Optimization and Modeling the Performance of a Mediator-less Microbial Fuel Cell using Butler-Volmer-Monod Model

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ABSTRACT
In this study, a one-dimensional model represented by Butler-Volmer-Monod (BVM) model was proposed to compute the anode overpotential and current density in a mediator-less MFC system. The system was fueled with various organic loadings of real field petroleum refinery oily sludge to optimize the favorable organic loading for biomass to operate the suggested system. The increase in each organic loading showed higher resistance to electrons transport to the anode represented by ohmic loss. On the contrary, both activation and mass transfer losses exhibited a noticeable decrement upon the increased organic loadings. However, current density was improved throughout all increased loads achieving a maximum current density of 5.2 A/m³. The BVM model perfectly expressed the bioelectrochemical reactions in the anodic-chamber. The experimental measurements for all the studied organic loadings agreed with the model predicted values by an estimated determination factor (R²) of 0.96, proving the validity of the proposed mathematical model to express the anodic bioelectrochemical reactions in the MFC. Also, the sustainable power generated from each cycle was evaluated, and it was found that higher sustainable energy can be harvested from higher organic loading 1000 g/L, which achieved maximum sustainable energy of 0.83 W/m³.

Keywords: Petroleum refinery oily sludge; Butler-Volmer-Monod; Organic loadings; Microbial fuel cell; Overpotential.

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1. INTRODUCTION
A microbial fuel cell (MFC) is a hybrid device of biological and electrochemical systems. It opens new opportunities for generating sustainable energy side by side with the bioelectrochemical treatment of domestic and industrial wastes. MFC converts the stored chemical energy in the organic matter into electrical power using a biocatalyst. However, this new technology implies challenges to the researchers to solve multiple scientific and engineering issues. On the other hand, the MFC exploits a common characteristic of microbiological systems, which is the ability to utilize a wide range of organic and inorganic substrates as the electron donors (Marcus, et al., 2007; Ismail and Habeeb, 2015).

To achieve a comprehensive understanding of the concepts and mechanisms governing the MFC operation and performance, extensive researches during the past years has led to significant progress in the awareness of MFC functional microbiology, electrode materials, membrane types, design, and operation. Based on these advancements, model-based designs and optimization approaches are considered to be essential tools for MFC development towards commercialization (Zhao, et al., 2014 and Recio-Garrido, et al., 2015). To express the behavior of the biocatalyst layer in a mathematical model of a microbial fuel cell, the minimal requirement for the electrode kinetic equation is to yield the volumetric current density due to the faradaic reaction in the catalyst layer. It is based on the volume of the substrate and as a function of the electrode/electrolyte potential difference, the concentration of the reactants (S), and the concentration of the products (P) if the process is reversible (Dickinson and Hinds, 2019). To describe the intracellular overpotential, the Monod model and Nernst Monod model are used. The Nemst-Monod model is a modified version of the Monod model by considering the anode as the final electron acceptor (Hamelers, et al., 2011). However, to describe the extracellular overpotential, a Bulter-Volmer-Model (BVM) is typically applied (Torres, et al., 2010). Hence, the BVM model, which describes the anode kinetics, enzymatic kinetics, plus the electrochemical kinetics, is the perfect candidate to understand the anode polarization. This model was established depending on simple mathematical expressions of the basic biochemical reactions and electrochemical reactions (Zhao, et al., 2016).

This study is intended to achieve a systematic understanding of the biological and electrochemical factors that control the overall performance of a dual-chambered mediator-less MFC fueled with real petroleum refinery oily sludge. This was accomplished via developing a kinetic mathematical model based on the BVM equation.

2. METHOD
2.1 Substrate
Real field petroleum refinery oily sludge (PROS) samples were collected from Al-Dura Oil Refinery, Baghdad, Iraq. The sludge samples were packed tightly in polythene containers
preserved and stored at 4°C, ready to be used. The sludge used in this study had an average initial COD concentration of 30000 mg/L. Different organic loadings (OL) were prepared to be fed to the MFC in a subsequently fill and draw mode operation. These organic loadings were prepared by mixing PROS with domestic wastewater (DWW) in four different proportions, which were 6 g, 60 g, 600 g, and 1000 g of PROS, in a liter of DWW.

2.2 MFC set-up
A dual-chamber cylindrical shape MFC designed with dual anodic electrodes constructed of perspex material, Fig. 1. A cation exchange membrane was used to separate the two chambers (Type: CMI-7000, Membrane International INC., NJ, USA). Two parallel uncoated graphite plates of 0.035 m² total surface area were used as anodes in the MFC and another identical graphite plate as the cathode. These electrodes were linked to an external electrical circuit of 100Ω by a wire which transfers the electrons to a data logger (Lascar EL-USB-3 Data Logger) to record the electrical data online (Radeef and Ismail, 2018). The system consisted of a hold and neutralization tank before MFC to ensure pH adjustment to 7 ± 0.2 of the substrate solution (using concentrated orthophosphoric acid (88%) or NaOH (1N)). In addition to a final receiving tank for the collection of the treated effluent. A peristaltic pump (variable speed pump 3386, USA) was used to feed the MFC directly from the neutralization tank at a flow rate of 8 ml/min to fill the chamber within two hours. The catholyte was continuously sparged with air using an air compressor (Yamamado-8000, China) at a flow rate of 0.1667 cm³/s to maintain the catholyte saturated with oxygen. The cathodic chamber was filled with a phosphate-buffer-solution (PBS) as a catholyte solution prepared by dissolving 20.7492 g Na₂HPO₄, 3.1167 g NaH₂PO₄ and 32.930 g of K₃Fe(CN)₆ in one liter of deionized water based on the procedure demonstrated by Wei et al. (2012). The pH of the catholyte solution was maintained at 7.2 ±0.2.

Figure 1. Schematic diagram of the dual-chambered MFC.
2.3 Model formulation
This study used a kinetic model represented by the Butler-Volmer-Monod (BVM) to describe the electrochemical reactions which are likely to control the anodic performance in the MFC system. Anode polarization curves were obtained for the four different PROS organic loads operated in fill and draw mode. In order to be able to apply the BVM model, further specific experiments were conducted using reference electrode (Ag/AgCl), as it is commonly used in electrochemical measurements for environmental purposes due to its simplicity, stability, and nontoxicity (Logan, et al., 2006). In a half cell measurement, the reference electrode should be considered as the reduced electrode (i.e., anode).

The main objectives of the modeling study are:
(1) Applying the Butler–Volmer–Monod model, which focuses on the bio-electrochemical reactions at the anodic chamber of MFC with the description of microbial populations.
(2) Understanding the effect of changing external resistance on anode, cathode, and cell potential, which accordingly, reflects on the MFC performance.
(3) Determining the extent of compliance between the model predictions and experimental work under similar operating conditions.

MATLAB software version (R2017b) was used to solve all the relative equations from including linear and nonlinear algebraic equations as well as differential equations.

2.3.1 Materials balances
The BVM model development relies on the hypothesis that the rate of substrate conversion into products, which are; CO₂, H⁺ and e⁻ by the anode respiring bacteria, is determined by enzyme kinetics, which can be modeled through breaking them down into three reversible reactions.

1) The enzymatic reaction of the substrate (S) and oxidized redox component (Xox) that forms the redox component complex (Xc).

\[ S + X_{ox} \xrightarrow{k_1, k_2} X_c \]  

2) The second reaction is when the redox component complex (Xc) reacts to form the products (P) and the reduced redox component (Xred).

\[ X_c \xrightarrow{k_3, k_4} P + X_{red} \]  

3) The oxidation of the reduced redox component (Xred) back into oxidized redox component (Xox) accompanied by electron libration. This process is carried out at the bio-anode surface.

\[ X_{red} \xrightarrow{k_5, k_6} X_{ox} + e^- \]  

where; K₁, K₃, and K₅ are forward constants (mole/m².s), respectively, while K₂, K₄, and K₆ are backward rate constants (mole/m².s), respectively. Fig. 2 demonstrates the bioelectrochemical reactions on the bio-anode.
Assuming quasi-steady-state conditions, where the concentration of the formed intermediates biocatalysts is constant upon the time. The differential mass balances for $X_{ox}$ and $X_{red}$ are as follows:

$$\frac{dX_{ox}}{dt} = -k_1 \cdot S \cdot X_{ox} + k_2 \cdot X_c + k_5 \cdot X_{red} - k_6 \cdot X_{ox}$$

(4)

$$\frac{dX_{red}}{dt} = k_3 \cdot X_c - k_4 \cdot P \cdot X_{red} - k_5 \cdot X_{red} + k_6 \cdot X_{ox}$$

(5)

Assuming that $X_{red}$ is at a constant value and quantity; hence, $X_c$ could be represented by the following equation:

$$X_c = X_T - X_{ox} - X_{red}$$

(6)

where:

$X_T$: total amount of redox, (mole/L)

The final formula of BVM (eq. 7) is obtained by solving the differential equations using the standard parameters suggested by Cleland (1963):

$$I = I_{max} \cdot \frac{1 - e^{-f \cdot \eta}}{K_1 \cdot e^{-(1-\alpha)f \cdot \eta} + K_2 \cdot e^{-f \cdot \eta} + (\frac{K_m}{S} + 1)}$$

(7)

Where, ($\eta$) is the anode overpotential vs. reference electrode. ($K_1$) and ($K_2$) is the lumped parameters representing the ratio between biochemical and electrochemical reaction rate constants, and between the forward and backward biochemical rate constants, respectively. ($I_{max}$) is the limiting current density, $\alpha$ is the transfer coefficient assumed to be (0.9) and ($K_m$) is the Substrate affinity constant.
2.3.2 Estimation of the standard parameters
As can be noticed from BMV mathematical expression, the solution of the equation is highly dependant on three basic parameters: $K_1$, $K_2$, and $K_m$. The substrate affinity constant ($k_m$), also known as Michaelis–Menten constant, is an empirical constant that illustrates the substrate influence on the biochemical reaction. This parameter is well known as the concentration at which half of the turnover is attained. The substrate affinity constant was determined experimentally by fueling the MFC with various concentrations of acetate (substrate) as described by (Hamelers et al., 2011) and by determining the concentration of substrate at which the current was first generated. On the other hand, $K_1$ and $K_2$; the two lumped parameters were estimated numerically by fitting the experimental data obtained from the polarization curves of the anode to the predicted model data until achieving an optimal fitting with a minimal residual sum of squares (RSS). RSS is defined as the difference between the experimental and the predicted data for each measurement. This model fitting was accomplished using the nonlinear least square method. The parameters of Eqs. (1) to (7) as well as the constants associated with the performance of MFC were described and adopted to obtain the predicted results for all models proposed for the investigation of MFC system are given in Table 1.

Table 1. Assumed, measured, and estimated parameters in addition to the physical constants used in the Butler-Volmer-Monod model.

| Symbol | Description | Value | Unit | Note |
|--------|-------------|-------|------|------|
| $F$    | Faraday’s constant | 96485 | Coulomb/mole | Constant |
| $R$    | Gas constant  | 8.314 | J/mole. K | Constant |
| $n$    | Number of exchange protons/mole of reactant | 8 | Dimensionless | Constant |
| $T$    | Temperature  | 318.15 | K | Constant |
| $I_{max}$ | The maximum current | | | |
|        | Organic load | $I_{max}$ | mA | Measured |
|        | 6 g/L | 1.73 | | |
|        | 60 g/L | 2.53 | | |
|        | 600 g/L | 4.24 | | |
|        | 1000 g/L | 5.20 | | |
| $I_\bar{\eta}$ | The overpotential | (0-3850) | mV | Measured |
| $K_1$  | A lumped parameter describing the ratio between biochemical and electrochemical rate constants | 40 | Dimensionless | Assumed |
| $K_2$  | A lumped parameter describing the forward over backward biochemical rate constants | 26.5 | Dimensionless | Assumed |
| $K_m$  | Substrate affinity constant | 0.001 | mole/L | Calculated |
| $\alpha$ | Transfer coefficient | 0.9 | Dimensionless | Assumed |
| S      | Substrate concentration | Organic load | S     | mole/L | Measured |
|--------|-------------------------|--------------|-------|--------|----------|
|        |                         | 6 g/L        | 0.019 |        |          |
|        |                         | 60 g/L       | 0.117 |        |          |
|        |                         | 600 g/L      | 0.232 |        |          |
|        |                         | 1000 g/L     | 0.285 |        |          |

| C_{S_{in}} | Average substrate concentrations | Organic load | C_{S_{in}} | mg/L | Measured |
|------------|----------------------------------|--------------|------------|------|----------|
|            |                                  | 6 g/L        | 1138       |      |          |
|            |                                  | 60 g/L       | 7000       |      |          |
|            |                                  | 600 g/L      | 13890      |      |          |
|            |                                  | 1000 g/L     | 17100      |      |          |

\[ f = \frac{F}{RT} \]

\[ 0.03855 \text{ V}^{-1} \]

2.5 Sustainable power

In general, the MFC system is considered to be at steady-state conditions when the power production is sustainable, and this is possible; if and only if the power generated is equal to the power consumed for an extended period of operation time. When the sustainable current reaches a maximum value, it is important to define these conditions in order to calculate the sustainable power that can be harvested from a certain MFC system. A relative decrease in anode potential (RDAP) as a function of the applied external resistance is usually used to compute the maximum sustainable power. Hence, the RDAP curve was plotted for the four different organic loadings by measuring anode potential as a function of the external circuit. The following equation can simply calculate RDAO:

\[
\text{RDAP} \% = \left( \frac{\text{EOCV} - \text{EA}}{\text{EOCV}} \right) \times 100
\]

Where \( \text{EOCV} \) is the open circuit potential of the anode (V), and \( \text{EA} \) is the measured anode potential at a specific external resistance (V).

3. RESULTS AND DISCUSSION

The performance of this MFC system was evaluated upon different concentrations of oily sludge represented by OL1, OL2, OL3 and OL4 for 6 g/L, 60 g/L, 600 g/L and 1000 g/L of PROS solution, respectively. This evaluation was investigated as the anode electrical performance governing the overall cell performance.

3.1 Anode polarization curves

Four different anode polarization curves were plotted for each organic load of PROS. It is obvious for the four plots that the current declined along with the drop of overpotential as the external resistance was increased. Furthermore, it can be noticed that with each increased organic load, the maximum current was relatively increased despite the high overpotential (i.e., losses). Maximum produced current densities achieved by MFC anode operated infill and draw mode were 1.73, 2.53, 4.24, and 5.2 A/m² for OL1, OL2, OL3, and OL4, respectively. Experimental and predicted results by the BVM model are shown in Fig. 3. The predicted results were significantly and reasonably in good compliance with the experimental data. It can be noticed that for the polarization curves of PROS at organic loadings of OL1 and OL2, the current dropped in almost a linear trend with
overpotential decrease upon the increased applied resistance. This linear relationship indicates a relatively low internal resistance. On the contrary, with the other plots; where the nonlinear relationship started to appear between current and overpotential upon increasing organic loads indicating higher internal resistance in comparison with organic loadings of OL1 and OL2. The obtained results were in a reasonable agreement with the results of (Velvizhi and Mohan, 2012) when they studied the effect of various pharmaceutical wastewater organic loads on the electrical behavior of the anode.

However, the predicted results successfully agreed with the experimental data sets by using Ag/AgCl reference electrode with determination coefficient ($R^2$) values of 0.967, 0.962, 0.966, and 0.953 for PROS organic loading of OL1, OL2, OL3, and OL4, respectively.

![Experimental and predicted polarization curves for the anode of MFC](image)

3.2 Effect of external resistance on MFC performance

During the operation of MFC with PROS at OL1 (6 g/L) and OL2 (60 g/L) cycles; anode, cathode and the cell, in general, showed positive increments in the potential along with increased applied resistances suggesting the possibility of effective electron discharge on the anode surface and effective electron delivery to the cathode surface. At 4.5 KΩ and 0.3 KΩ resistance for OL1 and OL2 cycles, respectively, all the curves had slightly increased in a linear pattern indicating the effect of ohmic loss at this linear part of the curve. Besides, it can be noticed clearly in Fig. 4 for OL1 and OL2; that anode, cathode, and cell all behaved in an identical pattern. This analogous
behavior means that both anode and cathode were controlling the current flow in the cell at these specific organic loads. However, a completely different behavior was noticed at the cathode while operating the MFC with PROS at OL3 (600 g/L) and OL4 (1000 g/L). In the beginning, the cathode potential was increased rapidly upon increasing external resistance indicating the effect of activation loss. Then the cathode potential remained constant at its open-circuit voltage (OCV). This type of behavior shows that the current generation at these cycles was only limited by the anode reactions as reported by (Mohan et al., 2008). On the other hand, anodic and hence cell potentials were dominated by activation and ohmic losses. This domination of the anodic reactions over cathodic reactions at higher organic loadings may be attributed to the higher ions content in OL3 and OL4 in the anodic chamber compared to the available ions in the cathodic chamber. This means much higher reaction rates at the anode are taking place, resulting in a negligible cathodic reaction rate when being compared.

Figure 4. Polarization curves for anode, cathode, and cell vs. reference electrode in the MFC system

3.3 Harvested sustainable energy
The variation of the relative decrease in the anode potential (RDAP) with applied external resistance for each different organic loading is shown in Fig. 5. The linear fit at high external
resistance represents the region in which the external resistance controls the power whereas the linear fit at low external resistances represents the region in which the power is limited by kinetics and/or internal resistances (Mohan, et al., 2011 and Pandit and Dass, 2013). When the external resistance was high, the RDAP increased linearly with decreasing external resistance because the external resistance only limited the electron delivery to the cathode. At low applied external resistance, the electron delivery to the cathode was limited by kinetic and/or internal resistance, and the RDAP increased linearly with decreasing external resistance. A horizontal line drawn from the intersection of linear fits of higher and lower resistances helps to estimate the peripheral resistor that allowed to measure sustainable power. The RDAP analysis showed a positive correlation between the substrate organic load and the RDAP, where the highest recorded sustainable energy was 0.26 and 0.83 W/m³ for OL3 and OL4, respectively, at external resistance of 14620 Ω for both. On the other hand, OL1 and OL2 achieved their maximum possible sustainable energy at a relatively lower resistance of 8180 Ω, attaining 0.07 and 0.13 W/m³, respectively.

![Figure 5](image)

**Figure 5.** Variation of the reduced decrease of anode potential RPAD as a function of external resistance and substrate organic load.

### 4. CONCLUSIONS

This study demonstrated the feasibility of the BVM model in describing the enzymatic reactions combined with the electrochemical reactions in the anodic chamber that is likely to control the overall MFC performance. The mathematical model was able to describe the measured anode polarization curves for a mediator less-MFC fed with various loadings of the PROS as the main substrate. The polarization curves of anode, cathode, and cell were verified against Ag/AgCl reference electrode, and the model predictions significantly approved with the experimental data.
referring to the feasibility of the BVM in approaching MFC actual reactions. In addition, the study demonstrated the energy barrier losses represented by the ohmic resistance upon the increased substrate load.

REFERENCES

- American Public Health Association (APHA), 2005. Standard methods of the examination of water and wastewater, Washington, DC.
- Cleland, W.W., 1963. The kinetics of enzyme catalysed reaction with two or more substrates or products, nomenclature and rate equations, *Biochimica et Biophysica Acta* 67, 104-137.
- Dickinson, E. J. F., Hinds G., 2019. The Butler-Volmer Equation for Polymer Electrolyte Membrane Fuel Cell (PEMFC) Electrode Kinetics: A Critical Discussion, *Journal of the electrochemical society*, 166, F221-F231.
- Hamelers, H. V. M., Heijne, T., Stein, N., Rozendal, R. A., Buisman, C. J. N., 2011. Butler-Volmer-Monod model for describing bio-anode polarization curves, *Bioresource Technology*, 102, 381-387.
- Ismail Z. Z., Habeeb A. A., 2015. Pharmaceutical Wastewater Treatment Associated with Renewable Energy Generation in Microbial Fuel Cell Based on Mobilized Electroactive Biofilm on Zeolite Bearer. *Journal of Engineering*, 21, 35-44.
- Logan, B. E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S. and Rabaey, K., 2006. Microbial fuel cells: methodology and technology, *Environmental science & technology*, 40, 5181-5192.
- Marcus, A. K., Torres, C. I., Rittmann, B. E., 2007. Conduction-Based Modeling of the Biofilm Anode of a Microbial Fuel Cell, *Biotechnology and bioengineering*, 98, 1171-1182.
- Mohan, S., MohananKrishna, G., Srikanth, S., Sarma, P., 2008. Harnessing of bioelectricity in microbial fuel cell (MFC) employing aerated cathode through anaerobic treatment of chemical wastewater using selectively enriched hydrogen producing mixed consortia, *Fuel*, 87, 2667–2676.
- Mohan, S., Chandrasekhar, K., 2011. Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation, *Bioresource Technology*, 102, 9532-9541.
- Pandit, S., Das, D., 2013. Improved energy recovery from dark fermented cane molasses using microbial fuel cells, *Frontiers of Chemical Science and Engineering*, 8, 1-13.
- Recio-Garrido, D., Perrier, M., Tartakovsky, B., 2015. Modeling, optimization and control of bioelectrochemical systems, *Chemical Engineering Journal*, 289, 180-190.
- Radeef A. Y., Ismail Z. Z., 2018. Biotreatment of Actual Potato Chips Processing Wastewater with Electricity Generation in Microbial Fuel Cell. *Journal of Engineering*, 24, 26-34.
- Rismani-Yazdi, H., Carverb, S. M., Christya, A.D., Tuovinen, O.H., 2008. Cathodic limitations in microbial fuel cells: An overview, *Journal of Power Sources*, 180, 683-694.
- Torres, C. I., Marcus, A. K., Lee, H.-S., Parameswaran, P., Krajmalnik-Brown, R., and Rittmann, B. E., 2010. A kinetic perspective, on extracellular electron transfer by anode-respiring- bacteria, *FEMS Microbiology Reviews*, 34, 3-17.
• Velvizhi, G., Mohan, V., 2012. Electrogenic activity and electron losses under increasing organic load of recalcitrant pharmaceutical wastewater, *International journal of hydrogen energy*, 37, 5969-5978.

• Wei, L., Yuan, Z., Cui, M., Han, H., Shen, J., 2012. Study on electricity generation characteristic of two-chambered microbial fuel cell in continuous flow mode, *International journal of hydrogen energy*, 37, 1067-1073.

• Zhao, L., Brouwer, J., Navlaux, J., Hochbaum, A., 2014. Modeling of polarization losses of a microbial fuel cell. Fuel cell, 6388, 1-6.

• Zhao, L., Li J., Battaglia, F., He, Z., 2016. Investigation of Multiphysics in Tubular Microbial Fuel Cells by Coupled Computational Fluid Dynamics with Multi-Order Butler-Volmer Reactions, *Chemical Engineering Journal*, 296, 377-385.