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Approximate Analytical Expressions for the Concentrations of Acetate and Methane in the Microbial Electrochemical Cell

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Abstract

Mathematical modeling of microbial electrochemical cells (MXCs) for both microbial fuel cell and microbial electrolysis cell is discussed. The model is based on the system of reaction diffusion of reaction-diffusion equation containing a non-linear term related to substrate consumption rates by electrogeneic and methanogenic microorganism in the bioflim. This paper presents the approximate analytical method to solve the non-linear differential equation that describes the diffusion coupled with acetate (substrate) consumption rates. Simple analytical expressions for the concentrations of acetate and methane have been derived for all experimental values of bulk concentration, distributions of microbial volume fraction, local potential in the biofilm and biofilm thickness. In addition, sensitivity of the parameters on concentrations is also discussed. Our analytical results are also validated with the numerical results and limiting cases results. Further, a graphical procedure for estimating the kinetic parameters is also suggested.

Keywords

Mathematical Modeling, Microbial Fuel and Electrolysis Cells, Waste Water Treatment, Boundary Value Problems, Non Linear Equations

1. Introduction

Microbial fuel cells (MFC) can be defined as a microbial catalyzed electrochemical system which can facilitate the direct conversion of substrate to electricity through a cascade of redox reactions, especially in the absence of

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oxygen [1]. The applications of MFC are widespread in different fields including waste water remediation, toxic pollutants/xenobiotics removal, recovery of commercially viable products, sequestration of CO_2 harvesting the energy stored in marine sediments, desalination, etc. [1]. Microbial electrochemical cells are recognized as a modern technology to directly utilize bioenergy stored in organic substances, especially in wastewater [2]. Several experiments have been conducted to evaluate MXCs main performance as a current or hydrogen generator fed with different organic matters [3] and [4]. A simple mediator based model with suspended cells was investigated [5]. A simple model with rapid implementation and computations is used to describe the effect of some operational conditions such as temperature and substrate concentration on in the MFC performance [6]. Pinto developed a time-dependent mathematical model with the uniform distribution of bacteria in the anode chamber. Although a number of MFC mathematical models have been developed and discussed. To the best of the knowledge, only one MEC model has been proposed [7]. Yahya modified this model for a fed-batch reactor. It is a multi population mediator-based model developed based on the Bernard's anaerobic digestion kinetics model [8]. Alavijeh [2] used a variety of approaches to develop the first generalized conduction-based model for MXCs including both MFCs and MECs. It is a one-dimensional spatial distribution and time-dependent model using Bernard's anaerobic digestion kinetics model and both biofilm and liquid bulk simulation. The purpose of this communication is to derive the analytical expression for acetate and methane concentration using the Adomain decomposition method. We also provide the tabular complication of concentration of acetate with limiting case results (first order and zero order kinetics).

2. Mathematical Formulation of the Problem

Anolyte contains fermentative microorganisms and acetoclastic methanogens. Biofilm contains acetoclastic methanogens and anode respiring bacteria (electrogens). Acetate is produced during fermentation process and then diffuses to the biofilm where electrogens consume it and conduct electrons to the anode surface [2]. The systematic diagram of the model is represented in **Figure 1**.

The acetate and methane mass transfer equations through the biofilm are described as follows [2]:

$$D_{AC,f}\frac{\mathrm{d}^2 S_{AC}}{\mathrm{d}z^2} - X_{E,a}q_{AC,E} - X_{AM,a}q_{AC,AM} = 0 \quad (1)$$

$$D_{CH_4,f}\frac{\mathrm{d}^2 S_{\mathrm{CH}_4}}{\mathrm{d}z^2} - Y_{\mathrm{CH}_4}X_{AM,a}q_{AC,AM} = 0 \quad (2)$$

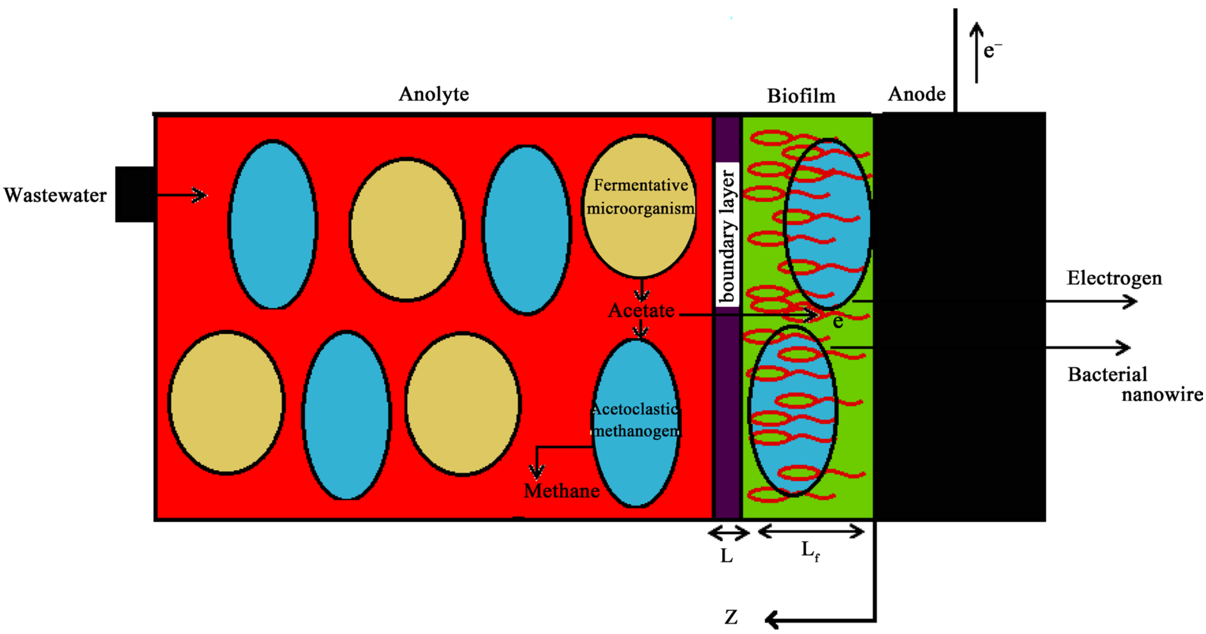

Figure 1. Schematic representation of the model [1].

where $D_{AC,f}$ and $D_{CH_4,f}$ the diffusion coefficient of acetate and methane in the bioflim $\left(m^2/day\right)$. S_{AC} and S_{CH_4} are the concentration of acetate on the biofilm $\left(kg\ COD_s\ m^{-3}\right)$ and methane concentration on the biofilm $\left(kg\ COD_s\ m^{-3}\right)$. $X_{E,a}$, $X_{AM,a}$ and Y_{CH_4} are the density of biomass $\left(kg\ COD_x\ m^{-3}\right)$ yield coefficient. The acetate consumption rate by electromagnetic microorganism in the biofuel $\left(kg\ COD_s\ kg\ COD_x\ m^{-1}\cdot day^{-3}\right)$ is represented by the Nenst-Monoid equation [2]

$$q_{AC,E} = q_{AC,AM,\max}\varphi_{E,a}\left(\frac{S_{AC}}{S_{AC}+K_{AC,E}}\right)\left(\frac{1}{1+\exp\left(-(F\eta)/(RT)\right)}\right) \tag{3}$$

where $q_{AC,AM,\max}$ is the maximum uptake $\left(kg\ COD_s\ kg\ COD_x\ m^{-1}\cdot day^{-3}\right)$, $\varphi_{E,a}$ and $K_{AC,E}$ are the volume fraction, and Half saturated constant $\left(kg\ COD_s\ m^{-3}\right)$. F, R, T and η are the Faraday constant, universal gas constant, temperature and local electrical potential of the biofilm respectively. The acetate consumption rate by acetoclastic methangen microorganism in the bioflim $\left(kg\ COD_s\ kg\ COD_x\ m^{-1}\cdot day^{-3}\right)$ is

$$q_{AC,AM} = \varphi_{AM,a}\left(\frac{S_{AC}}{S_{AC}+K_{AC,AM}}\right) \tag{4}$$

where $\varphi_{AM,a}$ and $K_{AC,AM}$ are the volume fraction and Half saturated constant $\left(kg\ COD_s\ m^{-3}\right)$. At the anode surface, there is no substrate flux and at the surface of the biofilm, there is an interface transfer. The boundary conditions for the above equations are given by [2]

$$\text{At } z=0,\quad \frac{dS_{AC}}{dz}=0 \tag{5a}$$

$$\text{At } z=L_f,\quad \frac{D_{AC,l}}{L}\left(S_{AC,bulk}-S_{AC}\right)=D_{AC,f}\frac{dS_{AC}}{dz} \tag{5b}$$

$$\text{At } z=0,\quad \frac{dS_{CH_4}}{dz}=0 \tag{5c}$$

$$\text{At } z=L_f,\quad \frac{D_{CH_4,l}}{L}\left(S_{CH_4,bulk}-S_{CH_4}\right)=D_{CH_4,f}\frac{dS_{CH_4}}{dz} \tag{5d}$$

where z, L_f, L represents the space coordinate in the biofilm (*m*), thickness of the biofilm (*m*) and boundary layer thickness (*m*) respectively. $D_{AC,l}$ and $D_{CH_4,l}$ are the diffusion coefficient of acetate and methane in the liquid $\left(m^2/day\right)$. $S_{AC,bulk}$ is the acetate concentration in the liquid bulk and in the biofilm interface $\left(kg\ COD_s\ m^{-3}\right)$ and $S_{CH_4,bulk}$ is the methane concentration in the liquid bulk and in the biofilm interface $\left(kg\ COD_s\ m^{-3}\right)$. We introduce the following set of dimensionless variables:

$$\begin{gathered} x=\frac{z}{L_f},\ s_{AC}=\frac{S_{AC}}{S_{AC,bulk}},\ s_{CH_4}=\frac{S_{CH_4}}{S_{CH_4,bulk}},\ m_1=\frac{D_{AC,l}L_f}{LD_{AC,f}},\ m_2=\frac{D_{CH_4,l}L_f}{LD_{CH_4,f}} \\ \varphi_1=\frac{L_f^2X_{E,a}q_{AC,AM,\max}\varphi_{E,a}}{D_{AC,f}K_{AC,E}\left(1+\exp\left(-Fn/RT\right)\right)},\quad \varphi_2=\frac{L_f^{\ 2}X_{AM,a}q_{AC,AM,\max}\varphi_{AM,a}}{D_{AC,f}K_{AC,AM}}, \\ \varphi_3=\frac{L_f^2X_{AM,a}q_{AC,AM,\max}\varphi_{AM,a}s_{AC,bulk}}{Y_{CH_4}S_{CH_4,bulk}D_{CH_4,f}K_{AC,AM}},\quad \alpha=\frac{S_{AC,bulk}}{K_{AC,E}},\quad \beta=\frac{S_{AC,bulk}}{K_{AC,AM}} \end{gathered} \tag{6}$$

Using the above dimensionless variables the non-linear reaction-diffusion Equations ((1) and (2)) are expressed in the following dimensionless form:

$$\frac{d^2s_{AC}}{dx^2}=\frac{\varphi_1 s_{AC}}{1+\alpha s_{AC}}+\frac{\varphi_2 s_{AC}}{1+\beta s_{AC}} \tag{7}$$

$$\frac{d^2s_{CH_4}}{dx^2}=\frac{\varphi_3 s_{AC}}{1+\beta s_{AC}} \tag{8}$$

The boundary conditions can be written as follows:

$$\text{At } x=0, \quad \frac{\mathrm{d}s_{AC}}{\mathrm{d}x}=0 \tag{9}$$

$$\text{At } x=1, \quad \frac{\mathrm{d}s_{AC}}{\mathrm{d}x}=m_1\left(1-s_{AC}\right) \tag{10}$$

$$\text{At } x=0, \quad \frac{\mathrm{d}s_{\mathrm{CH_4}}}{\mathrm{d}x}=0 \tag{11}$$

$$\text{At } x=1, \quad \frac{\mathrm{d}s_{\mathrm{CH_4}}}{\mathrm{d}x}=m_2\left(1-s_{\mathrm{CH_4}}\right) \tag{12}$$

3. Approximate Analytical Expression of Concentration of Acetate and Methane

Recently, many authors have been applied the Adomain decomposition method (ADM) to various problems and demonstrated the efficiency of the ADM for handling non-linear problem in physics and engineering sciences [9]-[13]. The modified Adomain decomposition method [11] is used to give the approximate solutions of the non-linear Equations ((7) and (8)). Many researchers find that the ADM requires less computational work than traditional approaches [11]-[13]. Other advantages include the ability to solve nonlinear problems without linearization, the wide applicability to several types of problems and scientific fields, and the development of a reliable, analytic solution. Many researchers find that the ADM requires less computational work than traditional approaches [11]-[13]. Other advantages include the ability to solve nonlinear problems without linearization, the wide applicability to several types of problems and scientific fields, and the development of a reliable, analytic solution. Using this method (refer **Appendix A**), we can obtain the concentrations acetate and methane as follows:

$$s_{AC}(x)=1-\left(\frac{\varphi_1}{1+\alpha}+\frac{\varphi_2}{1+\beta}\right)\left(\frac{1}{2}+\frac{1}{m}\right)+\left(\frac{\varphi_1}{1+\alpha}+\frac{\varphi_2}{1+\beta}\right)\frac{x^2}{2} \tag{13}$$

$$s_{\mathrm{CH_4}}(x)=k+\left[\phi_2x^2/2\phi_4\right]+\left\{\left[\phi_1-(\phi_2\phi_3)/\phi_4\right]\left[\left(\log\left(\phi_3+\phi_4x^2\right)/2\phi_4\right)-\left(\left(\tan^{-1}\left(\phi_4x/\sqrt{\phi_3\phi_4}\right)x\right)/\sqrt{\phi_3\phi_4}\right)\right]\right\} \tag{14}$$

where the constants

$$\begin{aligned}
&\phi_1=\varphi_3\left[1-\theta\left((1/m_1)+(1/2)\right)\right];\ \phi_2=(\varphi_3\theta)/2;\ \phi_3=1+\beta\left[1-\theta\left((1/m_1)+(1/2)\right)\right]\\
&\phi_4=(\beta\theta)/2;\ \theta=\left[\varphi/(1+\alpha)\right]+\left[\varphi_2(1+\beta)\right]\\
&k=1-\left[\phi_2/2\phi_4\right]+\left\{\left[\phi_1-(\phi_2\phi_3)/\phi_4\right]\left[\left(\log(\phi_3+\phi_4)/2\phi_4\right)-\left(\left(\tan^{-1}\left(\phi_4/\sqrt{\phi_3\phi_4}\right)\right)/\sqrt{\phi_3\phi_4}\right)\right]\right\}\\
&\quad\left[1/m_2\right]\left\{\left[\phi_2/\phi_4\right]-\left[\left[\phi_1-(\phi_2\phi_3)/\phi_4\right]\left[\left(\log(\phi_3+\phi_4)/2\phi_4\right)-\left(\left(\tan^{-1}\left(\phi_4/\sqrt{\phi_3\phi_4}\right)\right)/\sqrt{\phi_3\phi_4}\right)\right]\right]\right\}
\end{aligned} \tag{15}$$

Equations ((13) and (14)) are valid provided $\left(\frac{\varphi_1}{1+\alpha}+\frac{\varphi_2}{1+\beta}\right)\left(\frac{1}{2}+\frac{1}{m}\right)<1$ and $\left[\frac{\phi_1}{2\phi_4}-(\phi_2\phi_3)\right]>0$. This is the only limitations in this method.

4. Limiting Case

4.1. Unsaturated (First Order) Catalysis

We initially consider the situation where the concentration of acetate S_{AC} and methane $S_{\mathrm{CH_4}}$ is less than the half saturation constants $K_{AC,E}$ and $K_{AC,AM}$. In this case $\alpha s_{AC}<1$ and $\beta s_{AC}<1$. Hence, Equations ((7) and (8)) reduces to

$$\frac{\mathrm{d}^2s_{AC}}{\mathrm{d}x^2}=(\varphi_1+\varphi_2)s_{AC} \tag{16}$$

$$\frac{d^2 s_{CH_4}}{dx^2} = \varphi_3 s_{AC} \tag{17}$$

Hence, the non-linear Equations ((7) and (8)) have been reduces to linear equations. Now, the concentration of acetate S_{AC} and methane S_{CH_4} for corresponding boundary conditions (9a) to (9c) becomes as follows:

$$s_{AC}(x) = \left(\frac{m_1}{\sqrt{l_1}\sinh\sqrt{l_1} + m_1\cosh\sqrt{l_1}}\right)\cosh\sqrt{l_1}\,x \tag{18}$$

$$s_{CH_4}(x) = 1 + \frac{l_2\cosh\sqrt{l_1}\,x}{l_1} + \frac{l_2\cosh\sqrt{l_1}}{l_1} - \frac{l_2\sqrt{l_1}\sinh\sqrt{l_1}}{m_2} \tag{19}$$

where $l_1 = \varphi_1 + \varphi_2$ and $l_2 = \dfrac{\varphi_3 m_1}{\sqrt{l_1}\sinh\sqrt{l_1} + m_1\cosh\sqrt{l_1}}$. Equations ((18) and (19)) are the exact solution of Equations ((16) and (17)).

4.2. Saturated (Zero-Order) Catalysis

We now consider that the second major limiting situation found in practice, when the concentration of acetate and methane is very much greater than the half saturation constants $K_{AC,E}$ and $K_{AC,AM}$. In this case, $\alpha s_{AC} > 1$ and $\beta s_{AC} > 1$. Hence, the non-linear Equations ((7) and (8)) have been reduces to

$$\frac{d^2 s_{AC}}{dx^2} = \frac{\varphi_1}{\alpha} + \frac{\varphi_2}{\beta} \tag{20}$$

$$\frac{d^2 s_{CH_4}}{dx^2} = \frac{\varphi_3}{\beta} \tag{21}$$

The above Equations ((17) and (18)) are linear reaction-diffusion equations which are exactly solvable. By solving the above Equations ((17) and (18)), we can obtain the concentration of Acetate (16), and Methane (17).

$$s_{AC}(x) = 1 - \left(\frac{\varphi_1}{\alpha} + \frac{\varphi_2}{\beta}\right)\left(\frac{1}{m_1} + \frac{1}{2}\right) + \left(\frac{\varphi_1}{\alpha} + \frac{\varphi_2}{\beta}\right)\frac{x^2}{2} \tag{22}$$

$$s_{CH_4}(x) = 1 - \frac{\varphi_3}{\beta}\left(\frac{1}{m_2} + \frac{1}{2}\right) + \frac{\varphi_3 x^2}{2\beta} \tag{23}$$

Equations ((22) and (23)) are the exact solution of Equations ((20) and (21)).

4.3. Saturated Electrogenic Microorganism and Acetoclastic Methanogens Are Equal ($\alpha = \beta$)

In this case, Equations ((7) and (8)) become as follows:

$$\frac{d^2 s_{AC}}{dx^2} = \frac{(\varphi_1 + \varphi_2)s_{AC}}{1 + \alpha s_{AC}} \tag{24}$$

$$\frac{d^2 s_{CH_4}}{dx^2} = \frac{\varphi_3 s_{AC}}{1 + \beta s_{AC}} \tag{25}$$

In this case, the above non-linear equation can be solved using Adomain decomposition method. Now, the concentrations become

$$s_{AC}(x) = 1 - \frac{(\varphi_1 + \varphi_2)}{1 + \alpha}\left(\frac{1}{2} + \frac{1}{m_1}\right) + \frac{(\varphi_1 + \varphi_2)}{1 + \alpha}\left(\frac{x^2}{2}\right) \tag{26}$$

$$s_{CH_4}(x) = k + \left[\phi_2 x^2/2\phi_4\right] + \left\{\left[\phi_1 - (\phi_2\phi_3)/\phi_4\right]\left[\left(\log\left(\phi_3 + \phi_4 x^2\right)/2\phi_4\right) - \left(\left(\tan^{-1}\left(\phi_4 x/\sqrt{\phi_3\phi_4}\right)x\right)/\sqrt{\phi_3\phi_4}\right)\right]\right\} \tag{27}$$

where the constants ϕ_1 to ϕ_4 and k are given in Equation (12), when replacing $\theta = \left[(\phi_1 + \phi_2)/(1+\alpha)\right]$. Equations ((26) and (27)) are the approximate analytical expression of concentration of acetate and methane.

5. Discussion

Equations ((7) and (8)) represent the general closed-form of analytical expression for the concentrations of acetate and methane for non steady state condition and for various system parameters (potential, saturation parameter of electrogenic microorganism and acetoelastic methanogenes, the diffusion coefficient of acetate, ratio of the thickness of the biofilm and boundary layer). It is of interest to compare the influence of each parameter on the concentration of acetate and methane for various realistic experimental parameters.

Influence of Potential on the Concentration of Acetate. The influence of dimensionless potential on the concentration of the acetate for some experimental values of parameters is shown in **Figure 2(a)**. The microbial activity is strongly dependent on the redox potential of the anode. From this figure it is observed that the concentration of acetate decreases when ϕ_1 increases or potential decreases.

Influence of Saturation Parameter of Electrogenic Microorganism (m_1) and Acetoelastic-Methhanogenes (β) on Concentration of Acetate.-As shown in **Figure 2(b)** and **Figure 2(c)**, the concentration of

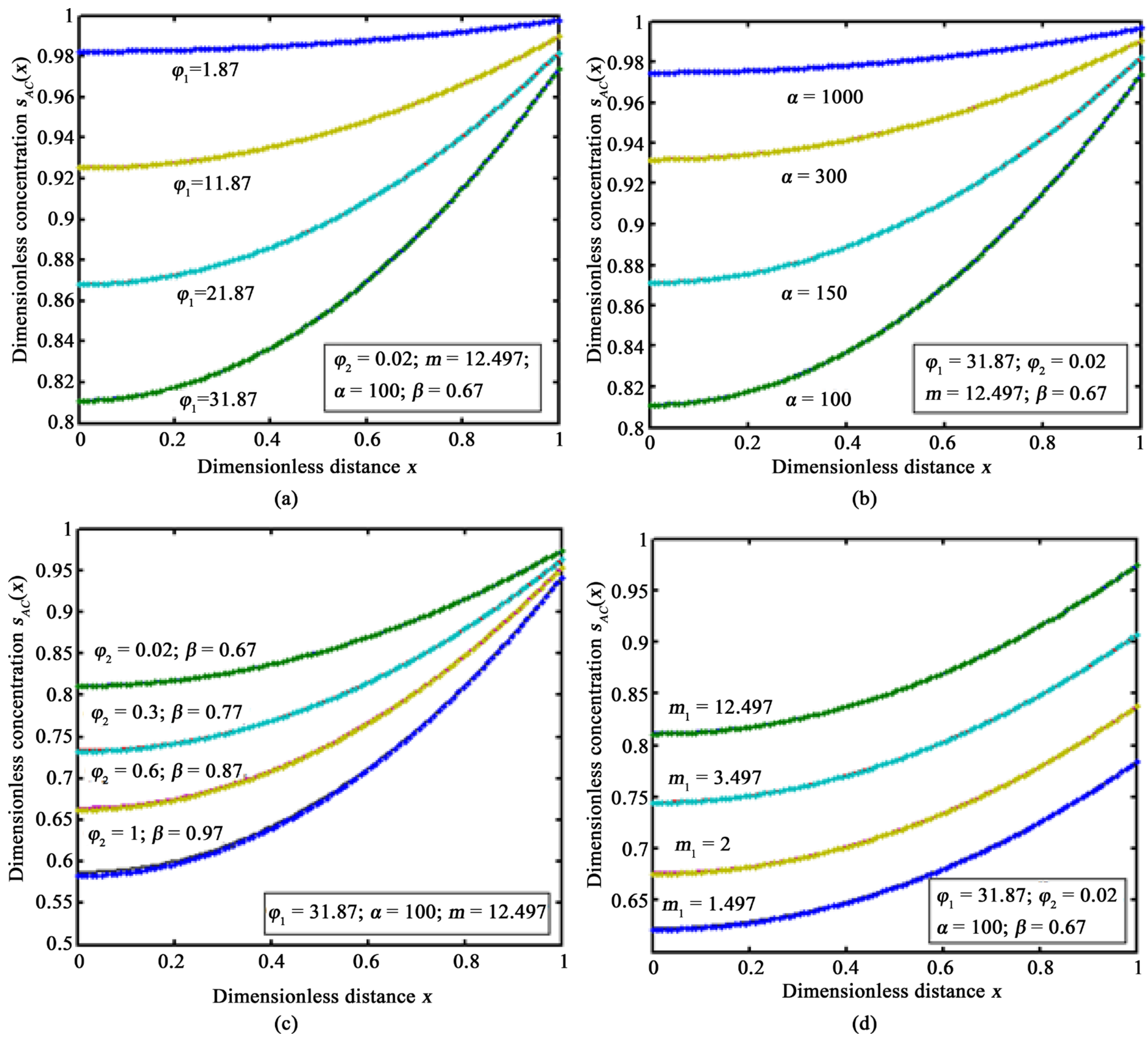

Figure 2. Plot of dimensionless concentration $s_{AC}(x)$ versus dimensionless distance x using Equation (10) for various values of the parameter (a) φ_1, (b) α, (c) φ_2 and β, (d) m_1 and for some fixed experimental values of other parameters.

acetate increases when saturation parameter of electrogenic microrganism (α) or bulk concentration of the acetate increases and saturation parameter of acetoelastic methanogenes (β) decreases. From **Figure 2(c)** it is also observed that the concentration of acetate is inversely proportional to diffusion coefficient of acetate.

Influnce of the Ratio of Thickness of the Biofilm and the Boundary Layer. **Figure 2(d)** represents the concentration verses distance from the anode surface for various values of m_1 or ratio of biofilm thickness and boundary layer thickness (L_f/L). From this figure, it is inferred that the concentration of acetate increases when the ratio of thickness increases.

Influence of Other Parameters of the Concentration of Methane and Acetate. The concentration of methane versus dimensionless distance *x* for various experimental values of parameters is plotted in **Figure 3**. From these figure, it is interfered that the concentration of methane increases when ϕ_1, ϕ_3, β increases or α decreases.

Figure 4 represents the dimensionless concentrations of acetate versus potential for various values of L_f, ϕ_2, α and β. From these figures, it is observed that the concentration of acetate increases when thickness L_f and α decreases. From **Figure 4(d)**, it is observed that the concentration of acetate does not differ significantly about the parameter β.

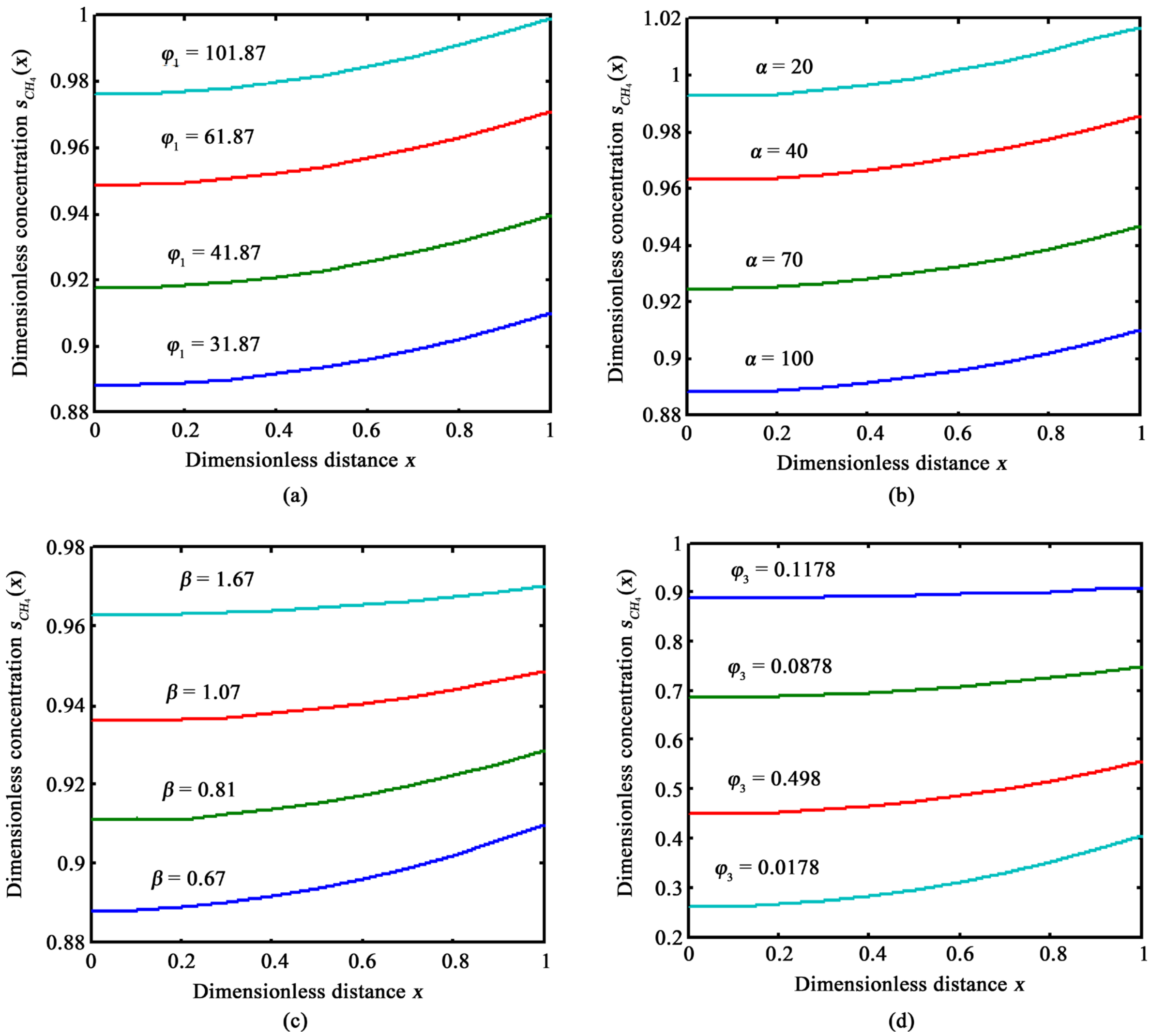

Figure 3. Plot of dimensionless concentration of $s_{CH_4}(x)$ versus dimensionless distance *x* using Equation (11). (a) For various values of the parameter (a) φ_1, (b) α, (c) φ_2 and β, (d) φ_3 and for some fixed experimental values of other parameters.

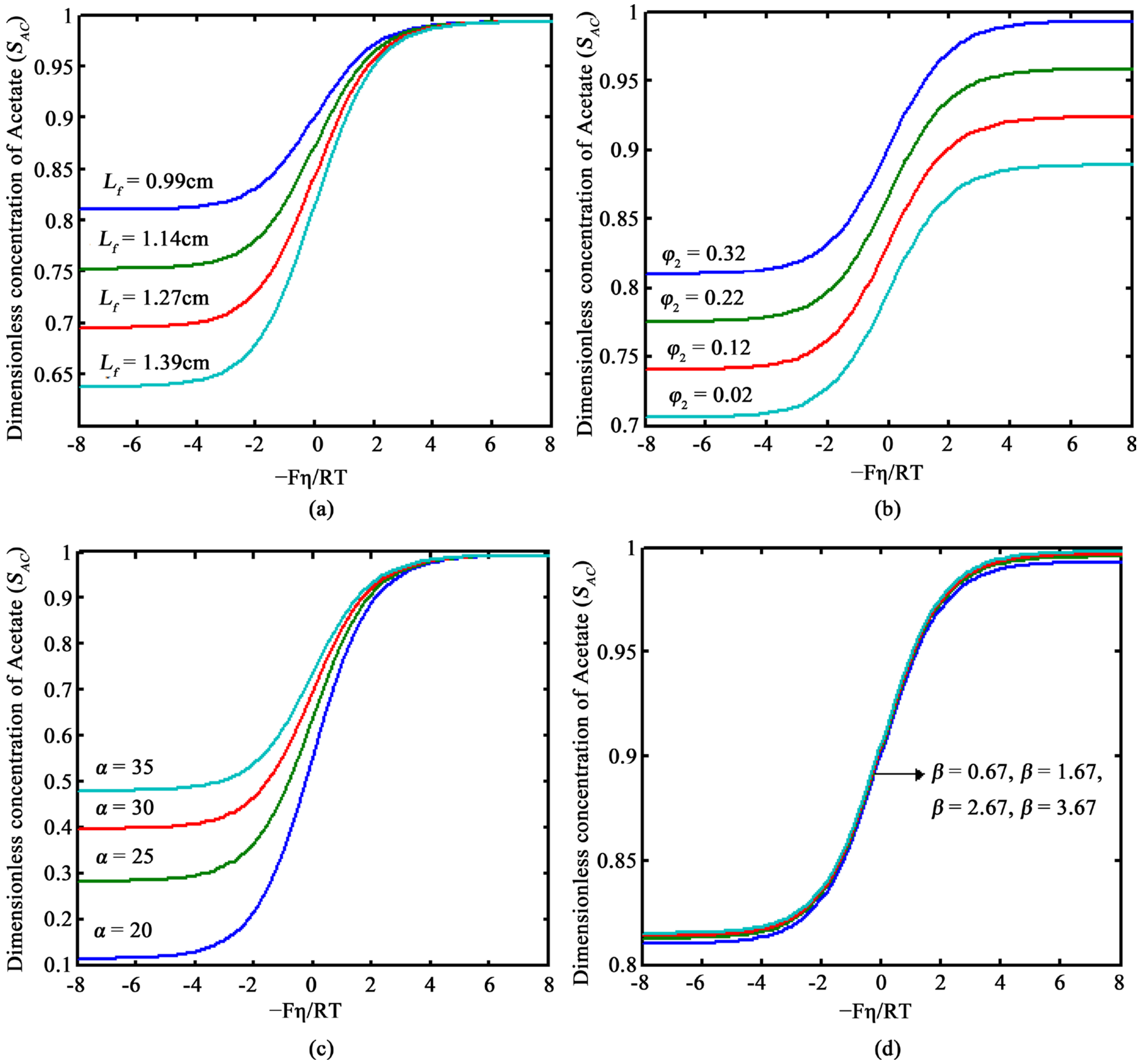

Figure 4. Plot of dimensionless concentration $s_{AC}(x)$ versus dimensionless potential using Equation (10) for various values of the parameter (a) L_f, (b) φ_2, (c) α, (d) β and for some fixed experimental values of other parameters.

6. Comparison with Numerical Data and Limiting Case Results

The non-linear differential Equations ((9) and (10)) for the given initial-boundary conditions are being solved numerically. The function pdex, in Matlab software which is a function of solving the initial-boundary value problems for non-linear ordinary differential equations is used to solve this equation. Its numerical solution is compared with analytical results in **Table 1**. The maximum relative error between our analytical result and the numerical result is 0.32%. The Matlab program is also given in **Appendix C**. The concentration of acetate and methane are also obtained for the following limiting cases, that is zero order kinetics, first order kinetics and saturated electrogenic microorganism and saturated acetoclastic methanogens are equal $(\alpha = \beta)$. Also our analytical results are compared with limiting case results in **Figure 5** and it gives a satisfactory agreement.

7. Determination of Kinetic Parameters $K_{AC,E}$, $q_{AC,AM,max}$, $\varphi_{E,a}$, α and β

The acetate consumption rate by electromagnetic microorganism in the microbial fuel cell (Equation (3)) can be written as follows:

Table 1. Comparison of the acetate concentration s_{AC} calculated using Equation (10) with the numerical simulation for various experimental values of φ_1 when $\varphi_2 = 0.02; \alpha = 100; \beta = 0.67; m_1 = 12.497$.

x	$\varphi_1 = 0.87$			$\varphi_1 = 31.87$			$\varphi_1 = 100.87$		
	Analytical Equation (10)	Numerical	% of derivation	Analytical Equation (10)	Numerical	% of derivation	Analytical Equation (10)	Numerical	% of derivation
0	0.418633	0.42057	0.460515	0.81091	0.80775	0.39996	0.9881	0.99000	0.19199
0.2	0.438648	0.440447	0.408479	0.81742	0.81435	0.38407	0.98851	0.99034	0.18524
0.4	0.498707	0.500134	0.285452	0.83709	0.83424	0.33744	0.98974	0.99137	0.16517
0.6	0.59885	0.599779	0.154921	0.86961	0.86739	0.26308	0.99171	0.99309	0.13176
0.8	0.739148	0.739587	0.059418	0.91529	0.91379	0.16528	0.99463	0.99553	0.08536
1	0.919696	0.919789	0.010118	0.97394	0.97347	0.04891	0.99837	0.99862	0.02622
	Average % of deviation		0.157141	Average % of deviation		0.31975	Average % of deviation		0.275781

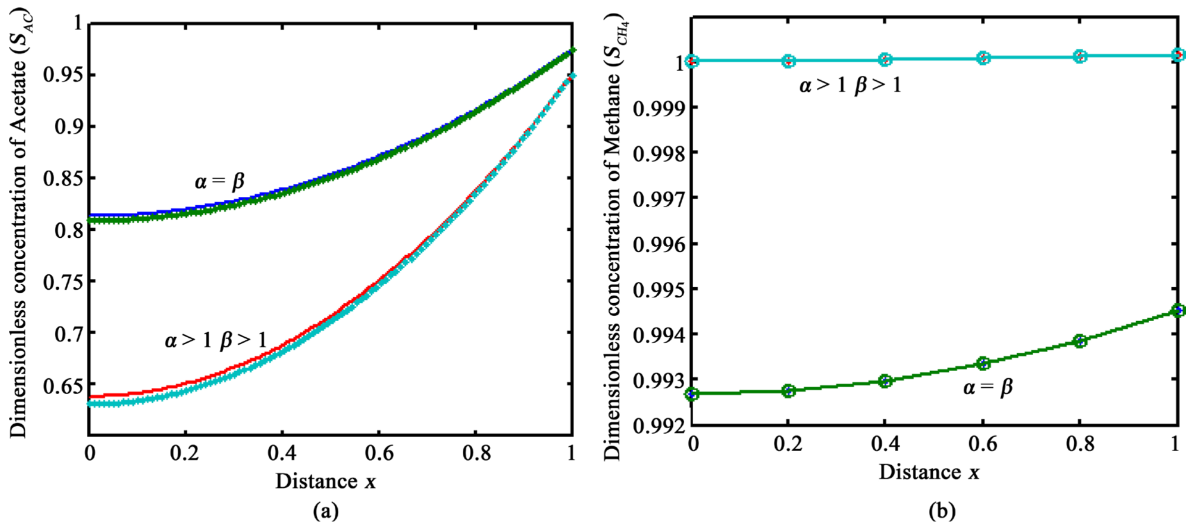

Figure 5. Plot of two dimensional comparative diagram of general solution of dimensionless Acetate concentration $s_{AC}(x)$ and methane concentration $s_{CH_4}(x)$ with the limiting cases (Zero order and in (a) and (b) respectively) for the experimental values Comparison of dimensionless concentration of $s_{AC}(x)$ and $s_{CH_4}(x)$ using Equations ((10), (11)), Equations ((22), (23)), Equations ((26), (27)).

$$\frac{1}{q_{AC,E}\left(1+\exp\left(-(Fn)/(RT)\right)\right)} = \frac{1}{q_{AC,AM,\max}\varphi_{E,a}}\left(1+\frac{K_{AC,E}}{S_{AC}}\right) \tag{28}$$

As shown in **Figure 6**, $1/\left(q_{AC,E}\left[1+\exp\left(-(Fn)/(RT)\right)\right]\right)$ is plotted against $1/S_{AC}$ to obtain the straight line with the slope $K_{AC,E}/q_{AC,AM,\max}\varphi_{E,a}$ and intercept $1/q_{AC,AM,\max}\varphi_{E,a}$. The slope and intercept yields the value of the parameters $K_{AC,E}$ and $q_{AC,AM,\max}\ \varphi_{E,a}$.

From Equation (10), we can obtain the concentration of acetate at bioflim and anode interface as

$$s_{AC}(x=0) = \left(1-\frac{\varphi_2\left(0.5+1/m_1\right)}{1+\beta}\right) - \frac{\left(0.5+1/m_1\right)}{1+\alpha}\varphi_1 \tag{29}$$

Now the plot of $S_{AC}(x=0)$ versus φ_1 gives the slope $-\left(0.5+1/m_1\right)/(1+\alpha)$ and intercept $1-\left[\left(\varphi_2\left(0.5+1/m_1\right)\right)/(1+\beta)\right]$. From these plot, we can obtain the kinetic constant α and β (**Table 2**).

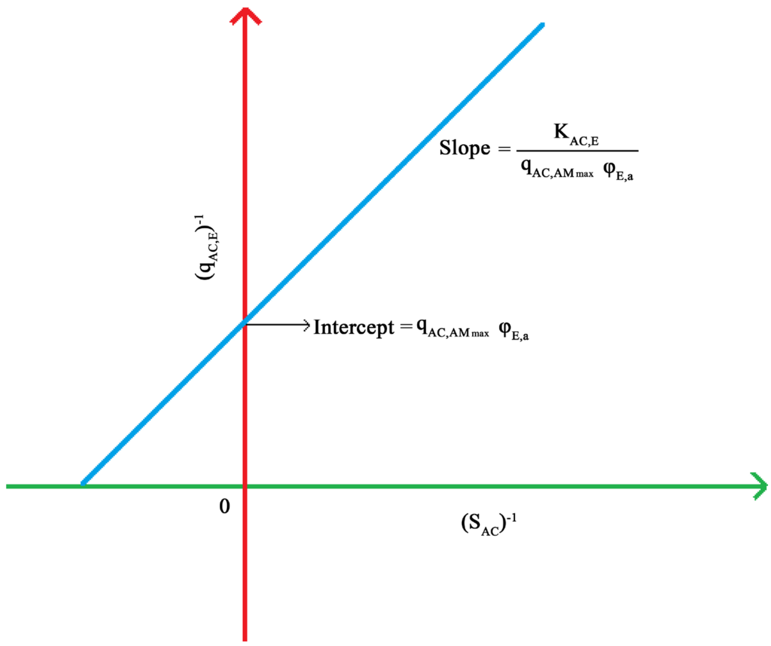

Figure 6. Estimation of kinetic parameters $K_{AC,E}$ and $q_{AC,AM,\max}\varphi_{E,a}$ from Equation (28).

Table 2. Nomenclature.

Symbols	Définitions	Units
s_{AC}	Acetate concentration in the biofilm	$(\text{kg COD}_s\ \text{m}^{-3})$
s_{CH_4}	Methane concentration in the biofilm	$(\text{kg COD}_s\ \text{m}^{-3})$
$s_{AC,bulk}$	Acetate concentration on the biofilm surface	$(\text{kg COD}_s\ \text{m}^{-3})$
$s_{CH_4,bulk}$	Methane concentration on the biofilm surface	$(\text{kg COD}_s\ \text{m}^{-3})$
$D_{AC,f}$	Diffusion coefficient of acetate	(m^2/day)
$D_{CH_4,f}$	Diffusion coefficient of methane	(m^2/day)
$X_{E,a}$	Density of biomass	$(\text{kg COD}_x\ \text{m}^{-3})$
$X_{AM,a}$	Density of biomass	$(\text{kg COD}_x\ \text{m}^{-3})$
$K_{AC,E}$	Half saturated constant of acetate consumed by acetoclastic methanogenic bacteria	$(\text{kg COD}_s\ \text{m}^{-3})$
$K_{AC,AM}$	Half saturated constant of acetate consumed by electrogenic bacteria	$(\text{kg COD}_s\ \text{m}^{-3})$
$q_{AC,AM,\max}$	Maximum acetate consumption rate	$(\text{kg COD}_s\ \text{kg COD}_x\ \text{m}^{-1}\cdot\text{day}^{-1})$
L_f	Thickness of the biofilm	*m*
L	Liquid concentration boundary layer thickness	*m*
$\phi_{E,a}$	Volume fraction of active electrogenic microorganism	*None*
$\phi_{AM,a}$	Volume fraction of active acetoclastic methanogenic microorganism	*None*
Y_{CH_4}	Yield coefficient	*None*
η	Local electrical potential	*v*
$F\eta/RT$	Dimensionless potential	*None*
m_1	Dimensionless parameter	*None*
m_1	Dimensionless parameter	*None*
φ_1	Dimensionless parameter	*None*
φ_2	Dimensionless parameter	*None*
φ_2	Dimensionless parameter	*None*

Continued

α	Dimensionless parameter	*None*
β	Dimensionless parameter	*None*
θ	Dimensionless parameter	*None*
S_{AC}	Dimensionless concentration of acetate in the biofilm	*None*
S_{CH_4}	Dimensionless concentration of methane in the biofilm	*None*
x	Dimensionless space coordinate in the bioflim	*None*
k	Dimensionless parameters	*None*

8. Conclusion

A theoretical model describing the bio energy production using microbial electrochemical cell via Nernst-Monoid kinetics is analyzed. The time independent non-linear partial differential equations have been solved analytically using the Adomain decomposition method. The primary result of this work is the approximate analytical expression of concentration of acetate and methane for all values of parameters. The influence of potential, ratio of thickness of biofilm and boundary layer, etc. on the concentration of acetate and methane is discussed. Our results are in excellent agreement with stimulation and limiting case results. Also two graphical procedures are suggested for estimating the kinetic parameters.

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Appendix A: Basic Concept of the Adomain Decomposition Method

This is given in the supplementary material of the manuscript.

Appendix B: Approximate Analytical Solution of Non Linear Equation (7) Using ADM

In this appendix, we indicate how Equation (6) in this paper is derived. Furthermore, an ADM is constructed to determine the solution of Equation (4) in the operator form,

$$Ls = \frac{\varphi_1 s_{AC}}{1+\alpha s_{AC}} + \frac{\varphi_2 s_{AC}}{1+\beta s_{AC}} \tag{B.1}$$

where $L = \frac{\mathrm{d}^2}{\mathrm{d}x^2}$. Applying the inverse operator L^{-1} on both sides of Equation (B.1) yields

$$s(x) = Ax + B + L^{-1}\left[\frac{\varphi_1 s_{AC}}{1+\alpha s_{AC}} + \frac{\varphi_2 s_{AC}}{1+\beta s_{AC}}\right] \tag{B.2}$$

where A and B are the constants of integration. We let,

$$s(x) = \sum_{n=0}^{\infty} s_n \tag{B.3}$$

$$N\left[s(x)\right] = \sum_{n=0}^{\infty} A_n \tag{B.4}$$

where

$$N\left[s(x)\right] = \frac{\varphi_1 s_{AC}}{1+\alpha s_{AC}} + \frac{\varphi_2 s_{AC}}{1+\beta s_{AC}} \tag{B.5}$$

From Equations ((B.3) to (B.5)), Equation (B.2) becomes

$$\sum_{n=0}^{\infty} s_n(x) = Ax + B + L^{-1}\left[\frac{\varphi_1 s_{AC}}{1+\alpha s_{AC}} + \frac{\varphi_2 s_{AC}}{1+\beta s_{AC}}\right] \tag{B.6}$$

We identify the zeroth component as

$$s_0(x) = Ax + B \tag{B.7}$$

and the remaining components as the recurrence relation

$$s_{n+1} = \gamma_E L^{-1} A_n ; n \geq 0 \tag{B.8}$$

where A_n are the Adomain polynomials of $s_0, s_1, \cdots, s_n$ .We can find the first two s_0 as follows:

$$s_0(x) = 1 \tag{B.9}$$

$$s_1(x) = \frac{\phi_1 + \phi_2}{1+\alpha}\left(\frac{x^2}{2} - \frac{1}{2} - \frac{1}{m}\right) \tag{B.10}$$

Adding (B.9) and (B.10), we can obtain the concentration of acetate as described in Equation (10) in the text. By substituting the values of s_{AC} in Equation (8), we get the concentration of the methane (Equation (11)) in the text.

Appendix C: Scilab/Matlab Program for the Numerical Solution of Equation

This is given in the supplementary material of the manuscript.

Supplementary Material of the Manuscript

Appendix A: Basic Concept of the Modified Adomain Decomposition Method

Consider the singular boundary value problem of $n+1$ order nonlinear differential equation in the form

$$\begin{aligned} & y^{(n+1)}+\frac{m}{x}y^{(n)}+Ny=g(x), \\ & y(0)=a_0,\ y'(0)=a_1,\cdots,y^{n-1}(0)=a_{n-1},\ y(b)=c \end{aligned} \tag{A.1}$$

where N is a non-linear differential operator of order less than n, $g(x)$ is given function and $a_0,a_1,\cdots,a_{n-1},c,b$ are given constants. We propose the new differential operator, as below

$$L=x^{-1}\frac{\mathrm{d}^n}{\mathrm{d}x^n}x^{1+n-m}\frac{\mathrm{d}}{\mathrm{d}x}x^{m-n}(.) \tag{A.2}$$

where $m\le n,n\ge 1$, so, the problem can be written as

$$L^{-1}(.)=g(x)-Ny \tag{A.3}$$

The inverse operator L^{-1} is therefore considered a $n+1$ fold integral operator, as below [11] [12]

$$L^{-1}(.)=x^{n-m}\int_b^x x^{m-n-1}\int_0^x\int_0^x\cdots\int_0^x x(.)\,\mathrm{d}x\cdots\mathrm{d}x. \tag{A.4}$$

By applying L^{-1} on (A.3), we have

$$y(x)=\phi(x)+L^{-1}(x)L^{-1}Ny \tag{A.5}$$

Such that

$$L\phi(x)=0$$

The Adomian decomposition method introduce the solution $y(x)$ and the nonlinear function Ny by infinite series

$$y(x)=\sum_{n=0}^{\infty}y_n(x) \tag{A.6}$$

and

$$Ny=\sum_{n=0}^{\infty}A_n \tag{A.7}$$

where the components $y_n(x)$ of the solution $y(x)$ will be determined recurrently. Specific algorithms were seen in [11] [12] to formulate Adomian polynomials. The following algorithm:

$$\begin{aligned} & A_0=F(u), \\ & A_1=F(u_0)u_1, \\ & A_2=F(u_0)u_2+\frac{1}{2}F''(u_0)u_1^2, \\ & A_3=F(u_0)u_3+\frac{1}{2}F''(u_0)u_1u_2+\frac{1}{3!}F'''(u_0)u_1^3, \\ & \quad\vdots \end{aligned} \tag{A.8}$$

can be used constant Adomian polynomials, when F is a nonlinear function. By substituting (A.6) and (A.7) in to (A.5)

$$\sum_{n=0}^{\infty}y_n=\phi(x)+L^{-1}g(x)-L^{-1}\sum_{n=0}^{\infty}A_n \tag{A.9}$$

Through using modified Adomian decomposition method, the components $y_n(x)$ can be determined as

$$y_0(x) = A + L^{-1}g(x)$$
$$y_{n+1}(x) = -L^{-1}(A_n), n \geq 0 \tag{A.10}$$

which gives

$$y_0(x) = A + L^{-1}g(x)$$
$$y_1(x) = -L^{-1}(A_0)$$
$$y_2(x) = -L^{-1}(A_1) \tag{A.11}$$
$$y_3(x) = -L^{-1}(A_2)$$
$$\vdots$$

From (A.8) and (A.11), we can determine the components $y_n(x)$, and hence the series solution of $y(x)$ in (A.6) can be immediately obtained. For numerical purposes, the *n*-term approximate

$$\psi_n = \sum_{n=0}^{n-1} y_k \tag{A.12}$$

can be used to approximate the exact solution. The approach presented above can be validated by testing it on a variety of several linear and nonlinear initial value problems.

Appendix C

Scilab/MatlabProgram for the Numerical Solution of Equation (4)

```
function pdex4
m = 0;
x = linspace (0, 1);
t = linspace (0, 100000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
%------------------------------------------------------------
Figure
plot(x,u1(end,:))
title('u1(x,t)')
xlabel('Distance x')
ylabel('u1(x,1)')
function [c,f,s] = pdex4pde(x,t,u,DuDx)
c =1;
f =1.* DuDx;
e=0.3;alpha=2;
F =-(e*u(1))/((1+(alpha*u(1))));
s =F;
% ------------------------------------------------------------
function u0 = pdex4ic(x);
u0 = [0];
% ------------------------------------------------------------
function [pl,ql,pr,qr] = pdex4bc(xl,ul,xr,ur,t)
j=10;
pl = [0];
ql = [1];
pr = [-j*(1-ur(1))];
qr = [1];
```