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Mathematical stimulation for bioelectrochemical behavior of a dual-chambered microbial fuel cell (MFC)

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Abstract

In this study, a steady-state bioelectrochemical model was developed to simulate the correlation between the acting overpotential and the produced current that is accounting for anode polarization. This study aimed to analyze the performance of a dual-chambered microbial fuel cell (MFC) equipped with two bio-anodes and fueled with real refinery oily sludge having a COD concentration of 13890 mg /L. Anode polarization data revealed a maximum current density of 6.07 A/m^3 of the substrate at an overpotential of 1.83 V. In addition, the behavior of the experimental measurements revealed the dominance of the ohmic losses in the overall anode overpotential compared to activation and mass transfer losses, respectively. On the other hand, the suggested mathematical model was verified significantly by the obtained experimental data, achieving a determination coefficient (R^2) of 0.96. Actual sustainable energy was also obtained using the reductive decrease of anode potential (RDAP) and it was found that the sustainable energy for this corresponding system can be attained when applying 17.6 KΩ as the external resistor.

Keywords: Butler-Volmer-Monod, Petroleum refinery oily sludge, Microbial fuel cell, sustainable energy, overpotential.

محاكاة رياضية للتصرف الكهروكيمياوي الإحيائي لخلية الوقود الإحيائية ثنائية الغرف (MFC)

الخلاصة:

في هذه الدراسة، تم تطوير نمذجة رياضية تعبر عن التفاعلات الكهروكيمائية الإحيائية عند حالة الإستقرار بهدف محاكاة العلاقة بين فرق الجهد المسيطر و التيار المنتج و التي تحسب لخسائر قطب الأنود. هدفت الدراسة الى تحليل أداء خلية الوقود الإحيائية ثنائية الغرف و المجهزة بقطبي أنود حيويين و التي غُذيَت بنماذج حقيقية من حمأة المصافي النفطية و التي تحتوي على المكون العضوي COD بتركيز ١٣٨٩٠ملغم\لتر. كشفت البيانات الكهربائية عن إنتاج كثافة تيار أقصاها ٠٧,٦ أمبير\م^{٣} عند فرق جهد ٨٣,١ فولت لهذا النوع من الوقود. بالإضافة الى ذلك، فإن تصرف النتائج العملية أظهر هيمنة الخسائر الأومية على مجموع الخسائر الأخرى في فرق جهد الأنود مقارنة مع خسارة التفعيل و خسارة انتقال الكتلة، بالتتابع. من جهة أخرى، فإن النموذج الرياضي المقترح قد أثبت تطابق كبير مع النتائج المختبرية، حيث وصل معامل التحديد (R^2) الى ٩٦,٠. تم قياس الطاقة المستدامة الفعلية المستحصلة من هذا النظام من خلال حساب نقصان الإختزال لجهد الأنود (RDAP) و وجِد بأن الطاقة المستدامة المنتجة من هذا النظام تظهر عند ربط مقاومة خارجية مقدارها ٦,١٧ كيلوأوم.

الكلمات الرئيسية: بوتلر-فولمر-مونود، حمأة المصافي النفطية، خلية الوقود الإحيائية، الطاقة المستدامة، فرق الجهد.

1. Introduction:

With the increasing demand of a new sustainable energy source to be an effective alternative for the fossil fuels and to solve the greenhouse emission crises, bioelectrochemical systems especially microbial fuel cell (MFC) have paid more attention in the last few decades as a possible main energy source [1]. MFC systems brought a lot of attention as they have the capability of simultaneously remediate and produce electricity directly from both domestic and industrial wastes. It has been proved by intensive studies that MFC can degrade high organic content wastes, inorganic constituents and even toxic contaminants [2]. This type of fuel cell has some common properties with chemical fuel cells since bothcases (anode and cathode side) are separated by a cation exchange membrane, the fuel is oxidized on the anode side and the oxidant (oxygen) reduced on the cathode side. However, MFC uses organic substrates as fuels to generate power and these organics are catalyzed by microbial communities while in chemical fuel cells, the fuel oxidation is catalyzed by noble metals [3]. Hence, power generation in MFC is conducted by bacterial catabolism, electron transfer from bacteria to the anode, reduction of electron acceptors at the cathode and proton transfer from the anode to the cathode via the separating membrane. The performance of any type of MFC relies on several parameters such as the type of biocatalyst and substrate components, membrane or separator characteristics, mixing and diffusion phenomena, surface area of electrodes [4]. In order to enhance the performance of MFC, it is necessary to optimize the design and operation of such fuel cells by developing mathematical models. Various mathematical models were developed to describe biofilm kinetics, biochemical reactions, and biosensors for toxic constituents, enzymatic reaction, electrochemical limitations, and polarization models. A comprehensive review on the most common mathematical models describing MFC, outlining the advantages and disadvantages of these models was conducted [5]. Moreover, a wide survey on the dynamic models of MFC and along with the general review on bioelectrochemical systems BES optimization and control was shown [6]. They point out that mathematical models that account for the biofilm growth dynamics catalyzed by mixed consortium of microbes can be most useful in BES system optimization. A detailed classification of MFC models into mechanism-based and application-based models was presented [7]. While describing these two categories of models, they presented the underlying approaches and usability of the different types of models.

In this study, a bioelectrochemical mathematical model was suggested through the use of Butler-Volmer-Monod model (BVM) kinetic equation. This model was intended to describe the enzymatic reactions taking place in the anodic chamber and controlling the whole cell consequently keeping in consideration that microbial kinetics is a limiting factor.

2. Methods:

2.1. MFC fuel

The MFC system was fueled with petroleum refinery oily sludge samples obtained from Al-Dura petroleum refinery wastewater treatment plant, located in Baghdad, Iraq. The type of used substrate was a mixture of the real oily sludge hydrolyzed in domestic wastewater acting as the anolyte required in the anodic chamber of MFC. The average initial COD concentration of the influent substrate was 13890 mg/L prepared by mixing 600 g of oily sludge in 1 liter of domestic wastewater.

2.2. MFC installation and operation

A cylindrical-shaped, dual-chambered MFC was constructed from the perspex material. The anodic chamber and cathodic chamber were identical in shape having the same full capacity of 1 liter as presented in Figure (1). These two chambers were separated by a cation exchange membrane (Type: CMI-7000, Membrane International INC., NJ, USA). Two circular uncoated graphite plates were employed as the anodes while another one identical graphite plate setting as the cathode. These electrodes were linked together through a wire to a fixed resistance of 100 Ω. This electrical circuit was eventually connected to a digital multimeter (Type: MT-1280) utilized for intensive monitoring of the electrical parameters.

This system comprised of a holding and neutralization tank prior to MFC to regulate the pH value at 7.0-7.2 and the TDS, EC and COD in the substrate influent. The MFC was fed via a peristaltic pump (variable speed pump 3386, USA) from the neutralization tank at flow rate of (0.35 ml/min). Finally, the treated effluent was collected in a final receiving tank for further measurements. The anodic chamber was maintained under anaerobic conditions by sparging nitrogen gas in the chamber prior to operation; on contrast for the cathodic chamber, which was filled with a catholyte solution and operated under fully saturated aerobic conditions.

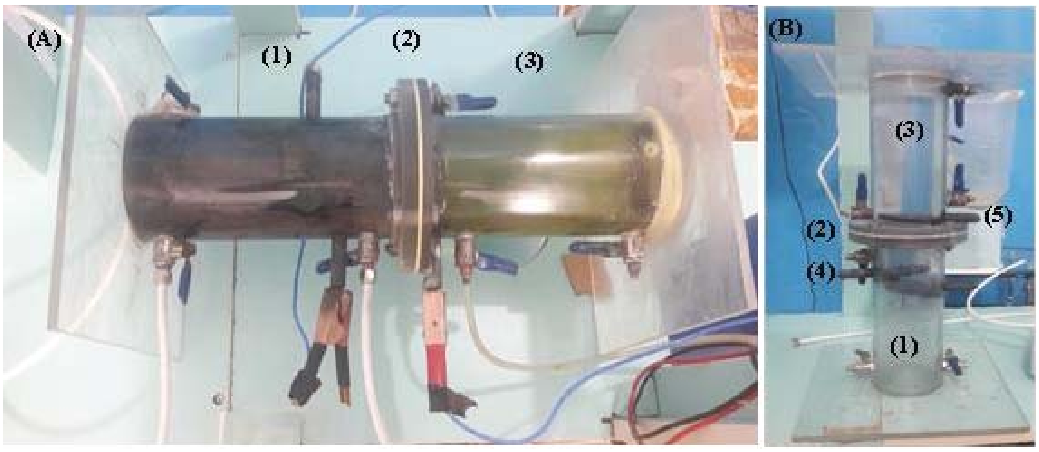

Fig. (1) Photos of the (A) complete cylindrical shaped dual-chambered MFC during operation; (B) MFC system during construction and setup; (1) anodic-chamber, (2) CEM separator, (3) cathodic chamber, (4) two graphite bio-anodes, (5) graphite cathode

3. Mathematical modeling:

3.1 Model description

This study proposed the butler-volmer-monod (BVM) model to evaluate the anodic reactions. The main objective of the proposed mathematical model of MFC focuses on the description of the electrochemical reactions and corresponding enzymatic reactions taking place at the anode surface of this MFC system.

The main assumptions of the study are:

(1) Quasi-steady state conditions, where the concentration of the formed intermediate biocatalysts is constant upon time.

(2) Electron transfer between the two chambers through the separating membrane were considered to be negligible, hence, all the produced electrons are either transformed directly into electricity or consumed in multiple paths in the anodic-chamber.

(3) The reduced redox component X_{red} is a constant value in the MFC and hence, the amount of redox component complex X_c can be expressed as the total amount of redox component subtracted from the oxidized X_{ox} and the reduced form of the redox component.

(4) The microbial kinetics is the limiting factor in the overall anode potential.

(5) Oxygen transport from the cathodic-chamber through the membrane was neglected.

(6) Constant temperature and pH were considered fully controlled and maintained constant.

3.2 Model Formulation

The Butler-Volmer-Monod (BVM) is a model established depending on easy mathematical expressions of the basic biochemical reactions and electrochemical reactions. The BVM uses the idea of redox state of microorganisms that controls the anodic processes. As the previously reduced microorganisms by chemical electron donors touch the anode, they transfer to the surface of anode their outer orbit electrons to return to its original oxidized form. Oxidized microorganisms are then free in interacting with another donor molecule [8]. In this work, the anode overpotential is precisely demonstrated by the Bulter-Volmer-Monod model as many researchers confirmed that the Butler-Volmer-Monod model was a better tool to describe experimental data than the Nernst-Monod model. The following three chemical equations are applied at the anode:

$$S + X_{ox} \underset{k_2}{\overset{k_1}{\rightleftarrows}} X_c \underset{k_4}{\overset{k_3}{\rightleftarrows}} P + X_{red} \qquad (1)$$

$$X_{red} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \mathrm{X_{ox}} + e^- \qquad (2)$$

where; K_1, K_3, K_5 and K_2, K_4 , K_6 are heterogeneous forward and backward rate coefficients, respectively. S and P are the substrate and product concentrations.

K_5 and K_6 was formulated as described by [8, 9]:

$$I = n \,.\, F \,.\, k_5 \,.\, X_{red} \qquad (3)$$

Where I is the forward current density, n number of electron moles participated in the reaction and F is the Faraday constant (96485 C/mol).

However, by assuming quasi-steady-state conditions, then X_{ox} and X_{red} can be expressed by the following differential equations depending on the mass balance of the biocatalyst:

$$\frac{d\,X_{ox}}{dt} = 0 = -k_1 \,.S \,.\; X_{ox} + k_2 \;.\, X_c + k_5 \,.\, Xr_{ed} - k_6\, X_{ox} \qquad (4)$$

$$\frac{d\,X_{red}}{dt} = 0 = k_3 \,.\, X_c - k_4 \,.\, P \,.\, X_{red} - k_5 \,.\, X_{red} + k_6\, X_{ox} \qquad (5)$$

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

$$X_c = X_T - X_{ox} - X_{red} \qquad (6)$$

Where X_T is the total amount of redox. In order to simplfy the eqs. (4) and (5), k_1, k_2 and k_3 were eliminated by introducing the substrate affinity (K_m) which can be defined as the half-saturation constant analogous to that of Michaelis-Menten enzyme kinetics [10], in addition to the product inhibition constant (Kp) refers to the effect of product concentration (P) at which an inhibition of the turnover rate is occured [11]:

$$K_m = \frac{k_2 + k_3}{k_1} \qquad (7)$$

$$K_p = \frac{k_2 + k_3}{k_4} \qquad (8)$$

Moreover, by assuming microbial activity is limiting in the overall anode performance as mentioned earlier, a maximum current density can be introduced and defined as the produced current when all microorganisms generate reduced intermediate X_{red}, thus:

$$I_{max} = n \,.\, F \,.\, k_3 \,.\, X_T \qquad (9)$$

Applying more simplifications and binding all the previously presented definitions with the differential balances in eqs. (4) and (5) yields the used Butler-Volmer-Monod equation:

$$I = I_{max} \frac{1 - e^{-f\,.\eta}}{\mathrm{K1}\,.e^{-(1-\alpha)f\,.\eta} + K2\; e^{-f\,.\eta} + (\frac{Km}{S} + 1)} \qquad (10)$$

Where, ɳ is the anode overpotential vs. reference electrode. (K_1) is a lumped parameter represent the ratio between biochemical and electrochemical reaction rate constants, while, (K_2) is a lumped parameter represent the ratio between the forward and backward biochemical rate constants, (α) is the anodic charge transfer coefficient.

4. Experimental procedure

The MFC system was continuously operated for 60 days of full operation period in a continuous mode. After a stable cell potential was achieved , a reference electrode was connected to the anode in the MFC. The (Ag/AgCl) reference electrode was selected to be utilized as it is commonly used in electrochemical measurements for environmental purposes due to its simplicity, stability and nontoxicity [12]. In a half cell measurement, the reference electrode should be considered as the reduced electrode (i.e. anode) and should be connected to the cell as demonstrated in Figure (2). Anode polarization curve was obtained and by connecting the MFC with various external resistances ranged from 10 Ω to

100 KΩ then recording the measured anode overpotential to be plotted against the produced current density.

In order to be able to perform the BVM model, it was necessary to obtain one essential standard parameter, the substrate affinity constant (K_m), which was specified and outlined [8]. The MFC was fed with several concentrations of acetate (as substrate) and by specifying the acetate concentration at which the current was first produced, this point represents the K_m.

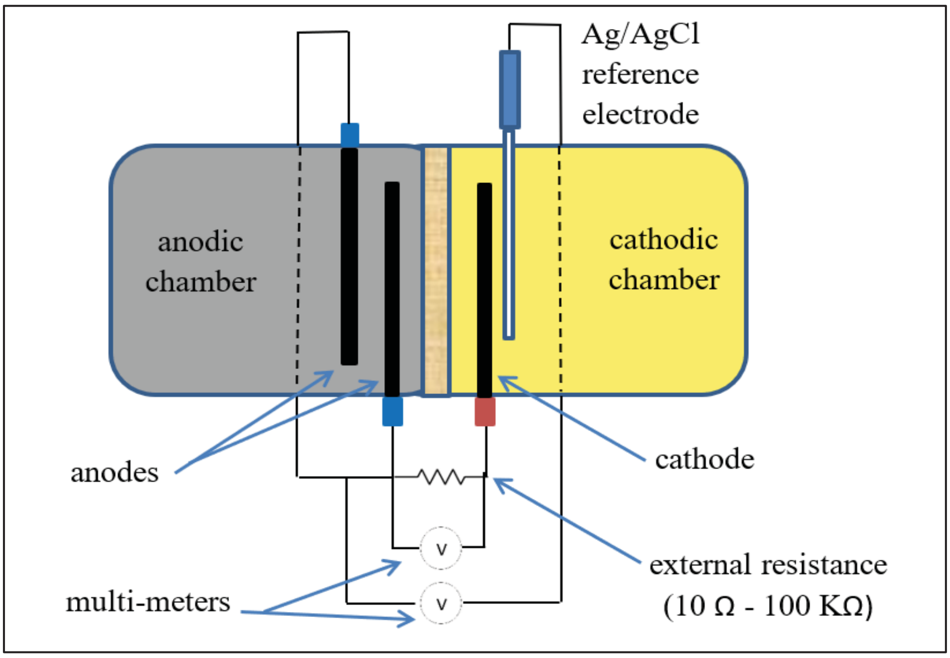

Fig. (2) Schematic description for reference electrode connection to MFC

5. Sustainable Energy

A steady-state operating MFC can only be attained, when the overall produced current equals the current consumed for an extended time operating at steady-state conditions and hence, the power production is then said to be sustainable. Many scholars have considered the steady-state operation to be sustainable [13, 14]. It is important to identify the steady state potential value to determine the maximum sustainable power that can be obtained from this MFC system. By increasing the external applied resistances within equal time intervals (10 min), anode current and potential was recorded to evaluate the harvested sustainable energy from the system. Sustainable power calculations were conducted by calculating the considering the relative decrease in anodic potential (RDAP) as described:

$$\mathrm{RDAP}\ \% = [(E_{OCV} - E_A) / E_{OCV}] * 100 \qquad (11)$$

Where, E_{OCV} is the open circuit potential of the anode (V) and E_A is the measured anode potential at a specific external resistance (V).

6. Results and Discussion

The performance of this MFC system was evaluated according to the anodic electrochemical performance which is likely to govern the overall cell power production.

6.1 Anode polarization curve

Figure (3) shows the conducted polarization curve for the anode against Ag/AgCl electrode. The plot clearly showed that upon increased applied external resistances, current density was collapsing simultaneously with the decline of the overpotential. Maximum anode current density obtained during continuous operation was 6.07 A/m^3 at an overpotential value and external resistance of 1.83 V and 10 **Ω**, respectively; while open-circuit voltage (OCV) recorded 1.89 V. However, the correlation between current and overpotential was a nonlinear correlation indicating a relatively high internal resistance due to the recalcitrant nature of the oily sludge and the high concentration of the substrate.

6.2 Model Verification

The BVM model was verified against the experimental data acquired from dual-chambered MFC with horizontal flow. The comparison between the measured and simulated current density and cell overpotential are given in Figure (4). The simulated results were in a good and reasonable compliance with the measured data. According to the obtained results, the BVM model succeeded in describing the anodic bioelectrochemical reactions by achieving a determination factor (R^2) of 0.96.

Figure (5) illustrates the variation of the produced current against different substrate feed concentrations. It was found that K_m =1 mM/L. This concentration of K_m represents the lowest concentration which can generate current in this MFC system. For the model verification process, limiting parameters such as charge transfer coefficients α, K_1 and K_2 were first evaluated and adjusted to obtain better fittings. For α, it was assumed to have the value of 0.9. This value was based on the behavior of the experimental curve, where it can be clearly noticed form Figure (6) that the region of the mass transfer loss was very minimal. A for the lumped parameters: K_1 and K_2, they were obtained by conducting a numerical method of fitting the experimental data to the simulated data using MATLAB software version (R2017b). It was It was found that the optimum K_1 and K_2 were 40 and 26.5, respectively, approaching the values estimated by [15]. The BVM model estimated, measured and assumed parameters and constants used in the simulation are given in Table (1).

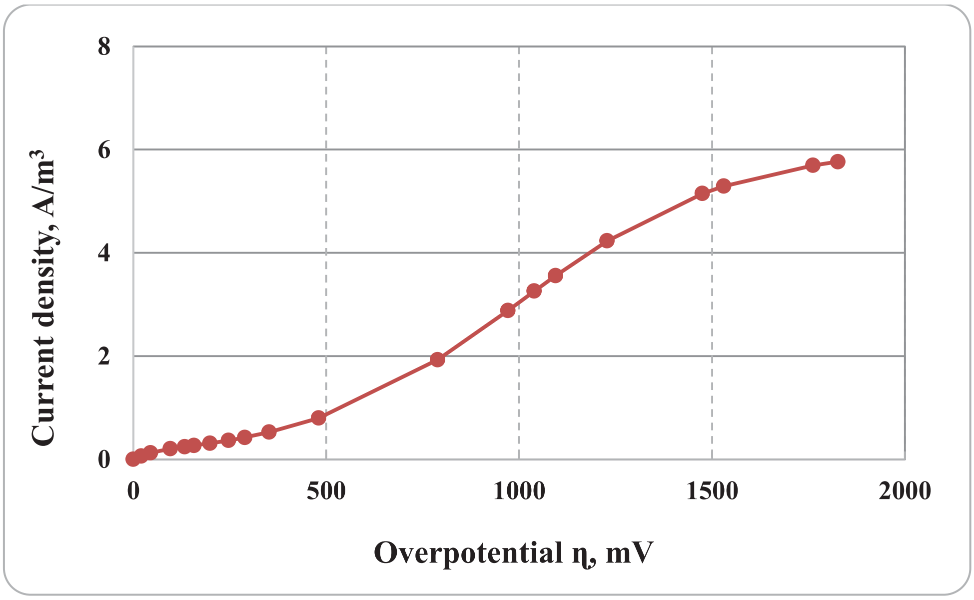

Fig. (3) Simulated anode polarization curve vs. Ag/AgCl reference electrode for a dual-chambered MFC

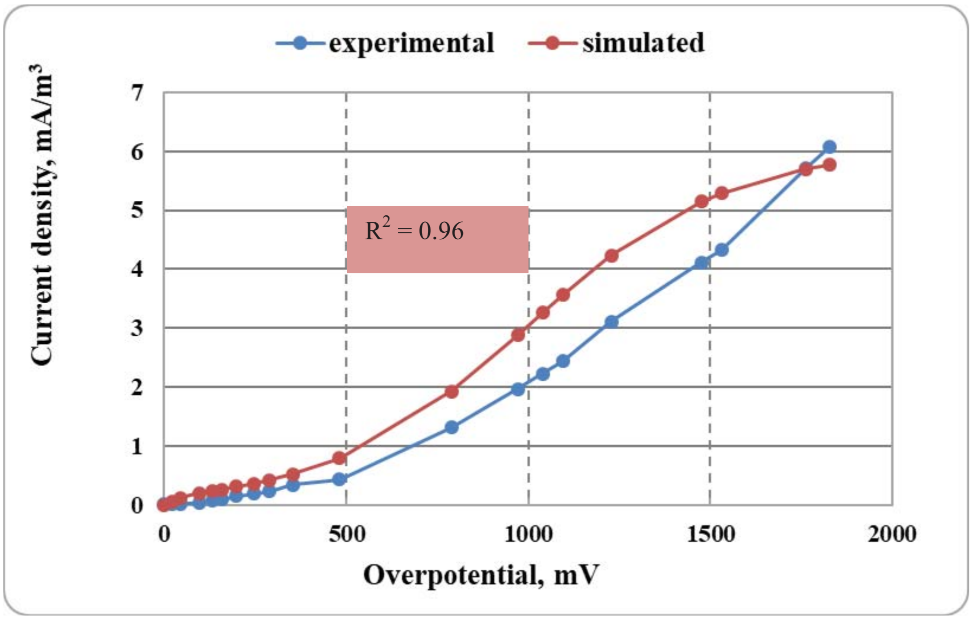

Fig. (4) A comparison between experimental and simulated polarization curves for anode in the MFC

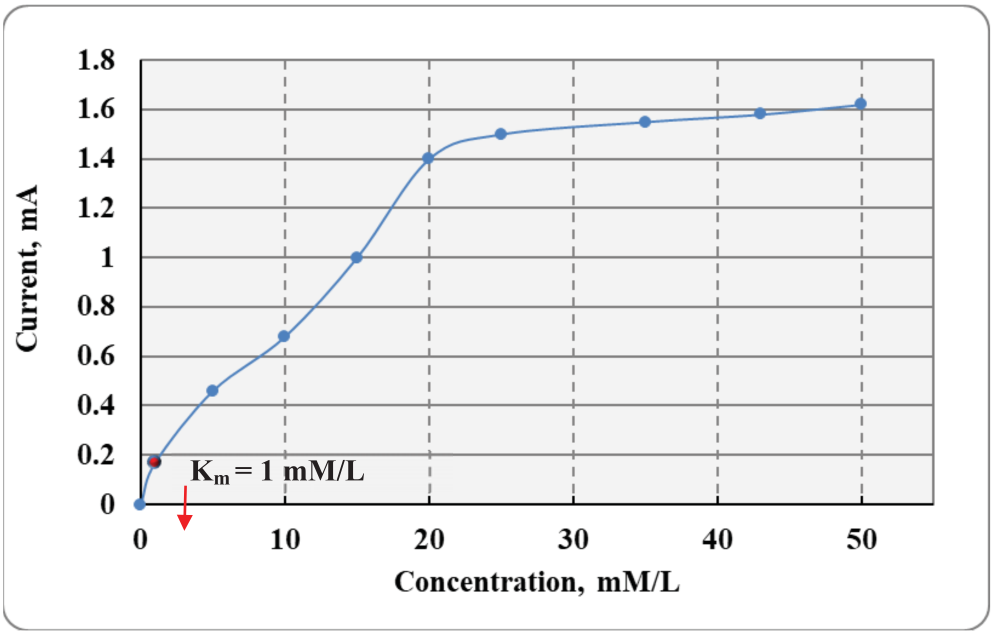

Fig. (5) Estimation of K_m for MFC system

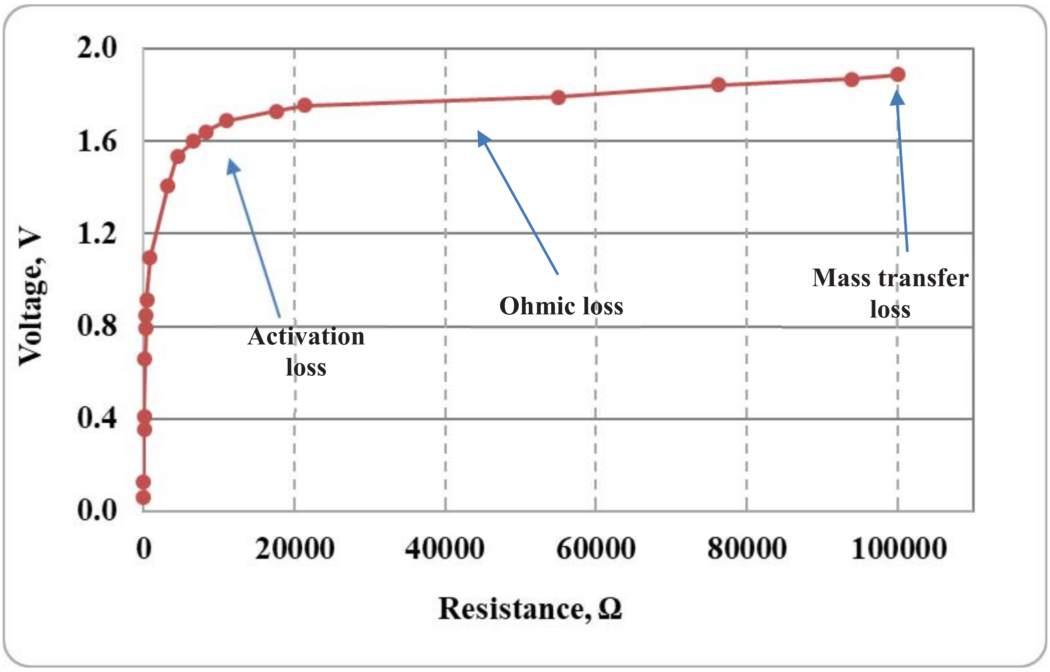

Fig. (6) The relation between voltage and the applied external resistance

6.3 Obtained sustainable energy

An estimation of the relative decrease in the anodic potential (RDAP) was conducted in order to assess the maximum sustainable power. The variation of percent deviation of anodic potential with respect to applied external resistance is shown in Figure (7). At lower resistances, the linear fit represents the region at which energy generation is only limited by kinetics or internal resistance. While, at higher external resistances, the explained linear fit represents the region at which the energy generation is only limited by the external resistance. At certain operating conditions, external resistance (R_{ext}) equals internal resistance (R_{int}) limitations; identifying this region is important to determine the external resistor at which the sustainable energy is approached [16]. This specific region always lays between the intersect of the two plotted lines. The dotted horizontal line plotted from the intersect point to meet the curve at a certain point, which represents the desired resistor value. As can be clearly seen in Figure (7), this point was spotted at 17600 Ω for this specific MFC system and the corresponding sustainable power generation was 0.17 W/m^3.

Table (1) Assumed, measured, and estimated parameters in addition to the physical constants used in Butler-Volmer-Monond 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
$\mathbf{I_{max}}$	The maximum current	6.07	mA	Measured
$\boldsymbol{\eta}$	The overpotential	(0-1.83)	V	Measured
$\mathbf{K_1}$	A lumped parameter describing the ratio between biochemical and electrochemical rate constants	40	Dimensionless	Assumed
$\mathbf{K_2}$	A lumped parameter describing the forward over backward biochemical rate constants	26.5	Dimensionless	Assumed
Km	Substrate affinity constant	0.001	mole/L	Calculated
$\boldsymbol{\alpha}$	Transfer coefficient	0.9	Dimensionless	Assumed
S	Substrate concentration	0.232	mole/L	Measured
Cs_{in}	Average substrate concentrations	13890	mg/L	Measured
f	f = F/RT	0.03855	V^{-1}	Calculated

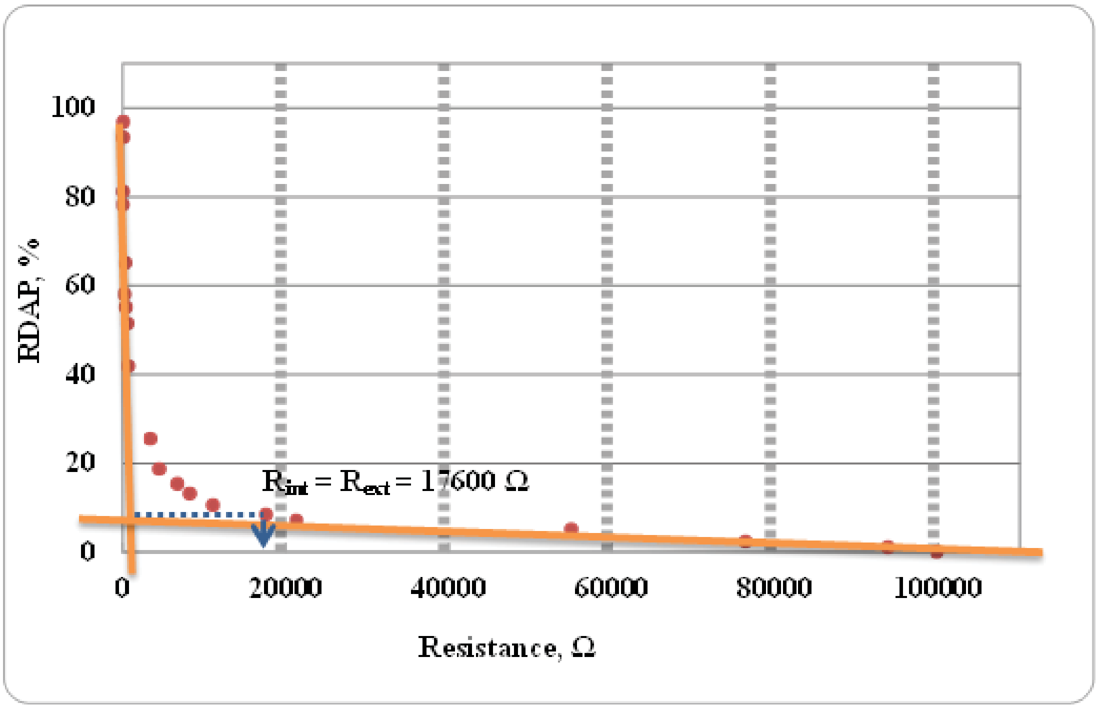

Fig. (7) Sustainable energy evaluation based on the variation of the relative decrease of anode potential (RDAP) with respect to applied external resistance.

7. Conclusions:

This study demonstrated the feasibility of the kinetic steady-state, one-dimensional model represented by Butler-Volmer-Monod model for describing the enzymatic reactions and the electrochemical reactions that governs the anode potential and consequently the MFC electrical generation. The simulated data showed a very good and reasonable match to the experimental data verifying the applicability of this model to this MFC system. Moreover, the good performance of the BVM model refers to the efficient adjustment of the assumed, estimated and fitted parameters such as the transfer coefficient α, the lumped parameters K_1 and K_2 and the substrate affinity constant K_m. Hence, the suggested model is a useful tool to improve MFC understanding and to optimize MFC design and operation. Nevertheless, this mathematical model is simple to be implemented and suitable for use in real-time MFC operation.

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