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Mathematical Modeling in Electrochemical Reactions of Homogeneous Catalysis "Split Waves" on the Rotating Disc Electrode

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ABSTRACT

A mathematical modeling of the electrochemical reactions at a rotating disc electrode is delivered. The pattern is constructed on stationary nonlinear diffusion equation associated to enzymatic reaction of the Michaelis-Menten kinetics. We described analytically nearly approximate appearance pertaining to substrate concentration profile for entirely possible significances of the reaction diffusion parameters K_m are K_{cat} at the RDE by employing homotopy perturbation method (HPM). The significance of few parameters is given in detail, leading to the ideas which can recover the analytical performance.

Keywords: Michaelis-Menten kinetics; Homotopy Perturbation Method; Mathematical Modeling; Analytical solution; Rotating disc electrode; Electrochemical reactions.

1. INTRODUCTION

RDE (Rotating Disk Electrode) is made from a disk of electrode material integrated in an insulating material rod. The electrode is incorporated into a motor and revolved at a specific frequency. We have exposed in a recent article[1], the technique which is used to establish the nature of curves of current-voltage of the rotating disc electrode is to be computed in favour of catalytic (EC') along with the associated mechanisms. Specifically, here the potential of half-wave was originated to extremely be sensitive in the speed of disc rotation as well as concentrations of the mediator and substrate used. The established concept was rooted which is mentioned in Hale-transformation [2-4] that employs in the non-linear space grid of the model

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processes developing inside the diffusion layer of the electrode. Moreover this is originated in the direction of success while the mechanisms scrutinized progress by moderate otherwise leisurely rates. Contrastly, Saveant et.al [5] utilized the depiction of EC' processes in the rotating discs to the Nernst diffusion layer model: it presumes so as to the kinetics is consequently fast so as to the explicit consideration of convection is ignored. An significant and presently topical kind of electrode reaction is named as catalytic (EC') mechanism where the electro generated species (the ''mediator'') oxidizes otherwise decreases few supplementary solution species (''the substrate'') owing to reactivation of the original electro active material that may be able to undertake, in additional the electron transfer ocurrs on the electrode. The progression has consequence together with synthesis as well as kinetic characterization to the reaction mediates [6-10]. Its unpretentious technique, the mechanism is well-explained by the resulting kinetic scheme and in Fig.1.is represented it's mechanism.

$$A + e^- \leftrightharpoons B \tag{I}$$

$$B + Y \rightarrow A + \text{products} \tag{II}$$

The transfer on electron is supposed to be electrochemically reversible in addition to Y is frequently occupied to be in surplus with intention that the chemical step follows pseudo- first –order kinetics [10].

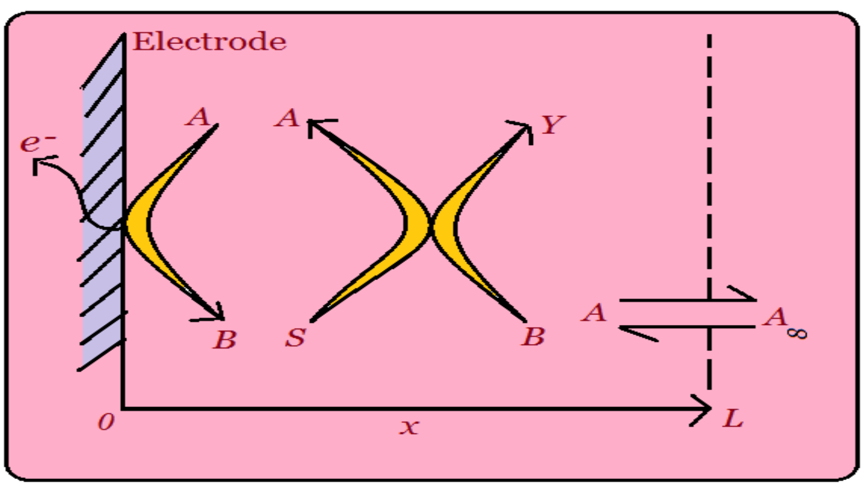

Fig:1 Schematic representation Reaction of EC'

To the greatest our facts, no simple analytical expression for concentration of species A, B in addition to that Y of reactions (I) and (II) in a rotating disc electrode for appropriate values of the

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parameters has been described. The determination of the statement is to develope the approximate expression of concentrations analytically by Homotopy perturbation method. This simple analytical expression is very abundant beneficial to the electrochemical scientists in support of the analysis in the experimental data.

2. MATHEMATICAL FORMULATION OF THE BOUNDARY VALUE PROBLEM

Consider the following coupled mass transport equations [11]:

$$\frac{\partial a}{\partial t} = D\frac{\partial^2 a}{\partial z^2} + Cz^2\frac{\partial a}{\partial z} + k_{(\mathrm{II})}yb \tag{1}$$

$$\frac{\partial b}{\partial t} = D\frac{\partial^2 b}{\partial z^2} + Cz^2\frac{\partial b}{\partial z} - k_{(\mathrm{II})}yb \tag{2}$$

$$\frac{\partial y}{\partial t} = D\frac{\partial^2 y}{\partial z^2} + Cz^2\frac{\partial y}{\partial z} - k_{(\mathrm{II})}yb \tag{3}$$

Here we have considered all the species of the diffusion coefficient to be identical and equivalent to D. Also t represents the time and z denotes the distance normal to the electrode surface, $k_{(\mathrm{II})}$ refers the rate of constant to the reaction (II) . Here Cz^2 defines the convective flow normal and near to the electrode $(C = 8.032\omega^{\frac{3}{2}}\upsilon^{\frac{-1}{2}}; \omega$ is the speed of disc rotation described by Hz; υ is the kinematic viscosity given by cm^2s^{-1}). We observe that there is refusal hypothesis is completed in the direction of the relative magnitudes of a along with y.

The boundary conditions of the equations (1) to (3) are given below:

If $z = 0$ $\quad a = be^{\phi}$ $\quad$ (where ϕ is the potential parameter) (4)

$$D\left.\frac{da}{dz}\right|_{z=0} = -D\left.\frac{db}{dz}\right|_{z=0} \tag{5}$$

$$D\left.\frac{dy}{dz}\right|_{z=0} = 0 \tag{6}$$

when $z \to \infty$: $\quad a \to a^*$ (7)

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$$b \to 0 \tag{8}$$

$$y \to y^* \tag{9}$$

3. DIMENSIONLESS MODEL

With the purpose of make the non-linear PDE equations (1), (2) and (3) dimensionless by defining the resulting parameters[11]:

$$a^* = \frac{a}{\xi},\ b^* = \frac{b}{\xi},\ y^* = \frac{y}{\xi},\ z^* = \frac{z}{\xi},\ t^* = \frac{tD}{\xi^2},\ \psi = \frac{k\xi^3}{D},\ \theta = \frac{c\xi^3}{D} \tag{10}$$

Now the equations (1) - (3) in the dimensionless preparation as below:

$$\frac{\partial a^*}{\partial t^*} = \frac{\partial^2 a^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial a^*}{\partial z^*} + \theta y^* b^* \tag{11}$$

$$\frac{\partial b^*}{\partial t^*} = \frac{\partial^2 b^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial b^*}{\partial z^*} - \theta y^* b^* \tag{12}$$

$$\frac{\partial y^*}{\partial t^*} = \frac{\partial^2 y^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial y^*}{\partial z^*} - \theta y^* b^* \tag{13}$$

In steady-state, the equations (11) - (13) as follows

$$\frac{\partial^2 a^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial a^*}{\partial z^*} + \theta y^* b^* = 0 \tag{14}$$

$$\frac{\partial^2 b^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial b^*}{\partial z^*} - \theta y^* b^* = 0 \tag{15}$$

$$\frac{\partial^2 y^*}{\partial z^{*2}} + \psi z^{*2}\frac{\partial y^*}{\partial z^*} - \theta y^* b^* = 0 \tag{16}$$

with boundary conditions:

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If $z^* = 0 \quad a^* = b^* e^{\phi}$ (17)

If $z^* = 0$, $\dfrac{da^*}{dz^*} = -\dfrac{db^*}{dz^*}$ and $\dfrac{dy^*}{dz^*} = 0$ (18)

If $z^* \to \infty$, $a^* = 1, b^* = 0$ and $y^* = 1$ (19)

5. ANALYTICAL SOLUTION TO THE CONCENTRATION BY HOMOTOPY PERTURBATION METHOD

Now a days, HPM is frequently working to resolve many analytical problems. Moreover, many groups established the proficiency and appropriateness of that HPM designed for resolving non-linear expressions as well as others electrochemical related problems [12-14]. In latest, several authors have employed HPM for solving several problems also make the competence of the HPM to identify the non-linear constructions as well as explaining several physics and also engineering problems [12-17]. This technique known as the mixture of homotopy in topology along with the methods of classic perturbation[18-21]. The HPM preserves the uniqueness of the applicabiliity, accurateness in addition to effectiveness also. The HPM [22-24] denotes the imbedding parameter *p* similar to the slight parameter, moreover just a very few iterations be required to analyse the asymptotic solution, we have obtained the approximate results of the equations (14) -(19) by homotopy perturbation method as given below:

$$a^*(z^*) = \frac{-0.3733\Gamma\left(\frac{1}{3}, \psi \frac{z^{*3}}{3}\right)}{(1+e^{\phi})} + 1 \tag{20}$$

$$b^*(z^*) = \frac{0.3733\Gamma\left(\frac{1}{3}, \psi \frac{z^{*3}}{3}\right)}{(1+e^{\phi})} \tag{21}$$

$$y^*(z^*) = 1 \tag{22}$$

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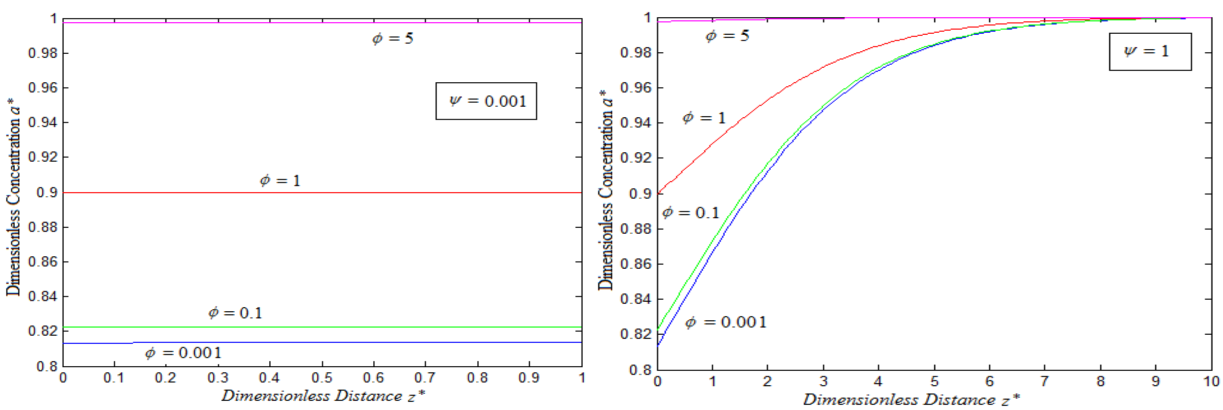
6. RESULTS AND DISCUSSION

Here,Equations (20)-(22) signify the easy and new expressions in the direction of the steady-state concentrations analytically of the rotating disc electrode where the electron transfer stage is supposed to electrochemically reversable designed using Homotopy Perturbation Method in support of the boundary conditions (17)-(19).Variation in dimensionless parameter ϕ can be archived by fluctuating alternative parameter Ψ. The parameter Ψ depends on the primary concentration. Figures (2a-2b) repersent incidental that the value of concentration a* increases if the value of ϕ rises for the fixed values of Ψ. For huge value of dimensionless parameter ϕ (> 5) the concentration remains constant. Figures (3a-3b) represent the product concentration b* for different values of ϕ and for few fixed values of Ψ. When the dimensionless parameter ϕ decreases, the concentration b* gradually increases moreover reaches the constant level. Figure:4 shows the concentration profile a* and b* verses dimensionless distance z* for different significances of ϕ and Ψ. Form figure 4, it is accomplished that dimensionless substrate concentration a^* increases and approaches its extreme value If the dimensionless parameter ψ increases and dimensionless product concentration b^* decreases and reaches its lowest value when the dimensionless parameter ψ increases. All over the reaction area, the concentration y^* remains same and it always one for any value of parameters ψ and ϕ.



(a) **(b)**

Fig. 2--- Scheme of dimensionless concentrations a^* versus dimensionless distance z^* while the dimensionless parameters (a) $\psi = 0.001$ (b) $\psi = 1$ with $\phi = 0.001, 0.1, 1$ and 5 using Eqn. (21).

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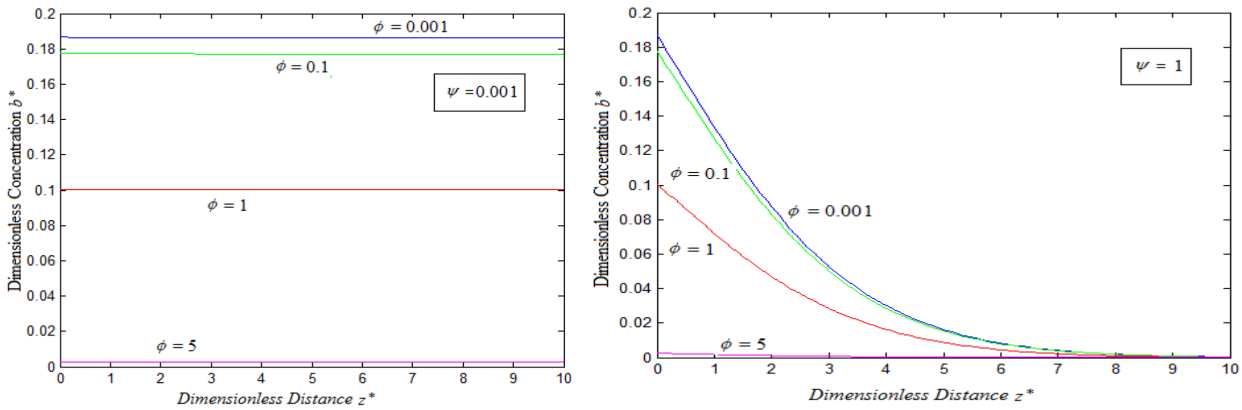

(a) **(b)**

Fig 3.--- Plotting of dimensionless concentrations b^* versus dimensionless distance z^* while the dimensionless parameters (a) $\psi = 0.001$ (b) $\psi = 1$ with $\phi = 0.001, 0.1, 1$ and 5 using Eqn. (21).

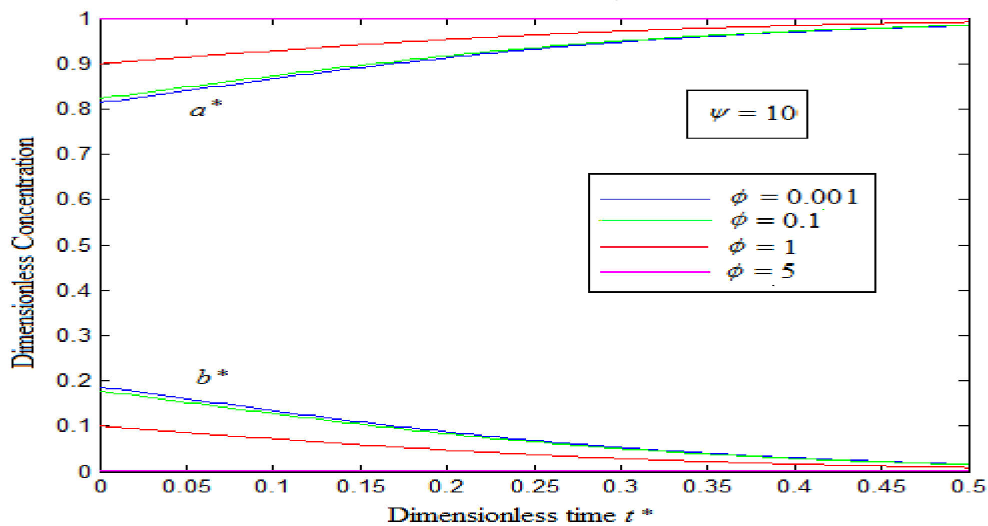

Fig 4.--- Graphical reperesentation of dimensionless concentrations a^* and b^* versus dimensionless distance z^* while the dimensionless parameters $\psi = 10$, $\phi = 0.001, 0.1, 1$ and 5 using Eqns. (20) and (21).

7. CONCLUSION

A nonlinear system of differential equations in electro chemical reactions in rotating disc electrode is explained analytically. This analytical approximate expressions relating to the concentration of species in favor of every value of the parameters are found by using Homotopy perturbation method. This analytical outcome assists for the improved realizing of the model. In forthcoming, the model can be prolonged on behalf of the non-steady reaction diffusion equations.

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