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A sustainable bioelectricity production from wastewater

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ABSTRACT

This study investigated the parameters affecting the performance of a 1000 mL dual-chamber MFC. A microbial fuel cell (MFC) reactor with two compartments has been constructed from cheap materials and used for electricity generation. The maximum power densities of 99.15 mW/m^2, 160.68 mW/m^2, 191 mW/m^2, and 204 mW/m^2 were obtained when aluminum electrode was used, the concentration of KCl in salt bridge was 6%, sodium acetate was used as a sole carbon source, and methylene blue used as a mediator; respectively. Changing the electrode materials, salt concentrations in the salt bridge, using different carbon sources and different mediators; had a great influence on electricity production from wastewaters using MFC**.** Microbial Fuel Cells (MFCs) offer the possibility of extracting electric current from a wide range of soluble or dissolved complex organic wastes and renewable biomass.

INTRODUCTION

Rapid industrialization contributes to large quantities of wastewater generation, and its treatment is highly imperative. Various technologies for reducing the wastewater treatment cost and finding ways to produce useful products from wastewater is gaining importance in view of environmental sustainability. During the anaerobic wastewater treatment process, chemical energy is used for converting waste to H_2, CO_2 and methane. Among them, hydrogen and methane can be used as fuel, but in microbial fuel cells (MFCs) chemical energy available in wastes are directly converted to electricity (Walter *et al*., 2019). Exploiting wastewater as a substrate to generate electricity is considered to be a sustainable and a promising approach to meet the increasing energy needs, and also as a substitute for fossil fuels (Pant *et al*., 2012; Logan, 2015; Cao *et al*., 2019). Therefore, the aim of this work is studying the effect of different anode material, different concentrations of salt in the salt bridge, different carbon sources, and different mediators on power generation.

MATERIALS AND METHODS

MFC setup

The cell was constructed (Fig. 1) using two round plastic containers of one-litre volume, working as the cathode and anode chambers, connected through agar salt-bridge made of 1.4 % agar and 0.4 % KCl. It was placed between anode and cathode compartments and rubber sheets inserted between each frame ensured the sealing

(Slate *et al*., 2019). The electrodes joined each other through variable external resistance (100-460 kΩ). Carbon rods were used as cathode electrodes while rod-shaped aluminum sheets were used as anode electrodes. Copper wires were used to connect electrodes and multimeter (Al-Shehri *et al.*, 2011).

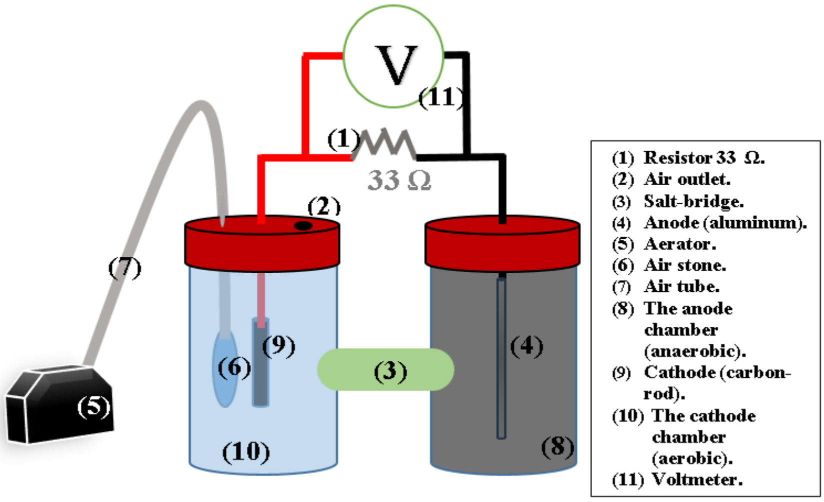

Fig. 1: A schematic diagram of the constructed double-chambered microbial fuel cell.

Medium, inoculum and operation

The anode chamber was filled with 990 ml medium composed of (g/l): yeast extract, 3; carbon source, 5; $MgSO_4.7H_2O$, 0.41; and vitamins, 0.75 ml. The pH of the medium was adjusted to 6.9 ± 0.2, by dissolving the components in 50 mM phosphate buffer saline solution. The medium was inoculated with 10 mL of wastewater. The cathode chamber was filled with 1 l catholyte which was composed of 1M potassium phosphate buffer solution (PPBS) and 1MNaCl (1:3, v:v) with pH 7.

The electrodes have been treated before using by 1 M HCl, 1 M NaOH, and distilled water, respectively. All parts of MFC have been assembled under sterilized conditions. The anolyte has been spared with N_2. Anode compartment has been closed tightly by parafilm, as well as the whole anode compartment have been enveloped by adhesive nylon. The anolyte was stirring continuously by magnetic bar stirrer. The catholyte was sparging continuously by 1 L/min. air. The experiments have been done at a temperature of 22 ± 2°C.

Measurements and calculations

For measuring voltage, a digital multi-meter was connected in parallel to the circuit by joining it to the alligator clips holding the resistor. The total volume of the cell (empty bed volume) was ~ 2 litres. The projected surface area of the cathode (carbon rod) was 0.000589 m^2, while that of the anode (a rod of aluminum foil) was about 0.0011 m^2.

MFC performance analysis

The MFC output was recorded in real-time in volts (V) using a digital multimeter. The current in amperes (A) was determined using ohm's law, E=IR; where "E" is the measured voltage in volts (V) and R is the loaded external resistance in ohms (Ω). Power (P) in watts (W) was calculated by multiplying the voltage by current, P=IE. Current density (I_d) and powder density (P_{cat}) were calculated in terms of the cathode electrode projected surface area, $I_d=I/A_{cat}$ and $P_{cat}=P/A_{cat}$, where A_{cat} is the total cathode surface area in square meters (m^2); or in terms of the volume of the anode chamber (1.86L), $I_d=I/V_{an}$ and $P_v=P/V_{an}$, where V_{an} is the total anodic volume in cubic meters (m^3). The surface area (S.A) was calculated from the following equation:

Surface area= Area of the top and bottom + Area of the side (Al-Sheheri, 2012)

$$\mathbf{S.A = 2(\pi r^2)+(2\pi r)h}$$

Where; π=3.141592, "h" is the length of the electrode which was 0.035m and "r" is the radius of the electrode which was 0.0025m.

The internal resistance (R_{int}) was calculated from the V/I curves of polarization data according to Jacobi's impedance matching law (maximum power transfer law).

Polarization data measurement

The output voltage of the closed-circuit (through the 33 Ω external resistance) was measured every 24 hours. When readings were steady for 2 successive days, polarization data were recorded via a periodical decrease of external resistors. The MFC was subjected to the following external resistors in decreasing order: 100, 220, 330, 560, 740 Ω, and 1, 1.2, 1.5, 2.2, 3.3, 4.7, 5.6, 6.5, 8.8, 10, 15, 33, 56, 88, 110, 220, 460 KΩ. The voltage produced at each external load was then recorded and calculations were made. The 33 Ω resistor was then returned to the circuit to watch for any further increase. The system was stopped when the output voltage at 33 Ω goes down from the highest voltage achieved. Comparisons between the performances of different cells were made based on the polarization data obtained.

Experimental investigation for parameter optimization on power generation

For a suitable anode material; three different anode materials; steel, aluminum and carbon, were individually tested. To optimize KCl concentration in the agar salt-bridge, different concentrations of KCl, 0.4, 2, 4, 6, and 8% were prepared. A comparative study was carried out to evaluate the performances of six different carbon sources (used as a sole carbon source): sodium acetate, carboxymethyl cellulose (CMC), glucose, lactose, soluble starch and sucrose. The effect of three different mediators on power output was also examined: Methylene blue, safranin O and crystal violet. In the last experiment, sodium acetate was used as a sole carbon source and the MFC was supplemented with 120 µM of each of the mediators.

RESULTS AND DISCUSSION

Effect of different anode materials on electricity generation

In this experiment, three separate MFCs were constructed with three different anode electrode materials: aluminum, steel, and carbon. All of the three MFCs were run under the same operational and environmental conditions.

According to the polarization data obtained (Table 1), the aluminum electrode showed the highest current density of 0.071 mA/cm^2; power density, 99.15 mW/m^2; and volumetric power density, 3.135 mW/m^3.

Table 1: Data obtained from the three microbial fuel cells with different anode materials.

Electrode material	Electric current $I_{(33\ \Omega)}$ (mA)	Voltage $E_{(33\ \Omega)}$ (mV)	Current density I_d (mA/cm^2)	Electric power P (mW)	Power density MPP (mW/m^2)	Volumetric Power density $P_{v\ (An)}$ (mW/m^3)	$R_{int\ (Pd\text{-}curve)}$ (Ω)
Aluminum	0.418	13.94	0.071	5.83	99	3.135	3300
Steel	0.328	10.94	0.056	3.59	61	1.932	4600
Carbon	0.078	2.58	0.013	0.20	3.4	0.108	8200

The anode material greatly affects the performance of microbial fuel cells as it impacts the biofilm formation, which functions as a living biocatalyst. The anode electrode also influences the rate of electron transfer with the bacteria present in the anode chamber itself as well as the interactions between bacteria and the electron acceptor. Therefore, the selection of proper anode material is crucial when it comes to the design of an MFC (Logan, 2008; Scott and Yu, 2016).

The results obtained are in consistence with Hussein *et al.*, (2012) who reported a high-power density for aluminum compared with carbon. In contrary, Ouitrakul *et al*. (2007) reported that aluminum had the lowest current and power densities of 2 mA/m^2 and 0.004 mW/m^2, respectively, when compared with carbon fiber that generated a current and power densities of 31 mA/m^2 and 1.8 mW/m^2, respectively. There are several factors affecting the interactions of microbes with the anode such as surface roughness, surface chemistry, material type, and porosity (Scott and Yu, 2016; Kalathil *et al.,* 2017, Oyiwona *et al.,* 2018, Hwang *et al*., 2019).

Effect of salt concentration in agar-salt bridge on power generation

The rate of proton transfer from the anode to the cathode can be a limiting factor in power generation, and it was found that the proton exchange system is the source of high internal resistance in two-chambered MFCs (Scott and Yu, 2016). This experiment, aims to optimize the concentration of potassium chloride to facilitate the maximum movement of protons towards the cathode that corresponds to higher current generation efficiency of the MFC. The experiment was carried out with 1.4% agar and 5 different concentrations of KCl ranging from 0.4 to 8% (Fig. 2).

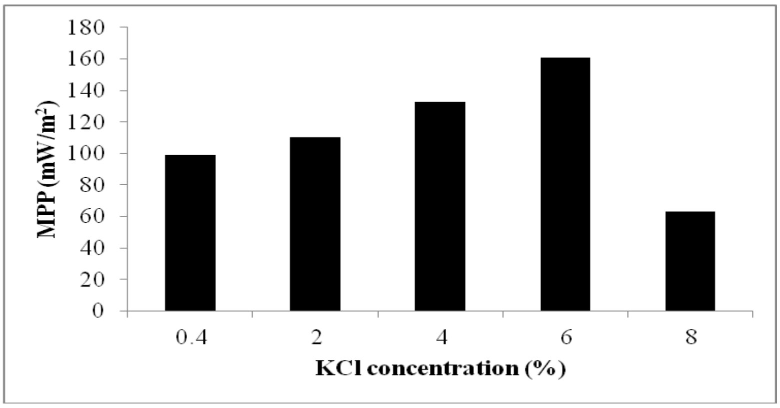

Fig. 2: Effect of different potassium chloride concentrations in salt-bridge of the MFC.

When salt (KCl) concentration was increased from 0.4% to 6%, the corresponding voltage, electric current, current density, electric power, power density, and volumetric power density increased to reach maximum values of, 17.76 mV, 0.533mA, 0.09047mA/cm^2, 9.46mW, 160.68mW/m^2, and 5.088 mW/m^3; respectively.

Increasing the salt concentration facilitated the transfer of more protons from the anode to the cathode chamber. However, a further increase in salt concentration to (8%), caused power density to decrease back to 63 mW/m^2 and lowered the overall performance of the cell (Fig. 1). Mangione *et al.*, (2005) stated that increasing the concentration of KCl increases the strength of the agar gel and the high KCl concentration against the low concentration of agar might have resulted in an adverse effect on the consistency of the gel, causing other ions to escape with protons from the anode to the cathode and air to escape from the cathode to the anode, which in turn might have caused the decrease in power generation. Sevda and Sreekrishnan (2012) reported an increase in volumetric power density from 1.71 mW/m^3 to 85 mW/m^3 and in power density from 0.32 mW/m^2 to 16.02 mW/m^2 when the concentration of salt was increased from 1 to 5% at 10% agar and increasing the salt concentration above 5% caused power density output to decrease back to 43.58 mW/m^2.

Comparative study for power output from MFCs with different carbon sources

In this study, the performance of six different carbon sources: sodium acetate, carboxymethyl cellulose (CMC), glucose, lactose, soluble starch and sucrose; was individually evaluated in six separate cells. An MFC with wastewater only was used as a control. Polarization data obtained from each of the six MFCs were summarized in Table 2.

Table 2: Data obtained from the six MFCs operated with different carbon sources

Carbon sources	Electric current $I_{(33\ \Omega)}$ (mA)	Voltage $E_{(33\ \Omega)}$ (mV)	Current density I_d (mA/cm^2)	Electric power P (mW)	Power density MPP (mW/m^2)	Volumetric Power density $P_{v\ (An)}$ (mW/m^3)	$R_{int\ (Pd\text{-}curve)}$ (Ω)
Control	0.533	17.778	0.091	9.483	161.000	5.098	1200
Sodium acetate	0.58097	19.364	0.099	11.250	191.000	6.048	1100
CMC	0.40973	13.656	0.070	5.596	95.000	3.008	3300
Glucose	0.40102	13.366	0.068	5.360	91.000	2.882	2200
Lactose	0.44489	14.828	0.076	6.597	112.000	3.547	1500
Starch Sol.	0.5027	16.755	0.085	8.423	143.000	4.528	1500
Sucrose	0.35171	11.723	0.060	4.123	70.000	2.217	2200

From the six tested carbon sources, sodium acetate showed the highest; voltage of 19.36mV, electric current of 0.58mA, current density of 0.099mA/cm^2, electric power of 11.25mW, power density of 191mW/m^2, and volumetric power density of 6.048mW/m^3. (Table 2).

The use of medium with sodium acetate as a sole carbon source improved the overall cell performance of voltage, electric current, current density, electric power, power density, and volumetric power density by 8.9, 9, 8.8, 18.6, 18.6, and 18.6 %, respectively; when compared with the control cell (wastewater only). The internal resistance of the sodium acetate-fueled cell was also lower by 8.3% when compared with the control cell.

Results obtained are consistent with Thygesen *et al*. (2009), who recorded a maximum power density of 130 ± 5 mW/m^2 and current density of 0.0550 ± 0.0050 mA/cm^2 when acetate was used as a carbon source. Sodium acetate was expected to perform better due to the simpler metabolic pathways associated with acetate biodegradation, compared with the other tested sources. Besides, the formation of by-products can reduce the electricity yield; no by-products are produced upon the bio-oxidation of acetate. Acetate can also increase the ionic strength of the solution and thereby decrease the internal resistance of the system (Thygesen *et al.,* 2009).

A great variety of substrates can be used in MFCs for electricity production ranging from pure compounds to complex mixtures of organic matter present in wastewater (Mishra *et al.,* 2017).

In MFCs, the bacterial abilities to oxidize substrates and transfer electrons are directly related to the production of current (Xu *et al*., 2019). The efficiency and economic viability of converting organic wastes to bioenergy depend on the characteristics and components of the waste material. Rozendal *et al.* (2007) and Lim *et al.*(2017) stated that the substrates not only influence the integral components of the bacterial community in the anode biofilm, but also the MFC performance, such as power density and Coulombic efficiency (CE).

Although many sorts of substrates could be oxidized by different species of bacteria, Pant *et al*. (2010) declared that it was difficult to make comparisons of MFCs performances with different substrates. This is mainly due to researchers being using different operating conditions (e.g. surface area and types of electrodes), different inoculated microorganisms, and different designs and volume of reactors (Parkash *et al.*, 2015).

Effect of different mediators on electricity generation

Some micro-organisms (exoelectrogens) have the ability to transfer electrons produced during electron transport chain to the anode without the aid of external mediators either through extensions (pili) on their outer surface known as nanowires (as found in *Shewanella Oneidensis)* (Gorby *et al.,* 2006), membrane-bound proteins (e.g. cytochromes as in *Geobacter sulferreducens*), or through the production of their mediators (e.g. phenazine as in

Pseudomonas spp.) (Gescher and Kappler, 2013; Feng *et al.*, 2014). Although electricity can be generated using a mediator–less MFC, the use of mediators can enhance both the coulombic efficiency of the cell as well as the electric output (Logan, 2008). Therefore, the aim of this experiment was to compare the effect of three different electron mediators: methylene blue, safranin O, and crystal violet; on MFC performance.

Three different cells were constructed with sodium acetate as the carbon source. The effect of the three different mediators; methylene blue, safranin O and crystal violet on MFC was tested with a final concentration of 120 µM. The concentration of the mediators was chosen based on the fact that some mediators are effective only at a concentration range of 120 µM (Alferov *et al.*, 2014). The resulting polarization data were compared with that of the control cell (mediator-less MFC) (Table 3).

Table 3: Data obtained from the three MFCs operated with three different mediators compared with the control cell.

Mediator	**Electric current $I_{(33\ \Omega)}$ (mA)**	**Voltage $E_{(33\ \Omega)}$ (mV)**	**Current density I_d (mA/cm^2)**	**Electric power P(mW)**	**Power density MPP (mW/m^2)**	**Volumetric Power density $P_{v\ (An)}$ (mW/m^3)**	**$R_{int\ (Pd\text{-}curve)}$ (Ω)**
Control	0.581	19.36	0.099	11.25	191	6.048	1100
Methylene Blue	0.600	20.01	0.102	12.02	204	6.460	1000
Crystal Violet	0.401	13.37	0.068	5.36	91	2.882	3300
Safranin-O	0.449	14.96	0.076	6.71	114	3.610	1500

The MFC amended with methylene blue showed the highest voltage of 20.01mV, electric current of 0.6mA, current density of 0.102mA/cm^2, electric power of 12.02mW, power density of 204mW/m^2, and volumetric power density of 6.46mW/m^3 (Table 3). Generally, mediators are used to increasing the current output by acting as electron shuttles between the anode electrode and the microorganisms. The polarization curve obtained from the methylene blue as an electron mediator had the lowest slope among the other tested mediators; indicating that the use of methylene lowered the internal resistance of the cell.

In this study, the observed power density obtained exceeded that obtained by Taskan *et al*. (2014), who reported an MPP of 36 mW/m^2, and Lohar *et al*. (2015), who reported an MPP of 69 mW/m^2 using methylene blue as an electron mediator.

The low power generation of safranin O-mediated cell is relevant to a previous study (Choi *et al.*, 2007), who reported safranin O to have virtually generated no current output. The volumetric power density obtained is lower than that reported by (Sevda and Sreekrishnan, 2012). They reported a maximum volumetric power density of 89 mW/m^3 compared with 6.46mW/m^3 obtained in this thesis. However, they reported much lower power densities ranging from 0.32 mW/m^2 to 18 mW/m^2 compared with the power density obtained in our work, 204 mW/m^2.

The results obtained with methylene blue as a mediator agreed with Al-Shehri *et al*. (2011), who reported that the highest recorded voltage at 33 ohms was 684 mV, with a power density of 1190.47 mW/m^2 and current density of 1.74 mA/m^2. Also, the results are by other researchers who demonstrated that the addition of mediators improved the power output (Mohan *et al.*, 2008; Daniel *et al.*, 2009; Liu *et al.*, 2009; Thygesen *et al.*, 2009).

CONCLUSION

Energy and water shortage are the main challenges that most countries face nowadays. Amongst the rising renewable energy technologies, MFCs are a unique technology capable of offering a solution for both sustainable energy and clean water demands. In order to take the MFC technology to a commercial level, more effort has to be spent in order to improve performance and treatment efficiency.

Conflict of Interest

The authors declare no conflict of interest

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