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Effects of organic loading rate and operating temperature on power generation from cassava wastewater by a single-chamber microbial fuel cell

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ABSTRACT

This research examined the effects of organic loading rate (OLR) and operating temperature on cassava wastewater treatment and the resulting power generated by a single-chamber microbial fuel cell. The OLRs were controlled to be 0.56, 1.44, 2.79, 4.14, and 6.25 kg COD/m^3 d at neutral pH 7.0. The selected operating temperatures were at normal mesophilic range at 30℃ and a transition temperature range between mesophilic and thermophilic at 45℃. The maximum efficiency of COD removal achieved from the OLR at 0.56 kg COD/m^3 d was 91.44 ± 0.72 and 90.72 ± 0.87% at 30 and 45℃, respectively. While the maximum power density obtained from the OLR at 6.25 kg COD/m^3 d was 28.68 and 27.85 W/m^3, respectively. The performance of COD removal decreases with increasing OLR. The power densities, the coulombic efficiency, and the internal resistance increases with decreasing OLR.

Keywords: Single-chamber microbial fuel cell (SCMFC); Cassava wastewater treatment; Power generation; Organic loading rate (OLR); Operating temperature; Polarization curves

1. Introduction

Cassava is a tropical plant. It is considered as an economically viable crop, and it is promoted in many parts of Thailand. The quantities of cassava wastewater were quite high and as were the COD concentrations. The typical process for treating cassava wastewater and the regulation requirement of the effluent industry wastewater (COD ⩽ 400 mg/L) was expensive. Microbial fuel cell (MFC) is at the moment considered only a future technology for sustainable wastewater treatment and simultaneous power generation. Electricity is produced by electrochemically activated micro-organisms via the use of organic compounds as substrate and an insoluble anode as electron acceptor in anaerobic condition [1]. In recent years, MFC has increasingly grown both in research and practical application [2]. Many studies have found that electricity can be generated from organic substrates in various sources, such as domestic wastewater [3], composite vegetable waste [4], mixed fatty acid [5], phenol [6],

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starch processing wastes [7], chocolate industrial wastewater [8], acetate, ethanol, and glucose [9]. Moreover, MFC can be used as an electron acceptor in the treatment of organic complexes such as diesel compounds, and demonstrates high removal efficiency up to 82% [10]. MFC can also be used with high efficiency for decolorization in wastewater treatment [11] or in leachate wastewater application [12]. Power generation showed improvement with an increase in the organic loading rate up to 0.911 kg COD/m^3 d, and showed a drop at the OLR of 1.589 kg COD/m^3 d, suggesting inhibition at higher carbon loading rates [13]. When using composite waste vegetables as a substrate, a higher power output was observed at loading 0.70 kg COD/m^3 d, and COD removal efficiency was 62.86% [14]. The test on various food industry wastes for electricity production suggested that yogurt wastewater could produce higher power output than fermented apple juice and wine lees [15]. In general, higher power density was achieved with the single-chamber microbial fuel cell (SCMFC) under mesophilic conditions, compared to lower temperature ranges [3]. In contrast, better growth of methanogens at low temperature range might possibly give high power density than at mesophilic temperature [16]. Some research work reported that changing the temperature might produce limited effects [17]. More research is needed to investigate effects of various temperature ranges on MFC performance. Nevertheless, temperature is onsidered as an important factor for survival of exoelectrogens and methanogens in anaerobic anode. The performance of enhanced MFC also depends on many key factors, because the processes of MFC are a combination of biochemical, electrochemical, and architecture of MFC. Therefore, examining the optimization of designs and operations for the MFC are of particular interest to this type of research.

In order to enhance the performance of MFCs, the optimization of operating conditions as temperature range and OLR should be evaluated. This research does so by examining a cassava wastewater treatment at a mesophilic temperature and a transition temperature (30 and 45˚C). The experiments worked on batch flow mode in a SCMFC system. The efficiency of SCMFC treatment was evaluated in terms of total COD removal efficiency, power generation, coulombic efficiency (CE), and also illustrated by the polarization curves. Examination of these factors will allow to exploration of the potential of using MFC to simultaneously produce direct electricity generation and wastewater treatment from the cassava wastewater as a promising substrate in hot climatic regions.

2. Methodology

2.1. Wastewater

The wastewater in this experiment was collected from the equalitzation pond before being fed to the wastewater treatment plant of Roi-Ed Flour factory, Roi-ed province, Thailand. The characteristics of the raw wastewater, which was kept in refrigerator at 4˚C before use, in general parameters were TCOD 14,500–21,800 mg/L, pH 3.84–3.92, TP 54 mgP/L, TKN 160 mg/L, sulfate 18,000–22,000 mg/L and conductivity 2.77 μS/cm. The pH was adjusted to 7.0 ± 0.1 by NaOH and diluted COD by deionized water to control OLRs of 0.56, 1.44, 2.79, 4.14 and, 6.25 kg COD/m^3 d.

2.2. Microbial fuel cell

A single-chamber microbial fuel cell (SCMFC) using carbon cloth for an anode and four layers of polytetrafluoroethylene on carbon cloth with proton exchange membrane and platinum 0.5 mg/cm^2 as a catalyst for the cathode [18] was made from polyvinylchloride tube with inside diameter 7 and 4 cm long as shown in Fig. 1. The empty volume was 150 mL. The carbon cloth anode A-1 acquired from the Clean Fuel Cell Energy company (LLC) was 7 cm in diameter with a total area of 38.48 cm^2. The carbon cloth cathode B-1 acquired from Clean Fuel Cell Energy company (LLC) was 7 cm in diameter and coated with platinum 0.5 mg/cm^2 and PEM (Nafion® solution 5% wt) on one side, and on the other side coated with Teflon four layers, the total

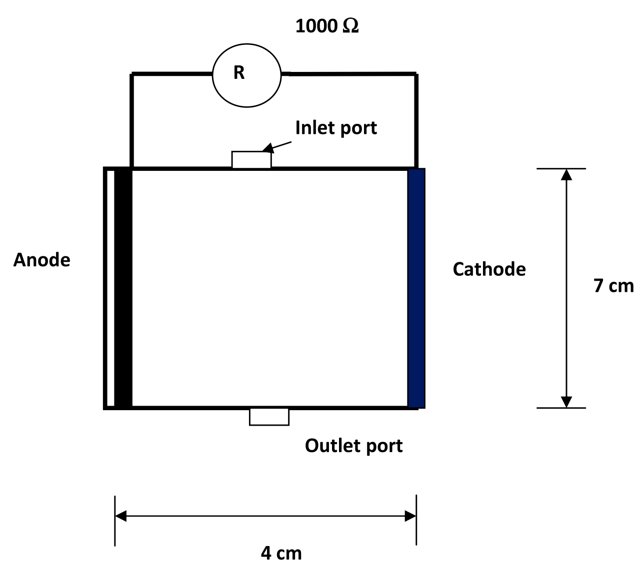

Fig. 1. A SCMFC used in this study.

area is 38.48 cm^2. The space between cathode and anode was 4 cm. Electrodes were connected with copper wire through external loading resistance of 1,000 ohm.

2.3. Inoculums and operation

SCMFC was inoculated with UASB sludge from the cassava factory. Before using in SCMFC, it was dried in daylight for 2 days and then heated at 60˚C for 1 h to remove methanogenic bacteria. Subsequently, it was grinded and screened by 1 mm^2 mesh. The resulting MLSS concentration was 3,000 mg/L. The first batch, fed cassava wastewater of 150 mL, contained no additions of any other nutrient or trace metal. At the end of the cycle, the 120 mL of liquid was withdrawn. The next batch, the wastewater of 120 mL, was filled and was withdrawn at the end of the cycle. The operating temperature was controlled at 30 and 45˚C. The cycle of batch mode flow operation was 24 h.

The experiments were considered to be stable when there was less than a 10% variation in power production, which then changed to another OLR. COD, pH, MLSS, and MLVSS were analyzed according to APHA standard methods [19]. The potential was measured and collected by a data logger at every 30 min. Polarization curves were obtained by varying the external resistance over a range of 10–10,000 ohm when the voltage output stabilized to a constant voltage at the end of each experimental run. The SCMFC was operated for three batches to ensure repeatable voltage outputs and the samples were collected for analysis.

2.4. Analyses and calculations

The power and the CE from SCMFC were expressed as follows:

$$P = (V^2)(R) \quad (1)$$

$$\mathrm{CE} = 8I/((F)(Q)(\Delta\mathrm{COD})) \quad (2)$$

where P = power (W), V = volt (V), R = resistance (ohm), I = current (A), F = Faraday constant (96,485 C/mol), Q = wastewater quantity (m^3) and ΔCOD = COD removal (g/m^3).

The internal resistance of the MFC was calculated from polarization slope method, in which the slope in a plot of current and voltage corresponds to internal resistance.

3. Results and discussion

3.1. Wastewater treatment

Table 1 shows a summary of the COD removal efficiency at the end of the experiment.

From Table 1, the efficiency of COD removal decreased when the OLR increased. At high OLR (6.25 kg COD/m^3 d), it took more time to reach a constant COD in the effluent than at low OLR (0.56 kg COD/m^3 d) (Fig. 2(a) and (b)), because at high substrate loading rate the ratio of F/M ratio at the beginning operation in the anode chamber was lower than at low substrate loading rate, thus the micro-organism was insufficient for reducing the organic matter, which meant a low efficiency of COD removal.

At high OLR (6.25 kg COD/m^3 d), there was only 30% of COD removal efficiency at the first stage of operation. However, the micro-organisms survived by increasing their quantity to balance with the food in the chamber and achieved a steady state after 400 h. When the COD reached a steady state (Fig. 2), the efficiency of COD removal increased to 73.7%. At low OLR condition (0.56 kg COD/m^3 d), it took only 250 h to reach the maximum value of COD removal efficiency. This study suggests that the microbes needed sufficient time for acclimatization when operating with high OLR. Comparing the efficiency of COD removal between low OLR and high OLR shows that COD removal efficiency decreases when the OLR increases, in both temperature conditions. However, as the operation time increased through steady state, the performance of COD removal efficiencies of both temperature ranges were similar. This steady state showed that micro-organisms could acclimatize themselves to the environment.

3.2. Power generation

When the anode chamber of an SCMFC was filled with cassava wastewater, the initial voltage was 0.12–0.40 V, depending on the OLR. It took 4 h to reach the stable value after the effluent was withdrawn and the new wastewater was filled, it dropped close to the initial value again. The initial circuit voltage of the latter batch was higher than the previous batch and also of the maximum circuit voltage.

Figs. 3(a) and 3(d), the circuit voltage at high OLR (6.25 kg COD/m^3 d) was constant during the first batch cycle to the second batch cycle, then decreased when the operating time increased during the second batch cycle to the fifth batch cycle. From the fifth batch cycle to the eighth batch cycle, the circuit voltage increased and reached a constant value. The

Table 1
The efficiency of COD removal

Temp (℃)	OLR (kg COD/m^3 d)				
	0.56	1.44	2.79	4.14	6.25
30	91.44 ± 0.72	86.14 ± 1.99	79.47 ± 2.16	78.37 ± 2.04	73.67 ± 2.99
45	90.72 ± 0.87	82.45 ± 1.34	76.83 ± 3.60	75.87 ± 2.61	70.74 ± 1.72

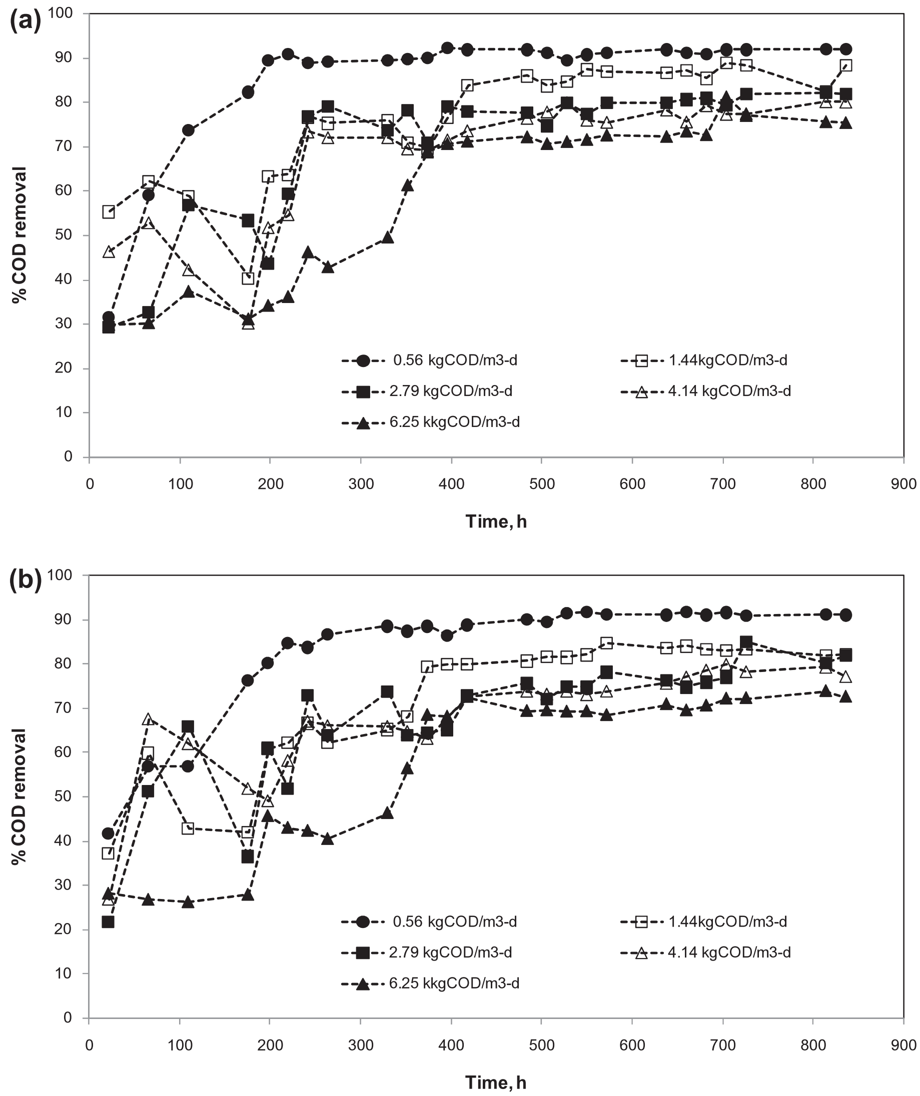

Fig. 2. The efficiency of COD removal as function of time (a) at 30℃ and (b) at 45℃.

constant circuit voltage at the first stage was due to an initially clean electrode. The decrease in circuit voltage at the second stage was due to voltage losses as result of slime or biofilm forming at the cathode surface. The increase in circuit voltage at the latter stage was due to an increase in microbial activities. The circuit voltage was constant from the eighth batch cycle to the end of experiment (Figs. 3(b) and 3(e)).

At the last batch cycle, the circuit voltage slightly decreased. This decrease in circuit voltage was due to mass transfer losses and oxygen leakage in the anode chamber.

The mass transfer losses increased when biofilm formed on the cathode surface accumulated in the cathode chamber. The proton accumulation in the cathode chamber was shown by the decrease of pH in

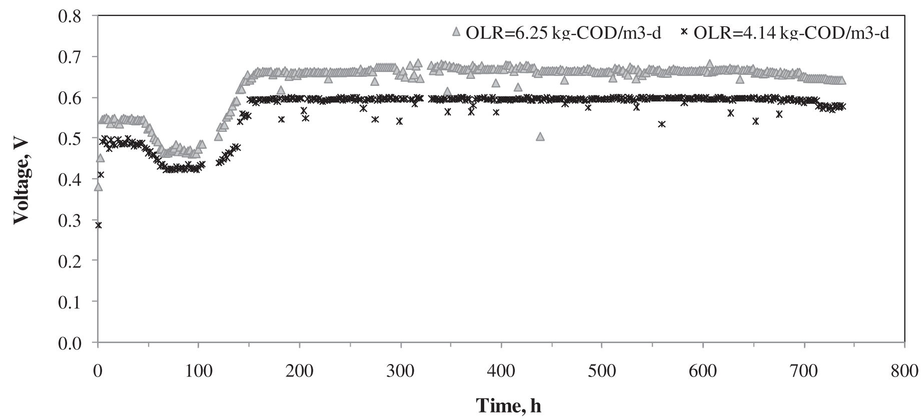

Fig. 3(a). The circuit voltage output from 6.25 to 4.14 kg COD/m^3 d at 30°C.

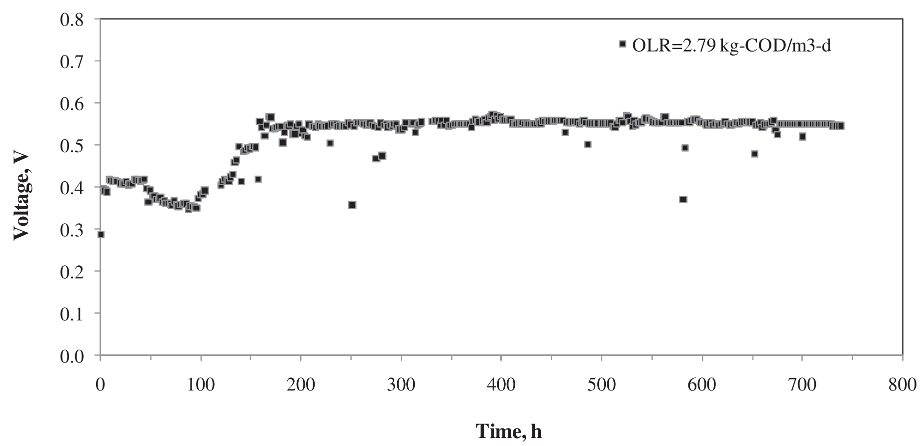

Fig. 3(b). The circuit voltage output from 2.79 kg COD/m^3 d at 30°C.

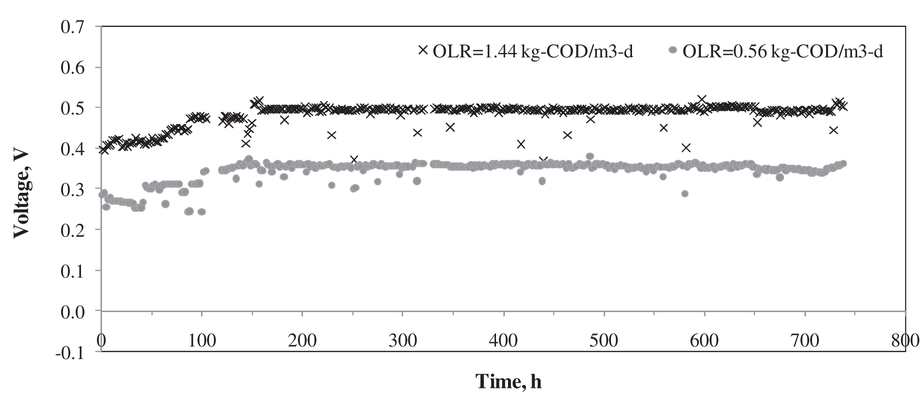

Fig. 3(c). The circuit voltage output from 1.44 to 0.56 kg COD/m^3 d at 30°C.

the effluent. In addition, organic matters at high OLR were accumulated at high rate more than at low OLR (the wastewater was filled and withdrawn every day).

Figs. 3(c) and 3(f), the circuit voltage at low OLR (0.56 kg COD/m^3 d) was constant during the first batch cycle to the sixth batch cycle. From the sixth batch cycle to the seventh batch cycle, the circuit voltage increased and reached a constant value through to the end of the seventh batch cycle. The occurrence of circuit voltage at low OLR was different from that at

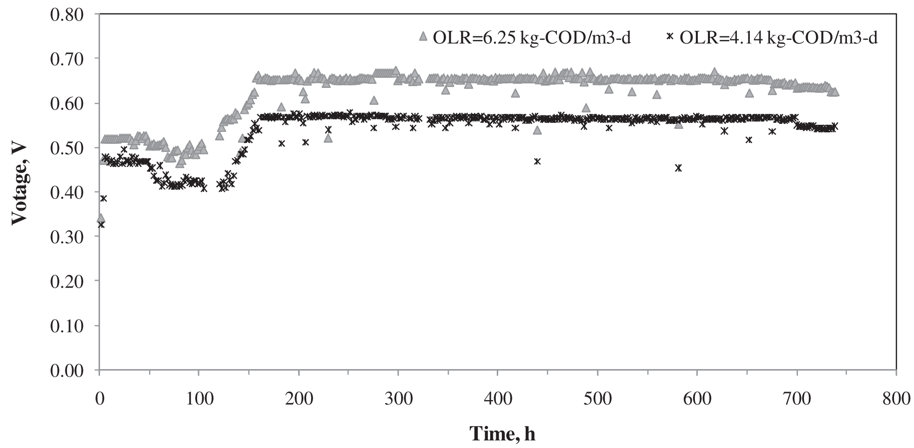

Fig. 3(d). The circuit voltage output from 6.25 to 4.14 kg COD/m^3 d at 45˚C.

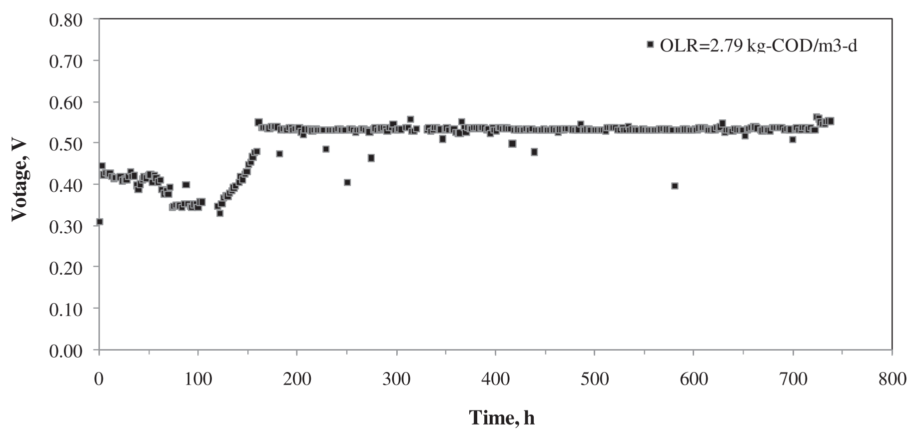

Fig. 3(e). The circuit voltage output from 2.79 kg COD/m^3 d at 45˚C.

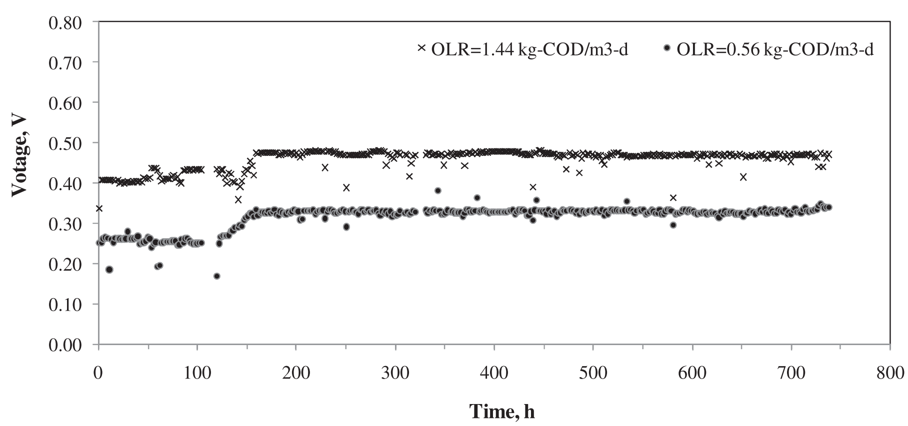

Fig. 3(f). The circuit voltage output from 1.44 to 0.56 kg COD/m^3 d at 45˚C.

high OLR as a result of the mass transfer losses and the food per micro-organism ratio (F/M). The organic matter accumulation in anode chamber at low OLR was lower at high OLR because the concentration of wastewater at low OLR was lower than that of the high OLR. Additionally, the wastewater was filled and withdrawn every day. The mass transfer losses at low OLR was lower than that of the high OLR, so the circuit voltage did not decrease. When compared to the F/M ratio, the F/M ratio at low OLR (0.21 kg COD/m^3 d) was lower than that of the high OLR (2.36 kg COD/m^3 d). The relation of circuit voltage and COD removal was a direct variation in MFC [20]. At low OLR, the circuit voltage reached the constant faster than that of the high OLR.

The pH in the effluent did not adversely affect the kinetic energy of the micro-organism, as pH in the effluent from anode chamber did not drop below 6.5 [21]. The alkalinity in the influent wastewater was used as buffer in the anode chamber. Sodium hydroxide solution (alkalinity) was added to influent wastewater to keep the initial pH feed of 7.0. The minimum concentration of alkalinity in the effluent was found at the lowest OLR (more than 200 mg/L as $CaCO_3$) (data not shown).

As the operating time increased, the micro-organisms appeared to acclimatizes with the environment. As they increased their cell numbers, some of them formed as a biofilm on the surface of the cathode. This biofilm increased the mass transfer losses in SCMFC, but a slight decrease in circuit voltage did not cause a major loss. Most of the micro-organisms formed as granules and attached at the surface of the anode. However, the effects of granules at the surface of anode enhanced the power generation because the granules at anode surface decreased the distance of electron shutter from solution to anode surface. The competition between the activities of the granules at anode surface and the biofilm at the cathode surface was effected by the values of the circuit voltage or the total loss. In this study, the circuit voltage did not drop significantly, so the electron lost by the biofilm was not the major effect on decreasing the circuit voltage. At both operating temperatures, a number of bands from the gels were cut for sequence analysis as shown in Fig. 4. At 30℃, the population could be assigned to four groups: Gammaproteobacteria, Betaprotobacteria, Bacteroidetes, and Firmicutes as shown in Fig. 5. At 45℃, the bacterial population could be assigned to three groups: Gammaproteobacteria, Betaprotobacteria, and Firmicutes as shown in Fig. 6.

Other factors enhancing the performance of SCMFC were on the characteristics of wastewater such as the solution conductivity. Our study demonstrated that the power generation increased with increasing the solution conductivity (the solution conductivity increased with the OLR). The solution conductivity in the effluent of 30℃ was 0.047 ± 0.003, 1.67 ± 0.22, 3.63 ± 0.30, 4.32 ± 0.34, and 5.70 ± 0.31 mS/cm as the OLR was 0.56, 1.05, 1.44, 2.76, and 6.25 kg COD/m^3 d, respectively and the solution conductivity at 45 ℃ condition was 0.047 ± 0.008, 1.71 ± 0.17, 3.57 ± 0.21, 4.27 ± 0.33, and 5.55 ± 0.22 mS/cm for the same OLR values.

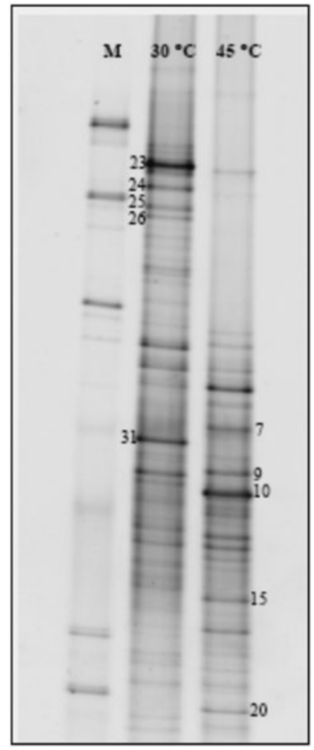

Fig. 4. PCR-DGGE fingerprints for bacterial communities in MFC. Each lane contains PCR-amplified 16S rRNA gene fragments from 30 to 45℃. Lanes labeled M contain a reference fingerprint used to correct for differences in fragment migration across the gel.

The solution conductivity increased from 46.74 to 5.70 μS/cm and the power density increased by 71.46% (data at 30℃). This result conformed to those of using the resulting beer brewery wastewater as a substrate by SCMFC [22]. Also, the effects of ionic strength, cation exchange, and inoculum age on the power generation were examined in a mediator MFC with methylene blue as the electron mediator [14].

The results of this study show that cassava wastewater can generate power by SCMFC effectively. The power achieved from the experiment is shown in Fig. 7. The results illustrate that the MFC can generate electricity using cassava wastewater as substrate. The OLRs of 0.56, 1.44, 2.79, 4.14, and 6.25 kg COD/m^3 d generate power outputs of 8.2, 16.0, 19.8, 22.9, and 28.7 W/m^3, respectively at operating temperature of 30℃. While the values of power generation at 45℃ were 7.18, 14.49, 18.49, 20.85, and 27.85 W/m^3, respectively and show the same trend at 30℃. The increased power occurred from increasing OLR or influent COD concentration.

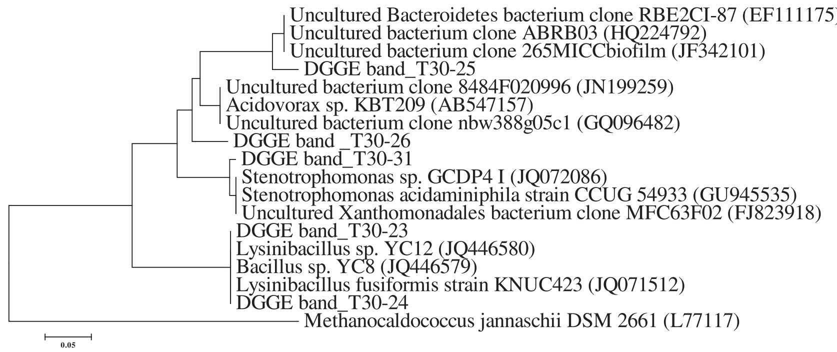

Fig. 5. Phylogenetic tree recovered from sludge in anode chamber at 30˚C.

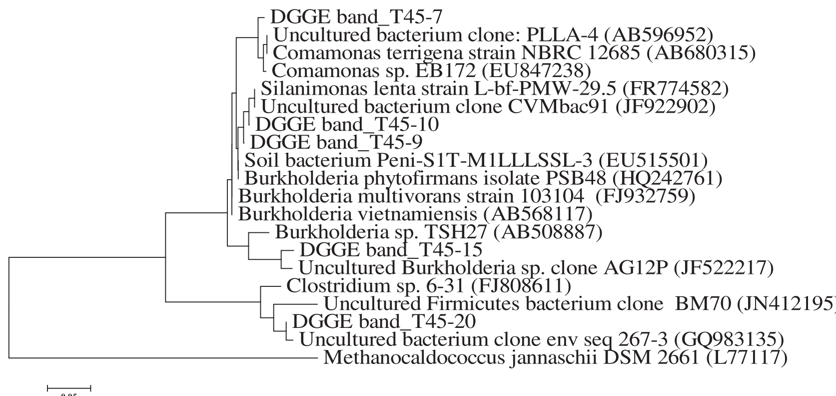

Fig. 6. Phylogenetic tree recovered from sludge in anode chamber at 45˚C.

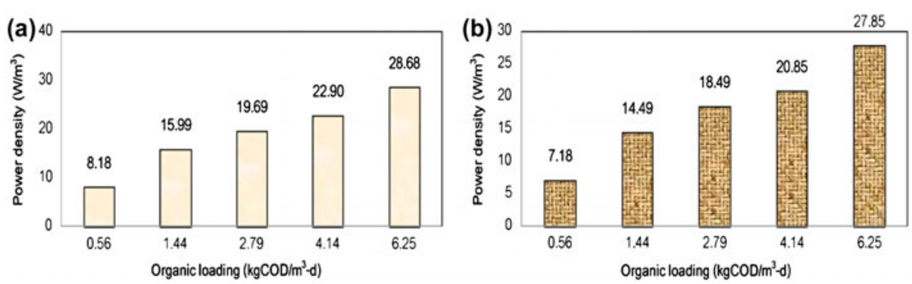

Fig. 7. Power density obtained from cassava wastewater by SCMFC (a) at 30˚C and (b) at 45˚C.

3.3. Coulombic efficiency

CE represents the conversion efficiency of organic carbon to electricity by micro-organism activities in an SCMFC. This study found that the CE decreases when the OLR increases, at both temperature conditions. At 30˚C, the highest OLR was found to be 6.25 kg COD/m^3 d, whereas CE was found to be 6.2%. CE value was found to be increased along with detention time. Low CE occurred at high OLR because there was high concentration of other electron acceptors such as sulfate in the wastewater, which caused the loss of electrons. Sulfate in cassava wastewater was from sulfuric acid, which was added in the production processes. We also found that sulfate concentration in the influent of cassava wastewater was very high at 1,038, 2,894, 6,052, 9,124, and 11,572 mg/L for OLRs of 0.56, 1.44, 2.79, 4.14, and 6.25 kg COD/m^3 d, respectively. The sulfate in the effluent was constant.

Moreover, sulfate removal loading reduced when the OLR increased in both the temperature conditions. The maximum sulfate removal loading occurred at the highest OLR. The amount of sulfate removal was used as an electron acceptor by substrate reduction. Theoretically, COD of 64 mg will reduce 96 mg of sulfate to sulfide of 1 mol, or 1 mg of sulfate will use COD of 0.67 mg. The amounts of COD consumed by sulfate reduction in theory at 30℃ are 652, 1,855, 3,654, 5,465, and 7,990 mg/L, and at 45℃ the figures are 653, 1,785, 3,585, 5,317, and 7,704 mg/L for OLR values of 0.56, 1.44, 2.79, 4.14, and 6.25 kg COD/m^3 d, respectively.

The COD lost by sulfate reduction caused a lower CE, while the maximum CE resulted from the lower OLR. The percentage of COD available for producing electricity was close to the CE value at both the temperatures. These results indicate that the amount of sulfate reduction affects the generation of electricity by SCMFC.

3.4. Polarization curve and internal resistance

In a plot of current density and voltage curve, the polarization slope method was used to examine the internal resistance and maximum power density by varying the external resistance from 10 to 996 ohm. Fig. 8 shows the maximum power density with OLR. The internal resistances of 30℃ were 115, 64, 55, 52, and 38 Ω and the internal resistances at 45℃ were 134, 83, 59, 59, and 48 Ω at OLR of 0.56, 1.44, 2.79, 4.14, and 6.25 kg COD/m^3 d, respectively.

The maximum internal resistance of this study was obtained from the lowest OLR of 0.56 kg COD/m^3 d. A high concentration of COD influent, as well as a high solution conductivity, cause high power production and lower internal resistance, similar to the previous reported from [14]. Decreasing anolyte conductivity might be the result of increasing the internal resistance to the flow of electrons in the anolytes, thereby increasing the ohmic losses [23]. The conductivity of our study increased from 0.047 mS/cm to 5.67 μS/cm. This caused the internal resistance to decrease from 115 to 38 ohms, which is a 67% decrease in the internal resistance at 30℃ operation.

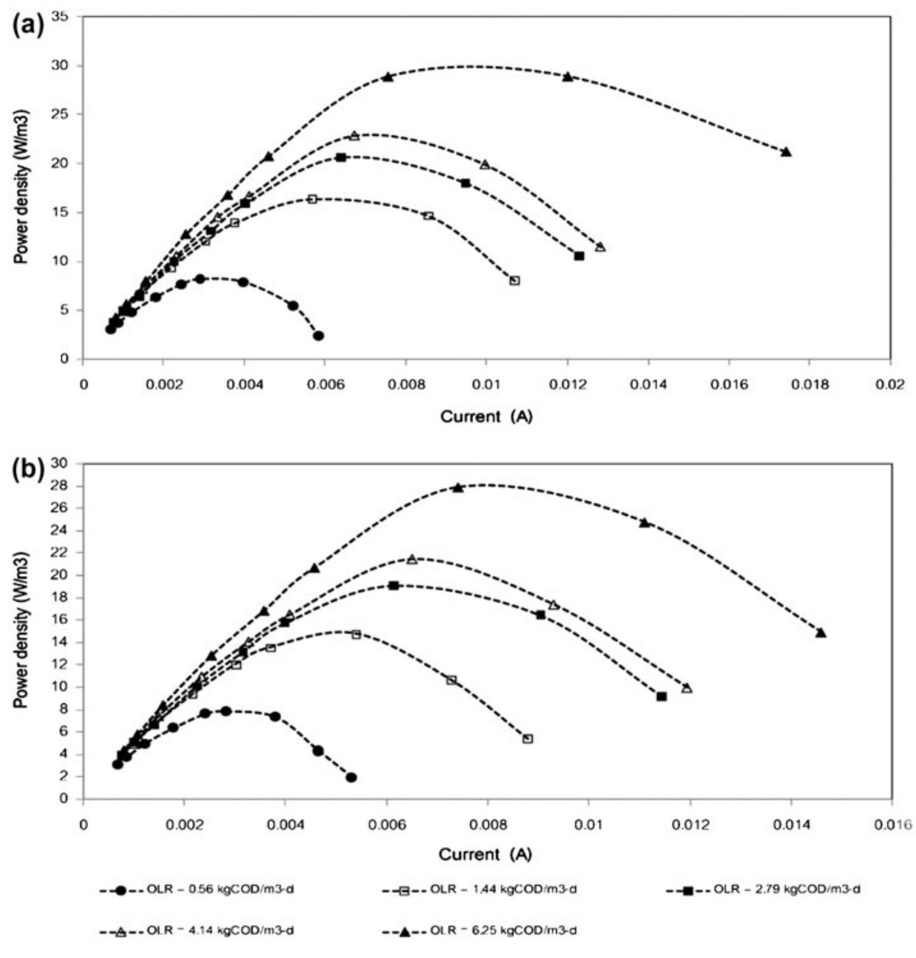

Fig. 8. The polarization curves: (a) at 30℃ and (b) at 45℃.

4. Conclusions

Cassava wastewater can be treated effectively by a single-chamber microbial fuel cell (SCMFC) at both mesophilic temperature of 30°C and a transition temperature of 45°C with COD removal efficiencies of 91.44 ± 0.72 and 90.72 ± 0.87%, respectively at the optimum OLR of 0.56 kg COD/m^3d and pH 7.0. The performance of COD removal decreases with increasing the OLR values. The power densities, the CE, and internal resistance were increased with decreasing the OLR of cassava wastewater treatment by the SCMFC.

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