Steady-State Catalytic Current of Bioelectrocatalysis Using Akbari-Ganji's Method

P. Jeyabarathi[1,2], L. Rajendran[2], Marwan Abukhaled[3], M.E.G. Lyons[4,], M. Kannan[1],*

[1] Department of Mathematics, Government Arts College, Ariyalur, Affiliated to Bharathidasan University, Thiruchirappalli, India
[2] Department of Mathematics, AMET, Deemed to be University, Chennai, India
[3] Department of Mathematics and Statistics, American University of Sharjah, Sharjah, UAE
[4] School of Chemistry and AMBER National Centre, University of Dublin, Trinity College Dublin, Dublin 2, Ireland
[*]E-mail: melyons@tcd.ie

This paper uses the efficient, reliable, and widely accessible Akbari-Ganji's method to solve the steady-state problem of mediator concentration by bioelectrocatalysis. Analytical expressions of the mediator concentration and the normalized current are derived for all values of parameters. Compared to numerical simulations, the derived approximate analytical expressions of the mediator concentrations are more accurate than the expressions obtained by the well-founded homotopy perturbation method. The derived results will help in evaluating several important enzyme kinetic parameters.

1. INTRODUCTION

An electrochemical process that uses biological materials as catalysts is called bioelectrocatalysis. The enzyme electrochemical reaction with an electrochemical regeneration of an electron acceptor of the enzyme is known as mediated bioelectrocatalysis [1, 2]. Bioelectrocatalysis yields the essential catalytic functions of redox enzymes to nonspecific electrode reactions. In recent years, the technology of bioelectrocatalysis has been widely used in various devices such as biosensors, biofuel cells, and bioreactors [3, 4].

The catalytic current is governed by the kinetics of the enzyme reaction and the electrode and the mass transport process.Therefore obtaining an analytical expression of the intensity of the catalytic current would lead to understanding other important enzyme kinetic parameters. For example, one

critical case study is an electrolysis period when the substrate concentration is sufficiently more than the corresponding Michaelis constant [2].

The case where the concentration of the mediator is significantly low compared to its Michaelis constant has been analytically discussed in [5, 6]. Ohgaru et al. [2] derived the steady-state limiting current of mediated bioelectrocatalysis for the case where the substrate concentration is sufficiently larger than its Michaelis constant. Thiagarajan et al. [7] employed the homotopy perturbation method to derive an approximate analytical solution of the steady-state nonlinear reaction-diffusion equation describing the Michaelis–Menten kinetics of the enzymatic reaction.

Mathematical models that emerge from modern complex bioelectrocatalysis are nonlinear differential systems for which exact solutions can't be found, and therefore researchers are opting for approximate numerical or analytical solutions. Though numerical solutions are relatively easy to obtain, some of their shortcomings cannot be avoided. In particular, the stability of the approximate numerical solution is not always guaranteed. In addition, with numerical solutions, it is difficult to adjust the model parameters to mimic the numerical data. With modern computational tools, many reliable and highly accurate analytical methods, which have been established in recent years, can be used to solve the underlying nonlinear steady-state catalytic current of mediated bioelectrocatalysis of the most common method that has shown remarkable success in solving complex nonlinear systems. These methods includes the variation iteration method[8], homotopy analysis method [9], differential transformation method [10], Green's function-fixed point method [11-13], exp-function method [14], and Taylor series method [15-17]. This article employs Akbari-Ganji's method [18], which is highly accurate, efficient, and widely accessible to scientists other than mathematicians.

2. THE MATHEMATICAL FORMULATION OF THE PROBLEM

The following two-substrate redox enzyme reaction describes the oxidation of the substrate (S) to the product (P) in solution [1]

$$S + M_{ox} \overset{K_M}{\Leftrightarrow} SM_{ox} \overset{k_{cat}}{\rightarrow} P + M_{red}, \tag{1}$$

where M_{ox} is the mediator and M_{red} is its reduced form. Under the assumption that the substrate concentration is larger than its Michaleis constant, the steady-state kinetic constant of the redox enzyme reaction (v_E) is expressed by the following Michaelis-Menten equation

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

where k_{cat} is the catalytic constant, $[E]$ is the soluble enzyme concentration, $[M_{ox}]$ and K_M are the concentration and the Michaelis constant of M_{ox}, respectively. In bioelectrocatalysis, M_{ox} is generated by the oxidization of M_{red} at the electrode surface, that is

$$M_{red} \rightarrow M_{ox} + ne^-, \tag{3}$$
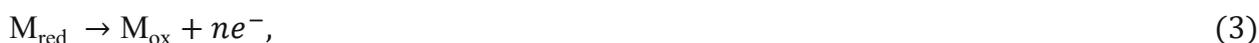
where n represents the number of electrons. The steady-state diffusion of the mediator with the enzyme reaction results as [1]

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

The boundary conditions become [1]

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

$$[M_{ox}]_{X=\delta} = 0, \tag{6}$$

$$\left(\frac{dM_{ox}}{dX}\right)_{X=\delta} = 0, \tag{7}$$

where

$$\delta = \sqrt{\frac{2\,D_M[M_{red}]^*}{k_{cat}[E]}} \quad \text{and } K = \frac{k_{cat}\,[E]}{K_M} \tag{8}$$

in which $[M_{red}]^*$ is the bulk concentration of M_{red}, K is a rate constant, and δ represents the diffusion layer thickness. The current is given by [7]

$$\frac{i}{nFA} = -D_M\left(\frac{d[M_{ox}]}{dX}\right)_{X=0}, \tag{9}$$

where F, A, and D_M are the Faraday constant, the surface area of the electrode, and the diffusion constant, respectively. Using Eq. (8) with algebraic manipulation, Eq. (4) can be written as

$$D_M\,\frac{d^2[M_{ox}]}{dX^2} - \frac{K[M_{ox}]}{1 + [M_{ox}]/K_M} = 0. \tag{10}$$

Introducing the following dimensionless parameters:

$$u = \frac{[M_{ox}]}{[M_{red}]^*}, x = \frac{X}{\delta}, k = \frac{K\,\delta^2}{D_M}, \text{ and } \alpha = \frac{[M_{red}]^*}{K_M}, \tag{11}$$

reduces Eq. (10) to the following dimensionless form

$$\frac{d^2u(x)}{dx^2} = \frac{k\,u(x)}{1 + \alpha\,u(x)}, \tag{12}$$

subject to the following dimensionless boundary conditions:

$$u(0) = 1, \tag{13}$$

$$u(1) = 0, \tag{14}$$

$$u'(1) = 0. \tag{15}$$

The dimensionless current can then be determined by

$$\psi = \frac{i\,\delta}{n\,F\,A\,D_M[M_{red}]^*} = -\left(\frac{du}{dx}\right)_{x=0}. \tag{16}$$

3. RESULTS AND DISCUSSION

3.1 Approximate analytical expression of the concentration using Akbari-Ganji method

First introduced by Akbari and Ganji in 2014, the AGM [18] has been successfully employed to obtain highly accurate approximate analytical solutions of many nonlinear differential models that have emerged in science and engineering [19-21]. In this section, we use the AGM to solve Eq. (12) subject to boundary conditions (13)-(15).

The approach begins by assuming that the solution to Eq. (12) is of the hyperbolic form:

$$u(x) = A_0\cosh(mx) + B_0\sinh(mx), \tag{17}$$

where A_0, B_0 and m are constant. From boundary conditions (13) and (14), the values of A_0 and B_0 are readily obtained, that is

$$A_0 = 1, B_0 = \frac{-\cosh(m)}{\sinh(m)}, \tag{18}$$

and hence Eq. (17) becomes

$$u(x) = \frac{\sinh(m(1-x))}{\sinh(m)}. \tag{19}$$

To determine the constant m in Eq. (19), we consider the functional form of Eq. (12)

$$F(x) = (1 + \alpha\, u(x))\frac{d^2\, u(x)}{d\, x^2} - k\, u(x) = 0. \tag{20}$$

By substituting Eq. (20) into Eq. (19), we obtain

$$F(x)|_{x=0} = \left(1 + \frac{\alpha \sinh(m)}{\sinh(m)}\right)\frac{m^2 \sinh(m)}{\sinh(m)} = k\frac{\sinh(m)}{\sinh(m)}, \tag{21}$$

which implies that

$$m = \pm\sqrt{\frac{k}{1+\alpha}}. \tag{22}$$

Substitute Eq. (22) into Eq. (19) gives the following analytical expression of a mediator concentration $u(x)$ for all dimensionless parameters k and α

$$u(x) = \frac{\sinh\left(\sqrt{\frac{k}{1+\alpha}}\,(1-x)\right)}{\sinh\left(\sqrt{\frac{k}{1+\alpha}}\right)}. \tag{23}$$

Now, from Eq. (16), the normalized current is given by

$$\psi = \sqrt{\frac{k}{1+\alpha}}\coth\left(\sqrt{\frac{k}{1+\alpha}}\right). \tag{24}$$

Notice that Eqs. (23) and (24) were derived using boundary conditions (13) and (14). However, if we use boundary conditions (13) and (15), then it is straightforward to derive, respectively, the following mediator concentration and normalized current:

$$u(x) = \frac{\cosh\left(\sqrt{\frac{k}{1+\alpha}}\,(1-x)\right)}{\cosh\left(\sqrt{\frac{k}{1+\alpha}}\right)}, \tag{25}$$

and

$$\psi = \sqrt{\frac{k}{1+\alpha}}\tanh\left(\sqrt{\frac{k}{1+\alpha}}\right). \tag{26}$$

3.2 Previous analytical results

Thiagarajan et al. used the homotopy perturbation method (HPM) to solve Eq. (12) with boundary conditions (13)-(14) [7]. They derived the following analytical expressions for the mediator concentration and normalized current, respectively,

$$u = e^{\sqrt{k}x} - e^{\sqrt{k}}\left[\frac{\sinh(\sqrt{k}x)}{\sinh(\sqrt{k})}\right] - \frac{\alpha e^{2\sqrt{k}x}\left[e^{-4\sqrt{k}(x-1)} + 1 + 6e^{-2\sqrt{k}(x-1)}\right]}{3\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)} + Ae^{\sqrt{k}x}$$
$$+ Be^{-\sqrt{k}x}, \tag{27}$$

$$\psi = (A - B + 1)\sqrt{k} - \frac{e^{\sqrt{k}}}{\sinh(e^{\sqrt{k}})} + \frac{2\alpha\left(e^{4\sqrt{k}} - 1\right)\sqrt{k}}{3\left(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1\right)}, \tag{28}$$

where

$$A = \frac{-\alpha[e^{3\sqrt{k}} - 7e^{2\sqrt{k}} - e^{\sqrt{k}} - 1]}{3(e^{\sqrt{k}} + 1)(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1)} \text{ and } B = \frac{\alpha[e^{4\sqrt{k}} + 6e^{2\sqrt{k}} + 1]}{3(e^{4\sqrt{k}} - 2e^{2\sqrt{k}} + 1)} - A. \tag{29}$$

And for boundary conditions (13) and (15), they found that the analytical expressions for the concentration and the normalized currents are, respectively, given by

$$u = e^{\sqrt{k}x} + \frac{\alpha\left(e^{\sqrt{k}x} - e^{2\sqrt{k}x}\right)}{3} - \frac{e^{\sqrt{k}}}{3\cosh(\sqrt{k})}\left[3\sinh(\sqrt{k}x) + 4\alpha e^{\sqrt{k}x} - \alpha e^{2\sqrt{k}x} - 3\alpha\right]$$
$$+ \frac{\alpha e^{2\sqrt{k}}}{6\cosh(\sqrt{k})^2}\left[4\,e^{\sqrt{k}x} - \cosh(2\sqrt{k}x) - 3\right] - 2\,G\,\alpha\sinh(\sqrt{k}x), \tag{30}$$

$$\psi$$
$$= \sqrt{k}\left(\frac{\alpha}{3} - 1\right) + \frac{\sqrt{k}\left(e^{\sqrt{k}}(3 + 2\alpha) + \alpha(e^{\sqrt{k}} - 2e^{2\sqrt{k}})\right)}{3\cosh(\sqrt{k})} + \frac{\sqrt{k}\left(2\alpha\left(-2\,e^{2\sqrt{k}} + e^{3\sqrt{k}}\right) - 2\alpha e^{2\sqrt{k}}\right)}{3\cosh(\sqrt{k})^2}$$
$$+ \frac{\alpha\sqrt{k}\left(2e^{3\sqrt{k}} - e^{2\sqrt{k}}\sinh(2\sqrt{k})\right)}{3\cosh(\sqrt{k})^3}, \tag{31}$$

where

$$G = \frac{(e^{\sqrt{k}} - 2e^{2\sqrt{k}})}{6\cosh(\sqrt{k})} - \frac{\left(2e^{2\sqrt{k}} - e^{3\sqrt{k}}\right)}{3\cosh(\sqrt{k})^2} + \frac{\left(2e^{3\sqrt{k}} - e^{2\sqrt{k}}\sinh\left(e^{2\sqrt{k}}\right)\right)}{6\cosh(\sqrt{k})^3}. \tag{32}$$

3.3 Validation of analytical results and discussion

In this section, we study the accuracy of the results obtained by the proposed AGM, analyze the results. Figure 1 shows the mediator concentrations obtained by AGM in Eqs. (23) and (25) are in solid agreement with the numerical results obtained by Maple RK45 procedure (Fehlberg fourth-fifth order Runge-Kutta method with degree four interpolant) for various values of the parameters α and k. To further confirm the accuracy of the concentration expressions obtained by the proposed AGM, we compared the results with those obtained by the well-founded homotopy perturbation method (HPM). Tables 1 and 2 show that the analytical expressions of the mediator concentrations obtained by the AGM yielded significantly less deviations from the numerical results than the HPM method.

From Figure 1, it is inferred that mediator concentration decreases as the reaction-diffusion parameter (k) and the distance x increase while saturation parameter $\alpha \leq 1$. When $\alpha k \leq 0.1$, the mediator concentration becomes a straight line with a negative slope, that is $u = -x + 1$. Notice that Eq. (11) can then be used to obtain $[M_{ox}]/[M_{red}]^* \approx 1 - X/\delta$, which can be used to compute the thickness of the diffusion layer δ. Figure 2 confirms the conclusions derived from Figure 1.

Figures 3 and 4 show several curves of the dimensionless current for various values of α and k. It is observed that the current and the reaction-diffusion parameter are proportionally related, whereas the current and the simulation parameter are inversely related.
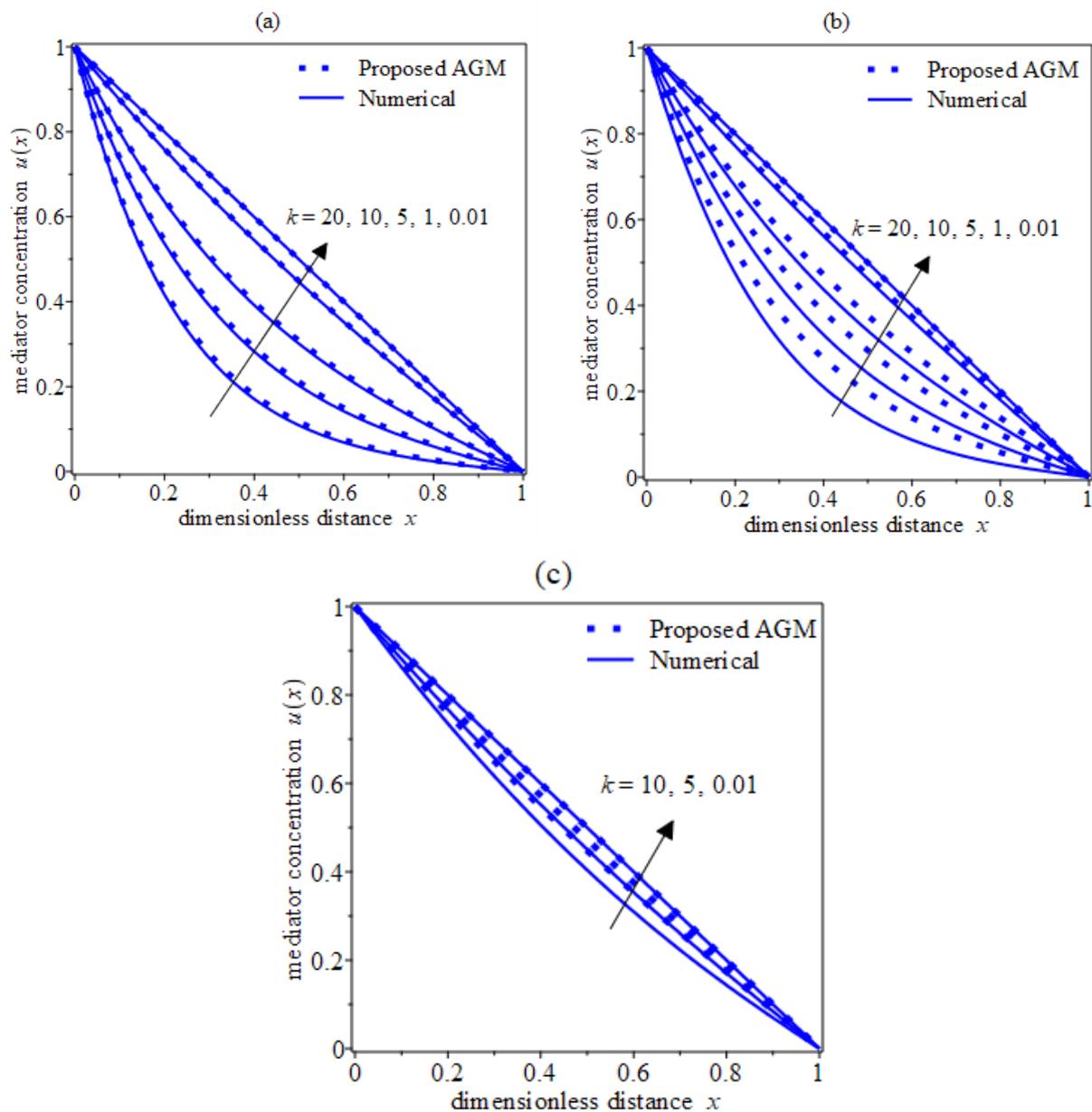
Figure 1. Mediator concentration curves $u(x)$ computed using Eq. (23) for various values k given that (a) $\alpha = 0.1$ (b) $\alpha = 1$ (c) $\alpha = 10$.
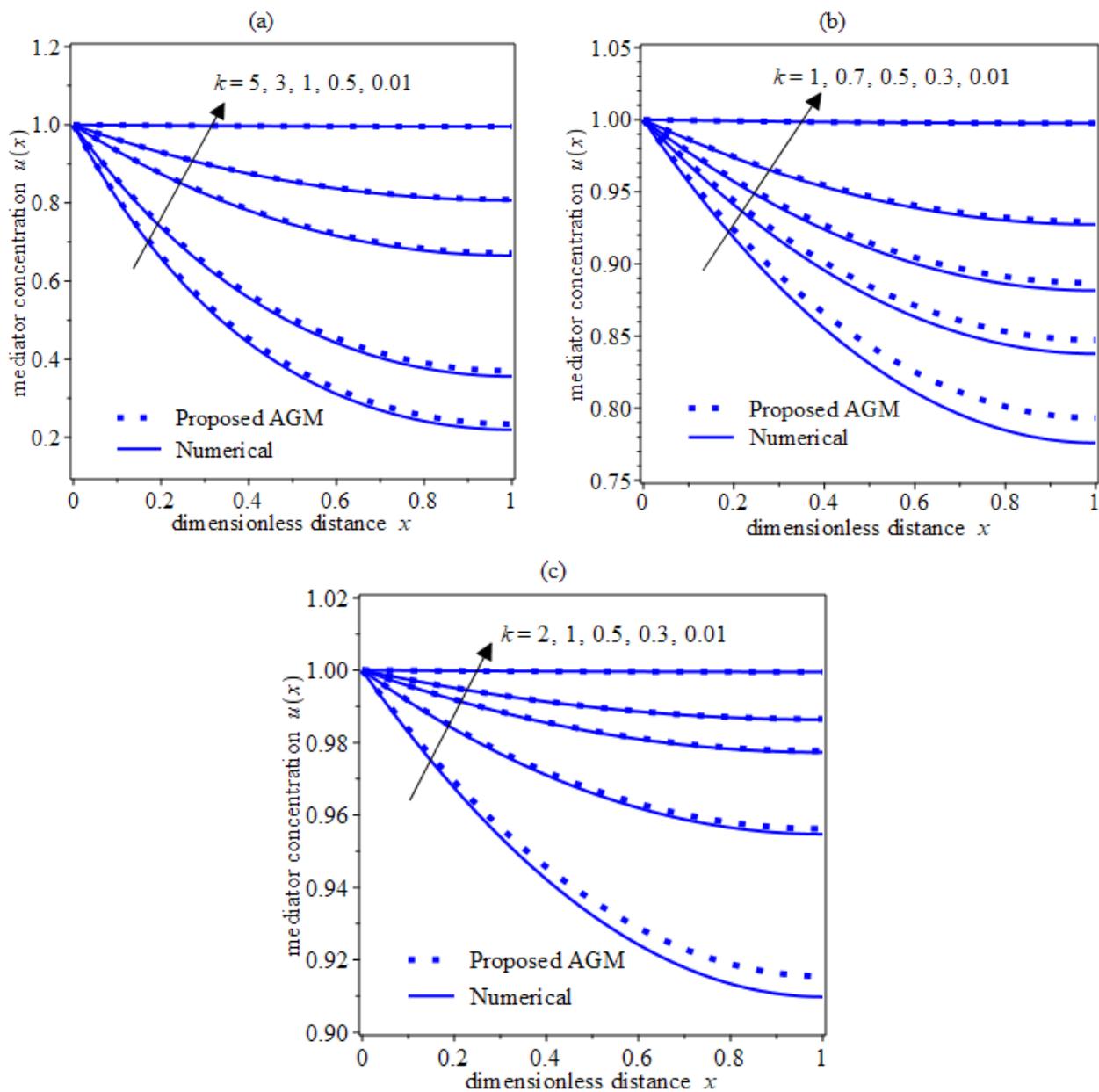
Figure 2. Mediator concentration curves $u(x)$ computed using Eq. (6.25) for various values k given that (a) α=0.1 (b) α =1 (c) α =10.

Figure 3. Dimensionless current ψ for various values of α and k using Eq. (24).

Figure 4. Dimensionless current ψ for various values of α and k using Eq. (26).

Table 1. Comparison beteween numerical and analytical results for dimensionless concentration of mediator $u(x)$ for various values of parameter k when $\alpha = 10$.

x	Num.	Approximate concentration		Error (%)		Num.	Approximate concentration		Error (%)		Num.	Approximate concentration		Error (%)	
		$k = 0.1$					$k = 0.5$					$k = 1$			
		Current AGM Eq. (23)	HPM [7] Eq. (27)	Current AGM Eq. (23)	HPM [7] Eq. (27)		Current AGM Eq. (23)	HPM [7] Eq. (27)	Current AGM Eq. (23)	HPM [7] Eq. (27)		Current AGM Eq. (23)	HPM [7] Eq. (27)	Current AGM Eq. (23)	HPM [7] Eq. (27)

x	Num.	Current AGM	HPM	Current AGM err	HPM err	Num.	Current AGM	HPM	Current AGM err	HPM err	Num.	Current AGM	HPM	Current AGM err	HPM err
0	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
0.2	0.7973	0.7975	0.8252	0.0251	3.4993	0.7946	0.7958	0.9213	0.1510	15.945	0.7913	0.7936	1.0180	0.2907	28.641
0.4	0.5954	0.5954	0.6277	0.0000	5.4249	0.5911	0.5931	0.7368	0.3383	24.649	0.5862	0.5902	0.8397	0.6824	43.245
0.6	0.3930	0.3934	0.4183	0.1018	6.4376	0.3892	0.3914	0.5003	0.5653	28.546	0.3845	0.3889	0.5739	1.1443	49.259
0.8	0.1913	0.1916	0.2042	0.1568	6.7433	0.1890	0.1905	0.2450	0.7936	29.630	0.1861	0.1891	0.2805	1.6120	50.725
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0147	0.0000	1.0000
	Average error (%)			0.0473	3.6842	Average error (%)			0.3080	8.2453	Average error (%)			0.6716	28.813

Table 2. Comparison beteween numerical and analytical results for dimensionless concentration of mediator $u(x)$ for various values of parameter k when $\alpha = 0.01$.

x	k = 0.1					k = 0.5					k = 1				
	Num.	Approximate concentration		Error (%)		Num.	Approximate concentration		Error (%)		Num.	Approximate concentration		Error (%)	
		Current AGM Eq. (25)	HPM [7] Eq. (30)	Current AGM Eq. (25)	HPM [7] Eq. (30)		Current AGM Eq. (25)	HPM [7] Eq. (30)	Current AGM Eq. (25)	HPM [7] Eq. (30)		Current AGM Eq. (25)	HPM [7] Eq. (30)	Current AGM Eq. (25)	HPM [7] Eq. (30)
0	1.0000	1.0000	0.9715	0.0000	2.8500	1.0000	1.0000	0.9625	0.0000	3.7500	1.0000	1.0000	0.9567	0.0000	4.3300
0.2	0.9826	0.9826	0.9568	0.0000	2.6257	0.9512	0.9513	0.9195	0.0105	3.3326	0.9235	0.9236	0.8885	0.0108	3.7899
0.4	0.9692	0.9693	0.9457	0.0103	2.4247	0.9140	0.9141	0.8865	0.0109	3.0087	0.8657	0.8659	0.8363	0.0923	3.3299
0.6	0.9598	0.9598	0.9382	0.0000	2.2505	0.8879	0.8880	0.8635	0.0113	2.7481	0.8255	0.8257	0.7996	0.0242	3.1375
0.8	0.9542	0.9542	0.9342	0.0000	2.0960	0.8725	0.8726	0.8502	0.0115	2.5559	0.8020	0.8022	0.7780	0.0249	2.9925
1	0.9524	0.9525	0.9337	0.0105	1.9635	0.8678	0.8679	0.8467	0.0115	2.4314	0.7947	0.7950	0.7714	0.0377	2.9319
	Average error %			0.0035	2.3684	Average error %			0.0093	2.9711	Average error %			0.0316	3.4185

4. CONCLUSIONS

We have derived an approximate analytical expression concentration profiles and catalytic current of mediated bioelectrocatalysis for steady-state conditions over a wide range of parameters. A nonlinear time-independent differential equation has been solved using the Akbari-Ganji method. The effects of the saturation and reaction diffusion parameters on concentration and current are discussed. The numerical results from the Matlab software are used to validate these analytical results. A satisfactory agreement is noted. In conclusion, the analytical expressions of the mediator concentration

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and catalytic current derived in this paper are reliable. Therefore, they can be applied to other mediated bioelectrocatalytic systems to compute the mediator's catalytic constant and the Michaelis constant.

NOMENCLATURE

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

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