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Research Article

Catalytic effect of acetate ($C_2H_3O_2$) on coulombic efficiency and bio-electricity generation from wastewater sample prepared from domestic kitchen waste using dual chamber microbial fuel cell technology

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Abstract
In recent times, the use of energy resources, particularly non-renewable resources, have increased manifolds due to the ever-increasing global demands. This has led to an increase in depletion of the resources and environmental pollution. Microbial Fuel Cells (MFC) are a new concept that has proved to be the solution to the problem as a green energy resource. The paper focuses on generating electricity from wastewater prepared from kitchen wet waste kept for about 168 hours in an attempt to address the energy crisis while also treating it. A comparative analysis of the sample as prepared and with acetate has been studied and power generation, coulombic efficiency and change in chemical oxygen demand (COD) for wastewater were calculated and also the catalytic effect of acetate was analyzed. It was observed that there was a substantial increase in coulombic efficiency and COD content . A coulombic Efficiency efficiency of 25.29% was obtained for the sample with acetate, whereas, without acetate it was calculated as 9.71%. The maximum power density was obtained from the polarization curves. It was observed that the maximum power density of pure kitchen wastewater was found to be 0.017 mW/m$^{2;}$ however, for kitchen wastewater with acetate, the power density increased considerably to 0.546 mW/m^2 at an external resistance of 1KΩ. Further, the maximum current densities observed were 2.239 mA/m^2 and 8.771 mA/m^{2,} respectively. The internal resistance of the constructed prototypes was also determined using the maximum power transfer theorem. In this study, a prototype was constructed and it was found that kitchen waste can be used as a source of electricity generation and leads to a green energy initiative.

Keywords: Bio-electricity generation, Coulombic efficiency, Internal resistance of MFC, Microbial fuel cell, Power density

INTRODUCTION

M. C. Potter first conceived the idea that microbes could be used to produce electricity in 1911. He showed the possible generation of electricity from the culture of E. Coli, which proved to be a revolutionary technological advancement (Potter, 1911). However, it gained attention in the 1980s when Robin M. Allen and H. Peter Bennetto published various papers describing the working of an MFC and various parameters that play a key role in determining the efficiency of the cell (Khera and Chandra, 2012). Thereafter, the technology was boosted and different MFC prototypes were investigated and constructed. The work started with the use of mediators in an MFC to transfer the electrons to the anode and this type of MFC was named Mediator MFC. Due to the fact that the mediators proved to be toxic to microbes, the research shifted from Mediator MFCs to Mediator-less MFCs in which the microbes like Geobacter, Shewanella etc. are capable of directly transferring the electrons to the anode (Gil *et al*., 2003) It has been observed that the energy output of the cell is majorly affected by several parameters such as type of design of the cell, the substrate, electrode material, the total internal resistance, ion concentration etc. (Khera and Chandra, 2012)(Logan, 2009) Hence, there is a need to optimize these parameters to increase the cell efficiency and the overall performance.

A Microbial Fuel Cell (MFC) is a promising biological technology that uses exoelectrogenic microorganisms' metabolic activity to generate electricity.(Chaturvedi and Verma, 2016) It is a bioreactor wherein the microorganisms such as *Geobacter*, *Shewanella*, *Pseudomonas* and others convert the chemical energy stored in the biodegradable organic matter present in the substrate to electrical energy through the breakdown of the organic matter (Konovalova *et al*., 2018). Hence, the organic-rich substrate is the fuel to the cell. A conventional MFC consists of an anode chamber and a cathode chamber separated by a Proton Exchange Membrane (PEM). The anode chamber has an anode immersed in the substrate. It operates under anaerobic conditions, whereas the cathode chamber consists of a cathode immersed in water and operates under aerobic conditions. The anode and cathode are connected via an external circuit (Li, 2013).

The PEM is an ion-exchange membrane that allows the flow of protons from the anode to the cathode chamber and blocks the diffusion of oxygen into the anode chamber. The principle behind the working of an MFC involves the oxidation of organic-rich substrate, i.e. the organic matter by microbes under the anaerobic condition to produce carbon dioxide, free electrons and protons. The electrons are then transferred to the anode extracellularly by the microbes. The electrons then flow to the cathode via an external load connection. At the same time, the protons diffuse to the cathode chamber via PEM. The protons then combine with electrons reaching the cathode in the presence of oxygen to produce water. The most widely used designs of an MFC that have been used for Bioelectricity generation are shown in Fig. 1.

The anodic and cathodic reactions governing this working principle is as follows :(Du *et al*., 2007)

Anodic reaction:

$$CH_3COO^- + 2\ H_2O \ \ ===> 2\ CO_2 + 7\ H^+ + 8\ e^- \qquad \ldots(1)$$

Cathodic reaction:

$$O_2 + 4e^- + 4H^+ \ \ ===> 2\ H_2O \qquad \ldots(2)$$

A large variety of MFCs have been designed and constructed for different configurations, substrates and electrode materials.

It has been observed that the energy output of the cell is majorly affected by several parameters such as type of design of the cell, the substrate, electrode material, the total internal resistance, ion concentration etc. (Logan, 2009; Khera and Chandra, 2012). Hence, there is a need to optimize these parameters to increase cell efficiency and overall performance.

The present work focuses on the enhancement of bioelectricity generation by the addition of an external substrate i.e. acetate to the kitchen wastewater. The paper, hence presents the catalytic effect of acetate to enhance the bio-electricity generation in comparison to that generated for the kitchen wastewater alone. In the present work, a prototype has been made to generate electricity using kitchen wet waste and further studied the catalytic effect of acetate to increase electricity production. A detailed comparative analysis has been done on various parameters such as coulumbic efficiency, COD(Chemical Oxygen Demand) etc. Also created an analogy of microbial fuel cell with an electric circuit to determine maximum power conditions

MATERIALS AND METHODS

MFC construction and sample preparation

Dual chamber microbial fuel cell (DCMFC) was constructed using two jars of Borosil. Two jars acted like anodic and cathodic chambers of DCMFC. The anodic chamber operated under completely anaerobic conditions, whereas the cathodic chamber operated under aerobic conditions (Rikame *et al*., 2012). The two chambers were separated by a proton exchange membrane (PEM), as shown in Fig. 2. The Nafion® 117 (Aldrich) 0.007 inches thick was used as the PEM. The working volume of the anode chamber and cathode chamber of MFC was 500 mL each. The MFC was operated under continuous mode. Carbon electrodes having cylindrical geometry and a surface area of 70.11 cm^2 (15.74 mm diameter and 13.4 cm long) were used as anode and cathode. The surface of the electrodes was rubbed using sandpaper to make it rough. The adhesion of bio-films on the rough surface is better than that on the smooth one. The electrodes were then connected externally with a 1 KΩ resistor via copper wire. The observations were taken continuously every 5hrs for 45 days.

Hence, two different DCMFC prototypes, viz. DCMFC A and DCMFC B were designed using the same configuration mentioned above but were fed with different substrates. Both the DCMFC were operated under continuous mode. The DCMFC A was operated for 30 days, whereas the DCMFC B was operated 45 days.

The anodic chamber of DCMFC A was fed with 400mL of kitchen wastewater and the cathodic chamber with 400 mL of pure water. The kitchen wastewater was prepared by decomposing the kitchen wet waste (tea leaves, potato peels, onion peels etc.), primarily consisting of fresh lime peels in water for one week in a closed container. The preparation was then strained and used as the substrate in the DCMFC A. The chambers were sealed using rubber cork after immersing the electrodes in it. Unlike the anodic chamber, the cathodic chamber had an opening on the upper side to ensure aerobic condition prevails in the cathodic chamber.

For DCMFC B, the sample was prepared by adding a small amount (8 grams) of acetate to the kitchen wastewater, as prepared above. The anodic chamber of DCMFC B was then fed with 400mL of this prepared sample and the cathodic chamber with 400 mL of pure water.

Methodology

Coulombic efficiency

The coulombic efficiency, CE, is the ratio of total coulombs actually transferred to the anode from the substrate to the maximum possible coulombs if all substrate removal produced current. It signifies how effectively the substrate can be used for the current generation (Chen *et al*., 2021). The samples' chemical oxygen demand (COD) concentration was measured at the start of the experiment and after 30 and 45 days of operation for both DCMFC A and DCMFC B, respectively. The initial value of COD for DCMFC A and DCMFC B was observed to be equal to 2003 mg/L and 3203 mg/L, respectively. After 30 days of operation of DCMFC A, the value of COD concentration reduced to 3.57 mg/L, whereas the value reduced to 4.78 mg/L after 45 days of operation of DCMFC B. This significant change observed in the values is attributed to the decomposition of the organic matter. Using the change in COD concentration, the coulombic efficiency (CE) was calculated from the COD removed per cycle of using equation (3) (Logan *et al*., 2006).

$$CE(\%) = \frac{M_s \int_0^{t_b} I\, dt}{F\, b\, V_{an}\, \Delta COD} * 100 \qquad \text{......(3)}$$

where,
M_S is the molecular weight of O_2 (32 g/mol),
I is the current density (mA cm^{-2}),
t_b is the operation time (days),
F is the Faraday's constant (96,487 C/mol),
b= 4 is number of e^- exchanged per mole of Oxygen,
V_{an} is the volume of the anode (L) and
ΔCOD is the change in COD (g L^{-1}) over time t_b

Polarization curves

The Polarization curves were plotted and analyzed for the constructed prototypes of DCMFC A and DCMFC B by varying the value of the external resistor from 10 Ω to 57KΩ. The corresponding values for voltage across the resistor and current flowing through it were recorded. The voltage and current values were also used to obtain the power density delivered to the load, i.e. the external resistor. The desired curves obtained and plotted are shown in Fig. 3.

Internal resistance

The internal resistance of the cell was then calculated by determining the slope of the line of voltage vs. current plot using the equation (4) (Adeniran *et al*., 2016)

$$R_{int}(\Omega) = \frac{dV}{dI} \qquad \text{...(4)}$$

where, dV is the change in voltage and dI is the change in current. Total internal resistance offered by MFC is calculated by including electrode resistance.

RESULTS AND DISCUSSION

The coulombic efficiency was found to be increased in DCMFC B. it was found to be 9.71 % for DCMFC A, whereas it was 25.29 % for DCMFC B. Previously, a coulombic efficiency of 5-7% and 25.01% has been reported for DCMFC using domestic wastewater mixed with primary sludge and a DCMFC using municipal wastewaster respectively (Adeniran *et al*., 2016; Ye *et al*., 2019). It implies that the addition of acetate in DCMFC B has led to the induction of more ions in the substrate and hence, an efficient recovery of energy from the MFC system than that in DCMFC A which results in more current production.

The maximum value of power density was obtained by generating the polarization curves by measuring the change in voltage across the load resistor with the vari-

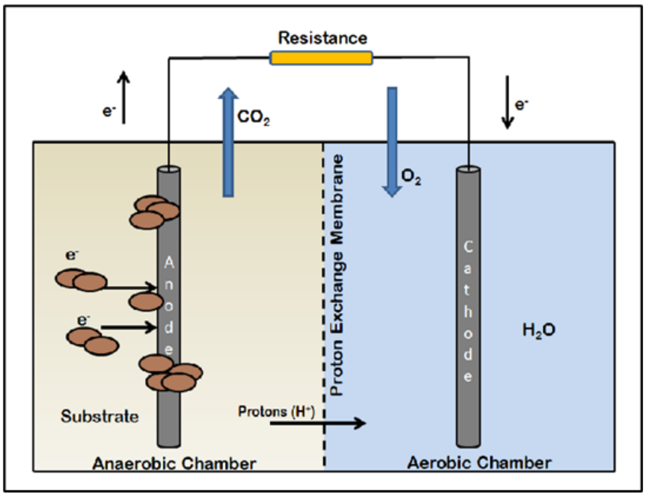


Fig. 1. *Schematic of a Double chamber MFC*

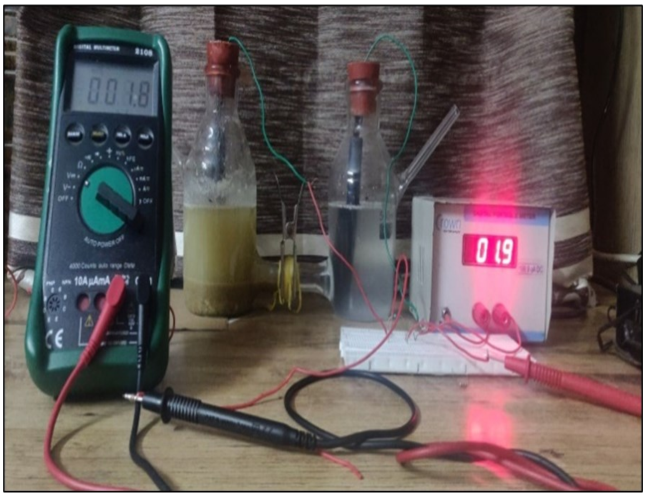
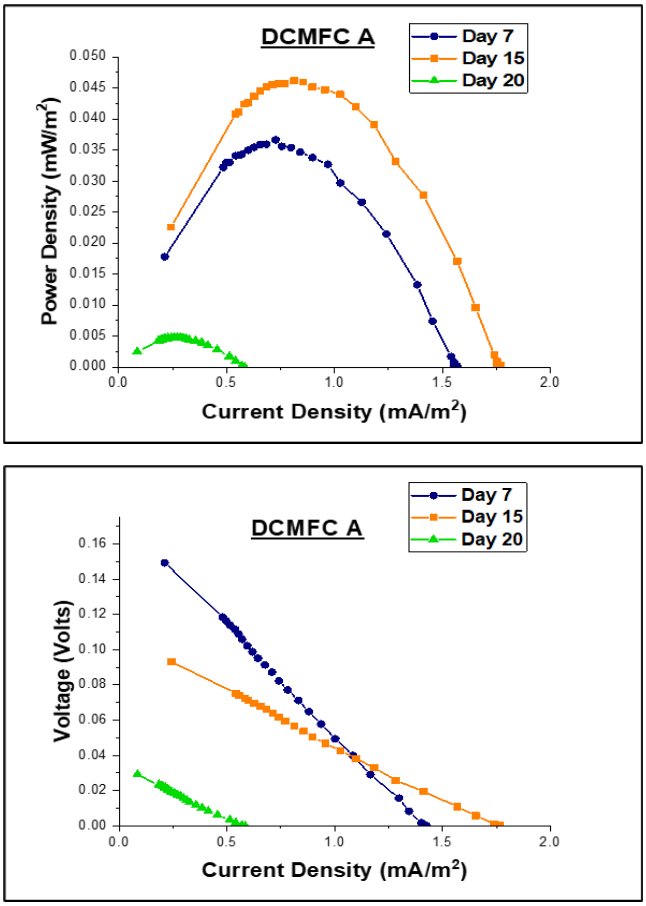


Fig. 2. *DCMFC constructed prototype*

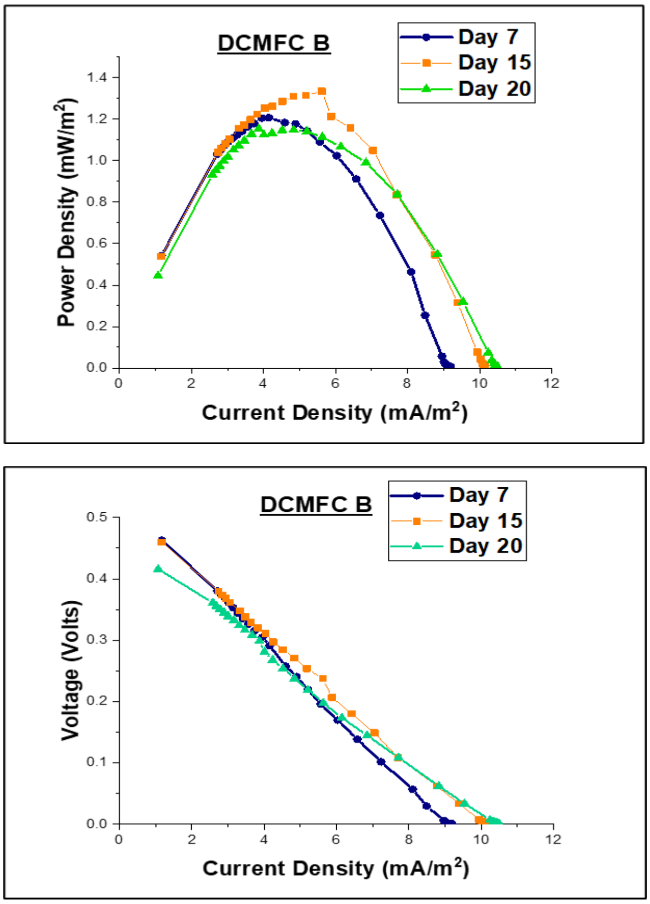
ation in the value of the external load resisitor. The maximum power density of pure kitchen wastewater is found to be 0.046 mW/m^2 at an external resistance of 10 KΩ however, for kitchen wastewater with acetate, the power density was determined to be equal to 1.148 mW/m^2 at an external resistance of 7 KΩ. For an external resistance of 1 KΩ, the power densities obtained for the pure kitchen wastewater and kitchen wastewater mixed with acetate were 0.017 mW/m^2 and 0.546 mW/m^2, corresponding to the current densities of 2.239 mA/m^2 and 8.771 mA/m^2 respectively. A variety of DCMFCs have been constructed in the past with different substrates and electrode materials. Rikame *et al.* (2012) demonstrated a DCMFC using food leachate as the substrate and obtained a power density of 15.14mW/m^3. Ali *et al.* (2017) reported use of glucose as a potential substrate toward enhanced electricity generation and constructed a DCMFC obtaining a power density of 136 mW/m^2. Sugarcane molasses were used as the substrate in a DCMFC constructed by Hassan *et al.* (2019) and a power density of 188.5 mW/m^2 was obtained. Marassi *et al.* (2020) developed an up-flow tubular air-cathode microbial fuel cell with diary wastewater as the substrate and achieved a maximum current density of 1.1 A/m^3.The polarization curves showed that the power density for DCMFC A and DCMFC B initially increased and then decreased, as shown in Fig. 3 (a) and 3(b).The polarization curve for both constructed prototypes obtained for a different number of days of operation showed that the value of power density obtained increased with time initially, which then started to decrease as time passed. The findings are consistent with the trends reported in previous studies that the value of power density is a function of time (Feng *et al.*, 2010; Miran *et al.*, 2015; Penteado *et al.*, 2016; Li *et al.*, 2018). The initial increase in power density with time is attributed to the generation of electrons due to the microbes' degradation of the organic matter present in the substrate. However, the decrease in the values observed later with time was due to the substrate's depletion of the organic matter. Hence, fewer or no electrons were generated.

Fig. 4 shows the variation of current density with the number of days. It can be seen that for DCMFC A, the current density was much higher than for DCMFC B. It implies that the addition of acetate had led to a considerable increase in the organic matter in DCMFC B than DCMFC A, which further led to increased power density and voltage values for the former. After reaching maximum value, the fall in current density implies depletion



(a)

Fig. 3.(a). *Polarization curves for DCMFC A*



(b)

Fig. 3(b). *Polarization curves for DCMFC B*

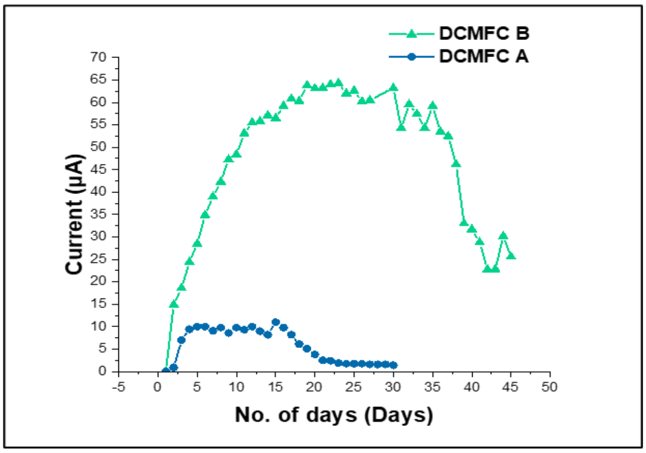


Fig. 4. *Graph showing the variation of current flowing through the load with time*

of electron in organic matter in samples as the time passes till the matter is completely decomposed.

The resistance of the electrode was measured using Ohm's Law and calculated to be equal to 67.9 Ω. Fig. 5 below shows the variation of voltage vs. current. For DCMFC A, the value of the internal resistance initially decreased with time. It was 10192 Ω and 8746 Ω on day 7 and 15, respectively as shown in Fig.5(a) . Later, the value of internal resistance began to increase with time and became 9549 Ω on 20th day of its operation. Similarly, for DCMFC B, the values of internal resistance that were determined from the plot were 8489 Ω, 7180 Ω, 6505 Ω and 16796 Ω on days 7, 15, 20 and 44, respectively as shown in Fig. 5(b). The initial increase in the value of internal resistance with time is due to the increase of concentration of ions in the substrate due to the breakdown of the organic matter present by the microbes. Since the microbes consume the organic matter gradually with time, the ion concentration decreases with time, so the value of internal resistance increases.

It has been observed that a microbial fuel circuit mimics an electric circuit. Hence an analogy can be made between them, as shown in Fig. 6. The values of voltage and current recorded by varying the value of the load resistor and the calculated power density were analyzed. A maximum power density was observed when the value of the external resistance became equal to the value of the internal resistance of the system. This infers that an MFC obeys the maximum power transfer theorem just like an electric circuit. The same result was also verified using a PSpice Simulation Software. The graphs obtained for both the constructed prototypes DCMFC A and B using the software are shown in Fig. 7.

Table 1 shows the comparison of experimental values of internal resistance, R_{int} (Ω) and power delivered to the load P_L (µW) (when the load resistance is equal to the internal resistance) and the same values calculated using PSpice for DCMFC A and B.

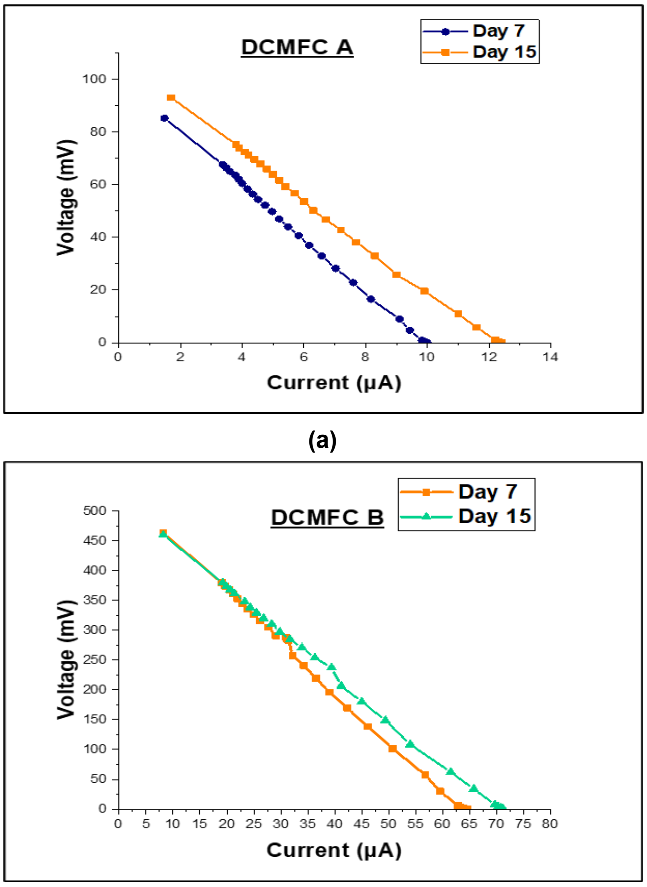
Hence, the fuel substrate is a key component of an MFC. A large number of substrates, such as acetate, sewage sludge, and swine wastewater, have been in-

Table 1(a). DCMFC A

Day	Experimental value		PSpice value	
	R_{int}(KΩ)	P_L (µW)	R_{int}(KΩ)	P_L (µW)
7	10.192	0.247	10.001	0.259
15	8.746	0.323	8.56	0.312
20	9.549	0.033	9.53	0.034

Table 1(b). DCMFC B

Day	Experimental value		PSpice value	
	R_{int}(KΩ)	P_L (µW)	R_{int}(KΩ)	P_L (µW)
7	8.489	8.928	8.509	8.924
15	7.180	9.361	7.197	9.357
20	6.505	8.054	6.412	8.050



(a)

(b)

Fig. 5. *V vs. I graph for (a) DCMFC A and (b) DCMFC B to obtain their internal resistance*

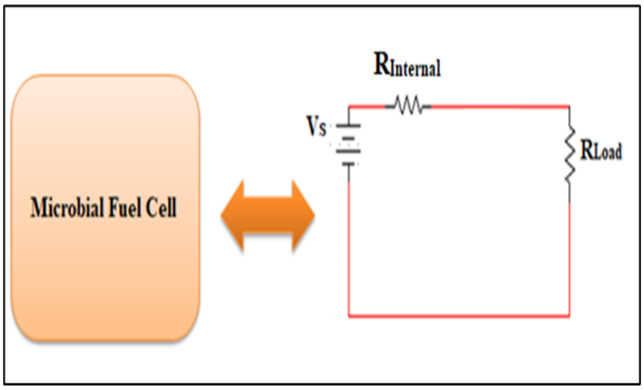


Fig. 6. *An analogy between an MFC and an electric circuit*

vested in an MFC for electricity generation (Pant *et al*., 2012). Different substrates have different amounts of organic matter in them. Thus, this leads to a variation in the energy outputs of an MFC using different substrates (Chandrasekhar *et al*., 2017). In addition to the substate, design, electrode materials and the total internal resistance of an MFC greatly impact the output power obtained using an MFC. A variation has been seen in the power densities obtained for different designs of an MFC using the same substrate and electrodes (Das and Mangwani, 2010), High values of current and power densities have been observed for SCMFC in comparison to DCMFC (You *et al*., 2006).

Several electrode materials have been explored and used for the construction of electrodes. There has been a shift from metallic electrodes to carbonaceous electrodes i.e. carbon and graphite-based electrodes. Recently, the Carbon nano tubes (CNT) and Graphene Oxide (GO) modified electrodes have gained attention. This is due to the high power densities that have been obtained using these (Cai *et al*., 2020). In some cases, the toxicity of these modified electrodes to the microbes and their growth is a limiting factor. The total internal resistance of an MFC proves to be another vital factor in determining the performance of the cell. The total internal resistance comprises an anode resistance, cathode resistance and ohmic resistance (in the case of membrane-less MFC) (Kondaveeti *et al*., 2017), The spacing between the electrodes contributes to the ohmic resistance, whereas the geometry or the structure of the anode and cathode affects the anode and cathode resistance. Hence, any change in the structure or spacing affects the resistance of the cell. This, in turn, affects the efficiency of the cell. In present scenario, the output current for the technology is low, which is greatly affected by the parameters mentioned above. Hence a need for the optimization of these parameters arises to obtain higher efficiency of current.

Conclusion

The prototype of a double chamber MFC was constructed for two different substrate samples. The power was successfully generated using kitchen wet waste as fuel using the MFC technology. It can be concluded that the generation of power in a DCMFC is greatly affected by the catalytic effect of acteate. Addition of acetate in substare results in an increase in the organic matter when it gets degraded by the microbes, leading to an increased ion concentration, which affects the internal resistance of the system. This, in turn, influences the amount of power generated by an MFC. In the comparative analysis, it can be seen that by adding a small amount of acetate to the substrate results in a considerable increase in coulombic efficiency. This is because the addition of the acetate has led to an increase in the organic content of the substrate present in the anodic chamber. Also, it has resulted in obtaining a higher power density for DCMFC B as compared to DCMFC A. Due to rich organic matter, the power den-

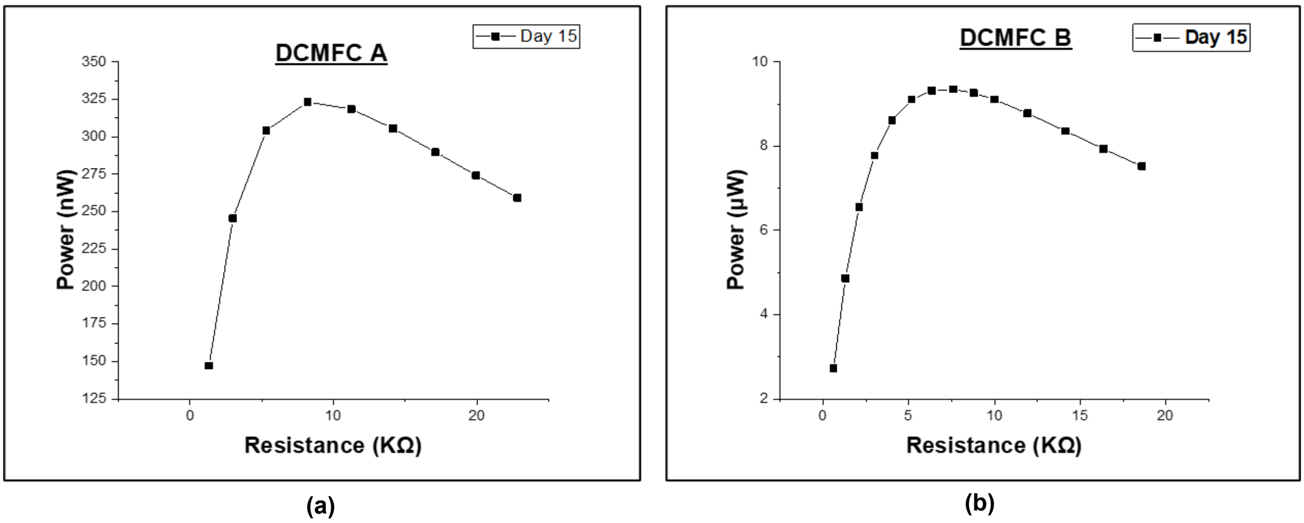


Fig. 7. *Graph plotted using PSpice simulation software showing the variation in values of power delivered to the load resistor for different values of load resistance for (a) DCMFC A, (b) DCMFC B*

sity initially increases with time and then once the matter degrades, the power density starts decreasing till the substrate is completely decomposed. An analogy has also been drawn between an MFC and an electric circuit. An MFC acts as an electric circuit that delivers maximum power output when the internal resistance of MFC becomes equal to the load resistance. The same has been verified using simulation An MFC is a low budget renewable form of energy capable of electricity generation and wastewater treatment. Also, the technology uses domestic kitchen waste as the fuel which is available in abundance to generate power. Therefore, this technology will be a significant source of power generation in the future, thereby tackling all the energy crises generated due to the depletion of non-renewable sources.

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Conflict of interest

The authors declare that they have no conflict of interest.

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