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Optimization of Electricity Generation and Palm Oil Mill Effluent (POME) Treatment from Microbial Fuel Cell

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Abstract: Natural micro-flora of Palm Oil Mill Effluent (POME) sludge was grown in dual-chamber Microbial Fuel Cells (MFC) to produce electricity by providing glucose at different concentration. A greater strength of Open Circuit Voltage (OCV) was observed with optimal biomass metabolism activity, as increasing glucose concentrations. The time Response Constant (RC) of OCV was taken everyday to estimate the total time needed to achieve steady state voltage at zero current. The lower value of RC indicates that the strength of OCV value is high and the biomass attached to the anode could be active in producing electrons. At 3 750 mg-COD L^{-1} with 10% added POME and 10 000 mg-COD L^{-1} synthetic wastewater, the values of RC for each medium were found as 3.36 and 1.95 h, respectively. The removal efficiency of COD was achieved 72.2% for 10% POME and 89.9% for synthetic wastewater. The initial COD level was found proportionally to the COD removal and maximum power density in the MFC system. However, the results shown that relation between RC value and initial COD level were inversely proportional. The highest power density (with present current density) in POME added and synthetic medium were 3.155 mW m^{-2} (9.322 mA m^{-2}) and 1.780 mW m^{-2} (3.996 mA m^{-2}), respectively. The optimal power density that conducted in different level of COD was occurred at day 2 before its start decrease at next consecutive day. The effects of electrochemical parameters to power densities at different initial COD level were also studied using polarization model. From the simulated data, averaged power densities (with present current densities) that could achieved at COD 3750 and 10000 mg L^{-1} were estimated 2.61 mW m^{-2} (4.5 and 1.38 mA m^{-2} (3.5 mA m^{-2})), respectively. The total losses due to current limitation were eliminated about 15-55 % at high initial COD level based on results mention above. The end of study showed that the maximum power density kept on increased although COD value had reached to the lower level and this could be due to the hydrolysis of inactive of the living cells undergone lysis, has contributed to COD level in the system.

Key words: Microbial fuel cell, open circuit voltage, polarization model, wastewater treatment, POME

INTRODUCTION

Microbial Fuel Cells (MFC) are a device or arrangements that provide bioactive conditions for converting substrates to electricity energy via microbial catalyzed-redox reactions (Du *et al*., 2007). The typical MFC consists of two chambers, representing an anode and a cathode, where the anode accepts electrons as a result of oxidation of the organic components and the cathode, in aerated condition, allows the reaction of electrons in the chamber. The two chambers are separated by placing a proton exchange membrane (PEM) allows cation, principally proton, transport toward the cathode. Microorganisms cultivated in the anodic chamber of MFCs are partially distributed (Du *et al*., 2007), while the rest are attached to the electrode (Bond and Lovely, 2003). Once the substrate are consumed and oxidized by the microbial via metabolism process, electrons will be generated and transfer to the anode surface. The electrons were transferred from anode to cathode by the way of external circuit with loading. On the other hand, the associated protons are transferred through PEM into the cathode by the internal electrolysis solution. MFC yields currents that caused by the transport of electrons and ions. These currents are limited by the following factors: (1) electrons activation in anode and cathode surfaces caused by oxidation and reduction process, (2) electron transfer from microbial cells to the anode and (3) internal resistances of the circuit and anions passing through the PEM (Fu *et al*., 2009). Therefore, concerning the above factors, this study was conducted to observe the change of electrochemical parameters at different level

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of COD. Various overvoltage loses based on fuel cell j-v behavior was represented using fuel cell polarization model. The changes of OCV during the experiment, that was only considered during the start-up and recovering of the MFC's voltage after maximum current operation (Fu *et al*., 2009; Wen *et al*., 2009) also was investigated. In the present study, microbial communities obtained from POME sludge, was cultured and tested in both POME and synthetic wastewater.

MATERIALS AND METHODS

Cultivation of POME sludge and biomass assay: The sludge culture was obtained from anaerobic digester pond at Sri Ulu Langat Palm Oil Mill in Dengkil, Selangor, Malaysia. It was cultivated in the Modified Wolfe's Medium (Atlas, 2004) containing (g L^{-1}): glucose 1.0; $NaH_2PO_4.H_2O$ 2.76; Na_2HPO_4 4.26; NH_4Cl 0.31 and KCl 0.13, 10 mL Wolfe's vitamin solution and 10 mL Wolfe's mineral solution. The cultivation was carried out in 2000 mL Duran bottle with 1000 mL of sludge together with 1000 mL of wastewater from the collection site. The sludge mixture was purged with Nitrogen gas to remove the oxygen and to keep the culture in anaerobic condition. The mixture was continuously stirred with magnetic stirrer to keep the culture active and the original POME sludge and wastewater that contain high COD level (30000-50000 mg L^{-1}) was removed in this stage. The feeding of glucose only was started after the formation bubble appeared on the surface had stopped intent to remove original high level of COD. The stock culture was feed with modified Wolfe's medium in room temperature with temperature range of 28-30°C, for at least 2 times to obtain a stable culture communities and controlled COD level in the sludge. Subsequently, the culture was harvested by dewatering the sludge and transfer into the chamber for MFCs experiment start-up.

Configuration of dual-chamber MFC: Two 500 mL MFCs were constructed by 0.8 cm thickness transparent poly-acrylic plastic and the dimension of each chamber has 8.2 (L), 9.0 (W) and 10.4 (H) cm. Plain carbon paper was used as electrodes for both anode and cathode, with size 9.0 (L), 5.0 (W) and 0.240 (T) cm. The electrodes were installed at the opposite end to each other or 7.3 cm apart. One of the electrodes was assigned as anode where the anaerobic culture was located, while the other one was assigned as a cathode. The electrode at cathode was coated with 0.5 mg cm^{-2} 50% Pt/C catalyst to increase the reduction of oxygen. The culture medium in anode compartment, the Modified Wolfe Medium, plays a role as anode electrolyte. The cathode chamber was filled with only 50 mM PBS (in g L^{-1}: $NaH_2PO4.H_2O$ 2.76; Na_2HPO_4 4.26; NH_4Cl 0.31 and KCl 0.13) and continuous air-sparged by aquarium pump. A proton-exchange membrane (Nafion 117) that clamped between the two compartments was used to separate the electrolytes while allowing transfer of H^+ion through the membrane. Prior to use in the MFC system, membrane was treated by boiling in 30% H_2O_2, 0.5 M H_2SO_4 and washed in running deionized water for about 1 h. The assembled MFC chambers were filled with deionized water overnight before operation.

Analysis of power generation and treatment efficiency from MFC operation: The two MFCs were operated at controlled temperature 35°C, in the water bath. Half of total volume of MFC was added with POME sludge and topped up mixed with Modified Wolfe's Medium for total operating volume of 450 mL. For long time operation, the readings of MFC voltage were registered every 15 min using a true-rms digital multimeter (Fluke 289, USA), that was clipped on the carbon paper by titanium binders. It was then connected to PC via USB-IR cable interface. Different levels of COD by varying glucose concentrations were studied to examine the effect on the open circuit voltage (OCV). The cell's electromotive force, OCV, without taking into account internal losses, is defined as the difference in chemical potentials or thermodynamic state between the two electrodes (Logan *et al*., 2006). The glucose concentration of 10.0 g L^{-1} was mixed into the culture medium to make final COD concentration of 10000 mg L^{-1}. Finally, the medium using fresh POME was also used and were prepared with distilled water in ratio 1:10. When the time interval of taking voltage reading had changed to 1 min, the performance of MFC and COD value were registered every day. The readings of voltage were recorded at variable resistance points and taken after 10 min to obtain the pseudo-steady state value. The adjustable resistance value was varied from 1.0 M ohm to 1.0 K ohm and power density were calculated according formula P_D (mW m^{-2}) = $I_D \times V$, where I_D is current density (mA m^{-2}) which can be calculated by $I_D = V/(R_{ext} \times A)$ based on external resistance (Ω) and projected surface area A (m^2). Polarization curves were constructed by plotting the value of cell voltage and power density against current density. COD was determined by standard method using 10 mL COD vial supplied with digester reagent COD range of 0- 1, 500 mg-COD L^{-1} (Hach, USA).

RESULTS AND DISCUSSION

MFC startup and OCV: Prior to start the experiments, the POME sludge was settled and filtered with to remove bigger suspended solid from the sludge. Amounts of 200 mL filtered sludge were taken and pour directly into the MFCs chamber before starting up. The Open Circuit Voltage (OCV) was recorded with the absence of current for some time (Fu *et al*., 2009), increased gradually from zero. From the observation, the systems only took less than 3 h to approach 0.8 V and the current remained zero during this change. Since, the startup experiment has caused contact of biomass with the electrode, the resulting transient dynamics of OCV responses occurred and can be regarded as a general exponential curve during initial run. For the OCV reading taking after phase of start up, the OCV was registered from the maximum current to zero current which is shown under same plot with the start up OCV. The transition of OCV responses is dependent upon the value of time constant (RC), which is known as the product of internal resistance and capacitance in MFC. The voltage, as function of both RC and time, is described in Eq. 1 (Floyd, 2004):

$$V = V_f\left(1 - e^{-\frac{t}{RC}}\right) \tag{1}$$

where V is the voltage reading, V_f is the OCV at the steady state, RC is the time constant and t is the time duration. To obtain the time as a constant, Eq. 1 can be further rearranged by linear relationship into Eq. 2:

$$\ln(V_f - V) = -\frac{1}{RC}\cdot t + \ln V_f \tag{2}$$

By using the linearization curve fitting method, RC can be determined from Fig. 1a, b and the results are summarized in Table 1. The value of RC was 3.36 h for 3 750 mg-COD L^{-1} (10% POME) and 1.95 h for 10000 mg-COD L^{-1}. High RC value occurred at low COD have indicated that the potential generated was unstable at the anode surface. However, the RC results from different level of COD have also shown that the bacteria community tends to produce strong potential at the anode with high range of COD supply and lower RC value. The time constant, RC represents the characteristic of electronic circuit, which defined the necessary of time space to reach 63.2% of the final steady state. The time constant and power could be varied simultaneously as the internal resistance is reduced.

Table 1: Summary on RC value, steady state OCV at initial, maximum power density and COD removal efficiency that achieved in different initial COD level

COD (mg L^{-1})	3750	10000
RC (h)	3.36	1.95
$V_{f,0}$ (V)	0.0728	0.4113
*$P_{D,max}$ (mW m^{-2}) with I_D (mA m^{-2})	1.780 (3.996)	3.115 (9.322)
Highest COD removal (%)	72.2	89.9

*Occurred at day 2 of experiment

As the COD increased from 3750 to 10000 mg L^{-1}, the respective initial OCV (V_{fo}) also showed the increments from 0.0728 to 0.4112. Most V_f value were close to the higher value for several day and then, gradually fall to lower value toward the last day of operation. The V_f for MFC with COD 10000 mg L^{-1}, was found fluctuated and unstable as show in Fig. 1b. However, the V_f was found more stable with COD 3 750 mg L^{-1}.

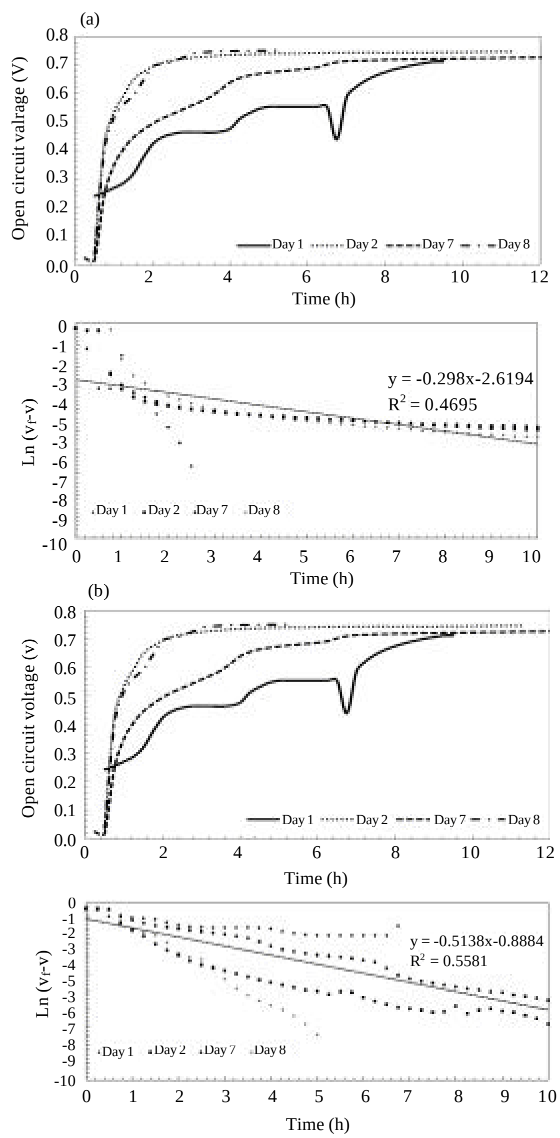

Fig. 1: OCV with RC value determination curve based on Eq. 2 at different initial COD level (a) 10% POME (3 750 mg L^{-1}); (b) synthetic wastewater (10000 mg L^{-1})

Effect of power output on COD concentration: The MFC runs with 10% POME supplied with different glucose concentrations was investigated to study the effect of initial COD level on electricity generated. For every 10.0 g L^{-1} of glucose concentrations, COD value contributed into the system will be of about 10000 mg L^{-1}. Fresh POME used in this study was diluted beforehand with distilled water in the ratio of 1:10. The initial MFC stabilized was at OCV of 0.8-0.9 V. However, when the resistance was applied to the MFC at certain resistance points, it caused the voltage to drop. The voltage had experienced a sudden drop of voltage to 0.68 V when a 90 KΩ resistance was applied and during that time, the scurrent density (current per electrode area) started to increase from 0 to 0.07 mA m^{-2}. In this experiment, various level of resistance was applied, from 1 kΩ to 1 MΩ with the aims to observe the effects of voltage and current density changes. Each of them took 10 min or more to approach new pseudo-steady state and each data was taken at 1 min interval. The time course of the current and power density generated by varying COD concentration at different consecutive day are shown in Fig. 2a, b.

To test the effect on biomass activity, the MFCs experiments were run at different COD and the power densities were noted everyday. Since the plot of voltage and current density against different resistance are known from the previous polarization experiments, power curve could be obtained. From the polarization curve, three zones can be divided into (1) activation loses, (2) ohmic loses and (3) mass transport losses, where each is subjected to the kinetics, overall resistance and ion transportation, respectively. The MFC performance was determined by ohmic losses based on power density and polarization curve. The power density was likely to increase at the beginning of the experiment but decreased after day 3. The optimal power densities of MFC at 10000 and 3750 mg-COD L^{-1} (10% POME), was determined to be 3.115 and 1.780 mW m^{-2}, respectively.

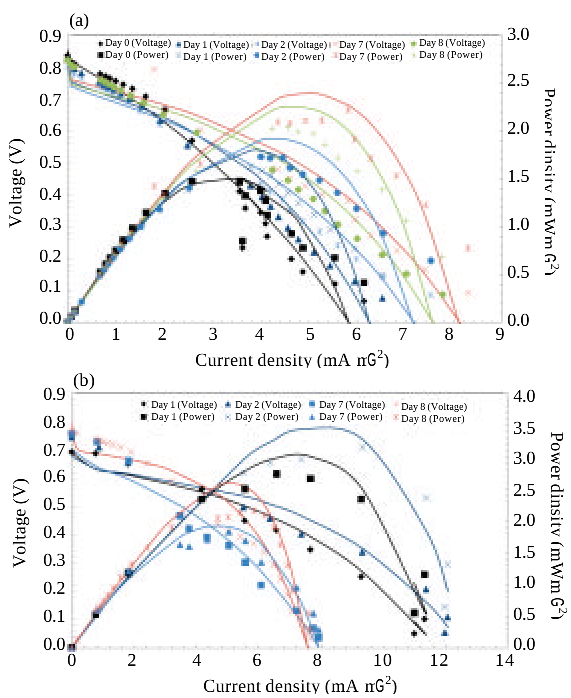

Fig. 2: Voltage and power performance curve for initial COD of (a) 10% POME (3 750 mg L^{-1}) and (b) Synthetic wastewater (10000 mg L^{-1}) (other days data are not show)

COD removal and treatment: The efficiency of MFC was observed by the power generation performance and removal of COD from the synthetic and real wastewater. After day 3 operations, the efficiency of total COD removal was 72.2% for the POME and 89.9% for the synthetic wastewater. Figure 3 shows COD removal at different initial glucose concentration begins from day 1 until day 13. The removal efficiencies were increase constantly from day 1 and reach maximum at day 10. The RC value, steady state OCV at initial, maximum power density and COD removal efficiency that achieved in different initial COD level was summarized in Table 1.

Polarization and power density at different COD condition: The maximum current and power density were monitored every day during experiments. The value of maximum current and power density that uses synthetic wastewater as starter culture were observed. It was found that the values tend to increase from day 1 until day 2, before the value was decreasing after fresh wastewater was replaced. From day 3 to day 8, the current and power

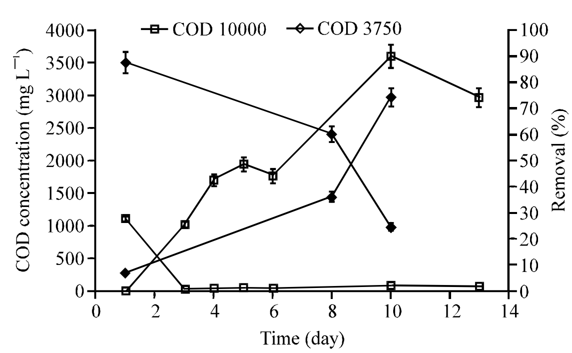

Fig. 3: COD removal using POME sludge culture at different initial COD level

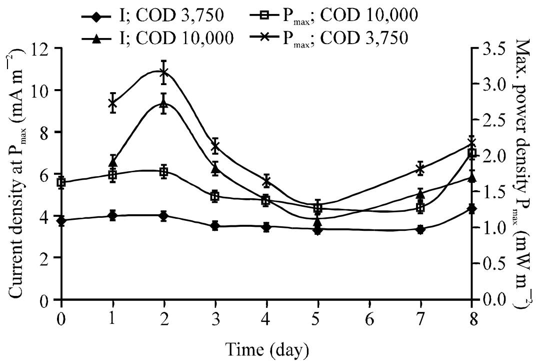

Fig. 4: Maximum power densities and the current densities at Pmax for POME and synthetic wastewater at different day of experiments

Table 2: Maximum current density & power density for COD 10% POME and 10 000 mg L^{-1} at different day of experiment (others day data are not shown)

t (day)	I_D at P_{max}(mA m^{-2})	$P_{D,max}$(mW m^{-2})
10% POME		
0	3.790	1.629
1	3.998	1.733
2	3.996	1.780
3	3.537	1.441
7	3.351	1.283
8	4.356	2.054
10 000 mg L^{-1}		
1	6.565	2.736
2	9.322	3.155
3	6.261	2.140
7	5.032	1.822
8	5.834	2.156

density were found slightly decrease due to the accumulation of metabolite product such as the accumulation of ion H^+ depressed microbial activities. The maximum value was constantly dropped after day 2 and finally maintain to constant for the next consecutive days as shown in Fig. 4 and the results are summarized in Table 2.

MFC modeling: The mathematical expression for MFC could be written using conventional fuel cell model (Wen *et al*., 2009):

$$V = E_o - \eta_{act} - \eta_{ohmic} - \eta_{conc} \quad (3)$$

where V is cell voltage when operating of fuel cell; E_o is predicted theoretical open circuitvoltage; η_{act}, η_{omic} and η_{conc} are voltage loses due to reaction kinetic, ohmic resistance and mass transport, respectively. The net fuel cell j-V behavior can be written in detail as:

$$V = E_o - b\log I_D - RI_D - \gamma\exp(\omega I_D) \quad (4)$$

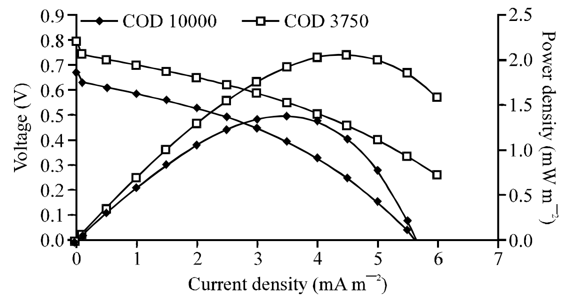

Fig. 5: Averaged performance of MFC simulated from polarization model using parameter as mention in Table 3

Table 3: Averaged electrochemical parameters subtracting from polarization model based on Eq. 4)

COD (mg L^{-1})	3750 Ave.	10000 Ave.	Differences (%)
R^2	0.95±0.00	0.95±0.00	0.0
P_{max} (mW m^{-2})	2.06±0.00	1.38±0.00	-32.9
$^*I_D$ (mA m^{-2})	4.50±0.00	3.50±0.00	-22.2
E_0 (V)	0.8247±0.0300	0.6962±0.1057	-15.6
b (V)	0.0125±0.0020	0.0095±0.0050	-24.1
R_i (Ωm^2)	0.0047±0.0012	0.0021±0.0011	-55.3
ã (V)	0.0905±0.0325	0.0724±0.0617	-20.0
ω (m^2 mA^{-1})	0.2925±0.0674	0.3954±0.1862	35.2

*Value at p_{max}

where ηact = b log I_D, represents activation losses from both electrodes in MFC based on natural logarithm of Tafel equation η_{omic} = RI_D, ohmic resistance losses based on current density I_D and resistance R; η_{conc} = $\gamma\exp(\omega_D)$ is combined fuel cell concentration loss, where γis a empirical constant and ù is fitting constant.

The experimental data was subjected to numerical simulation and was evaluate to obtain a best fit of electrochemical parameters. The simulation code was developed in MATLAB (version R2008a) using sum square error method (Mahreni, 2009). The regression value, R^2 indicated best fit between experimental and simulation data were set closed to 0.95.

The simulated results were show Fig. 2 (in different day and initial COD level) and Fig. 5 (averaged polarization curve) using electrochemical parameter from Table 3. The electrochemical parameters summaries in Table 3 indicated the effect of current limitation and total losses was eliminated at high COD level except ω value and increased power density. Figure 5 shows averaged power density that could achieve at different level of COD. Meanwhile, Fig. 6 shows current limitation due to voltage losses. Both curves show the concentration loss in MFC was dominant followed by ohmic and electrodes active loss.

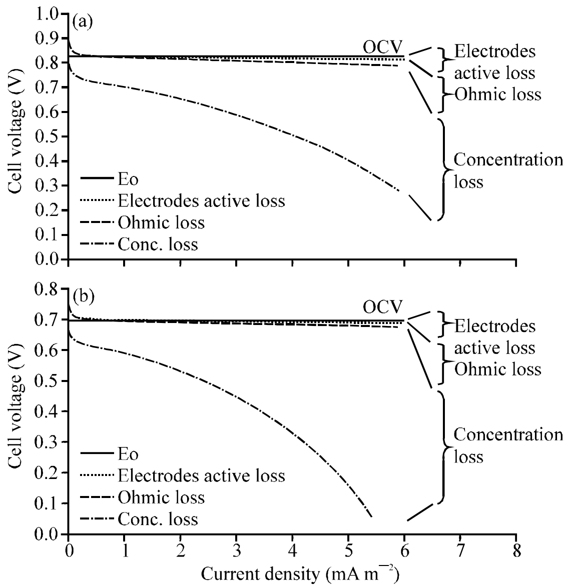

Fig. 6: Voltage losses analysis based on polarization model for initial COD level (a) 10 % POME (3 750 mg L^{-1}) (b) synthetic wastewater (10 000 mg L^{-1})

CONCLUSION

The RC obtained from OCV of MFC has shown getting lower value with higher COD concentration. The MFC needed longer time to reach its new steady stage OCV that recover from the maximum current operation. However, with the increment of lower initial COD level (3750 mg L^{-1}) to high COD level (10000 mg L^{-1}), maximum power density and COD removal were gradually increased. The COD removal efficiency has shown that the removal of 72.2% for higher COD concentration was obtained and for lower COD concentration, the removal was 89.9%. It means that the MFC work more efficient at lower COD concentration and produce higher power density at lower COD concentration. At 3750 and 10000 mg-COD L^{-1}, optimal maximum power density (present current density) were 3.155 mW m^{-2} (9.322 mA m^{-2}) and 1.780 mW m^{-2} (3.996 mA m^{-2}), respectively. The results shown that power densities and COD removals were proportionally increase with increment of initial COD level in MFC. However, the relationship between RC values was inversely proportionally regarding to initial COD levels. Most of electrochemical parameters simulated from polarization model were decreased from 15-55% indicated the total losses was eliminated at high initial COD level. From the results, concentration loss was major loss in MFC followed by ohmic and electrodes active loss.

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