CHAPTER I

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1.1 MATHEMATICAL MODELING

Mathematical modeling is an art of translating the problems from an application area into tractable mathematical formulations. Mathematical modeling is indispensable in many applications. It is a successful source to reach many further applications. It gives accuracy and solution for problems, and it enables a thorough understanding of the system model. Mathematical modeling also prepares the way for a better designing or control of a system [1]. Mathematical models are useful experimental tools for building and testing theories, assessing quantitative conjectures, answering specific questions, determining sensitivities to change in parameter values and estimating key parameters from data [2]. Modeling is an essential and inseparable part of all scientific activity, and many scientific disciplines have their own ideas about specific types of modeling. A model is a simplified abstract view of the complex reality. A scientific model represents empirical objects, phenomena, and physical processes in a logical way.

- Models are abstractions of reality.
- Models are a representation of a particular thing, idea, or condition.
- Mathematical models are simplified representations of some real world entity can be in equations or computer code are intended to mimic essential features while leaving out inessentials.
- Mathematical models are characterized by assumptions about:
Variables (the things which change)

Parameters (the things which do not change).

1.2 PROCESS OF MATHEMATICAL MODELING AND DIFFERENTIAL EQUATIONS

One can think of mathematical modeling as an activity or process that allows a mathematician to be a chemist, an ecologist, an economist, a physiologist. Instead of undertaking experiments in the real world, a modeller undertakes experiments on mathematical representations of the real world. The process of mathematical modeling is clearly represented diagrammatically in Fig1.

![Diagram](image)

Fig1. Process of mathematical modeling

The modeling process is a series of steps taken to convert an idea first into a conceptual model as well as into a quantitative model.

- A conceptual model represents our ideas about how the system works. It is expressed visually in a model diagram, typically involving boxes (state variables) and arrows (material flows or causal effects).
- Equations are developed for the rates of each process and are combined to form a quantitative model consisting of dynamic (i.e., varying with time) equations for each state variable.
- The dynamic equations can then be studied mathematically or to be translated into computer code to obtain numerical solutions for state variable trajectories.

Over the past decade there has been an increasing demand for suitable material in the area of mathematical modeling as applied to science but now more flexible and cost effective approaches are available for greater use of mathematical modeling and computer simulation [3]. It could be argued that, ordinary differential equations and partial differential equations are key areas of mathematical modeling. Provided that the model formulation is successful in producing an ODE, PDE or a primal/dual linear programming (L.P.) problem, there is a strong possibility of successful solution because of the wealth of appropriate analytical and numerical techniques.

1.3 NONLINEAR DIFFERENTIAL EQUATIONS

A differential equation is an equation for an unknown function that contains not only the function but also its derivatives. In general, the unknown function may depend on several variables and the equation may include various partial derivatives. Non-linear phenomena play a very important role in various scientific and engineering fields, such as fluid mechanics, plasma physics, optical fibers, solid state physics, chemical physics and geochemistry. Exact (closed-form) solution of non-linear reaction diffusion equations plays an
important role in the proper understanding of qualitative features of many phenomena and processes in various areas of natural science.

Particularly in physics, non-linear waves are encountered in numerous domains such as fluid mechanics [4], solid-state physics [5], plasma physics [6] and chemical physics [7]. New names like solitons, kinks, breathers, etc. are new commonly used in the vast literature [8] dealing with this subject. Unfortunately these topics are treated only in advanced courses and can rarely be found on an introductory level. Therefore, simple techniques and methods are needed to investigate these phenomena and to make them accessible for undergraduate study.

In chemistry, non-linear reaction-diffusion model and their study arise in various contents. Among them mention may be made of polymer electrode modifies with multilayered enzyme system [9], electrodes modified with nanostructure porous film [10]. In the above all fields the dimensionless non-linear reaction diffusion equation is of the form

\[
\frac{\partial S}{\partial \tau} = \nabla^2 S - f(R, \tau, S, P) \\
\frac{\partial P}{\partial \tau} = \nabla^2 P + g(R, \tau, S, P)
\]  

(1.1)

where \( S \) and \( P \) represent the dimensionless concentrations of the substrate and product, \( \tau \) represents the dimensionless time and \( R \) is the dimensionless radial co-ordinate of the particle. The first term on the right hand side of the above equation accounts for active species (substrate) diffusion, whereas the second term \( f(R, \tau, S, P) \) and \( g(R, \tau, S, P) \) represents the homogeneous reaction term (non linear term), generally polynomial in the concentrations and time. In
the subsequent chapters of this thesis, the behaviour of the system is considered with a CE mechanism.

1.4 MATHEMATICAL MODELING AT PLANAR ELECTRODE FOR THE CE MECHANISM

Electrochemistry has come a long way from the classical areas of physical chemistry. During this century, especially in electroanalytical chemistry, one can visualize two major contributing factors for this development. One is, the advances made in the electronic instrumentation, the second factor is the advances in mathematical modelling of the electrochemical processes, coupled with the numerical calculations and simulation. The initial boundary value problem which has to be solved in this case can be written in the dimension form as follows [11]:

\[
\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - k_f a + k_b b = 0
\]  \hspace{1cm} (1.2)

\[
\frac{\partial b}{\partial t} = D \frac{\partial^2 b}{\partial x^2} + k_f a - k_b b = 0
\]  \hspace{1cm} (1.3)

Where \( a \) and \( b \) denote the concentration of the species \( A \) and \( B \). \( x \) and \( t \) stand for space and time, respectively. \( \kappa_f \) and \( \kappa_b \) are described the forward and backward rate constants respectively. The boundary conditions reduce to

\[ t = 0; \ a = a_0; \ b = b_0 \]  \hspace{1cm} (1.4)

\[ x = l; \ a = a^*; \ b = b^* \]  \hspace{1cm} (1.5)

\[ x \to \infty; \ a \to a_0; \ b \to b_0 \]  \hspace{1cm} (1.6)
where $a_0$ and $b_0$ are the bulk concentrations of the species $A$ and $B$, $a'$ and $b'$ denote the concentrations at electrode surface. Ian Streeter et al. [11] derived the steady-state solution for the above equations (1.2) and (1.3). However, to the best of our knowledge, no purely analytical expressions for the non-steady-state concentrations of these CE mechanisms have been reported. In this thesis, the above partial differential equations (1.2) and (1.3) were solved analytically by Homotopy perturbation method.

1.5 MATHEMATICS MODELING OF COMPLEXES OF ARBITRARY LABILITY

Diffusion coupled with chemical reactions in the solution is widely used in electroanalysis and mechanistic electrochemistry for its many favorable attributes in an electrochemical experiment. In complexes of arbitrary lability [12], the dimensionless form of non-linear reaction diffusion equations with the mixed boundary conditions may be written as follows:

\[
\begin{align*}
\frac{\partial u}{\partial \tau} &= \frac{\partial^2 u}{\partial \chi^2} + \kappa_1 (v - u) \\
\frac{\partial v}{\partial \tau} &= \varepsilon \frac{\partial^2 v}{\partial \chi^2} + \kappa_1 (u - v)
\end{align*}
\]  

(1.7) (1.8)

\[
\begin{align*}
u(\chi,0) &= 1, \quad v(\chi,0) = 1 \\
u(1,\tau) &= 1, \quad v(1,\tau) = 1 \\
u(0,\tau) &= 0, \quad [\frac{\partial v}{\partial \chi}]_{x=0} = 0
\end{align*}
\]  

(1.9) (1.10) (1.11)

where $u$ represents the dimensionless concentrations of metal M and $v$ represents the dimensionless concentrations of complex ML. $\chi$ and $\tau$
represent the dimensionless distance and time respectively. $\kappa_1$ and $\kappa_2$ are the dimensionless rate constants. Salvador and co-workers [12] formulated the problem for the steady-state reaction-diffusion problem at an active planar surface for a finite diffusion region using a reaction layer approximation. However, to the best of our knowledge, no purely analytical expressions of concentrations for the non-steady state planar reaction-diffusion problem of a species that forms a complex have been reported. We adopt the Homotopy perturbation method (HPM) to present the approximate analytical expressions for the concentrations of the species of the metal ion and the complex for the non-steady state condition corresponding to small and medium values of the parameters. Simple expression of current is also reported.

### 1.6 MATHEMATICAL MODELLING IN IMMobilIZED GLUCOSE ISOMERASE OF PACKED-BED REACTORS

Pore networks are frequently used in the modelling of transport and reactions in porous materials. By representing the void space with a pore of idealised geometry, usually a cylindrical pore, the equations for diffusion and reaction may be solved. The model describes the mechanism by which glucose enzyme moves from the intermediate complex form to the fructose and back to the intermediate to the complex glucose enzyme. Mitra Dadvar and co-workers [13] formulated the problem for the steady-state response as dimensionless form of non-linear reaction diffusion equations with the boundary conditions may be written as [13]
\[
\frac{d^2 C}{dz^2} - \phi_p^2 \frac{C}{1 + \beta C} = 0
\]  
(1.12)

\[
C = \alpha_1 \text{ when } z = 0
\]  
(1.13)

\[
C = \alpha_2 \text{ when } z = 1
\]  
(1.14)

Where \( C \) is the dimensionless steady state concentration. The parameter \( \phi_p \) denotes Theiele modulus and \( \beta \) denotes the kinetic parameter and \( \alpha_1 \) and \( \alpha_2 \) are the dimensionless constants. However, to the best of our knowledge, till date no general analytical results for the steady-state substrate concentration and current for all values of parameters have been reported. In this thesis the steady-state substrate concentration and the current is derived for small values of parameters using the Homotopy perturbation method.

1.7 QUANTITATIVE ANALYSIS

Quantitative analysis can be done for a number of reasons such as measurement, performance evaluation or valuation of a experimental result. It can also be used to predict real world events. All the problems in physical sciences seeks to understand behavior by using complex mathematical and statistical modeling, measurement and research. By assigning a numerical value to variables, quantitative analysts try to replicate reality mathematically [14].
1.8 OBJECTIVES AND SCOPE OF THE PRESENT INVESTIGATION:

The objectives of the present investigation are as follows:

- To present the approximate analytical expression of non steady-state concentration profile by solving the coupled reaction-diffusion equations in CE mechanism with initial and boundary conditions corresponding to the potential step for all planar electrodes using Homotopy perturbation method.

- To solve the non-linear differential equation analytically for planar, spherical and cylindrical particles with immobilized enzyme and substrate inhibition kinetics. Closed and simple analytical expression for substrate concentration have been derived for all possible values of parameters.

- To develop the mathematical model of the finite planar diffusion in lability of complexes using the variable separable method and Homotopy perturbation method. The exact analytical solution is derived using complex inversion formula.

- To present the mathematical modelling of steady-state concentration and current in immobilized glucose isomerase of packed-bed reactor using Homotopy perturbation method.

1.9 ORGANIZATION OF THE RESEARCH WORK:

This thesis presents theoretical results on the development of mathematical expressions for analytical measurements of physical science problems. Particular emphasis is on mathematical model and quantitative
analysis of linear and non-linear partial differential equations (PDEs) which arise from the combination of mass transport limiting current response for the given mechanism at a microelectrode. The overall objective of the work is to produce analytical, approximate expressions and numerical solutions which predict the evaluation of the substrate and bulk concentrations in space which kinetics of the immobilized enzyme layer. There are two cases when enzyme activity is limited by diffusion of substrate to enzyme such as reaction limitation by external diffusion and internal diffusion. A variety of theoretical and numerical methods are used to obtain mathematical model for the steady state and non steady state conditions for all time scales.

Chapter one presents a short introduction to mathematical modeling and quantitative analysis of non-linear reaction diffusions in physical sciences with typical initial and boundary conditions.

Chapter two presents the analytical expression of non-steady state concentration profiles at planar electrode for the CE mechanism. The Homotopy perturbation method is used to predict the concentrations for all the values of the parameter.

Chapter three explains the substrate concentration in planar, spherical and cylindrical particles with immobilized enzyme and substrate inhibition kinetics using Homotopy perturbation method. These results are compared with numerical results and are found to be in good agreement. The obtained results are valid for whole solution domain.
Chapter four focuses on the theory of coupled system of transient reaction diffusion equations for complexes of arbitrary lability. The exact analytical solution of the reaction diffusion have been derived and compared with numerical simulation. Current is also given in terms of reaction and diffusion layer thickness.

Chapter five describes an analysis of pore networks used in the modeling of transport and reactions in porous materials. The steady-state substrate concentration and the current in closed form, for small values of parameters is derived using Homotopy perturbation method. The analytical results are compared with the numerical results and found to be in good agreement.

Chapter six is the overall conclusions and future directions of the thesis.