

Mathematical Modelling of Double Chamber Microbial Fuel Cell using Homotopy Perturbation Method



P. Jeyabarathi, M. Kannan, L. Rajendran

Abstract: A theoretical model and simulation of a two-chamber microbial fuel cell are discussed. The model is generated through the integration of the microbial fuel cell's bio-electrochemical kinetics and balance of mass and charge. Several parameters are examined that have a direct impact on the performance of the microbial fuel cells. Approximate analytical expressions for the concentration of acetate, dissolved carbon dioxide, hydrogen ion, biomass, dissolved oxygen, hydroxyl and cation M^+ in microbial fuel cell and glucose and glutamic acid in GGA fuel cell are obtained by solving the non-linear equation using new the homotopy perturbation method. The analytical result is compared with the numerical results and satisfactory agreement is noted.

Keywords: Mathematical modeling, Microbial fuel cell, Artificial wastewater, Numerical simulation, Homotopy perturbation method.

1. INTRODUCTION

A typical microbial two-chamber fuel cell shares certain similarities with chemical fuel cells like direct methanol fuel cells (DMFCs)[1] and direct ascorbic acid fuel cells (DAAFCS)[2]. A cation-exchange membrane divides anodic and cathodic chambers in both cases, oxidizes fuels in the anodic chamber and releases protons that move through the membrane to enter the cathodic chamber. By integrating biochemical reactions, Picioreanu et al [3] create an acetate solution based on a biofilm model of a redox-mediated microbial fuel cell (MFC). Oliveira et al.[4] extended Zeng's model and developed a model explaining the microbial fuel cells thermodynamic conduct. Since the microbial fuel cell is a multi-phase system involving simultaneous biological and electrochemical processes, mass, charging and energy transfer, the creation of a mathematical model is essential to the design and optimization of this type of cell. Zeng et al.[5] and Dannys et al.[6] present a one-dimensional model representing a two-chamber microbial fuel cell using an acetate substratum dependent expression of Butler-Volmer and mass/charge balances. The model of acetate was then extended to glucose and glutamic acid (GGA), confirming that it is indeed possible to extend the model to multiple substrates. Other than an acetate-fuelled microbial

fuel cell, the current method is also successfully applied to the use of artificial wastewater (glucose and glutamic acid solution) as fuel. In this paper, for all values of parameters, analytical expressions of the concentration of acetate, dissolved carbon dioxide, hydrogen ion, biomass, dissolved oxygen, hydroxyl, and cation M^+ are in Microbial fuel cell and Glucose and glutamic acid in GGA fuel cell is obtained by solving the non-linear equations using the homotopy perturbation method.

Nomenclature

Symbols	meanings	Value	Units
C_{AC}, C_{CO_2}, C_H, X	Concentration of acetate, dissolved CO_2 , hydrogen ion, biomass in anode components	-	$mol\ m^{-3}$
C_{O_2}, C_{OH}, C_M	Concentration of dissolved O_2 , hydroxyl, cation M^+ in cathode components	-	$mol\ m^{-3}$
C_6, C_5	Concentration of glucose, glutamic acid in GGA MFC	-	$mol\ m^{-3}$
$C_{AC.in}, C_{CO_2.in}, C_{H.in}, X_{in}$	Initial concentration of acetate, dissolved CO_2 , hydrogen ion, biomass in anode components	1	$mol\ m^{-3}$
$C_{O_2.in}, C_{OH.in}, C_{M.in}$	Initial concentration of dissolved O_2 , hydroxyl, cation M^+	1	$mol\ m^{-3}$
$C_{6.in}, C_{5.in}$	Initial concentration of glucose and glutamic acid in GGA MFC	1	$mol\ m^{-3}$

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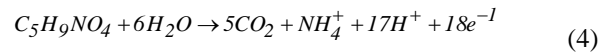
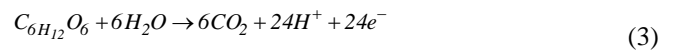
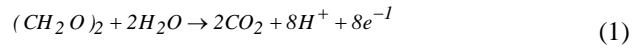
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$C_{AC}^{in}, C_{CO_2}^{in}, C_H^{in}, X^{in}$	Concentration of acetate, dissolved carbon dioxide, hydrogen ion, bacteria in the influent of anode compartment	1.56, 1, 1, 1	$mol\ m^{-3}$
$C_{O_2}^{in}, C_M^{in}, C_{OH}^{in}$	Concentration of dissolved oxygen, M^+ , OH^- in the influent of cathode compartment.	0.312, 1, 1	$mol\ m^{-3}$
C_6^in, C_5^in	Concentration of glucose, glutamic acid in the influent of anode compartment	1.2, 15	$mol\ m^{-3}$
F	Faraday's constant	96485.4	Coulombs mol^{-1}
R	Gas constant	8.3144	$J\ mol^{-1}\ K^{-1}$
T	Temperature	303	K
k^m, k^{aq}	Electrical conductivity of membrane and aqueous solution.	0.017	$Ohm^{-1}\ m^{-1}$
d^{cell}, d^m	Distance between anode and cathode in the cell and thickness.	0.777, 0.2	m
C_a, C_c	Capacitance of anode and cathode	500, 400	$F\ m^{-2}$
V_a, V_c	Volume of anode and cathode compartment	0.00001	$F\ m^{-2}$
Q_a, Q_c	Flow rate of fuel feed to anode and cathode	0.00001 0.00002	$m^3\ h^{-1}$
f_x	Reciprocal of wash-out fraction	10	None
k_1^0, k_2^0	Rate constant of anode and cathode reaction	0.2, 0.004	$mol\ m^{-2}\ h^{-1}$ $mol^{-4}\ m^{12}\ h^{-1}$
K_{AC}, K_{O_2}	Rate constant for acetate and dissolved oxygen	0.05, 0.004	$mol\ m^{-3}$
$\alpha, \alpha_1, \alpha_2$ and β	Charge transfer coefficient of glucose and glutamic acid at anode and cathode.	0.051, 0.76, 0.74, 0.663	None
U_{cell}	Cell voltage	-	Volt
U^0	Cell open circuit potential	0.77	Volt
Y_{ac}	yield	0.05	None
A_m	Area of membrane	0.0002	m^2
k_{dec}	Decay constant for acetate utilisers	0.08	h^{-1}
η_a, η_c	Overpotential at the anode and cathode	-	V

i_{cell}	Cell current density	4.8	$A\ m^{-2}$
N_M	Flux of M^+ ions	-	$mol\ m^{-2}\ h^{-1}$

II. MATHEMATICAL FORMULATION OF THE PROBLEM.

The reaction scheme of the anode, cathode chamber in microbial fuel cell and glucose and glutamic acid in GGA fuel cell [5] is



II(A). MASS BALANCES FOR ANODE COMPARTMENT [5]

The mass balances of the four components in the anode compartments namely, acetate, dissolved CO_2 , hydrogen ion and biomass are expressed by Eqns. (5-8).

$$V_a \frac{dC_{AC}}{dt} = Q_a (C_{AC}^{in} - C_{AC}) - A_m r_1 \quad (5)$$

$$V_a \frac{dC_{CO_2}}{dt} = Q_a (C_{CO_2}^{in} - C_{CO_2}) + 2A_m r_1 \quad (6)$$

$$V_a \frac{dC_H}{dt} = Q_a (C_H^{in} - C_H) + 8A_m r_1 \quad (7)$$

$$V_a \frac{dX}{dt} = \frac{Q_a (X^{in} - X)}{f_x} + A_m Y_{ac} r_1 - V_a K_{dec} X \quad (8)$$

The initial conditions are $C_{AC} = C_{AC_{in}}, C_{CO_2} = C_{CO_{2in}}, C_H = C_{H_{in}}, X = X_{in}$ at $t = 0$ (9)

where V, Q and A_m are the volume of the anode and cathode compartment, Y_{ac} the bacterial yield, and K_{dec} the decay constant for acetate utilizes, f_x the reciprocal of the wash-out fraction, C_{AC}, C_{CO_2}, C_H and X are concentration of acetate, dissolved CO_2 , hydrogen ion and biomass.

II(B). MASS BALANCES FOR CATHODE COMPARTMENT [5]

The mass balances of the three components in the cathode compartments namely, dissolved O_2 , hydroxyl and cation M^+ are expressed by Eqns. (10-13).

$$V_c \frac{dC_{O_2}}{dt} = Q_c (C_{O_2}^{in} - C_{O_2}) + r_2 A_m \quad (10)$$

$$V_c \frac{dC_{OH}}{dt} = Q_c (C_{OH}^{in} - C_{OH}) - 4r_2 A_m \quad (11)$$

$$V_c \frac{dC_M}{dt} = Q_c (C_M^{in} - C_M) + N_M A_m \quad (12)$$

The initial conditions are $C_{O_2} = C_{O_{2in}}, C_{OH} = C_{OH_{in}}, C_M = C_{M_{in}}$ at $t = 0$ (13)

where $N_M = \frac{3600i_{cell}}{F}$ is the flux of M^+ ions, i_{cell} is the cell current density, C_{O_2}, C_{OH}

and C_M are the concentration of dissolved O_2 , hydroxyl, and M^+ . By using Butler-Volmer equation [7] which is shown in the following equation:

$$r_1 = k_1^0 \frac{C_{AC}}{K_{AC} + C_{AC}} X \exp\left(\frac{\alpha F}{RT} \eta_a\right) \quad (14)$$

$$r_2 = -k_2^0 \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \exp\left(\frac{(\beta-1)F}{RT} \eta_c\right) \quad (15)$$

where k_1^0, k_2^0 are rate constants of anode and cathode reaction, K_{AC} and K_{O_2} are half velocity rate constant for acetate and dissolved oxygen. η_a, η_c is the over potential at the anode and cathode, α and β is the charge transfer coefficient of the anodic and cathodic reaction. R is the gas constant, F is the faraday constant and T is the temperature.

II(C). MASS BALANCES FOR ANODE COMPARTMENTS IN THE GGA FUEL CELL [5].

The mass balances of the five components in the anode compartments namely, glucose, glutamic acid, dissolved CO_2 , hydrogen ion and biomass are expressed by Eqns. (16-21).

$$V_a \frac{dC_6}{dt} = Q_a (C_6^{in} - C_6) - A_m r_{11} \quad (16)$$

$$V_a \frac{dC_5}{dt} = Q_a (C_5^{in} - C_5) - A_m r_{12} \quad (17)$$

$$V_a \frac{dC_{CO_2}}{dt} = Q_a (C_{CO_2}^{in} - C_{CO_2}) + 6A_m r_{11} + 5A_m r_{12} \quad (18)$$

$$V_a \frac{dC_H}{dt} = Q_a (C_H^{in} - C_H) + 24A_m r_{11} + 17A_m r_{12} \quad (19)$$

$$V_a \frac{dX}{dt} = Q_a \left(\frac{X^{in} - X}{f_x}\right) + A_m Y_{AW} (r_{11} + r_{12}) - V_a K_{DAW} A_m r_{12} \quad (20)$$

The initial conditions are

$$C_6 = C_{6m}, C_5 = C_{5m}, C_{CO_2} = C_{CO_{2m}}, C_H = C_{Hm}, X = X_{in} \text{ at } t=0 \quad (21)$$

where Y_{AW} the bacterial yield, C_6 and C_5 are the concentration of glucose and glutamic acid respectively. By using Butler-Volmer equation [7] which is shown in the following equation:

$$r_{11} = k_{11}^0 \frac{C_6}{K_6 + C_6} X \exp\left(\frac{\alpha_1 F}{RT} \eta_a\right) \quad (22)$$

$$r_{12} = k_{12}^0 \frac{C_5}{K_5 + C_5} X \exp\left(\frac{\alpha_2 F}{RT} \eta_a\right) \quad (23)$$

where k_{11}^0 and k_{12}^0 rate constants of glucose and glutamic acid, α_1 and α_2 are charge transfer coefficient of glucose and glutamic acid.

II(D). The charge balances at the anode and cathode [5]

The charge balance of the anode and cathode are given by the following Eqns. (24-25)

$$C_a \frac{d\eta_a}{dt} = 3600i_{cell} - 8F r_1 \quad (24)$$

$$C_c \frac{d\eta_c}{dt} = -3600i_{cell} - 8F r_2 \quad (25)$$

The initial conditions are

$$\eta_a = \eta_{a,in}, \eta_c = \eta_{c,in} \text{ at } t=0 \quad (26)$$

where C_a and C_c are the capacitances of anode and cathode. The cell voltage U_{cell} is calculated as

$$U_{cell} = U^0 - \eta_a + \eta_c - \left(\frac{d^m}{k^m} + \frac{d_{cell}}{k^{aq}}\right) i_{cell} \quad (27)$$

where U^0 is the open circuit voltage, d^m, d_{cell} are thickness, k^m and k^{aq} are the conductivities of the membrane. The steady state condition for acetate

$$C_{AC}(t) = C_{AC}^{in} - 450i_{cell} \frac{A_m}{FQ_a} \text{ where } r_1 = \frac{450i_{cell}}{F} \quad (28)$$

III. ANALYTICAL EXPRESSION OF CONCENTRATION USING HOMOTOPY PERTURBATION METHOD.

Recently, many authors applied the HPM to solve the various linear and nonlinear problems in physics and engineering sciences [8-10]. Suganya and Rajendran [11] derived the analytical solution of nonlinear equations in microbial fuel cells in wastewater treatment using the homotopy perturbation method. In this paper, the concentrations of acetate, dissolved carbon dioxide, hydrogen ion, biomass, dissolved oxygen, hydroxyl, and cation M^+ are in microbial fuel cell and glucose, and glutamic acid in GGA fuel cell can be obtained by solving Eqns. ((5-8),(10-12) and (16-20)) using HPM (see Appendix A) Eqn. (5) can be rewritten

$$\frac{dC_{AC}}{dt} = A_1 - A_2 \left(\frac{C_{AC}}{k_{AC} + C_{AC}}\right) \text{ where}$$

$$A_1 = \frac{Q_a C_{AC}^{in}}{V_a} - \frac{Q_a C_{AC,in}}{V_a}, A_2 = \frac{A_m k_1^0 X_{in} e^{\left(\frac{\alpha F}{RT} \eta_{a,in}\right)}}{V_a} \quad (29)$$

for some fixed experimental values of the parameter $Q_a = 0.00002, V_a = 0.00005, C_{AC}^{in} = 1.56, C_{AC,in} = 1, X_{in} = 1, A_m = 0.0005, k_1^0 = 0.207, F = 96485.4, K_{AC} = 0.592, \eta_{a,in} = 0.1$.

Solving the above equation we get

$$C_{AC}(t) = 0.067 + 0.67W(5.8e^{-2.7t}) \text{ where } A_1 = 0.2, A_2 = 2, \alpha = 0.01 \quad (31)$$

$$C_{AC}(t) = 0.052 + 0.65W(6.2e^{-3.5t})$$

where

$$(32)$$

$$C_{AC}(t) = 0.018 + 0.62W(7.8e^{-11t}) \text{ where } A_1 = 0.2, A_2 = 7, \alpha = 0.3 \quad (33)$$

$$C_{AC}(t) = 0.002 + 0.6W(8.7e^{-107.7t}) \text{ where } A_7 = 0.2, A_2 = 65, \alpha = 0.9 \quad (34)$$

$$C_{CO_2}(t) = A_3 \frac{Q_a}{V_a} + \left(C_{CO_2.in} - A_3 \frac{Q_a}{V_a} \right) e^{-\frac{Q_a t}{V_a}} \text{ where}$$

$$A_3 = \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{2 k_1^0 A_m C_{AC.in} X_{in} e^{\left(\frac{\alpha F \eta_{a.in}}{RT}\right)}}{V_a (K_{AC} + C_{AC.in})} \quad (35)$$

$$C_H(t) = A_4 \frac{Q_a}{V_a} + \left(C_{H.in} - A_4 \frac{Q_a}{V_a} \right) e^{-\frac{Q_a t}{V_a}} \text{ where}$$

$$A_4 = \frac{Q_a C_H^{in}}{V_a} + \frac{8 k_1^0 A_m C_{AC.in} X_{in} e^{\left(\frac{\alpha F \eta_{a.in}}{RT}\right)}}{V_a (K_{AC} + C_{AC.in})} \quad (36)$$

$$X(t) = \frac{-Q_a X^{in}}{A_5 f_x V_a} + \left(X_{in} + \frac{Q_a X^{in}}{A_5 f_x V_a} \right) e^{-A_5 t} \text{ where}$$

$$A_5 = \frac{-Q_a}{f_x V_a} + \frac{A_m Y_{ac} k_1^0 e^{\left(\frac{\alpha F \eta_{a.in}}{RT}\right)} C_{AC.in} - K_{dec}}{V_a (K_{AC} + C_{AC.in})} \quad (37)$$

$$C_{O_2}(t) = \frac{Q_c C_{O_2}^{in}}{V_c} + \left(C_{O_2.in} - \frac{Q_c C_{O_2}^{in}}{V_c} \right) e^{-A_6 t} \text{ where}$$

$$A_6 = \frac{Q_c}{V_c} + \frac{A_m k_2^0 e^{\left(\frac{(\beta-1)F \eta_{c.in}}{RT}\right)}}{V_c (K_{O_2} + C_{O_2.in})} \quad (38)$$

$$C_{OH}(t) = A_7 \frac{Q_c}{V_c} + \left(C_{OH.in} - A_7 \frac{Q_c}{V_c} \right) e^{-\frac{Q_c t}{V_c}} \text{ where}$$

$$A_7 = \frac{Q_c C_{OH}^{in}}{V_c} + \frac{4k_2^0 A_m C_{O_2.in} e^{\left(\frac{(\beta-1)F \eta_{c.in}}{RT}\right)}}{V_c (K_{O_2} + C_{O_2.in})} \quad (39)$$

$$C_M(t) = A_8 \frac{Q_c}{V_c} + \left(C_{M.in} - A_8 \frac{Q_c}{V_c} \right) e^{-\frac{Q_c t}{V_c}} \text{ where}$$

$$A_8 = \frac{Q_c C_M^{in}}{V_c} + \frac{3600 i_{cell} A_m}{V_c F} \quad (40)$$

III(A). ANALYTICAL EXPRESSION OF GGA MICROBIAL FUEL CELLS CONCENTRATION USING HOMOTOPY PERTURBATION METHOD.

Equation (16) can be rewritten

$$\frac{dC_6}{dt} = A_9 - A_{10} \left(\frac{C_6}{K_6 + C_6} \right) \text{ where}$$

$$A_9 = \frac{Q_a C_6^{in}}{V_a} - \frac{Q_a C_{6.in}}{V_a}, A_{10} = \frac{A_m k_{11}^0 X_{in} e^{\left(\frac{\alpha_1 F \eta_{a.in}}{RT}\right)}}{V_a} \quad (41)$$

for some fixed experimental values of parameter

$$Q_a = 0.00002, V_a = 0.00005, C_6^{in} = 1.2, C_{6.in} = 1, X_{in} = 1, A_m = 0.0005, k_{11}^0 = 0.005, K_6 = 0.3, F = 964854, \eta_{a.in} = 0.1. \quad (42)$$

Solving the above equation we get

$$C_6(t) = 0.038 + 0.336W(49.4e^{-1.9t}) \text{ where}$$

$$A_9 = 0.08, A_{10} = 0.72, \alpha_1 = 0.1 \quad (43)$$

$$C_6(t) = 0.012 + 0.316W(70.3e^{-4.8t}) \text{ where}$$

$$A_9 = 0.08, A_{10} = 1.6, \alpha_1 = 0.3 \quad (44)$$

$$C_6(t) = 0.007 + 0.306W(81.5e^{-10.5t}) \text{ where}$$

$$A_9 = 0.08, A_{10} = 3.3, \alpha_1 = 0.5 \quad (45)$$

$$C_6(t) = 0.005 + 0.30W(85.1e^{-46.4t}) \text{ where}$$

$$A_9 = 0.08, A_{10} = 4.8, \alpha_1 = 0.6 \quad (46)$$

Equation (17) can be rewritten

$$\frac{dC_5}{dt} = A_{11} - A_{12} \left(\frac{C_5}{K_5 + C_5} \right) \text{ where}$$

$$A_{11} = \frac{Q_a C_5^{in}}{V_a} - \frac{Q_a C_{5.in}}{V_a}, A_{12} = \frac{A_m k_{12}^0 X_{in} e^{\left(\frac{\alpha_2 F \eta_a}{RT}\right)}}{V_a} \quad (47)$$

for some fixed experimental values of parameter

$$Q_a = 0.00002, V_a = 0.00005, C_5^{in} = 1.15, C_{5.in} = 1, X_{in} = 1, A_m = 0.0005, k_{12}^0 = 0.0007, K_5 = 0.1, F = 964854, \eta_{a.in} = 0.1. \quad (48)$$

Solving the above equation we get

$$C_5(t) = 0.007 + 0.107W(10475e^{-15.7t}) \text{ where}$$

$$A_{11} = 0.06, A_{12} = 0.98, \alpha_2 = 0.7 \quad (49)$$

$$C_5(t) = 0.015 + 0.115W(44933e^{-3.48t}) \text{ where}$$

$$A_{11} = 0.06, A_{12} = 0.46, \alpha_2 = 0.5 \quad (50)$$

$$C_5(t) = 0.04 + 0.14W(6518.72e^{-1.07t}) \text{ where}$$

$$A_{11} = 0.06, A_{12} = 0.21, \alpha_2 = 0.2 \quad (51)$$

$$C_{CO_2}(t) = A_{13} \frac{Q_a}{V_a} + \left(C_{CO_2.in} - A_{13} \frac{Q_a}{V_a} \right) e^{-\frac{Q_a t}{V_a}} \text{ where}$$

$$A_{13} = \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{A_m X_{in}}{V_a} \left[\frac{6k_{11}^0 C_{6.in} e^{\left(\frac{\alpha_1 F \eta_a}{RT}\right)}}{K_6 + C_{6.in}} + \frac{5k_{12}^0 C_{5.in} e^{\left(\frac{\alpha_2 F \eta_a}{RT}\right)}}{K_5 + C_{5.in}} \right] \quad (52)$$

$$C_H(t) = A_{14} \frac{Q_a}{V_a} + \left(C_{CO_2.in} - A_{14} \frac{Q_a}{V_a} \right) e^{-\frac{Q_a t}{V_a}} \text{ where}$$

$$A_{14} = \frac{Q_a C_H^{in}}{V_a} + \frac{A_m X_{in}}{V_a} \left[\frac{24k_{11}^0 C_{6.in} e^{\left(\frac{\alpha_1 F \eta_{a.in}}{RT}\right)}}{K_6 + C_{6.in}} + \frac{17k_{12}^0 C_{5.in} e^{\left(\frac{\alpha_2 F \eta_{a.in}}{RT}\right)}}{K_5 + C_{5.in}} \right] \quad (53)$$

$$X(t) = \frac{-Q_a}{A_{15} F_x V_a} X^{in} + \left(X_{in} + \frac{Q_a}{A_{15} V_a F_x} X^{in} \right) e^{A_{15} t} \text{ where}$$

$$A_{15} = \frac{Q_a}{V_a F_x} + \frac{A_m Y_{AW}}{V_a} \left(\frac{k_{11}^0 C_{6in} e^{\frac{\alpha_1 F \eta_{a,in}}{RT}}}{K_6 + C_{6in}} + \frac{k_{12}^0 C_{5in} e^{\frac{\alpha_2 F \eta_{a,in}}{RT}}}{K_5 + C_{5in}} \right) - K_{dAW} \quad (54)$$

III(B). ANALYTICAL EXPRESSION OF OVER POTENTIAL AT THE ANODE AND CATHODE USING HOMOTOPY PERTURBATION METHOD.

Eqn. (24) can be rewritten

$$\frac{d\eta_a}{dt} = B_1 - B_2 e^{B_3 \eta_a(t)} \text{ where}$$

$$B_1 = \frac{3600 i_{cell}}{C_a}, B_2 = \frac{8 F k_1^0 C_{AC,in} X_{in}}{C_a (K_{AC} + C_{AC,in})}, B_3 = \frac{\alpha F}{RT} \quad (55)$$

Solving the above equation we get

$$\eta_a(t) = -\frac{1}{B_3} \log \left(\frac{e^{-B_3(B_1 t + \eta_{a,in})} [B_2 e^{B_3 \eta_{a,in}} (e^{B_1 B_3 t} - 1) + B_1]}{B_1} \right) \quad (56)$$

Eqn. (25) can be rewritten

$$\frac{d\eta_c}{dt} = -B_4 - B_5 e^{B_6 \eta_c(t)} \text{ where}$$

$$B_4 = \frac{3600 i_{cell}}{C_c}, B_5 = \frac{-4 F k_2^0 C_{O_2,in}}{C_c (K_{O_2} + C_{O_2,in})}, B_6 = \frac{(\beta - 1) F}{RT} \quad (57)$$

Solving the above equation we get

$$\eta_c(t) = \frac{-1}{B_6} \log \left(\frac{e^{B_4 B_6 t} [B_4 e^{-B_6 \eta_{c,in}} - B_5] + B_5}{B_4} \right) \quad (58)$$

Using Eqns. (56) and (58), the Eqn. (27) becomes

$$U_{cell} = \frac{1}{B_3} \log \left(\frac{e^{-B_3(B_1 t + \eta_{a,in})} [B_2 e^{B_3 \eta_{a,in}} (e^{B_1 B_3 t} - 1) + B_1]}{B_1} \right) - \frac{1}{B_6} \log \left(\frac{e^{B_4 B_6 t} [B_4 e^{-B_6 \eta_{c,in}} - B_5] + B_5}{B_4} \right) + U^0 - \left(\frac{d^m}{k^m} - \frac{d_{cell}}{k_{aq}^m} \right) i_{cell} \quad (59)$$

VI. NUMERICAL SIMULATION

Numerically, the non-linear Eqns.(5-8)and (10-12)) in Microbial fuel cells and Eqns. (16-20) in GGA Fuel cells are solved for the initial condition (equations (9),(13) and (21)). For ordinary differential equations, the function of ode 45 in

the Matlab program is used to solving the boundary value problems. The numerical results for all parameter values are also compared to the analytical expressions equations obtained (29-54).

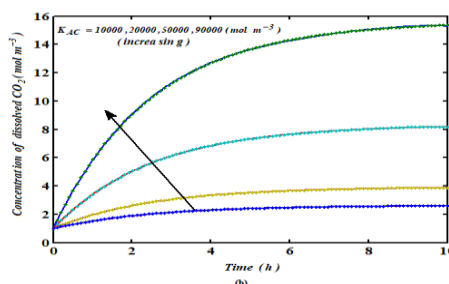
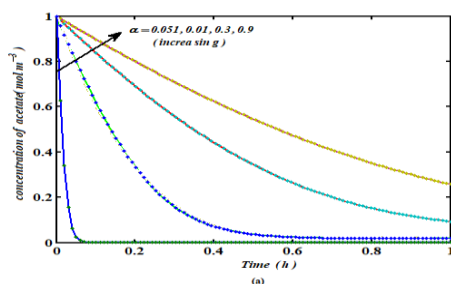
V. DISCUSSION

Eqns. (31-34) represents the concentration of acetate for various experimental values of parameters. Fig. 1(a) represents the concentration of acetate versus time for the various value of the decay constant for acetate utilisers k_{dec} . From the figure it is inferred that the concentration of acetate is the decreasing function. The concentration of dissolved carbon dioxide, hydrogen ion, and biomass versus time are represented in Fig. 1(b-d). From the figure, it is observed that dissolved carbon dioxide, hydrogen ion, and biomass are increase when time increases.

Fig .2 represents a concentration of dissolved oxygen, hydroxyl, and M^+ versus time for the various values of charge transfer coefficient of cathode β , rate constant of dissolved oxygen K_{O_2} , and volume of cathode V_c . From the figure, it is inferred that concentration dissolved oxygen, increases when time increases. From the figure it is observed that the concentration of hydroxyl, and M^+ is the decreasing function. Fig. 3 represents the concentration of glucose, glutamic acid, dissolved CO_2 , hydrogen ion, and biomass for various values of parameters. From the figure, it is noted that glucose, glutamic acid, dissolved CO_2 , hydrogen ion, and biomass are decreasing function.

Cell voltage U_{cell} versus time is represented that Fig. 4 for the various values of parameters. From the figure, it is observed that cell voltage increases when time increases and reaches the steady-state value when $t=10$ hour approximately.

Fig. 5 represents cell current density i_{cell} versus time for various values of parameters feed flow rate of anode Q_a and area of membrane A_m . From the figure, it is inferred that cell current density i_{cell} increases when time increases and reaches the steady-state when $t=1$ hour for all values of other parameters. The maximum value of cell current density depends upon Q_a and A_m



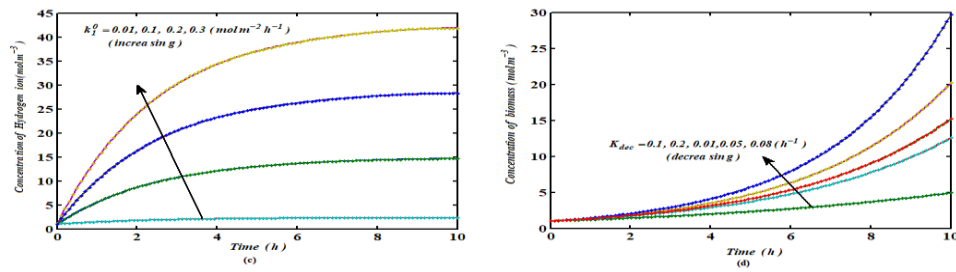


Fig.1 Comparison of analytical and numerical solutions of anode compartment in Microbial fuel cell.

- (a) Concentration of acetate versus time (Eqns.(31-34))
- (b) Concentration of dissolved CO_2 versus time (Eqn. (35))
- (c) Concentration of hydrogen ion versus time (Eqn. (36))
- (d) Concentration of biomass versus time (Eqn. (37))

Solid lines represent the numerical simulation and the dotted lines represent the analytical solutions

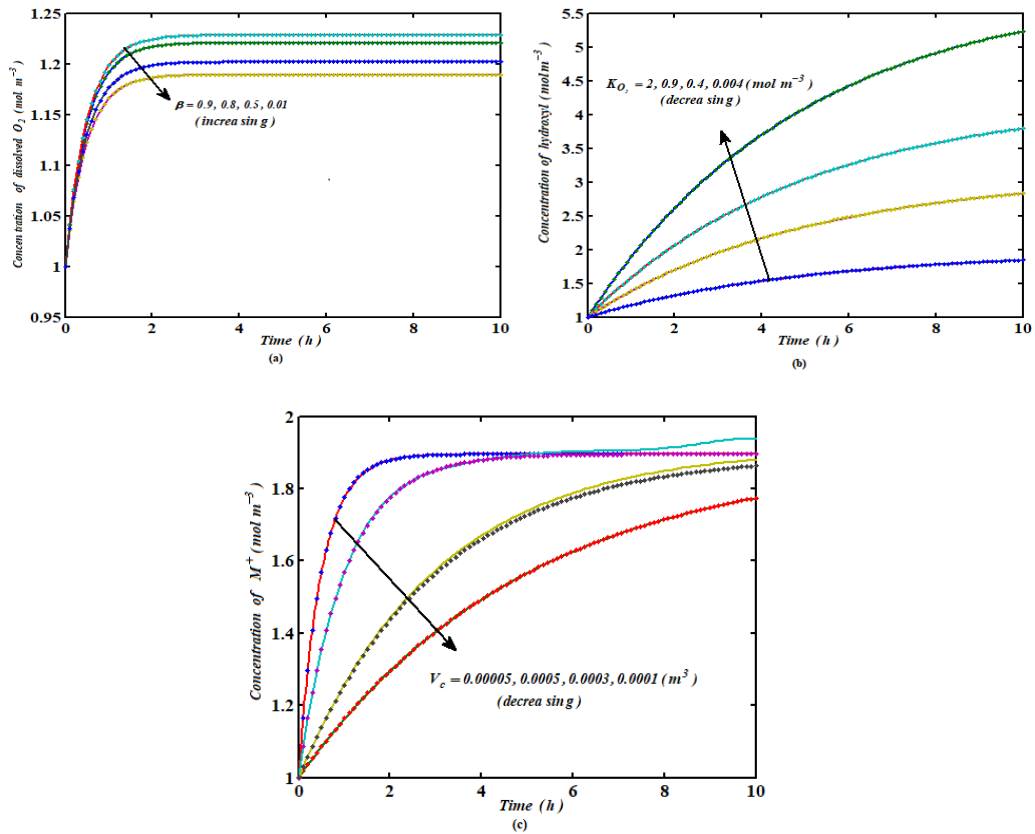


Fig.2 Comparison of analytical and numerical solutions of cathode compartment in Microbial fuel cell.

- (a) Concentration of dissolved O_2 versus time (Eqns.(38))
- (b) Concentration of hydroxyl versus time (Eqn. (39))
- (c) Concentration of M^+ versus time (Eqn. (40))

Solid lines represent the numerical simulation and the dotted lines represent the analytical solutions.

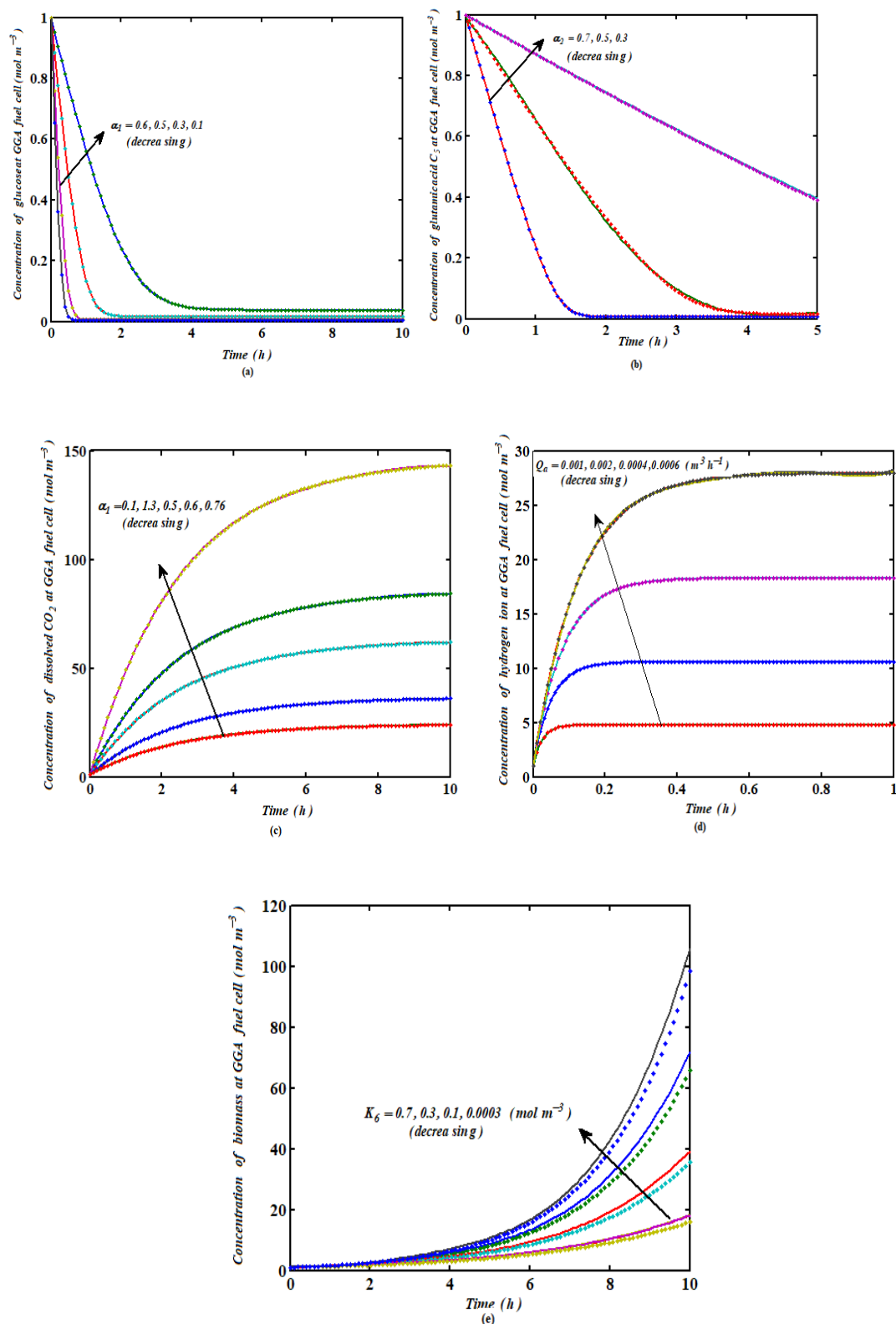


Fig.3 Comparison of analytical and numerical solutions of artificial waste water (glucose and glutamic acid.

- (a) Concentration of glucose versus time (Eqns. (43-46))
- (b) Concentration of glutamic acid versus time (Eqns. (49-51))
- (c) Concentration of dissolved CO_2 versus time (Eqn. (52))
- (d) Concentration of hydrogen ion versus time (Eqn. (53))
- (e) Concentration of biomass versus time (Eqn. (54))

Solid lines represent the numerical simulation and the dotted lines represent the analytical solutions.

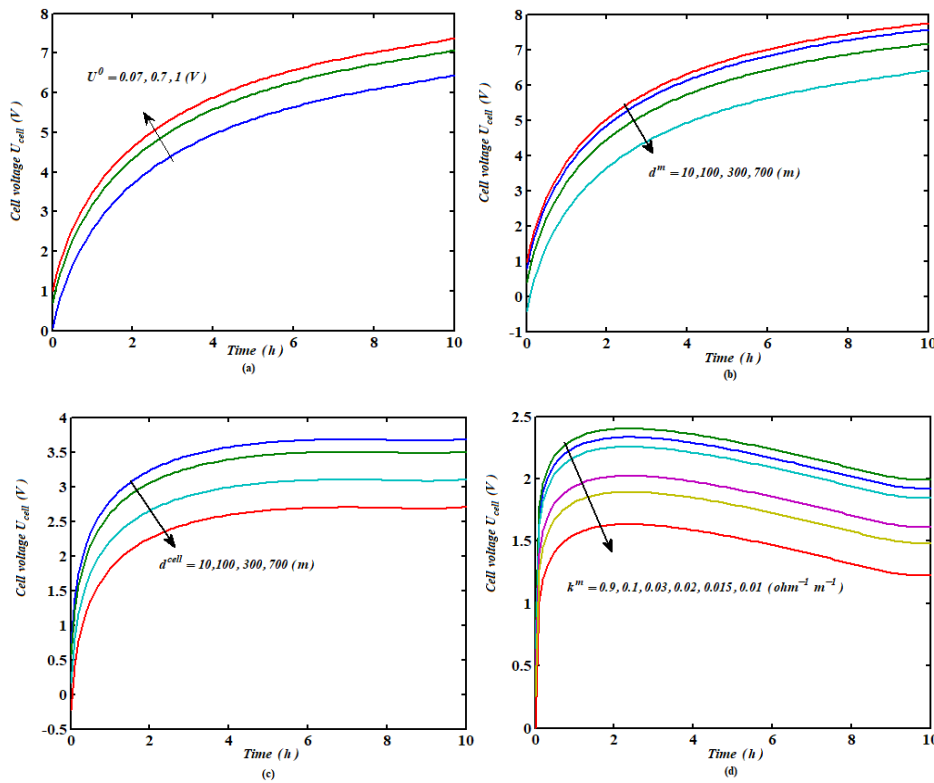


Fig. 4 plot of cell voltage U_{cell} versus time for various values of parameters U^0, d^m, d^{cell} and k^m using Eqn. (59)

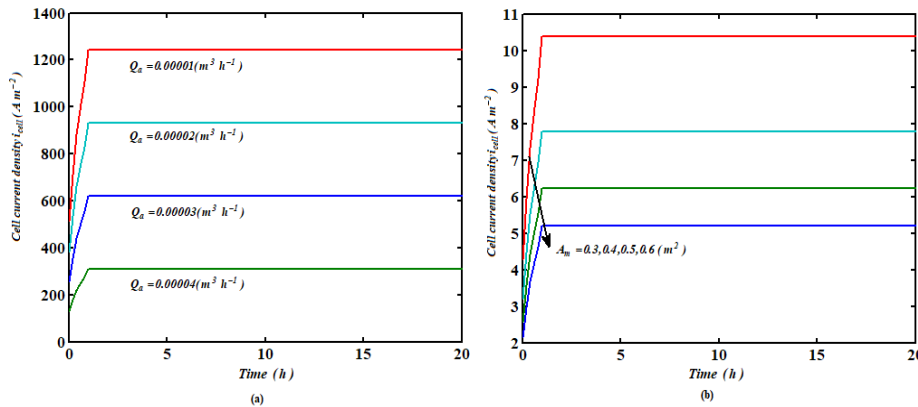


Fig. 5 plot of cell current density i_{cell} versus time for various values of parameters Q_a and A_m using Eqn. (27)

VI. CONCLUSION

The non-linear equations in two-chamber microbial fuel cells were solved analytically. The approximate analytical expression of concentration of acetate, dissolved carbon dioxide, hydrogen ion, biomass, dissolved oxygen, hydroxyl and cation M^+ in microbial fuel cell and GGA fuel cell for all experimental values of parameters are derived using the homotopy perturbation method. A satisfactory agreement with numerical simulation (Matlab program) is noted. These analytical expressions can be used to analyze the effect of various parameters such as decay constant, charge transfer coefficient of glucose and glutamic acid at anode and cathode, compartment. This theoretical result is also useful for the enzymatic microbial fuel cells.

APPENDIX

A. Approximate analytical solution of nonlinear Eqn. (6) using HPM for mass balances [5].

In this Appendix, we derive the general solution of the nonlinear reaction equation (6) using the new approach homotopy perturbation method. We begin by constructing the homotopy for Eqn. (34) as follows:

$$(1-p) \left[\frac{dC_{CO_2}}{dt} - \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{Q_a C_{CO_2}}{V_a} - 2 \frac{A_m k_j^0 C_{AC}(t=0) X(t=0)}{V_a (K_{AC} + C_{AC}(t=0))} e^{\left(\frac{\alpha F}{RT} \eta_a(t=0)\right)} \right]$$

$$p \left[\frac{dC_{CO_2}}{dt} - \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{Q_a C_{CO_2}}{V_a} - 2 \frac{A_m k_j^0 C_{AC} X}{V_a (K_{AC} + C_{AC})} e^{\left(\frac{\alpha F}{RT} \eta_a\right)} \right] = 0$$

(A1)



The approximate solution of the Eq. (A1) is

$$C_{CO_2}(t) = C_{CO_2_0}(t)p^0 + C_{CO_2_1}(t)P + C_{CO_2_2}(t)P^2 + \dots \quad (A2)$$

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

$$p^0 : \frac{dC_{CO_2_0}}{dt} - \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{Q_a C_{CO_2}}{V_a} - \frac{2A_m k_l^0 C_{AC.in} X_{in}}{V_a (K_{AC} + C_{AC.in})} e^{\left(\frac{\alpha F \eta_{a.in}}{RT}\right)} = 0 \quad (A3)$$

with initial condition for Eqn. (A3) given by

$$t = 0, C_{CO_2_0} = C_{CO_2.in} \quad (A4)$$

Solving Eqn. (A3) with initial condition (A4), using first iteration we get:

$$C_{CO_2}(t) = C_{CO_2_0}(t) = A \frac{Q_a}{V_a} + \left(C_{CO_2.in} - A \frac{Q_a}{V_a} \right) e^{-\frac{Q_a t}{V_a}} \quad \text{where}$$

$$A = \frac{Q_a C_{CO_2}^{in}}{V_a} + \frac{2 k_l^0 A_m C_{AC.in} X_{in}}{V_a (K_{AC} + C_{AC.in})} e^{\left(\frac{\alpha F \eta_{a.in}}{RT}\right)} \quad (A5)$$

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