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Effect of the Membrane Type and Resistance Load on the Performance of the Microbial Fuel Cell: A Step ahead of Microbial Desalination Cell Establishment

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One of the primary sources of drinking water and for non-potable applications is saline (sea) water. Conversely, a vast amount of wastewater is currently produced that needs to be treated before using or discharging. Ocean sea water is considered to be a raw material used in the desalination process and converted to usable water. In the initial stage of the study, a microbial fuel cell (MFC) with a cation exchange membrane (CEM) and an anion exchange membrane (AEM) were used as separators, in the experiments under different (1, 10, 100 and 1000 Ω) loads of resistance, to measure the efficiency in wastewater treatment and electricity production. The system using a CEM produced the maximum or optimal current of 1.8 mA, a columbic efficiency (CE) of 42% and 80% of chemical oxygen demand (COD) removal at 1 Ω external resistance. While the system running with an AEM achieved a maximum current of 1.8 mA, 40% CE and 77% COD removal at 1 Ω . It highlighted the minimal difference between the performances of the MFC either by using an AEM or CEM. In the second stage of this study, a microbial desalination cell (MDC) used as a novel bioelectrochemical system, was developed by modifying the enriched and optimised MFC system. The MDC was investigated for the desalination of salt water and wastewater treatment. The performance of the MDC with 10 g/l of NaCl salt was measured for desalination of brackish water and COD removal for wastewater treatment, CE and electrical current production. The COD removal of the system was greater than 80%, and the percentage of desalination was 100% after running for five days. The MDC system produced a maximum current of 1.3 mA. Therefore, the results from the study confirmed that the MDC was an appropriate technology used for simultaneous desalination and wastewater treatment applications and facilitating the production of green energy.

Key Words

Brackish water, Wastewater treatment, Desalination, Bioelectrochemical system

1. Introduction

The abundance of water located in and around our planet is a vital resource, fundamental to our ecology and enabling all life to flourish and coexist. More than 97% of the Earth's total water supply is found in our oceans. Saline or salt water as a potential source of drinking water is in ever increasing demand^{1) ~ 3)}. The amount of saline

water residing in our oceans could potentially supply our requirements for fresh water if, an appropriate desalination technique was available. High energy demands currently limit desalination methods, so for a technique to be effective and workable, an energy efficient mechanism for desalination is required^{4) 5)}. Over the past decade, microbial fuel cells (MFC) have been developed, representing a

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potentially new technology for the treatment of wastewater. An MFC is a device that simultaneously treats wastewater, by converting chemical energy into electrical energy. Microbes act as a biocatalyst to degrade organic substrates into protons and electrons through an oxidation process in the MFC. The generated electrons flow through to a cathode compartment via an external circuit^{(6) ~ (8)}. When the cathode is exposed to the air or any other aerobic liquid, bioelectricity is generated resulting from potential differences between the anode and cathode^{(9) ~ (11)}. The MFC can be modified to become a microbial desalination cell (MDC) by adding a chamber between the anode and cathode compartments, called a desalination chamber⁽¹²⁾. Cations and anions are moved to the anodic and cathodic chambers respectively in the MDC due to the potential cell differences existing between the anode electrode and the cathode electrode. The desalination process removes salt along with the treatment of the wastewater with electricity generated. Therefore, the motivating factor that exists for desalinating saline water in MDCs is related to the potential differences existing between the anode and cathode electrodes⁽¹³⁾.

A MDC consists of three chambers, each separated by a desalination chamber. An anode chamber is responsible for the degradation of the organic substrate (*e.g.* wastewater), and the middle chamber is responsible for salt water desalination with the cathode chamber completing the circuit^{(10) (14) (15)}.

The main problems associated with MDCs are the slow start up times, and pH drops which conflict with microbial metabolism and significant cathode catalyst costs. Compared to other desalination techniques or methods (*e.g.* such as the electrodialysis and reverse osmosis), MDC technology is recognised as being sustainable, by adopting a greater practical approach in conducting water desalination, given no energy input is required⁽¹⁶⁾.

The current study is performed on a pH controlled-recirculated MDC system. Salt (NaCl) in a concentration of 10 g/l is monitored for desalination efficiency. Before running the MDC system, the MFC system is enriched and examined by applying different loads of resistance in the circuit, in the presence of a cation exchange membrane (CEM) and an anion exchange membrane (AEM). The optimised MFC is converted to an MDC to examine the three simultaneous functions of the system regarding bioelectricity generation, wastewater treatment and the desalination of saline water.

2. Materials and Methodology

2.1 Experimental setup

The MDC was fabricated as a cubic shape out of a solid polycarbonate block consisting of three chambers which were; the anode chamber, the middle desalination chamber and the cathode chamber. The volume of the anode and cathode chambers were each, 48 ml ($4 \times 4 \times 3$ cm³ (wide, length, height)) while the desalination cell was 32 ml in volume ($4 \times 4 \times 2$ cm³). The anode chamber was separated from the desalination cell using an AEM (AMI-7001S Membranes International Inc.), while a CEM (CMI-7000S Membranes International Inc.) separated the desalination cell from the cathode chamber. Silicon gaskets were applied between the chambers to provide and ensure a proper water seal. Both the AEM and the CEM were preconditioned stored in a 5% NaCl solution for 24 hours before used in the experimental setup. Graphite felt was used as both a cathode and anode with an area of 16 cm² each (4×4 cm², and 5 mm thickness) coated with 0.5 mg-pt/cm² on each cathode. Graphite felt was cleaned and treated by soaking in ethanol (100%), HCl(1M), NaOH(1M) for 30 min, 1 hour and 1 hour respectively^{(17) (18)}.

2.1.1 Electrolyte

The anode chamber holding the bioelectrode inside was fed with a media consisting of a 50 mM phosphate buffer solution (4.58 g/l Na₂HPO₄, 2.45 g/l NaH₂PO₄·H₂O) and 0.1 g/l MgSO₄·7H₂O, 0.5 g/l NH₄Cl, 0.13 g/l KCl, 0.5 g/l NaCl, 0.05 g/l CaCl₂·2H₂O, 2 g/l sodium acetate, and respective amounts of Wolfe's vitamin and mineral solution. A desalination cell was filled with an understudied concentration of NaCl solution (10 g/l of NaCl) with 50 mM buffer solution in the cathodic chamber, and continuously aerated.

2.2 MFC operation

Before running the MDC system, the MFC mode was selected to enrich the anode biofilm. The performance of the MFC was monitored through applying different loads of resistance, in the presence of an AEM and a CEM, in running the individual experiments. Both the anolyte and catholyte were recirculated using a peristaltic pump (BT100-1L Multi-channels Peristaltic Pump, Longer pump, China) through a 500 ml circulation bottle, equipped with a pH meter (BL 981411 pH controller, Hanna, USA)⁽¹⁹⁾. The MFC operation also consisted of ports for purging and discharging anaerobic gas, sampling (samples were taken through a three-way stopcock), injecting and a circulating outlet, and an inlet in connection with anode and cathode chambers, as shown in Fig. 1. The chamber was inoculated using a mixed culture obtained from one of the palm oil

Fig. 1 MDC schematic system, demonstrating with detailed components: (1) anode chamber, (2) anode, (3) AEM, (4) desalination chamber, (5) CEM, (6) cathode, (7) cathode chamber, (8) applied external resistance, (9) data acquisition system (voltammeter and PC), (10) recirculation bottle, (11) pH monitoring system (pH probe and pH indicator), (12) anaerobic gas purging in, (13) anaerobic gas purging out, (14) injection port, (15) Peristaltic pump to pump feed in, (16) three-way stopcock for sampling

anaerobic ponds locally (Palm company, Selangor, Malaysia). A CEM was inserted between the two chambers, with 1000, 100, 10 and 1 ohmic external resistance applied in the circuit. The external resistance changed after the reproducible cycles were run and observed. Anolyte and catholyte were continuously recirculated via the recirculation bottles at a rate of 20 ml/min using a multichannel peristaltic pump (BT100-1L, Longer pump, China). The electrolyte used in the recirculation bottles was refreshed when the current level dropped to less than 10% of the maximum level reported. Consequently, the effect of similar external resistance ranges, (1, 10, 100 and 1000 Ω) were monitored when an AEM replaced the separator in the same experimental setup. MDC mode was conducted after the external resistance was fixed, based on the initial batch of experiments, by inserting the middle chamber and required accessories along with both the CEM and AEM. The catholyte and anolyte were recirculated and refreshed using the same procedure as used in the MFC mode. A 30-ml salt solution of NaCl in concentration of 10 g/l, was analysed during the experiment. The salt solutions used in the desalination cell had not been refreshed during the cycles until the maximum removal was detected throughout the microbial exoelectrogenic cycles^{20) 21)}.

2.3 Characterisation of biofilm and membranes

The morphology of membranes was observed using a field emission scanning electronic microscopic (FESEM). A scanning electron microscope (SEM) was used to examine the attached bacteria on the surface of the electrode. Before examining the surface of the electrode, any existing

moisture was removed from the electrode by thoroughly and critically drying. The biological specimens were then covered using a thin layer (20-50 nm) of conductive metal, making them conductive for the SEM analysis²²⁾.

2.4 Analysis

2.4.1 Current calculation

The voltage across the known external resistance (R_{ext}) was recorded every 30 minutes by using a multichannel multimeter (Keithley 2700 Multimeter) connected to a computer. The current was calculated using Ohm's law: $I = V/R_{ext}$ ²³⁾.

2.4.2 NaCl concentration

The NaCl concentration was measured using a conductivity evaluation method calibrated based on a broad range of NaCl concentrations (1 g/l and 5-50 g/l with an interval of 5 g/l of NaCl). Measurements were performed twice a day, at the beginning and end of each batch cycle.

2.4.3 Chemical Oxygen Demand (COD)

Samples were collected at the beginning and end of each cycle and analysed for COD content. COD was measured using a medium-range COD reagent (HI 93754B MR, Hanna, Romania) with 2 ml of the centrifuged sample added to the MR vials. This was then digested in a block heater reactor for two hours at 150 °C and recording the COD values using a photometer (HI 83099, Hanna, Romania) at ambient room temperature.

2.4.4 Coulombic Efficiency (CE)

The ratio of total coulombs transferred to the anode from the substrate to the maximum possible coulombs, which can be recovered, is defined as CE and calculated

using the following equation:

$$CE = \frac{8 \int_{t_1}^{t_2} Idt}{Fv_{an} \Delta COD}, \quad (1)$$

where t_1 and t_2 represent cycle duration, I = the corresponding current flowing in the circuit over the cycle duration, F = Faraday's constant, v_{an} = aqueous volume in the anode chamber and ΔCOD = the COD changes of anodic media consumed during the cycle^{24) 25)}.

3. Results and Discussion

3.1 Morphology of membranes and biofilm enrichment

The surfaces of the CEM and the AEM, shown in Figs. 2 (a) and (b) illustrate the surface textures of both membranes being smooth and with little difference in roughness. Also, the cross section of membranes reveals a very dense layer without any porosity.

The enrichment of the bacteria on the anode was carried out over a period of one month while running. Fig. 3 shows the surface of the bioanode after one month of enrichment. It was observed that the different types of bacteria attached to the surface of the electrode acted as a biocatalyst. The organic substrates inside the wastewater were degraded, producing protons and electrons. It was apparent that certain types of bacteria attached to the surface of the anode electrode could oxidise the organic materials in wastewater. Consequently, different loads of resistance were applied in the circuit when the bacteria was attached to the surface of the electrode and analysed²⁶⁾.

Fig. 2 Surface of the studied (a) CEM and (b) AEM

Fig. 3 Bacteria attached to the surface of the electrode in the anode compartment of the MFC

3.2 MFC mode

In the initial/first batch of experiments, both the electrical current generation and the CE were monitored with different resistances when an AEM and CEM were used as separators in the individual experiments. This was undertaken given the application of both the AEM and the CEM working together in the MDC system. Moreover, the electrical current is a focal point for the removal of salt in an MDC system.

3.2.1 Effect of different loads of resistance on the performance of the MFC using a CEM

Fig. 4 illustrates the MFC with a CEM used as a separator operating under different loads of resistance (1, 10, 100 and 1000 Ω). The cycles were repeated until the results were recorded. As shown in Fig. 4, the current increased from 0.4 to 1.8 mA when the load changed from 1000 to 1 Ω , respectively.

Therefore, at a constant voltage, a higher current can be achieved by using a lower resistance. It was observed that a high CE of 44% was obtained at 1 Ω external resistance compared to 6% achieved at a high resistance of 1000 Ω .

3.2.2 Effect of different loads of resistance on the performance of the MFC using an AEM

The results of the CE, COD removal and the electrical current over the duration of the process are shown in Fig. 5. When an AEM was used as a separator, the electrical current and CE of the MFC system with an AEM followed a similar trend due to the MFC system operating with a CEM. This was in agreement when comparing the internal resistance of 84 Ω for the AEM and 88 Ω for the CEM, in a cube chamber as reported by Logan in 2008²⁷⁾. The highest voltage and CE can be achieved in 1 Ω followed by 10, 100 and 1000 Ω . It should be mentioned that both systems had quite high COD removal which could be attributed to the high exoelectrogenic activity of the biocatalyst attached to the anode²⁸⁾. The results positively confirm that the MFC system is an appropriate system for the treatment of industrial and municipal wastewater treatment systems.

3.3 Microbial Desalination Cell (MDC)

Following the investigation of the MFC's performance in the initial batch of experiments, the desalination chamber was added as a middle chamber to the MFC, thereby converting it to an MDC. In respect to the concept of proof, desalination will occur when cations and anions pass through the CEM and the AEM leading to the potential difference between the anode and cathode being the motivating force for the desalination process²⁹⁾.

Fig. 4 Effect of different loads of resistance on the performance of the MFC (current production, coulombic efficiency and COD removal) in the presence of a CEM

Fig. 5 The effect of different loads of resistance on the performance of the MFC (current production, coulombic efficiency and COD removal) in the presence of an AEM

Fig. 6 illustrates the MDC operating with 10 g/l of NaCl in the desalination chamber. The electrical current produced uses a NaCl concentration and a percentage for removal of NaCl (salt) as shown the graph. The electrical current reached 1.3 mA in the first cycle, gradually decreasing to 1.1 mA in the second cycle and 0.9 mA in the third cycle. The concentration of NaCl decreased linearly whereas the rate of removal increased linearly. The complete removal of NaCl required was performed using three cycles, running over a period of 5 days.

4. Conclusion

Traditional desalination processes experience problems associated with high energy demand and significant capital costs. The application of a microbial desalination cell was applied in this study to demonstrate how desalinated NaCl, produces electrical energy and used

Fig. 6 Demonstration of the MDC performance in the form of the current production, NaCl concentration and salt removal rate in the presence of 10 g/l NaCl in the desalination chamber

for wastewater treatment. The results from the study confirmed that an MDC could successfully be used for sea water desalination. Furthermore, based on the results of the MFC enrichment and evaluation stage, it can be concluded that there were only minor differences in the performance of the MFC operating with either a CEM or AEM. However, the applied load for the external resistance should be carefully considered and selected to obtain the best performance and results in both the MFC and the MDC modes of operation. Both the MFC and MDC demonstrated a high capability for the treatment of wastewater ($\sim 100\%$). Therefore, in summary, it can be concluded that based on the results of the study, bioelectromchemical systems is shown to be a promising future technology, appropriate for wastewater treatment, the desalination process and facilitating green energy generation.

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