CHAPTER II

ANALYTICAL SOLUTIONS OF THE
CONCENTRATION IN A PACKED-BED
IMMOBILIZED ENZYME REACTOR USING
HOMOTOPY PERTURBATION METHOD

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2.1 INTRODUCTION

In many cases, for immobilized enzyme reactors, it is not possible to use the plug-flow model due to cannot suppress potentially disturbing effects such as mass transfer limitations, axial dispersion and bypassing. Therefore, any realistic analysis of the packed-bed enzymatic reactor should include some fundamental aspects of the process such as liquid-phase (external) and the solid-phase (internal) mass transfer, intrinsic kinetic parameters, and reactor hydrodynamics. These physical considerations determine a mathematical model representing reactor behavior as a function of operational conditions [1, 2]. Packed-beds are commonly employed for solid–fluid contacting in heterogeneous catalysis for several reasons: (i) it facilitates the contact and subsequent separation between reactant and catalyst; (ii) it allows reuse of the enzyme without the need for a prior separation; (iii) a continuous mode of operation can be used easily.

Immobilization of enzymes on suitable support materials has resulted in their extended use in batch and continuous bioreactors. For immobilized enzymes, however, there are several factors which affect the observed kinetics that could be significantly different from the intrinsic kinetics of the free enzyme. These factors include interparticle and intraparticle diffusion limitations, steric and conformation effects, the partitioning of substrate between
the support and bulk of the solution, conformation and spatial effects due to the immobilization mechanism which may cause disfiguration of the enzyme and micro-environmental effects due to the interactions of the support on the enzyme-substrate reaction resulting in a change in the enzymatic reaction mechanism.

Lilly et al. [3] proposed a method to characterize packed-bed immobilized enzyme (IME) reactors, in which the exit concentration of substrate consumed is linearly plotted against the logarithm of the exit unconverted fraction of substrate and the apparent Michaelis constant. On the other hand, Peter et al. [4] found that such a plot, made by using experimental data in the packed-bed immobilized β-galactosidase reactor, was deviated from linearity. Although several attempts [5, 6] were made to theoretically interpret the experimental results, no decisive conclusion has been derived because the models introduced were not sufficient. Shiraishi previously derived expressions for the apparent kinetic parameters of IME reactions [7]. Shiraishi studied the design equation for a packed-bed immobilized enzyme reactor is expressed in terms of apparent kinetic parameters and the relationship between the exit concentration of substrate consumed and the logarithm of the exit unconverted fraction of substrate [8].

However, to the best of author’s knowledge, no general analytical results of substrate concentration and effectiveness factor for all values of dimensionless parameters $\alpha$ and $\gamma_E$ have been published. The purpose of this chapter is to derive approximate analytical expressions for the steady-state concentrations for all values of parameters $\alpha$ and $\gamma_E$ using Homotopy perturbation method.

**2.2 MATHEMATICAL FORMULATION OF THE PROBLEM**

The boundary value problems which have to be solved in this case can be written in the following forms [8]:
\[
\frac{D_e}{x^{G-1}} \frac{d}{dx} \left( x^{G-1} \frac{dS}{dx} \right) = \frac{V_m S}{K_m + S} \tag{2.1}
\]

The boundary conditions are as follows:

\[
\frac{dS}{dx} = 0 \quad \text{when} \quad x = 0 \tag{2.2}
\]

\[
D_e \frac{dS}{dx} = k_L (S_b - S) \quad \text{when} \quad x = R \tag{2.3}
\]

The effectiveness factor \( E_f \) can be calculated as

\[
E_f = \frac{G(K_m + S_b)}{R V_m S_b} \left( \frac{De}{dx} \right)_{x=R} \tag{2.4}
\]

We introduce the following set of dimensionless variables:

\[
U = \frac{S}{S_b}, \quad X = \frac{x}{R}, \quad \gamma = \frac{V_m R^2}{De k_m}, \quad \alpha = \frac{S_b}{k_m}, \quad m = \frac{k_f R}{D_e} \tag{2.5}
\]

The governing non-linear reaction/diffusion equations (2.1 to 2.3) are expressed in the following non-dimensional form as:

\[
\frac{d^2 U}{dX^2} + \frac{G - 1}{X} \frac{dU}{dX} = \frac{\gamma E U}{1 + \alpha U} \tag{2.6}
\]

with the boundary conditions:

\[
X = 0, \quad \frac{dU}{dX} = 0 \tag{2.7}
\]

\[
X = 1, \quad \frac{dU}{dX} = m(1 - U) \tag{2.8}
\]
The effectiveness factor is given by

$$Ef = \frac{(1 + \alpha) \frac{dU}{dX} \bigg|_{X=1}}{\gamma_E}$$

(2.9)

### 2.3 ANALYTICAL SOLUTION OF STEADY STATE CONCENTRATION USING HOMOTOPY PERTURBATION METHOD (HPM)

Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [9-12]. This method is a combination in topology and classic perturbation techniques. Ji Huan He used the HPM to solve the Lighthill equation [13], the Duffing equation [14] and the Blasius equation [15]. The idea has been used to solve non-linear boundary value problems, integral equations and many other problems [16-17]. The HPM is unique in its applicability, accuracy and efficiency. The HPM uses the imbedding parameter $p$ as a small parameter and only a few iterations are needed to search for an asymptotic solution. Using this method (see Appendix B and C), we can obtain the following solution to Equations (2.6) to (2.8). For the case of slab ($G = 1$), the concentration of the substrate becomes

$$U(X) = 1 + \gamma_E \frac{X^2}{2} - \frac{(\gamma_E m + 2\gamma_E)}{2m} + \gamma_E \left[ \frac{\alpha}{m} + \frac{1}{6m} + \frac{\alpha}{2} + \frac{1}{24} - \frac{\alpha X^2}{2} - \frac{X^4}{24} \right]$$

$$+ \gamma_E \left[ \frac{1}{2m} + \frac{1}{4} + \frac{1}{m^2} + \frac{1}{2m} - \frac{X^2}{2m} - \frac{X^2}{4} \right]$$

(2.10)

The effectiveness factor is given by
\[ Ef = \frac{(1 + \alpha)}{\gamma_E} \left[ \gamma_E - \gamma_E \left( \frac{1}{6} + \alpha \right) - \gamma_E^2 \left( \frac{1}{m} + \frac{1}{2} \right) \right] \]  

(2.11)

For the case of rod \((G = 2)\), the concentration of the substrate becomes

\[ U(X) = 1 + \frac{\gamma_E^2}{24m^2} \left[ m^2 X^4 - 12mX^2 - 6m^2 X^2 + 20m + 24 + 5m^2 \right] + \frac{\gamma_E}{m} \left[ 2\alpha + \alpha m - \alpha mX^2 \right] \]  

(2.12)

The effectiveness factor is given by

\[ Ef = \frac{(1 + \alpha)}{\gamma_E} \left[ \frac{\gamma_E^2}{24m^2} \left( -8m^2 - 24m \right) - 2\gamma_E \alpha \right] \]  

(2.13)

### 2.4 RESULTS AND DISCUSSION

Figures 1(a)-(b) to 2(a)-(b) represent the normalized steady-state concentration of substrate \(U(X)\) for different values of dimensionless parameters \(\alpha\) and \(\gamma_E\). From this figure 1, it is evident that for the case of slab, the values of the concentration of substrate is constant when \(X = 0.1\) and then increases slowly. From this figure 2, it is obvious that the values of the concentration of substrate decreases when \(X \geq 0.1\). Also, from the figures 1(a)-2(b), it is known that, the concentration of substrate increases when dimensionless parameter \(\alpha\) and \(\gamma_E\) are increases for \(m = 0.01, 1\). The effectiveness factor \(Ef\) for various values of \(\gamma_E\) and \(\alpha\) is plotted in Figures 3 and 4. From these figures, it is obvious that, the values of the effectiveness factor slowly increases when \(\gamma_E\) and \(\alpha\) is increases.

Figures 5(a)-(b) to 6(a)-(b) represent the normalized steady-state concentration of substrate \(U(X)\) for different values of dimensionless parameters \(\alpha\) and \(\gamma_E\) for the case of rod \(G = 2\). From these figures, it is inferred that, the dimensionless concentration \(U(X)\) for
all values of $m$ and $\gamma_E$. The effectiveness factor increases quite rapidly as dimensionless reaction diffusion parameters $\gamma_E$ and $\alpha$ are increases, approaching to high values, which corresponds to internal diffusion controlled processes. Moreover, it is also well known that, a constant value of dimensionless parameters $\gamma_E$ and $\alpha$, the effectiveness factor increases with increasing value of $\gamma_E$ and $\alpha$. The effectiveness factor $Ef$ for various values of $\gamma_E$ and $\alpha$ is plotted in Figures 7 and 8. From these figures, it is apparent that, the value of the effectiveness factor is very small when $\gamma_E$ and $\alpha$ is less than 0.5. When $\gamma_E$ and $\alpha$ are greater than 1, the effectiveness factor is increases.
Figure 1(a-b): Normalised concentration profile $U(X)$ as a function of dimensionless parameter $X$. The concentrations were computed using equation (2.10) for various values of the reaction/diffusion parameter $\alpha$ and for the fixed values of $m=0.01, \gamma_E = 0.1$. 
Figure 2(a-b): Normalised concentration profile $U(X)$ as a function of dimensionless parameter $X$. The concentrations were computed using equation (2.10) for various values of the reaction/diffusion parameter $\gamma_E$ and for the fixed value of $m=1, \alpha = 5$. 


Figure 3: Dimensionless effectiveness factor $Ef$ versus $\alpha$ for various values of $\gamma_E$ for the fixed value of $m = 0.01$.

Figure 4: Dimensionless effectiveness factor $Ef$ versus reaction diffusion parameter $\gamma_E$ for various values of $\alpha$ for the fixed value of $m = 1$. 
Figure 5(a-b): Normalised concentration profile $U(X)$ as a function of dimensionless parameter $X$. The concentrations were computed using equation (2.12) for various values of the reaction/diffusion parameter $\alpha$ and for the fixed value of $m = 0.01, \gamma_E = 0.1$. 
Figure 6(a-b): Normalised concentration profile $U(X)$ as a function of dimensionless parameter $X$. The concentrations were computed using equation (2.12) for various values of the reaction/diffusion parameter $\gamma_E$ and for the fixed value of $m=1$, $\alpha=5$. 
Figure 7: Dimensionless effectiveness factor $E_f$ versus $\alpha$ for various values of $\gamma_E$ for the fixed value of $m = 0.01$.

Figure 8: Dimensionless effectiveness factor $E_f$ versus reaction diffusion parameter $\gamma_E$ for various values of $\alpha$ for the fixed value of $m = 1$. 
2.5 CONCLUSIONS

The time independent non-linear reaction-diffusion equation has been formulated and solved analytically. Analytical expressions for the concentration and effectiveness factor are derived by using the HPM. The primary result of this work is simple approximate calculations of concentration and effectiveness factor for all values of dimensionless parameters $\alpha$ and $\gamma_E$. The HPM is an extremely simple method and it is also a promising method to solve other non-linear equation. This method can be easily extended to find the solution of all other non-linear equations.

2.6 APPENDIX 2.A

In this appendix we outline the basic idea of Homotopy perturbation method. This method has eliminated the limitations of the traditional perturbation methods. On the other hand it can take full advantage of the traditional perturbation techniques, so there has been a considerable deal of research in applying Homotopy technique for solving various strongly nonlinear equations. To explain this method, let us consider the following function.

$$A(u) - f(r) = 0, \quad r \in \Omega$$  \hspace{1cm} (2.1)

with the boundary conditions of

$$B(u, \frac{\partial u}{\partial n}) = 0, \quad r \in \Gamma$$  \hspace{1cm} (2.2)

where $A$, $B$, $f(r)$ and $\Gamma$ denote a general differential operator, a boundary operator, a known analytical function and the boundary of the domain $\Omega$, respectively. Generally speaking, the operator $A$ can be divided into a linear part $L$ and a nonlinear part $N$. Equation (2.1) can therefore, be written as
\[ L(u) + N(u) - f(r) = 0 \] \hspace{1cm} (2.A3)

By the Homotopy technique, we construct a Homotopy \( v(r, p) : \Omega \times [0,1] \rightarrow R \) which satisfies

\[ H(v, p) = (1 - p)[L(v) - L(u_0)] + p[A(v) - f(r)] = 0. \quad p \in [0,1], r \in \Omega \] \hspace{1cm} (2.A4)

or

\[ H(v, p) = L(v) - L(u_0) + pL(u_0) + p[N(v) - f(r)] = 0. \] \hspace{1cm} (2.A5)

where \( p \in [0,1] \) is an embedding parameter, and \( u_0 \) is an initial approximation of equation (2.A1), which satisfies the boundary conditions. Obviously, from equations (2.A4) and (2.A5), we will have

\[ H(v,0) = L(v) - L(u_0) = 0 \] \hspace{1cm} (2.A6)

\[ H(v,1) = A(v) - f(r) = 0. \] \hspace{1cm} (2.A7)

When \( p = 0 \) equation (2.A4) or equation (2.A5) become a linear equation; when \( p = 1 \) it become a non-linear equation. So the changing process of \( p \) from zero to unity is just that of

\[ L(v) - L(u_0) = 0 \text{ to } A(v) - f(r) = 0. \]

We can first use the embedding parameter \( p \) as a “small parameter”, and assume that the solutions of equations (2.A4) and (2.A5) can be written as a power series in \( p \)

\[ v = v_0 + pv_1 + p^2v_2 + ..... \] \hspace{1cm} (2.A8)

Setting \( p = 1 \) results in the approximate solution of equation (2.A1)

\[ u = \lim_{p \rightarrow 1} v = v_0 + v_1 + v_2 + ..... \] \hspace{1cm} (2.A9)

The combination of the perturbation method and the Homotopy method is called the HPM.
2.7 APPENDIX 2.B

Solution of the equation (2.6) for $G=1$ using Homotopy perturbation method.

In this appendix, we indicate how equation (2.10) in this paper is derived. Furthermore, a Homotopy was constructed to determine the solution of equation (2.6) for $G=1$

$$(1-p)\left[ \frac{d^2 U}{dX^2} \right] + p\left[ \frac{d^2 U}{dX^2} + \alpha U \frac{d^2 U}{dX^2} - \gamma U \right] = 0$$

(2.B1)

The initial approximation is as follows:

$$X=0, \quad \frac{dU}{dX} = 0 \quad (2.B2)$$

$$X=1, \quad \frac{dU}{dX} = m(1-U) \quad (2.B3)$$

$$X=0, \quad \frac{dU_i}{dX} = 0 \quad (2.B4)$$

$$X=1, \quad \frac{dU_i}{dX} = m(1-U) \quad \forall \ i = 1, 2, \ldots \quad (2.B5)$$

The approximate solutions of (2.B1) is

$$U = U_0 + pU_1 + p^2U_2 + p^3U_3 + \ldots \quad (2.B6)$$

Substituting equation (2.B6) and into equation (2.B1) and comparing the coefficients of like powers of $p$

$$p^0: \quad \frac{d^2 U_0}{dX^2} = 0 \quad (2.B7)$$
\[ p^1 : \frac{d^2 U_1}{dX^2} + \alpha U_0 \frac{d^2 U_0}{dX^2} - \gamma E U_0 = 0 \]  
\[ (2.8) \]

\[ p^2 : \frac{d^2 U_2}{dX^2} + \alpha U_0 \frac{d^2 U_1}{dX^2} + \alpha U_1 \frac{d^2 U_0}{dX^2} - \gamma E U_1 = 0 \]  
\[ (2.9) \]

Solving the equations (2.7) to (2.9), and using the boundary conditions (2.2) and (2.3), we can find the following results.

\[ U_0(X) = 1 \]  
\[ (2.10) \]

\[ U_1(X) = \frac{\gamma E}{2} + \frac{2\gamma E}{2m} \]  
\[ (2.11) \]

\[ U_2(X) = \gamma E \left[ \frac{\alpha}{m} + \frac{1}{6m} + \frac{\alpha}{2} + \frac{1}{24} - \frac{\alpha X^2}{2} - \frac{X^4}{24} \right] \]
\[ + \gamma E^2 \left[ \frac{1}{2m} + \frac{1}{4} + \frac{1}{m^2} + \frac{1}{2m} - \frac{X^2}{2m} - \frac{X^2}{4} \right] \]  
\[ (2.12) \]

According to the HPM, we can conclude that

\[ U(X) = \lim_{\epsilon \to 1} U(X) = U_0 + U_1 + U_2 \]  
\[ (2.13) \]

Using equations (2.10), (2.11) and (2.12) in equation (2.13), we obtain the final result as described in equation (2.10).

2.8 APPENDIX 2.C

Solution of the equation (6) for \( G = 2 \) using Homotopy perturbation method.

In this appendix, we indicate how equation (2.12) in this paper is derived. Furthermore, a Homotopy was constructed for the equation (2.6) to determine the solution for the case of \( G = 2 \).
\[(1 - p) \left[ \frac{d^2 U}{dX^2} \right] + p \left[ \frac{d^2 U}{dX^2} + \frac{1}{X} \frac{dU}{dX} + \alpha U \frac{d^2 U}{dX^2} + \frac{\alpha U dU}{X} \frac{dU}{dX} - \gamma E U \right] = 0 \quad (2.C1)\]

The initial approximations are as follows:

\[X = 0, \quad \frac{dU}{dX} = 0 \quad (2.C2)\]

\[X = 1, \quad \frac{dU}{dX} = m(1 - U) \quad (2.C3)\]

\[X = 0, \quad \frac{dU_i}{dX} = 0 \quad (2.C4)\]

\[X = 1, \quad \frac{dU_i}{dX} = m(1 - U) \quad \forall \; i = 1, 2, \ldots \quad (2.C5)\]

The approximate solutions of (2.C1) is

\[U = U_0 + p U_1 + p^2 U_2 + p^3 U_3 + \ldots \quad (2.C6)\]

Substituting equation (2.C6) and into equation (2.C1) and comparing the coefficients of like powers of \( p \)

\[p^0 : \quad \frac{d^2 U_0}{dX^2} = 0 \quad (2.C7)\]

\[p^1 : \quad \frac{d^2 U_1}{dX^2} + \frac{1}{X} \frac{dU_0}{dX} + \alpha U_0 \frac{d^2 U_0}{dX^2} + \frac{\alpha U_0 dU_0}{X} \frac{dU_0}{dX} - \gamma E U_0 = 0 \quad (2.C8)\]

\[p^2 : \quad \frac{d^2 U_2}{dX^2} + \frac{1}{X} \frac{dU_1}{dX} + \alpha U_0 \frac{d^2 U_1}{dX^2} + \alpha U_1 \frac{d^2 U_0}{dX^2} + \frac{\alpha U_0 dU_1}{X} \frac{dU_1}{dX} + \frac{\alpha U_1 dU_0}{X} \frac{dU_0}{dX} - \gamma E U_1 = 0 \quad (2.C9)\]
Solving the equations (2.C7) to (2.C9), and using the boundary conditions (2.C2) and (2.C3), we can find the following results.

\[ U_0(X) = 1 \]  
\[ U_1(X) = \frac{\gamma_E X^2}{2} - \frac{\gamma_E}{m} \frac{X}{2} \]  
\[ U_2(X) = \frac{\gamma_E^2 X^4}{24} - \frac{\gamma_E^2 X^2}{2m} - \frac{\gamma_E^2 X^2}{4} - \alpha \gamma_E X^2 - \frac{\gamma_E X^2}{2} + \frac{\gamma_E^2}{m^2} + \frac{\gamma_E^2}{2m} + \frac{2 \alpha \gamma_E}{m} + \frac{\gamma_E}{m} - \frac{\gamma_E^2}{6m} - \frac{\gamma_E^2}{24} \]

According to the HPM, we can conclude that

\[ U(X) = \lim_{p \to 1} U(X) = U_0 + U_1 + U_2 \]  

Using equations (2.C10), (2.C11) and (2.C12) in equation (2.13), we obtain the final result as described in equation (2.12).
### 2.9 APPENDIX 2.D

Nomenclature and Units

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<th>Symbols</th>
<th>Meaning</th>
<th>Usual dimension</th>
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<td>$D_e$</td>
<td>Effective diffusivity of substrate in an IME support</td>
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<td>$Ef$</td>
<td>Effectiveness factor (-)</td>
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<tr>
<td>$G$</td>
<td>Geometric factor; 1, 2 and 3 for a slab, rod and sphere</td>
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<td>kg/m(^3)</td>
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<td>$K_L$</td>
<td>Mass transfer coefficient</td>
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<td>Reactor length</td>
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</tr>
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<td>$R$</td>
<td>Half-thickness of a slab, or radius of a rod or sphere</td>
<td>m</td>
</tr>
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<td>Substrate concentration in an IME support</td>
<td>kg/m(^3)</td>
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<td>Intrinsic maximum reaction rate</td>
<td>kg/m(^3)/s</td>
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