

A New Spectral Method Applied to Immobilized Biocatalyst Model Arising in Biochemical Engineering

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Abstract

The mathematical model of immobilized liver esterase and kinetics by flow calorimetry is discussed. In this paper, we have developed an efficient Legendre polynomial based spectral method to the model. To the best of our knowledge until now there is no rigorous Legendre spectral method has been reported for the above model. Illustrative examples are given to demonstrate the validity and applicability of the proposed method. The numerical results have been compared with modified Adomian decomposition method (MADM) and homotopy analysis method (HAM). Moreover the use of Legendre computational matrix method is found to be simple, accurate, flexible and an efficient tool.

Keywords: Reaction- diffusion equations; Mathematical model; homotopy analysis method; Legendre spectral method; operational matrices; modified Adomian decomposition method

1. Introduction

It has become a powerful tool for having applications in almost all the areas of engineering and sciences such as image coding, edge extraction, weather forecasting, statistical estimation and numerical solutions of ordinary and partial differential equations [1- 2]. Orthogonal functions play an important role in the

solution of nonlinear reaction- diffusion equations. The main aim in the current work is to establish the shifted Legendre polynomials and the operational matrix together with collocation method to discretize the nonlinear reaction- diffusion equation into a system of algebraic equations [2]. Hariharan and his coworkers [4 - 6] introduced the wavelet methods for solving differential equations arising in engineering. Recently, Hariharan and Kannan [7] reviewed the wavelet method for the solutions of reaction-diffusion problem. Boigues Muñoz et al. [31] established more accurate macro-models of solid oxide fuel cells through electrochemical and microstructural parameter estimation. Carlini et al. [32] presented mesophilic fermentation of SOMW in a micro pilot-scale anaerobic digester. Beginning from 1991, wavelet technique has been applied to solve differential equations. Wavelets, as very well-localized functions, are considerably useful for solving differential equations and provide accurate solutions. Hariharan and his coworkers [18-20] have introduced the wavelet based approach for solving the differential equations in science and engineering. The wavelet based approximation methods had been compared with Adomian decomposition method and other classical Recently, Rajaraman and Hariharan [25, 26] had introduced the efficient wavelet based spectral methods to singular boundary value problems and nonlinear reaction-diffusion problems. Hariharan and his coworkers [27-30] had developed the wavelet based approximation methods to differential equations.

2. Mathematical formulation of the problem [11 – 13]

The interaction of enzyme with substrate forms an enzyme-substrate complex (ES) and then converted to transition state (ES^*). It is then getting transformed to enzyme-product (EP) which finally splits into enzyme and product. [14]



where E is the enzyme, S the substrate k_1 is the rate constant for the formation of ES; also k_{-1} is the rate constant for the disassociation of ES back into $E+S$ and k_{cat} is the catalytic rate constant [13]. Assume that glucoamylase was immobilized in porous particles. The temperature difference between the column input and output, ΔT , is measured by thermistors and registered by a computer. The temperature of the system is 303.15 Kelvin and the buffer solution was continuously pumped through the column with constant flow rate of 1ml/min. Initially the buffer solution is replaced by the substrate solution containing 1 – 200 g/l of MDX in 0.1 M acetate buffer (pH 4.7). Two methods were adopted (i) single flow mode (ii) total recirculation mode. The single flow mode was performed with the switching valve 2 opened to the waste [12]. The equation of substrate balance in the particle is calculated from the substrate concentration gradient [12]. The biocatalyst particles are spherical shaped, the material balance reaction diffusion equation is given by:

$$D_e \left[\frac{d^2 S_{sc}}{dr^2} + \frac{2}{r} \frac{dS_{sc}}{dr} \right] - \nu_r = 0 \tag{2}$$

$$S_{sc} = 0 \quad \text{at } t = 0, \quad 0 \leq r \leq 1,$$

$$\frac{dS_{sc}}{dr} = 0 \quad \text{at } t = 0, \tag{3}$$

$$S_{sc} = S_c \quad \text{at } r = R_p,$$

where R_p is the particle radius and $\nu_r = \frac{V S_{sc}}{K_n + S_{sc} + \left(\frac{S_{sc}^2}{K_i} \right)}$ (4)

The parameters are made dimensionless by the following

$$x = \frac{r}{R_p}; \quad U = \frac{S_{sc}}{S_c}; \quad \delta_k = \frac{R_p^2 \nu}{\chi k_e m}; \quad \zeta = \frac{S_c}{k_m}; \quad \tau = \frac{S_c^2}{k_m k_i}$$

where δ_k is the reaction diffusion parameter, x is the dimensionless distance and $U(x)$ is the dimensionless concentration. Here ζ and τ are the saturation parameters.

Eq. (2) becomes

$$\frac{d^2 U}{dx^2} + \frac{2}{x} \frac{dU}{dx} - \frac{\delta_k U}{1 + \zeta U + \tau U^2} = 0 \tag{5}$$

with the boundary conditions

$$U = 1 \quad \text{at } x = 1$$

$$\frac{dU}{dx} = 0 \quad \text{at } x = 0 \tag{6}$$

3. Method of solution using LCMM [3]

The well known Legendre polynomials $P_n(z)$, defined on the interval $[-1, 1]$, have the following properties:

$$P_n(z) = (-1)^n P_n(-z), \quad P_n(-1) = (-1)^n, \quad P_n(1) = 1$$

The analytic form of the shifted Legendre polynomial $P_n^*(x)$ of degree n is given by;

$$P_n^*(x) = \sum_{k=0}^n (-1)^{n+k} \frac{(n+k)!}{(n-k)!(k!)^2 L^k} x^k \quad (7)$$

Let $\omega_L(x) = 1$, and the weighted space $L_{\omega_L}^2(0, L)$ is defined with the following inner product and norm.

$$(u, v)_{\omega_L} = \int_0^L u(x) v(x) \omega_L(x) dx, \quad \|u\|_{\omega_L} = (u, u)_{\omega_L}^{\frac{1}{2}}. \quad (8)$$

The orthogonality condition is of the form [10]

$$\int_0^L P_i^*(x) P_j^*(x) dx = \begin{cases} \frac{1}{2i+1} & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases} \quad (9)$$

The set of the shifted Legendre polynomials forms a complete

$L_{\omega_L}^2(0, L)$ orthogonal system and $\|P_n^*(x)\|_{\omega_L}^2 = \frac{L}{2} h_n = \frac{L}{2n+1}$ is obtained. The

function $u(x)$ which is square integrable in $[0, L]$, may be expressed in terms of shifted Legendre polynomials as;

$$u(x) = \sum_{i=0}^{\infty} c_i P_i^*(x), \quad \text{where the coefficients } c_i \text{ are given by;}$$

$$c_i = \frac{1}{\|P_i^*(x)\|_{\omega_L}^2} \int_0^L u(x) P_i^*(x) \omega_L(x) dx, \quad i = 0, 1, 2, \dots \quad (10)$$

It is suggested the solution $u(x) \in C^m[0, L]$ can be approximated in terms of the first $(m+1)$ terms of shifted Legendre polynomials only as;

$$u(x) = \sum_{i=0}^m c_i P_i^*(x). \quad (11)$$

The method which was suggested is applied when $m=2$, a system of 3 linear algebraic equations follows, out of this 2 from the initial conditions and one from the main equation using the collocation point $x_0=0.5$ which is the root of $P_1^*(x) = 0$ which can be written in the matrix form:

$$U(x) = P(x) A, \quad (12)$$

$$\text{where } P(x) = \begin{bmatrix} P_0^*(x) & P_1^*(x) & P_2^*(x) \end{bmatrix} = \begin{bmatrix} 1 & 2x-1 & 6x^2-6x+1 \end{bmatrix}, \quad (13)$$

$$A = \begin{bmatrix} C_0 & C_1 & C_2 \end{bmatrix}^T \quad (14)$$

Applying this procedure the given nonlinear differential equation takes the following form:

$$\left(P M_{(2)} + 4 P M_{(1)} - \frac{\delta_k P}{1 + \zeta P A^T + \tau(LA)^2} \right) A = 0 \tag{15}$$

where $P = (1 \ 0 \ -0.5)$, $M_{(2)} = \begin{pmatrix} 0 & 0 & 12 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ $M_{(1)} = \begin{pmatrix} 0 & 2 & 0 \\ 0 & 0 & 6 \\ 0 & 0 & 0 \end{pmatrix}$

The initial conditions are

$$P(1)A = 1, \quad P(0)M_{(1)}A = 0 \text{ where } P(0) = (1 \ -1 \ 1) \text{ and } P(1) = (1 \ 1 \ 1)$$

Eqs. (5) and (6) become the following system of linear algebraic equations

$$(1 + \zeta(C_0 - 0.5C_2) + \tau(C_0 - 0.5C_2)^2)(12C_1 + 8C_2) - \delta_k(C_0 - 0.5C_2) = 0 \tag{16}$$

$$C_0 + C_1 + C_2 = 1 \tag{17}$$

$$C_1 - 3C_2 = 0 \tag{18}$$

For various values of δ_k , ζ and τ the wavelet coefficients C_0 , C_1 and C_2 are obtained.

Using MADM $U(x)$ the substrate concentration,

$$U(x) = 1 - \frac{\delta_k}{6(1 + \zeta + \tau)} + \frac{7 \delta_k^2}{360(1 + \zeta + \tau)^3} + \left(\frac{\delta_k}{6(1 + \zeta + \tau)} - \frac{\delta_k^2(1 - \tau)}{36(1 + \zeta + \tau)^3} \right) \left(\frac{x^2}{6} \right) + \left(\frac{\delta_k^2(1 - \tau)}{6(1 + \zeta + \tau)^3} \right) \left(\frac{x^4}{20} \right) \tag{19}$$

The exact solution for the substrate concentration $U(x)$ [12] is

$$U(x) = \frac{\sinh(\sqrt{\delta_k} x)}{x \sinh(\sqrt{\delta_k})} \tag{20}$$

4. Comparison of dimensionless substrate concentration $U(x)$ with numerical solution for various values of δ_k , ζ and τ :

Case (i): Consider $\delta_k=1$ and $\zeta=0$ and $\tau=0$, in Eq. (5). Using the

aforsaid spectral method, one can obtain in the above case, when $m=3$, a system of 4 linear equations is obtained, two of them from the initial conditions and the other two from the main equation using 2 collocation points $x_0 = 0.211325$ and $x_1=0.788675$ which are the roots of $P_2^*(x) = 0$.

Then

$$P(x) = [P_0^*(x) \ P_1^*(x) \ P_2^*(x) \ P_3^*(x)] = [1 \ 2x-1 \ 6x^2-6x+1 \ 20x^3-30x^2+12x-1] \quad (21)$$

$$A = [C_0 \ C_1 \ C_2 \ C_3]^T \quad (22)$$

Applying this procedure to Eq.(15) when $\delta_k = 1$ and $\zeta = 0$ and $\tau = 0$

$$\left(P M_{(2)} + 4P M_{(1)} - \delta_k P \right) A = 0 \quad (23)$$

where $P_{x_0} = [1 \ -0.57735 \ 0 \ 0.38490]$ and $P_{x_1} = [1 \ 0.57735 \ 0 \ -0.38490]$,

$$M_{(1)} = \begin{bmatrix} 0 & 2 & 0 & 6 \\ 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 10 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad M_{(2)} = \begin{bmatrix} 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 60 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$P(0) = [1 \ -1 \ 1 \ -1]$$

The initial conditions are

$$P(1)A = 1, \quad P(0)M_{(1)}A = 0 \text{ where } P(0) = (1 \ -1 \ 1 \ -1) \text{ and}$$

$$P(1) = (1 \ 1 \ 1 \ 1)$$

Eq. (5) becomes the following system of linear algebraic equations for the two collocation points x_0 and x_1

$$[1 + \zeta [C_0 - 0.57735C_1 + 0.3849C_3] + \tau [C_0 - 0.57735C_1 + 0.3849C_3]^2][12C_1 - 34.641C_2] - \delta_k [C_0 - 0.57735C_1 + 0.3849C_3] = 0 \quad (24)$$

$$[1 + \zeta [C_0 + 0.57735C_1 - 0.3849C_3] + \tau [C_0 + 0.57735C_1 - 0.3849C_3]^2][12C_1 + 34.641C_2] - \delta_k [C_0 + 0.57735C_1 - 0.3849C_3] = 0 \quad (25)$$

If $\delta_k = 1$ and $\zeta = 0$ and $\tau = 0$, Eq. (25) and (26) become

$$[12C_1 + 34.641C_2] - \delta_k [C_0 - 0.57735C_1 + 0.3849C_3] = 0 \tag{26}$$

$$[12C_1 - 34.641C_2] - \delta_k [C_0 + 0.57735C_1 - 0.3849C_3] = 0 \tag{27}$$

Using the initial conditions,

$$C_1 - 3C_2 + 8C_3 = 0 \tag{28}$$

$$C_0 + C_1 + C_2 + C_3 = 1 \tag{29}$$

Consider $\delta_k=1$, $\delta_k=5$ and $\delta_k=10$ in Eq. (5) together with the initial conditions gives

$$U(x) = 0.0248x^3 + 0.142286x^2 - 0.000166x + 0.8509,$$

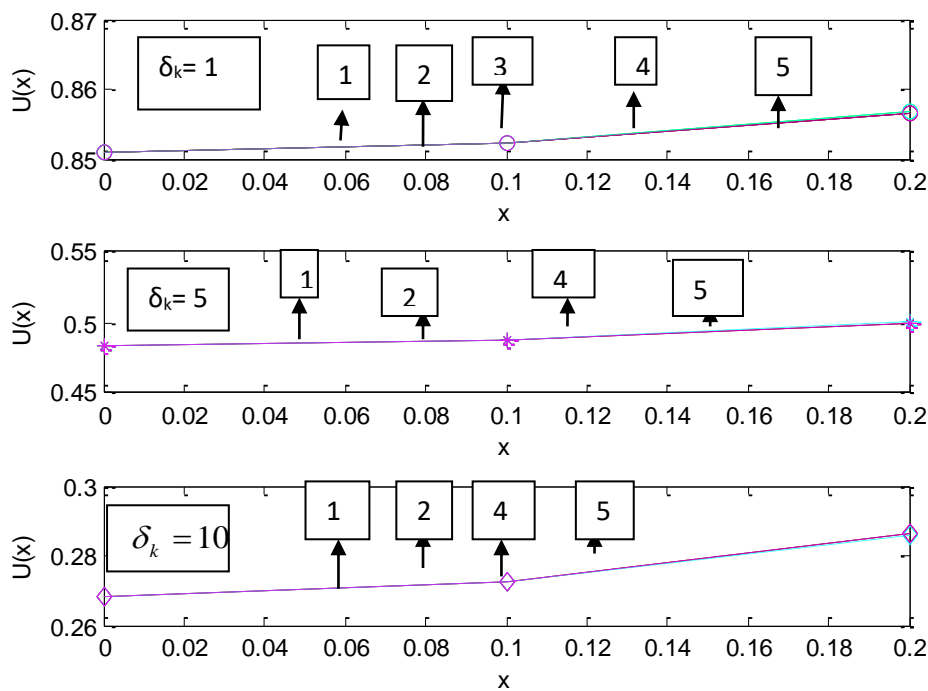
$$U(x) = 0.4062x^2 + 0.0028x + 0.4834 \text{ and}$$

$$U(x) = 0.44576x^2 - 0.00002x + 0.26829 \text{ respectively by LCMM.}$$

Table 1: Comparison between the MADM and LCMM for Eq.(5) and (6) when $\zeta = 0$ and $\tau = 0$

$\delta_k = 1$						$\delta_k = 5$			
x	Simulation	MADM	LCMM (m = 2)	LCMM (m = 3)	Exact Solution	Simulation	MADM	LCMM	Exact Solution
0.0001	0.8509	0.8509	0.85089	0.85089	0.8509	0.4835	0.4835	0.4834	0.48346
0.1	0.8523	0.8523	0.85233	0.85233	0.8523	0.4875	0.4875	0.4877	0.487535
0.2	0.8566	0.8566	0.85675	0.85675	0.8566	0.4998	0.4998	0.5002	0.499774

	$\delta_k = 10$			
x	Simulation	MADM	LCMM	Exact Solution
0.0001	0.2681	0.2682	0.26829	0.26819
0.1	0.2727	0.2727	0.27274	0.272686
0.2	0.2864	0.2864	0.28612	0.286435



1. Simulation 2. MADM 3. HAM 4. LCMM 5. Exact Solution.

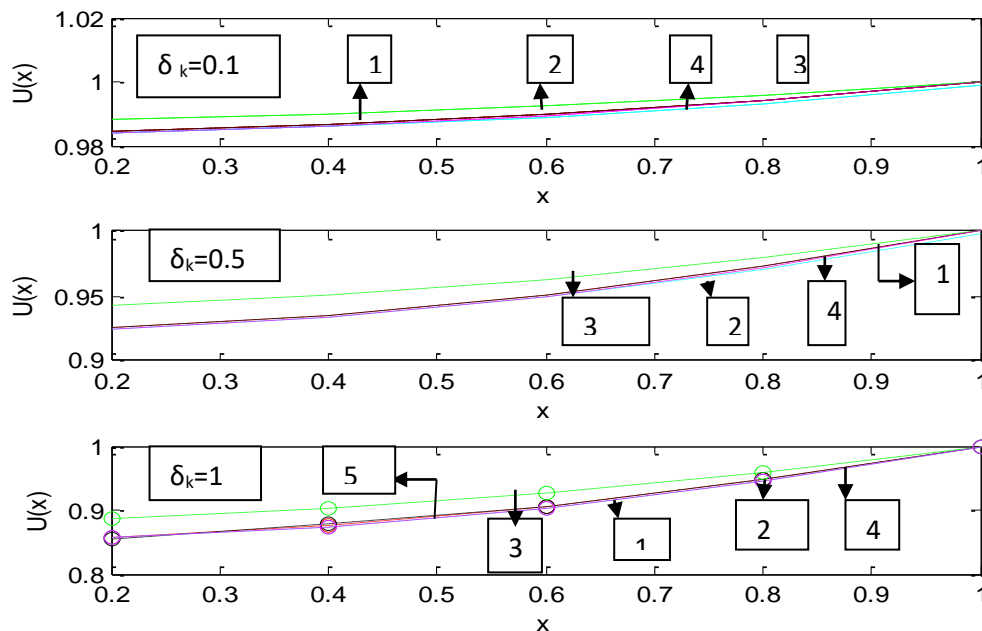
Fig 1: Comparison between the LCMM and MADM $\delta_k=1, \delta_k=5$ and $\delta_k=10$ for $\zeta = 0$ and $\tau = 0$

Case (ii): Comparison between the MADM and LCMM for Eq.(5) and (6) when $\zeta = 0.1$ and $\tau = 0.001$. Consider $\delta_k=0.1, \delta_k=0.5$ and $\delta_k=1$ in Eq. (5) together with the initial conditions, we obtain $U(x)=0.01534x^2+0.98348$ and $U(x)=0.07599x^2+0.9218$ and $U(x)=0.1468x^2+0.8509$ by using LCMM.

$\delta_k=0.1$						$\delta_k=0.5$				
x	Simulation	MADM	HAM	LCMM	Exact solution	Simulation	MADM	HAM	LCMM	Exact Solution
0.2	0.9844	0.9844	0.9884	0.9841	0.98418	0.9251	0.9254	0.9429	0.9248	0.9244
0.4	0.9864	0.9864	0.9899	0.98593	0.9861	0.9345	0.9347	0.9502	0.9339	0.9336
0.6	0.9897	0.9897	0.9924	0.9890	0.9894	0.9502	0.9504	0.9623	0.9491	0.9491
0.8	0.9943	0.9943	0.9958	0.9933	.99405	0.9725	0.9726	0.9793	0.9704	0.9712
1.0	1.0000	1.0000	1.0000	0.9988	1.0000	1.0000	1.0000	1.0000	0.9978	1.0000

Table 2: Comparison between the MADM, HAM and LCMM for Eq. (5) and (6)

$\delta_k=1$					
x	Simulation	MADM	HAM	LCMM	Exact Solution
0.2	0.8580	0.8554	0.8880	0.8568	0.856602
0.4	0.8754	0.8787	0.9021	0.8743	0.873792
0.6	0.9049	0.9057	0.9257	0.9037	0.902900
0.8	0.9471	0.9475	0.9591	0.9448	0.944632
1.0	1.0000	1.0000	1.0000	0.9977	1.000000



1. Simulation 2. MADM 3. HAM 4. LCMM 5. Exact Solution

Fig 2: Comparison between the LCMM, HAM and MADM for $\delta_k=0.1$, $\delta_k=0.5$ and $\delta_k=1$ and for $\zeta=0.1$ and $\tau=0.001$

5. Results and discussion

Our proposed numerical solutions have been compared with modified Adomian decomposition method and homotopy analysis method. The results of MADM and HAM are well satisfied with LCMM for various values of the reaction diffusion parameter δ_k . Figures (1- 3) show the comparison between the LCMM and MADM. The analytical expression of the concentration of substrate $U(x)$ increases when the dimensionless reaction diffusion parameter δ_k decreases. It attains maximum when $\delta_k = 0.1$, $\zeta = 0.1$, $\tau = 0.001$. It should be noted that the time-independent concentration of substrate $U(x)$ is less when $\delta_k = 10$ and error is also more. For larger M, we get the results closer to the real values. Tables (1-6) show the comparison between the LCMM, HAM and MADM for various values of δ_k . The proposed computation method is very efficient and convenient for solving nonlinear differential equations.

6. Conclusion

Since the Legendre Computational matrix method approximates the nonlinear initial and boundary value problems, it is very easy to implement and extend it to various nonlinear reaction-diffusion problems. In this section, an efficient LCMM has been used to investigate the kinetics of immobilized liver esterase by flow calorimetry. Our results have been compared with MADM and HAM results. Good agreement with the exact solution is observed. The results arrived are useful for design and optimization of immobilized liver esterase by flow calorimetry.

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