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Optimal Production of Biohydrogen Gas via Microbial Electrolysis Cells (MEC) in a Controlled Batch Reactor System

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A Microbial Electrolysis Cells (MECs) is a slightly modified microbial fuel cells (MFCs) where a small amount of electricity is applied to the anode chamber to suppress the production of methane. Oxygen is kept out of the cathode chamber to assist bacterial oxidation of organic matter present in the wastewater to produce hydrogen, a gas which is the becoming the most attractive energy source. While MECs has tremendous potential, the development of this technique is still in its infancy. The goal of this work is to optimize the production of biohydrogen gas by selecting the optimum current and controlling applied voltage in MECs using batch reactor. The mathematical model of the MECs is based on material balances with the integration of bio-electrochemical reactions describing the effect of applied voltage on the performance of MECs batch reactor. The behaviour of the system differs significantly as the value of applied voltage is changed and gives a significant influence on the hydrogen production rate. Finally, this study can be extended in the future to improve the optimization in MEC model and develop advanced control system study.

1. Introduction

MECs are a promising technology for wastewater treatment and simultaneous production of reduced value added compounds. The MECs performance strongly depends on the activity and efficiency of the anode and cathode (bio) catalysts (Villano et al., 2012). MFCs and MECs are part of the microbial electrochemical cell technology which is one of the renewable energy alternatives today. In MFCs, chemical energy of organic material in wastewater is converted into electrical energy through the use of a microbe as a catalyst to oxidize the substrates and produce electrons in the anode chamber. In MECs system, due to the addition of voltage into the cathode anaerobic-bioreactor, the reaction between protons and electrons leading to the formation of hydrogen gas is obtained (Logan, 2010). The performance of MFCs and MECs are greatly improved by shortening the interelectrode distance, and improving the fluid diffusion on the anode side (Sugiura et al., 2012).

MECs has tremendous potential but 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. Yet, efficient and scalable designs are required and investigated by biologists for the successful applications of the microbial electrolysis process (Hongqiang et al. 2008).

One of the important and interesting phenomena for MFC and MEC model is a competition between anodophilic and methanogenic microorganisms to consume the substrate in the anode compartment (Wang et al., 2009 and Pinto et al., 2011). Competition from microbial populations severely affects the performance of the MFC and MEC bioreactor. Several studies have been conducted and use the models, one of which is competition from anodophilic, methanogenic acetoclastic and hydrogenotrophic methanogenic microorganisms in the biofilm as reported by Pinto et al., (2010).

This study describes the mathematical models of MECs for hydrogen production by selecting the optimum current and controlling applied voltage in the batch reactor. The main goal of any development of mathematical models for MEC is to get the optimum hydrogen production rate by calculating the effect of electric current and voltage prediction of variations generated at different operating conditions. MEC model used here has been modified from the model presented by Pinto et al. (2011).

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2. Mathematical model

The mathematical models presented here aim to simulate the competition of three microbial in the MEC. The model takes into account the competition between anodophilic and methanogenic microorganisms from the source of carbon. The reactions at the anode and cathode are described as (Pinto et al. 2010):

$$C_2H_4O_2 + H_2O + 4M_{ox} \rightarrow 4M_{red} + CO_2 \quad (1)$$

$$4M_{red} \rightarrow 4M_{ox} + 8e^- + 8H^+ \quad (2)$$

$$C_2H_4O_2 \rightarrow CH_4 + CO_2 \quad (3)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (4)$$

where acetate represent substrate concentration; and $\mathrm{M_{ox}}$ and $\mathrm{M_{red}}$ are the reduced and oxidized forms of the intracellular mediator. The dynamic mass balance equations of the models are given below as:

$$\frac{dS}{dt} = -q_{max,a}\frac{S}{K_{A,a}+S}\frac{M_{ox}}{K_M+M_{ox}}x_a - q_{max,m}\frac{S}{K_{A,m}+S} \quad (5)$$

$$\frac{dx_a}{dt} = \mu_{max,a}\frac{S}{K_{A,a}+S}\frac{M_{ox}}{K_M+M_{ox}}x_a - K_{d,a}x_a - \alpha_1 x_a \quad (6)$$

$$\frac{dx_m}{dt} = \mu_{max,m}\frac{S}{K_{A,m}+S} - K_{d,m}x_m - \alpha_1 x_m \quad (7)$$

$$\frac{dx_h}{dt} = \mu_{max,h}\frac{H_2}{K_h+H_2} - K_{d,h}x_h - \alpha_2 x_h \quad (8)$$

$$\frac{dM_{ox}}{dt} = \frac{\gamma}{Vx_a}\frac{I_{MEC}}{mF} - Y_M q_{max,a}\frac{S}{K_{A,a}+S}\frac{M_{ox}}{K_M+M_{ox}} \quad (9)$$

$$Q_{H_2} = Y_{H_2}\left(\frac{I_{MEC}}{mF}\frac{RT}{P}\right) - Y_h\mu_h x_h V \quad (10)$$

$$E_{applied} = (\eta_{ohm} + \eta_{conc} + \eta_{act}) - E_{CEF} \quad (11)$$

$$I_{MEC} = \frac{E_{CEF}+E_{applied} - \frac{RT}{mF}ln\left(\frac{M_{Total}}{M_{red}}\right) - \eta_{act,C}(I_{MEC})}{R_{int}} \quad (12)$$

Where S is the substrate concentration (mg-S L^{-1}); x_a, $\mathrm{x_m}$, and $\mathrm{x_h}$ are the concentration of anodophilic, acetoclastic, and hydrogenotrophic microorganisms, respectively (mg-x L^{-1}); $\mathrm{M_{ox}}$ is the oxidized mediator fraction per electricigenic microorganism (mg-M mg-x^{-1}); Q_{H_2} is hydrogen production rate (mL/sec); $E_{applied}$ is electrode potential and $\mathrm{I_{MEC}}$ is the MEC current (A).

3. Measurement units and parameter estimation

Biohydrogen production process through microbial electrolysis cell is a nonlinear and complex process and non-linear. One of the solutions to overcome the problems posed by the MEC is to build a mathematical model that can be used for process design, optimization and develop process control strategies. In developing this model, several assumptions that carbon sources from wastewater is distributed both in the anode compartment and acetate gradient in biofilm is neglected. Due to the porosity of the fluid and the circulation rate is very high, it is assumed that the microorganisms in the anodic compartment is distributed homogeneously within each layer. Biofilm formation and retention of MEC-batch reactor in each biofilm layer is based on a two-phase biofilm growth model. Layer 1 represents the anode biofilm, containing anodophilic and acetoclastic methanogens microorganisms, while layer 2 is occupied by the cathode biofilm hydrogenotrophic methanogenic microorganisms. The transformation of organic substrates by glucose to acetate takes place in the anode biofilm layer 1. Thereafter acetate consumed by acetoclastic methanogenic microorganisms and produce methane and carbon dioxide, where $\mathrm{M_{red}}$ and $\mathrm{M_{ox}}$ are the reduced due to oxidation by intracellular mediator anodophilic microorganisms. Layer 2 assumed the cathode biofilm populated by hydrogenotrophic methanogenic microorganisms. On the other hand, microbes convert hydrogen to methane at the cathode and result in the formation of a biofilm layer around the cathode. Finally, pH and temperature assumptions are considered fully controlled and maintained at a constant value. The absence biomass growth in anodic liquid and mixing in the anode compartment is ideal. Parameters description, units and values of the model used for the simulation studies are provided in Table 1.

Table 1: System characteristics, kinetic and stoichiometric parameters of the Model used for the simulation [729]

Parameter	Value	Nomenclature
$\mu_{max,m}$	0.3	The maximum growth rate of the acetoclastic methanogenic microorganism [d^{-1}]
$\mu_{max,a}$	1.97	The maximum growth rate of the anodophilic microorganism [d^{-1}]
$\mu_{max,h}$	0.5	The maximum growth rate of the hydrogenotrophic microorganism [d^{-1}]
$K_{S,a}$	20	The half-rate (Monod) constant of the anodophilic microorganism [mg-AL^{-1} or mg-M l^{-1}]
$K_{S,m}$	80	The half-rate (Monod) constant of the acetoclastic methanogenic microorganism [mg-A l^{-1} or mg-M l^{-1}]
K_M	0.01	Mediator half-rate constant [mg-M l^{-1}]
H_2	1	H_2 saturation in water [mg-A l^{-1}]
K_h	0.001	Half-rate constant [mg l^{-1}]
Y_{H_2}	0.9	The dimensionless cathode efficiency [dimensionless]
Y_h	0.05	The yield rate for hydrogen consuming methanogenic microorganisms [ml-H_2 mg-x^{-1} d^{-1}]
R	8.314	The ideal gas constant [ml-H_2 atm K^{-1} mol-H_2^{-1}]
T	298.15	The MEC temperature [K]
M	2	The number of electrons transferred per mol of H_2 [mol-e^- mol-H_2^{-1}]
F	96.485	The Faraday constant [A d mol-e^{-1}]
E_{CEF}	-0.35	The counter-electromotive force for the MEC [V]
$X_{max,a}$	512.5	Anodophilic biofilm space limitation [mg-x l^{-1}]
$X_{max,m}$	1680/Y_h	Methanogenic biofilm space limitation [mg-x l^{-1}]
$K_{d,a}$	0.04	The microbial decay rates of the anodophilic microorganism [d^{-1}]
$K_{d,m}$	0.01	The microbial decay rates of the acetoclastic methanogenic microorganism [d^{-1}]
$K_{d,h}$	0.01	The microbial decay rates of the hydrogenotrophic microorganism [d^{-1}]
V	10	The anodic compartment volume [l]
S_0	1500	The initial conditions of organic substrate concentration in the influent and in the anodic compartment [mg-S l^{-1}]
X_{h0}	10	The initial conditions of hydrogenotrophic methanogenic microorganisms [mg-x l^{-1}]
X_{a0}	300	The initial conditions of anodophilic microorganisms [mg-x l^{-1}]
X_{m0}	20	The initial conditions of acetoclastic methanogenic microorganisms [mg-x l^{-1}]

4. Results and discussion

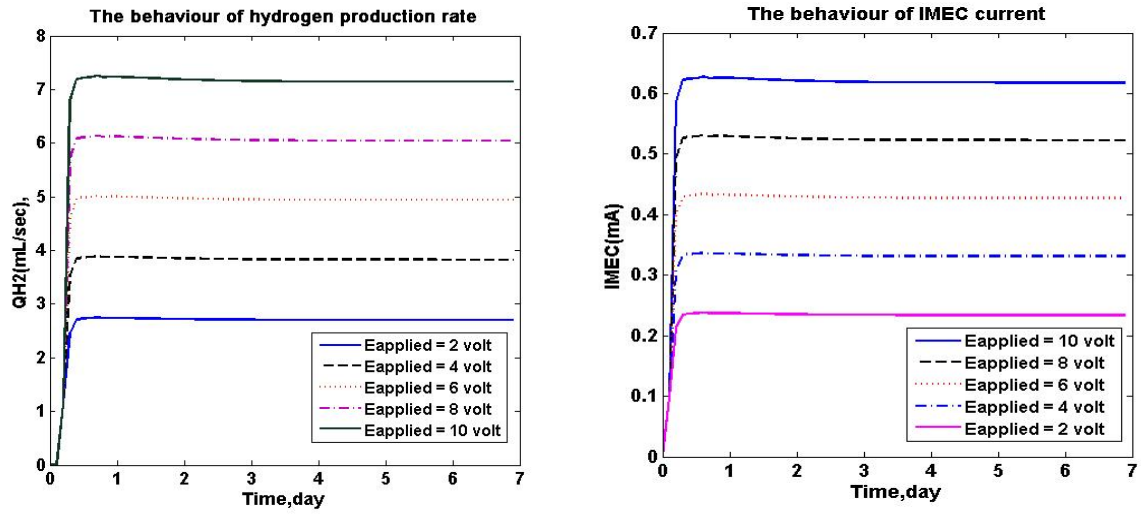
To gain knowledge about the dynamic behaviour of the microbial electrolysis cell process in batch reactor before designing the system controller, simulation study using the model described above was carried out. Various conditions in association with the change in varying the electrode potentials (V) with effects on the I_{MEC} current and the hydrogen production rate were performed. To optimize the process in order to obtain the maximum hydrogen production, the optimal operation of the electrode potentials and controlling of the current in the MEC process is very important to be achieved.

4.1 Behaviour of effect electrode potential changes in MEC

The behaviour of the system differs significantly as the value of applied voltage is changed and gives significant influence on the hydrogen production rate. It is demonstrated that the rate of hydrogen production could be maximized without excessive energy consumption by minimizing the apparent resistance of the MEC.

Figure 1 shows the behavior of the effect varying the electrode potentials (V) on the I_{MEC} current and the hydrogen production rate.

As shown in the Figure 1, the dependence of hydrogen production and I_{MEC} current were very significant to the process. In this process MEC batch reactor was operated at a voltage variation in the range of $2 \leq E_{applied} \leq 10$ V. Table 2, shows the maximum of the I_{MEC} current and the hydrogen production rate on varying the value of applied voltage (V) and counter-electromotive force.



(a) (b)

Figure 1: Behaviours of effect electrode potentials (V) changes on (a) hydrogen production rate (Q_{H2}) and (b) I_{MEC} current

Table 2: The Effect of varying the electrode potentials (V) and counter-electromotive force on I_{MEC} current and hydrogen production rate (Q_{H2}) at period 0.7 days

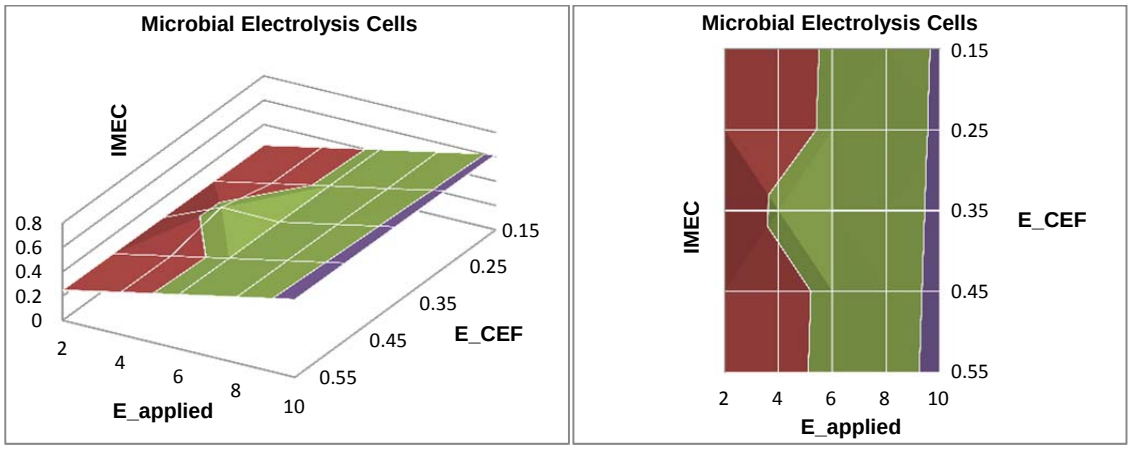
Parameters	Electrode (V) changes	Maximum I_{MEC} current (A)	Maximum hydrogen production rate (mL/s)
Electrode potential (V)	2	0.238	2.747
	4	0.336	3.888
	6	0.434	5.017
	8	0.531	6.138
	10	0.676	7.254
Counter-electromotive force (V)	0.15	0.327	3.775
	0.25	0.331	3.881
	0.35	0.336	3.888
	0.45	0.341	3.945
	0.55	0.346	4.001

In this study, the system performance of I_{MEC} current and the hydrogen production rate were affected significantly by variations in electrode potential. When applied voltage and counter-electromotive force are increased, the I_{MEC} current and hydrogen production rate is also increased as seen from Table 2.

4.2 Optimization of electrode potentials and counter-electromotive force

The Response Surface Methodology (RSM) is a statistical technique proposed for designing experiment, evaluating the influences of individual and effects of several factors, building models, reducing the number of experiments and finding the optimum conditions for the desired response. Since the objective of this work was to investigate the individual and interactive effects of electrode potentials and counter-electromotive force on the I_{MEC} current and the hydrogen production rate by using RSM approach is appropriate to be used. The RSM applied here is to determine the optimum electrode potentials and counter-electromotive force conditions for achieving optimum hydrogen production rate and I_{MEC} current in the reactor.

Figure 2 shows the optimum conditions for achieving maximum hydrogen production rate and I_{MEC} current were obtained at value of electrode potentials 4 volts and counter-electromotive force of 0.35 V. Repeating the condition, the highest hydrogen production rate and I_{MEC} current were obtained at values 3.888 mL/s and 0.336 A.

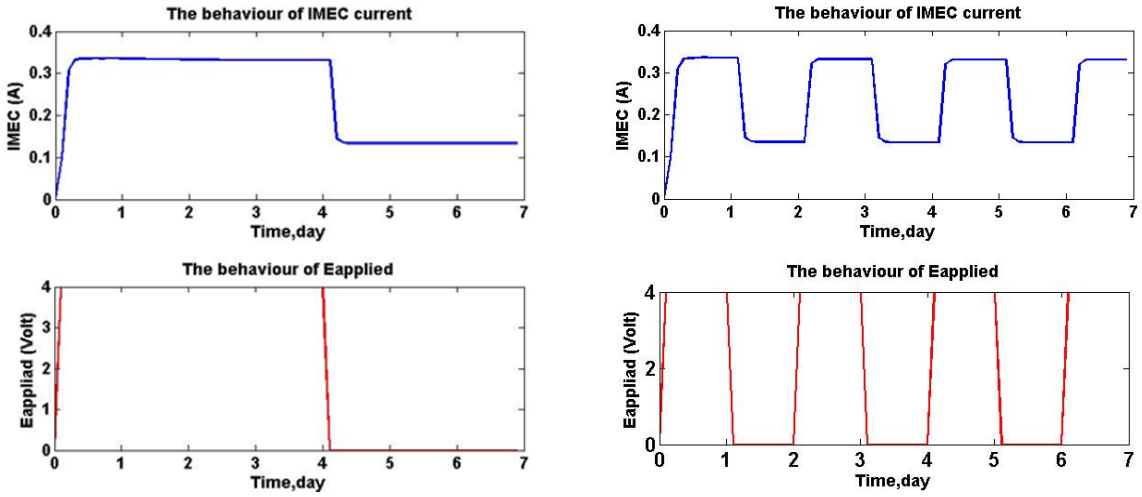


(a) (b)

Figure 2: Response surface; (a). Isometric and (b). Counter plot for optimum of electrode potentials and counter-electromotive force on I_{MEC} current and hydrogen production rate

4.3 Proportional integral derivative (PID) strategy for control of $\mathrm{I_{MEC}}$ current

The main objective of process control is to maintain the system performance in order to keep the value of the desired set-point, so that if an interruption occurs, the controller must be able to bring the process variable to set-point. In this work we use a PID controller as a control system to generate the maximum hydrogen production rate.

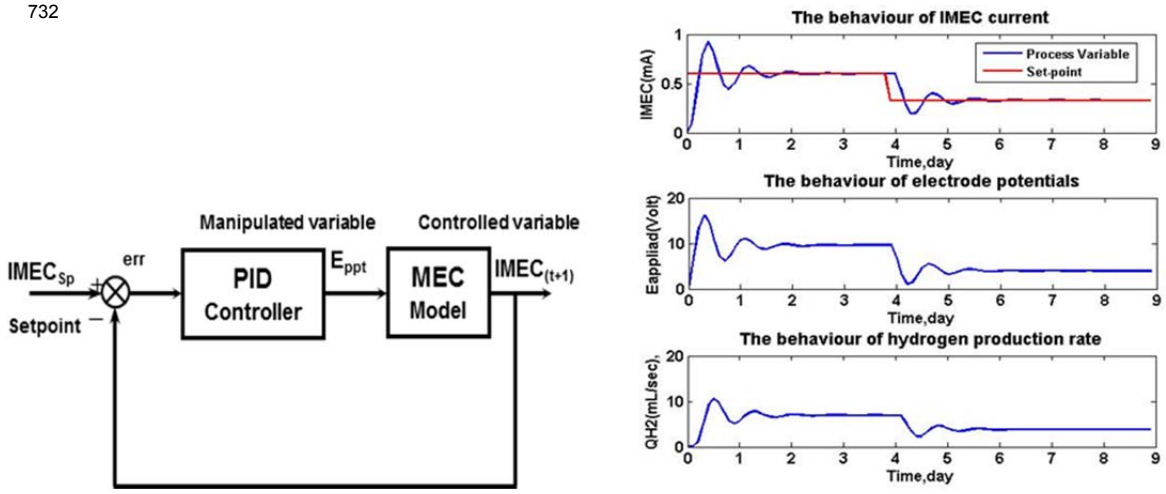


(a) (b)

Figure 3: Open loop test; (a) single pulse and (b) multiple tracking pulses for electrode potentials at 4 volt.

Figure 3 shows the simulation result for open loop using single and multiple tracking profile study were chosen to observe the effect of $\mathrm{I_{MEC}}$ current and hydrogen production rate process responses with the value of electrode potential at 4 V. This profile has been selected as one of the profiles for set-point tracking study for the controller design. Considering the electrode potentials as the control output and $\mathrm{I_{MEC}}$ current as the controlled variable with $I_{MEC_{sp}}$ is $\mathrm{I_{MEC}}$ current set-point and I_{MEC_t} is the $\mathrm{I_{MEC}}$ current controller response. The performance of the various controllers was assessed in this section based on its response characteristics which were investigated by observing the responses of the process under nominal and varying operating conditions.

Figure 4 shows the block diagram for the PID control strategy and controller response under single set-point tracking study to control the $\mathrm{I_{MEC}}$ current and electrode potential in the MEC batch reactor. The controller tuning was obtained by using the Ziegler and Nichols tuning method. The controller performs well and is successful in bringing the process to follow the given set point changes.



(a) (b)

Figure 4: Closed loop test; (a) Block diagram for PID control strategy and (b) Controller response for single set-point tracking study

5. Conclusions

This study presents the optimal production of biohydrogen gas via microbial electrolysis cells (MEC) in a controlled batch reactor system. The model is based on material balances with the integration of bio-electrochemical reactions. It was used for analysis and tested with open loop simulation result to get the maximum hydrogen production rate and I_{MEC} current by varying the applied potential and counter-electromotive force. The optimization of electrode potentials and counter-electromotive force was conducted by response surface methodology for maximizing of hydrogen production rate and I_{MEC} current. According to the results presented in this work, it was found that the optimum conditions on maximum of hydrogen production rate and I_{MEC} current were obtained at value for electrode potentials 4 V and counter-electromotive force was 0.35 V. The maximum hydrogen production rate was obtained at values 3.888 mL/s. Finally, this study can be extended in the future to improve and develop advanced control system study.

Acknowledgments

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