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Revolutionizing Electrochemical kinetics: Homogeneous Redox Catalysis unveiled through an innovative mathematical framework using the Homotopy Perturbation Method

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Abstract:

Introduction: In Redox homogeneous catalysis the catalyst couple merely plays the role of an electron in contrast with chemical catalysis. The mathematical modelling of homogeneous redox catalysis of electrochemical reactions for the EC scheme is described by the system of second order non-linear differential equations. This model was initially designed using the classical differential equations and it is extended to the Caputo fractional derivative (FDE's) of order α in particularly sequential fractional case. The aim is to obtain approximate analytical solutions of the system of FDE's using Homotopy Perturbation method (HPM) and analyze the impact of various parameters with different order of α. In addition, the solution of the sequential dynamic equations yields the solution of the corresponding integer-order differential equations as a special case.

Keywords: Electrochemical reaction, Fractional Differential Equations, Homotopy Perturbation Method.

1. Introduction

Fractional derivatives provide a special instrument for the description of the memory effects and hereditary properties of various materials and processes. In the comparison between fractional derivatives and integer-order derivatives, these effects are not taken into account. K.B. Oldham et al. [2] mentioned in their book that applications in physics, chemistry, and engineering play an outstanding role in the development of the subject of applied fractional calculus. In [1], M. Caputo published his book in 1969, in which he systematically used the original definition of fractional differentiation for formulating and solving various types of problems in various applications like viscoelasticity, rheological properties of rocks, and many other fields. See [14, 16, 21]. They observed in their research of sequential fractional differential equations with boundary value problems and experiments that the use of half-order derivatives and integrals led to a formulation of certain electro-chemical problems that was more useful than the classical approach. And also see [22], where the author mentions that we can compute the numerical solution of the sequential Caputo fractional equations with boundary conditions tend to the corresponding solution of the integer boundary value problems. Otherwise, it can be noted that it is non-sequential.

In the early 1990s, the perturbation method was one of the most effective methods. However, the solutions dealt with small parameters. The development of a new method called the Homotopy Perturbation Method (HPM) has been done to overcome this problem. Ji-Huan He was the first to introduce the homotopy perturbation method in 1998. He introduced this as a means of resolving problems in linear, non-linear, and coupled differential equations in ordinary and partial differential equations with boundary or initial conditions. HPM is a semi-analytical method that is widely used by mathematicians and engineers. This method is a highly effective and convenient way to overcome the difficulties of traditional methods.

Redox reactions generally involve the transfer of electrons between species. Redox reactions are part of everyday activities such as photosynthesis, respiration, coal combustion, and fertilizer production and use. Homogeneous redox catalysis involves analyzing and predicting the effectiveness of catalysis as a function of the potential separation of the catalyst, substrate, and stationary and quasi-stationary methods. C.P. Andrieux et al. [3-5] discussed the mathematical model of the homogeneous redox catalysis of electrochemical reactions. A mathematical model that includes boundary conditions features a system of second-order nonlinear differential equations.

This paper investigates the dynamics of the Electrochemical mechanism model in classical second-order non-linear differential equations with boundary value conditions [4] initially and then updated it to Caputo Sequential fractional equations. The Homotopy Perturbation method (HPM) is used to derive the approximate analytical solutions of the FDE system in fractional order. To analyze the effect of various values of each parameter with different order α on the concentration profile. Additionally, the HPM solutions of the EC mechanisms of fractional order tend to the integer-order HPM solution of the EC mechanism as a special case $\alpha \to 1$.

Nomenclature

P, Q	Catalyst Couple.
A	Substrate.
B	Product.
c_P, c_Q, c_A, c_B	Concentration of P, Q, A, B.
D_p, D_Q, D_A, D_B	Diffusion coefficients of P, Q, A, B in $cm^2 s^{-1}$.
K, K_1, K_2	Rate constants.
$\lambda, \lambda_1, \lambda_2$	Dimensionless rate parameters.
t	Time.
x	Distance to the Electrode.
E	Electrode Potential.
E_{PQ}^o	Standard potential of the Catalyst.
S	Electrode Surface area.
δ	Polarography of the Diffusion layer thickness.
v	Kinetic viscosity in $cm\, s^{-1}$.

ω	Angular rotation speed in $rad\ s^{-1}$.
ξ	Dimensionless potential scale.
ψ^{∞}	Dimensionless Plateau current.
i_1	Catalytic Plateau current.
i_{dP}	Diffusion-controlled Plateau current of P.
i_{dA}	Diffusion-controlled Plateau current of A.

2.Sequential Fractional Derivatives

This approach is based on the observation [2, 10] that the m-th order differentiation is simply a series of first order differentiations. That is,

$$\frac{d^m\varphi(t)}{dt^m} = \left(\frac{d}{dt}\cdot\frac{d}{dt}\dots(m\ times)\right)\varphi(t)$$

K.S.Miller and B.Ross first called the generalized fractional differentiation defined by D^{α} is the Riemann-Lioville fractional derivative and Sequential differentiation. That is a suitable method for replacing $\frac{d}{dt}$ with the derivative of non-integer order D^{α} where $0 \leq \alpha \leq 1$. Therefore, the general fractional differentiation series is written as

$$D^{m\alpha}\varphi(t) = \left(D^{\alpha}.D^{\alpha}\dots(m\ times)\right)\varphi(t)$$

3. Preliminaries

In this section, some basic definitions that will be used in the remaining sections are given,

Definition 1. A real valued function $\varphi(t)$, defined on $[a,b]$ lies in the function space $\mathbb{C}_{\mu}[a,b]$, $\mu \in \mathbb{R}$, if there exists a real number $k > \mu$ such that $\varphi(t) = (t-a)^k\bar{\varphi}(t)$, with $\bar{\varphi} \in \mathbb{C}[a,b]$, and it is said to be in the space $\mathbb{C}_{\mu}^{n}$ if and only if $\varphi^{(n)} \in \mathbb{C}_{\mu}$, n is positive integer number with zero. It is clear that $\mathbb{C}_{\mu_1} \subset \mathbb{C}_{\mu_2}$ for $\mu_1 \leq \mu_2$.

Definition 2. The Caputo fractional derivative of order $\alpha \in \mathbb{R}$ is defined as

$${}_{0}^{C}D_{t}^{\alpha}\varphi(t) = \frac{1}{\Gamma(n-\alpha)}\int_0^t (t-\tau)^{n-\alpha-1}\varphi^{(n)}(\tau)d\tau$$

where $\alpha > 0$. If $\alpha = n$ then ${}_{0}^{C}D_{t}^{\alpha}\varphi(t) = \frac{d^n\varphi(t)}{dt^n}$.

Definition 3. Let $m\alpha > 0$, and $\varphi(t) : (0,\infty) \to \mathbb{R}$. Then, the Caputo derivative of $\varphi(t)$ of order $m\alpha$ is given by

$${}_{0}^{C}D_{t}^{m\alpha}\varphi(t) = \frac{1}{\Gamma(n-m\alpha)}\int_0^t (t-\tau)^{n-m\alpha-1}\varphi^{(n)}(\tau)d\tau$$

where $m \in \mathbb{N}$ such that $(n-1) < m\alpha < n$. In particular, if $\alpha = 1$, then $m\alpha = m$ is an integer and ${}_{0}^{C}D_{t}^{m\alpha}\varphi(t) = {}_{0}^{C}D_{t}^{m}\varphi(t)$ and ${}_{0}^{C}D_{t}^{\alpha}\varphi(t) = \varphi^{1}(t)$.

Definition 4. The Caputo fractional derivative of $\varphi(t)$ of order $m\alpha$ for $(n-1) < m\alpha < n$ is said to be the sequential Caputo fractional derivative of order α if the relation is written as

$$ {}_0^C D_t^{m\alpha}\varphi(t) = {}_0^C D_t^{\alpha}\left({}_0^C D_t^{(m-1)\alpha}\right)\varphi(t) $$

holds for $m = 2,3,\ldots$

Definition 5. The Riemann-Lioville fractional integral operator $(\mathcal{J}^{\alpha})$ of order $\alpha > 0$, of a function $\varphi(t)$ is defined as

$$ \mathcal{J}^{\alpha}\varphi(t) = \frac{1}{\Gamma(\alpha)}\int_0^t (t-\tau)^{\alpha-1}\varphi(\tau)d\tau \qquad (\alpha > 0), $$

$$ \mathcal{J}^{0}\varphi(t) = \varphi(t) $$

where $\Gamma(\alpha)$ is the well-known gamma function.

Some of the properties for $\mathcal{J}^{\alpha}$ and D^{α} can be derived as follows

1) ${}_0^C D_t^{\alpha}\varphi^{\delta} = \frac{\Gamma(\delta+1)}{\Gamma(\delta-\alpha+1)}\varphi^{\delta-\alpha}, \quad \alpha > 0,\ \delta > -1,\ \varphi > 0,$
2) $\mathcal{J}^{\alpha}\varphi^{\delta} = \frac{\Gamma(\delta+1)}{\Gamma(\delta+\alpha+1)}\varphi^{\delta+\alpha}, \quad \alpha > 0,\ \delta > -1,\ \varphi > 0,$
3) $\mathcal{J}^{\alpha}\mathcal{J}^{\vartheta}\varphi(t) = \mathcal{J}^{\vartheta}\mathcal{J}^{\alpha}\varphi(t) = \mathcal{J}^{\alpha+\vartheta}\varphi(t), \quad \alpha,\vartheta > 0,$
4) ${}_a^C D_b^{\alpha}\,\mathcal{J}^{\alpha}\varphi(t) = \varphi(t), \quad a \le t \le b,$
5) $\mathcal{J}^{\alpha}\,{}_0^C D_t^{\alpha}\varphi(t) = \varphi(t) - \sum_k^{\mu-1}\varphi^{(k)}(0^+)\frac{t^k}{k!}\,, \quad \mu-1 < \alpha < \mu, t > 0.$

Lemma 1. If $m-1 < \alpha \le m$ is the order of Caputo fractional derivative ${}_a^C D_b^{\alpha}$, then it is consistent with the integer-order derivative $\frac{d^m}{dt^m}$ for $m \in \mathbb{N}$.

Proof. For $\varphi \in \mathbb{C}^{m+1}([0,\infty])$,then

$$ {}_0^C D_t^{\alpha}\,\varphi(t) = \frac{1}{\Gamma(m-\alpha)}\int_0^t \frac{\varphi^{(m)}(\tau)}{(t-\tau)^{1-(m-\alpha)}}d\tau $$

$$ = \frac{1}{\Gamma(m-\alpha)}\left[-\frac{(t-\tau)^{m-\alpha}}{m-\alpha}\,\varphi^{(m)}(\tau)|_{\tau=0}^{\tau=t} + \int_0^t \frac{(t-\tau)^{m-\alpha}}{m-\alpha}\,\varphi^{(m+1)}(\tau)d\tau\right] $$

$$ = \frac{1}{\Gamma(m-\alpha+1)}\left[0 + t^{m-\alpha}\varphi^{(m)}(0) + \int_0^t (t-\tau)^{m-\alpha}\,\varphi^{(m+1)}(\tau)d\tau\right] $$

and taking the limit: $\alpha \in \mathbb{R} \to m \in \mathbb{N}$ with $m-1 \le \alpha \le m$ yields:

$$ = \frac{1}{\Gamma(1)}\left[\varphi^{(m)}(0) + \int_0^t \varphi^{(m+1)}(\tau)d\tau\right] = \varphi^{(m)}(0) + \varphi^{(m)}(t) - \varphi^{(m)}(0) = \frac{d^m\varphi}{dt^m}(t). $$

4. Mathematical formulation of the problem

The simplest of the reaction sequences in which chemical reactions for Electrochemical (EC) mechanism can be represented in [4]

Electrode process

$$A + 1e \rightleftharpoons B \tag{1}$$

Redox catalyzed process

$$P + 1e \rightleftharpoons Q\left(E^0_{PQ}\right) \tag{2}$$

$$Q + A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} P + B \tag{3}$$

$$B \overset{K}{\rightarrow} C \tag{4}$$

A reduction process of the oxidized form P of the catalyst couple P/Q is introduced into the solution. Here, P/Q is introduced to fulfill the following conditions: the standard potential E^o_{PQ} is positive for the reduction potential of the substrate A; electron alteration between the electrode and P or Q is fast, both P and Q are chemically stable.

In [3, 4] C.P. Andrieux et.al. treat the system as governed by a set of differential equations with boundary conditions and a stationary-state assumption regarding B:

$$K_1 c_A c_Q = K c_B + K_2 c_B c_P \tag{5}$$

Introduce the dimensionless variables as follows:

$$y = x/\delta\,, \quad u = \frac{c_P}{c_P^0}\,, \quad v = \frac{c_Q}{c_P^0}\,, \quad w = \frac{c_A}{c_P^0}\,, \quad b = \frac{c_B}{c_P^0}\,, \quad \gamma = \frac{c_A^0}{c_P^0}\,,$$

$$\xi = -(F/RT)\left(E - E^0_{PQ}\right). \tag{6}$$

The dimensionless rate parameters[4]

$$\lambda_1 = \frac{K_1 c_p^0 \delta^2}{D}, \quad \lambda_2 = \frac{K_2 c_p^0 \delta^2}{D} \quad \lambda = \frac{K\delta^2}{D} \tag{7}$$

Substituting (6) , (7) in [4] gives

$$\frac{d^2u}{dy^2} = -\lambda_1 wv + \lambda_2 bu \tag{8}$$

$$\frac{d^2v}{dy^2} = \lambda_1 wv - \lambda_2 bu \tag{9}$$

$$\frac{d^2w}{dy^2} = \lambda_1 wv - \lambda_2 bu \tag{10}$$

Using (6) and (7) in (5)

$$\lambda b = \lambda_1 wv - \lambda_2 bu \text{ or } b = \frac{\lambda_1 wv}{\lambda + \lambda_2 u} \tag{11}$$

$$\text{when } y = 1\text{: } u = 1\,,\ v = b = 0\,, \quad w = \gamma \tag{12}$$

when $y = 0$:

$$\left(\frac{du}{dy}\right) + \left(\frac{dv}{dy}\right) = 0\,, \quad u = v\exp(-\xi), \quad \left(\frac{dw}{dy}\right) = -\left(\frac{db}{dy}\right) = 0 \tag{13}$$

From equations (8), (9), (11) and (12), It is clear that $u + v = 1$. In particular $u_0 + v_0 = 1$ and therefore,taking (13) into:

$$u_0 = \frac{1}{1 + \exp(\xi)}, v_0 = \frac{1}{1 + \exp(-\xi)}$$

Finally, the system of second order non-linear differential equation and substitute for b (11) in (8) − (10)

$$\frac{d^2u}{dy^2} + \lambda_1 wv - Cuvw = 0 \tag{14}$$

$$\frac{d^2v}{dy^2} - \lambda_1 wv + Cuvw = 0 \tag{15}$$

$$\frac{d^2w}{dy^2} - \lambda_1 wv + Cuvw = 0 \tag{16}$$

with the boundary conditions,

$$y = 1: \quad u = 1\,,\ v = 0\,,\ w = \gamma \tag{17}$$

$$y = 0: \quad u = \frac{1}{[1 + exp(\xi)]} = s \text{ (say)}, \frac{du}{dy} + \frac{dv}{dy} = 0\,, \ \frac{dw}{dy} = 0 \tag{18}$$

where $\frac{\lambda_1\lambda_2}{\lambda+\lambda_2} = C(\text{say})$.

A fractional model in Caputo Sequential derivative.

The fractional framework for the EC mechanism (14) − (16) is given as follows:

$${}_{0}^{CS}D_y^{2\alpha}u(y) + {\lambda_1}^{\alpha}wv - C^{\alpha}uvw = 0 \tag{19}$$

$${}_{0}^{CS}D_y^{2\alpha}v(y) - {\lambda_1}^{\alpha}wv + C^{\alpha}uvw = 0 \tag{20}$$

$${}_{0}^{CS}D_y^{2\alpha}w(y) - {\lambda_1}^{\alpha}wv + C^{\alpha}uvw = 0 \tag{21}$$

with $b = \frac{{\lambda_1}^{\alpha}wv}{\lambda^{\alpha} + {\lambda_2}^{\alpha}u}$. (22)

where ${}_{0}^{CS}D_y^{2\alpha}$ represents Caputo-Sequential derivative with Fractional order 2α.

5. Analysis of pre-equilibrium and stationary-state assumptions.

This section discusses the equilibrium points of the EC fractional model and the stationary-state of the model (14) − (16)

(i) Kinetic control by chemical reaction (4) with electrode process(1) acts as a pre-equilibrium.

In the context of homogeneous redox catalysis, when the follow-up chemical reaction (4) is slower than the backward solution electron transfer (3), the overall reaction kinetics are controlled by the follow-up chemical reaction, with the reaction (3) acting as a pre-equilibrium. The proceeding system $(8)-(10)$ of three differential equations can be reduced into a single differential equation that is

$$\frac{d^2u}{dy^2}+\left(\frac{\lambda\lambda_1}{\lambda_2}\right)[\psi(y-1)+1+\gamma-u]\frac{(1-u)}{u}=0 \tag{23}$$

where ψ is the dimensionless plateau current depends upon olnly two parameters γ and $\frac{\lambda\lambda_1}{\lambda_2}=(kk_1/k_2)(\delta^2/D)$.

In [4], which corresponds to general cases, some of the observations are represented as follows:

(i) The system depends on two kinetic parameters and γ, and for high values of $\frac{\lambda\lambda_1}{\lambda_2}$, the catalytic efficiency reaches unity, and the current-potential curves split into two waves.
(ii) An increase in δ shifts the catalytic efficiency of the system from low to high.
(iii) The catalytic efficiency is a function of $\lambda_1(7)$, and an increase in c^0 leads to an increase in λ_1, resulting in the function $\frac{\lambda\lambda_1}{\lambda_2}=(kk_1/k_2)(\delta^2/D)$ independent of c^0.

(ii) The stationary-state assumption regarding B.

Suppose there is no chemical reaction of the electron-transfer, i.e. when $\lambda=0$. Then the stationary-state assumption regarding B is no longer valid.

In [4], (i) The stationary-state assumption is valid when the follow-up chemical reaction is slower than the backward solution electron transfer, and the catalytic efficiency is low. (ii) The stationary-state assumption leads to two limiting situations for extreme values of k/k_2, which involve kinetic control of the overall reaction either by the forward reaction (3) or by reaction $(4)$with (3) as a pre-equilibrium. (iii) The polarization problem can be numerically solved for these two limiting cases as well as for the transition between them in the context of stationary or quasi-stationary electrochemical methods. (iv) The stationary-state assumption reduces the number of parameters needed to describe the reaction kinetics, making it easier to analyze and understand the kinetics of electrochemical reactions under homogeneous redox catalysis. (v) The stationary-state assumption has limitations and is only valid for certain ranges of catalytic efficiency and rate constants.

The previously established results concerning pre-equilibrium and the stationary-state assumption are relevant when addressing fractional differential equations with orders ranging from 0 to 1.

6.Basic idea of Homotopy Perturbation method for system of FDEs

First to illustrate the basic idea of Homotopy Perturbation method, many applications are modelled by systems of Fractional Differential equations which can be written in the form

$$D^{\alpha_1}\varphi_1(t)=f_1(t,\varphi_1,\varphi_2,\varphi_3,\dots,\varphi_n) \tag{25}$$

$$D^{\alpha_2}\varphi_2(t) = f_2(t, \varphi_1, \varphi_2, \varphi_3, \dots, \varphi_n) \tag{26}$$

.
.
.

$$D^{\alpha_n}\varphi_n(t) = f_n(t, \varphi_1, \varphi_2, \varphi_3, \dots, \varphi_n) \tag{27}$$

Subject to the initial condtions: $\varphi_n(t) = c_k,\ \ k = 1,2, \dots, n$.

where D^{α_i} is the fractional derivative of order $\alpha_i \ \ (m-1 < \alpha_i \le m)$ and f_i are arbitrary linear and nonlinar functions.

construct the following homotopy:

$$D^{\alpha_i}\varphi_i = pf_i(t, \varphi_1, \varphi_2, \varphi_3, \dots, \varphi_n) \tag{28}$$

where $i = 1,2, \dots, n$ and p is an embedding parameter which is monotonically increasing from 0 to 1. Using the parameter p, we expand the solution of the system $(25) - (27)$ in the form

$$\varphi_i(t) = \varphi_{i0} + p\varphi_{i1} + p^2\varphi_{i2} + p^3\varphi_{i3} + \cdots \tag{29}$$

Substituting (29) into (28) and the resultant equation is in terms with the same powers of p,

p^o: $\quad D^{\alpha_i}\varphi_{i0} = 0,$

p^1: $\quad D^{\alpha_i}\varphi_{i1} = f_{i1}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0}),$

p^2: $\quad D^{\alpha_i}\varphi_{i2} = f_{i2}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0},\ \varphi_{11}, \varphi_{21}, \varphi_{31}, \dots, \varphi_{n1}),$

p^3: $\quad D^{\alpha_i}\varphi_{i3} = f_{i3}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0},\ \varphi_{11}, \varphi_{21}, \varphi_{31}, \dots, \varphi_{n1}, \varphi_{11},\ \varphi_{22}, \varphi_{32}, \dots, \varphi_{n2}),$

etc., where the functions satisfies the following equation

$$\begin{aligned} &f_i(t, \varphi_{10} + p\varphi_{11} + p^2\varphi_{12} + \cdots, \varphi_{n0} + p\varphi_{n1} + p^2\varphi_{n2} + \cdots) \\ &\ = f_{i1}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0}) + pf_{i2}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0},\ \varphi_{11}, \varphi_{21}, \varphi_{31}, \dots, \varphi_{n1}) \\ &\qquad + p^2 f_{i3}(t, \varphi_{10}, \varphi_{20}, \varphi_{30}, \dots, \varphi_{n0},\ \varphi_{11}, \varphi_{21}, \varphi_{31}, \dots, \varphi_{n1}, \varphi_{11},\ \varphi_{22}, \varphi_{32}, \dots, \varphi_{n2}) + \cdots \end{aligned}$$

It can be easily solve by applying the $\mathcal{J}^{\alpha_i}$ that is the inverse of the operator D^{α_i}. By setting $p = 1$ in (28), Hence the components $\varphi_{ik}(k = 0,1,2, \dots)$ of the HPM solution can be determined.

7.The HPM of solving system of FDEs (19)-(21)

Construct the following homotopy

$${}_{0}^{CS}D_y^{2\alpha}u(y) = p(-{\lambda_1}^{\alpha}wv + C^{\alpha}uvw) \tag{30}$$

$${}_{0}^{CS}D_y^{2\alpha}v(y) = p({\lambda_1}^{\alpha}wv - C^{\alpha}uvw) \tag{31}$$

$${}_{0}^{CS}D_y^{2\alpha}w(y) = p({\lambda_1}^{\alpha}wv - C^{\alpha}uvw) \tag{32}$$

By perturbation technique, u, v and w can be written as a following series in p :

$$u = u_0 + pu_1 + p^2u_2 + \cdots \tag{33}$$

$$v = v_0 + pv_1 + p^2v_2 + \cdots \tag{34}$$

$$w = w_0 + pw_1 + p^2w_2 + \cdots \qquad (35)$$

Substituting $(33)-(35)$ into $(30)-(32)$ and equating terms of the same powers of p yields the following three sets of equations

$$\begin{aligned}
&p^0 \; : \; {}_0^{CS}D_y^{2\alpha}\, u_0 = 0 && p^0 \; : \; {}_0^{CS}D_y^{2\alpha}\, v_0 = 0\\
&p^1 \; : \; {}_0^{CS}D_y^{2\alpha}\, u_1 = -{\lambda_1}^{\alpha} w_0 v_0 + C^{\alpha} u_0 v_0 w_0 && p^1 \; : \; {}_0^{CS}D_y^{2\alpha}\, v_1 = {\lambda_1}^{\alpha} w_0 v_0 - C^{\alpha} u_0 v_0 w_0\\
&\quad\vdots && \quad\vdots
\end{aligned}$$

$$\begin{aligned}
&p^0 \; : \; {}_0^{CS}D_y^{2\alpha}\, w_0 = 0\\
&p^1 \; : \; {}_0^{CS}D_y^{2\alpha}\, w_1 = {\lambda_1}^{\alpha} w_0 v_0 - C^{\alpha} u_0 v_0 w_0\\
&\quad\vdots
\end{aligned}$$

Applying the operator of $\mathcal{J}^{\alpha}$ which is inverse operator of D^{α} in to $u_0, v_0, w_0, u_1, v_1, w_1, \ldots$

$u_0(y) = (1-s)y + s, \quad v_0(y) = (s-1)y + (1-s), \; w_0(y) = \gamma$

$$\begin{aligned}
u_1(y) = {} & \gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{y^{2\alpha}}{\Gamma(2\alpha+1)} + \gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)}\\
& -C^{\alpha}\gamma(1-s)^2\frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} + \{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)}\\
& -\gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{1}{\Gamma(2\alpha+2)} + \gamma(1-s)^2\frac{2}{\Gamma(2\alpha+3)}\}y^{\alpha}
\end{aligned}$$

$$\begin{aligned}
v_1(y) = {} & \gamma(1-s)[{\lambda_1}^{\alpha} - C^{\alpha}s]\frac{y^{2\alpha}}{\Gamma(2\alpha+1)} + \gamma(s-1)[{\lambda_1}^{\alpha} - C^{\alpha}s - C^{\alpha}(s-1)]\frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)}\\
& +C^{\alpha}\gamma(1-s)^2\frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} + \{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)}\\
& -\gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{1}{\Gamma(2\alpha+2)} - \gamma(1-s)^2\frac{2}{\Gamma(2\alpha+3)}\}y^{\alpha}
\end{aligned}$$

$$\begin{aligned}
w_1(y) = {} & \gamma(1-s)[{\lambda_1}^{\alpha} - C^{\alpha}s]\frac{y^{2\alpha}}{\Gamma(2\alpha+1)} + \gamma(s-1)[{\lambda_1}^{\alpha} - C^{\alpha}s - C^{\alpha}(s-1)]\frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)}\\
& +C^{\alpha}\gamma(1-s)^2\frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} + \{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)}\\
& -\gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{1}{\Gamma(2\alpha+2)} - \gamma(1-s)^2\frac{2}{\Gamma(2\alpha+3)}\}y^{\alpha}
\end{aligned}$$

Letting $p \to 1$ gives Therefore,

$$
\begin{aligned}
u(y) = {} & (1-s)y + s + \gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}] + \gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s] \\
& \frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)} - C^{\alpha}\gamma(1-s)^2 \frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} + \{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)} \\
& - \gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{1}{\Gamma(2\alpha+2)} \\
& + \gamma(1-s)^2 \frac{2}{\Gamma(2\alpha+3)}\}y^{\alpha}
\end{aligned}
\tag{36}
$$

$$
\begin{aligned}
v(y) = {} & (s-1)y + (1-s) + \gamma(1-s)[{\lambda_1}^{\alpha} - C^{\alpha}s]\frac{y^{2\alpha}}{\Gamma(2\alpha+1)} \\
& + \gamma(s-1)[{\lambda_1}^{\alpha} - C^{\alpha}s - C^{\alpha}(s-1)]\frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)} + C^{\alpha}\gamma(1-s)^2 \\
& \frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} + \{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)} - \gamma(s-1) \\
& [C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s]\frac{1}{\Gamma(2\alpha+2)} - \gamma(1-s)^2\frac{2}{\Gamma(2\alpha+3)}\}y^{\alpha}
\end{aligned}
\tag{37}
$$

$$
\begin{aligned}
w(y) = {} & \gamma + \gamma(1-s)[{\lambda_1}^{\alpha} - C^{\alpha}s]\frac{y^{2\alpha}}{\Gamma(2\alpha+1)} + \gamma(s-1)[{\lambda_1}^{\alpha} - C^{\alpha}s - C^{\alpha}(s-1)]\frac{y^{2\alpha+1}}{\Gamma(2\alpha+2)} \\
& + C^{\alpha}\gamma(1-s)^2\frac{y^{2\alpha+2}}{\Gamma(2\alpha+3)} \\
& +\{-\gamma(1-s)[C^{\alpha}s - {\lambda_1}^{\alpha}]\frac{1}{\Gamma(2\alpha+1)} - \gamma(s-1)[C^{\alpha}(s-1) - {\lambda_1}^{\alpha} + C^{\alpha}s] \\
& \frac{1}{\Gamma(2\alpha+2)} - \gamma(1-s)^2\frac{2}{\Gamma(2\alpha+3)}\}
\end{aligned}
\tag{38}
$$

Remark

Substituting the expressions of $u(y), v(y)$ and $w(y)$ in (22). The concentration of the product B can be obtained as $b(y)$.

8. Analysis and discussion

In this section, we established the significance of the parameters $\lambda, C, \gamma, \lambda_1, \lambda_2$ and ξ on the concentration of $P, Q, A,$ and B.

Fig 1 Dimensionless concentration u , v , w, b versus Dimensionless distance y computed using (36) to (38), (22) for various values of α, and for some fixed value of parameters λ , γ, λ_1, λ_2 and ξ .

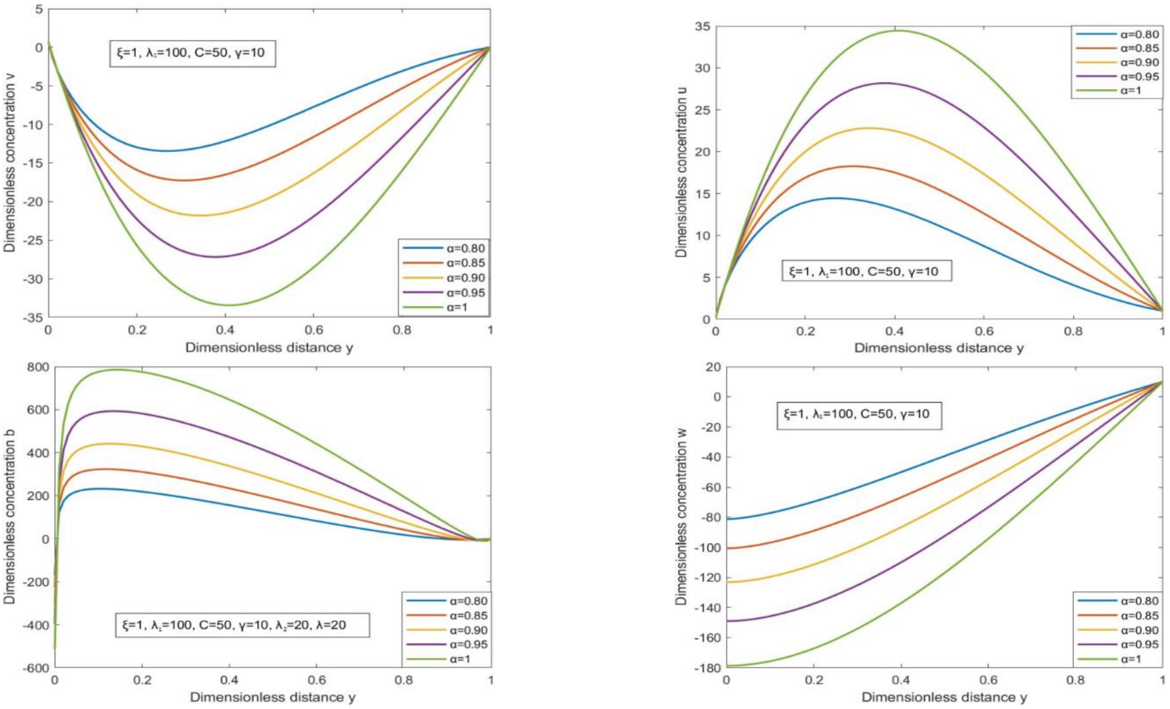


Fig 2 Dimensionless concentration u , v , w, b versus Dimensionless distance y computed using (36) to (38), (22) for various values of C, and for some fixed value of parameters λ , γ, λ_1, λ_2 and ξ .

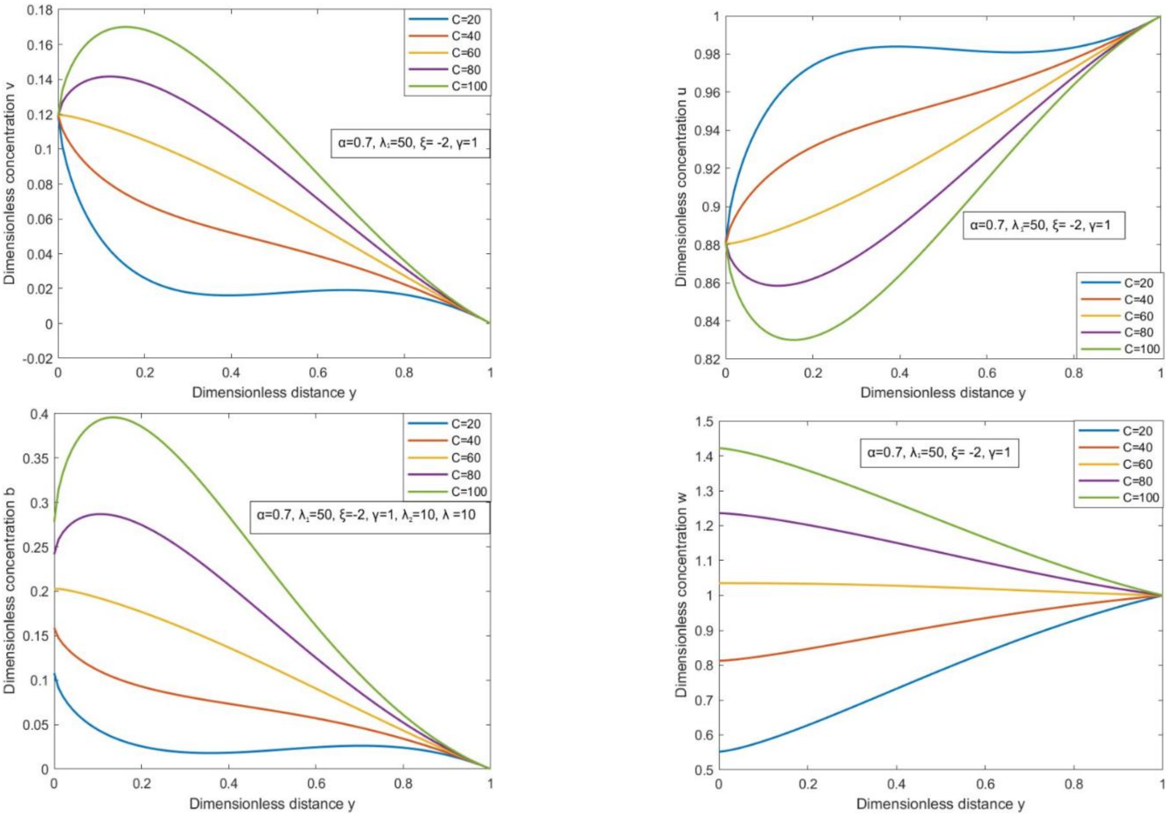


Fig 3 Dimensionless concentration u , v , w, b versus Dimensionless distance y computed using (36) to $(38), (22)$ for various values of dimensionless potential ξ and for some fixed value of parameters λ , C, λ_1, λ_2 and γ.

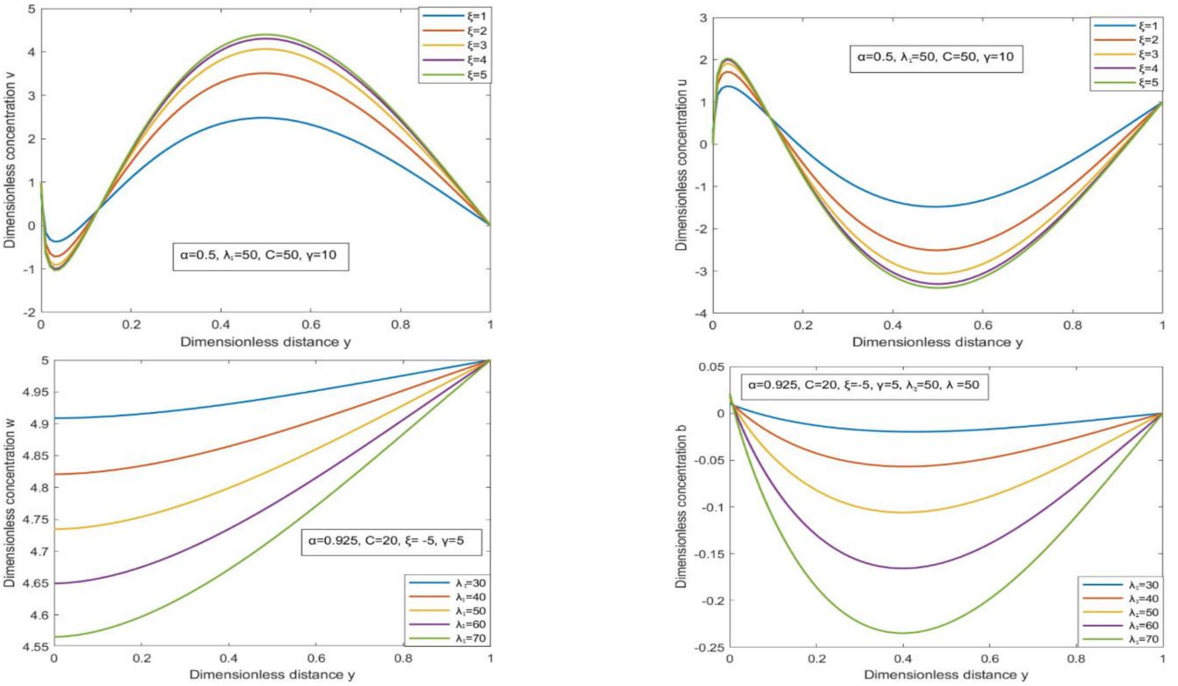


Fig 4 Dimensionless concentration u , v , w, b versus Dimensionless distance y computed using (36) to $(38), (22)$ for various values of λ_1, and for some fixed values of parameters ξ , C, λ_2 and γ.

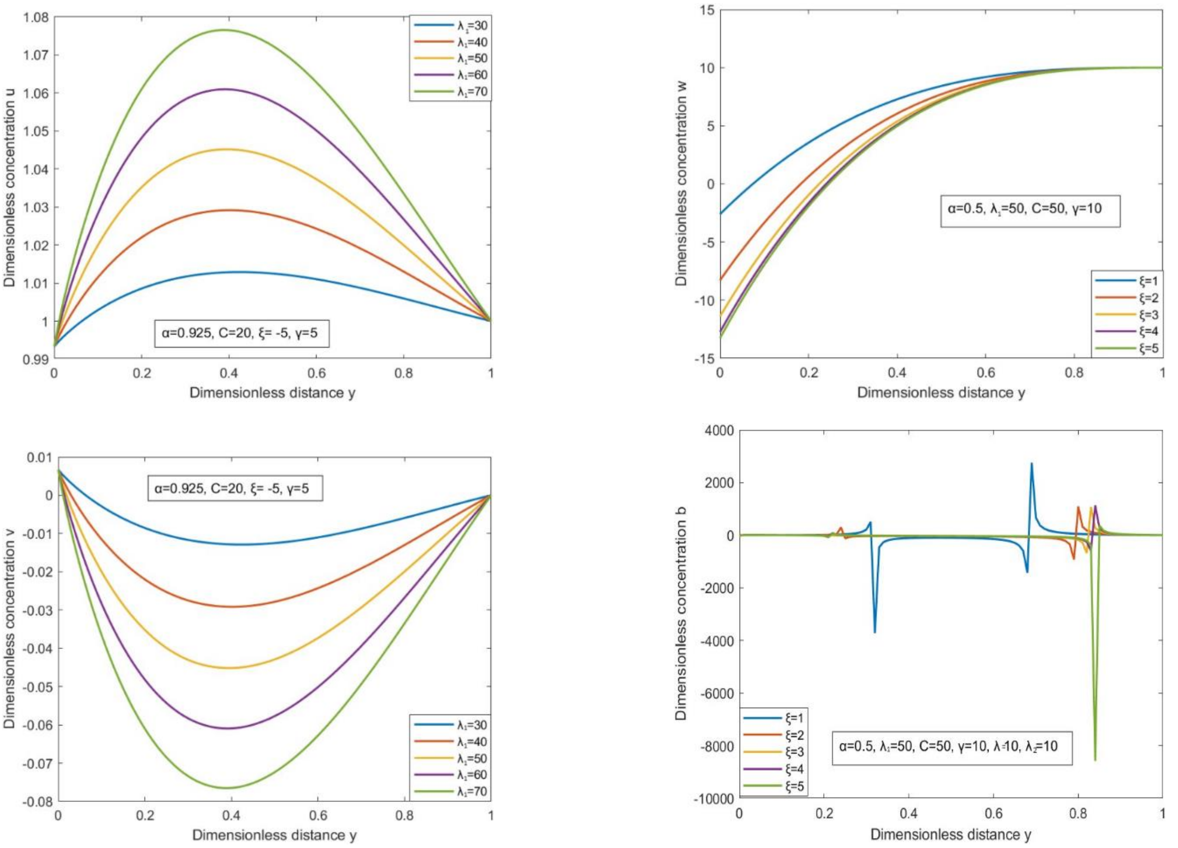
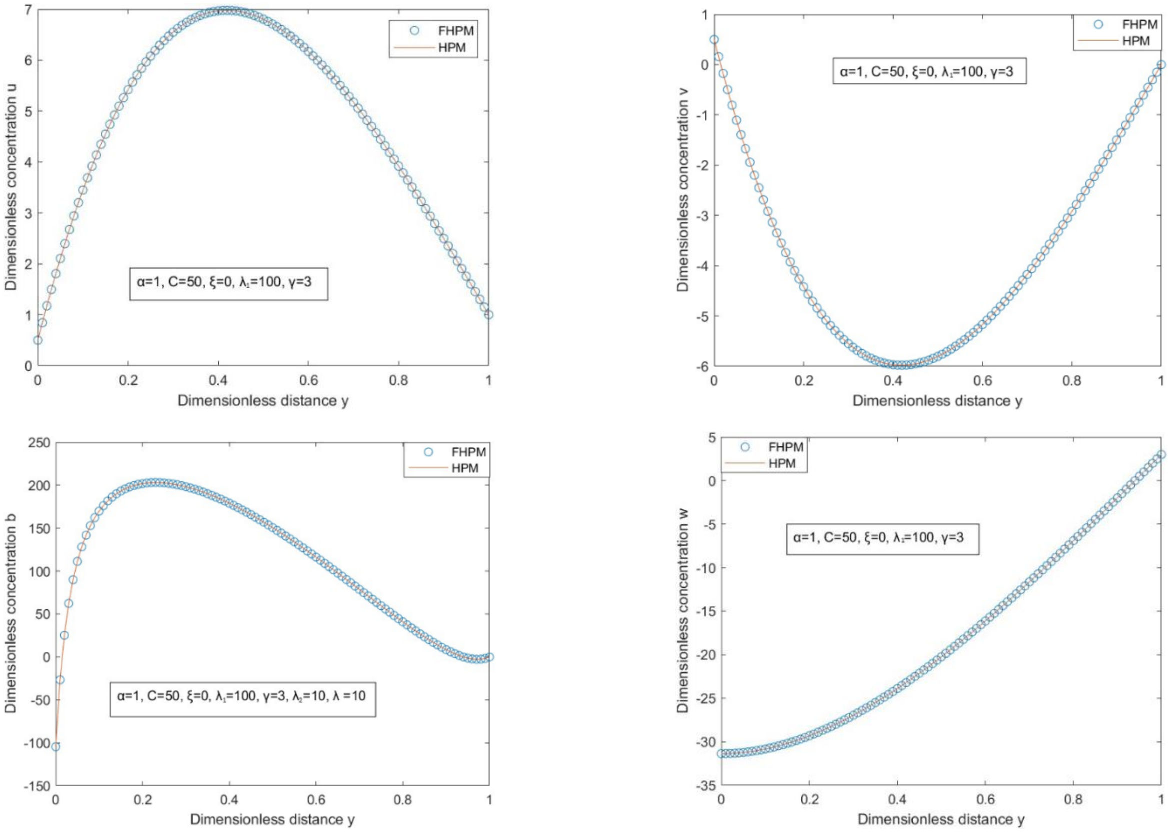


Fig 5 The HPM solution of the Caputo sequential system of fractional equations(36) to (38) yields the solution of the corresponding integer-order differential equations$(A23)$, $(A24)$ and $(A25)$ as a special case $\alpha \to 1$.



Equations $(36) - (38)$ and the remark represents the analytical expressions for the Dimensionless Concentration profile for Catalyst P and Q , and the substrate A and the product B for the different values of the parameters $\xi, \lambda_1, \gamma, C, \lambda, \lambda_2$ with the different non-integer order. In figures(1), demonstrate the Dimensionless concentration of P, Q, A, B for some fixed values of parameter with different values of fractional order α. This figures gives more accurate results compared to classical model. In figures(2), shows that the concentration of the Catalyst Q, the substrate A and the product B are directly proportional to C but concentration of the Catalyst P is inversely proportional to C. In figures(3), Catalyst P initially exhibits direct proportionality to potentialξ, changing to inverse proportionality at specific points. Similarly, Catalyst Q initially increases with ξ up to a certain point, then decreases. Simultaneously, product B undergoes a slight increase followed by a more significant decrease. In figures(4), shows that the concentration of the Catalyst P is directly proportional to λ_1,but concentration of the Catalyst Q, the substrate A and the product B are inversely proportional to λ_1. In figures(5), shows that the fractional HPM yields the solution of the corresponding integer-order differential equations$(A23)$, $(A24)$ and $(A25)$ as a special case.

9. Conclusion

In this paper, a new mathematical model based on the Caputo-Sequential fractional differential systems of the EC mechanism was investigated with steady-state assumptions. The fractional model of the EC mechanism gives more accurate results as compared to the classical integer-order model.

The dynamic system of non-linear equations with fractional order has been solved by the semi-analytical method, that is, HPM, which has very high accuracy. This method is effective and efficient not only for classical differential equations but also for fractional derivatives. The influence of the various parameters on catalytic efficiency was discussed. Additionally, we demonstrate that the sequential system of fractional equations yields the solution of the integer-order differential equations as a special case as $\alpha \to 1$.

Appendix A

The Homotopy Perturbation method of solving system of second order non-linear differential equation of EC mechanism

Here we can solve the system of second order non-linear differential equations $(14) - (16)$ with boundary conditions (17) and (18) analytically using Homotopy Perturbation method [4] in the following way.

Using Homotopy for the equations (14) to (16) are

$$(1-p)\left(\frac{d^2u}{dy^2}\right)+p\left[\frac{d^2u}{dy^2}+\lambda_1 wv - Cuvw\right]=0$$

$$\frac{d^2u}{dy^2}+p\lambda_1 wv - pCuvw = 0 \qquad (A1)$$

$$(1-p)\left(\frac{d^2v}{dy^2}\right)+p\left[\frac{d^2v}{dy^2}-\lambda_1 wv + Cuvw\right]=0$$

$$\frac{d^2v}{dy^2}-p\lambda_1 wv + pCuvw = 0 \qquad (A2)$$

$$(1-p)\left(\frac{d^2w}{dy^2}\right)+p\left[\frac{d^2w}{dy^2}-\lambda_1 wv + Cuvw\right]=0$$

$$\frac{d^2w}{dy^2}-p\lambda_1 wv + pCuvw = 0 \qquad (A3)$$

By Perturbation technique, u, v and w can be written as a series in p as follows :

$$u = u_0 + pu_1 + p^2u_2 + \cdots \qquad (A4)$$

$$v = v_0 + pv_1 + p^2v_2 + \cdots \qquad (A5)$$

$$w = w_0 + pw_1 + p^2w_2 + \cdots \qquad (A6)$$

Equating the identical powers of p on both sides of equation $(A1)$ and $(A4)$ to $(A6)$ gives,

$$p^0 \quad : \quad \frac{d^2u_0}{dy^2} = 0 \qquad (A7)$$

$$p^1 \quad : \quad \frac{d^2u_1}{dy^2} + \lambda_1 w_0 v_0 - Cu_0 w_0 \qquad (A8)$$

$$\vdots$$

At $y = 1,\ u_0 = 1\,,\ u_i = 0 \ \forall \ i = 1,2,3,\ldots$ $(A9)$

At $y = 0,\ u_0 = s\,,\ u_i = 0 \ \forall \ i = 1,2,3,\ldots$ $(A10)$

Equating the identical powers of p on both sides of equation $(A2)$ and $(A4)$ to $(A6)$ gives,

$$p^0 \quad : \quad \frac{d^2v_0}{dy^2} = 0 \qquad (A11)$$

$$p^1 \quad : \quad \frac{d^2v_1}{dy^2} - \lambda_1 w_0 v_0 + Cu_0 w_0 v_0 = 0 \qquad (A12)$$

$$\vdots$$

At $y = 1,$ $\quad v_0 = 0 \ \ \forall \ \ i = 0,1,2,3,\ldots$ $(A13)$

At $y = 0,$ $\quad \dfrac{du_i}{dy} + \dfrac{dv_i}{dy} = 0 \ \forall \ \ i = 0,1,2,3$ $(A14)$

Equating the identical powers of p on both sides of equation $(A3)$ and $(A4)$ to $(A6)$ gives,

$$p^0 \quad : \quad \frac{d^2w_0}{dy^2} = 0 \qquad (A15)$$

$$p^1 \quad : \quad \frac{d^2w_1}{dy^2} - \lambda_1 w_0 v_0 + Cu_0 w_0 \qquad (A16)$$

$$\vdots$$

At $y = 1,$ $\quad w_0 = \gamma \ \ w_i = 0 \ \forall \ i = 1,2,3,\ldots$ $(A17)$

At $y = 0,$ $\quad \dfrac{dw_i}{dy} = 0 \ \forall \ \ i = 0,1,2,3,\ldots$ $(A18)$

Integrating $(A7), (A8), (A11), (A12), (A15), (A16)$ with respect to y,

$$u_0(y) = y(1-s) + s; \quad v_0(y) = (s-1)y + (1-s); \qquad w_0(y) = \gamma \qquad (A19)$$

$$u_1(y) = \frac{C\gamma(2s - s^2 - 1)}{12} y^4 + \frac{\gamma(2Cs^2 - 3Cs + C - \lambda_1 s + \lambda_1)}{6} y^3 + \frac{\gamma(Cs - Cs^2 - \lambda_1 + \lambda_1 s)}{2} y^2 + \frac{(3Cs^2\gamma - 2Cs\gamma - C\gamma - 4\lambda_1 s\gamma + 4\lambda_1\gamma)}{12} \qquad (A20)$$

$$v_1(y) = \frac{C\gamma(s^2 - 2s + 1)}{12} y^4 + \frac{\gamma(3Cs - 2Cs^2 - C + \lambda_1 s - \lambda_1)}{6} y^3 + \frac{\gamma(Cs^2 - Cs + \lambda_1 - \lambda_1 s)}{2} y^2 + \frac{(2Cs\gamma - 3Cs^2\gamma + C\gamma - 4\lambda_1 s\gamma + 4\lambda_1\gamma)}{12}\, y \tag{A21}$$

$$w_1(y) = \frac{C\gamma(s^2 - 2s + 1)}{12} y^4 + \frac{\gamma(3Cs - 2Cs^2 - C + \lambda_1 s - \lambda_1)}{6} y^3 + \frac{\gamma(Cs^2 - Cs + \lambda_1 - \lambda_1 s)}{2} y^2 + \frac{2Cs\gamma - 3Cs^2\gamma + C\gamma + 4\lambda_1 s\gamma - 4\lambda_1\gamma}{12} \tag{A22}$$

Letting $p \to 1$ gives, therefore

$$u(y) = s + \frac{(12 - 12s + 3Cs^2\gamma - 2Cs\gamma - C\gamma - 4\lambda_1 s\gamma + 4\lambda_1\gamma)}{12} y + \frac{\gamma(Cs - Cs^2 - \lambda_1 + \lambda_1 s)}{2} y^2 + \frac{\gamma(2Cs^2 - 3Cs + C - \lambda_1 s + \lambda_1)}{6} y^3 + \frac{C\gamma(2s - s^2 - 1)}{12}\, y^4 \tag{A23}$$

$$v(y) = 1 - s - \frac{(12 - 12s + 3Cs^2 - 2Cs\gamma - C\gamma - 4\lambda_1 s\gamma + 4\lambda_1\gamma)}{12} y - \frac{\gamma(Cs - Cs^2 - \lambda_1 + \lambda_1 s)}{2} y^2 - \frac{\gamma(2Cs^2 - 3Cs + C - \lambda_1 s + \lambda_1)}{6} y^3 - \frac{C\gamma(2s - s^2 - 1)}{12}\, y^4 \tag{A24}$$

$$w(y) = \frac{(12\gamma + 2Cs\gamma - 3Cs^2\gamma + C\gamma + 4\lambda_1 s\gamma - 4\lambda_1\gamma)}{12} - \frac{\gamma(Cs - Cs^2 - \lambda_1 + \lambda_1 s)}{2} y^2 - \frac{\gamma(2Cs^2 - 3Cs + C - \lambda_1 s + \lambda_1)}{6} y^3 - \frac{C\gamma(2s - s^2 - 1)}{12} y^4 \tag{A25}$$

The equations $(A23)$, $(A24)$ and $(A25)$ gives the approximate analytical solution of the system $(14) - (16)$.

Remark

Substituting the expressions of $u(y), v(y)$ and $w(y)$ in (11). The concentration of the product B can be obtained as $b(y)$.

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