Staged Microbial Fuel Cells with Periodic Connection of External Resistance

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Abstract: Reactor staging is widely used in wastewater treatment where treatment norms are achieved by connecting two or more reactors in series. The first reactor operates at high carbon source loads and the last reactor performs the final polishing. Microbial Fuel Cells (MFCs) are bioelectrochemical devices designed for direct electricity production from organic matter. Periodic connection of the MFC external electrical resistance was demonstrated to increase performance. An engineering tool to understand this periodic mode of operation is developed. Effluent quality control can be ensured by developing control strategies able to reject variability in the influent concentration while tracking a desired set-point.

Keywords: Microbial fuel cell; dynamic modelling; reactors in series; intermittent operation; effluent quality control; PID.

1. INTRODUCTION
Microbial Fuel Cells (MFCs) are bioelectrochemical devices designed for direct electricity production from organic matter. Similar to conventional fuel cells, they consist of two electrodes connected by an external electrical circuit. The MFC anodic compartment benefits from the biocatalytic activity of exoelectricogenic bacteria, which externally release electrons from the oxidation of organic matter. The released electrons flow through the external electrical circuit while protons migrate to the cathode to reduce oxygen and form water (Logan 2008).

Microbial fuel cells are able to treat low strength wastewater. Their ability for energy recovery provides an opportunity to develop a novel wastewater treatment technology (Du et al. 2007). In such context, reactor staging is widely used where treatment norms are achieved by connecting two or more reactors in series with the first reactor operating at high carbon source loads and the last reactor performing the final polishing. Staging increases treatment performance (Pinto et al. 2010a) as it resembles a plug flow reactor. An increase in the reactor volume results in a decrease of the power density due to an increase of the internal resistance with the volume of the reactor (Clauwaert et al. 2008). Thus, stacking smaller MFCs in series and parallel is a way to increase voltage and current densities.

As any other electrical voltage source, the electrical power produced by the MFCs suffers dramatic losses when the external resistance does not match the value of the internal resistance of the reactor. For this reason, research has been devoted to tracking internal resistance in MFCs by adjusting the external resistance (Woodward et al. 2010). However, the external resistance cannot be changed in practical applications. Recent works have demonstrated that intermittent connection counteracts considerable losses in power output as compared to MFC operation with fixed external resistance (Grondin et al. 2012), particularly when operating at values of the external resistance which were below the internal resistance. While previous works study the effect of time connection and switching frequency experimentally (Gardel et al. 2012, Grondin et al. 2012, Coronado et al. 2013a), there is still a lack of an engineering tool useful to further extend the understanding of the periodic operation effect on MFC performance. Few studies have considered the effect of the connection time and switching frequency in the MFC performance and microbial structure. In this way, MFC dynamic modelling could shed some light in the subject and be used for developing MFC-based treatment systems with high volumetric power output.

The significant charge storage capacity of electrochemically active biofilms (Schrott et al. 2011) results in a complex non-linear behavior during intermittent connection of the external resistance in MFCs. This results in a combination of fast, i.e. time constants in the order of milliseconds, charge/discharge dynamics with much slower dynamics of microbial biofilm growth and decay, i.e. time constants in the order of hours to days. Such behavior has not been described by previous MFC models (Recio-Garrido et al. 2016a). Taking that into account, this study presents a combined bioelectrochemical-electrical (CBE) model of an MFC obtained by combining fundamental equations based on mass and electron balances with equations describing an equivalent electrical circuit. Accordingly, the presented CBE model describes both fast (milliseconds) and slow (hours and days) MFC dynamics and is used to describe the behavior of two staged MFCs operated under periodic connection of the external resistance. Steady-state values are used to study the effect of connection time ratio and switching frequency on MFC performance.
2. MATERIALS AND METHODS

2.1 MFC Design and Operation

Experiments were conducted in two membraneless air-cathode MFCs with an anodic compartment volume of 50 mL. The two MFCs were connected in series, i.e., the effluent of the first reactor was the influent of the second reactor. MFC design and operating conditions are provided elsewhere (Coronado et al. 2013a).

Throughout the tests, the two MFCs were operated using intermittent connection or pulse-width modulated connection of the external resistor (R-PWM mode). Each MFC was electrically independent. Such operation involved connecting the external resistor \( R_{ext} \) to MFC terminals with a low resistance (<0.4 \( \Omega \)) electronic switch (ADG801, Analog Devices Inc.). The switch was computer-controlled using a Labjack U3-LV data acquisition board (LabJack Corp., Lakewood, CO, USA). The data acquisition board was used to record MFC voltage at a maximum rate of 22,500 scans s\(^{-1}\). More details are provided in Coronado et al. (2013a).

2.2 Numerical Methods and Calculations

Matlab R2014a (Mathworks, Natick, MA, USA) was used for all calculations. Parameter estimation was performed using the \textit{fmincon} subroutine of the Matlab Optimization Toolbox\textsuperscript{TM} and the model equations were solved using a variable order integration method for stiff differential equations (\textit{ode15s}). Additional information can be found elsewhere (Recio-Garrido et al. 2016b, Pinto et al. 2010b). On-line estimations of the equivalent circuit model parameters were carried out using the algorithm described by Coronado et al. (2013b).

3. RESULTS AND DISCUSSION

3.1 Model Formulation and Structure

The CBE model structure (Fig. 1) was obtained by combining equations describing microbial, carbon source and electron balances of the bioelectrochemical model developed by Pinto et al. (2010b) with equations describing the equivalent electrical circuit (EEC) of a MFC presented by Coronado et al. (2013a). The EEC model only accounts for the internal capacitance and resistance of the anode thus lacking biomass and carbon source material balances. CBE model assumptions are inherited from Pinto et al (2010).

Similar to the EEC model, internal resistance \( R_1 \) represents the electrolyte ohmic resistance, while a resistor/capacitor circuit is included to describe the internal capacitance \( C \) and the activation losses \( R_2 \). Accordingly, MFC internal resistance \( R_{int} \) is defined as

\[
R_{int} = R_1 + R_2. \tag{1}
\]

MFC mass balances are given by the following equations:

\[
\frac{ds}{dt} = -q_e X_e - q_m X_m + D(S_{in} - S), \tag{2}
\]

\[
\frac{dX_e}{dt} = \left( \mu_e - K_{d,e} - \alpha_e D \right) X_e, \tag{3}
\]

\[
\frac{dX_m}{dt} = \left( \mu_m - K_{d,m} - \alpha_m D \right) X_m, \tag{4}
\]

\[
\frac{dM_{ox}}{dt} = -Y q_e + \gamma \frac{l_{cell}}{mFV X_e}, \tag{5}
\]

Where \( S \) is the substrate (acetate) concentration consumed by the electricigenic bacteria \( X_e \), capable of producing electricity by means of an intracellular mediator \( M_{int} \), or by the methanogenic archaea \( X_m \) that produce methane. \( S_{in} \) is the input substrate concentration, \( D = \text{Fin}/V \) is the dilution rate with the input flow rate \( F_{in} \) and the volume of the anodic compartment \( V \). \( K_a \) is the microbial decay rate, \( \gamma \) is the yield of oxidized mediator, \( \gamma \) is the mediator molar mass, \( m \) is the number of electrons transferred, \( F \) is the Faraday constant and \( I_{cell} \) is the current produced by the MFC. The corresponding microbial growth rates \( \mu \) and substrate consumption rates \( q \) are defined using multiplicative Monod kinetics as follows:

\[
\mu_e = \mu_{\text{max},e} \left( \frac{S}{K_{s,e}+S} \right) \left( \frac{M_{ox}}{K_{M}+M_{ox}} \right), \tag{6}
\]

\[
q_e = q_{\text{max},e} \left( \frac{S}{K_{s,e}+S} \right) \left( \frac{M_{ox}}{K_{M}+M_{ox}} \right), \tag{7}
\]

\[
\mu_m = \mu_{\text{max},m} \left( \frac{S}{K_{s,m}+S} \right), \tag{8}
\]

\[
q_m = q_{\text{max},m} \left( \frac{S}{K_{s,m}+S} \right), \tag{9}
\]

with \( K_s \) and \( K_M \) the Monod half rates for the substrate and oxidized mediator terms, respectively.

Fig. 1. Schematic diagram of the CBE model for MFCs presented in Recio-Garrido et al. (2016b).
The biomass retention parameter $\alpha$ used to represent the limiting effect of the biofilm in the microorganisms concentration is defined by the empirical expression

$$\alpha = \frac{1}{2} \left[ 1 + \tanh \left( K_e (X_e + X_m - X_{\text{max}}) \right) \right],$$  \hspace{1cm} (10)

where $K_e$ is a steepness factor and $X_{\text{max}}$ is the maximum microbial concentration in the biofilm.

The electrochemical balance is given by

$$I_{\text{cell}} = \frac{e_{\text{conc}} - e_{\text{conc}}^{\text{OC}} - V_c}{R_{\text{ext}} + R_{1}} \left( M_{\text{red}} - M_{\text{ox}} \right),$$  \hspace{1cm} (11)

Where $E_{\text{oc}}$ is the open circuit voltage, $V_c$ is the voltage at the capacitor, $R_{\text{ext}}$ is the external resistance applied to the MFC, $M_{\text{red}}$ is the reduced oxidized mediator concentration and $\varepsilon$ is the parameter for the Monod-like term which limits calculated MFC current at low values of $M_{\text{red}}$. The concentration losses $\eta_{\text{conc}}$ are defined as

$$\eta_{\text{conc}} = \frac{R_T m_p}{m_p} \ln \left( \frac{M_{\text{total}}}{M_{\text{red}}} \right),$$  \hspace{1cm} (12)

$$M_{\text{total}} = M_{\text{ox}} + M_{\text{red}}.$$  \hspace{1cm} (13)

with $R$ the ideal gas constant, $T$ the temperature of the MFC and $M_{\text{total}}$ the total concentration of intracellular mediator. Also, the following dynamic equation is used to describe the voltage at the internal capacitor:

$$\frac{dV_c}{dt} = \frac{1}{C} \left( I_{\text{cell}} - \frac{V_c}{R_{\text{int}} + 2} \right),$$  \hspace{1cm} (14)

The following empirical expressions were derived based on previously obtained experimental results (Pinto et al. 2010, Grondin et al. 2012, Coronado et al. 2013a) and are used to describe the dependence of the internal resistances $R_1$ and $R_2$, the internal capacitance $C$, and the open circuit voltage $E_{\text{oc}}$ on the anodic biofilm:

$$R_1 = R_{\text{min1}} + (R_{\text{min1}} - R_{\text{max}}) e^{-K_e X_e},$$  \hspace{1cm} (15)

$$R_2 = R_{\text{min2}} + (R_{\text{min2}} - R_{\text{max}}) e^{-K_e X_e (\frac{S}{S+3})},$$  \hspace{1cm} (16)

$$E_{\text{oc}} = E_{\text{oc, min}} + \left( E_{\text{oc, min}} - E_{\text{oc, max}} \right) e^{K_e X_e (\frac{S}{S+3})},$$  \hspace{1cm} (17)

$$C = C_{\text{min}} + (C_{\text{min}} - C_{\text{max}}) e^{K_e X_e (\frac{S}{S+3})},$$  \hspace{1cm} (18)

where $K_e$ is a steepness factor, $\text{min}$ and $\text{max}$ indicate the minimum and maximum values for the variables and $\xi$ is the parameter for the Monod-like term which links the EEC electrical variables to the substrate concentration.

Output electrical voltage and power are given by the following expressions:

$$V_{\text{cell}} = I_{\text{cell}} R_{\text{ext}},$$  \hspace{1cm} (19)

$$P_{\text{cell}} = V_{\text{cell}} R_{\text{ext}}.$$  \hspace{1cm} (20)

Finally, the rate of methane production, $Q$, by methanogenic microorganisms is assumed to be proportional, with yield $Y_{\text{CH}_4}$, to the substrate consumption rate by this trophic group

$$Q = Y_{\text{CH}_4} q m X_m V.$$  \hspace{1cm} (21)

The CBE model (1-21) describes fast and slow MFC dynamics in both MFCs. State variables, inputs and outputs of the model are summarized in Table 1. A more detailed description of the bioelectrochemical model can be found in Pinto et al. (2010b) and Recio-Garrido et al. (2016b).

### Table 1. State variables, inputs, outputs and estimated parameters for the CBE model.

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Units</th>
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<tbody>
<tr>
<td><strong>State variables</strong></td>
<td></td>
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<tr>
<td>Substrate</td>
<td>$S$</td>
<td>mg-S L$^{-1}$</td>
</tr>
<tr>
<td>Exoelectrogenic</td>
<td>$X_e$</td>
<td>mg-X L$^{-1}$</td>
</tr>
<tr>
<td>Methanogenic</td>
<td>$X_m$</td>
<td>mg-X L$^{-1}$</td>
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<tr>
<td>Oxidized mediator</td>
<td>$M_{\text{ox}}$</td>
<td>mg-M L$^{-1}$</td>
</tr>
<tr>
<td>Capacitor voltage</td>
<td>$V_c$</td>
<td>V</td>
</tr>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate</td>
<td>$F_{\text{in}}$</td>
<td>L d$^{-1}$</td>
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<tr>
<td>Input substrate</td>
<td>$S_{\text{in}}$</td>
<td>mg-S L$^{-1}$</td>
</tr>
<tr>
<td>External resistance</td>
<td>$R_{\text{ext}}$</td>
<td>$\Omega$</td>
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<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>$S$</td>
<td>mg-S L$^{-1}$</td>
</tr>
<tr>
<td>Voltage</td>
<td>$V_{\text{cell}}$</td>
<td>V</td>
</tr>
<tr>
<td>Methane production</td>
<td>$Q$</td>
<td>mL d$^{-1}$</td>
</tr>
<tr>
<td><strong>Estimated parameters</strong></td>
<td></td>
<td></td>
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<tr>
<td>Yield in (5)</td>
<td>$Y$</td>
<td>mg-M mg-S$^{-1}$</td>
</tr>
<tr>
<td>Consumption rate</td>
<td>$q_{m,e}$</td>
<td>mg-S mg-X$^{-1}$ d$^{-1}$</td>
</tr>
<tr>
<td>Steepness in (15-18)</td>
<td>$K_e$</td>
<td>L mg-X$^{-1}$</td>
</tr>
<tr>
<td>Monod half rate (16-18)</td>
<td>$\xi$</td>
<td>mg-S L$^{-1}$</td>
</tr>
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### 3.2 Parameter Estimation

To estimate model parameters, the difference between model simulations and the corresponding experimentally measured values was minimized. Thus, experimental values for the effluent concentration $S$ and voltage produced $V_{\text{cell}}$ were used for parameter estimation (Fig. 2). Additionally, on-line estimations using the EEC model (Coronado et al. 2013b) provided values for the open circuit voltage $E_{\text{oc}}$ and internal resistance $R_1$ (data not shown) that were also used during the optimization problem. A set of experimental data was used for parameter estimation and another set for model validation.

Experimentally, the input flow rate was maintained so that the total hydraulic retention time (HRT) within the two staged MFCs was about 6 h and the input substrate concentration was subjected to step-wise changes (Fig. 2 A). Also, the external resistance was set to $5 \Omega$ for the first MFC and $10 \Omega$ for the second MFC and controlled using the intermittent model of operation (R-PWM) at 100 Hz of switching frequency and a $90 \%$ connection time ratio. The connection time ratio (also called duty cycle) represents the ratio between the time when the circuit is connected with respect to the total cycle time.

Because of the limited number of measurable variables, the confidence intervals obtained from the Fisher information matrix were used to select parameters that can be estimated with an acceptable accuracy (Recio-Garrido et al. 2016b). The selected parameters for estimation were $Y$, $q_{m,e}$, $K_e$ and $\xi$. It should be mentioned that no methane production was observed during the experiments due to the operational
conditions favoring growth of the electricigenic bacteria (Kaur et al. 2014). Accordingly, equation (4) was not considered for parameter estimation and all the parameters related to the methanogenic population were taken from previous experiments where methane production was measurable (Pinto et al. 2010b). Any other parameters remaining were not considered because either they presented negligible magnitude effects on the outputs or their values could be assumed (e.g. physical constants) or experimentally measured and did not need to be re-estimated.

The estimated values of $Y$ in mg-M mg-S$^{-1}$, $q_{\text{max.e}}$ in mg-S mg-X$^{-1}$ d$^{-1}$, $K_r$ in L mg-X$^{-1}$, and $\xi$ in mg-S L$^{-1}$ for the models representing the two staged MFCs are 24.7, 16.87, 0.0198, and 14.85, respectively for the first MFC and 73.8, 15.0, 0.027, and 1.9, respectively, for the second MFC (units are indicated in Table 1). To evaluate the estimation accuracy, the confidence intervals were calculated. Assuming a 95% confidence level, the intervals of confidence were 3.7 %, 3.8 %, 0.039 % and 6.8 % for $Y$, $q_{\text{max.e}}$, $K_r$, and $\xi$, respectively for the first MFC and 8.5 %, 0.4 %, 0.1 % and 3.7 %, respectively for the second MFC. Such values are acceptable considering the complex microbial dynamics and the relatively small number of estimated model parameters.

On the other hand, parameters included in the empirical equations (15–18) were manually selected based on the results of the on-line estimation procedure (results not shown). Accordingly, parameters $R_{\text{max}}$, $R_{\text{min}}$, and $R_{\text{end2}}$ in (15) and (16) were set to 1,000 $\Omega$, 0.97 $\Omega$ and 3.01 $\Omega$ for the first MFC and to 1,000 $\Omega$, 2.27 $\Omega$ and 8.64 $\Omega$ for the second MFC, respectively. Also, parameters $E_{\text{max}}$ and $E_{\text{min}}$ in Eq. (17) were set to 0.26 V and 0.01 V for the first MFC and 0.35 V and 0.01 V for the second MFC, respectively. Finally, parameters $C_{\text{max}}$ and $C_{\text{min}}$ in Eq. (18) were set to 0.61 F and 0.01 F for the first MFC and 0.49 F and 0.01 F for the second MFC, respectively, based on the estimated capacitance values obtained during MFC startup and operation. Other parameters were taken from Pinto et al. (2010b).

Figure 2 compares model simulations with the corresponding measurements. The first part of experimental results corresponding to days 0 to 9 of operation was used for parameter estimation and the remaining set of data for model validation. Effluent acetate concentrations were well described by the model at all influent concentrations (Fig. 2 A). MFC output voltage was observed to depend on the influent acetate concentration (organic load) with voltage drops during low load operation (days 7 to 10, Fig. 2B). Effluent concentrations and voltage trends were correctly described with MSE values of 0.59 and 48.1 for the first MFC and 3.1 and 10.6 for second MFC, respectively for the effluent concentration and the output voltage experimental profiles, considering the two data sets. Concerning the microbial population, the profile of the concentration for the electricigenic bacteria showed a population decrease during the low influent concentration while attaining a plateau during substrate-replete conditions. This effect was especially notable in the case of the second MFC. Additionally, the model provided an adequate description of the intermittent output voltage during pulse-width modulated connection of $R_{\text{ext}}$. Fig. 2 C shows a zoom at the end of the 13th day.

A few recent publications show experimental results obtained from operating MFCs in an intermittent connection of the external resistance (Gardel et al. 2012, Grondin et al. 2012, Coronado et al. 2013a). Interestingly, in Gardel et al. (2012) microbial communities were found to be unaffected by such periodic operation in a broad range of switching frequencies. At the same time, MFC operation at different values of fixed external resistances was observed to result in different microbial populations (Lyon et al. 2010). However, the effect of the connection time ratio and switching frequency on the MFC performance still needs a deeper understanding. In this work, the CBE model is used to qualitatively study the effect of those two variables in the microbial distribution and substrate consumption as well as in the electrical performance of MFCs. All the parameter values are the same ones as used for the first MFC in section 3.2 and the minimum value of the applied external resistance is 5 $\Omega$.

Figure 3 shows the average steady-state values of the effluent, electricigenic and methanogenic concentrations as a function of the connection time ratio and for two different switching frequencies. Additionally, the upper x-axis represents the apparent external resistance seen by the MFC as if it were operated in a continuous mode. Exoelectricigenic bacteria demonstrate highest concentration at low values of the apparent external resistance (high connection time ratio)
while methanogenic bacteria proliferate in the regions where the external resistance is at its highest value (low connection time ratio). It can be observed that the effluent substrate concentration presents a maximum (lowest substrate consumption by the microorganisms) at around 30% duty cycle, the coexistence region between the two microbial populations. This result was already shown for the continuous operation mode in Pinto et al. (2010a). The increase of the switching frequency shifts all the profiles toward the left (or always disconnected region), thus expanding the range favorable to the electricigenic bacteria.

3.4 Simulation Example: Effluent Quality Control for two Staged MFCs

In parallel to investigating MFC staging, control strategies need to be developed in order for the process to counteract the unpredictable fluctuations in the environment that can directly affect its performance (Oh et al. 2010). Current control strategies only deal with the control of the electrical component in MFCs (Recio-Garrido et al. 2016a) while completely disregarding the treatment performance of MFCs. Their application to staged MFCs could result in failure of the process due to downstream MFC starvation. Control strategies dealing with the electrical and treatment performance of staged MFCs are expected to ensure a more stable operation.

This work presents a very simple control strategy (Fig. 5) to ensure the effluent quality control in two staged MFCs consisting on: (i) A PID controller that manipulates the treatment flow, and (ii) an ON/OFF controller that manipulates the connection time ratio in MFC 1 by switching from connected at a 90% duty cycle to fully disconnected. Both controllers consider the error with respect to the desired effluent concentration.
The operational conditions and the parameters presented in section 3.2 are used for the simulation. Under no other ground than to speed the simulation, a switching frequency of 0.1 Hz is used. The two controllers are discretized with sampling periods of 5 min for the ON/OFF controller and 10 min for the PID controller. The PID controller is used in discrete incremental form tuned at 2.5 mL d⁻¹, 240 min and 0 min for $K_c$, $\tau_1$ and $\tau_0$, respectively. The treatment flow presents lower and upper boundaries set at 0.1 L d⁻¹ and 0.5 L d⁻¹, respectively. Remark that the ON/OFF controller only acts when the error in the desired effluent is positive. Otherwise the effect of the ON/OFF controller would contribute to increase the error because an electrical disconnection of the first MFC results in a greater amount of substrate going into the second MFC.

Figure 6 shows a simulation of the performance of such control strategy after a sudden decrease of 33% in the influent concentration followed by an increase of 100% of the effluent desired concentration (set-point). It can be observed that the effect of the ON/OFF controller introduces oscillations in the effluent concentration with respect to the set point (lower than a 5% variation) but improves dramatically the disturbance rejection capability (5-25 h) and increases the response speed during regulation (at 30 h). Additionally, the treatment flow remains more stable around the initial value which can be desirable in wastewater treatment applications.

Fig. 6. Comparison of the effluent quality control performance on two staged MFCs using a PID to manipulate the treatment flow alone (blue) or with the help of an ON/OFF controller to manipulate the connection time in MFC 1 (red).

4. CONCLUSIONS

The CBE model adequately describes MFC dynamics under periodic connection/disconnection of the external resistance and represents a useful tool for simulation of staged MFCs. Such an engineering tool can be used for the study of the effect of connection time and switching frequency on MFC performance. The apparent external resistance obtained by changing the time of connection and the switching frequency has been found to affect the distribution of the effluent and microbial populations as well as the electrical performance of MFCs.

REFERENCES