CHEMICAL ENGINEERING TRANSACTIONS

VOL. 79, 2020

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Enrico Bardone, Antonio Marzocchella, Marco Bravi

ISBN 978-88-95608-77-8; **ISSN** 2283-9216

DOI: 10.3303/CET2079008

A Reduced Model for Microbial Fuel Cell

Dina Aboelela[a], Moustafa Aly Soliman[a*], Ibrahim Ashour[b]

[a] The British University in Egypt, Faculty of Engineering, Department of Chemical Engineering, El Shorouk City, Cairo 11837, Egypt
[b] El Minia University, Faculty of Engineering, Department of Chemical Engineering, ElMinia 61519, Egypt
moustafa.aly@bue.edu.eg

Microbial fuel cells (MFCs) are a group of microbial electrochemical cells (bioreactors) that are used to generate energy from organic waste found in wastewater. MFCs represent a promising method of waste disposal and production of electricity. Scaling up the use of MFCs requires extensive analysis and detailed grasp of the required processes. The current work aimed to study a model of an MFC, and find the optimum parameters needed for maximum energy production. The process was simulated and validated on continuous-flow MFCs with a Columbic efficiency of 162% and 35% COD removal. Sensitivity analysis of the model was performed. The studied model was found to be valid for both batch-cycle and continuous-flow MFCs. Parameters with less influence on MFCs were eliminated in order to obtain a simplified model of MFC performance. The new simplified model was then validated. Finally, optimization of operating external resistance was conducted to maximize energy generation.

1. Introduction

In MFC systems, organic wastes found in wastewater are converted into electricity (Debabov, 2008). In doing so, we benefit from the production of electricity whilst simultaneously conducting environmentally-friendly wastewater treatment. Anodophilic microorganisms which are attached to an anode decompose organic matter in wastewater into carbon dioxide, protons and electrons which are then transferred to a cathode. An electric current is generated due to the potential difference between the two electrodes. The inherent variability of possible types of microbial populations within wastewater, which may include populations of anodophilic, methanogenic and/or anaerobic microorganisms, invariably influence the performance of an MFC system. The existence of these multiple variables complicate attempts to understand and optimize the performance of such systems (Arcand et al., 1994, Moletta, et al., 1986, Quarmby and Forster, 1995).
One of the best tools in process optimization and design enhancement is process modelling, which facilitates the understanding of an operation and defines the bottlenecks. Few MFC models have been reported on in the literature. The model used in this study is the Pinto model (Pinto et al., 2010; Pinto et al., 2011) which produces the most accurate results when compared with other experimental data reported in the literature.

2. Materials and methods (MFC model)

MFC is a process which utilizes the microorganisms to produce electricity by oxidation of organic waste found in wastewater. Figure1 shows a simplified schematic diagram of an MFC. The anodic compartment of the model shows microbial populations participating in bio-electrochemical reactions.

Paper Received: 21 September 2019; Revised: 6 November 2019; Accepted: 4 March 2020
Please cite this article as: Aboelela D., Soliman M.A., Ashour I., 2020, A Reduced Model for Microbial Fuel Cell, Chemical Engineering Transactions, 79, 43-48 DOI:10.3303/CET2079008

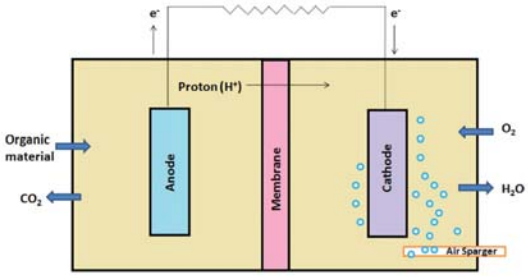

Figure 1: MFC schematic diagram

2.1 Microbial populations

The following equations describe the conceptual model reactions involving anodophilic microorganisms and acetoclastic methanogenic microorganisms:

1. **Anodophilic microorganisms:**

$C_2H_4O_2 + 2H_2O + 4\ M_{ox} \longrightarrow 4\ M_{red} + 2CO_2$

$4\ M_{red} \longrightarrow 4\ M_{ox} + 8e^- + 8H^+$

where M_{red} and M_{ox} represent the reduced and oxidized forms of an anodophilic intracellular mediator respectively.

2. **Acetoclastic methanogenic microorganisms:**

$C_2H_4O_2 \longrightarrow CH_4 + CO_2$

The dynamic equations below describe the model mass balance anodic compartment material balances as well as the intracellular material balances.

2.2 Anodic compartment Material balances

Material balances equations for MFC with continuous flow are:

$$\frac{dA}{dt} = -q_a x_a - q_m x_m + D(A_0 - A) \quad (1)$$

$$\frac{dx_a}{dt} = \mu_a x_a - K_{da}\, x_a - \alpha_1 x_a \quad (2)$$

$$\frac{dx_m}{dt} = \mu_m\, x_m - K_{dm}\, x_m - \alpha_1 x_m \quad (3)$$

where time is t in [d]; rates of acetate consumption for both of anodophilic and acetoclastic microorganisms are q_a, and q_m respectively in [mg-A mg-x^{-1} d^{-1}]; the concentration of anodophilic, acetoclastic, and hydrogenotrophic microorganisms are x_a and x_m, respectively in [mg-x L^{-1}]; the dilution rate is D in [d]= F_{in}/V, the feed flow rate is F_{in} in [L/d]; the anodic compartment volume is V in [L]; the acetate concentration in the feed stream is A_o and in the compartment of the anode is A in [mg-A L^{-1}]; the decay rate is K_d in [d^{-1}]; the growth rates of anodophilic and acetoclastic microorganisms are μ_a and μ_m respectively in [d^{-1}].

The biofilm retention constant can be determined from the below equation assuming stationary phase as thickness of the biofilm reaches the steady state.

$$\alpha_1 = \frac{(\mu_a - K_{da})X_a + (\mu_m - K_{dm})X_m}{(X_a + X_m)}\ if\ x_a + x_m \geq x_{max1} \quad (4) \qquad \alpha_1 = 0\ otherwise \quad (5)$$

where (x_{max1}) in [mg-x L^{-1}] is the maximum biomass concentration in the first layer of the biofilm.

Material Balances of Intracellular Anodophilic Microorganisms

For each anodophilic microorganism balance equations are as follows:

$$M_{Total} = M_{red} + M_{ox} \quad (6) \qquad \frac{dM_{ox}}{dt} = -Y_M\, q_a + \frac{\gamma\ I_{MFC}}{V\, X_a\, m\, F} \quad (7)$$

where M_{Total} in [mg-Mmg-x^{-1}] is the total fraction of mediator per microorganism; M_{red} in [mg-M mg-x^{-1}] is the fraction of the reduced mediator per anodophilic microorganism; M_{ox} in [mg-M mg-x^{-1}] is the fraction of the oxidized mediator per anodophilic microorganism; Y_M in [mg-M mg-A^{-1}] is the mediator's yield; γ in [mg-M mol med^{-1}] is the mediator's molar mass; I_{MFC} in [A] is the current produced by the MFC, and *m* in [mol-e- mol med^{-1}] is the number of electrons transferred per mol of mediator.

2.3 Kinetic Equations

Kinetics equations are detailed below:

$$\mu_a = \mu_{maxa}\frac{A}{Ksa+A}\frac{M_{OX}}{K_M+M_{OX}} \quad (8) \qquad \mu_m = \mu_{maxm}\frac{A}{Ksm+A} \quad (9)$$

$$q_a = q_{maxa}\frac{A}{Ksa+A}\frac{M_{OX}}{K_M+M_{OX}} \quad (10) \qquad q_m = q_{maxm}\frac{A}{Ksm+A} \quad (11)$$

where μ_{max} in [d^{-1}] is the maximum rate of growth; q_{max} in [mg-A mg-x^{-1} d^{-1}] is the maximum consumption rate of acetate, and K in [mg-A L^{-1}mg-M L^{-1}] is the half-saturation constant.

2.4 Electrochemical equations

MFC current was determined by the following equation

$$\mathrm{I_{MFC}} = \frac{E_{OCp}-\frac{RT}{F}\ln(\frac{M_{Total}}{M_{red}})}{R_{int}+R_{ext}} \quad (12)$$

Where E_{OCP} is voltage of open circuit; R_{int} is the internal resistance [Ω] and R_{ext} is the external resistance [Ω].

3. Results and discussion

3.1 Case study

The aforementioned model was used in Pinto's case study (Pinto et al., 2010; Pinto et al., 2011) with adjustments done to some parameters in order to verify the model. The initial parameters in the case study were 550; 100 and 10 mg/l of substrate, anodophilic and acetoclastic organisms respectively. The process was estimated to operate for 10 days. All parameters and equations were identified in MATLAB, then the equations were solved. Figure 2 represents of recorded concentrations.

Figure 2a shows the change in concentration of substrate. It was noted that a gradual decrease in concentration of the substrate (S) occurred during the initial stage of the reaction. By day 6, the concentration had declined to 370 mg/l. The concentration of the substrate then gradually increased until, by the end of the experiment, it had reached 380 mg/l; a reflection of a decreasing rate of decomposition.

Figure 2b shows the change in concentration of anodophilic (x_a) microorganisms. Apparently, sharp increase in the concentration of anodophilic microorganisms (x_a) had occurred by day 6, reaching 500 mg/l. The concentration then plateaued for the remainder of the process. Figure 2c shows the change in the concentration of acetoclastic microorganisms (x_m). The figure was a sharp increase in the concentration of acetoclastic microorganisms (x_m), reaching 16.7 mg/l at day 6.2. The concentration then decreased rapidly; reaching 12.5 mg x/l by the end of the process (day 10). Figure 2d shows the Voltage of the MFC model (E_{cell}). As illustrated, there was an initial sharp rise in the value of the E_{cell}; reaching 0.37 v after 6 days. Its value then remained constant until the end of the process.

3.2 Sensitivity analysis on MFC parameters

A preliminary sensitivity analysis on the operating and design parameters of the Pinto model was conducted. The sensitivity analysis aimed to define which parameters had the most significant effects on the density of the current generated during the operation of the system. One by one, each parameter was altered separately, while leaving other parameters unchanged. Analysis was conducted using the *relative sensitivity analysis method* (Zeng et al., 2010) in order to determine the ratio between the change in calculated current and the changes in each of the individual parameters. The following equation was used for each parameter, x_j

$$T_j = \frac{P(t,x_j+\delta x_j)-P(t,x_j)}{\delta x_j} * \frac{x_j}{P(t,x_j)}, j = 1, \dots, 6 \quad (13)$$

where T_j is the time dependent sensitivity for the parameter j; x_j is the value of parameter j; x_j is the change in x_j ; P is the current produced. The step of the change in this study was $x_j = 0.01x_j$.

3.2.1 Model parameters

Maximum growth rate and reaction rates

The results of sensitivity analysis of the effects of the maximum growth rates and the reaction rates on the current produced are shown in Fig. 3a. It is evident that maximum growth rate ($\mu_{m,a}$) of anodophilic microorganisms and their maximum reaction rate ($q_{max,a}$) were effectual parameters. On the other hand, analysis suggested that the maximum growth rate ($\mu_{m,m}$) of acetoclastic methanogenic microorganisms and their maximum reaction rate ($q_{max,m}$) had no significant effect on the current produced.

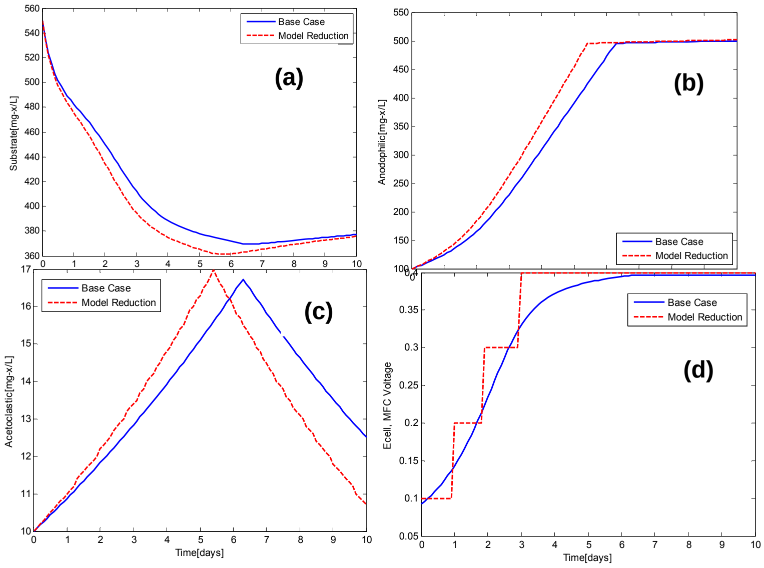

Figure 2: (a) substrate concentration, (b) Anodophilic concentration, (c) Acetolastic concentration, (d) MFC Voltage

Half rate and microbial decay rates

The results of sensitivity analysis of the effect of the half rates and microbial decay on the current produced are shown in Fig. 3b. It is evident that the mediator half-rate constant (K_M) and resistance curve steepness (K_R) were effectual parameters, whereas the anodophilic (K_{Sa}), acetoclastic methanogenic microorganism half-rate constant (K_{Sm}), the anodophilic (K_{da}) and acetoclastic methanogenic microorganism microbial decay rates (k_{dm}) did not represent parameters of significant effect on the current produced.

3.2.2 Operating parameters

The results of sensitivity analysis of the effect of operating parametrs on the current produced are illustrated by Fig. 3c. It is apparent that the open circuit voltage (E_{OCP}) and MFC temperature (T) were effectual parameters, whereas the total mediator weight percentage (M_{tot}), incoming flow (Fin) and pressure (P) did not represent parameters of significant effect on the current produced.

3.3.3 Design parameters

The results of sensitivity analysis of the effect of anodic compartment volume and anode surface area on current are shown in Fig. 3d. It is evident that anodic compartment volume (V) was an effectual parameter. This may have been due to the high levels of organic compounds in the system. Conversely, the anode surface area (A) did not represent a parameter of significant effect on the current produced.

3.4 MFC validation

The effectual parameters of MFC defined by the sensitivity analysis study were used to correlate the data prediction model of (Pinto et al., 2010) with experimental results of one batch acetate fed MFC by (Khater et al., 2017). Some of the parameters in (Pinto et al., 2010) model were adjusted, while the remaining parameters were kept the same. The results obtained through simulation were comparable to the actual experimental results. Figure 4a illustrates the acetate's decomposition as COD value across time. The concentration of substrate declined with time; the initial COD being 1210 mg and falling to 200 mg.

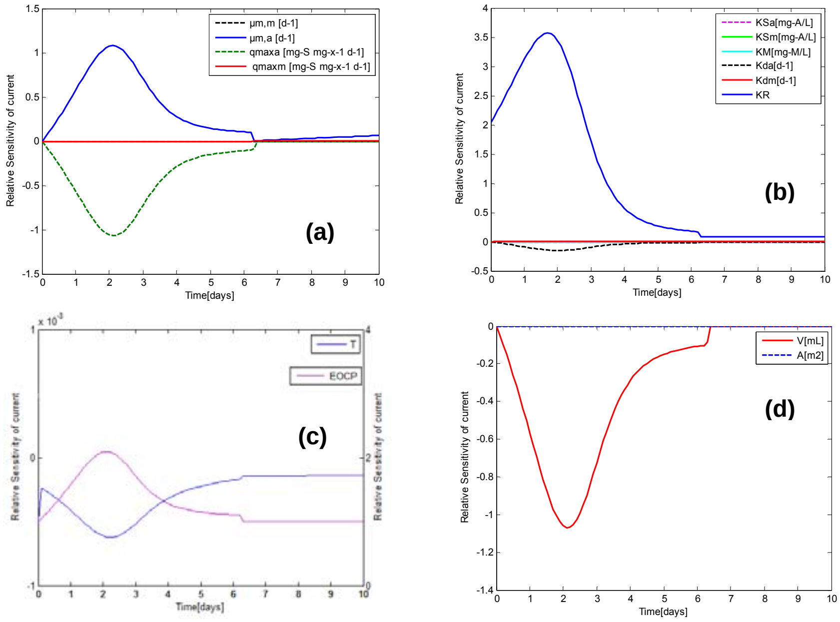

Figure 3: Current relative sensitivity with respect to: (a) maximum growth rates and reaction rates (b) half rate and decay rates, (c) operating parameters, (d) design parameters.

Figure 4b illustrates voltage production versus time. As shown, the produced voltage rose rapidly during the first period, then nearly plateaued for the next 3 days. The maximum produced voltage was 0.1856 mV. Following this maximum, the voltage decreased to around 0.1855 mV. This decrease could have been due to the drop in the acetate concentration.

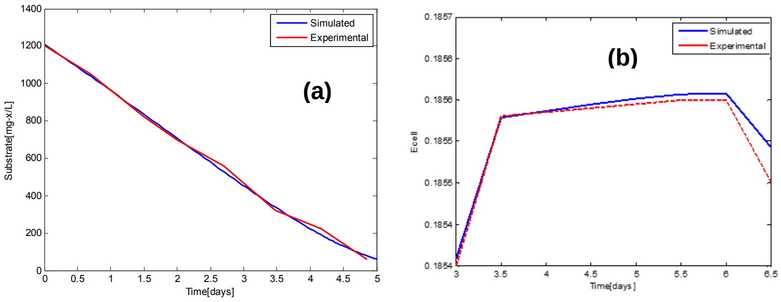

Figure 4: (a) Behaviour of COD for simulated results and experimental data, (b) voltage output versus time (the blue line represent simulated results and red line represent experimental data)

3.5 Model reduction

Results of the sensitivity analysis were used to simplify the MFC equation and obtain simplified analytical equations. These simplified equations were applied and comparable results were obtained.

Assuming that K_{da}, K_{dm}, K_{dh} and K_{sm} equal zero, the following simplified equations (14 - 24) were obtained:

$$\mu_m = \mu_{maxm} \quad (14) \qquad q_m = q_{maxm} \quad (15)$$

If $x_a+x_m<x_{max1}$

$$\frac{dA}{dt} = -q_{maxa}\frac{M_{OX}}{K_M + M_{OX}}\frac{A}{Ksa + A}x_a - q_{maxm}x_m + D(A_0 - A) \quad (16)$$

$$\frac{dX_a}{dt} = \mu_{maxa}\frac{M_{OX}}{K_M + M_{OX}}\frac{A}{Ksa + A}x_a \quad (17)$$

$$\frac{dX_m}{dt} = \mu_{maxm}\, x_m \quad (18) \qquad x_m = x_{m,0}\exp(\mu_{maxm}t) \quad (19)$$

$$0 = -Y_M q_{maxa} \frac{M_{OX}}{K_M + M_{OX}} + \frac{\gamma\ I_{MFC}}{V\ X_a\ m\ F} \quad (20) \qquad I_{MFC} = \frac{E_{OCp} - \frac{RT}{F} \ln(\frac{M_{Total}}{M_{red}})}{R_{int} + R_{Ext}} \quad (21)$$

If $x_a + x_m > x_{max1}$

$$\frac{dx_m}{dt} = -\frac{\mu_{maxa} - \mu_{maxm}}{X_{max,1}} x_a x_m \quad (22)$$

$$\frac{dx_a}{dt} = \frac{\mu_{maxa} - \mu_{maxm}}{x_{max,1}} x_a x_m \quad (23) \qquad \frac{x_a}{x_{max1}} = \frac{x_{a0}\ e^{(\mu_{maxa} - \mu_{maxm})t}}{(x_{max1} - x_{a0}) + x_{a0}\ e^{(\mu_{maxa} - \mu_{maxm})t}} \quad (24)$$

The results of the application of these equations to our model are shown in Figure 2. Excellent fitting of the reduced model with the full model is evident.

3.6 Optimizing energy productivity of MFC

The next step was to seek the maximization of energy productivity by computing the the optimum external resistance. Optimization was performed in order to tabulate the maximum sum of power outputs over the range of the experiment. MATLAB function fminsearch, based on the Nelder Mead simplex method, was used to obtain the maximum MFC productivity by manipulating external resistance. Results of optimization indicated that the maximum MFC power productivity was 0.0023 W, obtained at an external resistance of 67.0415 Ω and a produced potential of 0.4053V.

4. Conclusions

As indicated by this study, the MFC model represents an extremely complicated nonlinear and multivariable system. In this study MFC model was studied and validated. Sensitivity analysis indicated that the parameters with the highest effect on the cell and the current produced were $\mu_{m,a}$, $q_{m,a}$, K_M, K_R, T, P, V, A, E_{CEF}, R_{min} and R_{max}. These results were utilized to reduce the model and obtain simple equations. These simple equations were used to validate experimental results. Following this, the computations necessary for the optimization of the operating parameters of MFC were conducted. These computations indicated that that the maximum MFC power productivity was 0.0023 W, obtained at an external resistance of 67.0415 Ω and a produced potential of 0.4053V. Future work aimed at studying the combination of microbial electrolysis cell (MEC) and microbial fuel cell (MFC) is already under plans.

References

Arcand Y., Chavarie C., Guiot S., 1994, Dynamic modelling of the population distribution in the anaerobic granular biofilm. Water Sci. Technol, 30, 63–73.

Debabov V., 2008. Electricity from microorganisms, Microbiology, 77, 123–131.

Khater D.Z., El-Khatib K.M., Hassan H.M., 2017, Microbial diversity structure in acetate single chamber microbial fuel cell for electricity generation, J. Genet. Eng. Biotechnol, 15, 127–137. https://doi.org/10.1016/j.jgeb.2017.01.008

Moletta R., Verrier D., Albagnac G., 1986, Dynamic modeling of anaerobic digestion. Water Res. 20, 427–434.

Pinto R.P., Perrier M., Tartakovsky B., Srinivasan B., 2010, Performance analyses of microbial fuel cells operated in series, in: DYCOPS –Proceedings of 9th Inter- National Symposium on Dynamics and Control of Process Systems, Leuven, Belgium.

Pinto R.P., Srinivasan B., Escapa A., Tartakovsky B., 2011, Multi-population model of a microbial electrolysis cell. Env. Sci Technol, 45, 5039–5046.

Pinto R.P., Srinivasan B., Manuel M.F., Tartakovsky B., 2010, A two-population bio-electrochemical model of a microbial fuel cell. Bioresour. Technol, 101, 5256–5265. https://doi.org/10.1016/j.biortech.2010.01.122

Quarmby J., Forster C.F., 1995, An examination of the structure of UASB granules. Water Res, 29, 2449–2454.

Zeng Y., Choo Y.F., Kim B.H., Wu P., 2010, Modelling and simulation of two-chamber microbial fuel cell. J. Power Sources, 195, 79–89.