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.

I. 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, Picoreaneu 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

<table>
<thead>
<tr>
<th>Symbols</th>
<th>meanings</th>
<th>Value</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>( C_{\text{AC}}, C_{\text{CO}<em>2}, C</em>{\text{H}_{\text{X}}} )</td>
<td>Concentration of acetate, dissolved ( \text{CO}_2 ), hydrogen ion, biomass in anode components</td>
<td>-</td>
<td>mol ( \text{m}^{-3} )</td>
</tr>
<tr>
<td>( C_{\text{O}<em>2}, C</em>{\text{OH}}, C_{\text{M}} )</td>
<td>Concentration of dissolved ( \text{O}_2 ), hydroxyl, cation M⁺ in cathode components</td>
<td>-</td>
<td>mol ( \text{m}^{-3} )</td>
</tr>
<tr>
<td>( C_{\text{G}}, C_{\text{S}} )</td>
<td>Concentration of glucose, glutamic acid in GGA MFC</td>
<td>-</td>
<td>mol ( \text{m}^{-3} )</td>
</tr>
<tr>
<td>( C_{\text{AC}, \text{in}}, C_{\text{CO}<em>2, \text{in}}, C</em>{\text{H}_{\text{X}, \text{in}}} )</td>
<td>Initial concentration of acetate, dissolved ( \text{CO}_2 ), hydrogen ion, biomass in anode components</td>
<td>1</td>
<td>mol ( \text{m}^{-3} )</td>
</tr>
<tr>
<td>( C_{\text{O}<em>2, \text{in}}, C</em>{\text{OH}, \text{in}}, C_{\text{M}, \text{in}} )</td>
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<td>( C_{\text{G}, \text{in}}, C_{\text{S}, \text{in}} )</td>
<td>Initial concentration of glucose and glutamic acid in GGA MFC</td>
<td>1</td>
<td>mol ( \text{m}^{-3} )</td>
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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

\[
(CH_2)O_2 + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^- \\
O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \\
C_6H_5O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \\
C_3H_7NO_4 + 6H_2O \rightarrow 5CO_2 + NH_4^+ + 17H^+ + 18e^- 
\]

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 Eqs. (5-8).

\[
v_A \frac{dC_{AC}}{dt} = Q_A (C_{AC}^{in} - C_{AC}) - \lambda_{an} r \tag{5}
\]

\[
v_A \frac{dC_{CO_2}}{dt} = Q_A (C_{CO_2}^{in} - C_{CO_2}) + 2A_{an} r_i \tag{6}
\]

\[
v_A \frac{dC_H}{dt} = Q_A (C_H^{in} - C_H) + 8A_{an} r_i \tag{7}
\]

\[
v_A \frac{dX}{dt} = Q_A \left( \frac{X^{in} - X}{f_s} \right) + \lambda_{an} Y_{ac} r_j - V_A k_{dec} X \tag{8}
\]

The initial conditions are

\[
C_{AC} = C_{AC_{an}} \cdot C_{CO_2} = C_{CO_{2an}}, C_H = C_{H_{an}}, X = X_{an} \quad \text{at} \quad t = 0 \tag{9}
\]

where \( V, Q \) and \( A_{an} \) are the volume of the anode and cathode compartment, \( Y_{ac} \) the bacterial yield, and \( k_{dec} \) the decay constant for acetate utilizes, \( f_s \) 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 Eqs. (10-13).

\[
v_C \frac{dC_{O_2}}{dt} = Q_c (C_{O_2}^{in} - C_{O_2}) + r_2 A_m \tag{10}
\]

\[
v_C \frac{dC_{OH}}{dt} = Q_c (C_{OH}^{in} - C_{OH}) - 4r_2 A_m \tag{11}
\]

\[
v_C \frac{dC_M}{dt} = Q_c (C_M^{in} - C_M) + N_M A_m \tag{12}
\]

The initial conditions are

\[
C_{O_2} = C_{O_{2in}}, C_{OH} = C_{OH_{in}}, C_M = C_{M_{in}} \quad \text{at} \quad t = 0 \tag{13}
\]

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:

$$n_1 = k_1^0 \frac{C_6}{K_6 + C_6} X \exp \left( \frac{\alpha F}{RT} \eta_0 \right)$$

$$n_2 = k_2^0 \frac{C_5}{K_5 + C_5} X \exp \left( \frac{\beta F}{RT} \eta_0 \right)$$

where $k_1^0$ and $k_2^0$ are rate constants of anode and cathode reaction, $K_6$ and $K_5$ are half velocity rate constant for acetate and dissolved oxygen. $\eta_0$, $\eta_0$ is the over potential at the anode and cathode, $\alpha$ and $\beta$ 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 Eqsns. (16-21).

$$V_a \frac{dc_6}{dt} = Q_a \left( c_{in}^{m} - c_6 \right) - A_m \eta_{11}$$

(16)

$$V_a \frac{dc_5}{dt} = Q_a \left( c_{in}^{m} - c_5 \right) - A_m \eta_{12}$$

(17)

$$V_a \frac{dc_{CO_2}}{dt} = Q_a \left( c_{in}^{m} - c_{CO_2} \right) + 6 A_m \eta_{11} + 5 A_m \eta_{12}$$

(18)

$$V_a \frac{dc_H}{dt} = Q_a \left( c_{in}^{m} - c_H \right) + 24 A_m \eta_{11} + 17 A_m \eta_{12}$$

(19)

$$V_a \frac{dx}{dt} = Q_a \left[ \chi_{in}^{m} - x \right] + A_m Y_{AW} \left( \eta_{11} + \eta_{12} \right) - V_a K_d A_m \eta_{12}$$

(20)

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:

$$\eta_0 = \frac{\alpha F}{RT} \eta_0$$

where $k_1^0$ and $k_2^0$ rate constants of glucose and glutamic acid, $\alpha_1$ and $\alpha_2$ 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 Eqsns. (24-25)

$$C_a \frac{d \eta_0}{dt} = -3600 i_{cell} - 8 F n_1$$

(24)

$$C_c \frac{d \eta_0}{dt} = -3600 i_{cell} - 8 F n_2$$

(25)

The initial conditions are

$$n_0 = n_{in} \eta_0$$

(26)
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\[ C_{AC}(t) = 0.002 + 0.6W(8.7e^{-107.7t}) \] where \( \alpha_1 = 0.2, \alpha_2 = 65, \alpha = 0.9 \)

(34)

\[ C_{CO_2}(t) = A_3 \frac{Q_e}{V_a} + \left( C_{CO_2,in} - A_3 \frac{Q_e}{V_a} \right) e^{-\frac{Q_e}{V_a} t} \]

where

\[ A_3 = \frac{Q_e}{V_a} C_{CO_2,in} + \frac{2 k_{O_2} A_m C_{AC,in} X_m e^{\frac{\alpha F \eta_{in}}{RT}} + X_m e^{\frac{\alpha F \eta_{in}}{RT}}}{V_a (K_{AC} + C_{AC,in})} \]

(35)

\[ C_H(t) = A_4 \frac{Q_e}{V_a} + \left( C_{H,in} - A_4 \frac{Q_e}{V_a} \right) e^{-\frac{Q_e}{V_a} t} \]

where

\[ A_4 = \frac{Q_e}{V_a} C_{H,in} + \frac{8 k_{H_2} A_m C_{AC,in} X_m e^{\frac{\alpha F \eta_{in}}{RT}} + X_m e^{\frac{\alpha F \eta_{in}}{RT}}}{V_a (K_{AC} + C_{AC,in})} \]

(36)

\[ X(t) = -A_5 \frac{X}{f_x V_a} + \left( X - A_5 \frac{X}{f_x V_a} \right) e^{-A_5 t} \]

where

\[ A_5 = -\frac{Q_e}{V_a} + \frac{A_m k_{O_2} e^{\frac{\alpha F \eta_{in}}{RT}}}{V_a (K_{2O_2} + C_{2O_2,in})} - K_{dec} \]

(37)

\[ C_{O_2}(t) = A_6 \frac{Q_e}{V_c} + \left( C_{O_2,in} - A_6 \frac{Q_e}{V_c} \right) e^{-\frac{Q_e}{V_c} t} \]

where

\[ A_6 = \frac{Q_e}{V_c} + \frac{A_m k_{O_2} e^{\frac{\alpha F \eta_{in}}{RT}}}{V_c (K_{2O_2} + C_{2O_2,in})} \]

(38)

\[ C_{OH}(t) = A_7 \frac{Q_e}{V_c} + \left( C_{OH,in} - A_7 \frac{Q_e}{V_c} \right) e^{-\frac{Q_e}{V_c} t} \]

where

\[ A_7 = \frac{Q_e}{V_c} C_{OH,in} + \frac{4k_{O_2} A_m C_{O_2,in} e^{\frac{\beta \eta_{in}}{RT}} + C_{O_2,in} e^{\frac{\beta \eta_{in}}{RT}}}{V_c (K_{2O_2} + C_{2O_2,in})} \]

(39)

\[ C_M(t) = A_8 \frac{Q_e}{V_c} + \left( C_{M,in} - A_8 \frac{Q_e}{V_c} \right) e^{-\frac{Q_e}{V_c} t} \]

where

\[ A_8 = \frac{Q_e}{V_c} C_{M,in} + \frac{3600 \text{ i.cell} A_m}{V_c F} \]

(40)

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

Equation (16) can be rewritten

\[ \frac{dC_6}{dt} = -A_9 - A_{10} \frac{C_6}{K_6 + C_6} \]

(41)

for some fixed experimental values of parameter

\( Q_e = -0.00002, V_a = -0.00005, C_{CO_2}^* = 1.2, C_{H,in} = 1, X_m = 1, C_{M,in} = 1. \)

\( A_m = -0.0005, k_{O_2}^{012} = -0.005, K = -0.3, F = 96485.4, \eta_{in} = 0.1. \)

(42)

Solving the above equation we get

\[ C_6(t) = 0.038 + 0.336W(49.4e^{-1.9t}) \]

where

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

(43)

\[ C_6(t) = 0.012 + 0.316W(70.3e^{-4.8t}) \]

where

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

(44)

\[ C_6(t) = 0.007 + 0.306W(81.5e^{-10.5t}) \]

where

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

(45)

\[ C_6(t) = 0.005 + 0.30W(85.1e^{-46.4t}) \]

where

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

(46)

Equation (17) can be rewritten

\[ \frac{dC_5}{dt} = A_{11} - A_{12} \frac{C_5}{K_5 + C_5} \]

(47)

for some fixed experimental values of parameter

\( Q_e = -0.00002, V_a = -0.00005, C_{CO_2}^* = 1.15, C_{H,in} = 1, X_m = 1, \)

\( A_m = -0.0005, k_{O_2}^{012} = -0.0007, K = -0.1, F = 96485.4, \eta_{in} = 0.1. \)

(48)

Solving the above equation we get

\[ C_5(t) = 0.007 + 0.107W(10475e^{-15.7t}) \]

where

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

(49)

\[ C_5(t) = 0.015 + 0.115W(49933e^{-3.48t}) \]

where

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

(50)

\[ C_5(t) = 0.04 + 0.14W(651.782e^{-1.07t}) \]

where

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

(51)

\[ C_{CO_2}(t) = A_{13} \frac{Q_e}{V_a} + \left( C_{CO_2,in} - A_{13} \frac{Q_e}{V_a} \right) e^{-\frac{Q_e}{V_a} t} \]

(52)

where

\( A_{13} = \frac{Q_e}{V_a} C_{CO_2,in} + \frac{A_m X_m}{V_a} \left( \frac{a_1 \eta_{in}}{K_6 + C_6} \right) \]

(53)

\[ C_H(t) = A_{14} \frac{Q_e}{V_a} + \left( C_{H,in} - A_{14} \frac{Q_e}{V_a} \right) e^{-\frac{Q_e}{V_a} t} \]

where

\( A_{14} = \frac{Q_e}{V_a} C_{H,in} + \frac{A_m X_m}{V_a} \left( \frac{a_1 \eta_{in}}{K_6 + C_6} \right) \]
\[ X(t) = \frac{Q_0}{h_2 f_x} \left( x_m^I + \frac{Q_0}{h_2 f_x} \right) \alpha \eta \text{ where} \]

\[ \alpha = \frac{Q_0}{v} \left( \frac{\alpha f \epsilon \eta}{h_x} + \frac{\alpha f \epsilon \eta}{K_x + \epsilon \eta} \right) \]

\[ I(t) = B_1 - B_2 e^{\eta \alpha \epsilon (t)} \text{ where} \]

\[ B_1 = \frac{3600 \epsilon f_{cell}}{C_a} \left( \frac{8 F k_i C_{Ac,m} X_{m}}{C_n (K_{Ac} + C_{Ac,m})} \right) \]

Solving the above equation we get

\[ \eta_{i}(t) = -\frac{1}{B_3} \log \left( \frac{B_2 e^{\eta_{i}(0)} (B_3 + B_4) + B_5}{B_4} \right) \]

Eqn. (25) can be rewritten

\[ \frac{d\eta_c}{dt} = -B_4 - B_5 e^{\eta_c \epsilon (t)} \text{ where} \]

\[ B_4 = \frac{3600 \epsilon f_{cell}}{C_a} \left( \frac{4 F k_i C_{Ac,m}}{C_n (K_{Ac} + C_{Ac,m})} \right) \]

Solving the above equation we get

\[ \eta_{c}(t) = -\frac{1}{B_5} \log \left( \frac{B_6 e^{\eta_{c}(0)} (B_6 + B_7) + B_8}{B_7} \right) \]

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

\[ U_{cell} = \frac{1}{B_5} \log \left( \frac{e^{\eta_{c}(0)} + \epsilon_{cell} B_6 e^{\eta_{c}(0)} (\epsilon_{cell} - 1) + B_8}{B_7} \right) \]

\[ -\infty \epsilon_{cell} \left( \frac{e^{\eta_{c}(0)} - \epsilon_{cell} - 1 + B_8}{B_7} \right) + U \left( \epsilon_{cell} - \frac{d\eta_c}{dx} \log \frac{\epsilon_{cell}}{\epsilon_{cell}} \right) \]

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 \( B \), rate constant of dissolved oxygen \( K_{O_2} \), and volume of cathode \( V_c \). From the figure, it is inferred that concentration dissolved oxygen \( V_c \) 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 CO₂ 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 O₂ 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 $U^0, d^n, d^{10}$ and $k^n$ 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:

$$ (1 - p) \left( \frac{d C_{102}}{dt} - \frac{Q_a C_{102}}{V_a} + \frac{Q_a C_{102}}{V_a} \right) = 2 A_m \left( \frac{C_{102} X (t = 0) V_a (K_{a} + C_{102})^{\frac{1}{2}}}{(T_{R} + \frac{X (t = 0)}{C_{102}})^{\frac{1}{2}}} \right)$$

$$ p \left( \frac{d C_{102}}{dt} - \frac{Q_a C_{102}}{V_a} + \frac{Q_a C_{102}}{V_a} \right) V_a (K_{a} + C_{102})^{\frac{1}{2}} = 0 $$

(A1)
The approximate solution of the Eq. (A1) is
\[ C_{CO_2}(t) = C_{CO_2}(t)P_0 + C_{CO_2}(t)P + C_{CO_2}(t)P^2 + \ldots \]  
(A2)

Substituting equation (A2) into equation (A1) and equate the terms with identical power of \( P^0 \) we obtain
\[ p^a \frac{dC_{CO_2}}{dt} - \frac{Q_t C_{CO_2}}{V_T} + \frac{Q_t C_{CO_2}}{V_T} \frac{2\alpha_k^2 C_{AC,m} X_{in}}{V_T K_m + C_{AC,m}} + \frac{(\alpha_k^2 + \frac{\alpha_k^2}{\beta_T})}{V_T (K_m + C_{AC,m})} = 0 \]
(A3)

with initial condition for Eqn. (A3) given by
\[ t = 0, C_{CO_2} = C_{CO_2,m} \]  
(A4)

Solving Eqn. (A3) with initial condition (A4), using first iteration we get:
\[ C_{CO_2}(t) = C_{CO_2}(t) = \frac{Q_t}{V_T} \left( C_{CO_2,m} - \frac{Q_t}{V_T} \right) \epsilon^\frac{Q_t}{V_T} \text{ where} \]
\[ A = \frac{Q_t C_{CO_2,m}^2}{V_T} \frac{2\alpha_k^2 C_{AC,m} X_{in}}{V_T (K_m + C_{AC,m})} + \frac{(\alpha_k^2 + \frac{\alpha_k^2}{\beta_T})}{V_T (K_m + C_{AC,m})} \]
(A5)

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