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Research Article

Mathematical Analysis of Nonlinear Differential Equations in Polymer Coated Microelectrodes

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Abstract: A theoretical analysis is conducted on the electrochemical behaviour of micro disk electrodes coated with thin coatings of electroactive polymers. The main focus of efforts to characterize the planar diffusion chemical reaction within polymer-modified ultra-microelectrodes is the creation of a theoretical model that explicitly takes into account the potential for the polymer film to cover the inlaid micro disc support surface. Approximate formulae for the steady-state amperometric response and formulation of the boundary value problem are given. The impact of substrate concentration, mediator concentration and current responsiveness in the solution besides the polymer film is also investigated. Akbari-Ganji Method (AGM) and Differential Transformation Method (DTM), two adequate and widely available analytical methods, were utilized to determine the steady-state non-linear diffusion equation. The approximate analytical solution for the substrate concentration and mediator concentration and the current for the small experimental kinetic values and diffusion coefficients are presented. We additionally determine the problem's numerical solution using the MATLAB tool. A satisfactory agreement can be seen when the numerical outcomes verify with the analytical findings.

***Keywords*:** Nonlinear Differential Equation, Akbari-Ganji Method and Differential Transformation Method, Modified Polymer Ultra-Microelectrodes

MSC: 34A34, 34E05

Nomenclature

S^{∞}	The substrate's bulk concentration, μM
A	The electrode's radius, μm
C_{Σ}	The total amount of oxidised and reduced mediator species, μM
D_S	Substrate's diffusion coefficient, $\frac{\mu m^2}{s}$
D_E	Coefficient of diffusion of the oxidised mediator, $\frac{\mu m^2}{s}$
r	Radial unit, μm

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b	Oxidised mediator concentration, μM
s	Substrate concentration, μM
k	The mediator-substrate reaction's bimolecular rate constant, ms
A	Area of the hemispherical electrode, μm^2
F	Faraday constant, C/mol
u	Dimensionless substrate concentration
v	Dimensionless mediator concentration
$u(0)$	Dimensionless substrate concentration at electrode surface
$\rho = \dfrac{\gamma_E}{\gamma_S}$	Dimensionless parameter
γ_S	Substance diffusion in the film contrasted with catalytic reaction (Dimensionless diffusion parameters)
γ_E	Electron diffusion in the film contrasts with catalytic reaction (Dimensionless reaction parameters)
ψ	Normalized steady-state current
K	Partition coefficient
I	Net current, none
x	Radial distance without dimensions emitted from the Polymer hemisphere's source, none
n	Number of electrodes, none

1. Introduction

Throughout the previous fifteen years, two main areas have received the majority of electrochemistry research effort; the first focuses on researching and creating chemically modified electrode materials for specific technological uses domains like energy, electro catalysis, and chemical sensing conversion and storage [1–3]. The second area being studied is the creation of tiny electrode structures. The dimensions of these voltammetry ultra-microelectrodes are usually micrometres, ranging from 0.5 to 50 mm [4–6]. In this study, we provide an analytical model that explains the behaviour of the catalyst thin coatings of electronically conducting organic polymers on micro disk electrodes that have undergone chemical modification.

To create an electroactive thin film, oxidative electrochemical species-to-monomer polymerization deposits the macromolecular chemical microstructure onto a support electrode's surface. There is a sequence of ionic and electronic conductivity in the deposited coating.

Electrodes modified with polymers are especially appealing for applications involving chemical sensing [7–11]. A polymer sensor that functions under amperometric conditions has a simple concept; instead of reacting at the underlying support electrode, within the polymer film matrix, active receptor sites immobilised in three dimensions interact with the redox-active substrate of interest. In general, the polymer layer mediates substrate oxidation or reduction. The charge can pass through the polymer's chains and across the contact between the polymer and the support electrode because the polymer film is electroactive, which allows current to flow. The concentration of the substrate will have a direct bearing on this current flow. The kinetics of the substrate/product transition are inextricably governed by the properties of the mediating electroactive polymer film because electron transfer occurs between the substrate and the catalytic/receptor site. The polymer film's degree of conductivity, the mediating sites' catalytic properties, the interaction between the site and substrate, and the polymer film's structure will all be significant.

It is demonstrated that planar diffusion of the substrate within the layer may be used in place of planar diffusion when the radius of the inlaid micro disc is significantly larger than the thickness of the polymer film. This theoretical analysis considers simple planar diffusion and chemical reaction within a polymer-modified electrode. The precise geometrical pattern that an electrodeposited conducting polymer layer on microelectrode support will adopt is impossible to predict with any degree of accuracy. An effect known as the "spill over" layer will be seen. Without significantly spilling over into the nearby sheath, the layer may develop in an approximate pattern from the conductive ultra-micro-disc surface below, or it may extend onto and partially cover the latter region, which will be flush with the embedded micro-disc. When the equations describing transport and kinetic processes within the layer are solved, it is evident that any geometrical arrangement will result in a distinct set of mathematical boundary conditions and will need the employment of distinct distance normalization schemes.

Albery, Hillman [12], and Andrieux et al. have contributed fundamentally to enhanced electron transport in electroactive polymer films positioned on large electrode surfaces explained theoretically [13]. Although the latter methods are detailed differently, they provide similar results. Each technique considers the planar diffusion substrate inside the polymer matrix. When polymer sheet deposition over a microelectrode, many concepts can be applied to facilitate electron transfer utilising polymer-modified macro-sized electrodes. For example, the assumption that the response of net current is influenced by substrate diffusion through polymer matrix pores, charge percolation along the polymer strands, immobilised redox group and substrate will be subject to bimolecular chemical interaction.

We review the characteristics of ultramicrodisc electrodes with thin poly (pyrrole) coatings applied to them to change their electrical conductivity. We are concentrating on that materials as potential amperometric electrochemical sensors. No approximate analytical results were previously done for planar-modified polymer-coated ultra-micro electrodes. This connection aims to give approximate analytical formulas for the steady-state substrate and mediator concentration and the current for an ultra-microelectrode modified with polymer for all values of γ_S and γ_E using the Akbari-Ganji method and differential transformation method.

2. Formulation of the problem

The nonlinear reaction-diffusion equations contain nonlinear chemical reaction components; they are challenging to solve using traditional analytical techniques combined with initial and boundary conditions. As a result, approximations must be found. The solution layer close to the microelectrode is expected to have a significant substrate diffusion. This work aims to electrodeposit a conductive polymer coating with little spill over. The following is an expression for the nonlinear equations governing the steady-state conditions [14].

$$D_E b''(r) - ks(r)b(r) = 0 \tag{1}$$

$$D_S b''(r) - ks(r)b(r) = 0 \tag{2}$$

where s stands for the substrate concentration in the polymer film, while b stands for the oxidised mediator concentration, k is the bimolecular rate constant of the mediator-substrate reaction. Furthermore, r stands for the radial coordinate. Boundary conditions for this equation can be elucidated as follows:

$$r = 0,\ b = C_\Sigma,\ \frac{ds}{dr} = 0, \tag{3}$$

$$r = a,\ \frac{db}{dr} = 0,\ s = ks^\infty \tag{4}$$

Where $C_\Sigma = s + b$ represents the overall mediator concentration, both oxidised and reduced, electrode radius is a and s^∞ denotes the substrate concentration.

In Figure 1, the shape chosen by an electroactive polymer film placed over an inlaid micro disc electrode is represented diagrammatically. It is anticipated that the spill over of polymer onto the nearby insulating layer.

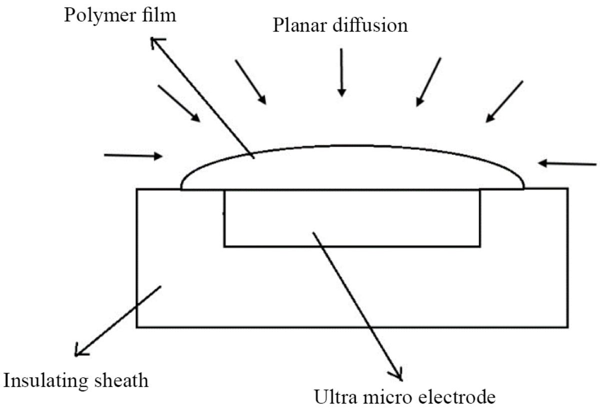


Figure 1. Diagrammatic depictions of the polymer-coated microelectrode onto an ultra-micro disc

Figure 2 illustrates the chemical interaction between the substrate and the species will be bimolecular, and radical substrate diffusion will occur inside the thin film. We also handle the deposited film as a homogeneous medium. r denotes the distance coordinator. The substrate splits into the layer with a partition coefficient of K and corresponding D_S and D_E. Electron hopping diffusion coefficient and substrate diffusion coefficient, respectively.

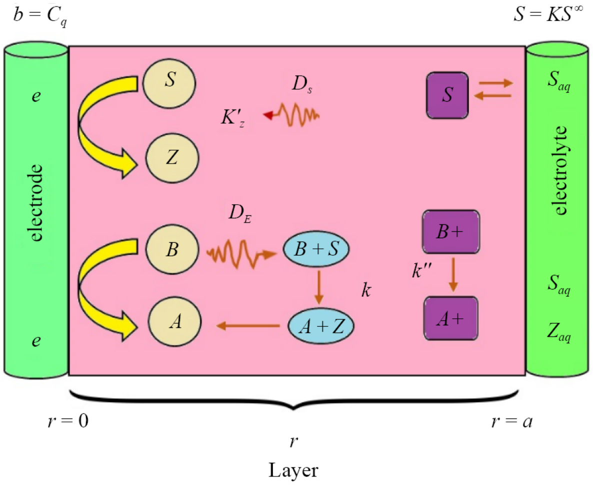


Figure 2. The model of the reaction system, where r is the radius from the polymer radical centre

The net current $'I'$ can be articulated as

$$I = \frac{i}{nFA} = -D_E \left(\frac{db}{dr}\right)_{r=0} = D_S \left(\frac{ds}{dr}\right)_{r=a} \tag{5}$$

F stands for the Faraday constant. A denotes the electrode area and the electrode reaction's charge number by n. We introduce dimensionless variables [15, 16] to make the non-linear differential equations described in Equations (1) and (2) dimensionless

$$u = \frac{s}{ks^{\infty}},\ v = \frac{b}{C_{\Sigma}},\ x = \frac{r}{a},\ \gamma_E = \frac{kKs^{\infty}a^2}{D_E},\ \gamma_S = \frac{kC_{\Sigma}a^2}{D_S} \tag{6}$$

The chemical reaction/diffusion parameters γ_E and γ_S estimate the proportion of charge percolation rates to chemical reaction rates. The subsequent nonlinear system of equations has the following expression.

$$\frac{d^2u(x)}{dx^2} - \gamma_S\, u(x)\, v(x) = 0 \tag{7}$$

$$\frac{d^2v(x)}{dx^2} - \gamma_E\, u(x)\, v(x) = 0 \tag{8}$$

at

$$x = 0,\ \frac{du}{dx} = 0,\ v = 1 \tag{9}$$

$$x = 1,\ u = 1,\ \frac{dv}{dx} = 0 \tag{10}$$

The normalized current is given by

$$\psi = ia/nFAD_s ks^{\infty} = \left(\frac{du}{dx}\right)_{x=1} \tag{11}$$

3. Analytical solution of the concentrations using Akbari Ganji Method

Recently some asymptotic methods such as the Adomian decomposition method [17], Variational iteration method [18], Homotopy perturbation method [19, 20], Taylor series method [21], differential transformation method [22] and Akbari-Ganji's method [23, 24]. Among all these method simplest approach for solving non-linear differential equations is Akbari-Ganji method and differential transformation method are used to solve the nonlinear equations.

Akbari Ganji method is a numerical technique for solving nonlinear differential equations, particularly boundary value problems. It is named after its developers, Akbari and Ganji, who introduced this method in 2014. It is initially assumed to be a solution function with an unknown constant coefficient that satisfies the initial condition and differential equation. The values of the unknown function are then found using the derivatives of the algebraic equations obtained from the initial conditions. This effective method makes it possible to solve complex non-linear differential equations without using any challenging process [25–33]. Approximate analytical solution of the non-linear differential equation (7), (8) is (Appendix A):

$$u(x) = \frac{\cos h(mx)}{\cos h(m)} \tag{12}$$

$$v(x) = \frac{\gamma_E}{\gamma_S}\left(\frac{\cos h(mx)}{\cos h(m)} - m\ \tan h(m) + \frac{\gamma_S}{\gamma_E} - \frac{1}{\cos h(m)}\right) \tag{13}$$

Where

$$m = \sqrt{\gamma_S} \tag{14}$$

3.1 *Analytical solution of the concentration using Differential Transformation Method*

A semi-analytical technique for solving differential equations is the Differential Transform Method (DTM). The differential transform concept, utilised to solve linear and nonlinear boundary value problems in electric circuit analysis, was first proposed by Zhou. Using DTM, differential equations yield an empirical polynomial solution, and it is possible to precisely find the nth derivative of an analytical function at a given position regardless of the knowledge of the boundary conditions. Unlike the usual high-order Taylor series procedure, which necessitates the symbolic computing of the data functions, this method is different. The primary benefit of this approach is that it can be used directly without the need for Discretization and linearization. The differential transformation method offers a combination of simplicity, accuracy, versatility, and efficiency, making it a valuable tool for solving differential equations in various scientific and engineering applications. A different iterative method for generating analytical solutions to differential equations is the DTM. The following approximate analytical expressions of concentrations obtained with the DTM approach are recognised (Appendix B):

$$u(x) = \frac{2 + \gamma_S x^2}{\gamma_S + 2} \tag{15}$$

$$v(x) = \frac{\gamma_E}{\gamma_S}\left(\frac{2 + \gamma_S x^2}{\gamma_S + 2}\right) + \frac{\gamma_E}{\gamma_S}\left(\frac{2 + \gamma_S}{\gamma_S + 2}\right)x + 1 - \frac{\left(2\left(\frac{\gamma_E}{\gamma_S}\right)\right)}{\gamma_S + 2} \tag{16}$$

From Equations (12) and (13) the current can be expressed as follows

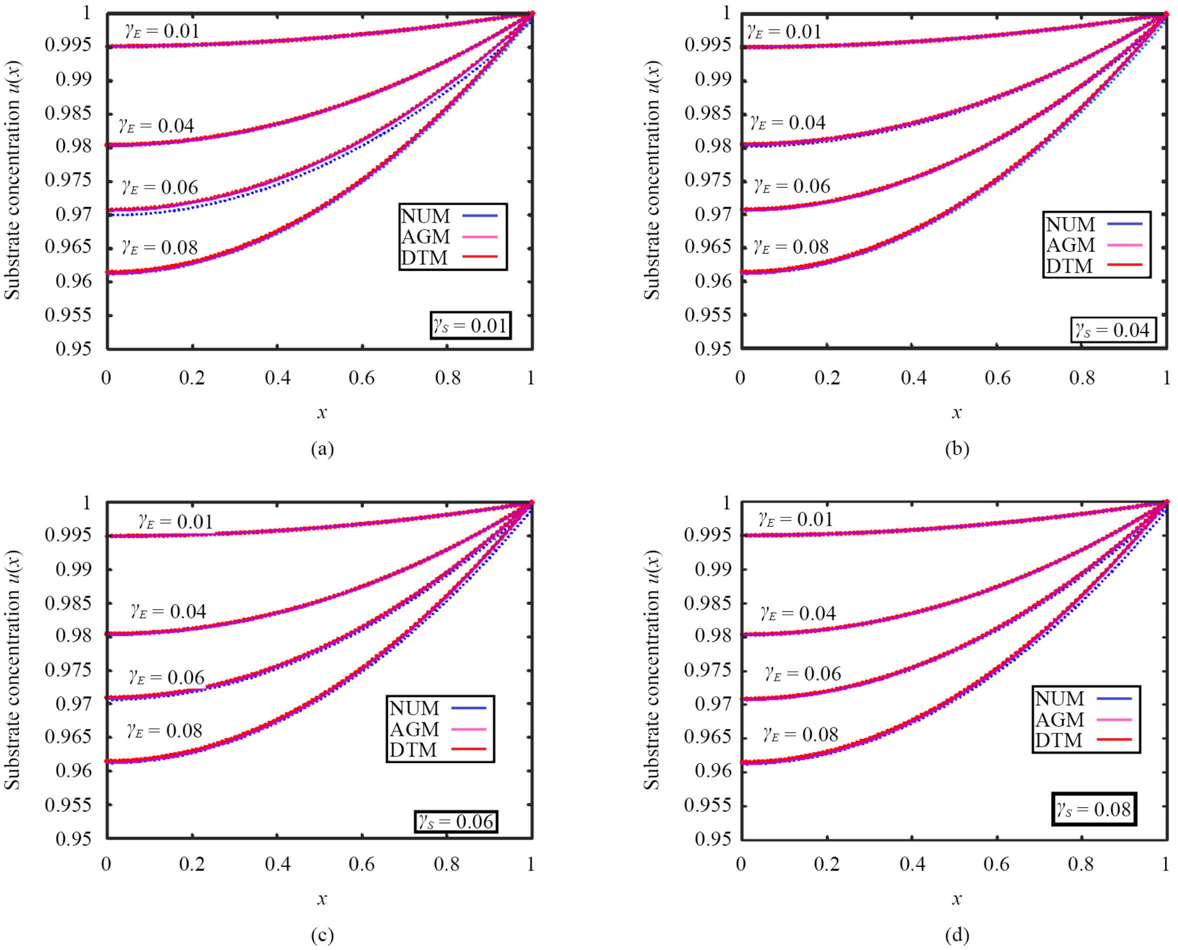
$$\Psi = \frac{2\gamma_E}{2 + \gamma_S} \tag{17}$$

4. Validation of analytical results

This scholarly work has placed considerable focus on the validation methodology. The numerical solution of the non-linear differential equations (7) and (8), along with the boundary conditions given by the equations (9) and (10), is carried out using the MATLAB program.

Figures 3-5 present a numerical comparison of substrate and mediator concentration obtained from Akbari-Ganji method equations (12) and (13) and differential transformation methodologies.

Tables 1 and 2 compare the analytical and numerical concentration of substrate and mediator by the Akbari-Ganji method and the differential transformation method for various parametric values. The table indicates that the average relative errors are less than 1%.



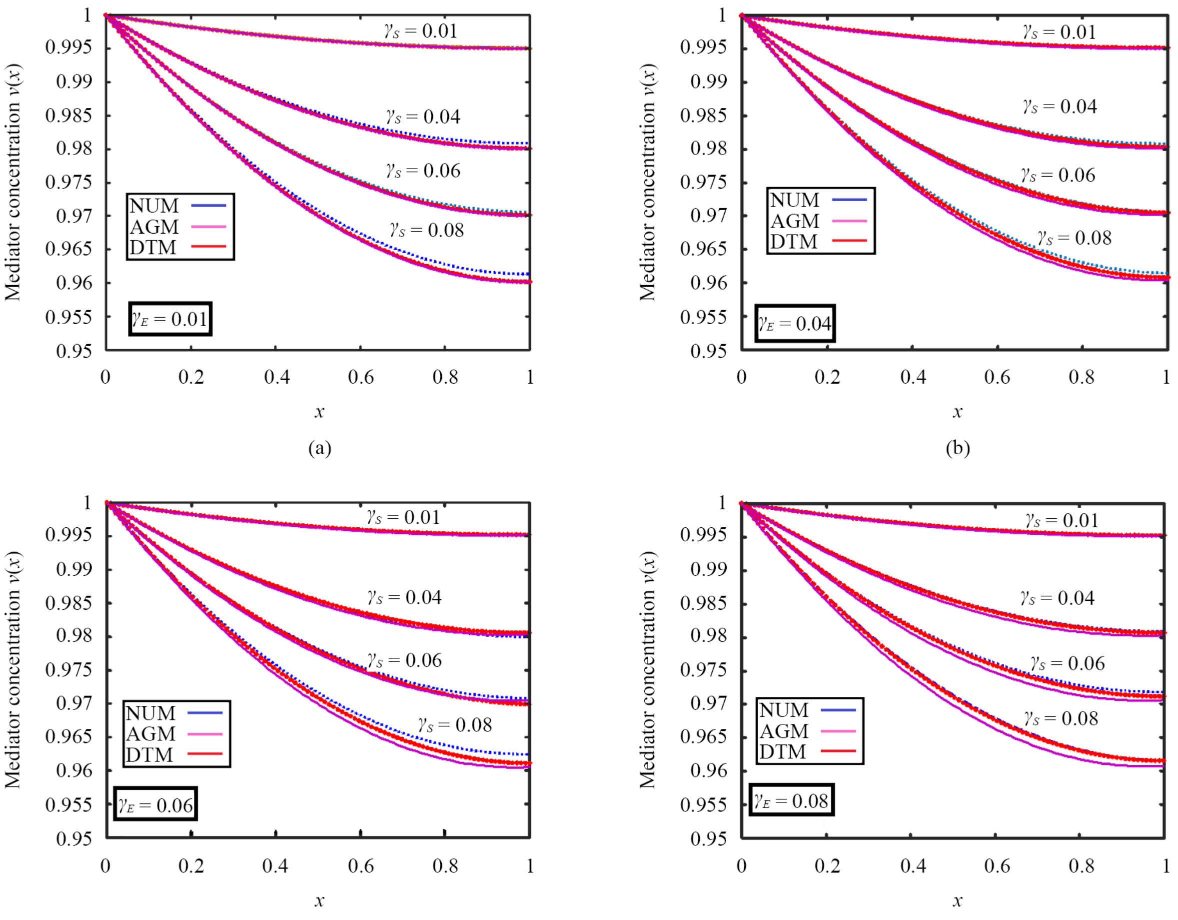
(a) (b) (c) (d)

Figure 3. (a-d): Profile of steady state substrate concentration u versus dimensionless distance x for different parametric values γ_S and γ_E

Table 1. Comparison of the substrate concentrations obtained by AGM and DTM for the parameters γ_S and γ_E between their numerical and analytical expressions

	$\gamma_S = 0.04,\ \gamma_E = 0.04$					$\gamma_S = 0.06,\ \gamma_E = 0.06$					$\gamma_S = 0.08,\ \gamma_E = 0.08$				
X	NUM	AGM	DTM	AGM ERR %	DTM ERR %	NUM	AGM	DTM	AGM ERR %	DTM ERR %	NUM	AGM	DTM	AGM ERR %	DTM ERR %
0	0.980	0.980	0.980	0	0	0.971	0.971	0.971	0	0	0.962	0.962	0.962	0	0
0.25	0.987	0.982	0.982	0	0	0.973	0.973	0.973	0	0	0.964	0.964	0.964	0	0
0.5	0.986	0.984	0.982	0	0	0.979	0.978	0.979	0	0	0.972	0.972	0.972	0	0
0.75	0.992	0.992	0.992	0	0	0.988	0.988	0.988	0	0	0.983	0.984	0.983	0.001	0
1	1	1	1	0	0	1	1	1	0	0	0.999	1	0.999	0.001	0
		Error %		0	0		Error %		0	0		Error %		0.002	0

Our analytical findings exhibit satisfactory substrate concentration and mediator consistency for small parametric values. Compared with these two methods, the differential transformation method provides more accurate results than the Akbari Ganji method.

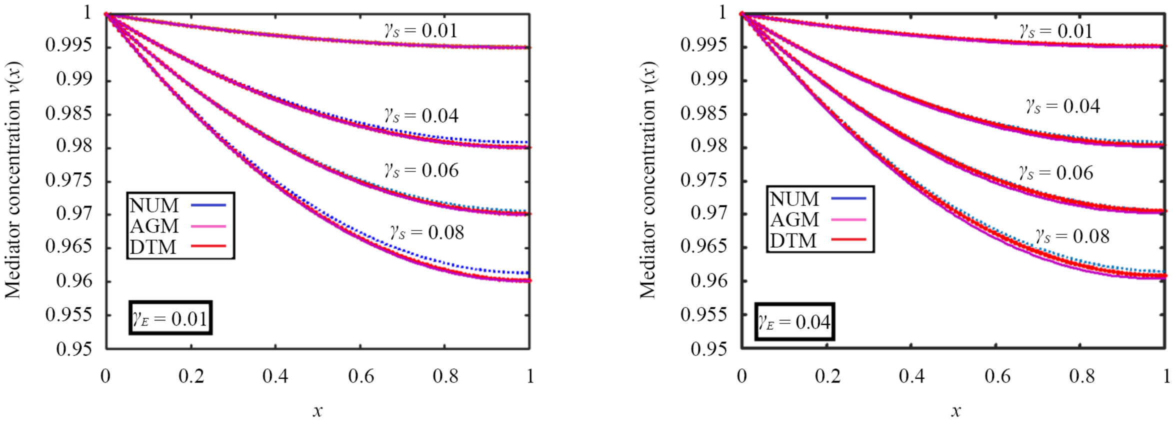


(a) (b) (c) (d)

Figure 4. (a-d): Profile of steady state mediator concentration v versus dimensionless distance x for different parametric values γ_S and γ_E

Table 2. Comparison of the mediator concentrations obtained by AGM and DTM for the parameters γ_S and γ_E between their numerical and analytical expressions

	$\gamma_S = 0.04,\ \gamma_E = 0.04$					$\gamma_S = 0.06,\ \gamma_E = 0.06$					$\gamma_S = 0.08,\ \gamma_E = 0.08$				
X	NUM	AGM	DTM	AGM ERR %	DTM ERR %	NUM	AGM	DTM	AGM ERR %	DTM ERR %	NUM	AGM	DTM	AGM ERR %	DTM ERR %
0	1	1	1	0	0	1	1	1	0	0	1	1	1	0	0
0.25	0.991	0.991	0.991	0	0	0.987	0.987	0.987	0	0	0.983	0.982	0.983	0.001	0
0.5	0.986	0.986	0.986	0	0	0.978	0.977	0.978	0.001	0	0.971	0.970	0.971	0.001	0
0.75	0.982	0.982	0.982	0	0	0.973	0.971	0.973	0.002	0	0.964	0.963	0.964	0.001	0
1	0.980	0.980	0.980	0	0	0.971	0.971	0.971	0	0	0.962	0.963	0.962	0.001	0
		Error %		0	0		Error %		0.003	0		Error %		0.004	0



(a)

(b)

Figure 5. (a) & (b): Normalised steady state current Ψ for different values of γ_S and γ_E

5. Result and discussion

The solution to the Non-Linear Differential equation in the Modified Polymer Ultra Microelectrode indicates a unique, closed form of an analytical expression for the concentration of mediator and substrate.

Figure 3 clearly shows that normalised Concentration of substrate $u(x)$ vary with Reaction Diffusion parameter γ_S and γ_E from the graph it is notice that γ_S increases the substrate concentration of u decreases at the electrode surface. At $x = 0$, u attains the minimum value denoted by $u(0)$, and when $x = 1$, u attains the maximum value. In Figure 3(a), it is noted that when the diffusion parameter $\gamma_S = 0.01$ and γ_E increases from 0.01, 0.04, 0.06 and 0.08, then the substrate concentration of $u(x)$ decreases and in Figure 3(b-d) diffusion parameter increases form $\gamma_S = 0.04, 0.06, 0.08$ and the reaction parameter carries the same constant values $\gamma_E = 0.01, 0.04, 0.06, 0.08$ then the substrate concentration $u(x)$ decreases.

Figure 4 shows the oxidised Mediator concentration $v(x)$ for all values of γ_S and γ_E, it can be noticed that minimal value of v attains at $x = 0$ and attains its maximal when $x = 1$, γ_E increases the mediator concentration of $v(x)$ decreases. Concentration of $v(x)$ decreases as γ_S and γ_E increases. In Figure 4(a) shows that reaction parameter $\gamma_E = 0.01$ and γ_s takes the values 0.01, 0.04, 0.06, 0.08 then the oxidised mediator concentration of $v(x)$ decreases and in Figure 4(b-d) states that reaction parameter increases from $\gamma_E = 0.04, 0.06, 0.08$ and the diffusion parameter takes the same constant values $\gamma_S = 0.01, 0.04, 0.06, 0.08$ then the oxidised mediator concentration $v(x)$ decreases.

Figure 5 display shows the study state current plotted against substrate concentration on the electrode surface for different parametric values, illustrating the influence of various factors on current. The graph shows the normalised current response for different substrate and electron diffusion values. Figure 5(a) shows that increase in γ_E leads to decrease in current, Figure 5(b) shows that increase in γ_S leads to increase in current.

6. Conclusion

This paper offers an in-depth theoretical examination of the mathematical model of polymer-coated ultra-micro electrodes. Approximate analytical expressions have been derived for the substrate concentration and mediator concentration for different parametric values. The Akbari Ganji and Differential Transformation methods are straightforward, featuring a simple solution process and yield precise outcomes when contrasted with other analytical techniques. The numerical results obtained from MATLAB were compared with the derived approximate analytical results. The research includes an examination of the steady-state concentration of substrate and mediator and steady-state current. Additionally, we assessed the transport and kinetics by considering the fundamental reaction/diffusion parameter of the polymer denoted by γ_S and γ_E. These techniques are also applicable to addressing non-steady state scenarios. The versatility and capabilities of ultra-microelectrodes make them indispensable tools in numerous scientific and technological fields, driving innovations and discoveries across various applications. This analytical approach can be expanded to encompass other spill over models for diverse electrode geometries, among other applications beyond the scope of the amperometric biosensor research.

Conflict of interest

The authors declare no competing interest.

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Appendix I

Relation between substrate and mediator concentration

The second order non-linear differential equation is as follows

$$\frac{d^2u(x)}{dx^2} - \gamma_S\, u(x)\, v(x) = 0 \tag{A1}$$

$$\frac{d^2v(x)}{dx^2} - \gamma_E\, u(x)\, v(x) = 0 \tag{A2}$$

Boundary conditions are

$$\frac{du}{dx} = 0,\ v = 1 \text{ when } x = 0 \tag{A3}$$

$$u = 1,\ \frac{dv}{dx} = 0 \text{ when } x = 1 \tag{A4}$$

subtracting (A1) and (A2) we get

$$\frac{d^2v(x)}{dx^2} = \frac{\gamma_E}{\gamma_S}\frac{d^2u(x)}{dx^2} \tag{A5}$$

Integrating (A5) twice we get

$$v(x) = \frac{\gamma_E}{\gamma_S}u(x) + c_1(x) + c_2 \tag{A6}$$

Analytical solution of the equation (A1) and (A2) using AGM

$$\frac{d^2u(x)}{dx^2} - \gamma_S\, u(x)\, v(x) = 0 \tag{A7}$$

$$\frac{d^2v(x)}{dx^2} - \gamma_E\, u(x)\, v(x) = 0 \tag{A8}$$

Boundary conditions are

$$\frac{du}{dx} = 0,\ v = 1 \text{ when } x = 0 \tag{A9}$$

$$u = 1,\ \frac{dv}{dx} = 0 \text{ when } x = 1 \tag{A10}$$

Using boundary conditions (A7) and (A8) in (A3), (A4)

$$u\left(x\right) = \frac{\cos h(mx)}{\cos h(m)} \tag{A11}$$

$$u'\left(x\right) = \frac{m \sin h(mx)}{\cos h(m)} \tag{A12}$$

$$u''\left(x\right) = \frac{m^2 \cos h(mx)}{\cos h(m)} \tag{A13}$$

$$v\left(x\right) = \frac{\gamma_E}{\gamma_S}\left(\frac{\cos h(mx)}{\cos h(m)} - m\tan h\left(mx\right) + \frac{1}{\frac{\gamma_E}{\gamma_S}} - \frac{1}{\cos h(m)}\right) \tag{A14}$$

By using Akbari Ganji Method, the value of *m* can be obtained as follows,

$$\frac{m^2 \cos h\left(mx\right)}{\cos h\left(m\right)} - \gamma_S\left(\frac{\cos h\left(mx\right)}{\cos hm}\right)\left(\frac{\gamma_E}{\gamma_S}\left[\frac{\cos h\left(mx\right)}{\cos hm} - m\tan h\left(mx\right) + \frac{1}{\frac{\gamma_E}{\gamma_S}} - \frac{1}{\cos hm}\right]\right) = 0$$

Solving for *m*, we get

$$m = \sqrt{\gamma_S} \tag{A15}$$

Appendix II

Analytical solution of the equation (A1) and (A2) using DTM

$$\frac{d^2u(x)}{dx^2} - \gamma_S\, u(x)\, v(x) = 0 \tag{A16}$$

$$u = l, \text{ when } x = 0 \tag{A17}$$

Transformed version of equation (A16) and (A17) are respectively

$$(n+2)(n+1)\,u(n+2) - \gamma_S \sum_{r=0}^{n} u(n)\, v(n-r) = 0 \tag{A18}$$

letting $n = 0$

$$2u(2) - \gamma_S(u(0)\, v(0) = 0$$

$$u(2) = \frac{\gamma_S l}{2} \tag{A19}$$

The differential inverse transforms of $u(n)$ is defined as

$$s(x) = \sum_{n=0}^{2} u(n)\,(x - x_0)^n \tag{A20}$$

Letting $x_0 = 0$, we get the second order closed form solution

$$u(x) = \sum_{n=0}^{2} u(n)(x)^n = l + \frac{l\gamma_S}{2}x^2 \tag{A21}$$

By using the boundary conditions $u = 1$ when $x = 1$, we get l value

$$l = \frac{2}{2 + \gamma_S} \tag{A22}$$

Hence the approximate analytical solution for the concentration of the substrate is

$$u(x) = \frac{2 + \gamma_S x^2}{\gamma_S + 2} \tag{A23}$$