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Mathematical Analysis for Electron Transfer Mediator/ Heterogeneous Catalyst Composites in Polymer Modified Electrodes

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Mathematical models of transport and kinetics of electrons and reactants in the layer of a modified electrode are discussed theoretically. The model comprises a system of reaction-diffusion equations that are nonlinearly connected. In this paper, the nonlinear differential equations that describe diffusion with a reaction term are solved using a highly accurate and conveniently accessible analytical method (AGM). A simple and closed approximate polynomial expression of substrate and mediator concentration and current has been developed for all parameter values. Furthermore, the numerical simulation of the topic is carried out in this paper utilizing a Matlab function. Simulated data and previously published limiting cases are used to validate the new analytical results. A reasonable agreement is observed.

Keywords: Redox polymer modified electrodes; Akbari Ganji method; Reaction diffusion equation; Mathematical modeling; Electron transfer mediator.

1. INTRODUCTION

The electrocatalytic process is a well-known phenomenon that has been widely used in the construction of biofuel cells, biosensors, and electrosynthesis systems. For many years, redox electrocatalysis inside thin surface films produced on electrode surfaces (Chemically Modified Electrodes) has piqued global attention and action. These electrodes have an organic or inorganic thin layer that is conductive and contains active sites that can catalyse solution-phase film reactions at the solution/film interface or within the layer. Microelectrodes are effective tools for deciphering the mechanism, behaviour, and kinetics of rapid reactions in electrochemical reactions. A modified electrode differs from a standard electrode. It has a thin film of some coated material on the metal surface prohibiting direct contact with the bulk electrolyte. Through that thin coating, electrochemical reactions of species in solution take to happen.The electron transfer is mediated through the thin layer's redox groups rather than a direct electron transfer from the metal's Fermi level to the ion in the solution. Many distinct modified electrodes have been produced during the previous two decades, with some systems receiving more attention than others.

Polymer-modified electrodes have received a lot of attention. For chemical sensing applications, polymer-modified electrodes are particularly appealing [1–4]. The idea behind a polymer sensor that operates under amperometric conditions is simple. Significant progress has been made in recent years in understanding the dynamics of coupled ion, solvent, and electronic transport in conducting electroactive organic thin-film materials for the use of voltammetric complex impedance, probe beam deflection, spectroscopic, and gravimetric measurements [5–8].

The transport and dynamics of reactions in chemically modified electrodes were previously studied using the approximate analytical solution [9-13]. Theoretical investigation of facilitated electron transport at electroactive polymer films placed on macro-sized electrode surfaces was provided by Albery and Hillman [14]. Theoretical investigation of the steady-state amperometric response for conducting polymer-modified ultra-microelectrodes was proposed by Senthamarai et al. [15]. Puida et al. [16] have developed a mathematical model for transport and electrocatalytic kinetics in surface-immobilized conducting polymer modified electrodes. Lyons [17] investigated the transport and kinetics of polymer-modified electrodes with a uniform distribution of spherical microparticle catalysts. More recently, Lyons dispersed an electron transfer mediator and spherical catalytic microparticles homogeneously within a polymeric matrix only for limiting cases [18]. Also, Eswari and Rajendran [19] have derived he analytical solution for electron transfer/ mediator catalyst composites in microelectrodes for small values of parameters using VIM.

In this study, we propose the Akbari- Ganji method for solving differential equations that occur in the setting of electron and reactant transport and kinetics in the layer of a modified electrode. To the best of our knowledge, no general analytical solution for the substrate and mediator concentration has been published yet. The primary goal of this paper is to use AGM to generate approximate analytical formulas for the concentration of species and current. Earlier limiting solutions and numerical simulations will be compared to the precision of the generated results.

2. MATHEMATICAL ANALYSIS OF THE PROBLEM

Within a polymeric matrix, the electron transfer mediator and spherical catalytic microparticles are uniformly dispersed. A relatively mobile redox-active component or a covalently bound polymeric backbone could be used as the mediator (a redox polymer). An electron transfer mediator, which acts as an electron relay between the support electrode and the catalytic site, is also an essential component of the system [18]. Using the rotating disc electrode arrangement, the effects of concentration polarisation in the solution are reasonably simple to incorporate into theoretical analysis and experimental study. Figure 1 shows a schematic representation of the multi-component system in this concept.

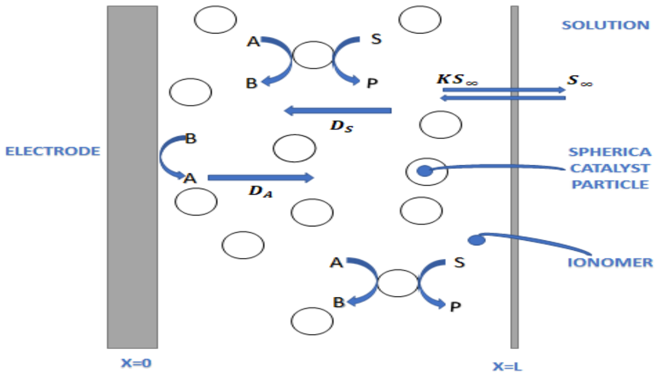

Figure 1. Modified electrodes with immobilised, tiny heterogeneous catalyst particles: particles immobilised in an ionomer or redox polymer matrix, as shown in the schematic diagram.

The transport and dynamics within the film can be represented using steady- state boundary value issues in dimensionless form as follows [18]:

$$D_A \frac{d^2a}{dx^2} - \frac{4\pi {r_0}^2 N D_A (k'_{A,0} k'_{S,0})^{1/2} (as)^{1/2}}{[D_A + r_0 (k'_{A,0} k'_{S,0})^{1/2} (s/a)^{1/2}]} = 0 \tag{1}$$

$$D_S \frac{d^2s}{dx^2} - \frac{4\pi {r_0}^2 N D_S (k'_{A,0} k'_{S,0})^{1/2} (as)^{1/2}}{[D_S + r_0 (k'_{A,0} k'_{S,0})^{1/2} (a/s)^{1/2}]} = 0 \tag{2}$$

where a is the concentration of the mediator and s is the concentration of the substrate. k'_S is electrochemical rate constant, r_0 is the radius of an electrode, D_S is the diffusion co-efficient for the substrate concentration , D_A is the diffusion co-efficient for the mediator, $N$is the number of particles per unit volume. The following boundary conditions must be applied to these coupled non-linear differential equations in order to solve them:

$$x = 0,\ \mathrm{d}s/dx = 0, a = a^\infty \text{ and } x = L, s = s^\infty,\ \mathrm{d}a/\mathrm{d}x = 0 \tag{3}$$

The following dimensionless parameters for substrate concentration u, mediator concentration v, and distance X are introduced:

$$u = \frac{s}{s^\infty}, v = \frac{a}{a^\infty}, X = \frac{x}{X_K}, X_k = \left(\frac{1}{4\pi r_0 N}\right)^{1/2}, \beta = (a^\infty D_A / s^\infty D_S)^{1/2}, \gamma = r_0 (k'_{A,0} k'_{S,0} / D_A D_S)^{1/2} \tag{4}$$

where X_k denotes a reaction layer thickness, β and γdimensionless parameters. Eqs. (1) and (2) are now reduced to the dimensionless form for the substrate, and mediator,

$$\frac{d^2u}{dx^2} - \frac{\gamma\beta (uv)^{1/2}}{1+\gamma\beta (v/u)^{1/2}} = 0 \tag{5}$$

$$\frac{d^2v}{dx^2} - \frac{\gamma (uv)^{1/2}}{\beta+\gamma (u/v)^{1/2}} = 0 \tag{6}$$

Accordingly for the mediator, we can suppose that the reaction layer thickness $X_K = L$ is in this case. The boundary conditions can now be written like this:

$$x = 0\ ,\ v = 1 \text{ and } \mathrm{d}u/dx = 0 \tag{7}$$

$$\text{and } x = 1, dv/dx = 0 \text{ and } u = 1. \tag{8}$$

If the kinetic lengths are significantly shorter than the layer thickness L, the reaction will take place in a reaction zone somewhere in the middle of the layer, with a transport-controlled supply of electrons from the electrode and a transport-controlled supply of substrate from the electrolyte. The flux j is given by

$$j= -D_A(da/dx)_{x=0} = D_S(ds/dx)_{x=L} \quad (9)$$

or in non-dimensional form:

$$j = -D_A a^{\infty}(4\pi r_0 N)^{1/2}(dv/dx)_{x=0} = D_S s^{\infty}(4\pi r_0 N)^{1/2}(du/dx)_{x=1} \quad (10)$$

The required expression of the normalized current is

$$I = \frac{j}{D_S s^{\infty}(4\pi r_0 N)^{1/2}} = (du/dx)_{x=1} \text{ or } I = \frac{j}{D_A a^{\infty}(4\pi r_0 N)^{1/2}} = -(dv/dx)_{x=0} \quad (11)$$

3. ANALYTICAL SOLUTION OF NONLINEAR EQUATIONS USING THE AKBARI- GANJI METHOD (AGM).

In physical chemistry, certain analytical methods have recently been employed to solve nonlinear issues [20-22]. Some nonlinear equations have recently been solved using the Adomian decomposition method [23], the homotopy analysis method [24,25], the homotopy perturbation method [26-28], the generalised [32], differential transformation method [29], the Taylor series method [30], hyperbolic functions [31], the residual method [33], a new analytical method [34], and the use of the Green's function coupled with a fixed point iteration scheme [35].

It's worth noting that this method has several substantial advantages, and that it can solve the vast majority of differential equations sets, whereas other methods have yet to provide a guarantee of satisfactory outcomes.The following are some of the method's advantages over other approaches: 1) It can solve differential equations directly; 2) It can solve equations without using any dimensionless procedures; and 3) It does not require converting variables into new ones. Furthermore, complicated nonlinear equations can be solved quickly and easily with this method without the use of complicated mathematical methods. Dharmalingam used the AGM approach to generate the general expression for current [36]. Lyons et al. [37] recently published a closed-form approximate analytical solution to the Michaelis – Menden kinetic rate equation when coupled to diffusion in thin confined films using the AGM approach. These earlier works represent the most recent advancement in the AGM technique.

3.1 Approximate analytical solution of the Eq. (8-11) using Akbari Ganji method

In this section, a novel approach to AGM was used to construct the approximate analytical expressions for the concentrations of substrate and mediator (see Appendix A for details), which are as follows:

$$u(x) = \frac{cosh(\delta x)}{cosh(\delta)} \quad (12)$$

$$v(x) = \frac{cosh(\alpha(1-x))}{cosh(\alpha)} \quad (13)$$

The unknown constant “δ *and* α” are obtained using the following equations.

$$\frac{\delta^2}{\cosh(\delta)} - \frac{\gamma\beta}{\gamma\beta\,\cosh(\delta)+\sqrt{\cosh(\delta)}} = 0 \;\; and \;\; \frac{\alpha^2}{\cosh(\alpha)} - \frac{\gamma}{\beta}\left(\frac{1}{\left(\frac{\gamma}{\beta}+\sqrt{\cosh(\delta)}\right)}\right) = 0 \tag{14}$$

Since $\cosh(\delta) \approx 1 \; and \; \cosh(\alpha) \approx 1$ for small $\delta \; and$, the above equation becomes

$$\delta = \sqrt{\frac{\gamma\beta}{1+\gamma\beta}} \quad \text{and} \quad \alpha = \sqrt{\frac{\gamma/\beta}{1+(\gamma/\beta)}} \tag{15}$$

The dimensionless current becomes

$$I = \frac{\delta\, sinh(\delta)}{cosh(\delta)} \text{ or } \quad I = \frac{\alpha\, sinh(\alpha)}{cosh(\alpha)} \tag{16}$$

4. THE VALIDATION OF THE RESULTS WITH PREVIOUS LIMITING CASE RESULTS

Tables 1-2 show that the Akbari Ganji approach is an effective tool for obtaining analytical expressions of substrate and mediator concentrations for electron and reactant transport and kinetics in the layer of a modified electrode. Also, when compared to earlier limiting case analytical results (Lyons et.al [18] and Eswari and Rajendran [19]) it can be concluding that our general analytical results are in very firstly obtained for all values of the reaction diffusion parameter $\gamma\beta, \gamma/\beta$. Our analytical expression of the dimensionless concentration of substrate u(χ) and mediator are compared with simulation results and previous results in Table 3 and 4 respectively. The maximum relative errors between numerical simulation with our results and earlier limiting cases work results are 0.0197% and 23.285% and 24.348% respectively.

5. VALIDATION OF THE ANALYTICAL RESULTS

The systems of differential equations represented by Eqs. (5)-(8) are numerically solved with the powerful Runge-Kutta method using the MATLAB function pdepe4 to investigate the accuracy of the analytical solution with a finite number of terms.

Appendix B has a complete Matlab function for numerical simulation. The results of the simulation are compared to our actual findings in Figures 2(a) and 2(b). Tables 1 and 2 summaries the suggested empirical representation of substrate and mediator concentrations with previous existing limiting case results.

The dimensionless concentrations versus normalized distance when the reaction diffusion parameter is too large (i.e.,) $\gamma\beta$ and $\gamma/\beta = 100$ is plotted in figure 3. In Tables 3 to 4, our results are also compared with numerical and previous limiting case analytical results. There is no significant difference in error percentage between the numerical and our analytical methods when the parameter $\gamma\beta << 1$ and $1/\gamma/\beta << 1$. But, the average error percentage between the numerical and other previous analytical methods is 23.285% and 24.348%. Therefore, our method has the simplest form when compared to all other previous methods. Up on comparison, in previous limiting case, the analytical solution of the mediator concentration is very vast error percentage with numerical solution.

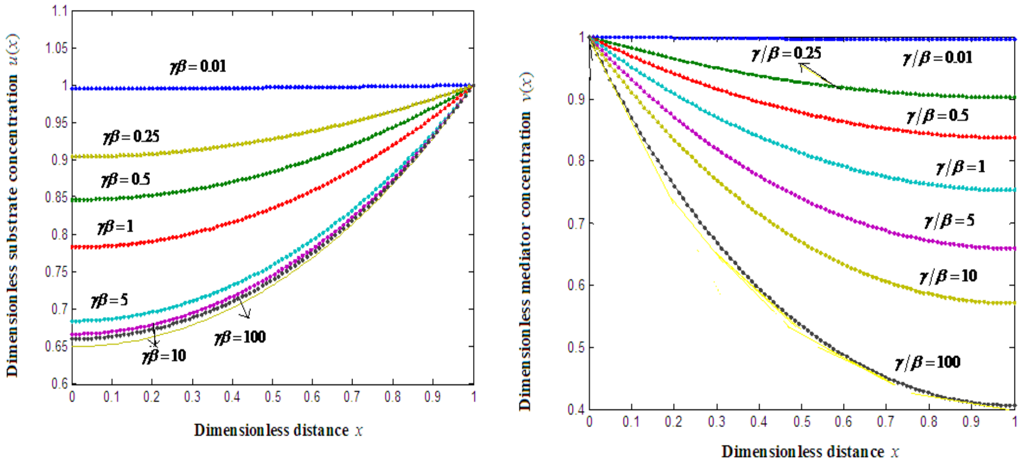

Figure 2. Comparison of concentration profile of (a) substrate (Eq. (12)) and (b) mediator (Eq. (13)) with simulation results for various values of parameter. Solid line represents analytical solution while dotted line is the numerical result.

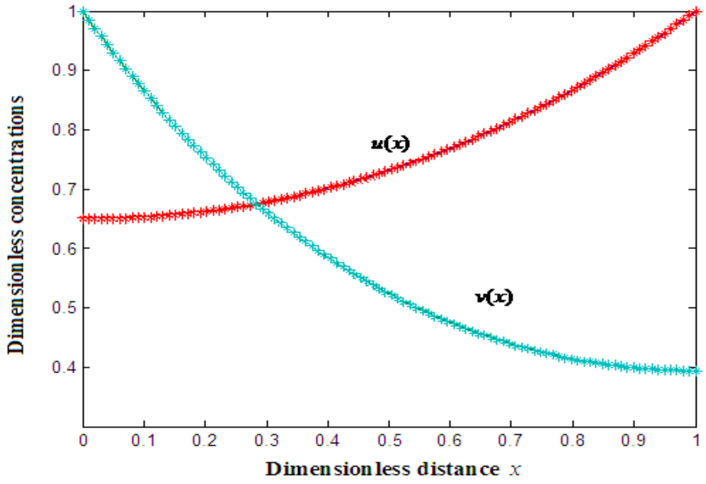

Figure 3. Dimensionless concentration of substrate and mediator $u(x), v(x)$ versus normalized distance x for large values of parameters $\gamma\beta = 100$ *and* γ/β. The dotted line represents the numerical results and solid line represents the analytical result.

6. RESULT AND DISCUSSION

The analytical expression of dimensionless concentration of substrate and mediator for transport and kinetics of electrons and reactant in the layer of a modified electrode in Eqs.12 and 13 is the general, new, simple and closed-form. Previously Lyons and Bartlett [18] obtained the approximate analytical expression of substrate and mediator concentrations and current for various limiting cases such as mediator-limited kinetics, substrate-limited kinetics. These expressions make use of an approximation which is valid only when reaction diffusion parameters $\gamma\beta$ and γ/β are not too large. In addition, the analytical expression fails to meet the boundary requirement. Later, using the variational iteration method, Eswari and Rajendran [19] derived an approximate solution for the mediator and substrate concentrations and current profiles in micro heterogeneous systems only when very small values of the parameters were used. Furthermore, compared to the variational iteration method, the proposed Akbari Ganji method is much easier and more accessible to all scholars. For all values of the parameters, a very simple and closed form of an approximate analytical equation is currently constructed for steady-state concentrations of substrate, mediator, and current in catalyst composites in micro electrodes.

In this study, Eqs. (12-14) are used to construct analytical equations for substrate and mediator concentrations versus distance for various reaction diffusion parameters (15). For all values of $\gamma\beta$, Figure 2(a) depicts the substrate concentration as a function of distance. It is noticed from Figure 2(a) that substrate concentration drastically decreases at the rising the distance while reaction diffusion parameter $\gamma\beta$ increases.The dimensionless concentration of substrate u(x) is uniform (i.e. $U\approx 1$) for the reaction diffusion parameter $\gamma\beta \geq 0.01$.

The concentrations curves of mediator versus distance from the micro electrode surface for all values of reaction diffusion parameter γ/β are plotted in Fig. 2(b). From Fig. 2(b), it is evident that the concentration of mediator increases with the decrease of the reaction diffusion coefficient. Figures S1 and S2 characterize the normalized three-dimensional steady-state substrate concentration in catalyst composites in microelectrodes for each dimensionless distance over the diffusion parameters. It is noted from Figure S3, the substrate concentration decreases with the increase of $\gamma\beta$. It can be found from Fig. S3 that when the dimensionless distance is very small and the reaction diffusion parameter $\gamma\beta$ exceeds 50, the least value of concentration is obtained. The mediator concentration over distance and γ/β is presented in Figure S4, where it is concluded that up to the small value of reaction diffusion, the mediator raised. The concentrations of substrate and mediator within the polymer film reaches the steady state when the $\gamma\beta$ and γ/β is less than or equal to one.

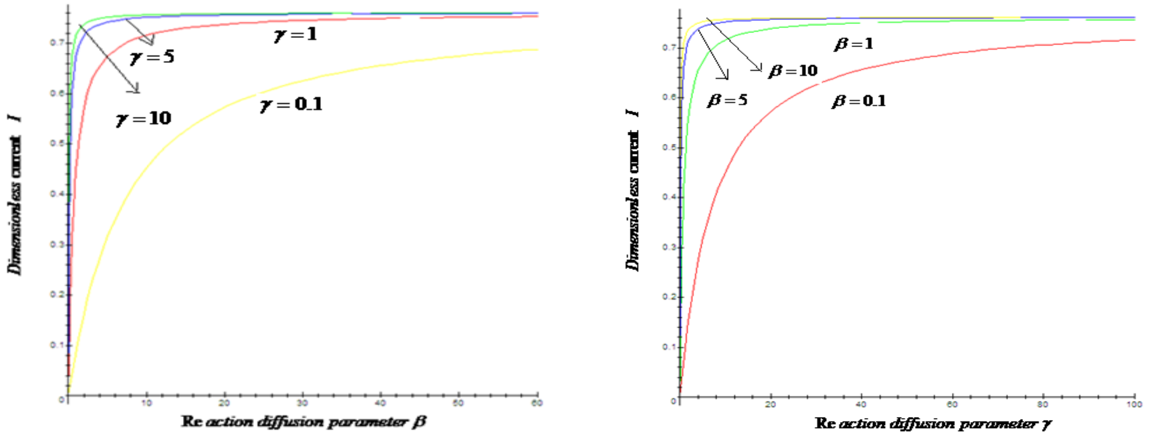

Figure 4. (*a*): Plot of dimensionless normalized current I versus dimensionless reaction diffusion parameter β for various values of the dimensionless reaction diffusion parameter γ for substrate layer. (*b*): Plot of dimensionless normalized current I versus dimensionless reaction diffusion parameter γ for various values of the dimensionless reaction diffusion parameter β substrate layer.

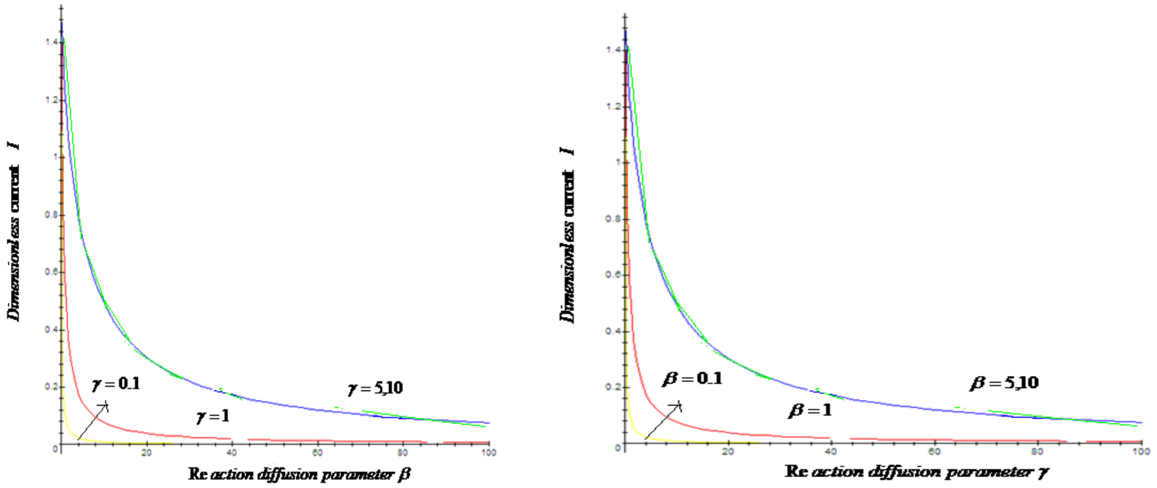

Figure 5. (*a*): Plot of dimensionless normalized current I versus dimensionless reaction diffusion parameter β for various values of the dimensionless reaction diffusion parameter γ for mediator layer. (*b*): Plot of dimensionless normalized current I versus dimensionless reaction diffusion parameter γ for various values of the dimensionless reaction diffusion parameter β mediator layer.

The dimensionless normalized current for various reaction-diffusion parameters using equation (16) is plotted in Figures 4 and 5. The current becomes stable for all large values of reaction-diffusion parameters, as seen in Figures 4 and 5. It's also easy to confirm that current is proportional to the thickness of the polymer film. An increase in the parameters leads to an increase in current.

The current is quantified in terms of fundamental reaction/diffusion parameters $\gamma\beta$ *and* γ/β. Table-1 represents the current for various limiting values of parameters. These findings are similar to Lyons et al. [18] and Eswari et al. [19].

Table 2. Various approximate analytical expression of current for the limiting cases

S.no	**Current**	**This work current for all values of parameters**	**Limiting cases**	**Current**
1.	Substrate current	$I=\frac{\delta\, sinh(\delta)}{cosh(\delta)}$	$\gamma\beta \ll 1$, $\delta=\sqrt{\gamma\beta}$	$I=\sqrt{\gamma\beta}\, Tanh(\sqrt{\gamma\beta})$
			$\gamma\beta \ll 1$, $\delta = 1$	$I = Tanh(1)$
2.	Mediator current	$I=\frac{\alpha\, sinh(\alpha)}{cosh(\alpha)}$	$\frac{\gamma}{\beta} \ll 1$ $\propto=\sqrt{\frac{\gamma}{\beta}}$	$I=\sqrt{\frac{\gamma}{\beta}}\, Tanh(\sqrt{\frac{\gamma}{\beta}}$
			$\frac{\gamma}{\beta} \gg 1$ $\propto= 1$	$I = Tanh(1)$

7. CONCLUSION

The Akbari Ganji method is being used because of the difficulties in solving the nonlinear differential equations in microelectrode. In this paper, a simple and effective method for solving the system of nonlinear reaction-diffusion equations is presented. The substrate and mediator concentration within the polymer film are analytically expressed after the transport and kinetics are quantified in terms of fundamental reaction/diffusion parameters $\gamma\beta$ and γ/β. The steady-state current response is given in a simple and closed-form of new analytical expression. The derived results are more numerically consistent than earlier limited case results. It's useful and straightforward, and finding an approximate analytical solution just takes a few iterations. The analytical results can be used to forecast and improve the kinetic characteristics of changed electrodes.

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CONFLICT OF INTEREST
There is no conflict of interest.

SUPPLEMENTARY MATERIAL:

APPENDIX A:

The solution of eqs. (5)-(6) is using Akbari Ganji method

The approximate analytical solutions for the Eqs.(5) and (6) are considered as follows:

$$u(x) = A_1 \cosh(\delta x) + B_1 \sinh(\delta x) \tag{A.1}$$

$$v(x) = A_2 \cosh(\alpha x) + B_2 \sinh(\alpha x) \tag{A.2}$$

Using the boundary conditions (Eqs.7-8), the constants becomes$A_1 = 1/\cosh(\delta), B_1 = 0$ and $A_2 = 1, B_2 = -\tanh(\alpha)$.Then the Eqs. (A.1) and (A.2) becomes,

$$u(x) = \frac{\cosh(\delta x)}{\cosh(\delta)} \tag{A.3}$$

$$v(x) = \frac{\cosh(\alpha(1-x))}{\cosh(\alpha)} \tag{A.4}$$

Substituting Eqs. (A.3) and (A.4) in Eqs. (5) and (6), we get

$$\frac{\delta^2 \cosh(\delta x)}{\cosh(\delta)} - \frac{\gamma\beta\left[\frac{\cosh(\delta x)\cosh(\alpha(1-x))}{\cosh(\delta)\quad \cosh(\alpha)}\right]^{1/2}}{1+\gamma\beta\left[\frac{\cosh(\alpha(1-x))\ \cosh(\delta)}{\cosh(\alpha)\quad \cosh(\delta x)}\right]^{1/2}} = 0 \tag{A.5}$$

$$\frac{\alpha^2 \cosh(\alpha(1-x))}{\cosh(\alpha)} - \frac{\gamma\left[\frac{\cosh(\delta x)\cosh(\alpha(1-x))}{\cosh(\delta)\quad \cosh(\alpha)}\right]^{1/2}}{\beta+\gamma\left[\frac{\cosh(\delta x)\quad \cosh(\alpha)}{\cosh(\delta)\ \cosh(\alpha(1-x))}\right]^{1/2}} = 0 \tag{A.6}$$

Solving Eqs. (A.5) and (A.6), we get $\delta$and αvalues.

$$\frac{\delta^2}{\cosh(\delta)} - \frac{\gamma\beta}{\gamma\beta\ \cosh(\delta)+\sqrt{\cosh(\delta)}} = 0 \tag{A.7}$$

$$\frac{\alpha^2}{\cosh(\alpha)} - \frac{\gamma}{\beta}\left(\frac{1}{\left(\frac{\gamma}{\beta}+\sqrt{\cosh(\delta)}\right)}\right) = 0 \tag{A.8}$$

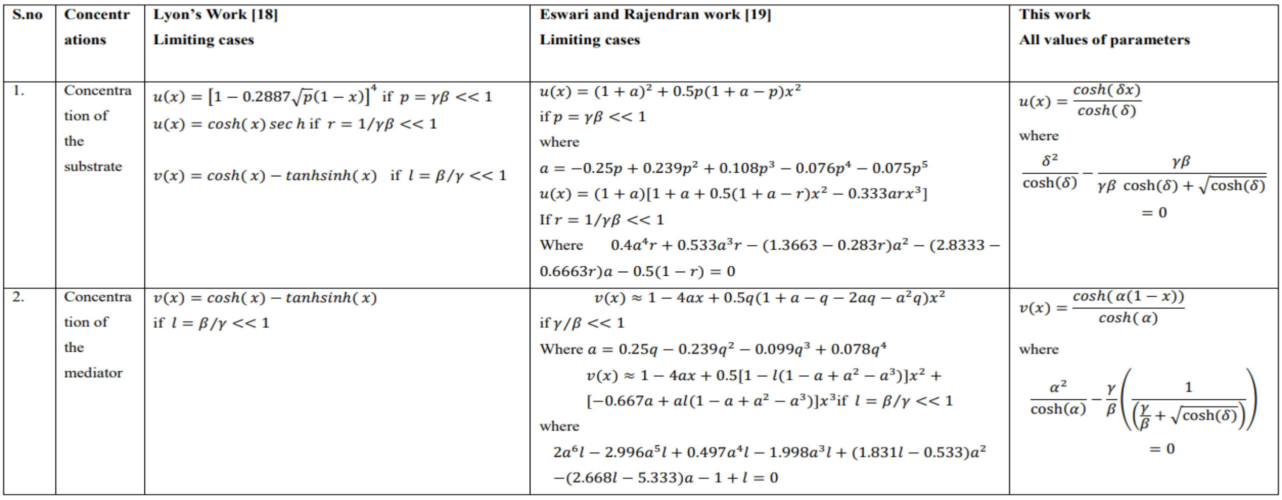
APPENDIX B:

Matlab Program for the Numerical Solution of Nonlinear Differential Eqs. (5)-(6).

```
function pdex4
m = 0;
x = linspace(0,1);
t=linspace(0,1);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
u2 = sol(:,:,2);
figure
plot(x,u1(end,:))
%————————————————————————————————
figure
plot(x,u2(end,:))
% ——————————————————————————————
% ---------------------------------------------------------------
function [c,f,s] = pdex4pde(x,t,u,DuDx)
c = [1; 1];
f = [1; 1] .* DuDx;
y = u(1) * u(2);
```

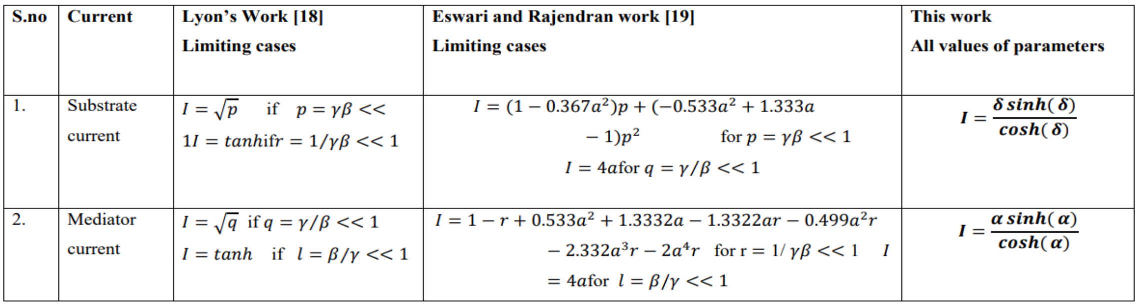
```
gamma=2;
beta=2;                                                  % parameters
F =(gamma*beta*sqrt(y))/(1+gamma*beta*(sqrt(u(2)/u(1))));
F1=(gamma*sqrt(y))/( beta+gamma*(sqrt(u(1)/u(2))));      % non linear terms
s=[-F;-F1];
% -----------------------------------------------------------
function u0 = pdex4ic(x);                                %create a initial conditions
u0 = [1; 0.001];
% -----------------------------------------------------------
function [pl,ql,pr,qr] = pdex4bc(xl,ul,xr,ur,t)          %create a boundary conditions
pl = [0; ul(2)-1];
ql = [1; 0];
pr = [ur(1)-1; 0];
qr = [0; 1];
```

Table S1. Various approximate analytical expression concentrations of substrate and a mediator.



S.no	Concentrations	Lyon's Work [18] Limiting cases	Eswari and Rajendran work [19] Limiting cases	This work All values of parameters
1.	Concentration of the substrate	$u(x) = \left[1 - 0.2887\sqrt{p}(1-x)\right]^4$ if $p = \gamma\beta << 1$ $u(x) = cosh(x)\, sec\, h$ if $r = 1/\gamma\beta << 1$ $v(x) = cosh(x) - tanhsinh(x)$ if $l = \beta/\gamma << 1$	$u(x) = (1+a)^2 + 0.5p(1+a-p)x^2$ if $p = \gamma\beta << 1$ where $a = -0.25p + 0.239p^2 + 0.108p^3 - 0.076p^4 - 0.075p^5$ $u(x) = (1+a)[1 + a + 0.5(1+a-r)x^2 - 0.333arx^3]$ If $r = 1/\gamma\beta << 1$ Where $0.4a^4r + 0.533a^3r - (1.3663 - 0.283r)a^2 - (2.8333 - 0.6663r)a - 0.5(1-r) = 0$	$u(x) = \frac{cosh(\delta x)}{cosh(\delta)}$ where $\frac{\delta^2}{\cosh(\delta)} - \frac{\gamma\beta}{\gamma\beta\ \cosh(\delta) + \sqrt{\cosh(\delta)}} = 0$
2.	Concentration of the mediator	$v(x) = cosh(x) - tanhsinh(x)$ if $l = \beta/\gamma << 1$	$v(x) \approx 1 - 4ax + 0.5q(1 + a - q - 2aq - a^2q)x^2$ if $\gamma/\beta << 1$ Where $a = 0.25q - 0.239q^2 - 0.099q^3 + 0.078q^4$ $v(x) \approx 1 - 4ax + 0.5[1 - l(1 - a + a^2 - a^3)]x^2 + [-0.667a + al(1 - a + a^2 - a^3)]x^3$if $l = \beta/\gamma << 1$ where $2a^6l - 2.996a^5l + 0.497a^4l - 1.998a^3l + (1.831l - 0.533)a^2 -(2.668l - 5.333)a - 1 + l = 0$	$v(x) = \frac{cosh(\alpha(1-x))}{cosh(\alpha)}$ where $\frac{\alpha^2}{\cosh(\alpha)} - \frac{\gamma}{\beta}\left(\frac{1}{\left(\frac{\gamma}{\beta} + \sqrt{\cosh(\delta)}\right)}\right) = 0$

Table S2: Various approximate analytical expression of current



S.no	Current	Lyon's Work [18] Limiting cases	Eswari and Rajendran work [19] Limiting cases	This work All values of parameters
1.	Substrate current	$I = \sqrt{p}$ if $p = \gamma\beta <<$ $1 I = tanh if r = 1/\gamma\beta << 1$	$I = (1 - 0.367a^2)p + (-0.533a^2 + 1.333a - 1)p^2$ for $p = \gamma\beta << 1$ $I = 4a$for $q = \gamma/\beta << 1$	$\boldsymbol{I = \frac{\delta\, sinh(\delta)}{cosh(\delta)}}$
2.	Mediator current	$I = \sqrt{q}$ if $q = \gamma/\beta << 1$ $I = tanh$ if $l = \beta/\gamma << 1$	$I = 1 - r + 0.533a^2 + 1.3332a - 1.3322ar - 0.499a^2r - 2.332a^3r - 2a^4r$ for r = $1/\gamma\beta << 1$ $I = 4a$for $l = \beta/\gamma << 1$	$\boldsymbol{I = \frac{\alpha\, sinh(\alpha)}{cosh(\alpha)}}$

Table S3: Comparison of analytical result with numerical result and various analytical results for substrate concentration $u(x)$for various values of parameter $\gamma\beta$**.**

	$\gamma\beta = 0.001$							$\gamma\beta = 0.01$							$\gamma\beta = 0.25$						
x	Numer. Simulat.	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]	Numer. Simulat.	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]	Numer. Simulat.	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]
0	0.9995	0.9995	0.9995	0.9640	0.0000	0.0000	3.6826	0.9950	0.9951	0.9949	0.8894	0.0100	0.0101	11.8732	0.9043	0.9042	0.9096	0.536	0.0111	0.5827	68.7127
0.2	0.9995	0.9995	0.9995	0.9712	0.0000	0.0000	2.9139	0.9952	0.9953	0.9955	0.911	0.0100	0.0301	9.2426	0.9082	0.9081	0.9132	0.6129	0.0110	0.5475	48.1808
0.4	0.9996	0.9996	0.9996	0.9784	0.0000	0.0000	2.1668	0.9958	0.9959	0.9960	0.9329	0.0100	0.0201	6.7424	0.9197	0.9196	0.924	0.6978	0.0109	0.4654	31.7999
0.6	0.9997	0.9997	0.9997	0.9857	0.0000	0.0000	1.4203	0.9968	0.9969	0.9962	0.9553	0.0100	0.0602	4.3442	0.9391	0.939	0.942	0.7912	0.0106	0.3079	18.6931
0.8	0.9998	0.9998	0.9998	0.9930	0.0000	0.0000	0.6848	0.9984	0.9983	0.9990	0.978	0.0100	0.0601	2.0859	0.9665	0.9664	0.9671	0.8937	0.0103	0.0620	8.1459
1.0	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000	0.9976	1.0000	0.0000	0.2406	0.0000
Average Error					**0.0000**	**0.0000**	1.8114	**Average Error**				**0.0083**	**0.0301**	**5.7147**	**Average Error**				**0.0090**	**0.3677**	**29.2554**

Table S4: Comparison of analytical result with numerical result and various analytical results for mediator concentration $v(x)$ for various values of parameter γ/β

	$\gamma/\beta = 5$							$\gamma/\beta = 10$							$\gamma/\beta = 100$						
x	Numer. Simulat	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]	Numer. Simulat.	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]	Numer. Simulat.	This work	Eswari et al. [19]	Lyon's et al. [18]	Error for This work (%)	Error for Eswari et al. [19]	Error for Lyon's et al. [18]
0	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000
0.2	0.8225	0.8224	0.8848	0.8656	0.0122	7.0411	4.9792	0.7942	0.7941	0.8723	0.8656	0.0126	8.9533	8.2486	0.7526	0.7525	0.8626	0.8656	0.0133	12.7521	13.0545
0.4	0.6947	0.6946	0.798	0.7666	0.0144	12.9449	9.3791	0.6484	0.6485	0.7767	0.7666	0.0154	16.5186	15.4187	0.5829	0.5827	0.7654	0.7666	0.0343	23.8437	23.9630
0.6	0.6091	0.609	0.7361	0.699	0.0164	17.2531	12.8612	0.5525	0.5523	0.7081	0.699	0.0362	21.9743	20.9585	0.4732	0.4731	0.6934	0.699	0.0211	31.7566	32.3033
0.8	0.5603	0.5602	0.6953	0.66	0.0179	19.4161	15.1061	0.499	0.498	0.6613	0.660	0.2008	24.5426	24.3939	0.4123	0.4122	0.6432	0.66	0.0243	35.8986	37.5303
1.0	0.5454	0.5453	0.6729	0.6481	0.0183	18.9478	15.8463	0.4817	0.4815	0.6323	0.6481	0.0415	23.8178	25.6751	0.3938	0.3939	0.6102	0.6481	0.0254	35.4638	39.2378
Average Error					**0.0132**	**12.6005**	**9.6953**	**Average Error**				**0.0511**	**15.9678**	**15.7825**	**Average Error**				**0.0197**	**23.2858**	**24.3482**

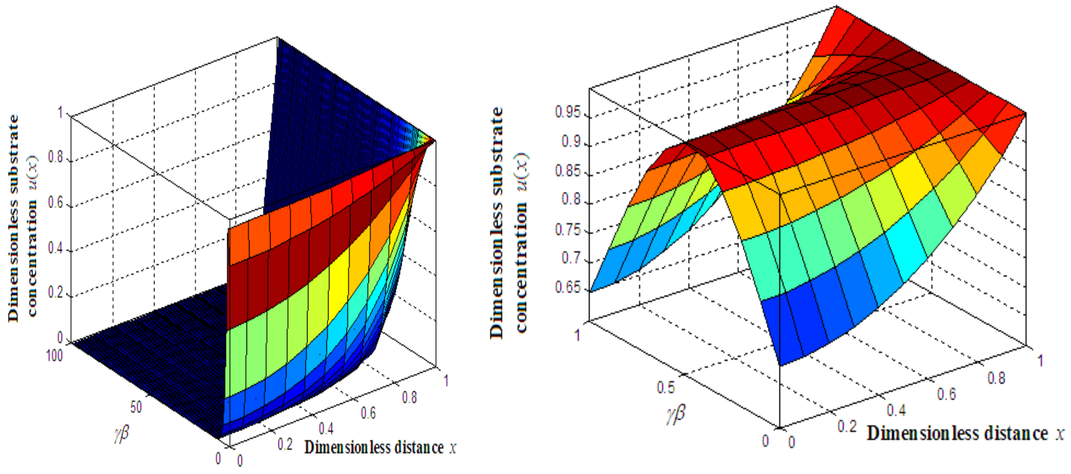


Figure S1: Three-dim substrate concentration versus reaction diffusion parameter and dimensionless distance. Figures (a) and (b) are generated using Eq. (12) for the empirical parameter values given in Fig. 2(a) respectively

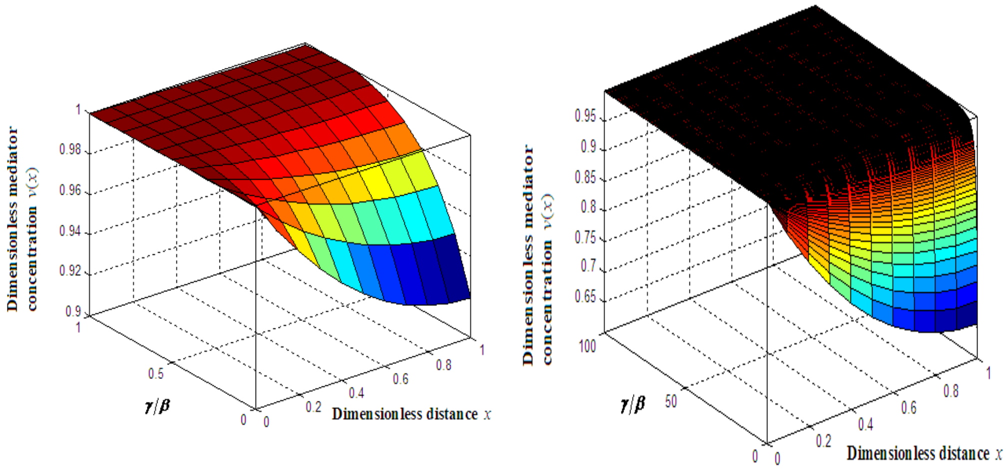


Figure S2: Three-dim mediator concentration versus reaction diffusion parameter and dimensionless distance. Figures (a) and (b) are generated using Eq. (13) for the empirical parameter values given in Fig. 2(b) respectively.

References

1. S.A. Wring, J.P. Hart, *Analyst.*, 117 (1992) 1215.
2. A.A. Karyakin, O.A. Bobrova, E.E. Karyakina., *J. Electroanal. Chem.*, 399 (1995) 179.
3. P.N. Bartlett, P.R. Birkin, E.K.N. Wallace, *J. Chem. Soc. Faraday Trans.*, 93 (1997) 1951.
4. M.E.G. Lyons, *Analyst.*, 199 (1994) 805.
5. D.J. Fermin, J. Mostany, B.R. Scharifker, *Curr. Top. Electrochem.*, 2 (1993) 131.
6. C. Barbero, M.C. Miras, O. Haas, R. Kotz, *J. Electrochem. Soc.*, 138 (1991) 669.
7. S.J. Higgins, P.A. Christensen, A. Hamnett, in: M.E.G. Lyons (Ed.), Electroactive Polymer Electrochemistry: Part II. Methods and Applications, Plenum Press, New York, (1996) 133.
8. W.J. Albery, Z. Chen, B.R. Horrocks, A.R. Mount, P.J. Wilson, D. Bloor, A.T.Monkman, C.M. Elliott, *Faraday Discuss. Chem. Soc.*, 88 (1989) 247.
9. D.J. Harrison and M.S. Wrighton, *J. Phys. Chem.*, 88 (1984) 3932.
10. C.P. Andrieux, J.M. Dumas-Bouchiat and J.M.Saveant, *J. Electroanal. Chem.*, 131 (1982) 1.
11. W. J. Albery and A. R. HiIlman., *J. EIectroanal. Chem.,* 170(1985) 27.
12. A.R.HiIlman in R.G. Linford (Ed.), Electrochemical Science and Technology of Polymers, EIsevier, Amsterdam, 22(1987)103.
13. W. J. Albery and AX. Hilhnan, AM. Rep. C., *Royal Society of Chemistry, London,* 78 (1981) 377.
14. W. John Albery, A. Robert Hillman, *J. Electroanal. Chem.*, 170 (1984) 27.
15. R.Senthamarai, L. Rajendran, *Electrochim. Acta.*, 55 (2010) 3223.
16. M. Puida, A. Malinauskas, F. Ivanauskas, *J. Math. Chem.,* 50 (2012) 2001.
17. M. E. G. Lyons, D. E. McCormack and P. N. Bartlett, *J. Electroanal. Chem.*, 261 (1989) 51.
18. M. E. G. Lyons, P. N. Bartlett, *J. Electroanal. Chem.*, 316 (1991) 1.
19. A. Eswari, L. Rajendran, *Natural Science.*, 2 (2010) 612.
20. A. Eswari, L. Rajendran, *J. Electroanal. Chem.*, 641 (2010)35.
21. A. Eswari, L. Rajendran, *J. Electroanal Chem.*, 648 (2010)36.
22. A. Eswari, L. Rajendran, *J. Electroanal Chem.*, 660 (2011) 200.
23. G. Adomian, *J. Math. Anal.Appl.*, 135 (1988) 501.

24. Shijun Liao, *Appl. Math.Comput*., 147 (2004) 499.
25. B Manimegalai, Michael EG Lyons, L Rajendran, *J. Electroanal. Chem.*, 902 (2021) 115775.
26. Ji-Huan He, *Comput. Methods Appl. Mech. Engrg.,* 178 (1999) 257.
27. Ji-Huan He, *Int. J. Nonlinear Mech*., 35 (2000) 37.
28. R. Saravanakumar, P. Pirabaharan, Marwan Abukhaled, L. Rajendran, *J. Phys.Chem*.B., 124 (2020) 443.
29. G. Adomian, *J. Math. Anal.Appl*., 135 (1988) 501.
30. R. Usha Rani, L. Rajendran, *Chem. Phys. Lett.*, 754 (2020) 137573.
31. A. Eswari, S. Saravanakumar, *J. Electroanal. Chem.*, 880 (2021**)** 114827**.**
32. K. Saranya, V. Mohan, L. Rajendran, J. Math. Chem., 58 (2020) 1230.
33. R. Joy Salomi, S. Vinolyn Sylvia, L. Rajendran, M. Abukhaled, *Sens. Actuators B Chem*., 321 (2020)128576.
34. J. Visuvasam, A. Meena, L. Rajendran, *J. Electroanal. Chem.,*869 (2020) 114106.
35. M. Abukhaled, S.A. Khuri, *J. Electroanal. Chem*., 792 (2017) 66.
36. K. M. Dharmalingam and M. Veeramuni, *J. Electroanal. Chem*., 844 (2019) 1.
37. Michael E.G. Lyons, *J. Electroanal. Chem.,* 872 (2020) 114278.