{3\sqrt{k}}\right)}{3\cosh\left(\sqrt{k}\right)^2} + \frac{\left(2e^{3\sqrt{k}} - e^{2\sqrt{k}}\sinh\left(2\sqrt{k}\right)\right)}{6\cosh\left(\sqrt{k}\right)^3} \tag{26}$$

The expression of current is

$$\psi = \left|\sqrt{k}\left(\frac{\alpha}{3} - 1\right) + \frac{\left(e^{\sqrt{k}}(3+2\alpha) + \alpha(e^{\sqrt{k}} - 2e^{2\sqrt{k}})\right)\sqrt{k}}{3\cosh\left(\sqrt{k}\right)}\right.$$
$$\left. + \frac{\left(2\alpha(-2e^{2\sqrt{k}} + e^{3\sqrt{k}}) - 2\alpha e^{2\sqrt{k}}\right)\sqrt{k}}{3\cosh\left(\sqrt{k}\right)^2} + \frac{\alpha\sqrt{k}\left(2e^{3\sqrt{k}} - e^{2\sqrt{k}}\sinh\left(2\sqrt{k}\right)\right)}{3\cosh\left(\sqrt{k}\right)^3}\right| \tag{27}$$

Substituting the value of $k = 2\alpha$ in the Eq. (27) we obtain the Eq. (28) for small values of α

$$\psi = \left|2\alpha + \frac{\sqrt{2}}{3}\alpha^{3/2} - 2\alpha^2 - 2\sqrt{2}\alpha^{5/2} + \frac{32}{9}\alpha^3\right| \tag{28}$$

In dimension form, the concentration of the mediator $[M_{ox}]$ and current i are as follows:

$$\frac{[M_{ox}]}{[M_{red}]^*} = e^{\sqrt{\beta}X} + \frac{[M_{red}]^*\left(e^{\sqrt{\beta}X} - e^{2\sqrt{\beta}X}\right)}{3K_M}$$
$$- \frac{e^{\sqrt{\beta}\delta}}{3\cosh\left(\sqrt{\beta}\delta\right)}\left[3\sinh\left(\sqrt{\beta}x\right) + \frac{[M_{red}]^*}{K_M}\left(4e^{\sqrt{\beta}X} - e^{2\sqrt{\beta}X} - 3\right)\right]$$
$$+ \frac{[M_{red}]^* e^{2\sqrt{\beta}\delta}}{6K_M\cosh\left(\sqrt{\beta}\delta\right)^2}\left[4e^{\sqrt{\beta}X} - \cosh\left(2\sqrt{\beta}X\right) - 3\right] - 2\frac{[M_{red}]^* G\sinh\left(\sqrt{\beta}X\right)}{K_M} \tag{29}$$

where

$$G = \frac{\left(e^{\sqrt{\beta}\delta} - 2e^{2\sqrt{\beta}\delta}\right)}{6\cosh\left(\sqrt{\beta}\delta\right)} - \frac{\left(2e^{2\sqrt{\beta}\delta} - e^{3\sqrt{\beta}\delta}\right)}{3\cosh\left(\sqrt{\beta}\delta\right)^2} + \frac{\left(2e^{3\sqrt{\beta}\delta} - e^{2\sqrt{\beta}\delta}\sinh\left(2\sqrt{\beta}\delta\right)\right)}{6\cosh\left(\sqrt{\beta}\delta\right)^3} \tag{30}$$

$$\frac{i\delta}{nFAD_M[M_{red}]^*} = \left| \begin{array}{l} \sqrt{\beta}\delta\left[\dfrac{\left(3e^{\sqrt{\beta}\delta} + 3[M_{red}]^*/K_M e^{\sqrt{\beta}\delta} - 2e^{2\sqrt{\beta}\delta}\right)}{3\cosh\left(\sqrt{\beta}\delta\right)} - 1\right] + \\ \dfrac{[M_{red}]^*}{K_M}\left(\dfrac{2\sqrt{\beta}\delta e^{3\sqrt{\beta}\delta}}{3\cosh\left(\sqrt{\beta}\delta\right)^3} - \dfrac{2\sqrt{\beta}\delta e^{2\sqrt{\beta}\delta}}{3\cosh\left(\sqrt{\beta}\delta\right)^2} - \dfrac{\alpha\sqrt{\beta}e^{2\sqrt{\beta}\delta}\sinh\left(2\sqrt{\beta}\delta\right)}{3\cosh\left(\sqrt{\beta}\delta\right)^3}\right) \end{array} \right| \tag{31}$$

5 Numerical simulation

The nonlinear differential Eq. (11) is also solved by numerical methods. The function bvp4c in MATLAB software which is a function of solving two-point boundary value problems (BVPs) for ordinary differential equations is used to solve this equation. Its numerical solution is compared with Homotopy perturbation method and it gives a satisfactory agremment. The Matlab program is also given in Appendix B.

6 Comparison of current with previous work

Recently Ohgaru et al. [3] obtained the current at $\alpha u << 1 \quad ([M_{red}]^* << K_M)$ as follows:

$$\psi = \sqrt{k} \tag{32}$$

Similarly when $\alpha u >> 1 \quad ([M_{red}]^* >> K_M)$

$$\psi = \sqrt{\frac{2k}{\alpha}} \tag{33}$$

Also Ohgaru et al. [3] proposed the following an approximate expression of current for all values of α:

$$\psi = \sqrt{\frac{2k}{2+\alpha}} \tag{34}$$

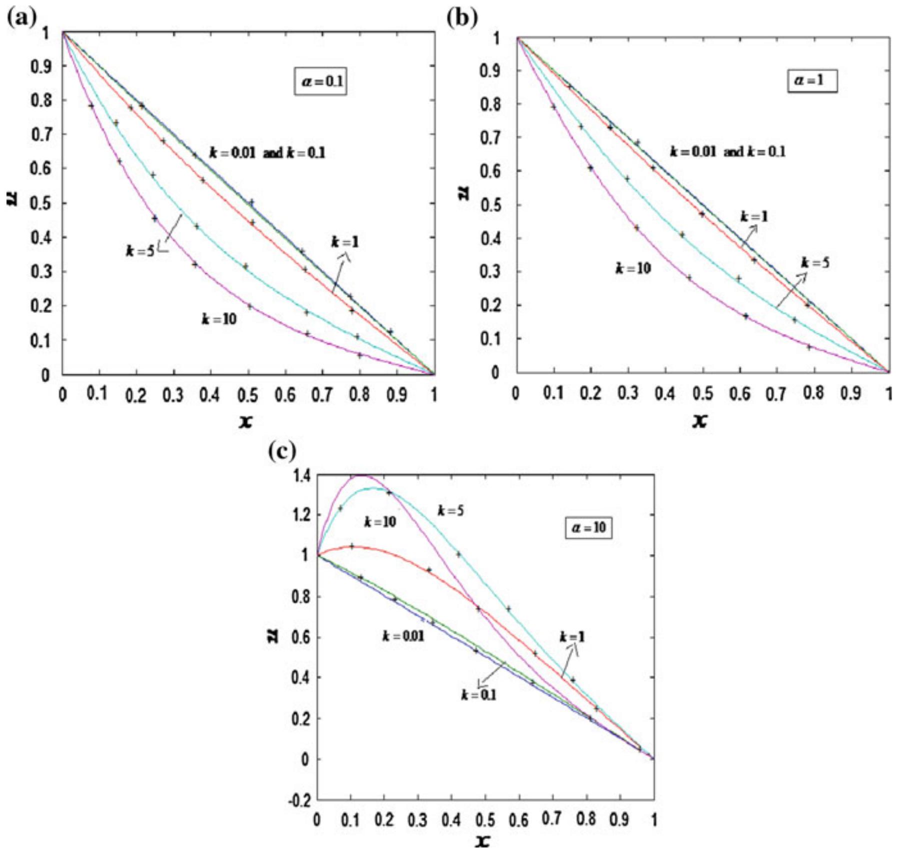

Fig. 1 Normalized steady-state mediator concentration u. The concentrations were computed using Eq. (14) for various values of the reaction diffusion parameters and saturation parameter α. $(-)$ denotes Eq. (14) and $(+)$ denotes the numerical simulation

7 Discussion

Equations (14) and (15) are the new and simple approximate analytical expressions for the concentrations of the mediator and the current calculated using Homotopy perturbation method for the boundary conditions (12a) and (12b). The closed approximate analytical expression for the concentration of mediator and current according to the boundary conditions (18) and (19) are represented by the Eqs. (25) and (26). The dimensionless mediator concentration $u(x)$ versus dimensionless distance x are given in Fig. 1a–c. From these figures, it is inferred that the value of the concentration decreases when the parameter k and distance x increases if $\alpha \leq 1$. Also when $\alpha k \leq 0.1$, the mediator concentration is $u = 1 - x \quad ([M_{ox}]/[M_{red}]^* \approx 1 - X/\delta)$. From this relation we can find the thickness of the steady-state diffusion layer δ. When α and k are both large, the value of u initially increases from the value zero and then decreases gradually (see Fig. 1c).

The dimensionless current ψ versus k for various values of α is given in Fig. 2. The value of the current increases when k increases and α decreases. In Fig. 3, the

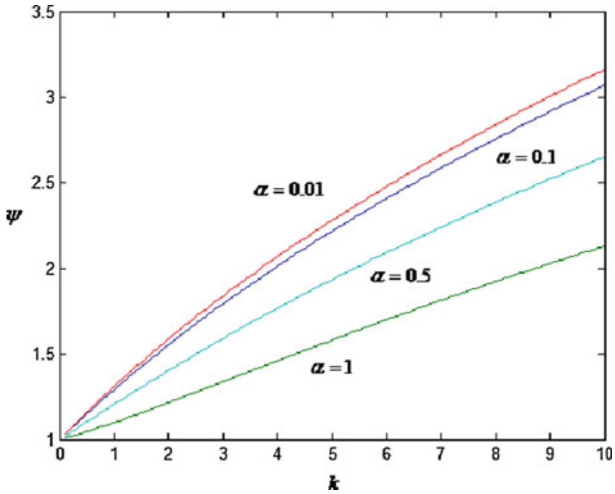

Fig. 2 Variation of normalized current ψ versus parameter k using Eq. (15) for various values of saturation parameter α

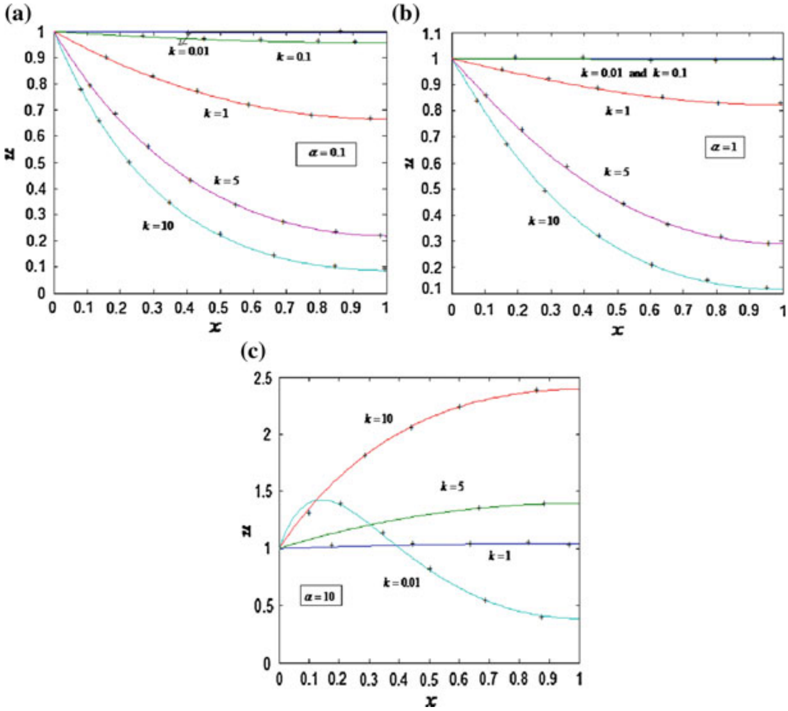

Fig. 3 Normalized steady-state mediator concentration u. The concentrations were computed using Eq. (25) for various values of the parameters k and saturation parameter α. (−) denotes Eq. (25) and (+) denotes the numerical simulation.

Table 1 Comparison of normalized steady-state current ψ for some value of $\alpha = 0.01$

k	This work Eq. (27) Analytical	Ohgaru et.al. [3] work	
		Small $\psi = \sqrt{k}$ Eq. (32)	Approximate $\psi = \sqrt{\frac{2k}{2+\alpha}}$ Eq. (34)
0.001	0.0009	0.0316	0.0315
0.01	0.0099	0.1000	0.0998
0.1	0.0958	0.3162	0.3154
1	0.7569	1.0000	0.9975
10	3.1403	3.1623	3.1544
100	9.9667	10.0000	9.9751

Table 2 Comparison of normalized steady-state current ψ for some value of $\alpha = 0.1$

k	This work Eq. (27) Anlytical	Ohgaru et.al. [3] work	
		Small $\psi = \sqrt{k}$ par Eq. (32)	Approximate $\psi = \sqrt{\frac{2k}{2+\alpha}}$ Eq. (34)
0.001	0.0009	0.0316	0.0309
0.01	0.0089	0.1000	0.0976
0.1	0.0877	0.3162	0.3086
1	0.7149	1.0000	0.9759
10	3.0444	3.1623	3.0861
100	9.6666	10.0000	9.7590

normalized mediator concentration u for various values of α and k are plotted. From this Figure it is known that $u(x)$ decreases when k increases (K_M decreases) for all values of α. Also $u \approx 1$ when $\alpha k \leq 0.1$. In Tables 1 and 2, our results are also compared with previous available analytical results. Our expression (Eq. 27) gives satisfactory agreement with small and large values of α (Eq. 32) From this tables, it is inferred that the value of the current increases when reaction diffusion parameter k and saturation parameter α increases.

8 Conclusion

In this work, the time independent non-linear reaction/diffusion equation has been formulated and solved analytically. We have presented approximate expression of mediated concentration using Homotopy perturbation method. Moreover, we have also presented an approximate analytical expression for the steady state current. Further, based on the outcome of this work it is possible to calculate the approximate amounts of mediator concentration and current corresponding to a non-linear Michaelis–Menten kinetics scheme. In addition, the transport and kinetics are quantified in terms of fundamental reaction/diffusion polymer parameter k and saturation parameter α.

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Appendix A

Solution of the equation (11) using Homotopy perturbation method

In this Appendix, we indicate how Eq. (14) in this paper is derived. In order, to determine the solution of Eq. (11), initially we construct a Homotopy as follows:

$$(1-p)\left[\frac{d^2u}{dx^2}-ku\right]+p\left[\frac{d^2u}{dx^2}+\alpha u\frac{d^2u}{dx^2}-ku\right]=0 \tag{A1}$$

and the initial approximations are as follows:

$$x=0,\quad u=1 \tag{A2a}$$

$$x=1,\quad u=0 \tag{A2b}$$

The approximate solution of (A1) is

$$u=u_0+pu_1+p^2u_2+\cdots \tag{A3}$$

Substituting the Eq. (A3) in the Eq. (A1), we have the following equations

$$p^0:\frac{d^2u_0}{dx^2}-ku_0=0 \tag{A4}$$

and

$$p^1:\frac{d^2u_1}{dx^2}-ku_1+\alpha u_0\frac{d^2u_0}{dx^2}=0 \tag{A5}$$

Solving the above equations and using the boundary conditions, we have

$$u_0=e^{\sqrt{k}x}-e^{\sqrt{k}}\left[\frac{e^{\sqrt{k}x}-e^{-\sqrt{k}x}}{e^{\sqrt{k}}-e^{-\sqrt{k}}}\right] \tag{A6}$$

and

$$u_1=-\frac{\alpha e^{2\sqrt{k}x}\left\lfloor e^{-4\sqrt{k}(x-1)}+6e^{-2\sqrt{k}(x-1)}+1\right\rfloor}{3\left(e^{4\sqrt{k}}-2e^{2\sqrt{k}}+1\right)}+Ae^{\sqrt{k}x}+Be^{-\sqrt{k}x} \tag{A7}$$

where

$$A = -\frac{\alpha\left\lfloor e^{3\sqrt{k}} - 7e^{2\sqrt{k}} - e^{\sqrt{k}} - 1\right\rfloor}{3\left(e^{\sqrt{k}}+1\right)\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)} \tag{A8}$$

and

$$B = \frac{\alpha}{3}\left[\frac{e^{4\sqrt{k}} + 6e^{4\sqrt{k}} + 1}{e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1}\right] - A \tag{A9}$$

According to the HPM, we can conclude that

$$u(x) = \lim_{p\to 1} u(x) = u_0 + u_1 \tag{A10}$$

After putting Eqs. (A6) and (A7) into Eq. (A10), the final results can be described in Eq. (14) in the text

Appendix B

```
function mt6bvp
solinit=bvpinit(linspace(0,1,10),@mat6init);
sol=bvp4c(@mat6ode,@mat6bc,solinit);
xint=linspace(0,1);
Sxint=deval(sol,xint);
plot(xint,Sxint(1,:));
title('numerical simulation')
xlabel('x')
ylabel('solution y')
function dydx=mat6ode(x,y)
a=0.1;
k=10;
dydx=[ y(2)
      (k*y(1))/(1 + a*y(1)) ];
function res=mat6bc(ya,yb)
      res =[ya(1) - 1
           yb(2)];
function yinit=mat6init(x)
        n=0.9495;
        yinit = [1 + n*(x - (x^2)/2)
               n*(1 - x)];
```

Appendix C

Nomenclature and units

Symbol	Meaning	Usual dimension
S	Substrate concentration	mole cm^{-3}
K_M	Michaelis–Menten constant	mole cm^{-3}
K_{cat}	Catalytic rate constant	sec^{-1}
$[E]$	Soluble enzyme concentration	mole cm^{-3}
D_M	Diffusion co-efficient	$cm^2 sec^{-1}$
$[M_{red}]^*$	Bulk concentration of M_{red}	mole cm^{-3}
n	No of electrons	None
F	Faraday constant	sec $mole^{-1}$
A	Area of the electrode surface	cm^2
X	Distance from the electrode surface	cm
δ	Thickness of the steady-state diffusion layer	cm
$[M_{ox}]$	Concentration of mediator	mole cm^{-3}
V_E	Kinetic constant	sec^{-1}
K	Kinetic rate constant	sec^{-1}
k	Normalized reaction diffusion parameter	None
α	Normalized saturation parameter	None
x	Dimensionless distance	None
I	Current density	A
u	Dimensionless mediator concentration	None
ψ	Dimensionless current	None

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