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Air-Cathode Microbial Fuel Cells by Utilizing Marine Electrogenic Bacteria: Enhancement with GAC Electrodes Coated with Biogenic Palladium Nanoparticles

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Microbial Fuel Cell (MFC) technology provides the potential of utilising wastewater treatment plants as power generation units. The biogenic bacteria cultures used in this study were collected from marine environment in South Africa (Saldanha Bay, South Africa). The MFC was configured to operate without a cathode chamber using an air-cathode configuration. Biological deposition of Pd(0) nanoparticles was used to improve the electrocatalytic activity of the anode. Solid material such as a carbon rod has a low surface area compared to dispersed material such as granular activated carbon (GAC) when using the same amount of mass. Therefore, GAC is a viable replacement to solid material anode electrodes which is proposed to improve MFC performance since the anode surface area plays a crucial role in MFCs. The use of parallel configuration is proposed in this study since it leads to a high current and power density operation.

1. Introduction

In recent years, Microbial Fuel Cells (MFCs) have been identified and developed in response to mankind's search for sustainable energy sources for future generations. MFC technology is constantly receiving research attention as it can easily be installed on existing waste treatment plants to act as an additional energy source. In doing so, the plant's energy cost is reduced and the sludge being processed contains less organic contaminants before downstream processing (Santoro et al., 2017). MFC technology is a relatively new field and is receiving a lot of attention from researchers (Medina Mori et al., 2022). Ultimately all research in this field aims at implementing the technology on existing sewage processing plants. To achieve this, laboratory scale setups must be scaled up to run continuously for tanks spanning the size of millions of liters per day.
In this study, we move from the traditional H-type microbial fuel cell a single chamber MFC with the objective of reducing internal resistance. It has been established in numerous studies the imitation of the H-type MFC is it's internal resistance due to ionic travel time of H^+ (proton) from the anode to the cathode to recombine with electrodes. Whereas the travel time of electrons from anode to cathode in a conductor is almost instantaneous, the journey of a proton through the aqueous phase is tedious and tenuous.
Various materials can be used to manufacture the air-cathode used in MFCs. Carbon is the most commonly used material in air-cathodes according to Jobin and Namour (2017). This is due to the relatively low cost of carbon's conductive form. It has been suggested that the performance of carbon air-cathodes can be increased by adding precious metals to the air-cathode. This creates composite materials that have higher electrical conductivities. Jadhav et al. (2017) performed various experiments to support these claims. Their research pointed out that the highest power output was achieved using a manganese-palladium mixture as an air-cathode.
Dual-compartment MFCs consist of two chambers | for the anode and cathode respectively and a proton exchange membrane (PEM) which separates the two compartments. Single-compartment MFCs contain one chamber for the anode, a PEM and a cathode which is open to the air otherwise known as an air-cathode

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microbial fuel cell. Stacked MFCs consist of several MFCs connected together either in series or parallel. This fuel cell stack focuses on increasing output power generation since single MFCs usually produce power levels which are only suitable for low-power-consumption devices (Najafpour, 2015). All three configurations have their own advantages, however, the air-cathode MFC is the most desirable.

Halophilic bacteria are extremophiles which thrive under super saline conditions (> 1M NaCl) and are commonly found in marine environments. Research has shown that utilizing electrogenic halophiles under super saline operating conditions can broaden the scope of industrial MFC applications and enhance MFC performance owing to the enreached electrolyte conductivity (Shrestha et al., 2018). Furthermore, physical conditions, such as temperature and pH, to which these microbes are exposed have shown direct effects on cellular activity and MFC performance (Malki et al., 2020). Research has indicated that these conditions are microbe specific. The problem is determining the optimal conditions for MFC performance relative to the utilized microbes. The present investigation aimed to evaluate and optimize the performance of an air cathode MFC which utilized marine bacteria collected from Saldanha Bay, South Africa.

The project objectives were to confirm the electrogenic potential of the collected samples, identify the best performing sediment sample and subsequent optimal operating conditions. In this work, the best performing sediment sample from Saldanha Bay was identified and the optimal pH and temperature conditions were determined to enhance MFC performance. System performance was evaluated on measured output potential, maximum 64 power output and internal resistance.

Currently, the laboratory scale set ups are being optimized to find the best reactor conditions and electrode materials. Jadhav et al. (2017) has previously indicated that by including palladium in air-cathodes of single cell MFCs greatly increased the power output of the MFCs. This study will mainly focus on improving the anode using biological deposition of Pd(0) nanoparticles and dispersed material such as granular activated carbon (GAC).

2. Materials and Methods

2.1 Microbial Samples and Growth Medium

2.1.1 Microbial samples

Sediment samples were collected from Saldanha Bay (Cape Town, South Africa) at three site locations: Site 1 (33°0'21.0"S 17°56'46"E), Site 2 (33°2'00.0"S 17°56'00"E) and Site 3 (33°5'35.0"S 18°1'48.5"E). Basal mineral media (BMM) was used as a growth medium and comprised of 0.80 mM sodium sulphate, 20 mM monopotassium phosphate, 0.20 mM magnesium sulphate, 30 mM disodium phosphate, 10 mM ammonium chloride, 0.20 μM copper(II) chloride, 0.10 μM zinc chloride, 0.10 μM potassium iodide, 25 μM iron(II) sulphate, 50 μM calcium chloride, 0.10 μM manganese(II) chloride, 0.10 μM cobalt(II) chloride, 0.050 μM sodium molybdate, 0.10 μM sodium bromide, 0.10 μM nickle(II) chloride and 0.20 μM boric acid | supplied in-house. The media was sterilised in an autoclave at 121 °C at 115 kg cm^{-2} for 15 minutes.

Luria-Bettani (LB) broth was prepared by dissolving 25 g of LB pellets in 1.0 L of deionized water. The broth was sterilised in an autoclave at 121 °C at 115 kg cm□2 for 15 minutes.

2.1.2 Basal mineral media (BMM)

BMM growth medium was prepared according to (Matsena et al., 2020) and was sterilized before use in an autoclave at 121 °C at 115 kg cm^{-2} for 15 minutes.

2.2 Anode chamber inoculation

Bacterial cultures were cultured anaerobically, in sterilized Erlenmeyer flasks containing 2.0 g of sample and 300 mL of sterilized Luria-Battani broth (LB), for 2 days at (30 ± 1 °C) in a shaker incubator operating at 150 rpm. The cultured cells were centrifuged at 4 °C and 6000 rpm for 15 minutes after incubation. The supernatant was disposed and the pellets were washed three times in a 0.85 % sterile solution of NaCl.

Experiments were carried out with an anode working volume of 320 mL consisting of the harvested cells, formate (5.0 g L^{-1}) and BMM. The anode chamber was purged with N_2 gas for 2 minutes and tightly sealed to prevent any air from entering prior to each experiment.

2.3 Air-Cathode MFC Set-Up

2.3.1 Set-Up

The MFC configuration can be observed in Figure 1.

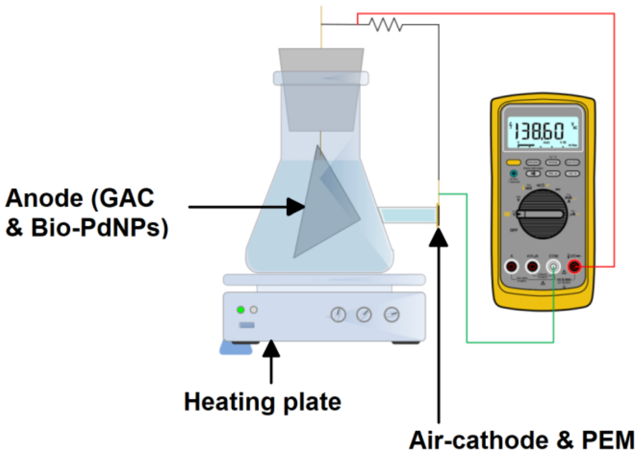

Figure 1: Configuration for an air-cathode Microbial Fuel Cell (MFC).

The anode chamber had an effective working volume of 320 mL and was separated from the cathode by a Nafion 117 (Fuel Cell Store, USA) PEM membrane. The anode electrode was constructed from carbon cloth, granular activated carbon, and bio-palladium nanoparticles. The anode chamber temperature was adjusted using a heating plate and batch operation was conducted at a fixed external resistance of 1 kΩ.

2.4 Performance analysis

Polarization curves were constructed by measuring the voltage across variable external resistance (2.7 kΩ – 1.2 MΩ) once the MFC had reached a maximum voltage output during batch operation at 1.0 kΩ external resistance. Current density was determined using Eq(1):

$$I = U_m/(R_{ext} \cdot V), \quad (1)$$

where I denotes current density (mA m^{-3}), U_m is the measure output potential (mV), V is the working chamber volume (m^3) and R_{ext} is the external resistance (Ω). Power density was calculated according to Eq(2):

$$P = (I \cdot U_m)/1000 \quad (2)$$

where P is power density (mW m^{-3}).

3. Results and Discussion

3.1 Anode Characteristics

Increased power outputs were associated with increased surface area available for attachment of microbial culture explained when the morphology of the GAC and the bacterial attachment is considered in Figure 2. The distinctive structures of morphology and attachment of the cells on GAC with varying average sizes of the particles were revealed by the scanning electron micrographs. The GAC of an average size of particles of 2–3 mm had a skeletal morphology as shown in Figure 2a. Skeletal structure then began to disappear with a decrease in particle size as shown in Figure 2b and c. The attachment of the bacteria is shown in blue squares depicted in micrograms of Figure 2a and b. However, as it can be seen in Figure 2c, there was no effective attachment of bacteria that was seen in the average size of particles of 0.45–0.6 mm.

3.2 Effect of GAC on an air-cathode MFC

The effect GAC on air-cathode MFC performance was studied. This was motivated by previous studies which observed that the change in surface area and particle size can help improve the attachment of electrogenic bacteria (Ahmed et al., 2015; Yang et al., 2018). Experiments involving the variation of average particle size were conducted to obtain the optimal size range for the improvement of air-cathode MFC performance.
The results in Figure 3a and Figure 3b show that GAC with an average size of particles in the range between 0.6-1.1 mm produced an output voltage of 254 mV and maximum power output of 322 mW m^{-3} at a current output of 1269 mA m^{-3}. However, a decrease in the average size of particles to 0.45-0.6 mm resulted in a decrease in MFC performance of an output voltage of 75 mV and a maximum power output of 28 mW m^{-3} at a current output of 375 mA m^{-3}.

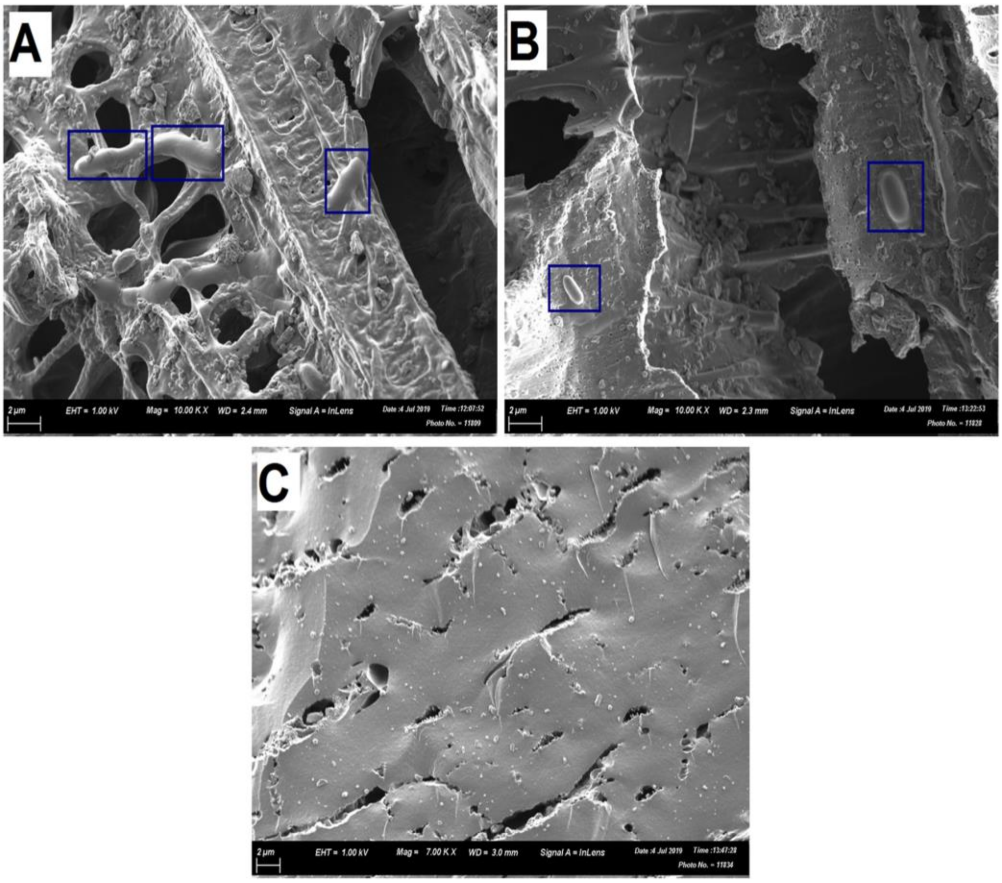

Figure 2: Morphology observation of GAC using SEM analysis at varying average sizes of particles of (a) 2–3 mm, (b) 0.6–1.1 mm, and (c) 0.45–0.6 mm.

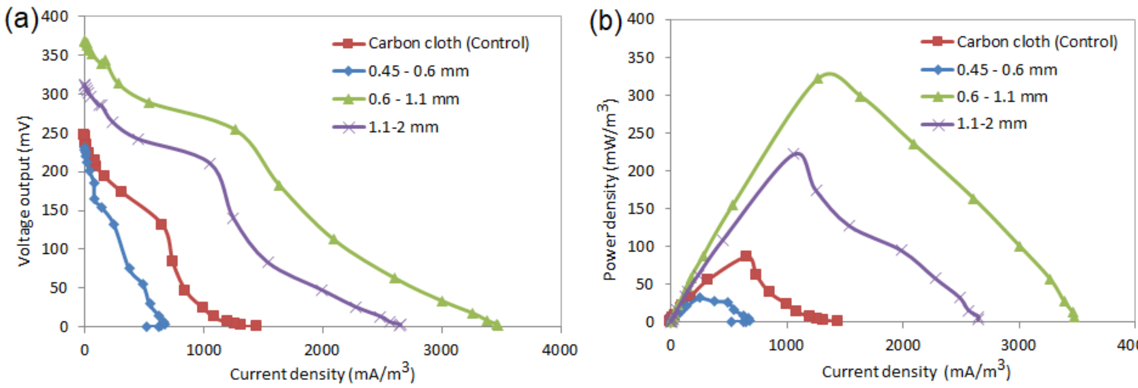

Figure 3: The effect of GAC with varying average sizes of the particles (0.45-0.6 mm, 0.6-1.1 mm, 1.1-2 mm) on (a) output voltage (polarization curve), (b) power output of an air-cathode MFC.

The average size of particles of 0.6-1.1 mm led to improved performance due to better attachment and the retention of bacteria since the surface is rough and irregular (Matsena et al., 2021b). Furthermore, the reason for performance deterioration for the average size particles of 0.45-0.6 mm is because there is a significant reduction in bacterial attachment due to lack of porosity (Matsena et al., 2021b).

3.3 Effect of Bio-PdNPs on an air-cathode MFC

The addition of the Bio-PdNPs to the unmodified GAC resulted in improved performance as both the output potential difference and maximum power output increased with increasing Bio-PdNPs loading. The results in Figure 4a and Figure 4b show that maximum improved performance occurred at an output voltage of 360 mV, a power output of 649 mW m^{-3} at a current output of 1802 mA m^{-3} using Bio-PdNP2.

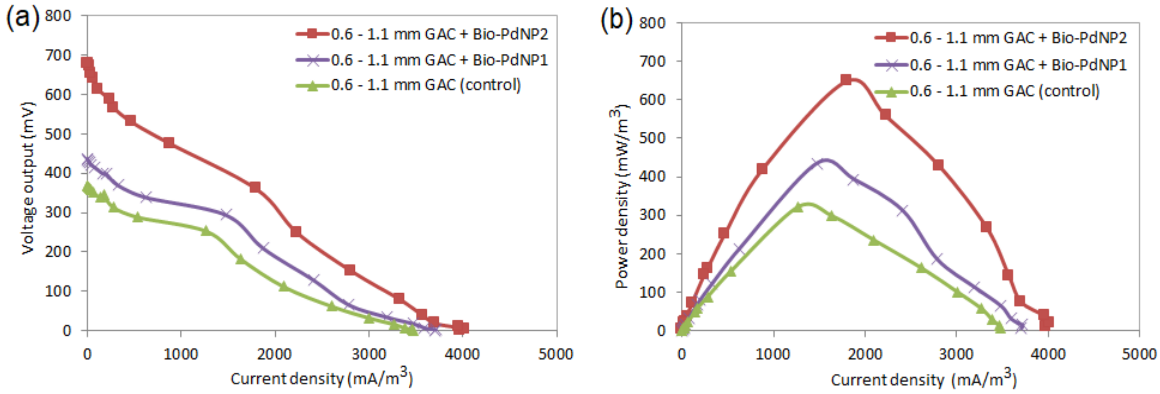

Figure 4: (a) Output potential difference (polarization curve), and (b) power density in air-cathode MFC with GAC anode modified with Bio-PdNP1 (2 mg Bio-PdNPs g-1 GAC), Bio-PdNP2 (6 mg Bio-PdNPs g-1 GAC), and an unmodified 0.6-1.1 mm GAC.

Besides the presence of microbes, further improvement in air-cathode MFC performance in the presence of Bio-PdNPs was attributed to enhanced catalyzation of formate oxidation by Bio-PdNPs and an increase in active sites with increased Bio-PdNPs loading (Matsena et al., 2021a).

3.4 Effect of air-cathode MFC configuration

The air-cathode MFC configuration was investigated. It was found that arranging two air-cathodes in a parallel configuration improves performance when compared to arranging them in a series configuration. The results in Figure 5a and Figure 5b show that maximum improved performance occurred at an output voltage of 504 mV, and power output of 1272 mW m^{-3} at a current output of 2522 mA m^{-3} using parallel configuration.
Similar observations in the ability of series configurations to increase output potential difference, and the ability of parallel configurations to increase the current density while maintaining high power densities were made by Aelterman et al. (2006) and Zhi et al. (2021).

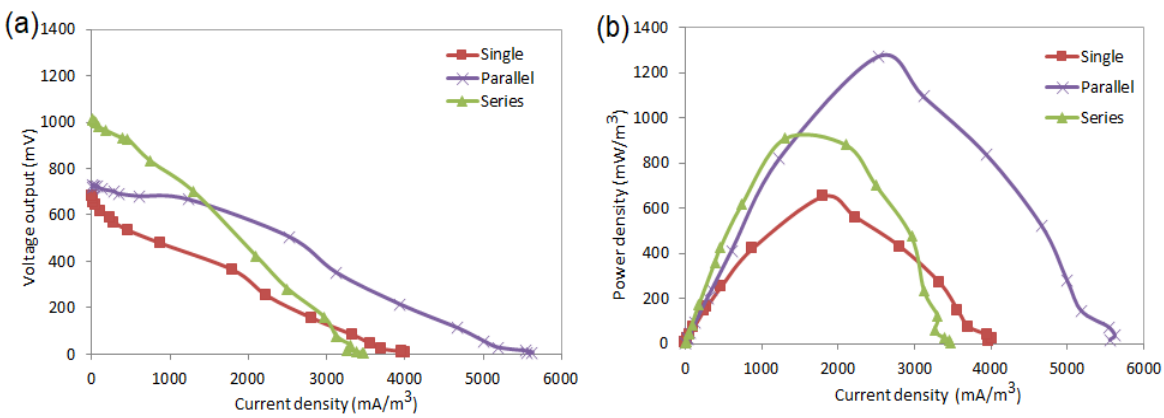

Figure 5: The (a) polarization and (b) power density curve of the air-cathode MFC under parallel and series configuration.

4. Conclusions

The potential of utilising wastewater treatment systems as generators of electricity was identified by the usage of microbial Fuel Cell (MFC) technology. The MFC was configured to operate without a cathode chamber using an air-cathode configuration. Biological deposition of Pd(0) nanoparticles was used to improve the electrocatalytic activity of the anode. Solid material such as a carbon rod has a low surface area compared to dispersed material such as granular activated carbon (GAC) when using the same amount of mass. Therefore, GAC is a viable replacement to solid material anode electrodes which is proposed to improve MFC performance since the anode surface area plays a crucial role in MFCs. The use of parallel configuration is proposed in this study since it leads to a high current and power density operation.

Acknowledgments

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