CHEMICAL ENGINEERING TRANSACTIONS

VOL. 76, 2019

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S. Varbanov, Timothy G. Walmsley, Jiří J. Klemeš, Panos Seferlis

ISBN 978-88-95608-73-0; **ISSN** 2283-9216

DOI: 10.3303/CET1976231

Microbial Fuel Cell Power Output and Growth: Effect of pH on Anaerobic Microbe Consortium

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The primary objective of all microbial fuel cell (MFC) research is currently to find ways to increase its efficiency by optimising design architecture and operating values. Microbial fuel cells (MFCs) are however very sensitive to changes in the configuration, source of inoculums and substrate initial pH values. This implies that power output results are hardly ever stable and there is need to find conditions which result in stable performance. A dual chambered batch MFC inoculated with small amount of untreated anaerobic digester sludge was initially operated at different external resistances of 120 Ω, 560 Ω and 1,000 Ω at a constant initial substrate pH of 7. After finding an external resistance that gives a high-power output, the MFC was operated using different substrate initial pH values of 6, 7, 8 and 9. Absorbance and voltage outputs were measured over a 5-d timespan and used to quantify the bacterial growth and electric output. High microbial activity was observed at pH 9, with electric output over a 1,000 Ω resistor, a voltage of 197.2 mV and power density of 10.3 $mW \cdot m^{-2}$. Power output inhibition was seen which was associated to membrane fouling. This study shows that microbial activities and methanogenic process can be controlled to stabilise maximum power output of the MFC by adjusting the initial substrate pH.

1. Introduction

Microbial Fuel Cells (MFCs) are devices that utilise electrogenic bacteria to generate an electric current by consuming the substrate in a wastewater solution (natural or synthetic). The investigation and development of MFCs as an alternative energy source is an active field of study. The primary objective of all MFC research is currently to find ways to increase its efficiency by optimising design architecture and operating values. Many species of electrogenic bacteria are easily accessible and many sources exist where some of these specimens can be acquired. Most studies made use of septic tank residue (Behera et al., 2010) and effluent from a primary clarifier (Tang et al., 2010) or secondary clarifier (Chen et al., 2013). Another suitable alternative inoculation source was anaerobic digester sludge (Kim et al., 2005). The sludge is readily obtainable from wastewater treatment plants and contains a wide variety of bacteria. The consensus is that a bacteria colony consisting of mixed species delivers higher power densities than pure colonies (Logan et al., 2006).

Due to the disadvantage of anaerobic digester sludge introducing methanogens into the MFC system, methods should be developed to reduce methanogenic activity during operation of MFCs. According to Kim et al. (2005), anaerobic digester sludge bacterial growth can overshoot leading to methanogens taking up space on the anode, rendering the MFC less efficient and stable, and it is also possible that in a batch setup the methanogens consume substrate which could otherwise be used by electrogenic bacteria for electricity generation. Methods for reducing methanogenic activity in the MFC should be explored, and they include pre-treatment of inoculum, anode surface altering, and optimising substrate initial pH.

The pH of the substrate will most likely influence the bacteria species with the highest population on the anode side. This logic follows from the fact that different species have different preferences for pH values. The objective of the pH adjustment would be to suppress or inactivate the methanogenic activity and enhance that of the electrogenic bacteria. Clemente et al. (2018) was able to evaluate microbial growth at different pH values and

Paper Received: 27/03/2019; Revised: 11/07/2019; Accepted: 12/07/2019
Please cite this article as: Igboamalu T.E., Bezuidenhout N., Matsena M.T., Chirwa E.M.N., 2019, Microbial Fuel Cell Power Output and Growth: Effect of pH on Anaerobic Microbe Consortium, Chemical Engineering Transactions, 76, 1381-1386 DOI:10.3303/CET1976231

Mahmood et al. (2017) did the same at a point where stable electric output was achieved but both didn't use anaerobic digester sludge where methanogenic activity is a problem.
In this study, the effect of substrate initial pH on the power output and bacterial growth was investigated. The aim was to show that substrate initial pH can be used to control bacterial growth and reduce methanogenic activities during operation of MFC, and this will maximise electricity output and increase its stability. The anaerobic digester sludge used was untreated to ensure a high bacterial variety. Having a variety of bacteria increases the chances of establishing a functional electrogenic system (Logan et al., 2006).

2. Materials and methods

A dual chamber MFC shown in Figure 1 was used to conduct experiments with each chamber having a volume of 640 mL. Anaerobic digester sludge from Brits Waste Water Treatment Works (North West Province, South Africa) was used as an inoculum. Nafion 117 was used as proton exchange membrane. Two 50 mm-25 mm irrigation pipe reducers were used to construct the connection between the two half-cell chambers. The electrolyte consisted of distilled water and KH_2PO_4 (13.6 g/L) which served as a pH buffer as well as electron conductive medium. The anode compartment was filled with 500 mL of synthetic wastewater. The composition of synthetic wastewater was glucose (3 g/L), Na_2HPO_4 (6 g/L), KH_2PO_4 (1.5 g/L), NH_4Cl (0.3 g/L), NaCl (0.5 g/L), $MgSO_4 \cdot 7H_2O$ (0.1 g/L), trace metals (2 mL/L), vitamin mixture [Biotin] (3 mL/L).
All runs were conducted in batch configurations under anaerobic conditions. The substrate initial pH was adjusted once at the beginning of each run using either NaOH or orthophosphoric acid. Inoculation was done with 1 mL sludge. The growth in the anode chamber and electricity output of the system was observed over 5 d.

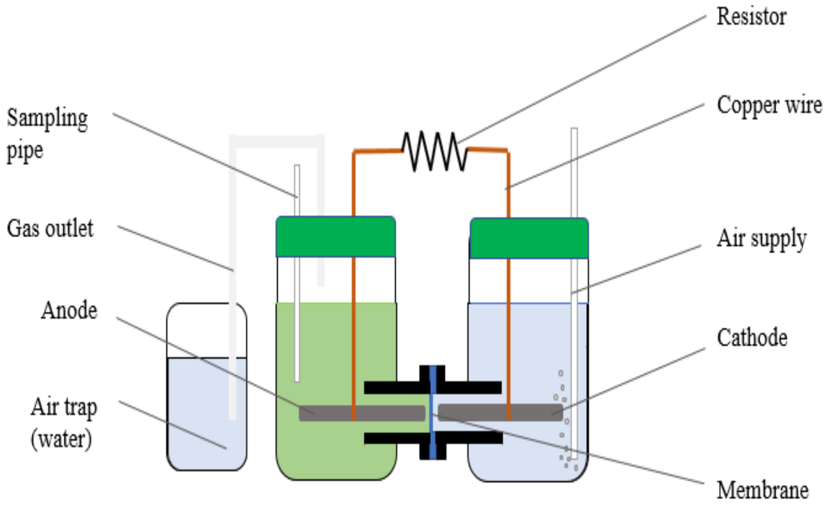

Figure 1: Microbial Fuel Cell configuration with Cathode and Anode

3. Results and discussion

Our result presentation focusses on the interpretation of Ohm's law of which current (power) is directly proportional voltage and inversely proportional to external resistance.

3.1 The effect of external resistance on MFC voltage output

Figure 2a shows the different voltage readings of pH 7 value over the experimental period using different resistances. From Figure 2, increasing the resistance corresponded to an increase in potential difference over the external circuit. In the case of most commercial galvanic cells, the potential difference measured across an external resistance is close to constant for a large range of resistance values. The reason for this is that the internal resistances in most galvanic cells are negligible and virtually no voltage drop is observed. In the MFC system investigated this assumption is similar since a clear difference in voltage readings can be observed for different external resistance values. This would then imply that the internal resistance of the MFC system is substantially high, and that changes in the external circuit will influence the output of the cell. According to Logan (2009), this is a common trait with dual chambered MFCs, since the proton transfer rate is low.

3.2 The effect of external resistance on MFC current output

From Figure 2b, it is evident that higher current densities were obtained when using lower external resistances at the pH of 7. This is in agreement with Ohm's law. The high current values observed for the low resistances then cause a high voltage dropped over the internal resistance of the cell leading to a lower measured voltage across the external resistance as observed in Figure 2a. And according to Sharma and Li (2010), the internal resistance in most dual chambered MFCs is in the range of 1,000 Ω. This means using only voltage readings to justify the performance of an MFC is not enough because even though a high voltage reading was recorded at resistance value of 1,000 Ω as shown in Figure 2, the current density was the lowest. The best way to possibly represent the performance of MFC is to also evaluate the power output of the MFC as shown in Figure 1.

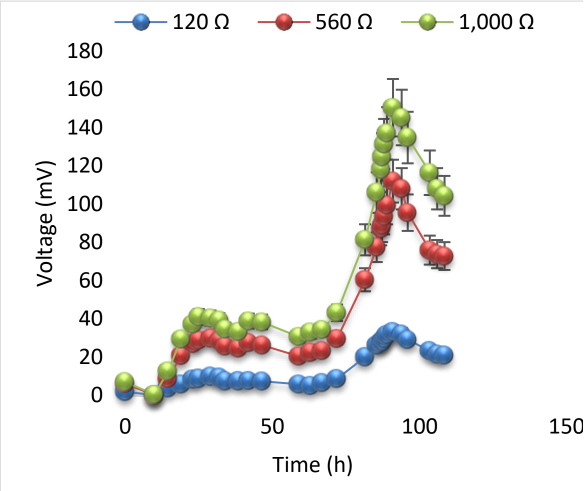

Figure 2a: Voltage output at pH 7 over different external resistances

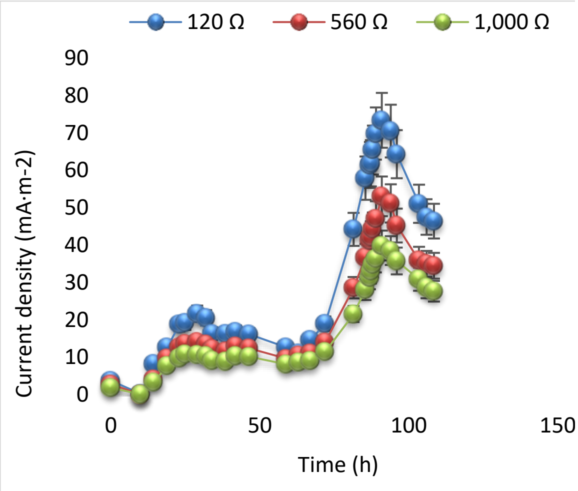

Figure 2b: Current output at pH 7 over different external resistances

3.3 The effect of external resistance on MFC power output

The power output of the MFC is shown in Figure 3, of which a high external resistance values lead to a high-power density was observed. This observation is supported by the reasoning that high resistance values will lead to low voltage drops over the internal resistance and more energy is available for consumption by the external circuit. Although both 560 Ω and 1,000 Ω have similar power densities, it can be concluded that at pH 7, a 1,000 Ω external resistor performed better for the dual microbial fuel cell since it also led to a high voltage output.

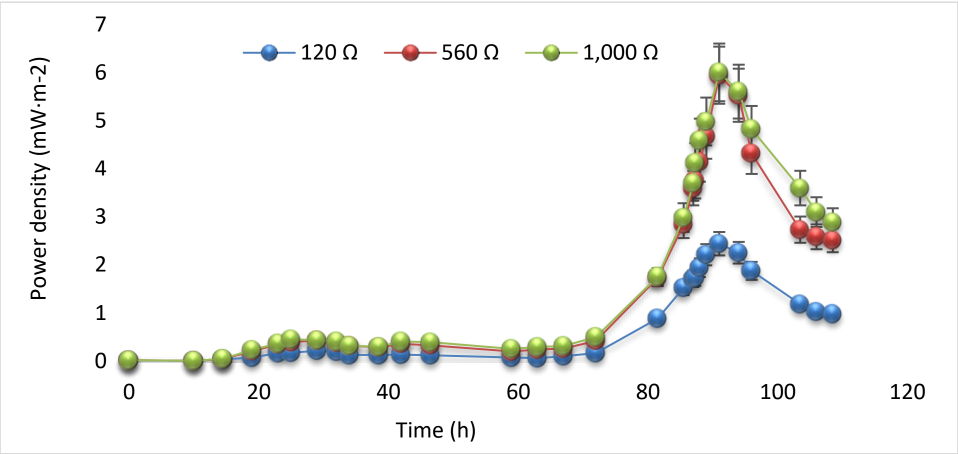

Figure 3: Power output at pH 7 over different external resistances.

3.4 The effect of pH on microbial growth and impact on voltage and power output

Figure 4 displays the absorbance measurements at 600 nm for an MFC with 1,000 Ω external resistor at different pH values over a period of 5 d. From Figure 4, a sudden rise in absorbance occurred much earlier for the pH 9 value than any of the other values and remained the highest for the longest time out of all the values. This implies indicate that that the activities of microorganism were at growth phase. This is a very advantageous quality since a stable output is essential for practical application of MFCs.

A very sharp increase in the absorbance was observed for pH 7 value at 60 h, this indicates high growth rates at pH 7. During this period, large quantities of bubble formation were also observed. The decline in absorbance after this increase was due to the fact that bacteria started approaching stationary or death phase. This was evident by the settling of dead cell at the bottom of the reactor. This could be associated to the depletion of organic carbon source and microbes did not have sufficient carbon for growth and metabolism.

A high peak absorbance was seen which is also significantly higher than the peak absorbances for any of the other values, is an indication that species other than electrogenic bacteria such as methanogens is very much active in the system (Kim et al. 2005). Methanogenesis is also most prominent over a pH range of 6.6 – 7.6 (Lay et al., 1997) which would support the higher peak at pH 7. This was also evident by the amount of bubbles that were forming in the process, something that was not occurring at pH 9. Both pH 8 and pH 6 achieved absorbances lower than 0.8, which means they had lower microbial growth.

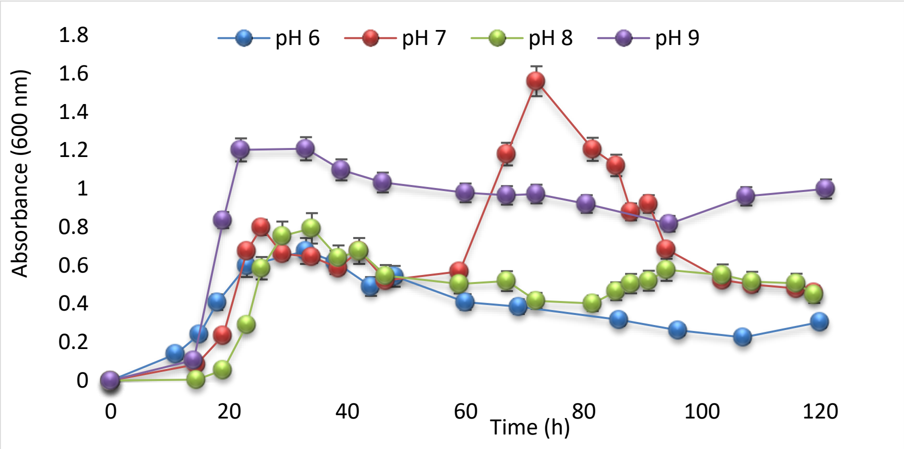

Figure 4: Absorbance measurements for MFC with 1,000 Ω external resistor at different pH values over a period of 5 d.

3.5 The effect of pH on proton liberation

Table 1 shows that the final pH of the anode chamber liquid will always be lower than the initial pH value. This acidification of the anode chamber is caused by the proton liberation during the substrate consumption. The proton flux to the cathode chamber is very limited and causes an accumulation of protons. This proton transfer limitation limits the process and is the main reason for the high internal resistance which causes the voltage output dependency on external resistance as stated in Table 1.

When the initial and final pH values of all the runs are compared, one can see that the initial pH order does not affect the order of the final pH values. In other words, as with pH 9, a very low final pH value can be obtained even though it had a high initial value. One can then gather that the final pH value is rather a measure of proton formation. The pH 9 value had a high change in pH than the other pH values and showed more protons were liberated in the anode chamber, which caused a lower pH value. It should be noted that although pH 7 value had the highest microbial growth as shown in Figure 4, it has the lowest change in pH and less protons being liberated.

Table 1: Changes in pH in the anode chamber for MFC with 1,000 Ω external resistor.

Initial pH	Final pH	Change in pH
6.03	4.71	2.48
7.19	6.73	0.46
8.03	7.19	0.84
9.03	6.46	2.57

3.6 The effect of pH on voltage and power output

From Figure 5a and 5b, it is evident that the highest voltage output was produced by the pH 9 substrate solution. It is also clear that the increase in voltage with time occurred much earlier for the pH 9 value than for any of the other values. This corresponds to the curve displayed in Figure 4 which indicates that a sudden rise in absorbance occurred much earlier for the pH 9 value than any of the other values. The power production was also relatively stable at its peak for a very long time compared to the other pH values. The most probable reason for this sustained output is the fact that the absorbance value of the pH 9 value was the highest for the longest time out of all the values and this implies that the microbes were alive and active for a long time

The pH 7 value produced the second highest power output among all the values as shown in Figure 5b. The rise in power output at pH 7 value was unstable compared to pH 9. This behaviour can be explained when the absorbance curve is considered. A very sharp increase in the absorbance at 60 h as shown in Figure 4 indicate very high growth rates which influenced the power output as shown in Figure 5b and the decline in absorbance after this increase which was due to the fact that bacteria started dying and settling at the bottom influenced the decrease in power output. This means that microbial growth had more impact on the power output since the power output was directly related to microbial growth. However, the increase in power output was not as high as the one of pH 9 due to the presence of methanogens. This means that pH 9 was able to suppress methanogenesis and produce more power output than pH 7 values. The lowest proton liberation of pH 7 as mentioned might have also influenced a lower power production at pH 7 than the one observed at pH 9. It should be noted that although pH 6 value had the second highest proton liberation as shown in Table 1, it showed the lowest microbial growth in Figure 4 which meant the lowest power output of all the values as shown in Figure 5b. This means that microbial growth influences power output more than proton liberation.

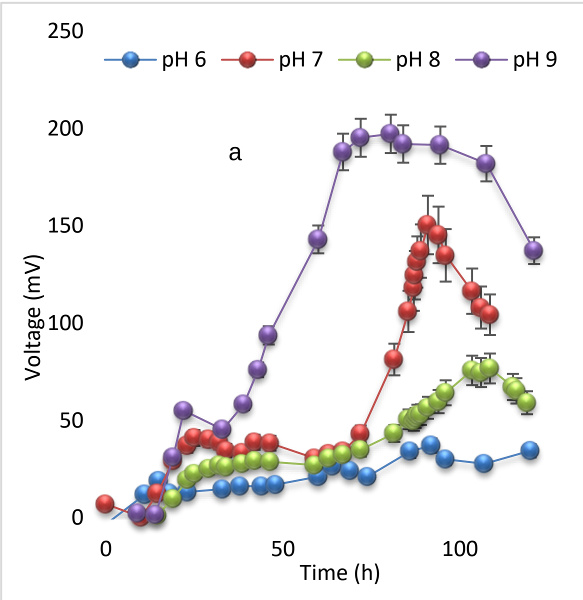

Figure 5a: Voltage output for different pH values using a 1,000 Ω external resistor.

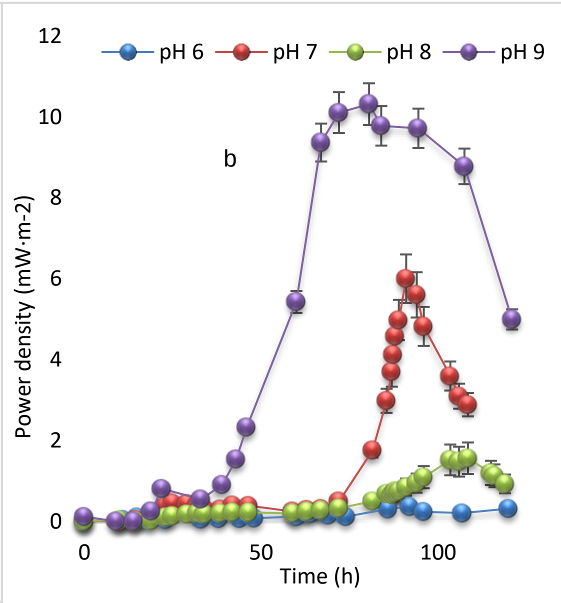

Figure 5b: Power output for different pH values using a 1,000 Ω external resistor.

3.7 Proton exchange membrane fouling

Upon disassembling the MFC chamber, it was found that fouling occurred on the anode chamber side of the proton exchange membrane (PEM). This fouling was observed for each of the pH values. Figure 6a shows that this fouling is clearly visible on the membrane and Figure 6b shows black residue on the anode and copper wire. Although some of the fouling substance could be removed by rubbing the membrane, it seems that permanent damage was done to the membrane which could not be removed. This fouling undoubtedly affected the proton transfer from the anode to the cathode chamber, which would have decreased the power output during the end of each run. However, it is clear that the fouling did not eliminate voltage generation since the runs were all carried out with significant success.

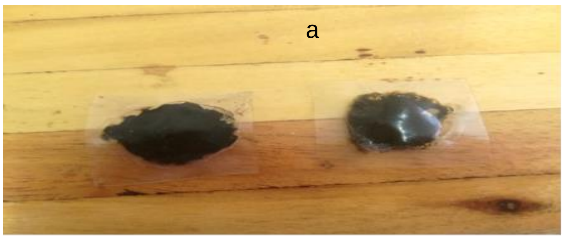

Figure 6a: Membrane fouling on the anode chamber side.

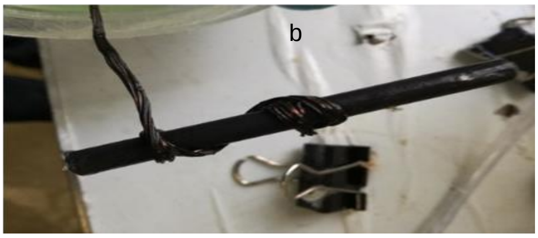

Figure 6b: Black residue formation on the anode and copper wire.

4. Conclusions

A dual chamber MFC was able to produce energy using anaerobic digester sludge from Brits Waste Water Treatment Works (North West Province, South Africa) as an inoculum under anaerobic values. Changing the pH was able to influence microbial growth which directly influenced power production. The results in this study show that microbial growth had more impact on power output than proton liberation, and that when proton flux is limited, proton liberation during the substrate consumption will cause an accumulation of protons in the anode chamber which is the main reason for the high internal resistance which causes the voltage output dependency on external resistance. This study also showed that changing the pH will be able to suppress methanogenesis, and in this study changing pH values from pH 7 to pH 9 suppressed methanogenesis. Membrane fouling did reduce power output at the end of each experiment and an improvement on the study will be to find ways to minimise it. A maximum potential difference of 197.2 mV and power density of 10.3 $mW \cdot m^{-2}$ was obtained at pH 9 over 1,000 Ω resistor. The bacterial growth rate was also fastest for pH 9 and the maximum voltage output was stabilised as compared to other pH values.

References

Behera, M., Jana, P.S., Ghangrekar, M.M., 2010, Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode, Bioresource Technology, 101, 1183 – 1189.

Chen, Y., Luo, J., Yan, Y., Feng, L., 2013, Enhanced production of short-chain fatty acid by co-fermentation of waste activated sludge and kitchen waste under alkaline values and its application to microbial fuel cells, Applied Energy, 102, 1197 – 1204.

Clemente, R.S., Igeno, M.S., Poblacion, A.G., Guijo, M.I., Merchan, F., Blasco, R., 2018, Study of pH changes in media during bacterial growth of several environmental strains, Proceedings, 2, 1297 –1301.

Kim, J.R., Min, B., Logan B.E., 2005, Evaluation of procedures to acclimate a microbial fuel cell for electricity production, Appl Microbiol Biotechnol, 68, 23 – 30.

Lay, J.J., Li, Y.Y., Noike, T., 1997, Influences of pH and moisture content on the methane production in high-solids sludge digestion, Water Res, 31, 1518 – 1524.

Logan B.E., 2009, Exoelectrogenic bacteria that power microbial fuel cells, Nature Reviews Microbiology, 7, 375 – 381.

Logan, B.E., Hamelers, B., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006, Microbial Fuel Cells: Methodology and Technology, American Chemical Society, 40, 5181 – 5192.

Mahmood, N.A.N., Ghazali, N.F., Ibrahim, K. A., Ali, M.A., 2017, Anodic pH evaluation on performance of power generation from palm oil empty fruit bunch (efb) in dual chambered microbial fuel cell (mfc), Chemical Engineering Transactions, 56, 1795 –1800.

Sharma, Y., Li, B., 2010, The variation of power generation with organic substrates in single-chamber microbial fuel cells (SCMFCs), Bioresource Technology, 101, 1844 – 1850.

Tang, X., Guo, K., Li, H., Du, Z., Tian, J., 2010, Electrochemical treatment of graphite to enhance electron transfer from bacteria to electrodes, Bioresource Technology, 102, 3558 – 3560.