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Mathematical Modeling of Microbial Fuel Cells in Wastewater Treatment - Homotopy Perturbation Method

S. ThamizhSuganya, P. Balaganesan, L. Rajendran

Abstract: Mathematical modeling of Microbial Fuel Cell (MFC), which accounts for the co-existence of methanogenic and anodophilic microbial populations for different operating modes and reactor configurations, is discussed. This model based on the system of non-linear rate equations, where the non-linear term is related to the rate of the reactions. The system of non-linear equations is solved by using homotopy perturbation method. In this paper closed form of analytical expression of the concentration of substrate, anodophilic, methanogenic, and the mediator is derived. The analytical expressions are compared with simulation results for the experimental values of parameters, and satisfactory agreement is noted. The influence of parameters on the concentration profiles are discussed.

Keywords: Microbial fuel cell,Mathematical modeling, Non-linear equation, Homotopy Perturbation Method, Cogeneration, Model-based design, Microbial Electrolysis Cell, Dynamic model.

I. INTRODUCTION

The MFCs are bioreactors with the ability to transform an oversized sort of extremely diluted natural thing of varied forms into electricity [1]. The main limitation of the application of MFC is its low power output. [2]. Also, using the wastewater as a substrate indicates the presence of mixed microbial populations, enzymatic, methanogenic, and anodophilic microorganisms [3-5], which affects the MFC's performance. One way to understand the complex problems that MFCs present is to create a dynamic mathematical model that can clarify the behavior of several microbial populations contesting the same substratum [6]. This paper represents a steady-state study of a dynamic system designed to explain two microbial coexisting in MFC [7]. This model takes into account the struggle for substrates between anodophilic and methanogenic microorganisms.
Apple (Maluspumila Mill.) is a prevalent arbor tree species in northern China, which makes China the most extensive area for apple fruit production [8].

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* Correspondence Author
S. Thamizh Suganya*, Department of Mathematics, AMET Deemed to be University, Kanathur, Chennai, Tamil Nadu, India,
Email: thamsuganms@yahoo,com
P. Balaganesan, Department of Mathematics, AMET Deemed to be University, Kanathur, Chennai, Tamil Nadu, India,
Email: balaganesanpp@gmail.com
L. Rajendran, Department of Mathematics, AMET Deemed to be University, Kanathur, Chennai, Tamil Nadu, India,
Email: raj_sms@rediffmail.com

Bioelectrochemical systems (BESs) are conventional technologies for the treatment of industrial wastewaters [9, 10]. Devinny et al. [11], explain the attempts that have been creating the mathematical illustrations of biofilters and bio-trickling filter. Kim and Deshusses [12],
simulate this effect, using an earlier grown up the empirical relationship to assessments the fraction of load surface wetted. Recently, Kirthiga and Rajendran[13] have obtained analytical expression on the concentrations of the output of biomass and ethanol from industrial wastewater. Analytical expressions of the concentrations of a substrate, biomass, and ethanol derived for solid-state enzymatic of biofuel production [14]. This paper presented a steady-state analysis of the MFC and the analytical expression of a substrate, anodophilic, methanogenic, and oxidized mediators obtained in all parameters.

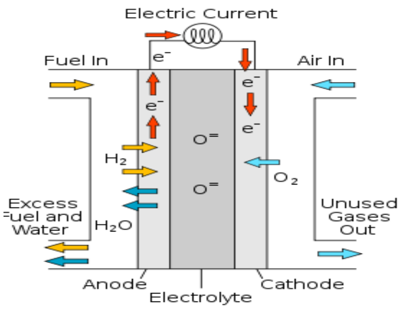

Figure 1: Microbial Fuel Cell in waste water treatment[1]

Table 1: Nomenclature of the given parameters [15]

Parameters	Meaning	Experimental value	Unit
S	Substrate concentration	-	$mg\text{-}S\ L^{-1}$
x_a	Anodophilic concentration	-	$mg\text{-}x\ L^{-1}$
x_m	Methanogenic concentraion	-	$mg\text{-}x\ L^{-1}$
M_{ox}	Oxidized mediator	-	$mg\text{-}M\ mg\text{-}x^{-1}$
S_o	Influent concentration	-	$mg\text{-}S\ L^{-1}$
t	Time	-	day
T	MFC temperature	298.15	K
R	Ideal gas constant	8.314	$J\ K^{-1}\ mol^{-1}$
F	Faraday constant	96485	$A\ d\ mole^{-1}$
D	Dilution rate	0.1	$L\ d^{-1}V^{1}$
Y	Yield in Eqn.(7)	22.75	$mg\text{-}M\ mg\text{-}S^{-1}$
$\mu_{max,m}$	Maximum methanogenic growth rate	0.1	d^{-1}

$\mu_{max,a}$	Maximum anodophilic growth rate	1.97	d^{-1}
$q_{max,m}$	Maximum methanogenic reaction rate	8.20	mg-S mg-x^{-1} d^{-1}
$q_{max,a}$	Maximum anodophilic reaction rate	1.97	mg-S mg-x^{-1} d^{-1}
R_{min}	Minimum internal resistance	25	Ω
R_{max}	Maximum internal resistance	2025	Ω
X_{max}	Maximal attainable biomass	525	mg-x L^{-1}
$K_{d,a}$	Decay rate of anodophils	0.04	d^{-1}
$K_{d,m}$	Decay rate of methanogens	0.0002	d^{-1}
$K_{s,m}$	Half-rate constant of methanogens	80	mg-S L^{-1}
$K_{s,a}$	Half-rate constant of anodophils	20	mg-S L^{-1}
γ	Mediator molar mass	663400	mg-M $mole_{med}^{-1}$
M	e^- transferred per mol of mediator	2	$mole^{-1}$ $mole_{med}^{-1}$
K_M	Mediator half-rate constant	0.01	mg-M L^{-1}
M_{total}	Mediator fraction	0.05	mg-M mg-x^{-1}
K_x	Parameter in Eqn.(8)	0.4	L mg-x^{-1}
E_{max}	Maximum E_{OCV}	0.674	V
E_{min}	Minimum E_{OCV}	0.01	V
K_R	Parameter in Eqns.(10) and (11)	0.024	L mg-x^{-1}

II. A MATHEMATICAL FORMULATION OF THE PROBLEM

This system reflects the substratum of anodophilic and methanogenic microorganisms that are modeled using an intracellular mediator in this case, the acetate charge transfer at the anode. The anode reactions are as follows [15]:

$$S + M_{ox} \rightarrow M_{red} + CO_2 \quad (1)$$

$$M_{red} \rightarrow M_{ox} + e^- \quad (2)$$

$$S \rightarrow CH_4 + CO_2 \quad (3)$$

where S is the substrate concentration, CH_4 and CO_2 is methane and carbon dioxide gas transport through the porous cathode is neglected and e^- is an electron and M_{red} and M_{ox} is the reduced and oxidized forms of the intracellular mediator are respectively.The dynamic mass balance equations as follows:

$$\frac{dS}{dt} = D(S_0 - S) - \frac{q_{maxa}S}{K_{S,a}+S}\frac{M_{ox}}{K_M + M_{ox}}x_a - \frac{q_{maxm}S}{K_{S,m}+S}x_m \quad (4)$$

$$\frac{dx_a}{dt} = \left(\frac{\mu_{maxa}S}{K_{S,a}+S}\frac{M_{ox}}{K_M+M_{ox}} - K_{d,a} - \alpha D\right)x_a \quad (5)$$

$$\frac{dx_m}{dt} = \left(\frac{\mu_{maxm}S}{K_{S,m}+S} - K_{d,m} - \alpha D\right)x_m \quad (6)$$

$$\frac{dM_{ox}}{dt} = \frac{\gamma I_{MFC}}{mFVx_a} - Y\frac{q_{maxa}S}{K_{S,a}+S}\frac{M_{ox}}{K_M+M_{ox}} \quad (7)$$

where $\alpha = \left(\frac{1+\tanh[K_x(x_a + x_m - X_{max})]}{2}\right)$ (8)

$$I_{MFC} = \left(E_{OCV} - \frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{ox}}\right)\right)(R_{ext}+R_{int})^{-1} \quad (9)$$

$$R_{int} = R_{min} + (R_{max} - R_{min})e^{-K_R x_a} \quad (10)$$

$$E_{OCV} = E_{min} + (E_{max} - E_{min})e^{-\frac{1}{K_R x_a}} \quad (11)$$

The initial conditions are

$$S = S_{in},\ x_a = x_{ain},\ M_{ox} = M_{oxin} \quad at \quad t=0 \quad (12)$$

The steady-state solution of (4) - (7) present the following possible solutions[15]:

Case (1): $A=0$ and $x_m = 0$ (anodophilic microorganisms)

Case (2): $A=0$ and $B=0$ (coexistence)

Case (3): $B=0$ and $x_a = 0$ (methanogenic microorganisms)

Case (4): $x_m = 0$ and $x_a = 0$ (wash-out solution)

where $A = \frac{\mu_{maxa}S}{K_{S,a}+S}\frac{M_{ox}}{K_M+M_{ox}} - \alpha D$, $B = \frac{\mu_{maxa}S}{K_{S,a}+S} - \alpha D$ (13)

III. ANALYTICAL EXPRESSIONS OF SUBSTRATE CONCENTRATION, THE CONCENTRATION OF MICROORGANISMS AND OXIDIZED MEDIATOR

The homotopy perturbation method was proposed by He [16]. In most cases, this approach results in a very fast accumulation of the solution, with several iterations leading to definite answers. Several researchers used different methods to research the solution of nonlinear equations. The benefit of this technique, they don't need a small parameter in the given system, leading to detailed application in nonlinear equations.

A. Case (1): Only anodophilic microorganisms:

In this case $A=0$ and $x_m = 0$ in equations (4), (5) and (7) we get the following equations

$$\frac{dS}{dt} = D(S_0 - S) - \frac{q_{maxa}}{\mu_{maxa}}\left[\frac{1+\tanh(K_x x_a - K_x X_{max})}{2}\right]x_a D \quad (14)$$

$$\frac{dx_a}{dt} = -K_{d,a}x_a \quad (15)$$

$$\frac{dM_{ox}}{dt} = \left\{\frac{\gamma\left[E_{min} + (E_{max}-E_{min})e^{-\frac{1}{K_R x_a}} - \frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{ox}}\right)\right]}{mFVx_a(R_{ext} + R_{min} + (R_{max}-R_{min})e^{-K_R x_a})} - YD\frac{q_{maxa}}{\mu_{maxa}}\left[\frac{1+\tanh(K_x x_a - K_x X_{max})}{2}\right]\right\} \quad (16)$$

Solving the above equations using HPM (Appendix-A)we get

$$S(t) = S_{in}e^{-Dt} + S_0(1-e^{-Dt}) + \left[\frac{q_{maxa}}{\mu_{maxa}}\frac{1+\tanh[K_x(x_{ain} - X_{max})]}{2}x_{ain}\right](e^{-Dt}-1) \quad (17)$$

$$x_a(t) = x_{ain}e^{-K_{d,a}t} \quad (18)$$

$$M_{ox}(t) = \frac{\gamma\left[E_{min} + (E_{max}-E_{min})e^{-\frac{1}{K_R x_{ain}}} - \frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{oxin}}\right)\right]}{mFVK_{d,a}x_{ain}[R_{ext} + R_{min} + (R_{max}-R_{min})e^{-K_R x_{ain}}]}(e^{k_{d,a}t}-1) + M_{oxin} - YD\frac{q_{maxa}}{\mu_{maxa}}\left[\frac{1+\tanh(K_x x_{ain} - K_x X_{max})}{2}\right]t \quad (19)$$

B. Case (2): Coexistence:

In this case $A=0$ and $B=0$ in equations (4) - (7)we get the following equations

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$$\frac{dS}{dt}=D(S_0-S)-\left[\frac{q_{max,a}}{\mu_{max,a}}x_a-\frac{q_{max,m}}{\mu_{max,m}}x_m\right]\left[\frac{1+\tanh(K_x(x_a+x_m-X_{max}))}{2}\right]D \quad (20)$$

$$\frac{dx_a}{dt}=-K_{d,a}x_a \quad (21)$$

$$\frac{dx_m}{dt}=-K_{d,m}x_m \quad (22)$$

$$\frac{dM_{ox}}{dt}=\frac{\gamma\left[E_{min}+(E_{max}-E_{min})e^{\frac{-1}{K_R x_a}}-\frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{ox}}\right)\right]}{mFVx_a[R_{ext}+R_{min}+(R_{max}-R_{min})e^{-K_R x_a}]}-y\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x(x_a+x_m-X_{max}))}{2}\right]D \quad (23)$$

Solving the above equation using HPM we get

$$S(t)=S_{in}e^{-Dt}+S_0(1-e^{-Dt})-\left[\left[\frac{q_{maxa}}{\mu_{maxa}}x_{ain}-\frac{q_{maxm}}{\mu_{maxm}}x_{min}\right]\left[\frac{1+\tanh(K_x(x_{ain}+x_{min}-X_{max}))}{2}\right]\right](1-e^{-Dt}) \quad (24)$$

$$x_a(t)=x_{ain}e^{-K_{d,a}t} \quad (25)$$

$$x_m(t)=x_{min}e^{-K_{d,m}t} \quad (26)$$

$$M_{ox}(t)=\frac{\gamma\left[E_{min}+(E_{max}-E_{min})e^{\frac{-1}{K_R x_a}}-\frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{oxin}}\right)\right]}{(R_{ext}+R_{min}+(R_{max}-R_{min})e^{-K_R x_a})(mFVx_{ain})K_{d,a}}(e^{K_{d,a}t}-1)+M_{oxin}-yD\frac{q_{maxa}}{\mu_{maxa}}\left[\frac{1+\tanh(K_x(x_{ain}+x_{min}-X_{max}))}{2}\right] \quad (27)$$

C. Case (3): Only methanogenic microorganisms:

In this case $B=0$ and $x_a=0$ in equations (4) and (5) we get the following equations

$$\frac{dS}{dt}=D(S_0-S)-\frac{q_{max,m}}{\mu_{max,m}}\left[\frac{1+\tanh[K_x(x_m-X_{max})]}{2}\right]Dx_m \quad (28)$$

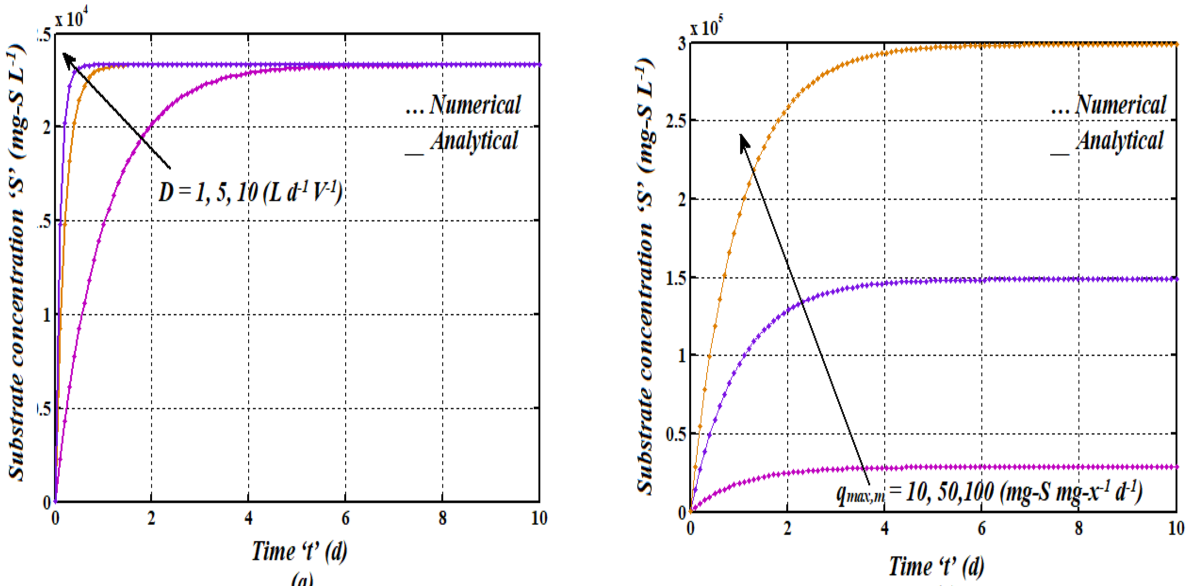
$$\frac{dx_m}{dt}=-K_{d,m}x_m \quad (29)$$

By solving the above equations using new approach of HPM, the following concentration of the substrate, anodophilc, methanogenic, and mediator are obtained.

$$S(t)=S_{in}e^{-Dt}+S_0(1-e^{-Dt})+\left[\frac{q_{maxm}}{\mu_{maxm}}\frac{1+\tanh[K_x(x_{min}-X_{max})]}{2}x_{min}\right](e^{-Dt}-1) \quad (30)$$

$$x_m(t)=x_{min}e^{-K_{d,m}t} \quad (31)$$

where S is a substrate concentration, S_0 is influent substrate concentration, x_a is a concentration of anodophilic, x_m is a methanogenic concentration, M_{ox} is an oxidized mediator fraction per anodophilic microorganism. D is a dilution rate, $q_{max,a}$ is a maximum anodophilic reaction rate, $K_{S,a}$ is a half-rate constant of anodophilics, K_M is a mediator half-rate constant, $q_{max,m}$ is a maximum methanogenic reaction rate, $K_{S,m}$ is a half-rate constant of methanogens, $\mu_{max,a}$ is a maximum anodophilic growth rate, $K_{d,a}$ is a decay rate of anodophilic microorganisms, α is a dimensionless biofilm retention parameter, $\mu_{max,m}$ is a maximum methanogenic growth rate, $K_{d,m}$ is a decay rate of methanogenic microorganisms, γ is a mediator molar mass, I_{MFC} is the MFC current, F is a Faraday constant, K_x is a parameter in α, X_{max} is a maximal attainable biomass, E_{OCV} is the MFC open circuit, R_{ext} is an external resistance, R_{int} is an internal resistance, R is an ideal gas constant, T is a MFC temperature, M_{total} is a mediator fraction, R_{min} is minimum internal resistance, R_{max} is a maximum internal resistance, E_{max} is a minimum MFC open circuit voltage, E_{min} is a maximum MFC open circuit voltage, K_R is a parameter in internal resistance and MFC open circuit voltage and $Y$is yield in mediator. Where the all parameters are constants.



(a) (b)

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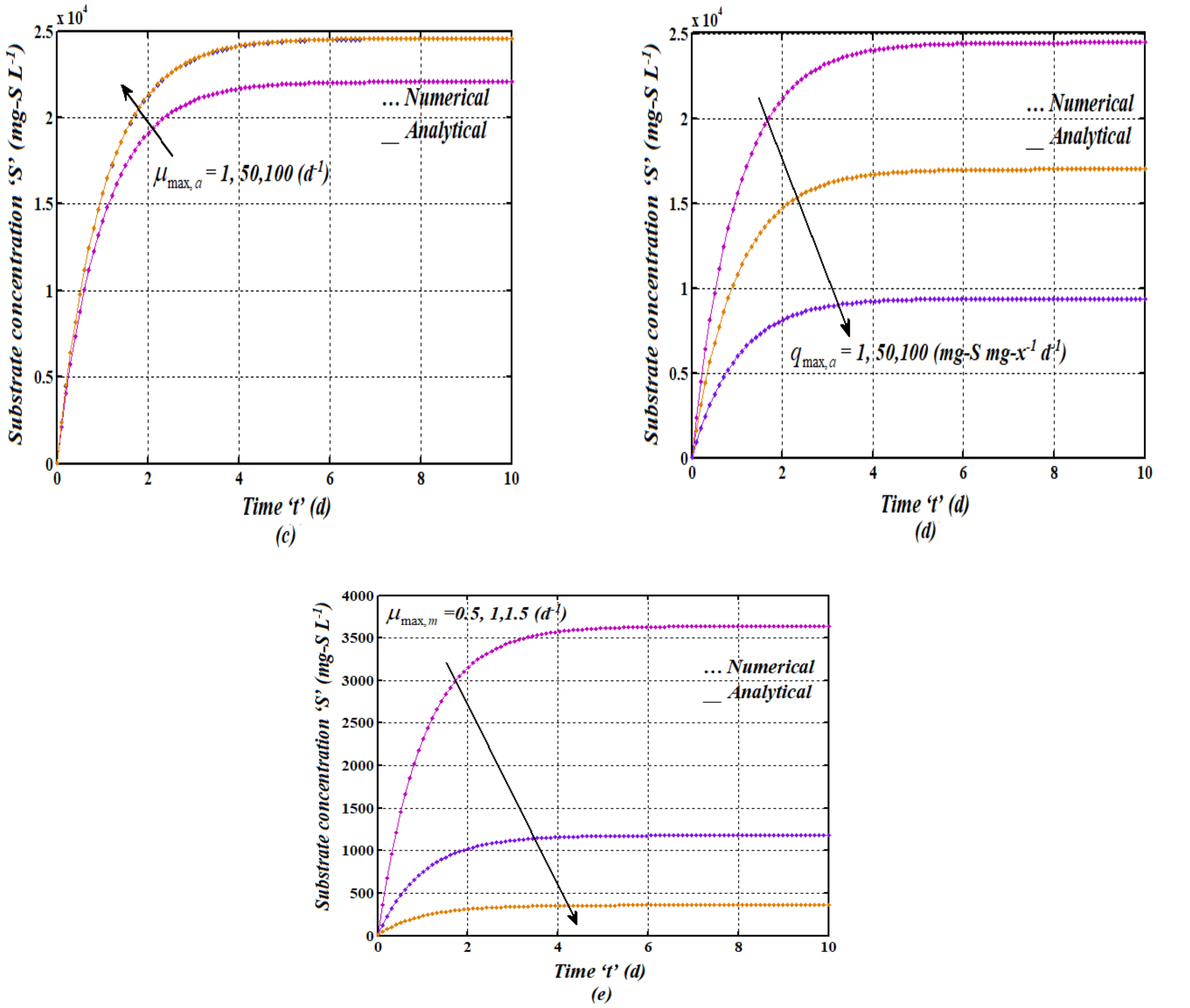

Figure 2: Comparison of analytical and simulation results for the substrate concentration using various values of the parameters

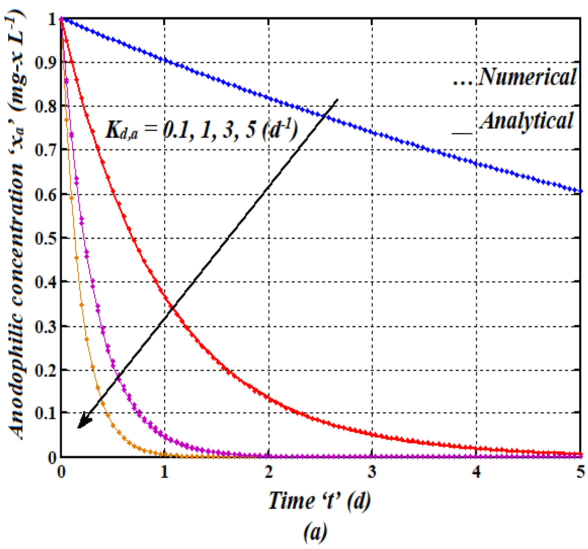

Figure 3: Comparison of analytical and simulation results for the anodophilic concentration using various values of the parameters

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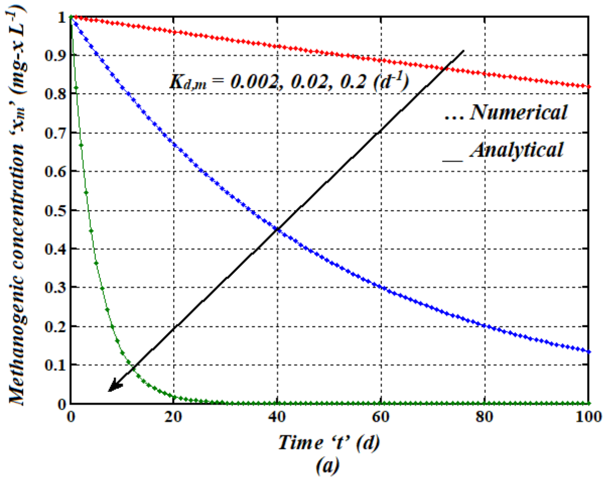

Figure 4: Comparison of analytical and simulation results for the methanogenic concentration using various values of the parameters

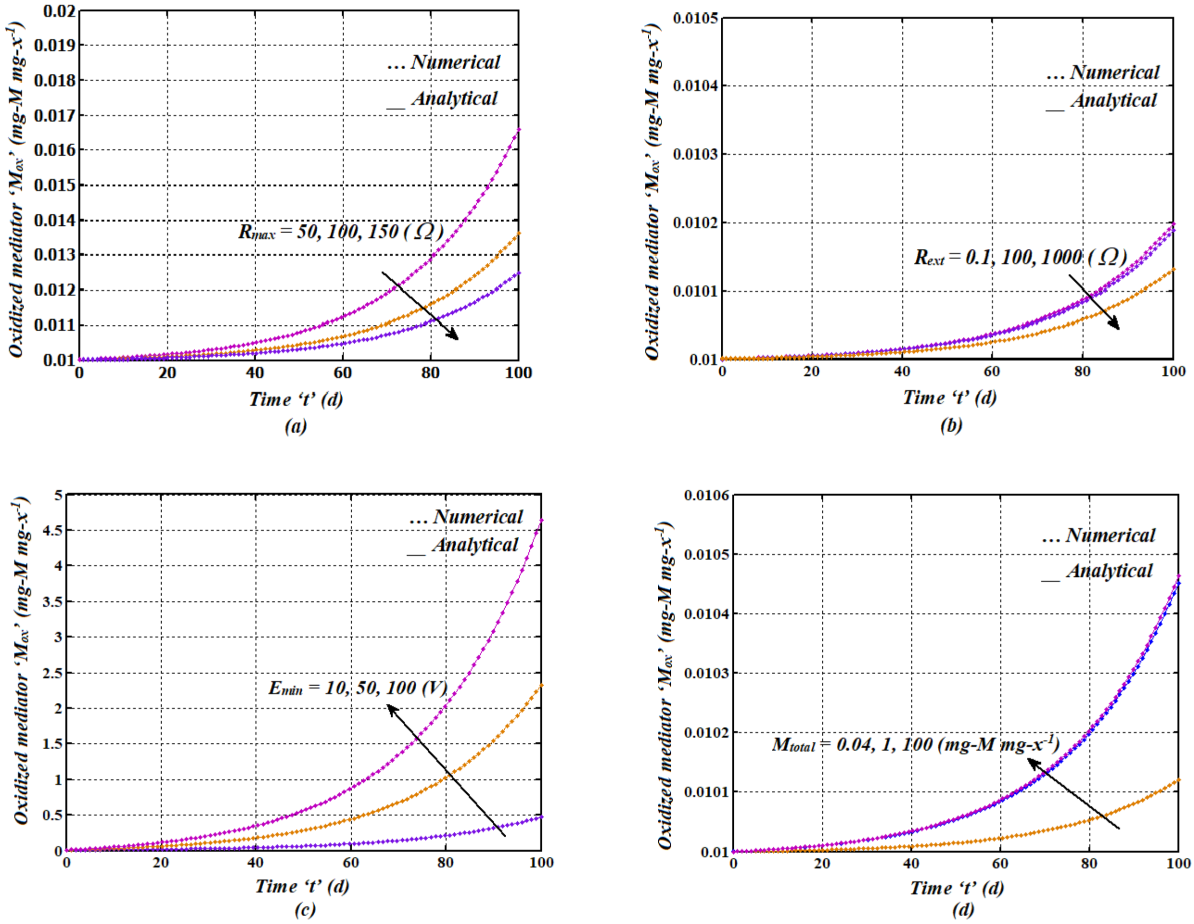

Figure 5: Comparison of analytical and simulation results for the Oxidized mediator using various values of the parameters

IV. NUMERICAL SIMULATION

For the given system of nonlinear differential equations (4)-(7) is solved numerically. To solve this equation, the function "ode45" in MATLAB software is used to solve the initial value issues for nonlinear differential equations. This program is given in the section of the Appendix.

V. RESULTS AND DISCUSSION

The above solutions represent the new approximate analytical expression for the substrate, anodophilic, methanogenic, and mediator concentration profiles using homotopy perturbation approach for all values of parameters. Itsatisfies the initial condition Eqn. (12).

Figs. 2(*a*), 2(*b*) and 2(*c*), represents the substrate concentration for different values of *D*, $q_{max,m}$,and $\mu_{max,a}$. It is observed that an increase in the parametersleads to an increase in concentration.Figs. 2(*d*) and 2(*e*) that the substrate concentration decreases as the values of maximum anodophilic reaction rate $q_{max,a}$ and maximum methanogenicgrowth rate $\mu_{max,m}$increases.Mathuriya and Sharma [17]

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was represented in the current generation decreases with reduce in wastewater organic material concentration.At less substrate concentration, the highest power generation is proportionally attached to substrate concentration [18].

The effects of the anodophilc$K_{d,a}$ on the concentration profile shown in Fig. 3(a), where it is noticed that an decrease in $K_{d,a}$ leads to an increase in the anodophilic concentration. Similarly, Fig. 4(a) represents the $K_{d,m}$ on the concentration profile, where it is noticed that a decrease in $K_{d,m}$ leads to an increase in the methanogenic concentration.

The mediator concentration profiles versus time expressed in Figures 5(a)-(d). From these Figures, it represented that the value of the mediator concentration reducing when the resistance increase. Lower or higher concentration leads to increased internal resistance and decreases efficiency. Increasing the operating temperature rises bacterial activity, reduces internal resistance, and improves efficiency.But the mediator concentration increases when the Mediator fraction $M_{total}$and minimum voltage E_{min} increases.

VI. CONCLUSION

A steady-state one-dimensional mathematical model for the prediction of the concentration of anodophilic and methanogenic microorganisms in microbial fuel cells is discussed. The system of non-linear equations is solved using the homotopy perturbation method for various limiting cases. The effects of varies parameters on concentration profiles are explained. Our analytical results agree very well with numerical results. The presented theoretical model is a useful tool to improve MFC understanding and to optimize fuel cell design and operation.

APPENDIX – A

A. Analytical solutions of non-linear equations (14) and (16) using HPM

Equation (14) and (16) can be written as follows:

$$\frac{dS}{dt}=D(S_0-S)-\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a-K_x X_{max})}{2}\right]x_a D \quad \text{(A.1)}$$

$$\frac{dM_{ox}}{dt}=\frac{\gamma I_{MFC}}{mFVx_a}-YD\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a-K_x X_{max})}{2}\right] \quad \text{(A.2)}$$

The initial conditions are

$$S=S_{in},\quad M_{ox}=M_{oxin}\quad at\quad t=0 \quad \text{(A.3)}$$

where

$$x_a(t)=x_{ain}e^{-K_{d,a}t},\ I_{MFC}=\left(E_{OCV}-\frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{ox}}\right)\right)(R_{ext}+R_{int})^{-1},$$
$$R_{int}=R_{min}+(R_{max}-R_{min})e^{-K_R x_a},\ E_{OCV}=E_{min}+(E_{max}-E_{min})e^{-\frac{1}{K_R x_a}}$$

(A.4)

Construct thehomotopy for the equation (A.1) and (A.2) method as follows [19]:

$$(1-p)\left[\frac{dS}{dt}-D(S_0-S)+\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a(t=0)-K_x X_{max})}{2}\right]x_a(t=0)D\right]$$
$$+p\left[\frac{dS}{dt}-D(S_0-S)+\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a-K_x X_{max})}{2}\right]x_a D\right]=0$$

(A.5)

$$(1-p)\left[\frac{dM_{ox}}{dt}-\frac{\gamma I_{MFC}}{mFVx_a(t=0)}+YD\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a(t=0)-K_x X_{max})}{2}\right]\right]$$
$$+p\left[\frac{dM_{ox}}{dt}-\frac{\gamma I_{MFC}}{mFVx_a}+YD\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_a-K_x X_{max})}{2}\right]\right]=0$$

(A.6)

The approximate solution of equations (A.1) and (A.2) are

$$S=S_0+pS_1+p^2S_2+p^3S_3+.... \quad \text{(A.7)}$$

$$M_{ox}=M_{ox_0}+pM_{ox_1}+p^2M_{ox_2}+p^3M_{ox_3}+.... \quad \text{(A.8)}$$

Substituting equations (A.7) and (A.8) into equations (A.5) and (A.6), and equate the terms with the identical powers of p^0, we obtain

$$p^0:\frac{dS_0}{dt}-D(S_0-S)+\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_{ain}-K_x X_{max})}{2}\right]x_{ain}D=0$$

(A.9)

$$p^0:\frac{dM_{ox_0}}{dt}-\frac{\gamma I_{MFC}}{mFVx_{ain}}+YD\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_{ain}-K_x X_{max})}{2}\right]=0$$

(A.10)

The initial conditions for equations (A.9) and (A.10) ar

$$S_0(t=0)=S_{in},\ and\ M_{ox_0}(t=0)=M_{oxin} \quad \text{(A.11)}$$

Solving equations (A.9) and (A.10) for the above initial conditions, we can obtained $S(t)$ and $M_{ox}(t)$ as follows.

$$S(t)=S_{in}e^{-Dt}+S_0(1-e^{-Dt})+\left[\frac{q_{max,a}}{\mu_{max,a}}\frac{1+\tanh[K_x(x_{ain}-X_{max})]}{2}x_{ain}\right](e^{-Dt}-1)$$

(A.12)

$$M_{ox}(t)=\frac{\gamma\left[E_{min}+(E_{max}-E_{min})e^{-\frac{1}{K_R x_{ain}}}-\frac{RT}{F}\ln\left(\frac{M_{total}}{M_{total}-M_{oxin}}\right)\right]}{mFVK_{d,a}x_{ain}[R_{ext}+R_{min}+(R_{max}-R_{min})e^{-K_R x_{ain}}]}(e^{k_{d,a}t}-1)$$
$$M_{oxin}+-YD\frac{q_{max,a}}{\mu_{max,a}}\left[\frac{1+\tanh(K_x x_{ain}-K_x X_{max})}{2}\right]t$$

(A.13)

The same procedure is used to obtained the concentration profiles for other limiting cases.

Appendix – B:

Numerical solution of non-linear differential equations (4) – (7) using Matlab coding

```
function main1
options= odeset('RelTol',1e-6,'Stats','on');
xo = [1; 1; 1];
tspan = [0,100];
tic
[t,X] = ode45 (@ TestFunction,tspan,Xo,options);
toc
figure
hold on
plot  (t, x(:,1))


plot  (t, x(:,2))
plot  (t, x(:,3))
return
function [dx_dt]= TestFunction(t,x)
          D=0.1; S1=10; S=1; q=9; K=1; a=1; b=10; N=0.1;
k=1;g=5;k=1;E=1+9*exp(1);R=8.314;T=100;F=96485;M1=
10;M=1;m=.1;v=1;R1=10;
r1=1+19*exp(-1);
y=2;D=.1;K=3;a=1;b=10;q=1;N=1;
dx_dt(1)=-D*(S1-S)+((D*q*(1+tanh((K*a)-
(K*b))))/(2*N));
dx_dt(2)=-k*x(2);
dx_dt(3)=((((g*exp(k*t))*(E-((R*T)*log(M1/(M1-
M)))/F)))/((m*F*v*a)*(R1+r1)))-
((y*D*q*(1+tanh((K*a)-(K*b))))/(2*N));
dx_dt = dx_dt';
```

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AUTHORS PROFILE

S. Thamizh Suganya, born at Pavuppattu, Thiruvannamalai, Tamil Nadu, India on 11.05.1992. Obtained her M.Sc. in Mathematics from Government arts and Science College, Thiruvannamali, Tamil Nadu, India during 2015. Also she is doing her Ph.D. in ''Analysis, Computation and Mathematical modelling of reaction diffusion processes" at AMET Deemed to be university University under the guidance of Dr. P. Balaganesan, Assistant Professor in Mathematics, AMET Deemed to be University, Kanathur, Chennai, Tamil Nadu, India.

P. Balaganesan is an Associate Professor in the Department of Mathematics, AMET Deemed to be University, Chennai 603112. He has been serving in the field of academic for more than two decades. He obtained his Bachelor of Science and Master of Science in Bharathidasan University. He has completed his master of Philosophy in Mathematics in Madurai Kamaraj University. He has completed Ph.D in Mathematics at Hindustan University. He published 20 Research papers in reputed National and International Journals.

L. Rajendran is a Professor at the Department of Mathematics, Academy of Maritime Education and Training (Deemed to be University), Chennai, India. He has published 110 papers in international/SCI journals and 100 papers in national journals. He has also written four books. He serves as a reviewer in many International Journals. He completed 6 research projects from various funding agencies in India. More than 35 students completed the Ph.D under his guidance. He visited Germany and Poland under INSA fellowships.