FORMULATION AND PRELIMINARY APPLICATION OF AN INTEGRATED MODEL OF MICROBIAL FUEL CELL PROCESSES

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ABSTRACT

Microbial Fuel Cells (MFCs) are bioelectrochemical systems that directly convert chemical energy contained in organic matter bioconvertible substrate into electrical energy. Since the mid-90's, researchers have attempted to simulate the bioelectrochemical activity of MFCs: in this paper, in order to develop an enhanced model capable of describing a complex bacterial community, such as that of a MFC, an earlier model formulated by Pinto et al. (2010) has been integrated with the ASM2d model, representing complex biological systems with multiple substrates (Henze et al., 2013). The resulting model is herein described, together with its application to long series of MFC operational data. Results are discussed, confirming the good performance of the new model.

INTODUCTION

Microbial Fuel Cells (MFCs) are bioelectrochemical systems that directly convert the chemical energy contained in bioconvertible organic matter substrate into electrical energy. For this to happen, exoelectrogenic bacteria catalyze one, or both, reactions occurring at the electrodes, that is, substrate oxidation at the anode and oxidant reduction at the cathode (Rabaey and Verstraete, 2005). When wastewater containing organic matter is used as anode fuel, the MFC effectively performs wastewater treatment while recovering energy, thus leading to the future possibility of designing energy-producing wastewater treatment plants.

Several practical issues remain still to be solved, before MFC systems can be deemed ready for full-scale practical applications: among them, the reduction of the systems' internal resistance, that would allow higher substrate-electricity conversion rates, cathode technology improvements, efficient, scalable, design, and reduction of electrochemical losses (Capodaglio et al., 2015). Deeper process understanding and its mathematical reproducibility can also play an important role in the quest for improvement of this technology.

Since the mid-90's, researchers have attempted to simulate the bioelectrochemical activity of MFCs: Zhang and Halme (1995) proposed a simple model based on a single anodic population and focused on the generated power in relationship to substrate concentration and cathodic-chamber mediator. Later, models by Kato Marcus et al. (2007) were developed, neglecting the contribution of the mediator, but considering a complex bacterial population composed by exoelectrogen and non-exoelectrogen species. In the same year, Picioreanu et al. (2007) proposed a 3-dimensional model considering both adhese and suspended microorganisms. Zheng et al., (2010) developed a dual-chamber MFC model that simulated transient conditions, including cathodic compartment reactions, while Pinto et al. (2010) published a 2-population, anodic dynamic model representing the competition between exoelectrogens and methanogens. In 2013, Oliveira et al. proposed a steady-state MFC model, focusing on the effect of some parameters such as: cell temperature, substrate concentration, biofilm thickness and current density.

In this paper, in order to develop an enhanced model capable of describing a complex bacterial community, such as that of a MFC, as well as the complexity of feed substrates, the model by Pinto et al. (2010) has been integrated with the ASM2d model (Henze et al., 2013). The resulting model is herein described, together with its application to long series of MFC operational data. Results are discussed, confirming the good performance of the new model.

SELECTION OF THE BASIC MFC MODEL

Table 1 summarizes the characteristics of MFC models published in the literature.

Table 1. Literature-reported models summary

Model	Compartment	Mediator	Species	Time resolution	Space resol.
Zhang e Halme,1995	Anodic	Yes	Single	Dynamic	1D
Marcus et al., 2007	Anodic	No	Multiple	Dynamic	1D
Oliveira et al., 2013	Anodic/ cathodic	No	Single	Steady st.	1D
Picioreanu et al., 2007	Anodic	Yes	Multiple	Dynamic	3D
Zeng et al., 2010	Anodic/ cathodic	No	Single	Dynamic/ Steady st.	1D
Pinto et al., 2010	Anodic	Yes	Multiple	Dynamic	1D

The model herein proposed is based on the previous work by Pinto et al. (2010): theirs, as shown in the Table above is a dynamic, 1-dimensional (completely mixed), multi-species model. It considers the presence of two microbial populations in the anodic chamber: exoelectrogen and methanogenic microorganisms co-existing in competition for available substrate, as observed by the authors in previous studies (Molognoni et al., 2015). The

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presence of an endogenous mediator, either in reduced or oxidized form is responsible for the extracellular electronic transfer by exoelectrogenic bacteria. It is assumed that these bacteria adhere to the anode as a biofilm, while methanogenic ones can be both suspended or adhese. The model focuses on the anodic compartment, assuming that dynamics at the cathode's end are nonlimiting (Figure 1).

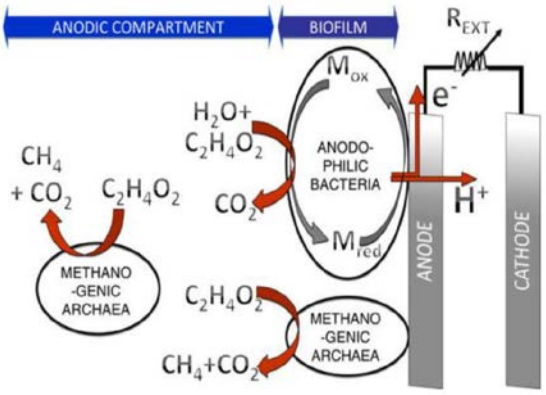

Figure 1. Conceptual model (Pinto et al, 2010)

The model therefore describes:
-substrate (S_a) oxidation to CO_2 by exoelectrogens (X_a), with reduction of the mediator: ($M_{ox} \rightarrow M_{red}$)
- mediator reoxydation, with release of free electrons and protons: $M_{red} \rightarrow M_{ox} + e^- + H^+$
-methane and carbon dioxide production by methanogens: $S_a \rightarrow CH_4 + CO_2$
The above can be expressed by the following mass balance equations (Eqs. 1-3):

$$\frac{dS_a}{dt} = -q_a x_a - q_m x_m + D(S_{a0} - S_a) \quad (1)$$

$$\frac{dx_a}{dt} = \mu_a x_a - K_{d,a} x_a - \alpha_a D x_a \quad (2)$$

$$\frac{dx_m}{dt} = \mu_m x_m - K_{d,m} x_m - \alpha_m D x_m \quad (3)$$

where D=1/(retention time in anodic chamber) [t^{-1}]; q_a, q_m substrate conversion rates for exoelectrogens and methanogens; μ_a, μ_m (Monod) growth rates, and K_{da} , α_a bacterial endogenous decay and washout coefficients, respectively. Monod kinetics are assumed for bacteria: specifically, exoelectrogens' growth is limited by both substrate (acetate) and oxidized mediator concentrations, while methanogens' only by acetate's.
Pinto et al. assume that biomass growth occurs in two phases: growth, during which there is no microorganism dispersion/washout (α_a = 0), and steady state, where a dynamic equilibrium between growth, endogenous decay and washout is established. A switch in the model converts between modes. Total mediator's concentration (in reduced AND oxidized forms) is assumed constant in the system.
One of the most important aspects in the characterization of MFCs performance, is the electric current that they produce: in the model of Pinto et al., this is calculated from the cell's tension through Ohm's First Law: $E_{cell} = I_{MFC} R_{ext}$.

The electromotive force (Equation 4) is considered equal to the Open Circuit Voltage od the cell, neglecting activation losses:

$$I_{MFC} = \frac{(E_{OCV} - \eta_{conc})}{(R_{ext} + R_{int})} \left(\frac{M_{red}}{\varepsilon + M_{red}}\right) \quad (4)$$

Methane production is calculated as proportional to acetate uptake through a specific yield coefficient, Y_{CH4}:

$$Q_a = Y_{CH4}\, q_m\, X_m\, V \quad (5)$$

While this model has the advantage of representing the ongoing competition between exoelectrogen and methangenic populations in the anodic chamber, at the same time it completely neglects the fact that other bacterial species (e.g. heterotroph bacteria) can be present in the cell, as well. Furthermore, the model only considers acetate as the only substrate present: in reality, especially when MFCs are applied to the treatment of urban/industrial wastewaters, the composition of the incoming substrate will be much more complex.

MODEL INTEGRATION

In order to compensate the above mentioned shortcomings, therefore, it was decided to modify the model by integrating in its structure elements of the well-known ASM2d model (Henze et al., 1999).
ASM2d was designed to simulate the processes normally occurring in traditional activated sludge models, such as degradation of organic compounds, and N and P removal, both by aerobic (oxygen as electron acceptor) and anaerobic/anoxic (nitrates and other compounds as electron acceptors). The model considers basic substrate measured as COD (Chemical Oxygen Demand), although in diverse forms.
In the ASM2d model, substrate id expressed as COD in particulate (X) and soluble (S) forms: S_f substrate that can be fermented to S_a (acetate), inert substrate, S_i and X_i, slowly degradable particulate, X_s, nitrogenous, S_{NO3}, and ammonia, S_{NH4} matter.
Although, in theory, heterotrophic, autothrophic (nitrifiers) and phosphate-accumulating bacteria can be present in wastewater treatment plants, the presence of heterotrophs was herein considered since, due to their characteristics, they are more likely to be present in a MFC's anodic chamber. For the same reason, bio-P accumulation processes are not represented in the integrated model. All the degradation processes present in ASM2d can be represented by Monod-type kinetics. The equations describing the model can therefore be written as:

$$\frac{dS_a}{dt} = -\frac{1}{Y_H}\rho_7 X_H + \rho_8 X_H \quad (6)$$

$$\frac{dX_S}{dt} = -\rho_2 X_H - \rho_3 X_H + (1 - f_{XI})\rho_9 \quad (7)$$

$$\frac{dS_{NH4}}{dt} = \upsilon_{NH4}(\rho_2 + \rho_3) X_H \quad (8)$$

$$\frac{dS_I}{dt} = f_{SI}(\rho_2 + \rho_3) X_H \quad (9)$$

$$\frac{dX_H}{dt} = \rho_6 X_H + \rho_7 X_H - \rho_9 \quad (10)$$

$$\frac{dS_f}{dt} = (1 - f_{SI})(\rho_2 + \rho_3) X_H - \frac{1}{Y_H}\rho_6 X_H - \rho_8 X_H \quad (11)$$

$$\frac{dX_I}{dt} = f_{XI}\rho_9 \quad (12)$$

$$\frac{dS_{NO3}}{dt} = -\frac{1-Y_H}{2.86 Y_H}(\rho_6 + \rho_7) X_H \quad (13)$$

$$\frac{dS_{N2}}{dt} = \frac{1-Y_H}{2.86 Y_H}(\rho_6 + \rho_7) X_H \quad (14)$$

where the constants ρ_i are represented by:

$$\rho_1 = K_h \frac{S_{O2}}{K_{O2}+S_{O2}} \frac{\frac{X_S}{X_H}}{K_{x,S}+\frac{X_S}{X_H}} \quad (15)$$

$$\rho_2 = K_h \eta_{NO3,i} \frac{K_{O2}}{K_{O2}+S_{O2}} \frac{S_{NO3}}{K_{NO3}+S_{NO3}} \frac{\frac{X_S}{X_H}}{K_{x,S}+\frac{X_S}{X_H}} \quad (16)$$

$$\rho_3 = K_h \eta_{fe} \frac{K_{O2}}{K_{O2}+S_{O2}} \frac{K_{NO3}}{K_{NO3}+S_{NO3}} \frac{\frac{X_S}{X_H}}{K_{x,S}+\frac{X_S}{X_H}} \quad (17)$$

$$\rho_4 = \mu_h \frac{S_{O2}}{K_{O2}+S_{O2}} \frac{S_f}{K_f+S_f} \frac{S_f}{S_f+S_a} \frac{S_{NH4}}{K_{NH4}+S_{NH4}} \frac{S_{alk}}{K_{alk}+S_{alk}} \quad (18)$$

$$\rho_5 = \mu_h \frac{S_{O2}}{K_{O2}+S_{O2}} \frac{S_a}{K_a+S_a} \frac{S_a}{S_f+S_a} \frac{S_{NH4}}{K_{NH4}+S_{NH4}} \frac{S_{alk}}{K_{alk}+S_{alk}} \quad (19)$$

$$\rho_6 = \mu_h \eta_{NO3} \frac{K_{O2}}{K_{O2}+S_{O2}} \frac{S_{NO3}}{K_{NO3}+S_{NO3}} \frac{S_f}{K_f+S_f} \frac{S_f}{S_f+S_a} \frac{S_{NH4}}{K_{NH4}+S_{NH4}} \frac{S_{alk}}{K_{alk}+S_{alk}} \quad (20)$$

$$\rho_7 = \mu_h \eta_{NO3} \frac{K_{O2}}{K_{O2}+S_{O2}} \frac{S_{NO3}}{K_{NO3}+S_{NO3}} \frac{S_a}{K_a+S_a} \frac{S_a}{S_f+S_a} \frac{S_{NH4}}{K_{NH4}+S_{NH4}} \frac{S_{alk}}{K_{alk}+S_{alk}} \quad (21)$$

$$\rho_8 = q_{fe} \frac{K_{O2}}{K_{O2}+S_{O2}} \frac{K_{NO3}}{K_{NO3}+S_{NO3}} \frac{S_f}{K_f+S_f} \frac{S_a}{S_f+S_a} \frac{S_{alk}}{K_{alk}+S_{alk}} \quad (22)$$

$$\rho_9 = b_h X_H \quad (23)$$

Model integration therefore resulted in:
-a combined equation (Eqs. 1+6) for S_a

$$\frac{dS_a}{dt} = -q_a x_a - q_m x_m + D(S_{a0} - S_a) - \frac{1}{Y_H}\rho_7 X_H + \rho_8 X_H \quad (24)$$

-addition of the inflow term for all COD components (S_a, S_i, S_f, X_i, X_s), i.e, for S_f

$$\frac{dS_f}{dt} = (1 - f_{SI})(\rho_2 + \rho_3) X_H - \frac{1}{Y_H}\rho_6 X_H - \rho_8 X_H + \boldsymbol{D(S_{f0} - S_f)} \quad (25)$$

-addition of the lysis component for all microorganism in the X_s and X_i mass balance equations;
-addition of the washout coefficient for heterotrophs:

$$\frac{dX_H}{dt} = \rho_6 X_H + \rho_7 X_H - \rho_9 - \boldsymbol{\alpha_h D x_h} \quad (26)$$

The effects of aerobic activity of heterotrophs have also been included in the model, considering a small influent oxygen concentration (S_{O2} = 2 mg/L), and the diffusive oxygen transfer from the cathode to the anodic chamber through the ion exchange membrane, by means of an oxygen mass balance equation:

$$\frac{dS_{O2}}{dt} = \left(1 - \frac{1}{Y_H}\right)(\rho_4 X_H + \rho_5 X_H) + D(S_{O20} - S_{O2}) \quad (27)$$

In the original model by Pinto et al., internal resistance (R_{int}), and Open Circuit Voltage (E_{OCV}), are represented as constant values to be declared as initial conditions. In the integrated model, however, their dynamic formulas have been included, in order to better correlate their values with the actual concentration of exoelectrogens estimated at any time in the cell:

$$R_{int} = R_{min} + (R_{max} - R_{min}) e^{-K_r X_a} \quad (28)$$

$$E_{OCV} = E_{min} + (E_{max} - E_{min}) e^{-K_r^{-1} X_a^{-1}} \quad (29)$$

The resulting, integrated MFC model was then implemented in MATLAB environment, and the representing differential equations solved by means of the MATLAB ode23t function.

MODEL APPLICATION AND RESULTS

The model was applied to the observations gathered from an intensely monitored, dual chamber, laboratory MFC with anodic volume of 0.42 L, continuously fed with swine wastewater at 1.5 L/d, operating in steady state at 21°C for a prolonged period (Molognoni et al., 2014). A subset of these data was used to initially calibrate the integrated model.
Initially, literature-reported parameter values were selected. If these were not available, "reasonable" best estimates (guesses) were used. A Least Squares estimation method was subsequently applied to determine more significative values based on the experimental observations's initial subset.
The calibrated model was then applied to the observed experimental series.
Figure 2 shows the simulated temporal trend of the exoelectrogen, methanogen and heterotropic populations in the MFC, over time. After day 53 (when a decrease in COD load from 11.2 kg/m^{3}d to 5.3kg/m^{3}d occurred, Figure 3), exoelectrogens grow more rapidly than other groups, reaching a concentration of 380 mg/L, against methanogen and heterotroph concentrations decreasing to 80 and 40 mg/L, respectively. The high concentration of exoelectrogenic biomass allows a higher production of electric current, from 11 mA during the previous period to 13 mA when the organic load is lower (Figure 4). All the above results are in general agreement with the experimental observations of actual MFC behavior.

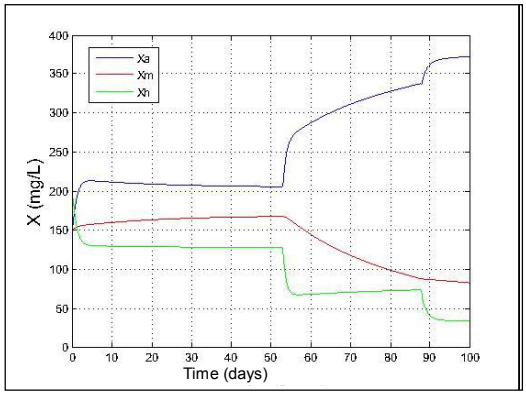

Figure 2. MFC biomass distribution over time

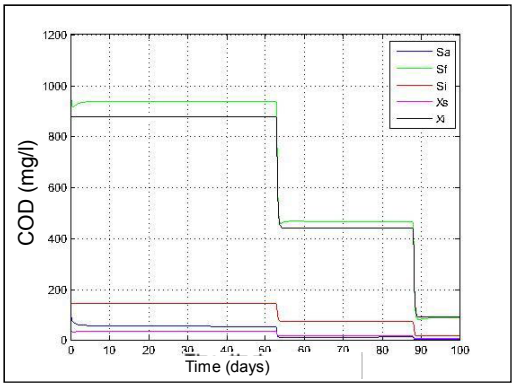

Figure 3. Substrate inflows over time

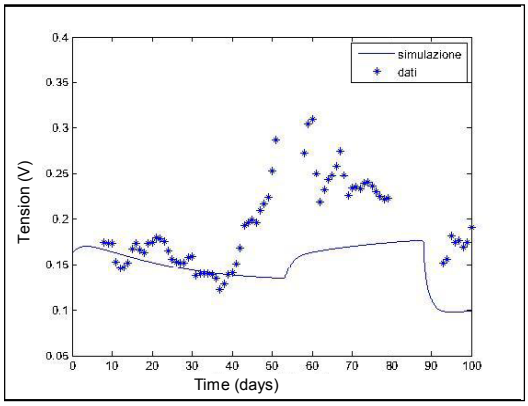

Figure 4. Cell voltage over time

Table 2 reports average measured and simulated COD removal, η_{CODs}, and Coulombic Efficiency (CE) values for the entire simulation period.

Table 2. COD removal and CE values

	η_{CODs} (%)		CE (%)	
period	**observed**	**simulated**	**observed**	**simulated**
I	31 ± 21	23	6 ± 3	6
II	36 ± 10	25	10 ± 2	15
III	33 ± 18	29	39 ± 9	36

CE is a measure of the cell's electric efficiency, consisting in the ratio between the amount of substrate converted to electricity and the total removed in the anodic chamber. Figure 4 shows simulated methane production compared with available observations. Also in this case (although only two values were measured) model results seem in accordance with experimental data.

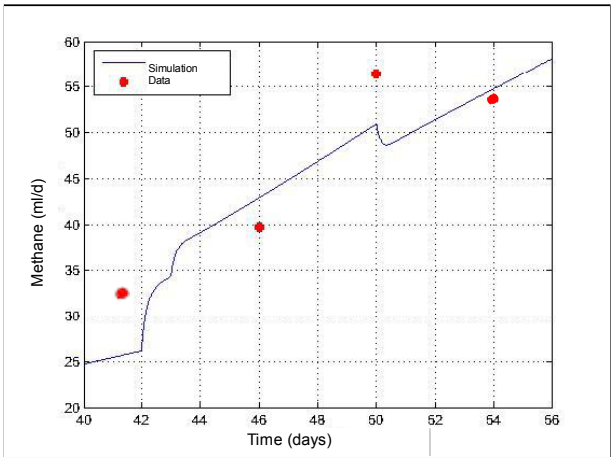

Figure 5. Simulated and observed methane production

The integrated model did not include the retention effect of particulate substrate within the MFC volume: in first approximation, this was in fact assumed as an empty, complete-mixed reactor, while in reality the anodic chamber was filled with granular graphite with the purpose of improving the electric efficiency of its electrode. Addition of a retention term for X_i and X_s will be implemented in a future version with the aim of improving model representation of the actual system simulated.

CONCLUSIONS

An integrated, dynamic, multi-species model for a completely mixed MFC is presented in this paper. The model is obtained by combining the Pinto et al. (2010) model of an acetate-fed MFC, with the ASM2d activated sludge model (Henze et al. 1999), representing biological treatment systems fed by complex substrates. In this way, the presence of various microorganism species (exoelectrogens, methanogens and heterotrophs), and of a complex influent substrate, were taken into account, and their different methabolic processes simulated.

The model was implemented in a MATLAB platform; its equations, solved by a numerical solutor, allowed to reproduce the growth dynamics of microorganisms, organic matter degradation, current and methane production within a MFC. Monitoring observations from a laboratory system were used to calibrate the model and to compare results obtained from the simulations.

Observations and simulation results are reasonably in accordance with each other and with the expected (theoretical) behavior of the system, save for some differences that can be explained by the lack of a

particulate substrate retention term, and limited calibration data availability.

Further improvements of the proposed model are foreseeable. Refinement of the model can be of importance for future studies on MFC behavior, especially in view of their possible, larger scale application. A better understanding of MFC response to operational conditions could eventually lead to a better, more efficient design and their larger scale applicability.

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