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Article

Alkalinity of Cassava Wastewater Feed in Anodic Enhance Electricity Generation by a Single Chamber Microbial Fuel Cells

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Abstract. This study was demonstrated that the alkaline feeding in the anode chamber could enhance the electricity generation from a single chamber microbial fuel cell (SCMFC). The SCMFC was operated in batch mode. The substrate was cassava wastewater from a flour factory in Roi-Et province, Thailand and the concentration of COD value was controlled between $1,086 \pm 50.06$ mg/L. The pHs were varied from acidity (pH 5.0 and 6.0), neutral (pH 7.0) and alkalinity (pH 8.0 and 9.0) by adding NaOH. The temperature was controlled at 30°C. The maximum power density could be generated to 22.19 W/m³ from pH feed at 9.0. Whereas at pH feed of 8.0, the second highest power density at 16.70 W/m³ was gained. The maximum efficiency of COD removal ($92.83 \pm 1.37\%$) was obtained from pH of 8.0. The maximum of coulombic efficiency (CE) was 47.8% which was obtained from pH feed of 9.0. The alkalinity feed enhanced the power generation by increasing the alkalinity and conductivity in the anode chamber more than other feeds. It was also found that the pH feed which was nearly close to neutral would enhance the wastewater treatment by SCMFC.
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Keywords: Single microbial fuel cell, cassava wastewater treatment, alkaline feed, pH.

1. Introduction

Cassava has been long well known as a food plant and recently it is also promoted as a power plant in many parts of Thailand. The wastewater from cassava factory carried high strength and high of solids contained. Anaerobic treatment and the oxidation pond are typical technologies of cassava wastewater treatment in order to meet the requirement of industrial effluent standard regulation (COD ≤ 400 mg/L). Biogas production from the anaerobic treatment can be indirectly used to produce electricity by thermodynamic processes. Microbial fuel cells should be considered as a modern technology for the wastewater treatment and at the same time generating electricity. Therefore, there was the feasibility that cassava wastewater could be used to generate the power through the treatment by microbial fuel cell.

Fuel cell could be used to produce power by generating H_2 [1] or directly generating electricity [2]. In microbial fuel cell, electricity would be produced by electrochemically processes of microorganisms oxidizing on organic compounds. The electrons were produced by oxidation processes and then released outside their cells. Those electrons were accepted by anode electrode as the electron acceptor in anaerobic condition. In many studies it was found that electricity can be generated from various sources of organic matters such as domestic [3], composite vegetable waste [4], various food industries [5], starch processing [6, 7], brewery wastewater [8, 9], cheese whey [10], palm oil mill effluent [11], sewage sludge [12], decolorization in wastewater treatment [13], leachate wastewater [14]. Those reports had also proved that microbial fuel cell could be used for wastewater treatment and simultaneously producing electricity in various conditions. The optimized conditions depend on the characteristic of the wastewater, architectures of reactor including the types of cathode, anode and connection wire, environment conditions such as pH, temperature, conductivity, quantity and source of sludge.

In general, cassava wastewater has low pH level due to the production processes. pH is one of the most important factors that influences the microbial fuel cell treatment performance and power generation. The result of this research can be literally applied with the real cassava wastewater treatment in any tropical countries. The treatment efficiency was evaluated in terms of total COD removal. The power density generation and the coulombic efficiency were analyzed from the circuit voltage.

2. Methodology

2.1. Wastewater

The raw wastewater used in the experiments was collected from Roi-Et Flour Factory, Roi-Et province, Thailand. The general characteristics of the raw wastewater in parameters: TCOD 14,500-21,800 mg/L., BOD_5 10,000 -12,500 mg/L., pH 3.84-3.92, TP 54-60 mgP/L., TKN 360-400 mg/L., Sulfate 18,000-20,000 mg/L. and conductivity 2.77 mS/cm. The pH in feeding was adjusted to 5.0, 6.0, 7.0, 8.0 and 9.0 by adding NaOH. COD influent was diluted by tap water to be 1,088±60 mg/L.

2.2. Microbial Fuel Cell

A carbon cloth, a single-chamber microbial fuel cell, was used for anode and another carbon cloth wrapped with four layers of polytetrafluoroethylene (PTFE) with proton exchange membrane and platinum 0.5 mg/cm² was used as the catalyst for cathode (Fig. 1). The chamber was made from polyvinylchloride tube with the inside diameter of 7 cm with the length of 4 cm. The empty volume was 150 mL. The anode was the Carbon cloth A-1 from Clean Fuel Cell Energy LLC with the diameter of 7 cm, so the total area was 38.48 cm². The cathode was the Carbon cloth B-1 from Clean Fuel Cell Energy, LLC with the diameter of 7 cm coated with Platinum 0.5 mg/cm² and PEM (Nafion® solution 5% wt.) on one side and another side was coated with Teflon 4 layers, so the total area is 38.48 cm². The spacing between cathode and anode was 4 cm. Anode and cathode was connected with the external copper wire and the resistance of 100 Ohms.
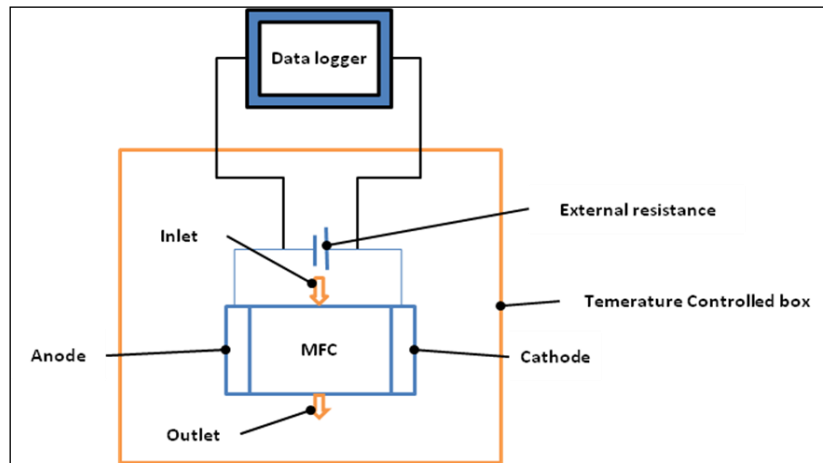
Fig. 1. Schematic diagram of a single chamber microbial fuel cell.

2.3. Inoculums and Operation

The SCMFC was inoculated with activated sludge that received from UASB wastewater treatment in the cassava factory. The sludge was left drying on daylight for 2 days and heated at 60 °C for 1 hour to suppress methanogens bacteria. When it was cool down to room temperature lather, it was grounded and sieved through 1 mm sieve. The initial MLSS in anode chamber was kept as 3,000 mg/L (MLVSS = 2,650 mg/L). The cycle of batch operation was controlled to be 22 hours. The first batch was set up by feeding 150 mL of the cassava wastewater into anode chamber. At the end of the 22nd hour, the effluent of 80 mL was withdrawn. The process of filling the new influent and withdrawing the effluent took about 2 hours. The temperature was controlled at 30°C and 45°C. TCOD and pH were analyzed according to APHA standard methods for the examination of water and wastewater [15]. The circuit voltage was measured and collected by a data logger every 30 minutes. Polarization curves were obtained by varying the external resistance over a range from 10 to 996 Ohms at the end of the experiment.

2.4. Analyses and Calculations

The power from SCMFC was calculated according to $P = (I)(V)$, where P = Power (W), I = Current (A), V = Volt (V) and $V = I.R$, where R = Resistant (Ohm) so, $P = V^2/R$. The coulombic efficiency (CE) was estimated by measuring current relative to the theoretical current on the basis of consumed COD as Eq.(1)[16]

$$CE = 8I/((F)(Q)(\Delta COD)) \tag{1}$$

where I = Current (A)

F = Faraday Constant (96,485 C/mol)

Q = Wastewater quantity (m³)

$\triangle COD$ = COD removal (g/m³)

Internal resistance of the MFC was calculated from polarization slope method which the slope in a plot of current and voltage was internal resistance.

3. Results and Discussions

3.1. Power Generation

The findings showed that the power could be generated through the cassava wastewater by using SCMFC. During the operation, the initial voltage varied from 0.1-0.3 V depending on the pH feeds. The circuit

voltage increased when increasing the numbers of batch cycle. The circuit voltage was almost constant at the end of the 2th cycle (40 hours) as shown in Fig. 2. From Fig. 2, the circuit voltage of extreme acidic feed (pH 5.0) and alkaline feed (pH 9.0) were slightly fluctuated and higher than one with the neutral feed. Besides in comparison, it was clearly seen that the feeding of pH 5.0 and 9.0 had inhibited the microbial activity more than in the neutral feed so the lower biochemistry reaction was found in both extreme pHs feed. However, the high conductivity was found in both extreme pHs, so the circuit voltage value were higher than that of neutral feed.

Power density achieved from the study is shown in Fig. 3. The maximum power density obtained from the alkaline feed (pH 9.0) as 22.19 W/m³ and the second order was 16.70 W/m³ which obtained from pH 8.0. When the pH feed was decreased from pH 9.0 to 6.0, it caused the lower of power density generation. But when pH feed was decreased from 6.0 to 5.0, the power density was increased from 5.60 W/m³ to 10.61 W/m³. The result from our study agreed with previous results which stated that the highest value of power generation could be reached when the value of pH in anode was at 10.0 and cathode was 2.0 [17]. The result from our study was lower than the powers density generation from two chambers microbial fuel cell by synthetic wastewater. The values of power densities were 36.72 W/m³ and 15.51 W/m³ at pH 8.0 and pH 6.0, respectively and pH 8.0 favoured more power production than pH 6.0 [18]. When air-cathode microbial fuel cell was used to produce electricity with a mixed bacteria culture, the optimal initial pH for electrical generating was between 8.0 to 10.0 [19]. The power output from our study was caused from the combination of biochemistry reaction and the electron transferring in anode chamber. Alkaline feed had directly promoted the microbial metabolism in using substrate and enhanced power generation. During the alkaline feed, there was the increasing of the alkalinity concentration comparing to acidic feed which later the alkalinity concentration. Alkalinity was used as a buffer in anaerobic reaction and caused the better growth of methanogens [17]. Comparison of power generation obtained from microbial fuel cells with different substrates and pH feed is shown in Table 1.
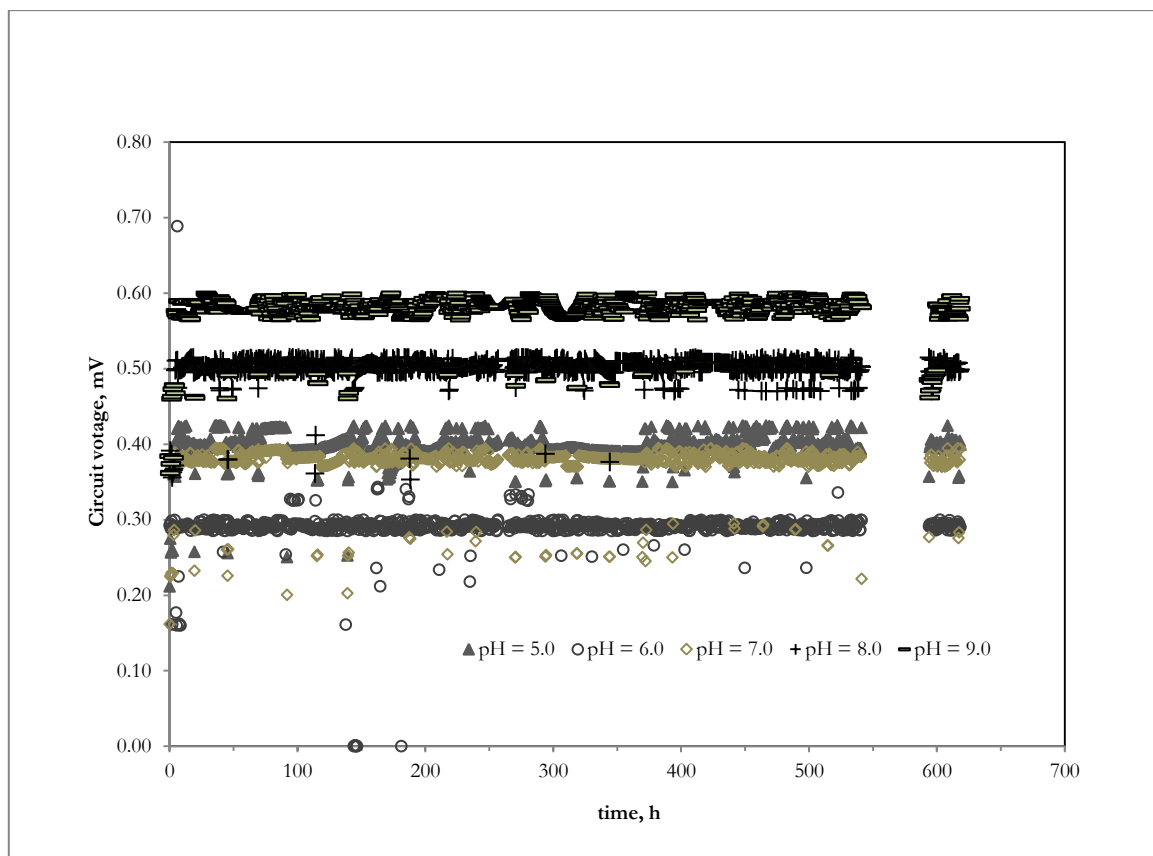

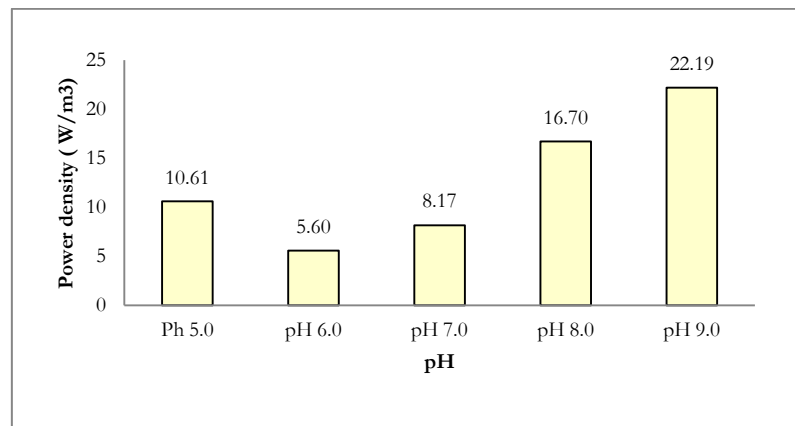Fig. 2. The circuit voltage in a function of time.

Fig. 3. Power density in terms of pH feed.

Table 1. Comparison of power generation obtained from microbial fuel cells with different substrates and pHs feed.

Substrate	Initial inoculums	pH feed	COD removal efficiency	Power density base on anode surface or anode volume	Reference
Cassava wastewater, COD of 1,086 ± 50.06 mg/L. (0.56 kgCOD/m³-d)	Mixed culture from UASB plant	5.0 6.0 7.0 8.0 9.0	81.19±1.10% 89.88±0.68% 91.46±1.10% 92.83±1.37% 89.78±0.86%	10.61 W/m³ 5.60 W/m³ 8.17 W/m³ 16.70 W/m³ 22.19 W/m³	This study
Domestic wastewater, COD of 210 -220 mg/L.	Pure culture (*Geobacter metallireducens)*	7.3-7.6	70%	0.009 W/m² (1.06 mW/m³)	[3]
Vegetable-based waste, COD of 52,000 mg/L. (0.56 kgCOD/m³-d)	Mixed culture from UASB plant	7.0	62.86%	0.173 W/m² (2.81 W/m³)	[5]
Corn starch wastewater, COD of 4,852 mg/L. (0.54 kgCOD/m³-d)	Mixed culture in starch processing wastewater	7.0±0.1	98.0%	0.239 W/m² (1.41 W/m³)	[6]
Cassava wastewater, COD of 16,000 mg/L. (2.67 kgCOD/m³-d)	Mixed culture from cassava mill factory	5.5±0.2	88.0%	1.77 W/m² (18.2 W/m³)	[7]
Brewery wastewater, COD of 1,250±100 mg/L. (4.08-4.43 kgCOD/m³-d)	Anaerobic mixed sludge from brewery	6.5±0.4	45.1-49.4%	0.83 W/m³)	[8]

3.2. Wastewater Treatment

This study was operated under semi-batch mode conditions, with at feed cycle time of 24 h. At the end of 5th batch cycles, the COD in the effluent reach stable conditions. Figure 4 showed the COD in the effluent in a function of operating time. When operating time increased, the COD in the effluent decreased. The microbial in anode chamber took time for 5 days to acclimate with the pH feeds. The efficiency of COD removal was observed after the 5th of batch cycle through the end of experiments. The COD removal efficiency of 81.19 ± 1.10%, 89.88 ± 0.68%, 91.46 ± 1.10%, 93.83 ± 1.37% and 89.78 ± 0.86% was obtained from pH feed of 5.0, 6.0, 7.0, 8.0 and 9.0, respectively (Fig. 5). The highest efficiency of COD removal occurred at the pH feed of 8.0 followed by pH feed of 7.0. The lowest of COD removal efficiency was observed from acidic feed (pH 5.0). The pH values in the effluent of pH 8.0 and 7.0 feed closed to neutral pH as shown in Fig 6. At neutral pH enhanced the activities of microorganisms for utilizing substrate in the wastewater treatment. Alkalinity is necessary in anaerobic treatment. Our results were clearly showed that pH 8.0 feed and pH 7.0 feed increased the efficiency of COD removal.

In the early batch cycles, the amount of alkalinity was used as buffer for neutralization with H^+ in the wastewater influent only and in the lather batch cycles, alkalinity was decreased by the accumulating of proton in the anode chamber. So the pH in the effluent decreased and might be toxic to microorganism especially in the latter batch of pH 5.0 feed. Alkaline feed of wastewater favoured the microbial activities in a single chamber microbial fuel cell rather than feeding with acidic wastewater. This condition (pH 8.0 feed) was not strongly inhibited the activities of microorganism. Whereas, the pH 9.0 feed might be strongly inhibited to the microorganism activities.
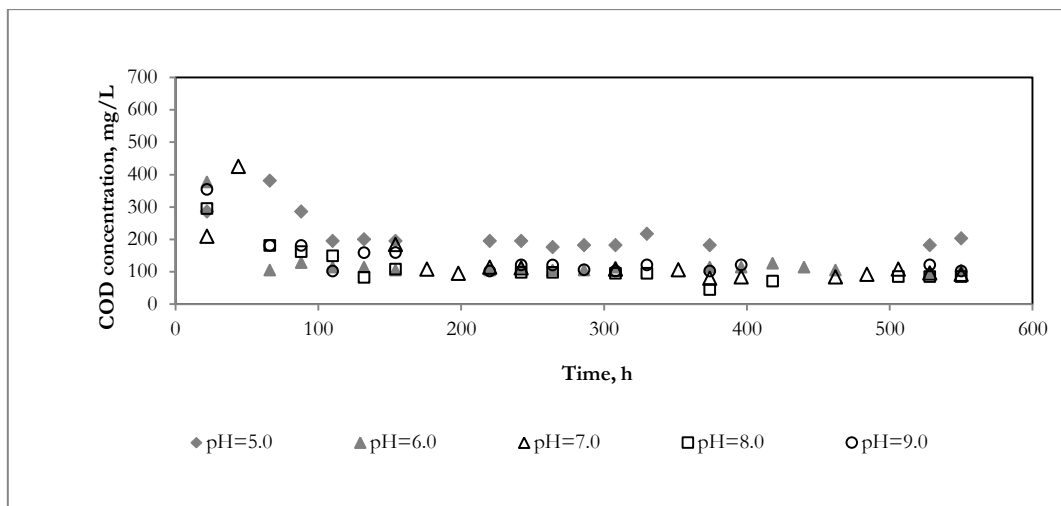

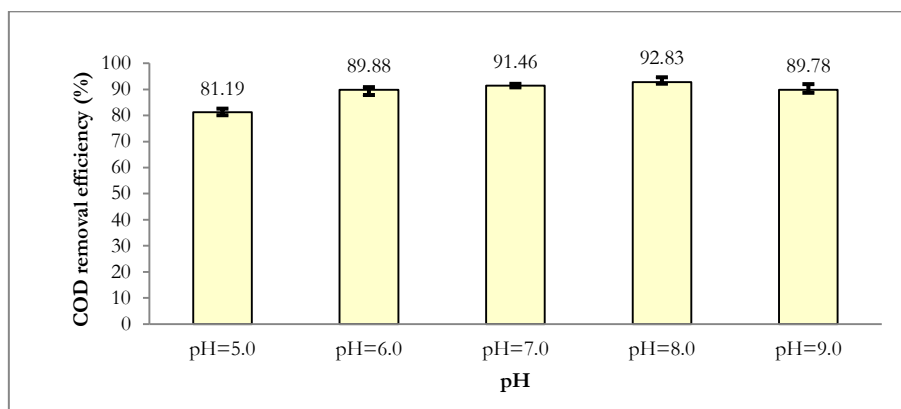Fig. 4. The COD concentration in the effluent.

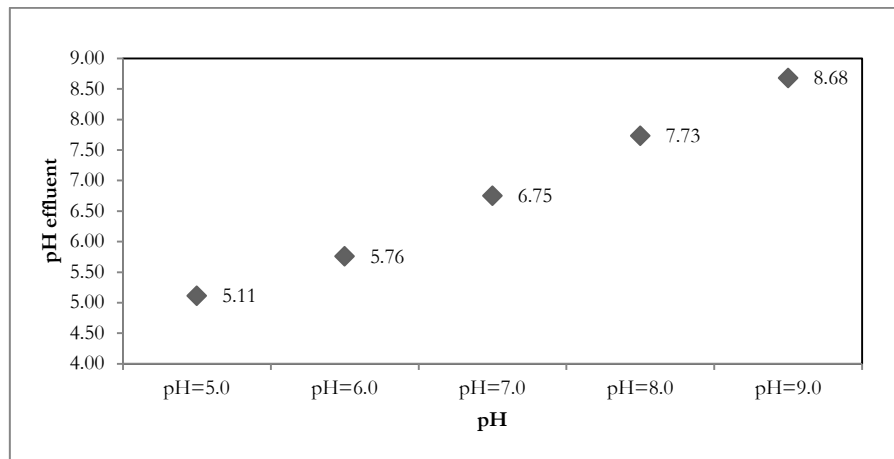Fig. 5. COD removal efficiency in terms of pH feed.

Fig. 6. The pH in the effluent.

The COD removal efficiency of pH 8.0 feed (92.83%) was higher than at neutral feed (91.46%). The later order was observed from pH 6.0 feed (89.88%) and pH 9.0 feed (89.78%). Both of pH feed (pH 6.0 feed and pH 9.0 feed) contributed the same values of COD removal efficiency, but the mechanisms in substrate reducing were different. Higher COD removal from pH 6.0 feed might be caused from methanogens or acidogens. Whereas pH 9.0 feed was suppressed the ability of methanogens or acidogens but its increased alkalinity in the anode chamber which might be promoted others microorganisms to reduce substrate.

Our results were not agreed with previous study. The substrate degradation was effective at neutrophilic conditions (58.98%) followed by alkaliphilic (55.76%) and acidophilic (47.80%) conditions [20]. The air-cathode microbial fuel cell was investigated the influence of pH on COD removal. The study was under continuous flow mode operation and seeding was inoculated from anaerobic sludge (25 °C temperature operation). The COD removal of OLR 3.72 kgCOD/m³-d at pH of 7.0 and 6.25 were 82.3% and 76.6%, respectively and pH values below 6.6 was favoured for methane production [21]. Whereas the organic matter removal efficiency was always higher in case of pH 6.0 than that of pH 8.0 [18]. The result of previous study [18] was different from our study because they used yeast as the inoculums and pH 6.0 was favoured for yeast growth more than pH 8.0.

3.3. Coulombic Efficiency

The result of CE is shown in Fig. 7. It was found that the CE was as high as 47.8% at pH 9.0 feed. The alkaline feed of pH 8.0 presented high CE as 37.5%, followed by pH 5.0 feed (39.3%) and pH 7.0 feed (30.2%). The minimum CE was obtained at pH 6.0 feed. The CE retrieved from pH 6.0 was only 24.4% which was lower about 49% than pH 9.0.

The low CE occurred at pH 6.0 feed because that condition promoted the methanogens growth. The COD at pH 6.0 might be removed by methanogens or others acidogens accordingly, the current obtained from substrate reduction was lower when compared to other conditions.

Extreme of alkaline feed was contributed higher CEs than that of others feed conditions. The higher of CE achieved from the extreme of alkaline feed because at this solubility, it was high conductivity as shown in Fig. 8. High conductivity enhanced the power generation by SCMFC. By the way, extreme of acidic feed was also contributed to high CE, too. But the mechanism at low pH feed was different from high pH feed. In low pH feed condition was not favoured the microorganism to reduce the substrate, thus substrate was removed a little amount. By these of two reasons, extreme pH feed enhanced the efficiency of coulombic efficiency. The results were clearly supported that reason. When focussed on pH 5.0 feed, the CE (39.3%) was higher than that of pH 6.0 feed (CE, 24.4%) because conductivity at pH 5.0 feed was higher than that of pH 6.0 feed and methanogens was suppressed by pH 5.0 feed.

Relatively higher specific power yield was observed at acidophilic microenvironment (46 mW/kg CODR) compared to neutral (35 mW/kg CODR) and alkaline (34 mW/kg CODR) conditions [20]. The two chamber of MFC treated a synthetic wastewater of 100 − 600 mg/L COD concentration under 20 - 35

°C operation [22]. The pH different between the anodic and cathodic solutions affected the internal resistance of MFC [22].
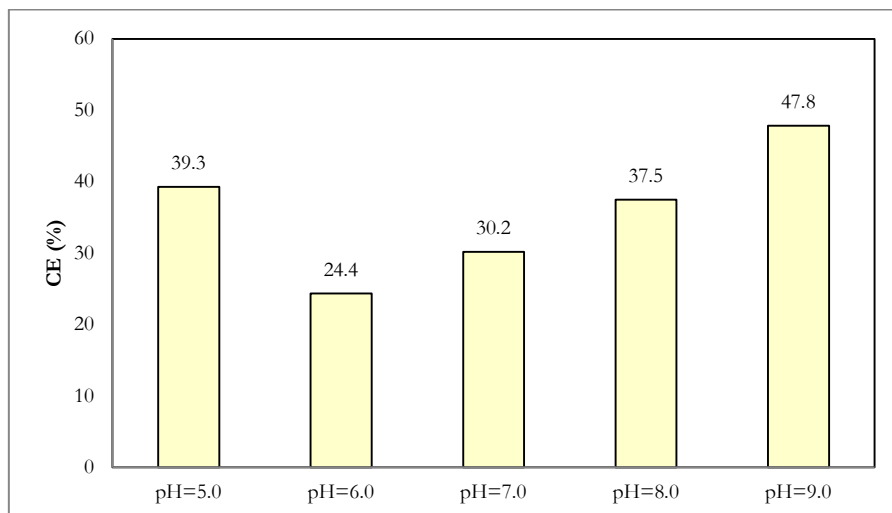

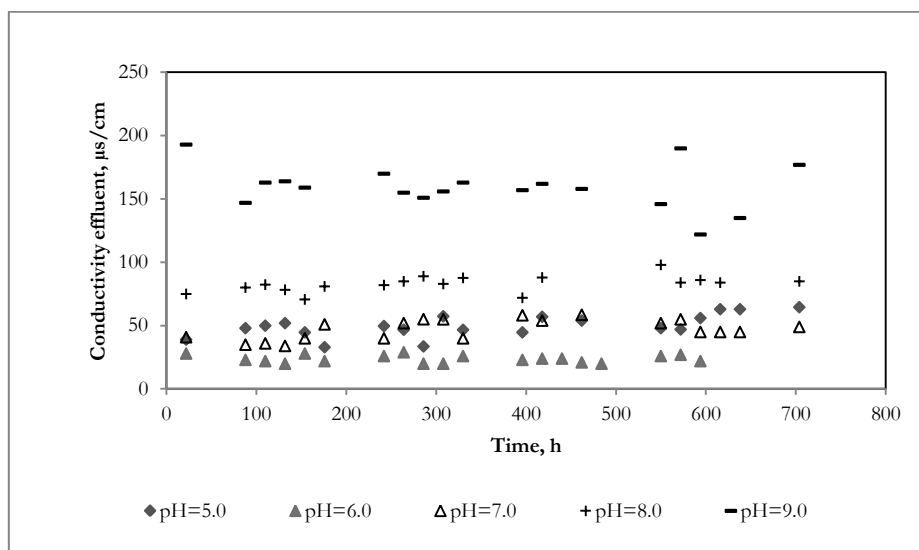Fig. 7. The coulombic efficiency in terms of pH feed.

Fig. 8. The conductivity in the effluent.

3.4. Polarization Curve and Internal Resistance

The polarization slope method in a plot of current and voltage curve was used to examine the internal resistance and maximum power density by varying the external resistance from 10 Ohms to 996 Ohms. Figures 9(a) and 9(b) show the slope from polarization method and the polarization curve in terms of pH feed. The internal resistant of pH feed of 5.0, 6.0, 7.0, 8.0 and 9.0 were as 115 Ohms, 142 Ohms, 115 Ohms, 71 Ohms and 55 Ohms, respectively.

The maximum of internal resistance of 142 Ohms was obtained from the pH 6.0 feed. Therefore, at pH of 6.0 feed, the solution conductivity was the lowest of all pH feed. The minimum of internal resistance of 55 Ohms was observed from pH 9.0. The internal resistant decreased with the conductivity increased except for pH 5.0 feed and pH 7.0 feed. The internal resistant of both feed conditions were equal, but the conductivity of pH 5.0 feed was higher than pH 7.0 feed. The pH 7.0 feed was favoured to microorganism producing electricity better than pH 5.0 feed. The internal resistance decreases with increasing pH difference between anode and cathode solutions. When the pH difference was 2 units, the internal

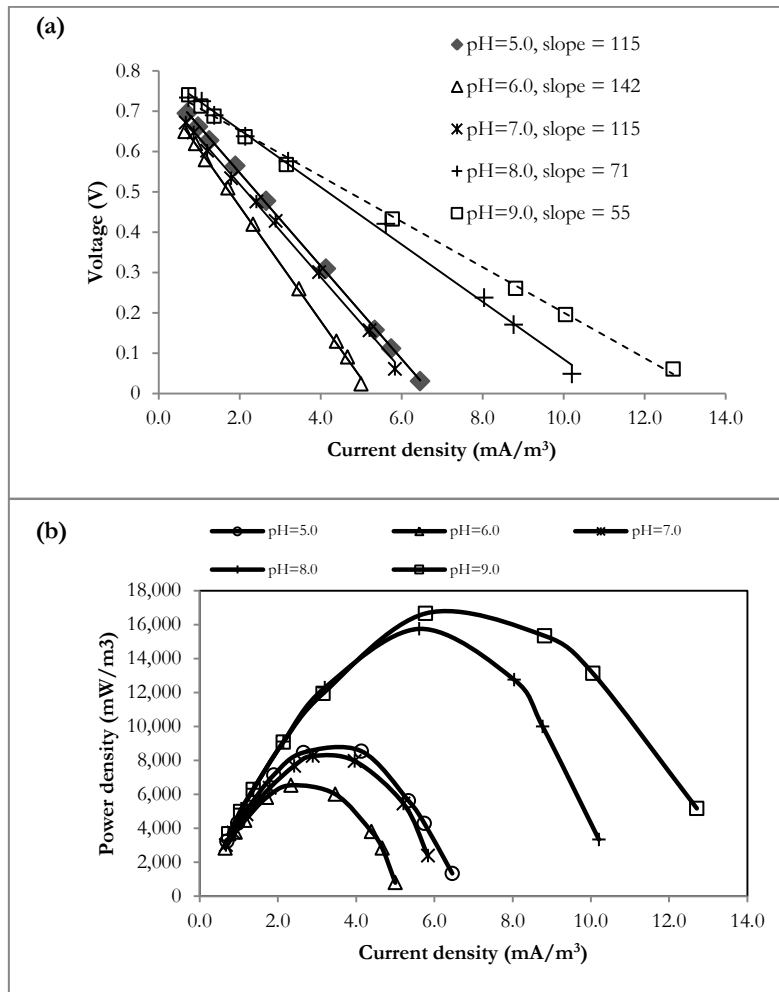resistance of the cell was 523 Ohms and for zero unit pH difference the internal resistance was 547 Ohms [20].

Fig. 9. (a) Slope from polarization method and (b) the polarization curve.

4. Conclusions

Cassava wastewater could be treated by SCMFC. The pH feed of 9.0 enhanced the electricity generation as 22.19 W/m³ which had the efficiency of COD removal of 89.78 ± 0.86%. When kept the pH feed as 8.0 at mesophillic temperature, the COD removal efficiency increased up to 92.83 ± 1.37%. The maximum CE and the minimum internal resistance of cassava wastewater treatment by microbial fuel cell were observed from the pH 9.0 feed. The low pH feed (pH 5.0) presented the power as 10.61 W/m³ and COD removal efficiency was 81.19 ± 1.10%. The COD concentration in the effluent of pH 5.0 feed was low as 113 mg/L which was lower than the requirement of regulation. That SCMFC could apply to treat the cassava wastewater and producing electricity as the same time.

Acknowledgement

References

[1] A. Suttichai, P. Janewit and A. Amornchai, "Fuel processing technologies for hydrogen production from methane," *Engineering Journal*, vol. 16, no. 2, pp. 1-4. March, 2012.

[2] W. Wisitsree, "Reviews on fuel cell technology for valuable chemicals and energy co-generation," *Engineering Journal*, vol. 14, no. 3, pp. 1-14. July, 2010.

[3] H. Liu, R. Ramnarayanan, and B. E. Logan, "Production of electricity during wastewater treatment using a single chamber microbial fuel cell," *Environmental Science and Technology*, vol. 38, no. 7, pp. 2281-2285, 2004.

[4] S. V. Mohan, G. Mohanakrishna, and P. N. Sarma, "Composite vegetable waste as renewable resource for bioelectricity generation through non-catalyzed open-air cathode microbial fuel cell," *Bioresource Technology*, vol. 101, pp. 970-976, 2010.

[5] B. Cercado-Quezada, M.-L. Delia, and A. Bergel, "Testing various food-industry wastes for electricity production in microbial fuel cell," *Bioresource Technology*, vol. 101, pp. 2748-2754, 2010.

[6] N. Lu, S.-G. Zhou, L. Zhuang, J.-T. Zhang, and J.-R. Nia, "Electricity generation from starch processing wastewater using microbial fuel cell technology," *Biochemical Engineering Journal*, vol. 43, pp. 246-251, 2009.

[7] P. Kaewkannetra, W. Chiwes, and T. Y. Chiu, "Treatment of cassava mill wastewater and production of electricity through microbial fuel cell technology," *Fuel*, vol. 90, pp. 2746-2750, 2011.

[8] Q. Wen, Y. Wu, L. X. Zhao, Q. Sun, and F. Y. Kong, "Electricity generation and brewery wastewater treatment from sequential anode-cathode microbial fuel cell," *J. Zhejiang Univ Sci B*, vol. 11, no. 2, pp. 87-93, 2010.

[9] X. Wang, Y. J. Feng, and H. Lee, "Electricity production from beer brewery wastewater using single chamber microbial fuel cell," *Water Science and Technology*, vol. 57, no. 7, pp. 1117-1121, 2008.

[10] G. Antonopoulou, K. Stamatelatou, S. Bebelis, and G. Lyberatos, "Electricity generation from synthetic substrates and cheese whey using a two chamber microbial fuel cell," *Biochemical Engineering Journal*, vol. 50, pp. 10-15, 2010.

[11] J. Cheng, X. Zhu, J. Ni, and A. Borthwick, "Palm oil mill effluent treatment using a two-stage microbial fuel cells system integrated with immobilized biological aerated filters," *Bioresource Technology*, vol. 101, pp. 2729-2734, 2010.

[12] Y. Zhang, L. G. Olias, P. Kongian, and I. Angelidaki, "Submersible microbial fuel cell for electricity production from sewage sludge," *Water Sci Technol*, vol. 64, no. 1, pp. 50-55, 2011.

[13] J. Sun, Y. Y. Hu, Z. Bi, and Y. Q. Cao, "Simultaneous decolorization of azo dye and bioelectricity generation using a microfiltration membrane air-cathode single-chamber microbial fuel cell," *Bioresour Technol*, vol. 100, no. 13, pp. 3185-92, 2009.

[14] A. Gálvez, J. Greenman, and I. Ieropoulos, "Landfill leachate treatment with microbial fuel cells; scale-up through plurality," *Bioresource Technology*, vol. 100, pp. 5085-5091, 2009.

[15] American Public Health Association, American Water Works Association, Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater 19th ed.*, American Public Health Association, Washington, DC, 1995.

[16] B. E. Logan, "Power generation," *Microbial Fuel Cells*, New Jersey, John Wiley & Son, ch. 4, sec. 4.2, pp. 44-60, 2007.

[17] L. Zhuang, S. Zhou, Y. Li, and Y. Yuan, "Enhanced performance of air-cathode two-chamber microbial fuel cells with high-pH anode and low-pH cathode," *Bioresource Technology*, vol. 101, pp. 3514-3519, 2010.

[18] M. Behera, and M. M. Ghangrekar, "Performance of microbial fuel cell in response to change in sludge loading rate at different anodic feed pH," *Bioresource Technology*, vol. 100, pp. 5114-5121, 2009.

[19] Z. He, Y. Huang, A. K. Manohar, and F. Mansfeld, "Effect of electrolyte pH on the rate of the anodic and cathodic reactions in an air-cathode microbial fuel cell," *Bioelectrochemistry*, vol. 74, pp. 78-82, 2008.

[20] S. V. Raghavulu, S. V. Mohan, M. V. Reddy, G. Mohanakrishna, and P. N. Sarma, "Behavior of single chambered mediatorless microbial fuel cell (MFC) at acidophilic, neutral and alkaline microenvironments during chemical wastewater treatment," *International Journal of Hydrogen Energy*, vol. 34, pp. 7547-7554, 2009.

[21] E. Martin, O. Savadogo, S. R. Guiot, and B. Tartakovskyb, "The influence of operational conditions on the performance of a microbial fuel cell seeded with mesophilic anaerobic sludge," *Biochemical Engineering Journal*, vol. 51, pp. 132-139, 2010.

[22] G. S. Jadhav and M. M. Ghangrekar, "Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration," *Bioresource Technology*, vol. 100, pp. 717-723, 2009.