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MATHEMATICAL MODELING OF AMPEROMETRIC ENZYME ELECTRODES IN THE HOMOGENEOUS MEDIATED MECHANISM USING HOMOTOPY PERTURBATION METHOD

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ABSTRACT

A mathematical model of amperometric enzyme electrodes is re-studied using Homotopy perturbation method. An analysis of diffusion and kinetics in amperometric immobilized enzyme electrodes, containing a non-linear term related to Michaelis-Menten kinetics, for reaction of enzyme and substrate is presented. In this paper, we obtain approximate analytical solutions of non-linear equations, describing diffusion and reaction within the film, by employing the homotopy perturbation method (HPM). The obtained analytical results are compared with the available analytical and numerical results and found to be in satisfactory agreement.

Keywords: *Mathematical modeling; Homogeneous mechanism; Diffusion and Kinetics; Amperometric enzyme electrode; Homotopy perturbation method.*

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1. INTRODUCTION:

Nowadays, there has been much more attention in the use of mediators which effect electron transfer reactions between electrodes [1] and biological molecules (enzymes or NADH). On two major areas, the importance of this work has been focused. Firstly, the basis of a selective Amperometric enzyme electrode is provided by the transduction of the rate of an enzymatic reaction into a current. Secondly, the information about the electron transfer in biological system [2- 14] using Homotopy perturbation method [14, 15] mechanism is studied.

The complete theoretical treatment for an enzyme electrode is presented by John Albery's et al [1], where the electron transfer is achieved by a mediator reacting in homogeneous solution from the enzyme to the electrode. John Albery's et al. [1] solved the second order differential equations only for the various limiting values of the parameter γ, K_E and K_M to describe the mediator in the diffusion layer of the electrode and the transport and kinetics of the enzyme. The definition about the parameters is given below in the equation (2). The purpose of this paper is to derive the concentration of the mediator and enzyme for all values of reaction parameter γ, K_E and K_M . Using Homotopy perturbation method [14, 15].

2. MATHEMATICAL FORMULATION OF THE BOUNDARY – VALUE PROBLEM AND ANALYSIS:

At the electrode, in the biological system

$$M' \rightarrow M$$

It is expressed by homogeneous solution

$$M + E' \xrightarrow{K_M} M' + E$$

$$E \xrightarrow{K_E} E'$$

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K_E is the rate constant with which the enzyme reacts with its substrate S. K_M is the rate constant with which the enzyme reacts with the mediator. On the electrode, the mediator redox couple $\frac{M}{M'}$ is converted and react with the enzyme in the solution. When the substrate concentration is sufficiently large the enzyme is saturated. Now the rate constant K_E will be equal to K_{cat}. The differential equations for the above reacting scheme are reduced to the following dimensionless form [1]:

$$\frac{\partial^2 u}{\partial x^2} = K_M uv \tag{1}$$

$$\frac{\partial^2 v}{\partial x^2} = \gamma K_E uv - K_E(1-v) \tag{2}$$

The parameter K_M is the probability of the mediator M escapes from the diffusion layer before it reacts with the enzyme. The parameter K_E is the probability of the conversion of enzyme E and E' by substrate within the diffusion layer. The parameter γ is the local steady state between the two enzyme forms at the electrode surface. It must obey the following boundary conditions,

$$u = 1, \quad u' = 0 \text{ and } \frac{\partial v}{\partial x} = 0 \qquad \text{for } x = 0 \tag{3}$$

$$u = 0, \quad u' = 0 \text{ and } v' = 1 \qquad \text{for } x = 1 \tag{4}$$

The flux of the electron is given by

$$j = \left(\frac{nD_M m_\circ}{Z_D}\right)\left(\frac{\partial u'}{\partial x}\right)_{x=0} \tag{5}$$

The dimensionless current is given by

$$I = \frac{j}{(nD_M m_\circ / Z_D)} = (\partial u/\partial x)_{x=0} \tag{6}$$

we get

$$I = -\left(\frac{\partial u'}{\partial x}\right)_{x=0} \tag{7}$$

$$I = -\left(\frac{\partial u}{\partial x}\right)_{x=0} - 1 \tag{8}$$

when $v = 1$ the Eq. (1) reduces to a simple first order case [16,17]. In this paper the nonlinear Eqs. (1) and (2) are solved for the boundary conditions given by the Eqs. (3) and (4) using Homotopy perturbation method, proposed by He [14,15].

3. HOMOTOPY PERTURBATION METHOD:

Nonlinear phenomena play a crucial role in physical chemistry and biology (heat and mass transfer, filtration of liquid, diffusion in chemical reactions etc.). Constructing of particular exact solution for these equations remains an important problem. Finding an exact solution that has a physical chemical or biological interpretation is of fundamental importance. This model combines the processes of diffusion and enzymatic reactions in the membrane. This model is based on non-stationary system of diffusion equations containing a non-linear reaction term. It is not possible to solve this equations using standard analytical technique. The investigation of an exact solution of non-linear equation is interesting and important. In the past several decades, many authors mainly had paid attention to study the solution of nonlinear equations by using various methods, such as Backlund transformation [18], Darboux transformation [19], Inverse scattering method

[20], Bilinear method [21], The tanh method [22], Variational iteration method [23] and Homotopy perturbation method [24-28] etc.

The Homotopy perturbation method [24-28] has been extensively worked out over a number of years by numerous authors. The HPM was first proposed by He and was successfully applied to autonomous ordinary differential equations to nonlinear polycrystalline solids and other fields. This method has been proved by many authors to be a powerful mathematical tool for various kinds of nonlinear problems. It is a promising and evolving method. Besides its mathematical importance and its link to other branches of mathematics, it is widely used in all ramifications of modern sciences. The HPM is unique in its applicability, accuracy and efficiency. In this method the solution procedure is very simple and only few iterations lead to high accurate solutions which are valid for the whole solution domain.

4. ANALYTICAL SOLUTION OF THE CONCENTRATION AND CURRENT USING HOMOTOPY PERTURBATION METHOD:

Using Homotopy perturbation method [14, 15] (see Appendix A), the concentration of the mediator and the enzyme are

$$
\begin{aligned}
u(x) = 1 &- \frac{\gamma K_M^2 \tan\sqrt{K_E}}{K_E^{5/2}} - \frac{2\gamma K_M^2}{K_E^3} + \frac{\gamma K_M^2 \tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{5/2}} \\
&+ \frac{2\gamma K_M^2 \tan\sqrt{K_E}\sin\sqrt{K_E}\,x}{K_E^3} - \frac{\gamma K_M^2 \sin\sqrt{K_E}\,x}{K_E^{5/2}} \\
&+ \frac{2\gamma K_M^2 \cos\sqrt{K_E}\,x}{K_E^3} + x\left[\begin{aligned} &-1-\frac{K_M}{3}-\frac{\gamma K_M^2\tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{5/2}}+\frac{\gamma K_M^2\sin\sqrt{K_E}\,x}{K_E^{5/2}}- \\ &\frac{2\gamma K_M^2\left[\tan\sqrt{K_E}\sin\sqrt{K_E}+\cos\sqrt{K_E}-1\right]}{K_E^3}-\frac{\gamma K_M^2}{4K_E}+\frac{K_M^2}{45}+\frac{\gamma K_M^2\tan\sqrt{K_E}}{K_E^{5/2}}\end{aligned}\right] \\
&+ x^2\left(\frac{K_M}{2}+\frac{\gamma K_M^2}{2K_E}\right) - x^3\left(\frac{K_M^2}{18}+\frac{K_M}{6}+\frac{2\gamma K_M^2}{K_E}\right) + x^4\left(\frac{\gamma K_M^2}{12K_E}+\frac{K_M^2}{24}\right) - x^5\left(\frac{K_M^2}{120}\right)
\end{aligned} \tag{8}
$$

$$
v(x) = 1 - \frac{\gamma K_M \tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{3/2}} + \frac{\gamma K_M \sin\sqrt{K_E}\,x}{K_E^{3/2}} + \frac{\gamma K_M(1-x)}{K_E} \tag{9}
$$

We get dimensionless current,

$$
\begin{aligned}
I &= \left(\frac{\partial u}{\partial x}\right)_{x=0} = -\left(\frac{\partial u}{\partial x}\right)_{x=0} - 1 \\
&= \frac{-2\gamma K_M^2}{K_E^{5/2}}\tan\sqrt{K_E} + \frac{2\gamma K_M^2}{K_E^3}\left[\tan\sqrt{K_E}\sin\sqrt{K_E}+\cos\sqrt{K_E}-1\right] + \frac{\gamma K_M^2}{K_E^2} + \frac{\gamma K_M^2}{4K_E} - \frac{K_M^2}{45} + \frac{K_M}{3}
\end{aligned} \tag{10}
$$

5. COMPARISON WITH THE LOGHAMBALWORK [25]:

Using Variational iteration method , Loghambal and Rajendran [25] obtain the concentration of the mediator and the enzyme as follows :

$$
u(x) = 1-(a+1)\,x + \frac{K_M}{2}(1+b)\,x^2 - \frac{K_M}{6}(1+b+a+ab)\,x^3 + \frac{K_M}{12}(a+ab-b)\,x^4 + \frac{K_M}{20}(ab+b)\,x^5 - \frac{K_M}{30}abx^6 \tag{11}
$$

$$v(x) = 1+b+\frac{K_E}{2}\left(\gamma+b+\gamma b\right) x^2 - \frac{\gamma K_E}{6}\left(1+b+ab+a\right) x^3 + \frac{K_E}{12}\left(\gamma a+\gamma ab-\gamma b-b\right) x^4 + \frac{\gamma K_E b}{20}\left(a+1\right) x^5 - \frac{\gamma K_E ab}{30} x^6 \tag{12}$$

where

$$a = \frac{100}{96\gamma K_E}\left[\begin{array}{l} 2.16\gamma K_E + 3K_E + 7.2 + 0.6K_M + 0.25K_E K_M \\ -\left(\begin{array}{l} 43.2K_E + 8.64K_M + 31.104\gamma K_E + 7.2K_E K_M + 51.84 - 0.84\gamma K_E^2 K_M \\ -2.016\gamma K_E K_M + 1.5K_E^2 K_M + 0.3K_E K_M^2 + 0.36K_M^2 + 0.0625K_E^2 K_M^2 \\ +4.6656\gamma^2 K_E^2 + 12.96\gamma K_E^2 + 9K_E^2 \end{array}\right)^{1/2} \end{array}\right] \tag{13}$$

$$b = \frac{-5}{2}\left[\frac{12a + K_M a - 4K_M}{K_M\left(2a-9\right)}\right] \tag{14}$$

The dimensionless current

$$I = \left(\frac{\partial u'}{\partial x}\right)_{x=0} = -\left(\frac{\partial u}{\partial x}\right)_{x=0} - 1 = a \tag{15}$$

6. DISCUSSION:

Eqs. (8) and (9) are the new and simple analytical expressions of concentration profiles for the mediator u and enzyme v. The approximate solutions of second order differential equations describing the transport and kinetics of the enzyme and the mediator in the diffusion layer of the electrode are derived. Albery and co-workers [1] derived the different approximate solutions for various limiting cases only.

The concentration of mediator in most cases is in the linear form where as the concentration of the enzyme is in the parabolic type. Our analytical results (Eqs. (8) and (9)) are compared with previously available analytical and our numerical results. In Table 1-6 our analytical expression of dimensionless concentration u and v are compared with previous analytical (VIM) results and our numerical methods for various values parameter γ, K_E and K_M. In all the cases our expression of dimensionless concentration u are within 0.18% of the simulated data whereas previous analytical results within 0.24% simulated data. Similarly our expression of dimensionless concentration v is within 1.65% of the simulated data whereas previous analytical results within 3.01% simulated data. Figures 1-5 represents the comparison of dimensionless concentration of u and v.

Figures 6 and 7, show the dimensionless current I for various values of γ and K_M. From Figure 6, it is inferred that, the value of the current decreases when γ increases. From the Figure 7, it is known that the value of the current increases when K_M increases.

7. CONCLUSIONS:

The studies observed in this paper are of theoretical nature. The simple analytical expressions of the concentration of the mediator and the enzyme are reported, for all values of reaction parameters γ, K_E and K_M using Homotopy perturbation method. These values are compared with previously available limiting case results. A satisfactory agreement with available data for limiting cases is noted. The extension of this procedure to other reaction mechanism apart from the study of mediated enzyme reaction mechanism in biosensor [24] with complex boundary condition seems possible.

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REFERENCES:

[1] W. John Albery , P.N. Bartlett, J. Driscoll and R. Bruce lennox , J. Electroanal. Chem., 323 (1992), 77.

[2] A.E.G. Cass, D.G. Francis, H.A.O. Hill, W.J. Aston, I.J. Higgins, E.V. Plotkin, L.D.L. Scott and A.P.F. Turner. Anal. Chem., 56 (1984) 667.

[3] A.E.G. Cass, G. Davis, H.A.O. Hill and D.J. Nancarrow, Biochim. Biophys. Acta., 828 (1985) 51–57.

[4] A.E.G.Cass, G. Davis, M.J. Green and H.A.O.Hill, J. Electroanal.Chem., 190 (1985) 51–57.

[5] P. Schlapfer, W. Mindt, P. Racine, Clin. Chim. Acta., 57 (1974) 283.

[6] R. M. Ianniello, T. J. Lindsay, and *A*. M. Yacynych, Anal. Chem., 54 (1982), 1980.

[7] J. M. Johnson, H. B. Halsall and W. R. Heineman, Biochemistry, 24 (1985) 1579.

[8] J.J. Kulys, and A.S. Samalius, Bioelectrochem. Bioenerg., 10 (1983) 385.

[9] J.J. Kulys, A.S. Samalius and G.-J.S. Svirmickas , Electron exchange between the enzyme active centre and organic metal. FEBS Lett., 114 (1980) 7–10.

[10] W.J. Albery, P.N. Bartlett and D.H. Craston, Amperometric J. Electroanal. Chem., 194 (1985) 223–235

[11] W.J. Albery, P.N. Bartlett, M . Bycroft, D.H. Craston and B.J. Driscoll,J. Electroanal. Chem., 218 (1987) 119.

[12] W.J. Albery, P.N. Bartlett, A.E.G. Cass, and B.G.D. Haggett, J. Chem. Soc. Faraday Trans. I, 82 (1986), 1033.

[13] M. Dixon and E.C. Webb, Enzymes (3rd edn.,), Longman, London, (1979) 483.

[14] M. E. G. Lyons, S. Rebouillat, Int. J. Electrochem. Sci. 4 (2009) 481.

[15] M.E.G. Lyons, Int. J. Electrochem. Sci., 4 (2009) 77

[16] J.H. He, G.C. Wu and F. Austin, Physics and Mechanics., 1.1 (2010) 1.

[17] J.H. He and X.H. Wu, Int J Computers Math Appl., 54 (2007) 881.

[18] A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, (1980) 455.

[19] N.K. Cenas and J.J. Kulys, Bioelectrochem. Bioenerg., 8 (1981) 103.

[20] Lu Junfeng, J Comput Appl Math., 207 (2007) 92.

[21] M.A. Abdou and A.A. Soliman, J Comput Appl Mat., 181(2005) 245.

[22] G. Rahamathunissa and L. Rajendran, J Math Chem., 44(2007) 849.

[23] J.H. He, J Comput Appl Math., 207(2007) 1.

[24] Kenji Yokoyama, Satoshi Koide and Yoshihiro Kayanuma, Anal Bioanal Chem., 372

[25] S. Loghambal and L. Rajendran, Int. J. Electrochem. Sci., 5(2010) 327

APPENDIX A

SOLUTION OF THE EQUATIONS USING HOMOTOPY PERTURBATION METHOD:

In this Appendix, to find the solution we first construct a Homotopy as follows

$$(1-p)\left(\frac{\partial^2 u}{\partial x^2}\right)+p\left[\frac{\partial^2 u}{\partial x^2}-K_M uv\right]=0 \tag{A1}$$

$$(1-p)\left(\frac{\partial^2 v}{\partial x^2}-K_E(1-v)\right)+p\left[\frac{\partial^2 v}{\partial x^2}-\gamma K_M uv-K_E(1-v)\right]=0 \tag{A2}$$

and the initial approximations are as follows:

$$\begin{aligned}
&x=0; \quad u_\circ=1; \quad \frac{\partial v_\circ}{\partial x}=0\\
&x=1; \quad u_\circ=0; \quad v_\circ=1\\
&x=0; \quad u_i=1; \quad \frac{\partial v_i}{\partial x}=0\\
&x=1; \quad u_i=0; \quad v_i=1 \qquad \forall\, i=1,2,......
\end{aligned} \tag{A3}$$

and

$$\begin{cases} u=u_0+pu_1+p^2u_2+p^3u_3+.......\\ v=v_0+pv_1+p^2v_2+p^3v_3+....... \end{cases} \tag{A4}$$

Substituting Eq. (A4) into Eqs. (A1) and (A2) and arranging the coefficients of powers p

$$p^\circ \;:\quad \frac{\partial^2 u_\circ}{\partial x^2}=0 \tag{A5}$$

$$p^1 \;:\quad \frac{\partial^2 u_1}{\partial x^2}-\frac{\partial^2 u_\circ}{\partial x^2}+\frac{\partial^2 u_\circ}{\partial x^2}-K_M u_\circ v_\circ=0 \tag{A6}$$

$$p^2 \;:\quad \frac{\partial^2 u_2}{\partial x^2}-\frac{\partial^2 u_1}{\partial x^2}+\frac{\partial^2 u_1}{\partial x^2}-K_M\left(u_\circ v_1+u_1 v_\circ\right)=0 \tag{A7}$$

and

$$p^\circ \;:\quad \frac{\partial^2 v_\circ}{\partial x^2}-K_E+K_E V_\circ=0 \tag{A8}$$

$$p^1 \;:\quad \frac{\partial^2 v_1}{\partial x^2}-\frac{\partial^2 v_\circ}{\partial x^2}+K_E-K_E V_\circ+K_E V_1+\frac{\partial^2 v_\circ}{\partial x^2}-\gamma K_M u_\circ v_\circ-K_E+K_E v_\circ=0 \tag{A9}$$

$$p^2 \;:\quad \frac{\partial^2 v_2}{\partial x^2}-\frac{\partial^2 v_1}{\partial x^2}+K_E V_2-K_E V_1+\frac{\partial^2 v_1}{\partial x^2}-\gamma K_M\left(u_\circ v_1+u_1 v_\circ\right)+K_E v_1=0 \tag{A10}$$

Solving equations (A5) to (A10) using reduction of order, and using the initial conditions (A3), we can find the following results

$$u_\circ=1-x \tag{A11}$$

$$u_1=\;x\left(-\frac{K_M}{3}\right)+x^2\left(\frac{K_M}{2}\right)+x^3\left(-\frac{K_M}{6}\right) \tag{A12}$$

$$\begin{aligned}
u_2 = {} & \frac{\gamma K_M^2 \tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{5/2}} + \frac{2\gamma K_M^2 \tan\sqrt{K_E}\sin\sqrt{K_E}\,x}{K_E^3} - \frac{\gamma K_M^2 \sin\sqrt{K_E}\,x}{K_E^{5/2}} + \frac{2\gamma K_M^2\cos\sqrt{K_E}\,x}{K_E^3} - \frac{\gamma K_M^2\tan\sqrt{K_E}}{K_E^{5/2}} - \frac{2\gamma K_M^2}{K_E^3} \\
& + x\left(\frac{\gamma K_M^2\sin\sqrt{K_E}\,x}{K_E^{5/2}} - \frac{\gamma K_M^2\tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{5/2}} - \frac{2\gamma K_M^2\left[\tan\sqrt{K_E}\sin\sqrt{K_E}+\cos\sqrt{K_E}-1\right]}{K_E^3} - \frac{\gamma K_M^2}{4K_E} + \frac{K_M^2}{45} + \frac{\gamma K_M^2\tan\sqrt{K_E}}{K_E^{5/2}}\right) \\
& + x^2\left(\frac{\gamma K_M^2}{2K_E}\right) - x^3\left(\frac{2\gamma K_M^2}{6K_E} + \frac{K_M^2}{18}\right) + x^4\left(\frac{\gamma K_M^2}{12K_E} + \frac{K_M^2}{24}\right) - x^5\left(\frac{K_M^2}{120}\right)
\end{aligned} \tag{A13}$$

$$v_\circ = 1 \tag{A14}$$

$$v_1 = -\frac{\gamma K_M}{3} + x^2\left(\frac{\gamma K_M}{2}\right) - x^3\left(\frac{\gamma K_M}{6}\right) \tag{A15}$$

$$\begin{aligned}
v_2 = {} & 1 - \frac{\gamma K_M \tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{K_E^{3/2}} + \frac{\gamma K_M\sin\sqrt{K_E}\,x}{K_E^{3/2}} + \frac{\gamma K_M}{K_E} - \frac{\tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{\sqrt{K_E}}\left(-\frac{\gamma^2K_M^2\tan\sqrt{K_E}}{4K_E^{5/2}} + \frac{5\gamma^2K_M^2}{2K_E^2} + \frac{\gamma K_M^2}{3K_E} - \frac{\gamma K_M^2}{K_E^2}\right) \\
& + \frac{\gamma^2K_M^2\tan^2\sqrt{K_E}\cos\sqrt{K_E}\,x}{2K_E^2} - \frac{\gamma^2K_M^2\tan\sqrt{K_E}\cos\sqrt{K_E}\,x\left(1+\sqrt{K_E}\tan\sqrt{K_E}\right)}{4K_E^{5/2}} + \frac{\gamma^2K_M^2\cos\sqrt{K_E}\,x}{2K_E^2} \\
& + \frac{\gamma^2K_M^2\cos\sqrt{K_E}\,x\left(\tan\sqrt{K_E}-\sqrt{K_E}\right)}{4K_E^{5/2}} - \frac{\gamma^2K_M^2\cos\sqrt{K_E}\,x}{K_E^2\cos\sqrt{K_E}} + \frac{\cos\sqrt{K_E}\,x}{K_E\cos\sqrt{K_E}}\left(\frac{2\gamma^2K_M^2}{K_E} + \frac{\gamma K_M^2}{3}\right) \\
& - \frac{\cos\sqrt{K_E}\,x}{K_E\cos\sqrt{K_E}}\left(\frac{\gamma^2K_M^2}{K_E} + \frac{\gamma K_M^2}{2} - \frac{2\gamma^2K_M^2}{K_E^2} - \frac{2\gamma K_M^2}{2K_E}\right) + \frac{\cos\sqrt{K_E}\,x}{6K_E\cos\sqrt{K_E}}\left(\gamma K_M^2 - \frac{6\gamma K_M^2}{K_E}\right) - \frac{2}{K_E^2}\left(\frac{\gamma^2K_M^2}{K_E} + \frac{\gamma K_M^2}{2}\right) + \frac{\gamma^2K_M^2}{K_E^2} \\
& + \frac{\sin\sqrt{K_E}\,x}{\sqrt{K_E}}\left(-\frac{\gamma^2K_M^2\tan\sqrt{K_E}}{4K_E^{5/2}} + \frac{5\gamma^2K_M^2}{2K_E^2} + \frac{\gamma K_M^2}{3K_E} - \frac{\gamma K_M^2}{K_E^2}\right) \\
& + x\left(-\frac{\gamma K_M}{K_E} - \frac{\gamma^2K_M^2\tan\sqrt{K_E}\sin\sqrt{K_E}\,x}{2K_E^2} + \frac{\gamma^2K_M^2\tan\sqrt{K_E}\cos\sqrt{K_E}\,x}{4K_E^{5/2}} - \frac{\gamma^2K_M^2\cos\sqrt{K_E}\,x}{2K_E^2} - \frac{\gamma^2K_M^2\sin\sqrt{K_E}\,x}{4K_E^{5/2}} - \frac{2\gamma^2K_M^2}{K_E^2} - \frac{\gamma K_M^2}{3K_E} + \frac{\gamma K_M^2}{K_E^2}\right) \\
& + x^2\left(\frac{\gamma^2K_M^2\sqrt{K_E}\tan\sqrt{K_E}\sin\sqrt{K_E}\,x}{4K_E^{5/2}} + \frac{\gamma^2K_M^2\sqrt{K_E}\cos\sqrt{K_E}\,x}{4K_E^{5/2}} + \frac{\gamma^2K_M^2}{K_E^2} + \frac{\gamma K_M^2}{2K_E}\right) - x^3\left(\frac{\gamma K_M^2}{6K_E}\right)
\end{aligned} \quad \text{A16)}$$

APPENDIX B

MATLAB PROGRAM TO FIND THE NUMERICAL SOLUTION OF THE EQUATIONS (1) AND (2):

```
function pdex4
m = 0;
x = linspace(0,1);
t=linspace(0,100000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
u2 = sol(:,:,2);
figure
plot(x,u1(end,:))
title('u1(x,t)')
xlabel('Distance x')
ylabel('u1(x,2)')
%-----------------------------------------------------------------
figure
plot(x,u2(end,:))
title('u2(x,t)')
xlabel('Distance x')
ylabel('u2(x,2)')
```



```
% --------------------------------------------------------------
function [c,f,s] = pdex4pde(x,t,u,DuDx)
c = [1; 1];
f = [1; 1] .* DuDx;
y = u(1) * u(2);
%y1=u(1)*u(3);
p=0.1;
q=0.01;
k=0.1;
%lamta=0.0001;% parameters
%F =(-lamta*y-y1);
F1=(-q*y);      % non linear terms   %
F2=(-p*q*y)-k+k*u(2);
s=[F1;F2];
% --------------------------------------------------------------
function u0 = pdex4ic(x);                              %create a initial conditions
u0 = [0; 1];
% --------------------------------------------------------------
function[pl,ql,pr,qr]=pdex4bc(xl,u1,xr,ur,t)            %create a boundary conditions
pl = [u1(1)-1; 0];
ql = [0; 1];
pr = [ur(1);ur(2)-1];
qr = [0,0];
```

Table 1: Comparison of dimensionless concentration u and v with simulation result for various values of x and $\gamma = 0.1$, $K_E = 0.1$ and $K_M = 0.01$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.9997	0.9997	0.9968	0.0000	0.2901
0.2	0.7995	0.7995	0.7995	0.0000	0.0000	0.9997	0.9997	0.9970	0.0000	0.2701
0.4	0.5994	0.5994	0.5994	0.0000	0.0000	0.9997	0.9997	0.9975	0.0000	0.2201
0.6	0.3994	0.3994	0.3995	0.0000	0.0250	0.9998	0.9998	0.9982	0.0000	0.16001
0.8	0.1997	0.1997	0.1997	0.0000	0.0000	0.9999	0.9999	0.9990	0.0000	0.09001
1	0.0000	0.0042	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Average				0.0000	0.0042	Average			0.0000	0.1717

Table 2: Comparison of dimensionless concentration u and v with simulation result for various values of x and $\gamma = 0.1$, $K_E = 0.01$ and $K_M = 1$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.9997	0.9997	0.9968	0.0000	0.2901
0.2	0.7995	0.7995	0.7995	0.0000	0.0000	0.9997	0.9997	0.9970	0.0000	0.2701
0.4	0.5994	0.5994	0.5994	0.0000	0.0000	0.9997	0.9997	0.9975	0.0000	0.2201
0.6	0.3994	0.3994	0.3995	0.0000	0.0250	0.9998	0.9998	0.9982	0.0000	0.16001
0.8	0.1997	0.1997	0.1997	0.0000	0.0000	0.9999	0.9999	0.9990	0.0000	0.09001
1	0.0000	0.0042	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Average				0.0000	0.0042	Average			0.0000	0.1717

Table 3: Comparison of dimensionless concentration u and v with simulation result for various values of x and $\gamma = 5$, $K_E = 0.1$ and $K_M = 0.1$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.8512	0.8264	0.8610	2.9135	1.1513
0.2	0.7958	0.7959	0.7958	0.0126	0.0000	0.8592	0.8361	0.8688	2.6885	1.1173
0.4	0.5944	0.5945	0.5944	0.0168	0.0000	0.8814	0.8624	0.8898	2.1557	0.9530
0.6	0.3950	0.3952	0.3950	0.0506	0.0000	0.9146	0.9013	0.9208	1.4542	0.6779
0.8	0.1971	0.1972	0.1971	0.0507	0.0000	0.9553	0.9485	0.9586	0.7118	0.3454
1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Average				0.0218	0.0000	Average			1.6540	0.7075

Table 4: Comparison of dimensionless concentration u and v with simulation result for various values of x and $\gamma = 0.1$, $K_E = 0.1$ and $K_M = 1$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.9685	0.9653	0.9971	0.3304	2.9530
0.2	0.7565	0.7574	0.7569	0.1190	0.0529	0.9703	0.9672	0.9973	0.3195	2.7826
0.4	0.5427	0.5440	0.5438	0.2395	0.2027	0.9751	0.9725	0.9977	0.2666	2.3177
0.6	0.3503	0.3515	0.3519	0.3426	0.4568	0.9822	0.9803	0.9984	0.1934	1.6494
0.8	0.1717	0.1724	0.1730	0.4077	0.7571	0.9907	0.9897	0.9992	0.1009	0.8580
1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
Average				0.1848	0.2449	Average			0.2018	3.0173

Table 5: Comparison of dimensionless concentration u and v with simulation result for various values of x and γ =0.1, $K_E = 1$ and $K_M = 0.1$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.9946	0.9944	0.9771	0.0201	1.7595
0.2	0.7953	0.7953	0.7953	0.0000	0.0000	0.9949	0.9947	0.9785	0.0201	1.6484
0.4	0.5937	0.5937	0.5938	0.0000	0.0168	0.9957	0.9955	0.9821	0.0201	1.3659
0.6	0.3945	0.3945	0.3946	0.0000	0.0253	0.9969	0.9968	0.9872	0.0100	0.9730
0.8	0.1968	0.1968	0.1969	0.0000	0.0508	0.9984	0.9983	0.9934	0.0100	0.5008
1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	0.9999	0.0000	0.0100
Average				0.0000	0.0155	Average			0.0230	1.7879

Table 6: Comparison of dimensionless concentration u and v with simulation result for various values of x and $\gamma = 0.01$, $K_E = 1$ and $K_M = 0.01$

x	u					v				
	Simulation u	This work HPM Eq.(8)	Logambal et al [25] VIM Eq.(11)	Error %		Simulation v	This work HPM Eq.(9)	Logambal et al [25] VIM Eq.(12)	Error %	
				HPM	VIM				HPM	VIM
0	1.0000	1.0000	1.0000	0.0000	0.0000	0.9999	0.9999	0.9974	0.0000	0.2500
0.2	0.7995	0.7994	0.7995	0.0125	0.0000	0.9999	0.9999	0.9975	0.0000	0.2400
0.4	0.5994	0.5992	0.5994	0.0334	0.0000	1.0000	1.0000	0.9979	0.0000	0.2100
0.6	0.3994	0.3991	0.3995	0.0751	0.0251	1.0000	1.0000	0.9984	0.0000	0.1600
0.8	0.1997	0.1993	0.1997	0.2003	0.0000	1.0000	1.0000	0.9990	0.0000	0.1000
1	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	0.9996	0.0000	0.0400
Average				0.0535	0.0042	Average			0.0000	0.1667

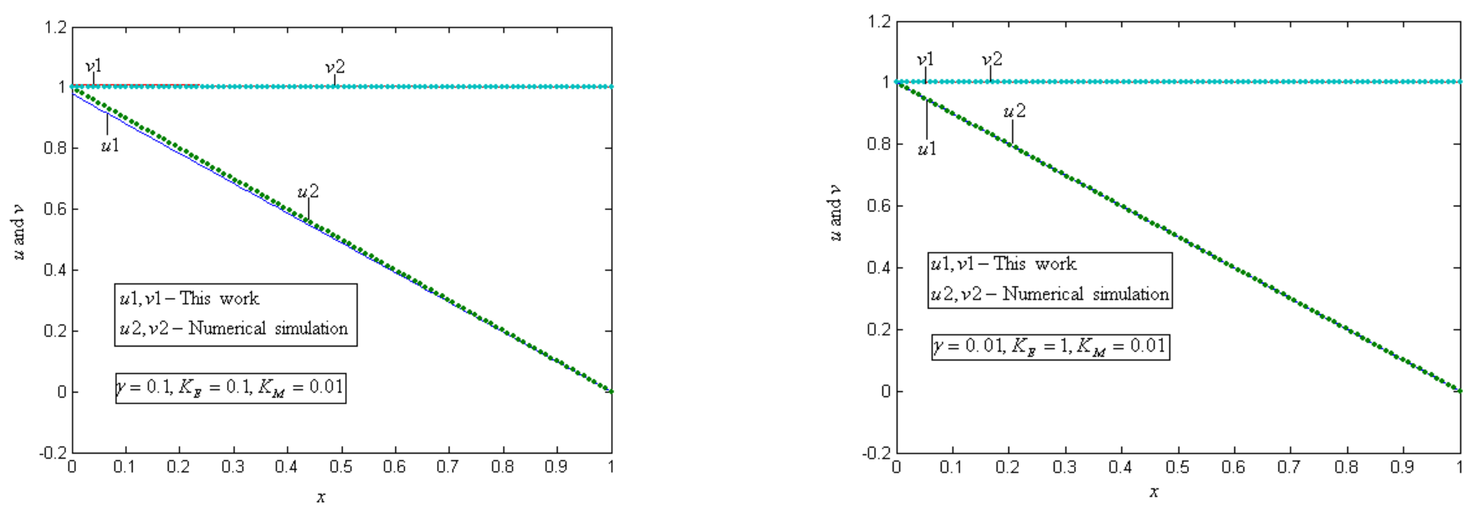

Fig. 1: Comparison of dimensionless concentration u and v with simulation result for various values of γ, K_E and K_M

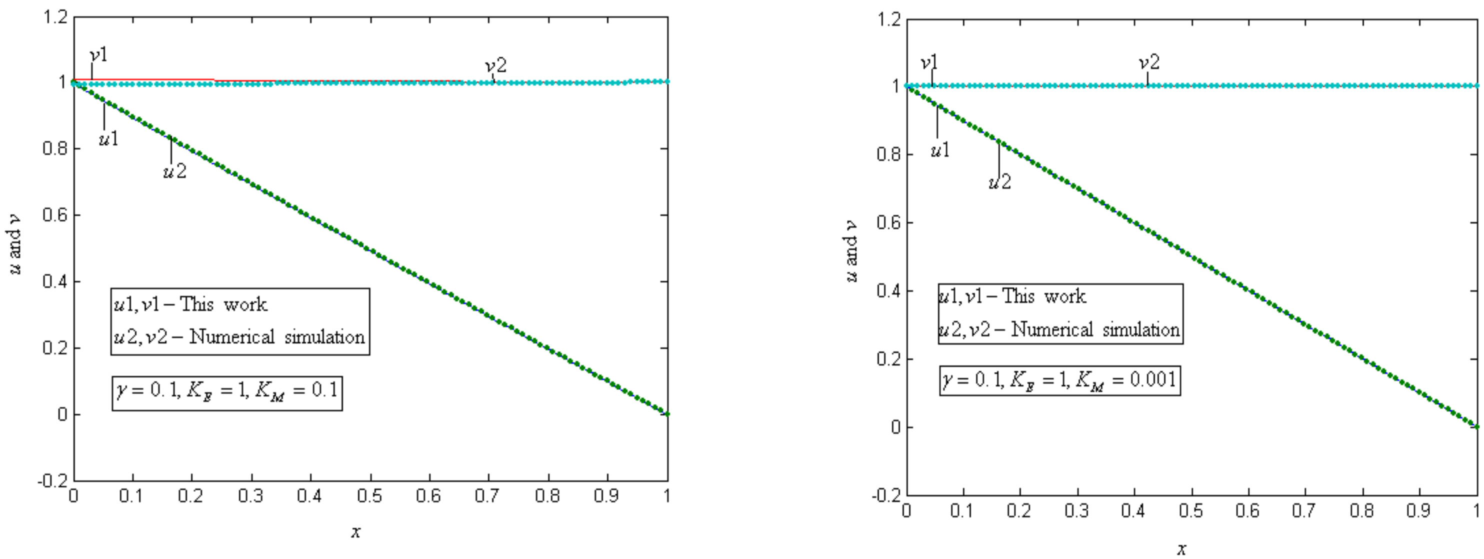

Fig. 2: Comparison of dimensionless concentration u and v with simulation result for various values of γ, K_E and K_M

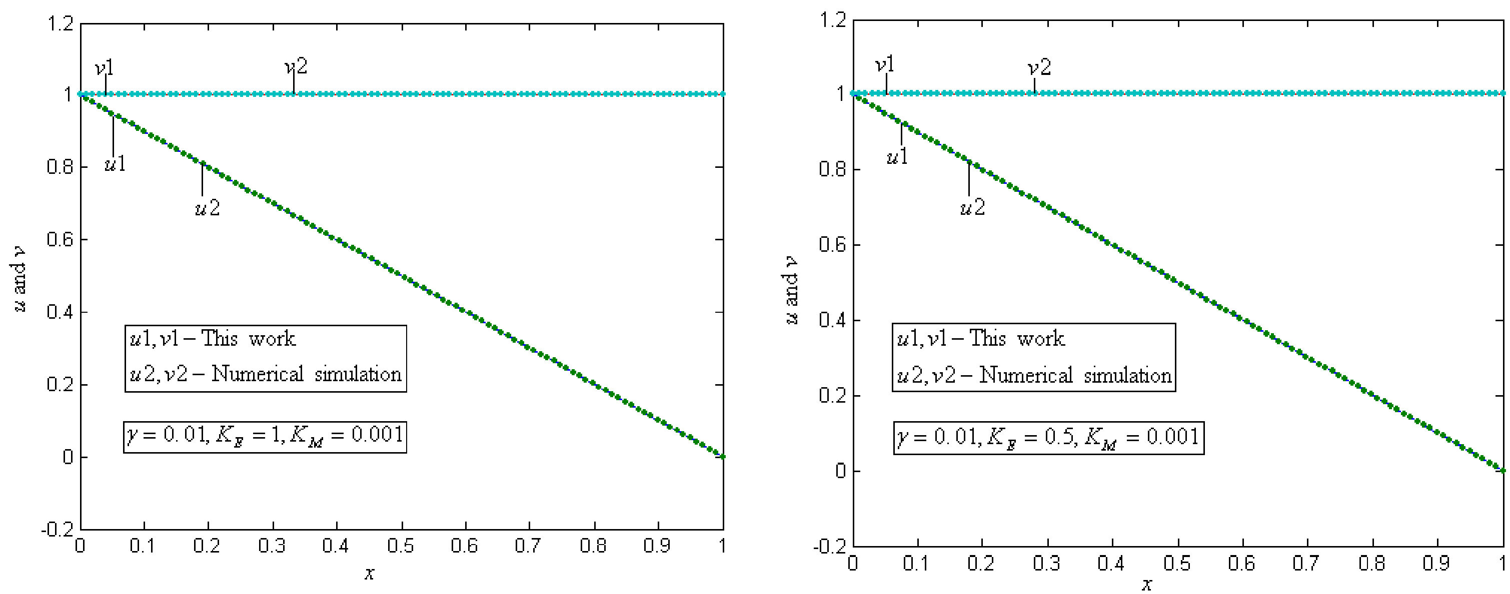

Fig. 3: Comparison of dimensionless concentration u and v with simulation result for various values of γ, K_E and K_M

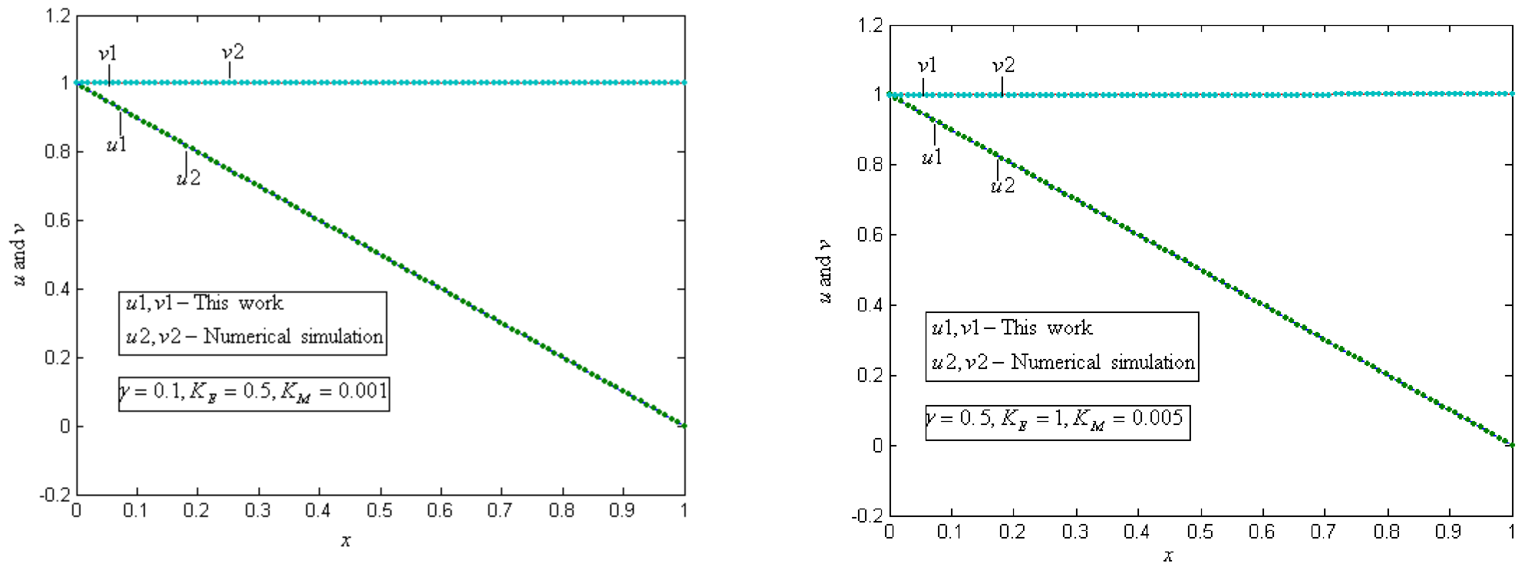

Fig. 4: Comparison of dimensionless concentration u and v with simulation result for various values of γ, K_E and K_M

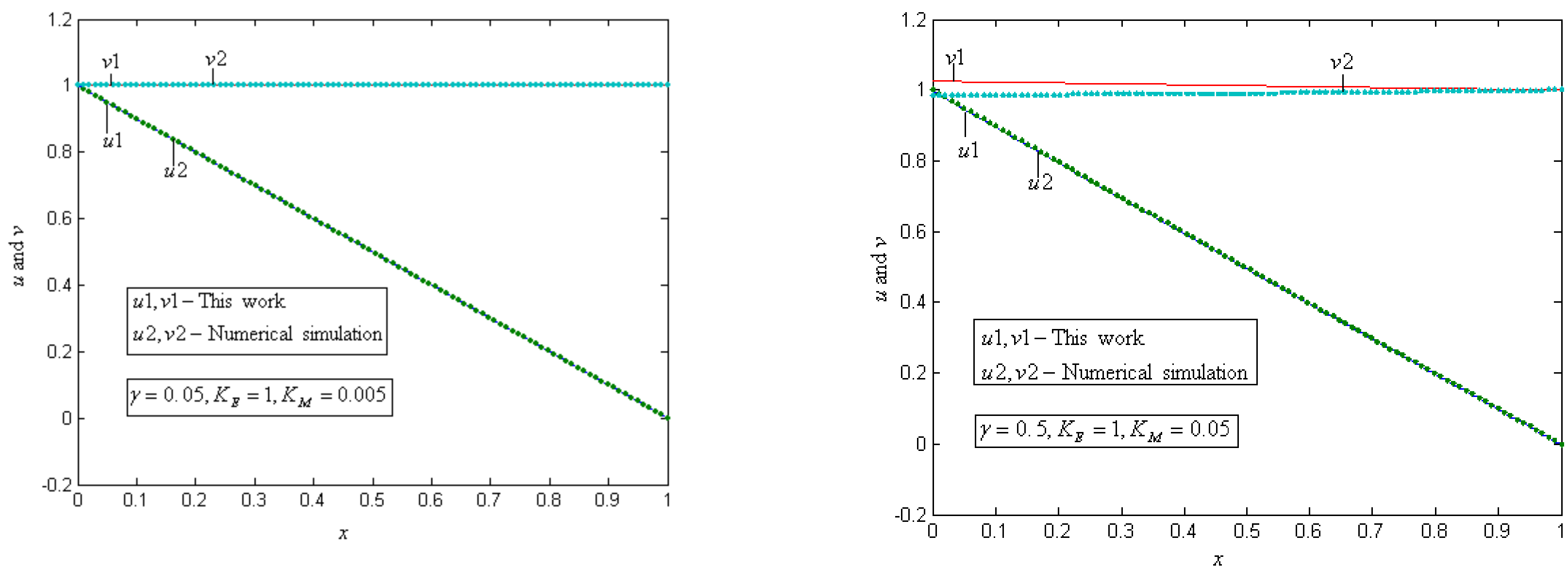

Fig. 5: Comparison of dimensionless concentration u and v with simulation result for various values of γ, K_E and K_M

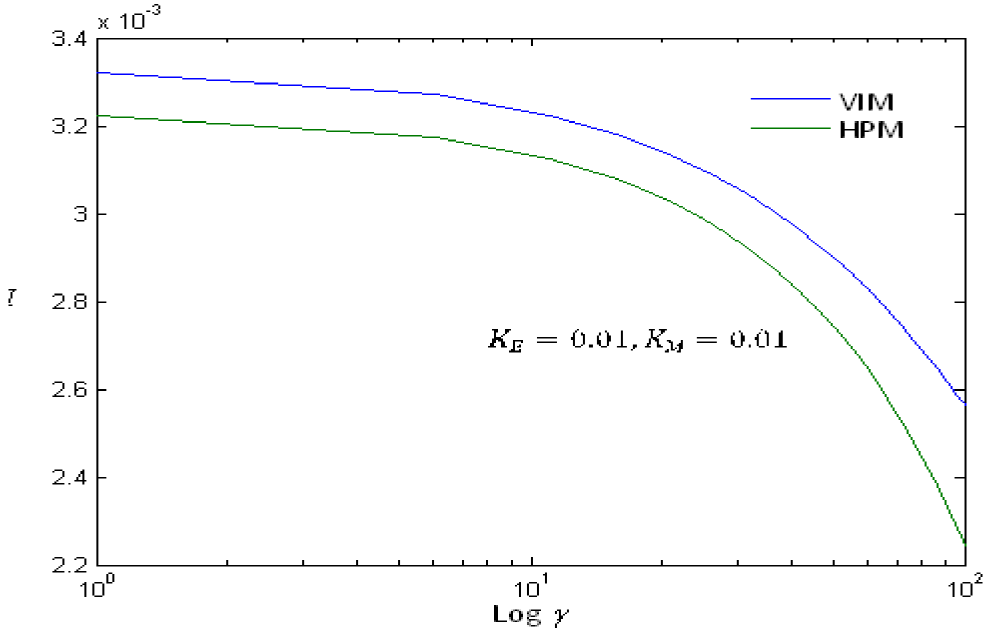

Fig. 6: Comparison of current between VIM [25] and HPM [This work] for various values of γ.

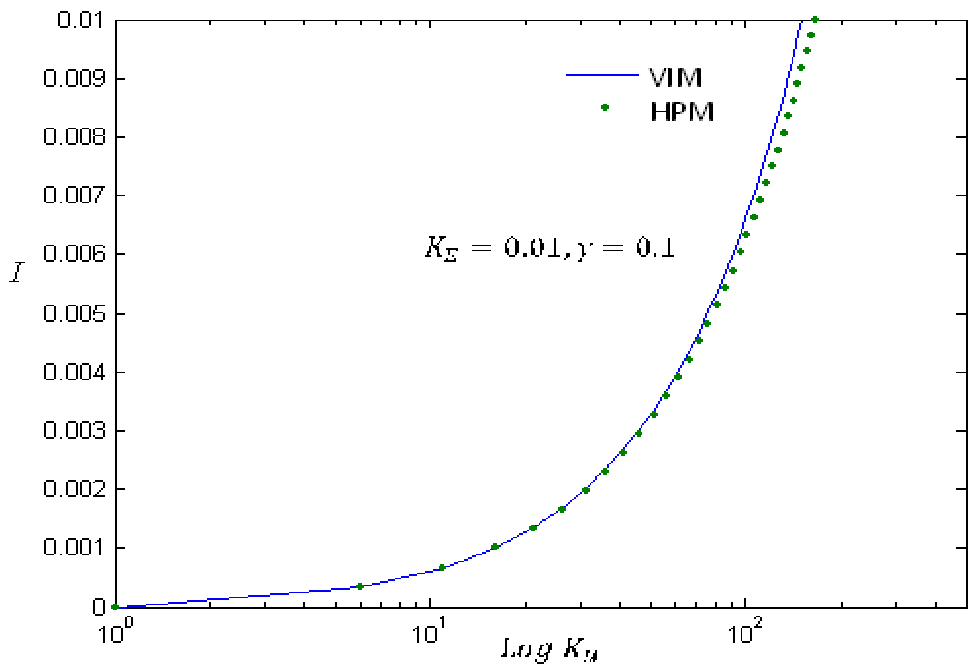

Fig. 7: Comparison of current between VIM [25] and HPM [This work] for various values of K_M.

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