

Chapter 2

The Effect of Internal Parameters on Biohydrogen Production in Batch Microbial Electrolysis Cell Reactor

M. Azwar, M. A. Hussain and A. K. Abdul-Wahab

Abstract Production of biohydrogen has the potential to be a renewable energy alternative to current technology. Microbial electrolysis cell (MEC) system is new bio-electrochemical processes that are capable of producing hydrogen gas and has higher efficiency when compared with other processes. This study describes the mathematical model of MEC for hydrogen production from wastewater batch reactor. The model is based on material balances with the integration of bio-electrochemical reactions describing the steady-state behaviour of biomass growth, consumption of substrates, hydrogen production and power current characteristics. The model predicts the concentration of anodophilic, acetoclastic methanogenic and hydrogenotrophic methanogenic microorganisms. In this study the effect of varying changes of initial concentration, effect of stoichiometric and kinetic parameters on MEC in a batch reactor to be used with open-loop identification test. In this model will also be examined effect of competition between the three microbial populations between anodophilic, hydrogenotrophic and acetoclastic.

Keywords Mathematical model • Batch microbial electrolysis cells reactor • Hydrogen gas • Internal parameter

List of Symbols

S	Substrate concentration (mg-S L^{-1})
x_a	Concentration of anodophilic microorganisms
x_m	Concentration of acetoclastic microorganism
x_h	Concentration of hydrogenotrophic microorganisms

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Q_{H_2}	Hydrogen production rate (mL/day)
$q_{max,a}$	Maximum reaction rate of the anodophilic microorganism [mg-A mg-x ⁻¹ d ⁻¹]
$q_{max,m}$	Maximum reaction rate of the acetoclastic methanogenic microorganism [mg-A mg-x ⁻¹ d ⁻¹]
$K_{S,a}$	Half-rate (Monod) constant of the anodophilic microorganism [mg-A l ⁻¹ or mg-M l ⁻¹]
$K_{S,m}$	Half-rate (Monod) constant of the acetoclastic methanogenic microorganism [mg-A l ⁻¹ or mg-M l ⁻¹]
K_M	Mediator half-rate constant [mg-M l ⁻¹]
$K_{d,a}$	Microbial decay rates of the anodophilic microorganism [d ⁻¹]
$K_{d,m}$	Microbial decay rates of the acetoclastic methanogenic microorganism [d ⁻¹]
$K_{d,h}$	Microbial decay rates of the hydrogenotrophic microorganism [d ⁻¹]
K_h	Half-rate constant [mg l ⁻¹]
Y_M	Oxidized mediator yield [mg-M mg-A ⁻¹]
Y_{H_2}	Dimensionless cathode efficiency [dimensionless]
Y_h	Half-rate constant [mg l ⁻¹]
V_r	Anodic compartment volume [l]
m	Number of electrons transferred per mol of H ₂ [mol-e ⁻ mol-H ₂ ⁻¹]
F	Faraday constant [A d mol-e ⁻¹]
R	Ideal gas constant [ml-H ₂ atm K ⁻¹ mol-H ₂ ⁻¹]
T	MEC temperature [K]
P	Anode compartment pressure [atm]
$E_{applied}$	Electrode potentials [V]
R_{ext}	External resistance [Ω]
R_{int}	Internal resistance [Ω]
I_{MEC}	MEC current [A]
E_{CEF}	Counter-electromotive force for the MEC [V]
M_{Total}	Total mediator weight percentage [mg-M mg-x ⁻¹]
M_{red}	<i>Reduced mediator fraction per each</i> electricigenic microorganism (mg-M mg-x ⁻¹)
M_{ox}	<i>Oxidized mediator fraction per each</i> electricigenic microorganism (mg-M mg-x ⁻¹)
$A_{sur,A}$	Anode surface area [m ²]

Greek letters

$\mu_{max,a}$	Maximum growth rate of the anodophilic microorganism [d ⁻¹]
$\mu_{max,h}$	Maximum growth rate of the hydrogenotrophic microorganism [d ⁻¹]
β	Reduction or oxidation transfer coefficient [dimensionless]
i_0	Exchange current density in reference conditions [A m ⁻²]
γ	Mediator molar mass [mg-M mol _{med} ⁻¹]
α_1	Dimensionless biofilm retention constant for layers 1

α_2	Dimensionless biofilm retention constant for layers 2
μ_h	Hydrogen growth rate [d^{-1}]
η_{ohm}	Ohmic losses due to resistance to the flow of ion in the electrolyte and electrode [V]
η_{conc}	Concentration loss due to mass transfer limitation [V]
η_{act}	Activation loss due to activation energies and electrochemical reactions [V]

2.1 Introduction

Electrochemical systems represent a novel alternative for energy recovery from organic waste and biomass residue, where microorganisms can be employed to catalyze electrochemical oxidation-reduction reactions. Microbial electrochemical cells such as Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cell (MEC) are among such bioelectrochemical systems. Performance of MFC and MEC largely depends on anaerobic biofilm occupied by anodophilic (electrogenic) microorganisms, which transfer electrons to the anode during their metabolism [3]. Though anodic compartments in all MFC and MEC are similar, the cathode reactions differ. MFCs operate with cathodes exposed to air resulting in oxygen reduction reaction at the cathode and electricity production [6]. In contrast, MEC require a small additional input of electrical energy provided by an external power supply to facilitate the reaction of hydrogen formation on the cathode [13].

Microbial electrolysis cells (MEC) and microbial fuel cells (MFC) are part of the microbial electrochemical cell technology which is one of the renewable energy alternatives today. Anodophilic microorganisms in anaerobic bioreactor is capable of oxidizing substrate containing organic materials in the compartment anode into electric energy [8]. Anodophilic microorganisms or microbial electrigenic is able to break the organic material and wastewater that has been diluted or low concentrations of organic compounds [3, 6]. MFC can generate spontaneous current due to the oxidation and reduction of the electron-proton from the organic material in the cathode bioreactor, whereas in MECs system, due to the addition of voltage into the cathode anaerobic- bioreactor, reaction between protons and electrons occurs leading to the formation of hydrogen gas [7, 13].

A Microbial Electrolysis Cell (MEC) is a slightly modified MFC where a small amount of electricity is applied to the anode chamber to suppress the production of methane and oxygen is kept out of the cathode chamber to assist bacterial oxidation of organic matter present in wastewater, to produce hydrogen. Although Microbial Electrolysis Cell (MEC) has tremendous potential, the development of this technique is still in its infancy. Information about the anode materials and microorganisms used in MFCs are also applicable to MEC systems due to their similar anodic process.

However the MEC present many technological challenges that goes beyond modelling studies, that need to be overcome before commercial application. For instance, the nonlinear and highly complex process in this hydrogen production process is due to the microbial interaction which also depends on the microbial activity. These difficulties and complexity makes the MEC system difficult to be operated and control under the best of condition.

These problems can be alleviated using an integrated process system engineering approach involving process modelling, optimisation, and control simultaneously in the study of the MEC system. To improve the productivity of bioreactor one alternative is to find the optimum conditions so that the rate of hydrogen production can be increased. Through the study of the experimental work for predicting the behavior of MEC in the bioreactor in a variety of operating conditions, the optimum value of the MEC can be obtained [5] or through developing the mathematical model of the MEC system.

One of the important and interesting phenomena for MFC and MEC model is the competition between anodophilic and methanogenic microorganisms to consume the substrate in the anode compartment [11]. Competition from microbial populations severely affect the performance of the MFC and MEC bioreactor. Several studies have been conducted to analyse the models, one of which is competition from anodophilic, methanogenic acetoclastic and hydrogenotrophic methanogenic microorganisms in the biofilm as conducted by Pinto et al. [10].

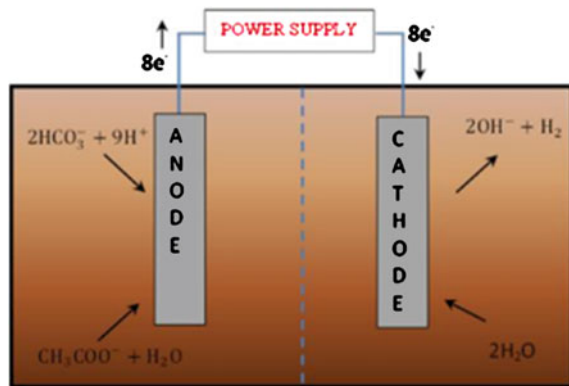
This study describes the mathematical models of MECs for hydrogen production modified from Pinto et al. [10] model based on the anaerobic digestion model proposed by Bernard et al. [2]. One method to improve the performance of MECs process is to design a proper mathematical model that can be used to optimize the design and develop process control strategies of the MECs system. This study has assessed the maximum hydrogen production rate by varying the anodic compartment volume, electrode potentials applied, effect of varying changes of initial concentration, effect of stoichiometric and kinetic parameters on MECs in the batch reactor. It was used for analysis and tested with open loop identification. In this model the effect of competition between the three microbial populations between anodophilic, hydrogenotrophic and acetoclastic will also be examined. The equation of this model involves unified model as well as activity of microbes in the anode chamber of a microbial fuel cells and microbial electrolysis cells in the cathodic reaction.

2.2 Modified Model of MEC in Batch Reactor

2.2.1 Mathematical Models

The main goal of any development of mathematical models for MEC is to get the maximum hydrogen production rate by calculating the effect of electric current and voltage prediction at different operating conditions. The MEC model used here

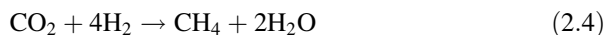
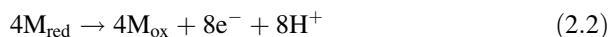
Fig. 2.1 A simplified diagram of the microbial electrolysis cells set-up showing anode and cathode in batch reactor



has been modified as the model presented by Pinto et al. [12]. The modification to Pinto model involves: batch process operation, phase of biofilm growth, metabolic activities, and the reactor size. In this model, to some assumptions such as that the acetate is to be the only carbon source, the fermentation process involving the conversion of the hydrolysis of acetate organic is ignored, and the carbon source in the anode compartment well distributed so that acetate gradient in the biofilm is neglected have been made.

This section presents a model for the MEC in batch reactor, developed from Pinto et al. [10] based on the anaerobic digestion model (ADM) proposed by Bernard et al. [2]. The mathematical models presented here aim to simulate the competition of three microbial in MECs. The model represents competition between anodophilic and methanogenic microorganisms for the substrate. Charge transfer at the anode is modeled using substrate (acetate) and intracellular mediator by three microbial populations between anodophilic, acetoclastic methanogenic and hydrogenotrophic methanogenic. The proposed MEC model system is shown in Fig. 2.1.

The reactions at the anode and cathode are described as [10]:



where acetate represent substrate concentration; and M_{ox} and M_{red} are the reduced and oxidized forms of the intracellular mediator.

The influent and effluent of flow rate for MEC in batch reactor are the same and the dynamic mass balance equations of the model for substrate and microorganisms can be written as:

$$\frac{dS}{dt} = \frac{F_{in}}{V} (S_0 - S) - q_{max,a} \frac{S}{K_{A,a} + S} \frac{M_{ox}}{K_M + M_{ox}} x_a - q_{max,m} \frac{S}{K_{A,m} + S} \quad (2.5)$$

$$\frac{dx_a}{dt} = \mu_{max,a} \frac{S}{K_{A,a} + S} \frac{M_{ox}}{K_M + M_{ox}} x_a - K_{d,a} x_a - \alpha_1 x_a \quad (2.6)$$

$$\frac{dx_m}{dt} = \mu_{max,m} \frac{S}{K_{A,m} + S} - K_{d,m} x_m - \alpha_1 x_m \quad (2.7)$$

$$\frac{dx_h}{dt} = \mu_{max,h} \frac{H_2}{K_h + H_2} - K_{d,h} x_h - \alpha_2 x_h \quad (2.8)$$

$$\frac{dM_{ox}}{dt} = \frac{\gamma}{V x_a} \frac{I_{MEC}}{mF} - Y_M q_{max,a} \frac{S}{K_{A,a} + S} \frac{M_{ox}}{K_M + M_{ox}} \quad (2.9)$$

$$M_{Total} = M_{red} + M_{ox} \quad (2.10)$$

$$Q_{H_2} = Y_{H_2} \left(\frac{I_{MEC}}{mF} \frac{RT}{P} \right) - Y_h \mu_h x_h V \quad (2.11)$$

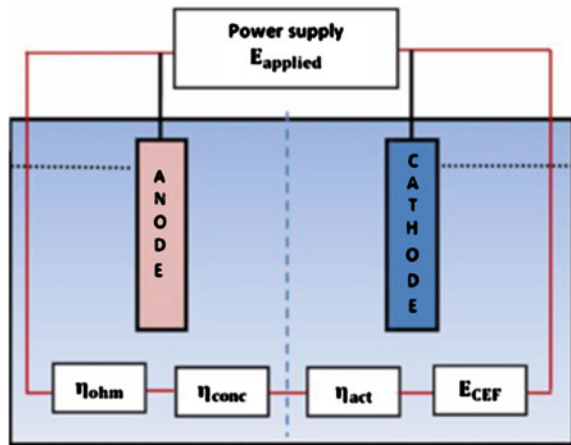
The model as given by Eq. (2.5) is for filling time period (t_f) in the process. During reaction time in the batch reactor process, the volumetric flow rate (F_{in}) is nil and the V_f is constant at V_o . The values of the coefficients can be found in Pinto et al. [11].

2.2.2 Electrochemical Equations

The potential losses of internal resistance can give additional information about the performance of an MEC, especially when comparing different systems [4]. Since the voltage needed for hydrogen production is constant, the current density depends on the total internal resistance of the system, which in itself is a function of the current density. The total internal resistance is a sum of the partial resistances of the system [1].

Figure 2.2 gives an overview of partial internal resistances in an MEC, which can be represented by a series of resistances in an equivalent circuit. These partial resistances consist of: (i) counter-electromotive force (E_{CEF}), (ii) activation loss (η_{act}), concentration loss (η_{conc}), ohmic loss (η_{ohm}). Each of these polarizations has a different magnitude for different current density degrees. At low current densities, activation losses are dominant due to reaction energy barriers at the electrode-electrolyte interface, which need to be overcome to start the reaction. At high current densities, reactant and product diffusion limitations lead to high concentration losses. Finally, ohmic losses increase linearly with current due to electron and ion conduction at the electrodes, electrolytes, and contact resistance across

Fig. 2.2 The potential losses of microbial electrolysis cells in batch reactor



each material's interface, and interconnections to electrodes. Note that the output voltage of a fuel cell is directly proportional to the cell current, following Ohm's law:

$$E_{\text{output}} = R_{\text{ext}} I_{\text{cell}} \quad (2.12)$$

MEC voltage can be calculated using theoretical values of electrode potentials by subtracting ohmic, activation, and concentration losses. Therefore the following electrochemical balance can be written as [9]:

$$-E_{\text{applied}} = E_{\text{CEF}} - \eta_{\text{ohm}} - \eta_{\text{conc}} - \eta_{\text{act}} \quad (2.13)$$

Here, concentration losses at the cathode can be neglected due to the small size of H_2 molecules resulting in a large diffusion coefficient of H_2 in a gas diffusion electrode used as a cathode. The concentration losses at the anode are then calculated using the Nernst equation.

$$\eta_{\text{conc,A}} = \frac{RT}{mF} \ln \left(\frac{M_{\text{Total}}}{M_{\text{red}}} \right) \quad (2.14)$$

The cathodic activation losses can be calculated by the Butler-Volmer equation. Assuming that the reduction and oxidation transfer coefficients that express the activation barrier symmetry are identical, the Butler-Volmer equation can be approximated as

$$\eta_{\text{act,C}} = \frac{RT}{\beta mF} \sinh^{-1} \left(\frac{I_{\text{MEC}}}{A_{\text{sur,A}} i_0} \right) \quad (2.15)$$

Therefore, the MEC current can be calculated by combining Eqs. (2.13)–(2.15):

$$I_{MEC} = \frac{E_{CEF} + E_{applied} - \frac{RT}{mF} \ln\left(\frac{M_{Total}}{M_{red}}\right) - \eta_{act,C}(I_{MEC})}{R_{int}} \frac{M_{red}}{\varepsilon + M_{red}} \quad (2.16)$$

where ε is null [mg-M mg-x⁻¹]; $\varepsilon \approx 0$, Eq. (2.16) can be written as:

$$I_{MEC} = \frac{E_{CEF} + E_{applied} - \frac{RT}{mF} \ln\left(\frac{M_{Total}}{M_{red}}\right) - \eta_{act,C}(I_{MEC})}{R_{int}} \quad (2.17)$$

2.3 Results and Discussion

In all simulations studies, the total time was set at 20 days. Figure 2.3 shows the block diagram which consists of multi input and multi output parameters. All input and output parameter are divided in two types namely; internal and external parameters. Internal input is the parameter that we assume or are taken from literature. However, external output is the parameter that can be seen and manipulated such as volume reactor; substrate feed concentration, electrode potential applied and MEC current (external load).

The model described previously is used to study the sensitivity of effect internal parameters changes in biohydrogen production via microbial electrolysis cells in batch reactor. Figures 2.4 and 2.5 shows the dynamic behaviour of initial concentration of the anodophilic microorganisms (X_{ao}) on the I_{MEC} current and the hydrogen production rate.

Figures 2.4 and 2.5 illustrate the results for the effect of initial concentration of the anodophilic microorganisms (X_{ao}), varied with values of 0.1 mg/l, 0.5 mg/l, 1.0 mg/l and 1.5 mg/l, on the hydrogen production rate profiles and the I_{MEC} current. The investigation was carried out for the anodophilic microorganisms initial concentration (X_{ao}) range of $0.1 \leq X_{ao} \leq 1.5$ (mg-x/l), the balance (i.e. the difference from the base value X_{ao} which is 1.0) was added to X_{ao} . As the growth rate of the hydrogenotrophic and initial concentration of X_{ao} increased, the I_{MEC} current and hydrogen production rate also increases up to the period of 2 days. Hence, it is evident from Figs. 2.4 and 2.5 that performance of I_{MEC} current and the hydrogen production rate were affected by changes in initial concentration of the anodophilic microorganisms.

Figures 2.6 and 2.7 shows the behaviour of the effect of internal parameters changes of initial concentration of the hydrogenotrophic microorganisms (X_{ho}) on the I_{MEC} current and the hydrogen production rate. The investigation was carried out for hydrogenotrophic microorganism's initial concentration (X_{ho}) in the range

Fig. 2.3 Schematic description of input–output model block diagram

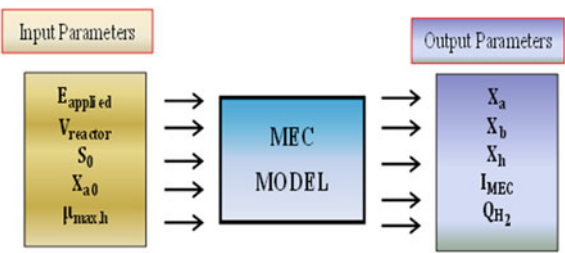
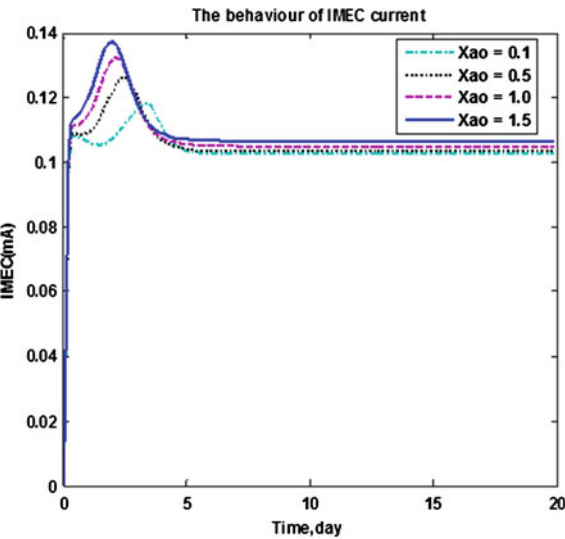


Fig. 2.4 The effect of initial concentration of the anodophilic microorganism on the I_{MEC} current



of $1 \leq X_{ao} \leq 15$ mg/l. Figure 2.6 illustrate the simulation results for the internal parameters changes of initial concentration of the hydrogentrophic microorganisms (X_{ho}) on the I_{MEC} current with the values varied at 1 mg/l, 5 mg/l, 10 mg/l and 15 mg/l. Figure 2.6 shows that the effect of changing the initial conditions of the hydrogentrophic concentration (X_{ho}) has no significant on the I_{MEC} current variations.

Figure 2.7 shows the hydrogen production rate increased with increasing the hydrogentrophic microorganisms initial concentration (X_{ho}). As mentioned previously, by increasing the initial concentration of the hydrogentrophic microorganisms, the hydrogen production rate is also increased. In summary, the hydrogen production rate is correlated with the initial concentration of the hydrogentrophic microorganism.

Fig. 2.5 The effect of initial concentration of the anodophilic microorganism on the hydrogen production rate

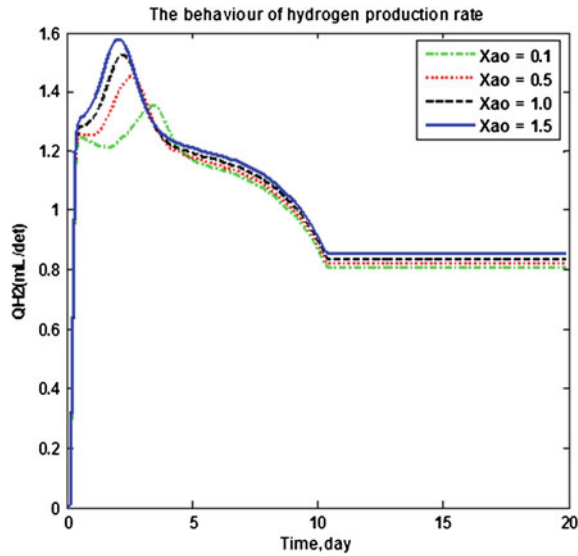


Fig. 2.6 The effect of initial concentration of the hydrogentrophic microorganisms on the I_{MEC} current

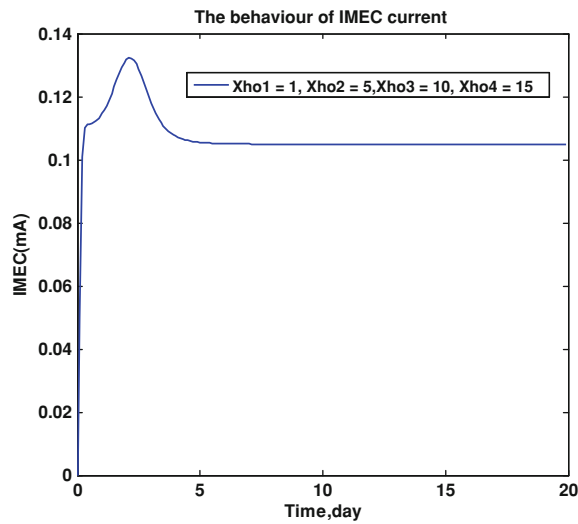
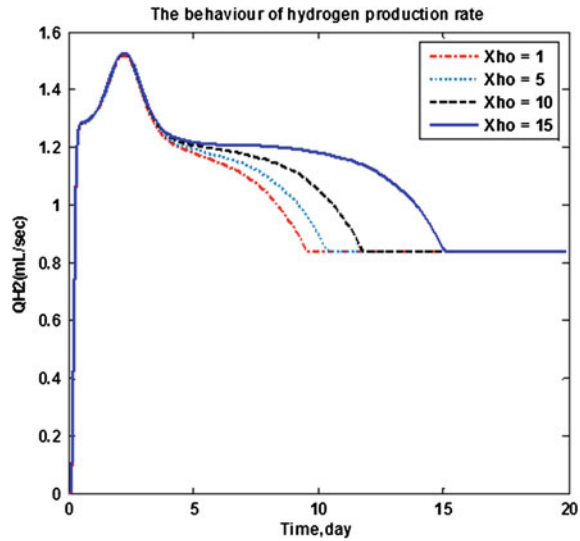


Fig. 2.7 The effect of initial concentration of the hydrogenotrophic microorganisms on the hydrogen production rate



2.4 Conclusions

The study has assessed the maximum hydrogen production rate by varying the effect of varying changes of initial concentration and kinetic parameters on the MECs in a batch reactor. In this paper, the effect of varying changes of initial concentration of the anodophilic microorganisms (X_{ao}) and hydrogenotrophic microorganisms on the I_{MEC} current and the hydrogen production rate has been studied. The model is based on material balances with the integration of bio-electrochemical reactions. The model examined the performance and competition between the three microbial populations involving anodophilic, acetoclastic methanogenic and hydrogenotrophic methanogenic microorganisms. This model is also capable of predicting the growth of Populations of microorganisms and biofilm composition. The results show that the initial concentration of the anodophilic microorganisms (X_{ao}) has significant effect on the I_{MEC} current and the hydrogen production rate as compared to the effect of initial concentration of the hydrogenotrophic microorganisms (X_{ho}).

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