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Mathematical Modelling Of A Biofilm-Based Microbial Fuel Cells Using Homotopy Perturbation Method

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Abstract*—The theoretical model for biofilm-based microbial fuel cells is analyzed. Some biological, chemical and electrochemical reactions occur in the bulk liquid, in the biofilm and at the electrode surface, involving glucose and redox mediators. The homotopy perturbation method (HPM) is used to solve the nonlinear diffusion equations in Microbial fuel cells. Simple and approximate polynomial expression of a substrate (acetate), oxidized mediator and reduced mediator concentration is obtained at the biofilm. *The analytical result is compared with the numerical results and satisfactory agreement is noted.

Keywords—Mathematical modeling, Numerical simulation, Microbial fuel cell, Biofilm, mediators, Homotopy perturbation method.

I. INTRODUCTION

A microbial fuel cell can use complex organic substrates as a source of electricity, including domestic, industrial and agricultural wastewater, attracting attention as a promising technology that links renewable energy and waste treatment[1,2].The biocatalytic cycle performed by the microorganisms in fuel cells varies from the natural situation, as the electron flow goes to a solid electrode[3].In an electrochemical reaction at the anode the reduced mediator is re-oxidised. In the anolyte and in the biofilm attached to the anode, multiple species of methanogenic and electroactive microorganisms co-exist suspended.This model will also integrate information from many areas into mass balances for soluble and biomass components: electro-chemical reactions on the surface of the anode, biochemical reactions in suspended and biofilm cells, transport mechanisms for soluble components and microbial cells. Picioreanu et al. [4] developed a general model describing the MFC behavior with both suspended cell and added electron transfer mediator. In this paper, analytical expressions of the concentration of substrate (acetate), oxidized and reduced mediator in bulk liquid/biofilm is obtained by solving the non-linear equations using the homotopy perturbation method for all values of parameters,

Nomenclature

Symbols	Meanings	Value	Unit
$S_{B,Ac}, S_{B,Mred}$ $S_{B,Mox}$	Concentration of bulksubstrate(acetate),reduced and oxidized mediator.	-	$gCODm^{-3}, mM, mM$
X_B	Concentration of bulk biomass	-	$gCODm^{-3}$
$S_{F,Ac}$, $S_{F,Mred}$ $S_{F,Mox}$	Concentration of biofilm substrate(acetate),reduced and oxidized mediator.	-	$gCODm^{-3}, mM, mM$
$S_{0,Ac}$, $S_{0,Mred}$ $S_{0,Mox}$	Initial concentration ofbulk liquid/biofilmsubstrate(acetate),reduced and oxidized mediator.	1	$gCODm^{-3}, mM, mM$
D_{Mred}, D_{Mox}	Diffusion coefficient of mediator	0.06	$m^2\ day^{-1}$
D_{Ac}	Diffusion coefficient of substrate(acetate)	0.06	$m^2\ day^{-1}$
$q_{Ac.max}$	Maximum specific rate constant for microbial consumption of acetate	10	$(acetate)(biomass)^{-1}$ day^{-1}
L_L	Thickness layer	1	μm
V_B	Bulk liquid volume	0.2	m^3

A_F	Electrode area	25	m^2
V_c	Cathode potential	0.68	V
$R_{int}+R_{ext}$	Total cell resistance	–	Ω
$i_{0,ref}$	Exchange current density in r eference conditions for media tor oxidation ($S_{ref,Mred}=S_{ref,Mox}=1mM$)	0.0002	Am^{-2}
I	Current	-	mA
$E^0_{Mox/Mred}$	Standard reduction potential for the pair of mediator	0.477	V
b	Tafel coefficient for mediator oxidation	0.12	V
Y_{Mox}, Y_{Mred} Y_X	Yield mediator , biomass from substrate	$0.051,0.5,1$	$(mol\ mediator)(gCOD\ acetate)^{-1}$, $(biomass)(acetate)^{-1}$
K_{Ac}	Monod coefficient for substrate(acetate)	100	$gCODm^{-3}$
K_{Mox}	Monod coefficient for oxidized mediator	0.01	mM
z	Distance from anode surface	10	mM
t	Time	-	s

II. MATHEMATICAL FORMULATION OF THE PROBLEM.

The reaction scheme of electrochemical oxidation of a reduced mediator [5] is

$$M_{red} \leftrightarrow M_{OX} + 2H^+ + 2e^- \quad (1)$$

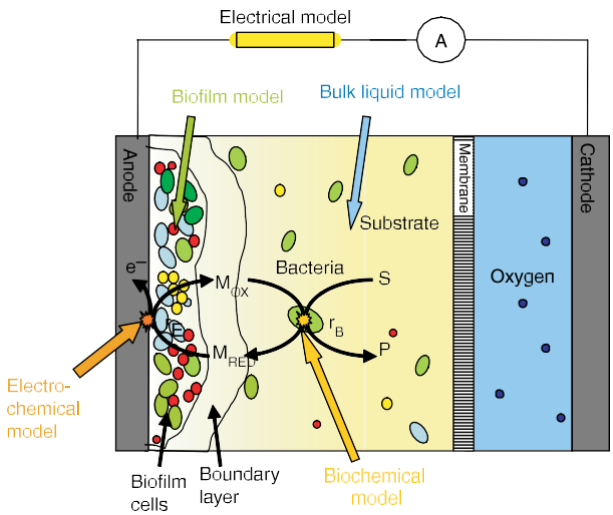

Fig. 1. Schematic design of biofilm and bulkliquid [6].

A. Mass balances in bulk liquid

The mass balance equation in the bulk liquid for soluble and biomass components [5].

$$\frac{dS_B}{dt}=\frac{\phi(S_{in}-S_B)}{v_B}+r_{S,B}+\frac{1}{v_B}\int_{v_F} r_{S,F}\,dV+\frac{1}{v_B}\int_{A_F} r_{S,E}\,dA \quad (2)$$

$$\frac{dX_B}{dt}=\frac{\phi(X_{in}-X_B)}{v_B}+r_{X,B}+r_{det}\frac{A_F}{v_B}-r_{ata}\frac{A_F}{v_B} \quad (3)$$

Since $\phi=0$, where $r_{S,B}$, $r_{S,F}$ is the net rates of reaction in the bulk and in the biofilm, $r_{S,E}$ is the electrochemical rates of solute components change on the electrode surface, v_B, v_F is the bulk and biofilm liquid volume (m^3) and A_F is the anode surface area (m^2) ,and r_{det}, r_{ata} is a rates of biomass detachment and attachment has been ignored $(r_{det}, r_{ata}=0)$.

The initial conditions are

$S_B=S_0$ at $t=0$ for all soluble components. (4)

$X_B=X_0$ at $t=0$ for all biomass components (5)

The net rates for acetate, oxidized and reduced mediator and biomass are as follows:

$$\rho=q_{Ac,max}\ X\frac{S_{Ac}}{K_{Ac}+S_{Ac}}\frac{S_{Mox}}{K_{Mox}+S_{Mox}} \quad (6)$$

$$r_{Ac}=-\rho,\ r_{Mred}=Y_M\,\rho,\ r_{Mox}=-Y_M\,\rho,\ r_X=Y_X\,\rho \quad (7)$$

$$r_{E,Mred}=\frac{-i}{2F},\ r_{E,Mox}=\frac{i}{2F} \quad (8)$$

where S_{Ac}, S_{Mox} and X is the concentration of substrate(acetate), oxidized mediator and biomass, and K_{Ac}, K_{Mox} is the Monod coefficient for substrate(acetate) and oxidized mediator, and $q_{Ac,max}$ is maximum specific rate constant for microbial consumption acetate Y_M, Y_X is the yield mediator and biomass from substrate.By using the Butler-Volmer equation[7] , the electrode surface concentrations S_E inEqn. (9)shown in the formula below:

$$i=i_{0,ref}\left(\frac{S_{E,Mred}}{S_{ref,Mred}}\right)\left(\frac{S_{E,Mox}}{S_{ref,Mox}}\right)^{-1}\left(\frac{S_{E,H}}{S_{ref,H}}\right)^{-2}\left[exp\left(\frac{2.303}{b}\eta_{A,act}\right)-exp\left(-\frac{2.303}{b}\eta_{A,act}\right)\right] \quad (9)$$

The over- potential activation $\eta_{A,act}$ is a function of the current I passing through the fuel cell:

$$\eta_{A,act} = V_C - I(R_{int} + R_{ext}) - \left(E^0_{Mox/Mred} - 0.059pH + \frac{0.059}{2} log \frac{S_{E,Mox}}{S_{E,Mred}} \right) \quad (10)$$

Where $i_{0,ref}$ is the exchange current density for mediator oxidized in reference conditions, b is a tafel coefficient, i is the current density, and V_C is cathode potential, $E^0_{Mox/Mred}$ is the mediator's standard reduction potential, $R_{int} + R_{ext}$ is total cell resistance, I is total current .

i) The mass balance equation in thebulk liquid for acetate, two mediator, and biomass[5].

$$\frac{dS_{B,Ac}}{dt} = r_{B,Ac} + r_{F,Ac} \frac{v_F}{v_B} \text{ since } r_{E,Ac} = 0, \quad (11)$$

$$\frac{dS_{B,Mox}}{dt} = r_{B,Mox} + r_{F,Mox} \frac{v_F}{v_B} + r_{E,Mox} \frac{A_F}{v_B} \quad (12)$$

$$\frac{dS_{B,Mred}}{dt} = r_{B,Mred} + r_{F,Mred} \frac{v_F}{v_B} + r_{E,Mred} \frac{A_F}{v_B} \quad (13)$$

$$\frac{dX_B}{dt} = r_{X,B} \quad (14)$$

Where $S_{B,Ac}, S_{B,Mox}, S_{B,Mred}$ is the concentration of substrate(acetate), oxidized and reduced mediator and X_B is the concentration of biomass are bulk liquid. The rates Eqn. (7) are applied in mass balances for components in biofilm(with $S_{F,Ac}, S_{F,Mox}, S_{F,Mred}$ and X_F all variable in time and space) as well as in the bulk liquid(with $S_{B,Ac}, S_{B,Mox}, S_{B,Mred}$ and X_B all variable in time)

The initial conditions are given as follows:

$$S_{B,Ac} = S_{F,Ac} = S_{0,Ac} \text{ at } t = 0 \quad (15)$$

$$S_{B,Mox} = S_{F,Mox} = S_{0,Mox} \text{ at } t = 0 \quad (16)$$

$$S_{B,Med} = S_{F,Med} = S_{0,Med} \text{ at } t = 0 \quad (17)$$

$$X_B = X_0 \text{ at } t = 0 \quad (18)$$

B.Mass balances in biofilm

The mass balance equation in the biofilm for soluble components [5] are

$$\frac{\partial S_F}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial S_F}{\partial x} \right) + \frac{\partial}{\partial y}\left(D \frac{\partial S_F}{\partial y} \right) + \frac{\partial}{\partial z}\left(D \frac{\partial S_F}{\partial z} \right) + r_{S,F} \quad (19)$$

$$\frac{\partial S_F}{\partial t} = \frac{\partial}{\partial z}\left(D \frac{\partial S_F}{\partial z} \right) + r_{S,F} \text{ Since } \left(\frac{\partial}{\partial x} = 0, \frac{\partial}{\partial y} = 0 \right) \quad (20)$$

The boundary conditions are

$$S_F = S_B \text{ at } z = L_z \quad (21)$$

$$D \frac{\partial S_F}{\partial z} + r_{S,E} = 0 \text{ at } z = 0 \quad (22)$$

The mass balance equations for acetate, oxidized mediator and reduced mediator in the biofilm are given as follows for steady-state conditions [5]:

$$\frac{d^2 S_{F,Ac}}{dz^2} + \frac{r_{F,Ac}}{D_{Ac}} = 0 \quad (23)$$

$$\frac{d^2 S_{F,Mox}}{dz^2} + \frac{r_{F,Mox}}{D_{Mox}} = 0 \quad (24)$$

$$\frac{d^2 S_{F,Mred}}{dz^2} + \frac{r_{F,Mred}}{D_{Mred}} = 0 \quad (25)$$

where $S_{F,Ac}, S_{F,Mox}, S_{F,Mred}$ is the concentration of substrate(acetate), oxidized and reduced mediator and X_B is the concentration of biomass in the biofilm. D_{Ac}, D_{Mox} and D_{Mred} is the diffusion coefficient of substrate(acetate), oxidized and reduced mediator.

The boundary conditionsare

$$S_{F,Ac} = S_{B,Ac},\ S_{F,Mox} = S_{B,Mox},\ S_{F,Mred} = S_{B,Mred} \text{ at } z = L_z \quad (26)$$

$$\frac{dS_{F,Ac}}{dz} = 0, D\frac{dS_{F,Mox}}{dz} + r_{E,Mox} = 0, D\frac{dS_{F,Mred}}{dz} + r_{E,Mred} = 0, \text{ at } z = 0 \quad (27)$$

III. Analytical expression of concentration using homotopy perturbation method.

We derive the general solution of the nonlinear reaction equations (11-14) using the homotopy perturbation method. Recently He and Rajendran et al. [8-12] solved many nonlinear problems in engineering andchemical sciences. The initial approximations can be freely chosen with possible unknown constants which can be determined by imposing the boundary and initial conditions. In this paper, the concentrations of bulk liquid can be obtained by solving the equations (11-14) using HPM (see Appendix A) as follows:

$$S_{B,Ac}(t) = S_{0,Ac}\, e^{k_1 t} + S_{0,Ac} \frac{v_F}{v_B}\left(e^{k_1 t} - 1 \right) \text{ where}$$

$$k_1 = -\frac{q_{Ac,max} X_0 S_{0,Mox}}{(K_{Ac} + S_{0,Ac})(K_{Mox} + S_{0,Mox})} \quad (28)$$

$$S_{B,Mox}(t) = \frac{-k_3}{k_2} + \left(S_{0,Mox} + \frac{k_3}{k_2} \right) e^{k_2 t} \text{ where}$$

$$k_2 = -\frac{Y_{Mox} q_{Ac,max} X_0 S_{0,Ac}}{(K_{Ac} + S_{0,Ac})(K_{Mox} + S_{0,Mox})},$$

$$k_3 = \frac{k_2 A_F S_{0,Mox}}{v_B} + \frac{A_F i_{0,ref} S_{E,Mred}}{4 V_B F S_{E,Mox} (S_{E,H})^2}$$

$$sinh\left(\frac{2.303}{b} \left[V_c - I(R_{int} + R_{ext}) - E^0_M + 0.354 + 0.0295 log\left(\frac{S_{E,Mox}}{S_{E,Mred}} \right) \right] \right) \quad (29)$$

$$S_{B,Mred}(t)=\frac{-k_5}{k_4}+\left(S_{0,Mred}+\frac{k_5}{k_4}\right)e^{k_4 t}$$ where

$$k_4=-\frac{Y_{Mred}\,q_{Ac,max}\;X_0\,S_{0,Ac}}{(K_{Ac}+S_{0,Ac})(K_{Mox}-S_{0,Mred})},$$

$$k_5=\frac{k_4\,A_F\,S_{0,Mred}}{v_B}-\frac{A_F\,i_{0,ref}\;S_{E,Mred}}{4V_B\,F\,S_{E,Mox}(S_{E,H})^2}$$
$$\sinh\left(\frac{2.303}{b}\left[V_c-I(R_{int}+R_{ext})-E_M^0+0.354+0.0295\log\left(\frac{S_{E,Mox}}{S_{E,Mred}}\right)\right]\right) \quad (30)$$

$$X_B(t)=X_0\,e^{k_6 t}$$ where $$k_6=\frac{Y_X\,q_{Ac,max}\;S_{0,Mox}\,S_{0,Mred}}{(K_{Ac}+S_{0,Ac})(K_{Mox}+S_{0,Mox})} \quad (31)$$

A . Analytical expression of concentration in biofilm using homotopy perturbation method.

By solving the Eqns. (23-25) using HPM (Appendix B), we can obtain the concentration of substrate (glucose), oxidized mediator and reduced mediator at biofilmas follows:

$$S_{F,Ac}(z)=S_{B,Ac}\frac{\cos\left(\sqrt{\frac{k_1}{D_{Ac}}}\;z\right)}{\cos\left(\sqrt{\frac{k_1}{D_{Ac}}}\;L_z\right)} \quad (32)$$

$$S_{F,Mox}(z)=S_{B,Mox}\frac{\cos\left(\sqrt{\frac{k_2}{D_{Mox}}}\;z\right)}{\cos\left(\sqrt{\frac{k_2}{D_{Mox}}}\;L_z\right)}$$
$$+k_7\left(-\sin\left(\sqrt{\frac{k_2}{D_{Mox}}}\;z\right)+\tan\left(\sqrt{\frac{k_2}{D_{Mox}}}\;L_z\right)\cos\left(\sqrt{\frac{k_2}{D_{Mox}}}\;z\right)\right) \quad (33)$$

Where

$$k_7=\frac{i_{0,ref}\;S_{E,Mred}}{4\sqrt{k_2 D_{Mox}}\;F\,S_{E,Mox}(S_{E,H})^2}$$
$$\sinh\left(\frac{2.303}{b}\left[V_c-I(R_{int}+R_{ext})-E_M^0+0.354+0.0295\log\left(\frac{S_{E,Mox}}{S_{E,Mred}}\right)\right]\right) \quad (34)$$

$$S_{F,Mred}(z)=S_{B,Mred}\frac{\cos\left(\sqrt{\frac{k_4}{D_{Mred}}}\;z\right)}{\cos\left(\sqrt{\frac{k_4}{D_{Mred}}}\;L_z\right)}$$
$$+k_8\left(\sin\left(\sqrt{\frac{k_4}{D_{Mred}}}\;z\right)-\tan\left(\sqrt{\frac{k_4}{D_{Mred}}}\;L_z\right)\cos\left(\sqrt{\frac{k_4}{D_{Mred}}}\;z\right)\right) \quad (35)$$

Where

$$k_8=\frac{i_{0,ref}\;S_{E,Mred}}{4\sqrt{k_4 D_{Mred}}\;F\,S_{E,Mox}(S_{E,H})^2}$$
$$\sinh\left(\frac{2.303}{b}\left[V_c-I(R_{int}+R_{ext})-E_M^0+0.354+0.0295\log\left(\frac{S_{E,Mox}}{S_{E,Mred}}\right)\right]\right)$$

(36)

IV. Numerical simulation

Numerically, the non-linear equations (11-14) are solved for the initial condition equations (15-18). For ordinary differential equations, the function ode 45 in Matlab software is used to solve problems with two-point boundary value (BVPs). The analytical expressions of the concentration of substrate (acetate), oxidized mediator and biomass have compared with simulation results inTables1-3. A satisfactory agreement is noted.

V.Discussion

Equations (28-36) represent the new closed-form of approximate analytical expressions of substrate (acetate), oxidized and reduced mediator, and biomass concentrations for all parameter ($K_{Mox}, q_{Ac.max}, Y_{Mox}, Y_{Mred}, Y_X, V_C$ and $i_{0,ref}$) values. Figs (2-5) show the profiles of the substrate (acetate), the oxidized and reduced mediator, and the concentration of biomass. As the standardized parameter K_{Mox} rises, the concentrations of substrates increase and q_{Acmax} decreases, the concentrations of substrates decrease. As the standardized parameter K_{Mox} increases, substrate concentrations increases and $q_{Ac.max}$ decreases, substrate concentrations decreases (see Fig.1).

From Fig. 3a, it is observed that the concentration of oxidized mediator decreases when the yield mediator Y_{Mox} decreases. There is no significant difference in the concentration of oxidized mediator about the parameter $V_C = 0.1, 1, 10$ (see Fig.3b).From Fig4a, it is observed that an increase in the parameter Y_{Mred}, the concentration of reduced mediator increases. Also exchange current density $i_{0,ref}$ decreases, when the concentration decreases (Fig 4b). From Fig.5 it is inferred that a yield biomass Y_X increases biomass concentration in bulk increases. Figure 6 shows that the thickness layer increases, the concentration of substrates (acetate) and the oxidized mediator in biofilm increases. The reduced mediator concentration for various anode distance and thickness values is shown in Fig. (6)(c).From the figure it is noticed that a decrease in z and L_z leads to decrease in the concentration of reduced mediator in biofilm.

VI.Conclusion

The non-linear reaction-diffusion equation in the modelling of biofilm-based microbial fuel cells was solved analytically. The approximate analytical expression of biofilm/bulk liquid of concentration of substrate (acetate), oxidized mediator, and reduced mediator, and biomass are obtained for all experimental values of parameters using the homotopy perturbation method. A satisfactory agreement with numerical simulation is noted. These analytical expressions can be used to analyze the effect of various parameters such as thickness layer, yield substrate and mediators, Monod coefficient for substrate and oxidized mediator, cathode potential, exchange current density and rate constant.

APPENDIX

A. Approximate analytical solution of Eqn. (11) using HPM [5].

In this Appendix, we derive the general solution of the nonlinear reaction equation (11) using the new approach of the homotopy perturbation method. We begin by constructing the homotopy for Eqn. (28) as follows:

$$(1-p)\left[\frac{dS_{B,Ac}}{dt}-\frac{q_{Ac,max}S_{B,Ac}\,S_{B,Mox}(t=0)X(t=0)}{(K_{Ac}+S_{B,Ac}(t=0))(K_{Mox}+S_{B,Mox}(t=0))}-\frac{q_{Ac,max}S_{F,Ac}(t=0)S_{F,Mox}(t=0)X(t=0)}{(K_{Ac}+S_{F,Ac}(t=0))(K_{Mox}+S_{F,Mox}(t=0))}\right]+$$

$$p\left[\frac{dS_{B,Ac}}{dt}-\frac{q_{Ac,max}S_{B,Ac}\,S_{B,Mox}X}{(K_{Ac}+S_{B,Ac})(K_{Mox}+S_{B,Mox})}-\frac{q_{Ac,max}S_{F,Ac}\,S_{F,Mox}X}{(K_{Ac}+S_{F,Ac})(K_{Mox}+S_{F,Mox})}\right]=0 \qquad \text{(A1)}$$

The approximate solution of the Eq. (A1) is

$$S_{B,Ac}(t)=S_{B,Ac_0}(t)\,p^0+S_{B,Ac_1}(t)\,p^1+S_{B,Ac_2}(t)\,p^2+\ldots \qquad \text{(A2)}$$

Substituting equation (A2) into equation (A1) and equate the terms with identical power of p^0 we obtain

$$p^0:\ \frac{dS_{B,Ac}}{dt}-\frac{q_{Ac,max}S_{B,Ac}\,S_{0,Mox}X_0}{(K_{Ac}+S_{0,Ac})(K_{Mox}+S_{0,Mox})}-\frac{q_{Ac,max}S_{0,Ac}\,S_{0,Mox}X_0}{(K_{Ac}+S_{0,Ac})(K_{Mox}+S_{0,Mox})}=0 \qquad \text{(A3)}$$

The initial condition for Eqn. (A3) is given by

$$t=0,\ S_{B,Ac_0}=S_{0,Ac} \qquad \text{(A4)}$$

Solving Eqn. (A3) with initial condition (A4) we get:

$$S_{B,Ac_0}(t)=S_{0,Ac}\,e^{k_1 t}+S_{0,Ac}\frac{v_F}{v_B}\left(e^{k_1 t}-1\right) \qquad \text{where}$$

$$k_1=-\frac{q_{Ac,max}\,X_0\,S_{0,Mox}}{(K_{Ac}+S_{0,Ac})(K_{Mox}+S_{0,Mox})} \qquad \text{(A5)}$$

B.A**nalytical solution of non linear diffusion equation (23) in biofilm using HPM [5].**

In this Appendix, we derive the general solution of the nonlinear reaction equation (23) using the new approach homotopy perturbation method. We begin by constructing the homotopy for Eqn. (23) as follows:

$$(1-p)\left[\frac{\partial^2 S_{F,Ac}}{\partial z^2}-\frac{q_{Ac,max}S_{F,Ac}\,S_{F,Mox}(t=0)X(t=0)}{D_{Ac}(K_{Ac}+S_{F,Ac}(t=0))(K_{Mox}+S_{F,Mox}(t=0))}\right]$$

$$+\,p\left[\frac{\partial^2 S_{F,Ac}}{\partial z^2}-\frac{q_{Ac,max}S_{F,Ac}\,S_{F,Mox}X}{D_{Ac}(K_{Ac}+S_{F,Ac})(K_{Mox}+S_{F,Mox})}\right]=0 \qquad \text{(B1)}$$

The approximate solution of the Eq. (B1) is

$$S_{F,Ac}(z)=S_{F,Ac_0}(z)p^0+S_{F,Ac_1}(z)P^1+S_{F,Ac_2}(t)P^2+\ldots \qquad \text{(B2)}$$

Substituting equation (B2) into equation (B1) and equate the terms with identical power of p^0 we obtain

$$p^0:\ \frac{\partial^2 S_{F,Ac_0}}{\partial z^2}-\frac{q_{Ac,max}S_{F,Ac}\,S_{0,Mox}X_0}{D_{Ac}(K_{Ac}+S_{0,Ac})(K_{Mox}+S_{0,Mox})}=0 \qquad \text{(B3)}$$

with boundary condition for Eqn. (B3) given by

$$S_{F,Ac_0}=S_{B,Ac}\ \text{at}\ z=L_z \qquad \text{(B4)}$$

$$\frac{\partial S_{F,Ac_0}}{\partial z}=0\ \text{at}\ z=0 \qquad \text{(B5)}$$

Solving Eqn. (B3) with boundary conditions (B4) and (B5) we get:

$$S_{F,Ac_0}(z)=S_{B,Ac}\frac{\cos\left(\sqrt{\frac{k_1}{D_{Ac}}}\,z\right)}{\cos\left(\sqrt{\frac{k_1}{D_{Ac}}}\,L_z\right)} \qquad \text{(B6)}$$

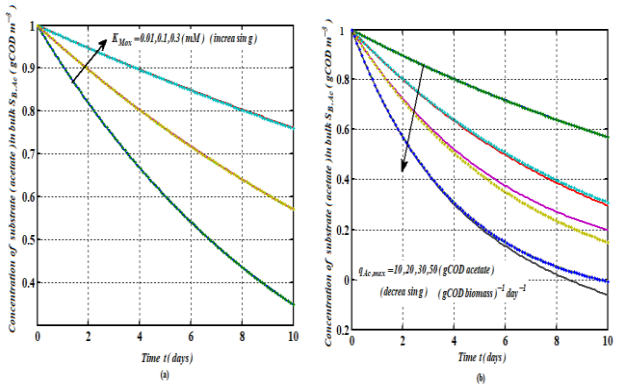

Fig.2 Plot of concentration of substrate (acetate) in bulk $S_{B,Ac}$ versus time t. The curves are plotted using equation (28). (-) denotes the analytical results and (…) denotes the numerical simulations.

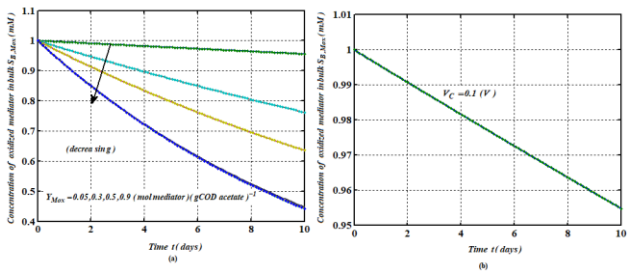

Fig. 3 Plot of concentration of oxidized mediator in bulk $S_{B,Mox}$ versus time t. The curves are plotted using equation (29). (-) denotes the analytical results and (…) denotes the numerical simulations.

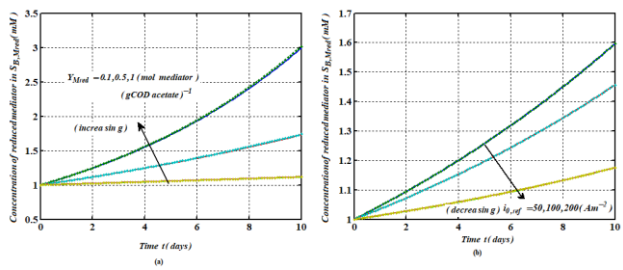

Fig.4 Plot of concentration of reduced mediator in bulk $S_{B,Mred}$ versus time t. The curves are plotted using equation (30). (-) denotes the analytical results and (…) denotes the numerical simulations.

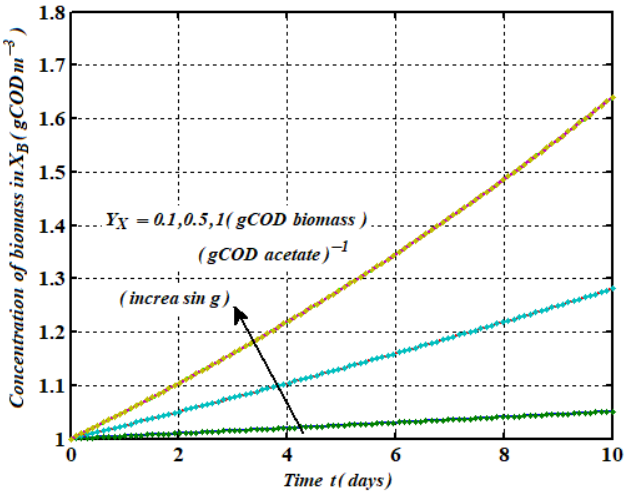

Fig.5 Plot of concentration of biomass in bulk X_B versus time t. The curves are plotted using equation (31). (-) denotes the analytical result and (…) denotes the numerical simulations.

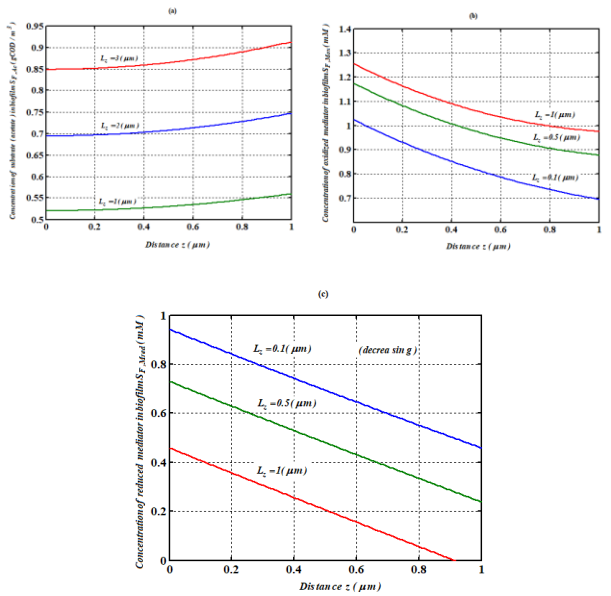

Fig.6 Plot ofconcentration of (a) substrate (acetate) in biofilm versus distance (Eqn. (32))

(a) oxidized mediator in biofilm versus distance (Eqn. (33))

(b) reduced mediator in biofilm versus distance (Eqn. (35))

Table 1: Comparison of substrate (acetate) concentration $S_{B,Ac}$ with simulation results for various values of parameters $q_{Ac.max} = 10, S_{0,Ac} = 1, X_0 = 1, S_{0,Mox} = 0.1, K_{Ac} = 100, K_{Mox} = 0.01$.

t	$K_{Mox} = 0.5$			$K_{Mox} = 0.7$			$q_{Ac.max} = 10$			$q_{Ac.max} = 30$		
	Num. Eqn. (9)	This work Eqn. (27)	Error % of Eqn. (27)	Num. Eqn. (9)	This work Eqn. (27)	Error % of Eqn. (27)	Num. Eqn. (9)	This work Eqn. (27)	Error % of Eqn. (27)	Num. Eqn. (9)	This work Eqn. (27)	Error % of Eqn. (27)
0	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000
2	0.964	0.964	0.041	0.973	0.973	0.031	0.817	0.817	0.000	0.527	0.537	1.934
4	0.930	0.929	0.064	0.947	0.946	0.063	0.665	0.665	0.000	0.280	0.269	3.750
6	0.896	0.895	0.112	0.921	0.920	0.087	0.537	0.537	0.000	0.119	0.114	4.037
8	0.864	0.863	0.150	0.896	0.895	0.112	0.431	0.431	0.000	0.028	0.024	14.54
10	0.833	0.833	0.000	0.872	0.872	0.000	0.347	0.347	0.000	-0.03	-0.026	0.385
	Average error %		0.062	Average error %		0.049	Average error %		0.000	Average error %		4.107

Table 2: Comparison of oxidized mediator concentration $S_{B,Mox}$ with simulation results for various values parameters

$q_{Ac.max} = 10, X_0 = 1, S_{0,Ac} = 1, S_{0,Mox} = 1, A_F = 0.001, V_B = 0.2, K_{Ac} = 100,$
$K_{Mox} = 0.1, i_{0,ref} = 0.0002, S_{E.Mred} = 0.5, S_{E.Mox} = 1, S_{E.H} = 1, V_c = 0.68,$
$R_{int} + R_{ext} = 0, E_M = 0.477, b = 0.120, F = 96480$

t	$Y_{Mox} = 0.1$			$Y_{Mox} = 0.5$		
	Num. Eqn. (10)	This work Eqn. (28)	Error % of Eqn. (28)	Num. Eqn. (10)	This work Eqn. (28)	Error % of Eqn. (28)
0	1.0000	1.0000	0.0000	1.0000	1.0000	0.0000
2	0.9821	0.9819	0.0200	0.9135	0.9127	0.0880
4	0.9645	0.9641	0.0410	0.8344	0.8329	0.1797
6	0.9472	0.9295	0.0630	0.7622	0.7601	0.2755
8	0.9302	0.9295	0.0750	0.6961	0.6936	0.3591
10	0.9135	0.9135	0.0000	0.6358	0.6358	0.0000
	Average error %		0.0330	Average error %		0.1503

t	$Y_X = 0.01$			$Y_X = 0.5$			$Y_X = 1$		
	Num. Eqn. (12)	This work Eqn. (30)	Error % of Eqn. (30)	Num. Eqn. (12)	This work Eqn. (30)	Error % of Eqn. (30)	Num. Eqn. (12)	This work Eqn. (30)	Error % of Eqn. (30)
0	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000
2	1.001	1.001	0.000	1.051	1.051	0.000	1.104	1.105	0.090
4	1.002	1.002	0.000	1.104	1.105	0.090	1.219	1.221	0.164
6	1.003	1.003	0.000	1.160	1.162	0.172	1.346	1.350	0.297
8	1.004	1.004	0.000	1.219	1.221	0.164	1.486	1.492	0.405
10	1.005	1.005	0.000	1.281	1.281	0.000	1.641	1.641	0.000
	Average error %		0.000	Average error %		0.071	Average error %		0.159

Table 3:Comparison of biomass concentration X_B with simulation results for various value parameters $q_{Ac.max} = 10, S_{0,Ac} = 1, X_0 = 1, S_{0,Mox} = 0.1, K_{Ac} = 100, K_{Mox} = 0.1$.

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