Substrate mass transfer: analytical approach for immobilized enzyme reactions

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Abstract: In this paper, the boundary value problem in immobilized enzyme reactions is formulated and approximate expression for substrate concentration without external mass transfer resistance is presented. He’s variational iteration method is used to give approximate and analytical solutions of non-linear differential equation containing a non linear term related to enzymatic reaction. The relevant analytical solution for the dimensionless substrate concentration profile is discussed in terms of dimensionless reaction parameters $\alpha$ and $\beta$.

1. Introduction

The greater part of chemical transformation inside the cells is carried out by proteins called enzymes. Enzymes accelerate the rate of chemical reaction without being in the process and tend to be very selective with a particular enzyme accelerating only a definite reaction [1]. To understand the role of enzymes kinetics, the researcher has to study the rate of reactions, the temporal behaviors of the various reactants and the conditions which influence the enzyme kinetics. For immobilized enzymes, there are several factors which observed kinetics that could be notably different from the intrinsic kinetic of free enzyme. The extent of external mass transfer limitations depends on the diffusivity of the substrate in the bulk fluid phase, the velocity of the fluid phase over the support pellets, density and viscosity of the fluid phase and the substrate concentration [2,3]. Michaelis-Menten equation is the most common rate expression used for enzyme reaction [4].

A mathematical model of the kinetics of single-substrate-enzyme-catalyzed reactions was first developed by V. C. R. Henri in 1902. Kinetics of simple enzyme–catalyzed reactions is often referred to as Michaelis-Menten kinetics or saturation kinetic [4]. Recently Shiraishi [5] developed a boundary value problem in immobilized enzyme reactions, Substrate concentration by Michaelis-Menten constant. To the best of our knowledge, no rigorous analytical solutions of the model have been reported. The purpose of this communication is to provide the approximate analytical solutions for the dimensionless substrate concentrations without mass transfer resistance for various values of dimensionless reaction diffusion parameters $\alpha$ and $\beta$. 
2. Mathematical model

The following differential equation and associated boundary conditions express the dimensionless substrate concentration \( C \) in the pellet [5]:

\[
\frac{d^2 C}{dX^2} + \frac{g-1}{X} \frac{dC}{dX} = \alpha^2 \frac{C}{1+\beta C}
\]

(1)

at \( X = 0, \frac{dC}{dX} = 0 \) \hspace{1cm} (2)

at \( X = 1, C = 1 \) (without mass transfer resistance) \hspace{1cm} (3)

where \( X \) is the dimensionless distance to the center of the surface of symmetry of the pellet and \( g \) is the pellet shape factor which for slab, cylindrical and spherical pellets respectively. Parameter is a Theile modulus and is a constant viz. ratio of the substrate concentration in the bulk fluid phase and Michaelis constant.

3. Approximate analytical solution of the nonlinear Eqns.(1) using Variational Iteration Method

Under steady state conditions the reaction rate can be evaluated from the concentration profile obtained from the solution of equation (1) by He’s Variational Method. Recently, He’s variational method is often employed to solve several analytical problems. In addition, several groups demonstrated the efficiency and suitability of the VIM for solving non-linear equations and other Enzyme kinetics reaction and boundary value problems, many authors have applied the VIM to solve various physics and engineering problems [6- 8]. This method is basic enzyme kinetics to test the effectiveness of an analytical method. Using He’s Variational Iteration Method (refer Appendix A), we obtained the approximate solutions of the eqns. (1), (2) and (3) as follows

\[
C(x) = l + \frac{x^2}{2(1-g)}[2(1-l)-\alpha^2 l + \alpha^2 \beta l^2] + \frac{x^4}{4(1-g)}[2\alpha^2 \beta(1-l)-(1-l)\alpha^2] + \frac{x^6}{6(1-g)}[\alpha^2 \beta(1-l)^2]
\]

(4)

where \( l = \frac{-(2\alpha^2 \beta - 3\alpha^2 - 12g) - \sqrt{((2\alpha^2 \beta - 3\alpha^2 - 12g)^2 - 8\alpha^2 \beta(2\alpha^2 \beta - 3\alpha^2 + 12g)}}}{4\alpha^2 \beta} \)

(5)

4. Result and Discussion

Equation (4) represents the most general new analytical expressions for the dimensionless substrate concentration \( C \) in the pellet for various values of \( \alpha, \beta \) and \( g \). It satisfies the boundary conditions given in eqns. (2) and (3). From figures 1, 2 and 3, it is inferred that the concentration increases when the distance increases. When \( \alpha, \beta \) and \( g \) are very small and closer to zero, the dimensionless concentrations remains constant and it is equal to one always. When \( \alpha = \beta = 0.01 \) and \( g \) value varies, the concentration is nearer to one.
Figure 1. Dimensionless substrate concentration $C$ versus dimensionless distance $X$ for some fixed values of parameters $\alpha = 0.01, g = 0.0001$ and various values of $\beta$.

Figure 2. Dimensionless substrate concentration $C$ versus dimensionless distance $X$ for some fixed values of parameters $\beta = 0.01, g = 0.0001$ and various values of $\alpha$. 
5. Conclusion
A boundary value problem in immobilized enzyme reactions is formulated and approximate expression for substrate concentration without external mass transfer resistance using He’s variational iteration method is presented. The relevant analytical solution for the dimensionless substrate concentration profile is discussed in terms of dimensionless reaction parameters $\alpha$ and $\beta$ and the pellet shape factor $g$. The He’s variational iteration method is a simple method and it is also a promising method to solve other non-linear equations. This method can be easily extended to find the solution of all other non-linear equations.

Appendix A
In this appendix, we derived the general solution of non-linear reaction diffusion equation (1) using He’s variational iteration method. To illustrate the basic concept of variational iteration method (VIM). We consider the following non-linear partial differential equation

$$L[u(x)] + N[u(x)] = f(x)$$  \hspace{1cm} (A.1)

where $L$ is a Linear operator, $N$ is a non-linear operator and $f$ is a given continuous function. According to the variational iteration method, we can construct a correct functional as follows

$$u_{n+1}(x) = u_n(x) + \int_0^x \lambda [L[u_n(\tau)] + N[\tilde{u}_n(\tau)] - f(\tau)] d\tau$$  \hspace{1cm} (A.2)

where $\lambda$ is a general Lagrange multiplier which can be identified optimally via variational theory. $u_n$ is the $n^{th}$ approximate solution, and $\tilde{u}_n$ denotes a restricted variation, i.e. $\delta \tilde{u}_n = 0$. In is method a trial function (an initial solution) is chosen with some unknown parameters, which is identified after a few
iterations according to the given boundary conditions. Using above variational iteration method we can write the correction functional of equation (1) as follows

\[ C_{n+1}(x) = C_n(x) + \int_0^1 \lambda \left[ s C''(s) + (g-1)C'(s) - \alpha^2 s C(s) + \alpha^2 \beta s C^2(s) \right] ds \]  \hspace{1cm} (A.3) 

where \( s C''(s), \alpha^2 s C(s) \) and \( \alpha^2 \beta s C^2(s) \) considered as restricted variations. i.e \( \delta C_n = 0 \).

\[ \delta C_{n+1}(x) = \delta C_n(x) + \int_0^1 \lambda \left[ (g-1)C'(s) \right] ds \]  \hspace{1cm} (A.4) 

Taking variation with respect to the independent variable \( C_n \)

\[ \delta C_{n+1}(x) = \delta C_n(x) + (g-1)[\lambda \delta C_n(s) - \lambda \int_0^1 \delta C_n(s) ds] \]  \hspace{1cm} (A.5) 

Making the above correction functional stationary.

\[ \delta C_n(x) : 1 + (g-1)\lambda = 0 \] \hspace{1cm} \[ \delta C_n(x) : -(g-1)\lambda' = 0 \] \hspace{1cm} (A.6) 

The above equations are called Lagrange-Euler Equations. The above Lagrange multiplier \( \lambda \) can be identified as

\[ \lambda = \frac{1}{1-g} \] \hspace{1cm} (A.7)

Substituting the Lagrangian multiplier and \( n = 0 \) in the iteration formula (equation (A.3)) we obtain,

\[ C_1(x) = C_0(x) + \int_0^1 \frac{1}{1-g} \left[ s C_0''(s) + (g-1)C_0'(s) - \alpha^2 s C_0(s) + \alpha^2 \beta s C_0^2(s) \right] ds \]  \hspace{1cm} (A.8) 

We assume the initial approximation \( C_0(x) = l + (1-l)x^2 \) \hspace{1cm} (A.9) By the iteration formula (A.8), we have

\[ C_1(x) = l + \frac{x^2}{2(1-g)}[2(1-l) - \alpha^2 l + \alpha^2 \beta l^2] + \frac{x^4}{4(1-g)}[2\alpha^2 \beta(1-l) - (1-l)\alpha^2] + \frac{x^6}{6(1-g)}[\alpha^2 \beta(1-l)^2] \]  \hspace{1cm} (A.10) 

Considering the boundary condition (2) and (3) we identify the unknown constant \( l \) given in equation (5). The remaining compounds of \( C_n(x) \) be completely determined such that each term is determined by previous term using equation (A.8). \( C_1 \) is convergent series we are taking \( C_1(x) = C(x) \).
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