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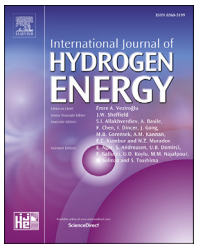

Dynamic modeling of a continuous two-chamber microbial fuel cell with pure culture of *Shewanella*

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ABSTRACT

Microbial fuel cell is a bioreactor which converts the chemical energy stored in chemical bonds of the organic compounds to electrical energy through the catalytic reactions. In this work, the previous model which was proposed by our group [M. Esfandyari, M.A. Fanaei, R. Gheshlaghi, M.A. Mahdavi, Chemical Engineering Research and Design, 117 (2017) 34–42] for a batch two-chamber microbial fuel cell (MFC) is extended to the continuous operation. In the selected continuous MFC, lactate is used as the substrate, *Shewanella* as the microbial agent, and oxygen of air as the final electron acceptor in the cathode chamber. An experimental setup is applied for the collection of data needed for the verification of the proposed model. A Good agreement was observed between the predicted and the experimental data of the current and voltage produced by MFC as well as the substrate and carbon dioxide concentration in the liquid bulk of anode chamber of MFC. The proposed model has simple structure and can be used for the optimization, and design of control system of microbial fuel cell.

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Introduction

Energy is an integral part of human life and from the beginning of history, mankind is looking for a way to control it to provide the basic needs. One of the available energy sources is fossil energy that has been considered due to the huge amount of energy.

These types of fuels have some limitations such as non-renewability, consequent run off in near future, and emission of greenhouse gases [1,2]. The use of renewable energies provides different options for us. One of such technologies is microbial fuel cell (MFC) [2,3]. Nowadays, managing waste and wastewater originated from mankind activities is a challenge. Releasing wastewater to environment threatens the human health in some aspects [4]. So, the ability of MFC in the use of household and industrial waste and wastewater as a substrate is of interest. Accordingly, MFC technology has attracted the attention of researchers in recent years. As yet, most of researches related to MFC, have been allocated to the laboratory studies and investigation of the effects of different operative parameters on the cell function. Although, in the advent of a technology, laboratory studies is necessary to identify the mechanisms involved, but mathematical modeling of the process also plays a crucial role in the scrutiny and assessment.

MFC is a set of physical, electrochemical, and biological interdependent processes, which together perform the same task. Mathematical modeling help the researchers exploring

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processes from each other, and determining the role of each ones in the MFC. Mathematical modeling also can help to provide solutions to improve the efficiency of MFCs. Further, modeling leads to better design, scale up, and control of MFCs [5].

In previous paper of us [6], after reviewing the research published about the MFC modeling, a dynamic mathematical model was proposed for batch two-chamber MFC with *Shewenella* culture. In the current study, that pervious model is extended to the continuous operation and its performance is compared to empirical data revealed from an experimental setup.

In the following sections, after describing the materials and methods, the model equations are presented. According to these equations, the voltage and current of MFC as well as

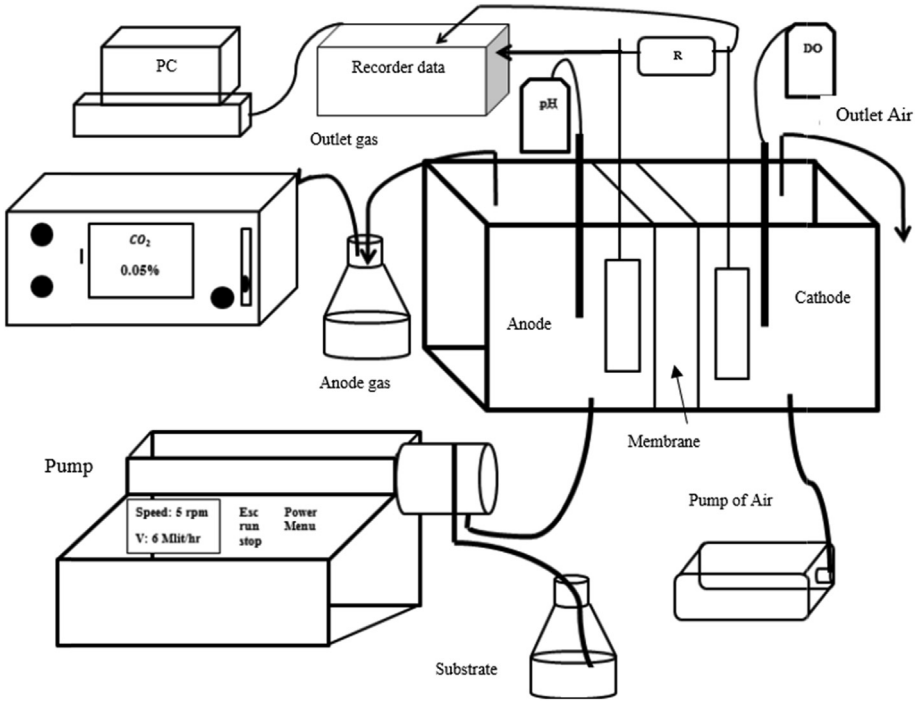

Fig. 1 – Structure of experimental setup.

Table 1 – The proposed model equation.

Description of the equation	Equation
Rate of substrate consumption (Nernst-Monod equation)	$r_s(t) = r_{max}\phi_a \frac{C_S(t)}{K_s+C_S(t)} \frac{1}{1+\exp\left(-\frac{F}{RT}\eta\right)}$
Mass balance of active biomass in biofilm	$\frac{d}{dt}(\phi_a(t)) = Y_{ac}r_s(t) - b_{ina}\phi_a(t) + \frac{\phi_a(t)}{L(t)}\delta(t) - \frac{\phi_a(t)}{L(t)}\frac{d}{dt}(L(t))$
Mass balance of non-active biomass in biofilm	$\frac{d}{dt}(\phi_i(t)) = b_{ina}\phi_a(t) + \delta(t)\frac{\phi_i(t)}{L(t)} - \frac{\phi_i(t)}{L(t)}\frac{d}{dt}(L(t))$
Biofilm thickness change rate	$\frac{dL(t)}{dt} = Y_{ac}r_s(t)L(t) + \delta(t)$
Mass balance of substrate in biofilm	$\frac{d}{dt}(C_S(t)) = \frac{D_s}{L_l L(t)}(C_{S_b}(t) - C_S(t)) - \rho r_s(t) - \frac{C_S(t)}{L(t)}\frac{d}{dt}(L(t))$
Mass balance of carbon dioxide in biofilm	$\frac{d}{dt}(C_{CO_2}(t)) = \frac{D_{CO_2}}{L_l L(t)}(C_{CO_{2_b}}(t) - C_{CO_2}(t)) + 3\rho r_s(t) - \frac{C_{CO_2}(t)}{L(t)}\frac{d}{dt}(L(t))$
Mass balance of hydrogen in biofilm	$\frac{d}{dt}(C_H(t)) = \frac{D_H}{L_l L(t)}(C_{H_b}(t) - C_H(t)) + 12\rho r_S(t) - \frac{C_H(t)}{L(t)}\frac{d}{dt}(L(t))$
Bulk liquid volume change	$\frac{dV_L(t)}{dt} = -A_m(Y_{ac}r_s(t)L(t) + \delta(t))$
Mass balance of substrate in bulk liquid	$\frac{d}{dt}(C_{S_b}(t)) = \frac{1}{V_L(t)}\left(Q_a(t)C_{S_{in}}(t) - Q_a(t)C_{S_b}(t) - \frac{A_m D_s}{L_l}(C_{S_b}(t) - C_S(t))\right)$
Mass balance of carbon dioxide in bulk liquid	$\frac{d}{dt}(C_{CO_{2_b}}(t)) = \frac{1}{V_L(t)}\left(Q_a(t)C_{CO_{2_{in}}}(t) - Q_a(t)C_{CO_{2_b}}(t) - \frac{A_m D_{CO_2}}{L_l}(C_{CO_{2_b}}(t) - C_{CO_2}(t))\right)$
Mass balance of oxygen in cathode	$\frac{dC_{O_2}}{dt} = k_L a(C^*_{O_2} - C_{O_2}) - q_{O_2}C_{O_2}$
Current	$i = i_{0,ref}\left[\exp\left(\frac{2.303}{b}\eta_{act}\right) - exp\left(-\frac{2.303}{b}\eta_{act}\right)\right]$
Activation overpotential	$\eta_{act} = \frac{b}{2.303}sinh^{-1}\left[\frac{i}{2i_{0,ref}C_S}\right]$
Ohmic overpotential	$\eta_{ohm} = \left(\frac{d_m}{k_m} + \frac{d_{cell}}{k^{aq}}\right)i$
Concentration overpotential	$\eta_{con} = \frac{RT}{nF}\ln\left(\frac{i_l}{i_l - i}\right)$, $i_l = \frac{nFD_sC_{S_b}}{L_l}$
Output voltage	$E_{output} = E_{thermo} - \eta_{ohm} - \eta_{con} - \eta_{act}$

substrate and carbon dioxide concentration in the liquid bulk of the anode chamber are calculated. Finally, the predicted results of the proposed model are compared with the experimental data.

Materials and methods

Two-chamber microbial fuel cell, made of poly glass and cubic shape is used. The volume and effective volume of each of the anode and cathode chambers are 150 and 135 *ml*, respectively. These two chambers were designed in such a way that the chambers were separated from each other by cation exchange membrane (CMI7000S, Membrane International Inc).

Electrode plates (anode and cathode) made of carbon felt with cubic shape was used (PANEX35, Zoltek). The surface area of these electrodes are 54 cm^2 and installed on either side of the cell by a distance of 2.5 *cm*.

For proper sealing of the cell, silicone gaskets with thick of 0.5 *mm* were used between the components. Aeration was done in anode chamber using aquarium pump.

To prevent contamination in aerated flow path of the cathode chamber, sterile filter with the pore size of 0.45 μm was used [3,7,8].

Experimental setup include microbial fuel cell, peristaltic pumps, aquarium pumps, carbon dioxide analyzers, pH meter, DO meter, data recording system, and a computer device is shown in Fig. 1.

Cation exchange membrane used in the cell was made from PTFE with a surface area of 32 cm^2. Bacteria *Shewanella* as the bacteria was supplied from Iranian Research Organization for Science and Technology (IROST) [9].

The output voltage and electric current during operation of microbial fuel cell, was recorded online with sampling time of 1 min. Lab View™ software (version 10) were used in order to data obtaining and analyzing. Based on the measured voltage and current, external resistance, power, power density, and current density was calculated and recorded by the software on the basis of anode surface area.

In normal situations, external resistor of 100 Ω was placed in the path of the electron movement. The resistance of the external resistor could be changed by potentiometer. All experiments were conducted under strictly sterile conditions.

One liter of anolyte medium contains of 3 gr NaOH, 1.5 gr NH_4Cl, 0.1 gr KCl, 0.6 gr KH_2PO_4, 5.8 gr NaCl, 10 cm^3 mineral solution and 10 cm^3 Amino acid solution (adjusted to pH of 7). Lactic acid was used as the substrate (adjusted to pH of 7). Before adding medium and substrate to MFC, solutions were sterilized at 121 °C for 15 min in an autoclave.

The cathodic chamber of the MFC was filled with phosphate buffer solution of 25 *mM* (2.678 kg m^{-3} K_2HPO_4, 1.310 kg m^{-3} KH_2PO_4, adjusted to pH of 7).

The concentration of biomass and substrate (lactate) were determined by the direct measurement of the optical density (OD) of the samples, taken from the anode chamber, at a wavelengths of 600 nm and 570 nm, respectively, using a spectrophotometer (UV-2100, U.S.A.).

The Volume fraction of carbon dioxide in the gas phase was measured by carbon dioxide analyzer (SB 1000 Portable Gas Analyzer) with the accuracy of 0.01. The concentration of carbon dioxide dissolved in the liquid phase was calculated as follows (Henry law):

$$C_{Co_2,b} = H^{cc} C_{Co_2,g} \quad (1)$$

where $C_{Co_2,b}$ and $C_{Co_2,g}$ are the carbon dioxide concentrations in liquid and gas phases, respectively. H^{cc} is the Henry constant.

The Electrical conductivity of anolyte solution was measured using a conductivity meter (Mi306 Conductivity) with the accuracy of 0.01.

The value of dissolved oxygen was measured using a portable DO meter (SevenGo® pro Portable Dissolved Oxygen Meter, METTLER TOLEDO®) with the accuracy of 0.01.

Table 2 – Numerical values of model parameters.

Symbol	Value	unit	Reference
D_s	0.2544	$cm^2.day^{-1}$	[10]
L_l	0.02	cm	[11]
ρ	50	$mgr.Cm^{-3}$	[11]
Y_{ac}	0.212	mgr dry cell.mgr $lactate^{-1}$	[12]
k_d	0.05	day^{-1}	[13]
D_{CO_2}	0.996	$cm^2 \cdot day^{-1}$	[10]
D_H	2.3328	$cm^2 \cdot day^{-1}$	[10]
A_m	54	cm^2	constant
b_{ina}	0.03	day^{-1}	[13]
F	96450	$C.mol^{-1}$	constant
T	303	K	constant
R	8.314	$J.mol^{-1}K^{-1}$	constant
V_c	135	Cm^3	constant
V_a	135	Cm^3	constant
$E_{0,anode}$	340	mV	[2]
$E_{0,cathode}$	1299	mV	[2]
$i_{0,ref}$	0.001	mA	[14]
b	0.15	V	[15]
d^{cell}	2.5	cm	constant
k^{aq}	35	$mS.\ cm^{-1}$	measured
E_{KA}	−155	mV	[16]
d^m	45	mm	[12]
k^m	17	$mS.\ cm^{-1}$	constant
$C^*_{O_2}$	7.26	$mgr.lit^{-1}$	measured
$k_L a$	17.25	hr^{-1}	estimated
q_{O_2}	0.11	hr^{-1}	estimated
r_{max}	4.20	hr^{-1}	estimated
K_s	1.27	$mgr.lit^{-1}$	estimated
k^{aq}	35	$mS.cm^{-1}$	measured
pH_{anode}	7	–	measured
$pH_{cathodee}$	7	–	measured

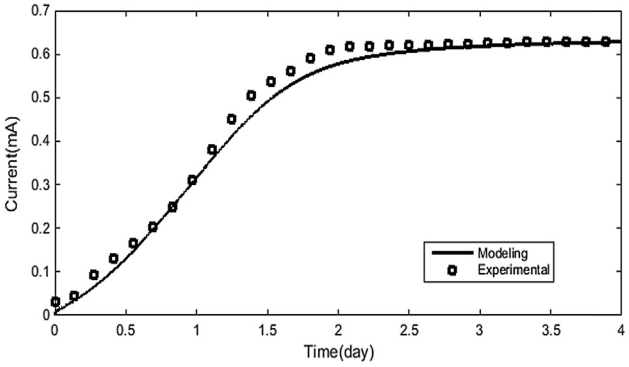

Fig. 2 – Predicted and experimental values of current vs. time.

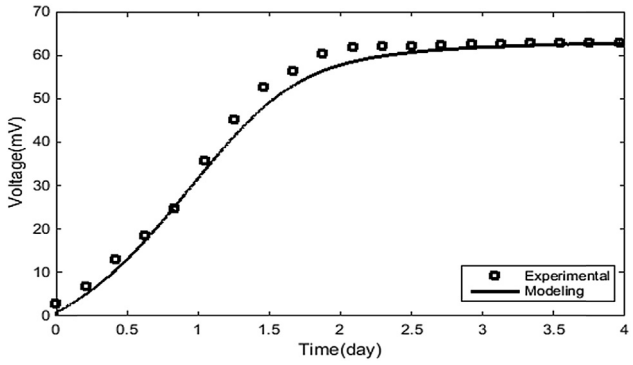

Fig. 3 – Predicted and experimental values of voltage vs. time.

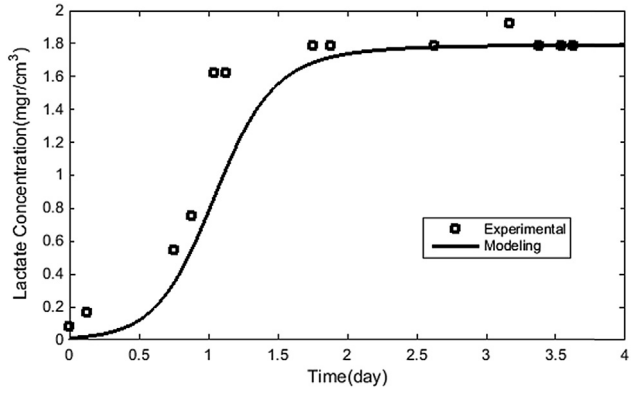

Fig. 4 – Predicted and experimental values of substrate concentration in liquid bulk of anode chamber vs. time.

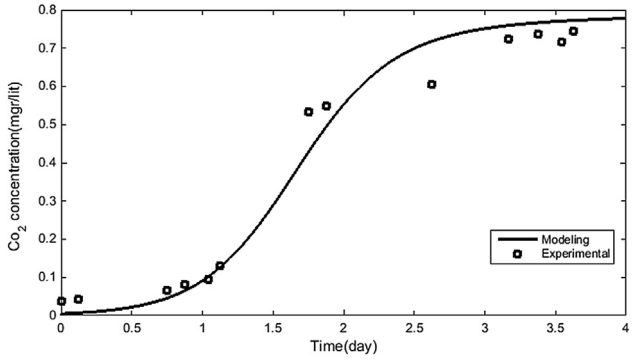

Fig. 5 – Predicted and experimental values of dissolved carbon dioxide concentration in the liquid bulk of anode chamber vs. time.

Model description

In this section the mathematical model proposed by Esfandyari et al. [6] for a batch two-chamber MFC with the pure culture of *Shewenella* is extended to the continuous operation. The resulted model equations are summarized in Table 1.

The Numerical values of some of the required parameters in the proposed model, have been collected from the previous works, and the others are estimated or measured based on the experimental data. These parameters are presented in Table 2.

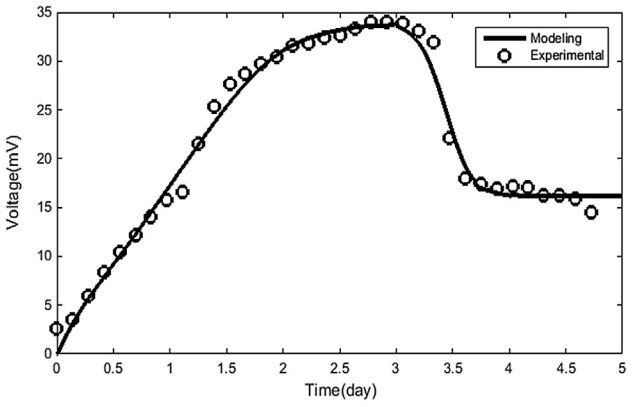

Fig. 6 – Predicted and experimental values of voltage vs. time for a negative step change in substrate flow rate (4.5 $cm^3 \cdot hr^{-1}$–3 $cm^3 \cdot hr^{-1}$).

Validation of the proposed model

To validate the proposed model, the experimental data of a continuous MFC with the substrate volumetric flow rate of 6 $cm^3.hr^{-1}$ and concentration of 4.5 $mgr.Cm^{-3}$ were used.

The values of current and voltage predicted by the model and the experimental corresponding data are shown in Figs. 2 and 3, respectively. As it can be observed the electric current started from a zero initial value and after about 3 days it reached to its steady value of 0.62 mA. The good agreement exist between the predicted and experimental data.

The variations of substrate and carbon dioxide concentration in the liquid bulk of anode chamber in comparison with the experimental data are shown in Figs. 4 and 5, respectively. As it can be observed in these figures, an acceptable match is exists between the predicted and experimental data.

The effectiveness of the proposed model is investigated in the case of changing the input flow rate of substrate into the anode chamber. For this purpose a step change of −1.5 $cm^3.hr^{-1}$ is applied in the inlet substrate volumetric flow rate of anode chamber after 3 days (changing from 4.5 to 3 $cm^3 \cdot hr^{-1}$). Fig. 6 shows the changes of the experimental data for the voltage with time for the above mentioned test along with the predicted values. As it is obvious there is a good agreement between these two sets of data.

Conclusion

A simple and comprehensive model was presented to investigate the performance of a continuous MFC with pure culture of *Shewanella*. Using this model the substrate, dissolved CO_2, and hydrogen concentration in biofilm, substrate and CO_2 concentration in the liquid bulk of anode chamber, oxygen concentration in the cathode chamber, biofilm thickness,

current, and voltage can be predicted. The results showed that a good agreement was seen between the model predictions and experiment data. Considering the features of the proposed model, it can be used to optimize and control the MFC in continuous and batch modes.

Nomenclature

Symbol

A_m	Area of membrane, (m^2)
b	Tafel coefficient, (mV)
b_{ina}	Inactivation coefficient, (day^{-1})
b_{det}	Detachment coefficient, (day^{-1})
$C_{CO_{2in}}$	The initial concentration ofCarbon dioxide in bulk liquid, (kgm^{-3})
$C_{H_{in}}$	The initial concentration ofhydrogen in bulk liquid, (kgm^{-3})
$C_{CO_{2b}}$	The concentration of Carbon dioxide in bulk liquid, (kgm^{-3})
C_{H_b}	The concentration of Hydrogen in bulk liquid, (kgm^{-3})
C_{O_2}	The concentration of oxygen in cathode chamber, (kgm^{-3})
C_{CO_2}	The concentration of Carbon dioxide in biofilm, (kgm^{-3})
$C^*_{O_2}$	The equilibrium or saturation concentration of the oxygen, (kgm^{-3})
C_H	The concentration of Hydrogen in biofilm, (kgm^{-3})
$C_{S_{in}}$	The initial concentration of lactate, (kgm^{-3})
C_{S_b}	The concentration of lactate in bulk liquid, (kgm^{-3})
C_S	The concentration of lactate in biofilm, (kgm^{-3})
D_{CO_2}	The diffusivity of Carbon dioxide, (m^2day^{-1})
D_H	The diffusivity of hydrogen, (m^2day^{-1})
D_s	The diffusivity of lactate, (m^2day^{-1})
d_m	Membrane thickness, (m)
d_{cell}	Distance between electrodes, (m)
$E_{0.anode}$	Standard anode voltage, (mV)
$E_{0.cathode}$	Standard cathode voltage, (mV)
F	Faraday's constant, ($Cmol^{-1}$)
i	Current, (mA)
i_l	Limited current, (mA)
$i_{0,ref}$	Exchange current in reference conditions, (mA)
k_m	Membrane conductivity, (mS m^{-1})
k_{aq}	Solution conductivity, (mS m^{-1})
K_s	Half-max-rate lactate concentration, (kgm^{-3})
k_La	The overall volumetric oxygen mass transfer coefficient, (day^{-1})
L_f	The thickness of biofilm, (m)
L_l	The thickness of the laminar diffusion sublayer
q_{O_2}	The specific uptake rate of oxygen, (day^{-1})
Q_a	Flow rate liquid bulk to anode, (Cm^3day^{-1})
r_{max}	Reaction rate constant, (day^{-1})
T	Universal gas constant, ($Jmol^{-1}K^{-1}$)
T	Temperature, (K)
V_l	Bulk liquid Anode chamber volume, (m^3)
Y_{ac}	The bacterial yield, (kg dry cellkg^{-1})
$\varnothing_a$	Volume fraction of the active biomass
$\varnothing_i$	Volume fraction of the inactive biomass
ρ	The biomass density, (kgm^{-3})
δ	detachment rate
η	overpotential, (mV)
η_{ohm}	Ohmic overpotential, (mV)
η_{act}	Activation overpotential, (mV)
η_{conc}	Concentration overpotential, (mV)

Abbreviation

DO	dissolved oxygen
OTR	oxygen transfer rate
OUR	oxygen uptake rate
MFC	Microbial fuel cell
UV	Ultraviolet
OD	optical density

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