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Analytical and Computational Investigation of Non-Steady State Reaction and Kinetics at Spherical Ultramicroelectrodes Concerning Conducting Polymer Modification using Homotopy Perturbation Method

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Abstract:

In this work, mathematical modelling of non-steady state reaction and kinetics at spherical ultramicroelectrodes within conducting polymer modification is considered. The main objective of this work is to propose a new analytical formulation for the system of nonlinear non-steady state reaction diffusion equation in spherical ultramicroelectrodes. Employing Homotopy Perturbation Method, the concentrations of species, mediator and current may all be obtained analytically for all conceivable experimental results of the parameter. The accumulated analytical outcomes are analyzed with numerical simulations and implemented to investigate various parameters. By comparing the analytical solution with numerical findings, the accuracy of the method is presented. In order to better understand the system dynamics, a numerical simulation of the issue is also provided through Matlab Software. The new analytical results contribute to optimizing the consistency of this model. These novel approaches produce a compact set of analytical approximations that possess straightforward to compute and verify as well.

Keywords: Nonlinear equation, Non-steady state, reaction diffusion process, Spherical ultramicroelectrodes, Homotopy Perturbation Method.

1.Introduction

In the electrochemical process and the kinetics of rapid reactions, Ultra microelectrodes serve as a practical aid for interpreting the system's functioning. Last 10 years, many voltammetric investigations have employed UME with tip diameters of the order of a micrometre along with ten percent of μm[1]. It demonstrates a time-independent current reaction with a spherical or disc shape, which has both practical as well as theoretical benefits[2-4]. Numerous sensing applications might use modified microelectrodes within Polymer layer[5-6]. Fleischmann et al.[7] discussed the electrochemical characteristics of spherical ultramicroelectrodes. Special structures like fibers and embedded reticulated foams are needed for the moderate commercialization of reactions at microelectrodes. The use of the unique benefits of microelectrodes for the synthesis such as the simplicity of setup and the enlargement of the fluid region when the support electrolyte is absent. Even so, certain electrode and cell designs are needed, such the utilizing electrodes in three dimensions. Rebouilat et al.[8] have issued an empirical investigation of the equilibrium current response anticipated for a Conducting spherical ultramicroelectrodes with polymer modification beneath amperometric circumstances. Albery et al.[9]

have made significant contributions to the theoretical explanation of facilitated electron transport at electroactive polymer films that have been formed on large-scale electrode surfaces. In contrast, the later strategies yield identical outcomes but are distinct in specifics.

Within Conducting Polymer modified ultramicroelectrodes, Anitha et al.[10] worked at the solution of coupled time-varying nonlinear reaction-diffusion equations. Sentamarai et al.[11] and Yogeshwari et al.[12] determine the substrate concentration and mediated profiles within UME by adopting the Variational Iteration Method and Taylor Series Method, respectively.

The present work intends to utilize HPM to construct an analytical formulation for the concentration of mediator and current based on non-steady state reaction-diffusion equations at an electrode surface within spherical Ultramicroelectrodes along with Conducting Polymer Modification.

2.Mathematical formulation

A mathematical model has determined the relationship between the substrate reaction and diffusion in the electro conductive polymer. We will simply give a quick summary because a detailed analysis of the underlying assumptions and physical depiction of the issue has already been done by Fleischmann et al.[7]and Rebouillat et al.[8] . The governing equations are derived while considering the following assumptions.

1. The substrate will diffuse spherically in the thin film, and the mediator and substrate species will intent chemically in a bio molecular way.
2. Consider the deposited film to be a uniform medium.
3. A partition and diffusion coefficient cause the substrate to divide into layers.

The equation regarding non-steady state reaction-diffusion within the polymer layer could be phrased in the following manner.

$$\mathfrak{D}_{S_1}\frac{\partial^2 s_1}{\partial u^2}+\frac{2\mathfrak{D}_{S_1}}{u}\frac{\partial s_1}{\partial u}-\rho s_1 s_2=\frac{\partial s_1}{\partial t} \tag{2.1}$$

$$\mathfrak{D}_{S_2}\frac{\partial^2 s_2}{\partial u^2}+\frac{2\mathfrak{D}_{S_2}}{u}\frac{\partial s_2}{\partial u}-\frac{\rho}{2}s_1 s_2=\frac{\partial s_2}{\partial t} \tag{2.2}$$

$$\mathfrak{D}_{\mathcal{M}}\frac{\partial^2 m}{\partial u^2}+\frac{2\mathfrak{D}_{\mathcal{M}}}{u}\frac{\partial m}{\partial u}+\rho s_1 s_2=\frac{\partial m}{\partial t} \tag{2.3}$$

Following are the boundary conditions that describe the problem

At $t=0,\ s_1=0;\ s_2=0; m=0.$ (2.4)

At $u=0,\ \frac{ds_1}{du}=0\ ;\ \frac{ds_2}{du}=0;\ \frac{dm}{du}=0.$ (2.5)

At $u=r,\ s_1=\mathbb{K}{s_1}^T;\ s_2=\mathbb{K}{s_2}^T; m=m^T$ (2.6)

The Net flux is represented as

$$\mathcal{C}_{\mathfrak{J}}=\mathfrak{D}_{S_1}\left(\frac{\partial s_1}{\partial u}\right)_{u=r} \tag{2.7}$$

The results of the final evaluation should be presented in dimensionless parameters before we progress on to a complete mathematical review of the boundary value problem described in the equations (2.1)-(2.7)

We introduce the Non-Dimensional Parameters as,

$$\zeta = \frac{s_1}{\mathbb{K}s_1{}^T};\ \eta = \frac{s_2}{\mathbb{K}s_2{}^T};\ \theta = \frac{m}{m^T};\ X = \frac{u}{r};\ T = \frac{Dt}{r^2};$$

$$\chi_{\mathcal{S}_1} = \frac{\rho m^T r^2}{\mathfrak{D}_{\mathcal{S}_1}};\chi_{\mathcal{S}_2} = \frac{\rho m^T r^2}{\mathfrak{D}_{\mathcal{S}_2}};\ \chi_{\mathcal{M}} = \frac{\rho \mathbb{K}s_1{}^{\infty} r^2}{\mathfrak{D}_{\mathcal{M}}} \tag{2.8}$$

The reaction diffusion parameters $\chi_{\mathcal{S}_1}, \chi_{\mathcal{S}_2}$ and $\chi_{\mathcal{M}}$ are used to measure the correlation between the chemical reaction rate and the amount of charge percolation or substrate diffusion.

The system of non-steady state nonlinear reaction-diffusion equation can be written as

$$\frac{\partial^2\zeta(X)}{\partial X^2} + \frac{2}{X}\frac{\partial\zeta(X)}{\partial X} - \chi_{\mathcal{S}_1}\zeta(X)\theta(X) = \frac{\partial\zeta}{\partial T} \tag{2.9}$$

$$\frac{\partial^2\eta(X)}{\partial X^2} + \frac{2}{X}\frac{\partial\eta(X)}{\partial X} - \frac{\chi_{\mathcal{S}_2}}{2}\,\zeta(X)\theta(X) = \frac{\partial\eta}{\partial T} \tag{2.10}$$

$$\frac{\partial^2\theta(X)}{\partial X^2} + \frac{2}{X}\frac{\partial\theta(X)}{\partial X} + \chi_{\mathcal{M}}\zeta(X)\theta(X) = \frac{\partial\theta}{\partial T} \tag{2.11}$$

The appropriate boundaries were expressed as

$$\zeta(X) = \eta(X) = \theta(X) = 0 \text{ when } T = 0 \tag{2.12}$$

$$\frac{\partial\zeta(X)}{\partial X} = \frac{\partial\eta(X)}{\partial X} = \frac{\partial\theta(X)}{\partial X} = 0 \text{ when } X = 0 \tag{2.13}$$

$$\zeta(X) = \eta(X) = \theta(X) = 1 \text{ when } X = 1 \tag{2.14}$$

The following equation represents the normalized current response

$$\Delta = -D\left(\frac{\partial\zeta(X)}{\partial X}\right)_{X=1} \tag{2.15}$$

3. Analytical solution of the concentrations using Homotopy Perturbation Method

Many writers have focused on researching the solution of nonlinear equations during the past few decades using a variety of techniques, including the Homotopy perturbation Method[14-17], Taylor Series Method[18-20], Akbari Ganji Method[21-28], Variational iteration method[29,30]. Homotopy perturbation Method is conservative in its efficiency, applicability, and accuracy. The non-steady state nonlinear equations (2.9) through (2.15) may be solved using this technique to provide the analytical formulation for the concentration of species and mediator.

We construct the homotopy for (2.9) – (2.11) as,

$$(1-p)\left[\frac{\partial\zeta}{\partial T} - \frac{\partial^2\zeta}{\partial X^2} - \frac{2}{X}\frac{\partial\zeta}{\partial X} + \chi_{\mathcal{S}_1}\zeta\theta\right] + p\left[\frac{\partial\zeta}{\partial T} - \frac{\partial^2\zeta}{\partial X^2} - \frac{2}{X}\frac{\partial\zeta}{\partial X} + \chi_{\mathcal{S}_1}\zeta\theta\right] = 0 \tag{3.1}$$

Equation (1) - (3) has an analytical solution as,

$$\zeta = \zeta_0 + p\zeta_1 + p^2\zeta_2 + \dots..$$

$$\theta = \theta_0 + p\theta_1 + p^2\theta_2 + \ldots \quad (3.2)$$

Substituting (3.2) in (3.1) and comparing the coefficients of p, we get

$$p^0 = \frac{\partial \zeta_0}{\partial T} - \frac{\partial^2 \zeta_0}{\partial X^2} - \frac{2}{X}\frac{\partial \zeta_0}{\partial X} - \chi_{s_1}\zeta_0 = 0 \quad (3.3)$$

In Laplace plane, (3.3) can be written as,

$$\frac{d^2\zeta_0}{dX^2} + \frac{2}{X}\frac{d\zeta_0}{dX} - (s + \chi_{s_1})\zeta_0 = 0 \quad (3.4)$$

Subject to the boundary conditions,

$$\frac{d\zeta_0}{dX}(0) = 0\,;\ \zeta_0(1) = \frac{1}{s} \quad (3.5)$$

By reduction of order, we consider the equation

$$\frac{d^2\zeta_0}{dX^2} + P\frac{d\zeta_0}{dX} - Q\zeta_0 = R \quad (3.6)$$

Comparing (3.4) and (3.6),

$$P = \frac{2}{X}\,;\ Q = -(s + \chi_{s_1})\,;\ R = 0 \quad (3.7)$$

Consider $\zeta_0 = \theta\eta$ (3.8)

The general solution of (21) represented as $2\frac{d\theta}{dX} + P\theta = 0$ (3.9)

Then $\theta = \frac{1}{X}$ (3.10)

Equation (3.6) and (3.7) reduces to

$$\eta'' - (s + \chi_{s_1})\eta = 0 \quad (3.11)$$

Integrating (3.11) twice, we get

$$\eta = Ae^{\left(\sqrt{s+\chi_{s_1}}\right)X} + Be^{\left(-\sqrt{s+\chi_{s_1}}\right)X} \quad (3.12)$$

Substituting (3.12) and (3.10) in (3.8) and then using boundary conditions, we obtain

$$\zeta_0(X,s) = \frac{1}{X}\left[\frac{\sinh\left(\sqrt{s+\chi_{s_1}}X\right)}{s.\sinh\left(\sqrt{s+\chi_{s_1}}\right)}\right] \quad (3.13)$$

Employing inverse Laplace transform, the concentration of species s_1 can be represented as,

$$\zeta(X,T) = \frac{\sinh\left(\sqrt{\chi_{s_1}}X\right)}{X\sinh\left(\sqrt{\chi_{s_1}}\right)} + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)e^{-(n^2\pi^2+\chi_{s_1})T}}{(n^2\pi^2+\chi_{s_1})}\right] \quad (3.14)$$

3.1. Relation between the concentration of species s_1 and s_2

Utilizing equation (2.9) and (2.10), we derive the equation as,

$$\frac{\partial^2}{\partial X^2}\left(\frac{\zeta\chi_{s_2}}{2} - \eta\chi_{s_1}\right) + \frac{2}{X}\frac{\partial}{\partial X}\left(\frac{\zeta\chi_{s_2}}{2} - \eta\chi_{s_1}\right) - \frac{\partial}{\partial T}\left(\frac{\zeta\chi_{s_2}}{2} - \eta\chi_{s_1}\right) = 0 \quad (3.15)$$

Consider $K = \frac{\zeta \chi_{s_2}}{2} - \eta \chi_{s_1}$ (3.16)

Equation (3.15) can be written as $\frac{\partial^2 K}{\partial X^2} + \frac{2}{X}\frac{\partial K}{\partial X} - \frac{\partial K}{\partial T} = 0$ (3.17)

Subject to the boundary conditions,

At T = 0, K = 0 ; (3.18)

At X = 0, $\frac{\partial K}{\partial X} = 0$; (3.19)

At X= 1, $K = \frac{\chi_{s_2}}{2} - \chi_{s_1}$ (3.20)

Applying Laplace transform for equation (3.17) and then solving by the use of the boundary conditions (3.18)-(3.20), we get

$$K(X,T) = \left(\frac{\chi_{s_2}}{2} - \chi_{s_1}\right)\left[1 + 2\pi \sum_{n=1}^{\infty} n(-1)^{n+1} \sin(n\pi X) e^{-(n^2\pi^2 T)}\right] \quad (3.21)$$

By (3.16), we obtain the concentration of species s_2 as expressed as

$$\eta(X,T) = \frac{\chi_{s_2}[\zeta(X,T)]}{2\chi_{s_1}} - \left(\frac{\chi_{s_2}}{2\chi_{s_1}} - 1\right)\left(1 + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)e^{-(n^2\pi^2 T)}}{n^2\pi^2}\right]\right) \quad (3.22)$$

3.2. Relation between the concentration of species s_1 and mediator

Employing equation (2.9) and (2.11), we express the equation as,

$$\frac{\partial^2}{\partial X^2}(\zeta\chi_{\mathcal{M}} - \theta\chi_{s_1}) + \frac{2}{X}\frac{\partial}{\partial X}(\zeta\chi_{\mathcal{M}} - \theta\chi_{s_1}) - \frac{\partial}{\partial T}(\zeta\chi_{\mathcal{M}} - \theta\chi_{s_1}) = 0 \quad (3.23)$$

Take $L = \zeta\chi_{\mathcal{M}} - \theta\chi_{s_1}$ (3.24)

Equation (3.15) becomes $\frac{\partial^2 L}{\partial X^2} + \frac{2}{X}\frac{\partial L}{\partial X} - \frac{\partial L}{\partial T} = 0$ (3.25)

The corresponding boundary conditions are

At T = 0, L = 0 ; (3.26)

At X = 0, $\frac{\partial L}{\partial X} = 0$; (3.27)

At X= 1, $L = \chi_{\mathcal{M}} - \chi_{s_1}$ (3.28)

Using Laplace transform in the equation (3.25) and solving by the use of the boundary conditions (3.26)-(3.28) and then applying inverse Laplace formula, we get

$$L(X,T) = (\chi_{\mathcal{M}} - \chi_{s_1})\left[1 + 2\pi\sum_{n=1}^{\infty} n(-1)^{n+1}\sin(n\pi X)e^{-(n^2\pi^2 T)}\right] \quad (3.29)$$

By (3.24), we get the mediator concentration is expressed as

$$\theta(X,T) = \left(\frac{\chi_{\mathcal{M}}}{\chi_{s_1}}\right)\left(1 + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)e^{-(n^2\pi^2 T)}}{n^2\pi^2}\right]\right) - \left[\frac{(\chi_{\mathcal{M}}[\zeta(X,T)]}{\chi_{s_1}}\right] \quad (3.30)$$

The normalized flux can be derived as,

$$\Delta = -D(\frac{\partial\zeta(X)}{\partial X})_{X=1} = \frac{-D.s_1{}^T}{r}(1-\sqrt{\chi_{S_1}}coth\sqrt{\chi_{S_1}} - 2\sum_{n=1}^{\infty}\left[e^{-(n^2\pi^2T)}\right]$$

$$+2\pi^2\sum_{n=1}^{\infty}\left[\frac{n^2(-1)^{n+1}e^{-(n^2\pi^2+\chi_{S_1})T}}{(n^2\pi^2+\chi_{S_1})}\right]) \quad (3.31)$$

4. Specifying cases

As X→ 0, the concentration of species and mediator closely reaches at the center of the conducting polymer and it can be expressed as,

$$\zeta(0,T) = \zeta(0,\infty) + 2\pi^2\sum_{n=1}^{\infty}\left[\frac{n^2(-1)^{n+1}e^{-(n^2\pi^2+\chi_{S_1})T}}{(n^2\pi^2+\chi_{S_1})}\right] \quad (4.1)$$

$$\eta(0,T) = \frac{\chi_{S_2}[\zeta(0,T)]}{2\chi_{S_1}} - (\frac{\chi_{S_2}}{2\chi_{S_1}} - 1)(1 + 2\sum_{n=1}^{\infty}\left[(-1)^{n+1}e^{-(n^2\pi^2T)}\right]) \quad (4.2)$$

$$\theta(0,T) = \left(\frac{\chi_{\mathcal{M}}}{\chi_{S_1}}\right)(1 + 2\sum_{n=1}^{\infty}\left[(-1)^{n+1}e^{-(n^2\pi^2T)}\right]) - \left[\frac{(\chi_{\mathcal{M}}[\zeta(0,T)]}{\chi_{S_1}}\right] \quad (4.3)$$

As T→ 0, the concentration of substrates and mediator closely relative to the boundary of the conducting polymer and the analytical expression of the concentrations becomes

$$\zeta(X,0) = \frac{\sinh(\sqrt{\chi_{S_1}}X)}{X\sinh(\sqrt{\chi_{S_1}})} + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)}{(n^2\pi^2+\chi_{S_1})}\right] \quad (4.4)$$

$$\eta(X,0) = \frac{\chi_{S_2}[\zeta(X,0)]}{2\chi_{S_1}} - (\frac{\chi_{S_2}}{2\chi_{S_1}} - 1)\left(1 + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)}{n^2\pi^2}\right]\right) \quad (4.5)$$

$$\theta(X,0) = \left(\frac{\chi_{\mathcal{M}}}{\chi_{S_1}}\right)\left(1 + \frac{2\pi}{X}\sum_{n=1}^{\infty}\left[\frac{n(-1)^{n+1}\sin(n\pi X)}{n^2\pi^2}\right]\right) - \left[\frac{(\chi_{\mathcal{M}}[\zeta(X,0)]}{\chi_{S_1}}\right] \quad (4.6$$

As T→ ∞ in the above non-steady state analytical expression for the concentrations of species s_1, s_2 and mediator becomes steady state and concentrations can be written as

$$\zeta(X,T) = \frac{\sinh(\sqrt{\chi_{S_1}}X)}{X\sinh(\sqrt{\chi_{S_1}})} \quad (4.7)$$

$$\eta(X,T) = \frac{\chi_{S_2}[\zeta(X,T)]}{2\chi_{S_1}} - (\frac{\chi_{S_2}}{2\chi_{S_1}} - 1) \quad (4.8)$$

$$\theta(X,T) = \left(\frac{\chi_{\mathcal{M}}}{\chi_{S_1}}\right) - \left[\frac{(\chi_{\mathcal{M}}[\zeta(X,T)]}{\chi_{S_1}}\right] \quad (4.9)$$

5. Numerical simulation

The non-dimensional form of equations (2.9)-(2.11) that relate to boundary conditions (2.12)-(2.14) were numerically solved in order to test the accuracy of the HPM solution. Graphical comparisons between our analytical findings and numerical results demonstrate the effectiveness of the current approach. The new analytical results with a dimensionless concentration of substrate s_1 and substrate s_2 in its numerical representation are compared in Tables 1 and 2. It offers an acceptable agreement for each parameter setting that is being compared. The highest typical error of 0.06% in the substrate s_1 and 0.3% in the species s_2 separates the prior numerical result from the latest analytical outcome derived by using HPM Method.

Table 1. Comparison among the new analytical results with numerical results for the species s_1 concentration for different reaction diffusion parameter values.

Species s_1 Concentration									
T= 1 and χ_{S_1} = 1				T= 1 and χ_{S_1} = 5			T= 1 and χ_{S_1} = 10		
T	**Numerical result Eqn. (2.9)**	**Analytical result using HPM Eqn. (3.14)**	**% of variation between (2.9) and (3.14)**	**Numerical result Eqn. (2.9)**	**Analytical result using HPM Eqn. (3.14)**	**% of variation between (2.9) and (3.14)**	**Numerical result Eqn. (2.9)**	**Analytical result using HPM Eqn. (3.14)**	**% of variation between (2.9) and (3.14)**
0.1	0.8580	0.8523	0.0057	0.4992	0.4875	0.0117	0.2809	0.2727	0.0082
0.2	0.8626	0.8566	0.006	0.5098	0.4997	0.0101	0.2948	0.2864	0.0084
0.3	0.8691	0.8637	0.0054	0.5295	0.5205	0.009	0.3160	0.3103	0.0057
0.4	0.8785	0.8738	0.0047	0.5584	0.5505	0.0079	0.3506	0.3456	0.005
0.5	0.8908	0.8868	0.004	0.5973	0.5907	0.0066	0.3989	0.3947	0.0042
0.6	0.9060	0.9029	0.0031	0.6473	0.6421	0.0052	0.4639	0.4607	0.0032
0.7	0.9244	0.9221	0.0023	0.7102	0.7065	0.0037	0.5497	0.5475	0.0022
0.8	0.9460	0.9446	0.0014	0.7881	0.7859	0.0022	0.6622	0.6611	0.0011
0.9	0.9712	0.9705	0.0007	0.8836	0.8826	0.001	0.8088	0.8085	0.0003
Average Error %			**0.0037**			**0.0064**			**0.0043**

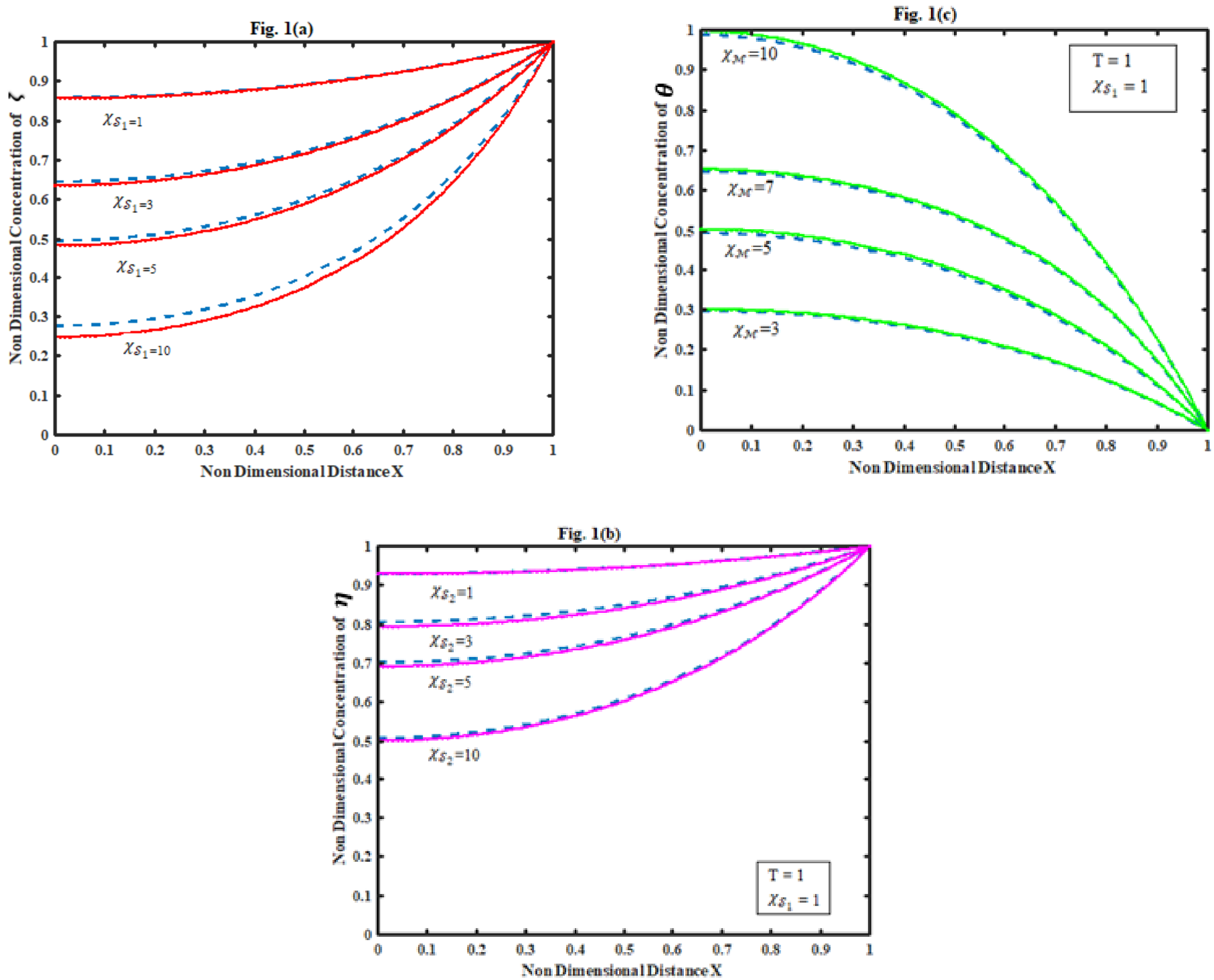
Table 2. Deviation of New analytical solution with Numerical findings of concentration of species s_2 for various values of reaction diffusion parameters

Species s_2 Concentration									
T= 1 , χ_{S_1} = 1 , χ_{S_2} = 0.1				T= 1 , χ_{S_1} = 1 , χ_{S_2} = 1			T= 1 , χ_{S_1} = 1 , χ_{S_2} = 4		
T	**Numerical result Eqn. (2.10)**	**Analytical result using HPM Eqn. (3.22)**	**% of variation between (2.10) & (3.22)**	**Numerical result Eqn. (2.10)**	**Analytical result using HPM Eqn. (3.22)**	**% of variation between (2.10) & (3.22)**	**Numerical result Eqn. (2.10)**	**Analytical result using HPM Eqn. (3.22)**	**% of variation between (2.10) & (3.22)**
0.1	0.9926	0.9926	0.0000	0.9294	0.9261	0.0033	0.7528	0.7046	0.0482
0.2	0.9929	0.9928	0.0001	0.9316	0.9283	0.0033	0.7595	0.7132	0.0463
0.3	0.9932	0.9932	0.0000	0.9350	0.9318	0.0032	0.7709	0.7274	0.0435
0.4	0.9937	0.9936	0.0001	0.9404	0.9369	0.0035	0.7871	0.7476	0.0395
0.5	0.9944	0.9943	0.0001	0.9461	0.9434	0.0027	0.8059	0.7736	0.0323
0.6	0.9952	0.9951	0.0001	0.9538	0.9515	0.0023	0.8348	0.8058	0.029
0.7	0.9962	0.9961	0.0001	0.9632	0.9611	0.0021	0.8637	0.8442	0.0195
0.8	0.9973	0.9972	0.0001	0.9742	0.9723	0.0019	0.9019	0.8892	0.0127
0.9	0.9987	0.9986	0.0001	0.9869	0.9853	0.0016	0.9470	0.9410	0.006
Average Error %			**0.0000**			**0.0027**			**0.3078**

6. Results and discussion

The equations (3.14), (3.22) and (3.30) provides a newly developed analytical formulation of the concentration of species s_1, species s_2 and mediator in simple closed form respectively. The reaction rate constants and time affects the species concentrations . Simple new analytical formulae (3.31) describe how much normalized current is present.

Figure 1. Analytical and numerical evaluations of the solutions for various values of reaction diffusion parameter (a) $\chi_{S_1} = 1, 3, 5, 10$ and T = 1 (b) $\chi_{S_2} = 1, 3, 5, 10$ and for fixed T = 1, $\chi_{S_1} = 1$ (c) $\chi_{\mathcal{M}} = 3, 5, 7, 10$ and for fixed T = 1, $\chi_{S_1} = 1$.



The standardized species s_1 concentration is shown in Figure 1(a) for various amounts of the diffusion parameter χ_{S_1}. The dotted line indicates Analytical results and solid line indicate Numerical results. This graph demonstrates that for each value of $\chi_{\mathcal{M}}$ and χ_{S_1} that are lower or equal to 1, ζ is approximately comparable to 1. As the concentration of substrate S_1 goes down, χ_{S_1} increases. The concentration of species s_1 reach the peak value at the large amount of the non-dimensional distance in the range of X≥ 0.9.

Figure 1(b) shows that the concentration of substrate S_2 for numerous values of χ_{S_2} depends on the constant value of χ_{S_1}.The concentration slowly decreases whenever the diffusion parameter χ_{S_2} increases. At the time T = 1, the concentration of species s_2 reaches the constant state for very small amount of reaction rate constant $\chi_{S_2} \leq 1$.

The series of normalized concentration profiles for a mediator is present in Figure 1(c) for various values of the $\chi_{\mathcal{M}}$ and χ_{S_1} reaction diffusion parameters. All values of $\chi_{\mathcal{M}}$ and χ_{S_1} that are both less than or equal to 1 can be deduced that it is substantially equal to 1. As θ increases either $\chi_{\mathcal{M}}$ increases.

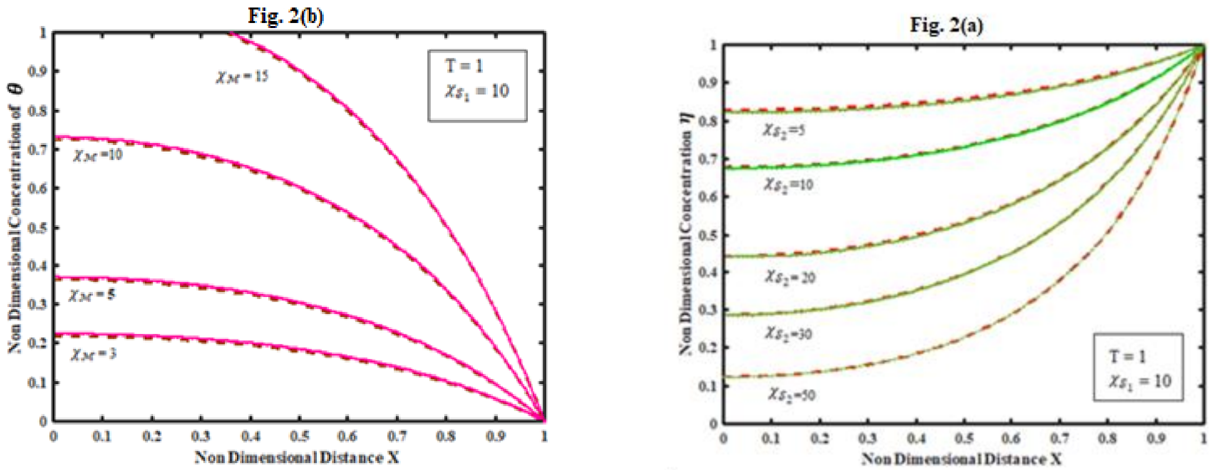


Figure 2. Comparison of the solutions both analytically and numerically for different values of (a) $\chi_{S_2} = 5, 10, 20, 30, 50$ and for fixed T = 1, $\chi_{S_1} = 10$ (b) $\chi_{\mathcal{M}} = 3, 5, 10, 15$ and for fixed T = 1, $\chi_{S_1} = 10$. The numerical solution is shown by solid line and the analytical finding is depicted by the dotted line.

Figure 2(a) which states that η quickly falls down when the diffusion parameter increases as well as the for large value of $\chi_{S_1} \geq 10$. The concentration slowly falls down and reaches the steady state for very large value of reaction rate constant $\chi_{S_2} \geq 50$. That is, the concentration of species s_2 is inversely proportional to the reaction rate constant χ_{S_2}. As the very large amount of non-dimensional distance at X = 1, the concentration attains its maximum value and the concentration falls for X≤ 1. According to the range X≤0.1, the mediator concentration is uniform. That is the inclined curve turned into the straight line.

Figure 2(b) delivered that the concentration of mediator rises for all large values of diffusion parameter $\chi_{\mathcal{M}}$. For the maximal value of reaction rate constant, the concentration is perpendicular to the dimensionless distance X. The concentration of mediator approaches the stable state for the reaction rate constant $\chi_{\mathcal{M}} \geq 10$. The influence of the parameter $\chi_{\mathcal{M}}$ which is directionally proportional to the concentration of mediator. The analytical and numerical values are coincide for increasing values of the reaction rate constant $\chi_{\mathcal{M}}$.

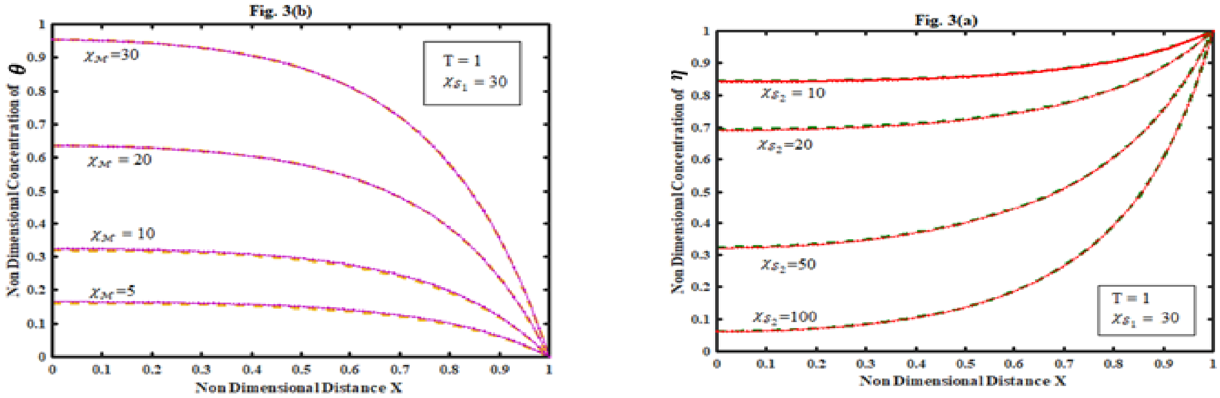


Figure 3. The analytical solutions compare to the numerical findings for different values of (a) $\chi_{S_2} = 10, 20, 50, 100$ and for fixed T = 1, $\chi_{S_1} = 30$ (b) $\chi_{\mathcal{M}} = 5, 10, 20, 30$ and for fixed T = 1, $\chi_{S_1} = 30$. The solid line represents Numerical findings and dotted line indicates Analytical findings.

Figure 3(a) illustrates the intricate relationship between the species s_1 concentration and the reaction rate constant χ_{S_2} and for fixed $\chi_{S_1} = 30$. This representation shows that when the nondimensional distance increases, the concentration drops with a decreasing parameter χ_{S_2}. The variation of the concentration profile also rises with an increase in total concentration. As a result, when χ_{S_2} is al lowest, the species concentration approaches zero. The relationship between the species diffusion parameter χ_{S_2} and the concentration is inversely correlated whereas the species diffusion coefficient is directly correlated.

As seen in figure 3(b), the fluctuation of mediator concentration for various system characteristics is approximated using Eqn.(3.30) and the results are compared to numerical data. The rate of progress at which mediator is extracted from the film drops when the diffusion parameter for mediator $\chi_{\mathcal{M}}$ improves over the layer interface. It can be deduced that $\chi_{\mathcal{M}}$ is in reverse proportion to mediator concentration, meaning that when the diffusion parameter rises, the substrate diffusion coefficient declines or the layer thickness grows.

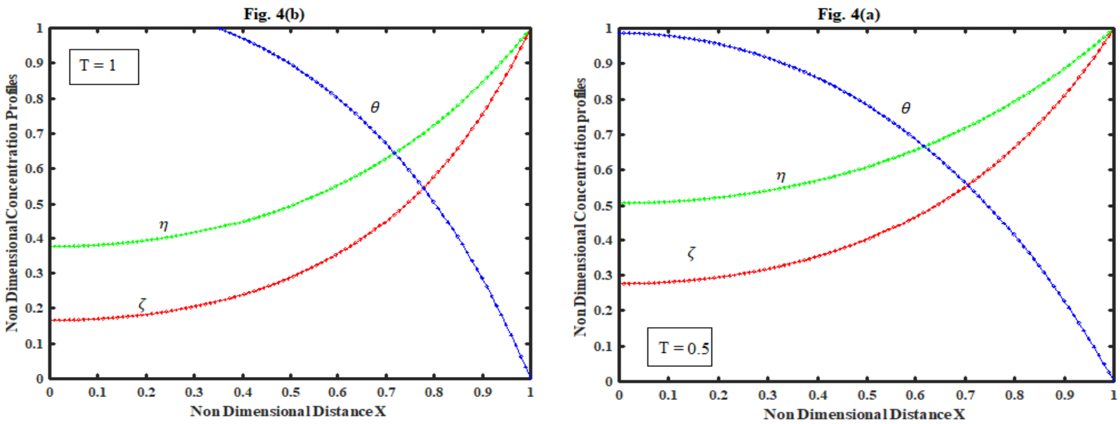


Figure 4. Graph concentration profiles of species s_1, s_2 and mediator versus dimensionless time T.

Figure 4(a) and 4(b) represent the comparison of concentration of species s_1, s_2 and mediator with the various values of non-dimensional time. The concentration of s_1 and s_2 falls down as the dimensionless time increases. As well as the mediator concentration grows up for all greater amount of time. It depicts that the concentration of mediator inversely proportional to the species concentration depends on the increasing value time.

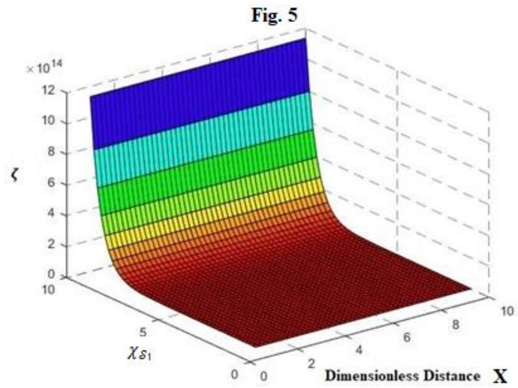


Figure 5. Plot of Three-dimensional substrate concentration s_1 versus dimensionless distance X and various values of diffusion parameter $\chi_{\mathcal{S}_1}$.

Figure 5 indicates the three-dimensional representation of concentration of species for various diffusion parameter versus dimensionless distance. It evident that the dimensionless diffusion parameter increases, the concentration of species gradually decreases depends on the distance X.

7. Conclusion

The system of nonlinear reaction diffusion equations in the spherical ultramicroelectrodes alongside conducting polymer modification at non-steady state have been determined analytically in the present study. Homotopy Perturbation Method is used to achieve the closed analytical formulation of concentration of species, mediator and current. The non-steady state current response is provided in intuitively by a novel analytical expression. The kinetic properties of the spherical ultramicroelectrodes will be discovered by the excellent analytical outcomes. These analytical findings allow one to qualitatively evaluate the characteristics of spherical ultramicroelectrodes with polymer modification. Concerning other analytical procedures, this method is clear-cut, has a straightforward solution, and produces precise results. This technique can solve other boundary value issues in the physical and chemical sciences without difficulty.

Nomenclature

$\mathfrak{D}_{\mathcal{S}_1}$	Diffusion coefficient of species s_1 $\mu m^2/s$	$\chi_{\mathcal{S}_1}$	Dimensionless diffusion parameter for s_1
$\mathfrak{D}_{\mathcal{S}_2}$	Diffusion coefficient of species s_2 $\mu m^2/s$	$\chi_{\mathcal{S}_2}$	Dimensionless diffusion parameter for s_2
$\mathfrak{D}_{\mathcal{M}}$	Diffusion coefficient of mediator $\mu m^2/s$	$\chi_{\mathcal{M}}$	Dimensionless reaction parameter
s_1	Concentration of species μm	ζ	Dimensionless Concentration species s_1
s_2	Concentration of species μm	η	Dimensionless concentration of species s_2
m	Concentration of oxidized mediator μm	θ	Dimensionless concentration of mediator
ρ	Biomolecular rate constants ms	X	Dimensionless distance
u	Distance from the electrode μm	T	Dimensionless Time

m_T	Total concentration of mediator & Substrate	r	Layer thickness
s^T	Bulk concentration of substrate μm	$\mathbb{K}$	Partition coefficient
$\mathcal{C}_{\mathfrak{J}}$	Net flux	Δ	Dimensionless normalized current

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