environmental sciences proceedings

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Proceeding Paper

Integration of Microalgae-Microbial Fuel Cell with Microbial Electrolysis Cell for Wastewater Treatment and Energy Production †

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† Presented at the 7th International Electronic Conference on Water Sciences, online, 15–30 March 2023; Available online: https://ecws-7.sciforum.net.

Abstract: The microalgae-microbial fuel cell (mMFC) enables us to perform secondary and tertiary treatment of domestic wastewater while simultaneously producing green electricity**.** In this work, treatment of wastewater and producing electricity using a dual chambered microalgae based microbial fuel cell (mMFC) is demonstrated. Furthermore, the electricity produced by mMFC is utilized to drive microbial electrolysis cell (MEC) for hydrogen synthesis. Primary treated domestic wastewater was treated in the anodic compartment of mMFC. Chemical oxygen demand (COD) removal of 67.2% and 54% was achieved in anodic compartment of batch and continuous mode respectively. Wetland treated water filled the cathodic compartment, and *Scenedesmus* sp was used as catholyte. The overall voltage of 1.85 V was used to run a 1-L microbial electrolysis cell (MEC). Industrial wastewater was treated with COD removal of 73% in the MEC and biohydrogen produced at a rate of 9.8 ± 0.2 mL L^{-1} d^{-1}.

Keywords: microalgae-microbial fuel cell; microbial electrolysis cell; wastewater treatment; energy production; microalgae

Citation: Mansoor, B.; Ashraf, S.; Rehman, U.; Ullah, Z.; Sheikh, Z. Integration of Microalgae-Microbial Fuel Cell with Microbial Electrolysis Cell for Wastewater Treatment and Energy Production. *Environ. Sci. Proc.* **2023**, *5*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s):

Published: 15 March 2023

1. Introduction

Globally, around four hundred billion cubic meter of untreated wastewater is discharged each year [1]. Furthermore, the world's energy need is increasing all the time. Most of our energy requirement is fulfilled by burning of fossil fuels. The combustion of fossil fuels produces a large amount of carbon dioxide, which is a greenhouse gas and causes climate change. We need to shift to sustainable green energy sources now more than ever. Microalgae-microbial fuel cell (mMFC) has attracted attention as a long-term wastewater treatment technology because it does not require an external power supply for wastewater treatment (WWT). It uses exoelectrogens to convert the organic matter in wastewater to electricity, domestic wastewater contains 2–5 kWh/m^3 of energy [2]. In addition, mMFCs can be used in a variety of WWT applications because their biofilm contains not only electroactive microorganisms but also non-electroactive microorganisms such as fermentative, sulfate-reducing, nitrate-reducing, denitrifying, and aerobic microorganisms that can be used for a variety of functions ranging from the breakdown of complex organics to fermentation [3]. Microbial electrolysis cell (MEC) is a modification of MFC which when operated under anaerobic conditions treats industrial wastewater and produces biohydrogen which is an excellent green fuel.

In addition to producing bioelectricity and value-added products from microalgal biomass, microbial fuel cells based on microalgae are effective systems for removing CO_2, nitrogen, and phosphorus from wastewater. These mMFCs have been demonstrated to be effective for the removal of N and P through symbiotic relationship between microalgae and bacteria in wastewater treatment together with power generation. Since mechanical aeration would otherwise require power, the oxygen produced by microalgae during the day eliminates the need for mechanical aerators [4]. MEC systems need external power at an electrical potential that is substantially lower than the theoretical one utilized in water electrolysis to create hydrogen. A conventional power source, photovoltaics, wind power, thermoelectric generators, or MFCs are all potential options for this external power source [5].

In this study, the basic purpose of mMFCs was to perform secondary and tertiary wastewater treatment as well as producing electricity [4]. The secondary wastewater treatment was done in the anodic compartment that contained sludge while the tertiary treatment was performed in the cathodic compartment containing microalgae. A detailed comparison of batch mode mMFC and continuous flow mMFC was also performed in this study. On the other hand, the main objective of MEC was to consume the electricity provided by the mMFCs to produce hydrogen using microbial phenomenon. The MEC also helped in treating industrial wastewater, since high strength wastewater containing large amounts of COD is required for the synthesis of hydrogen [6].

2. Materials and Methods

2.1. Construction of mMFC and MEC

For mMFC, a two-compartment H shaped prototype made of acrylic sheet was used. Graphite rods, abraded by sandpaper to increase the surface area, were used as electrodes. Cation exchange membrane (CMI-7000s) which was soaked in a 5% NaCl solution for 12 h prior to its use was used as a separator. The working volume of mMFC was 1700 mL while total volume was 2000 mL. The anodes and cathodes were connected to complete the circuit with low resistance white copper wires. A stirrer was used to keep the algae in suspension and LED bulbs were used to provide light for growth of algae. A peristaltic pump was also used to provide a continuous flow to the continuous flow mMFC.

For MEC, a 1000 mL stock bottle was used with similar graphite electrodes as mMFC. The working volume was 900 mL and the total volume was 1000 mL. Gas syringe and pipes were used for collection of hydrogen.

2.2. Inoculum and substrate for mMFC and MEC

mMFC: 30% activated sludge, obtained from I-9 wastewater treatment plant, Islamabad was used to perform secondary treatment of domestic wastewater in the anodic compartment. In the cathodic compartment microalgae (*Scenedesmus* sp*)* was used to perform tertiary treatment of domestic wastewater and as a photosynthetic electrolyte. Primary treated domestic wastewater from membrane bio reactor (MBR) plant of National University of Sciences and Technology (NUST) was used in the anodic compartment while wetland treated wastewater was used in cathodic compartment.

MEC: 20% anaerobic sludge was mixed with 5% cow dung to treat synthetic food industrial wastewater with an initial COD value of 10,000 mg/L.

The obtained sludge was acclimatized to anaerobic conditions before using in both mMFC and MEC.

2.3. Operation of mMFC and MEC

mMFC: One mMFC was run in continuous flow mode (MFC-C) and two in batch mode (MFC-B). The mMFC was operated at a lab scale at ambient temperature. In anodic compartment a pH of 7 was maintained while a pH of 7.5 was maintained the in cathodic compartment. The HRT was 24 h for both MFC-B and for MFC-C.

MEC: MEC was also operated at a lab scale at ambient temperature in batch mode. The HRT was 10 days and a pH of 4.5–5.5 was maintained to suppress the growth of methanogens. The MEC was sparged with N_2 gas prior to the start of each batch to ensure there was no oxygen present to combine with the produced hydrogen.

The mMFC were linked in series with the copper wires to get the combined voltage to be supplied to the MEC. A combined voltage of 1.8–1.9 V of all the three mMFCs was provided to the MEC.

2.4. Analysis and Calculations

The closed reflux titrimetric method was used to obtain the values of COD. pH was measured by using a Hach multimeter (Model-156). The values of orthophosphate and ammonium nitrogen were obtained using the ascorbic acid method and salicylate method respectively [7]. The water samples from both the compartments of mMFC were obtained via valves positioned at the center of the respective compartments. The water was stirred to ensure proper mixing prior to obtaining samples. A digital multimeter was used to obtain values of open circuit voltage while a datalogger (Picolog 6) was used to continuously obtain value of voltages in a closed circuit when a resistor of 470 Ω was used. The polarization curves were obtained by varying resistances ranging from 1 MΩ to 1 Ω. Voltages corresponding to these resistances were obtained and current was calculated for each value using Ohm's law. Current density was found by dividing the value of current by the surface area of the anode which was 0.0024 m^2. Power and power density was calculated using the formulas in equation (1) and (2) respectively. For algae growth a UV visible spectrophotometer (PG Model T6OU, PG Instruments, UK) was used to measure optical density (OD) at 680 nm [7]. The Columbic efficiency was found using the formula reported in [8].

$$P = VI \tag{1}$$

$$P = \frac{VI}{A} \tag{2}$$

where, V—Voltage drop across each resistor, I—corresponding current, A—surface area of anode.

3. Results and Discussions

3.1. Sludge and Wastewater Characteristics

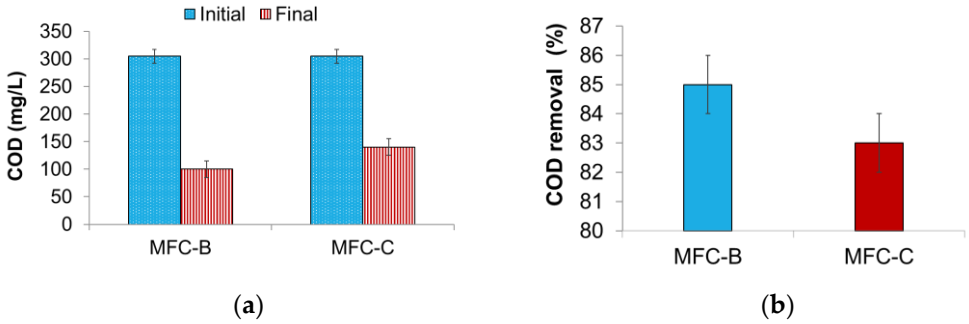
The sludge had a pH of 6.5–7, Total solids (TS) 15–25%, Volatile Solids 30–35% (of TS), moisture content (MC) 75–85%, Oxidation Reduction Potential (ORP) −360 to −380 mV, TKN 1800–2500 mg/L. The primary treated domestic wastewater used in mMFCs had an initial COD value of 240 mg O_2/L (varied each day), ortho phosphate 18.5 mg/L, turbidity 136 NTU, conductivity 1636 μs/cm, pH 7.3, TSS 20 mg/L, TDS 780 mg/L, ammonia nitrogen 50 mg/L, nitrate nitrogen 11.4 mg/L, nitrite nitrogen 1.6 mg/L, organic nitrogen 20.16 mg/L.

3.2. Results of mMFC

The maximum open circuit voltage (OCV) was 784 mV in MFC-B while the maximum OCV was 723 mV in MFC-C.

As shown in Figure 1a, the COD decreased in the anodic chamber of both MFC-B and MFC-C. The initial COD was 305 mg/L for both MFC-B and MFC-C. The final COD for batch mode was 100 mg/L, the removal efficiency was thus 67.2%. In case of continuous flow mode, the final COD was 140 mg/L, the removal efficiency thus was 54%. There was a difference of 13.2% in the removal efficiency. The possible reason for high COD removal in batch mode was that there was more time available for the microorganisms to consume the already existing COD, while in continuous flow mode new COD was being pumped in the reactor continuously. Another similar study quotes their COD removal efficiency

to be in the similar range of 50 to 65% [8]. Figure 1b shows the COD removal in cathodic chamber. The removal from cathodic chamber in MFC-B was 85% while in MFC-C it was 83%.



(**a**) (**b**)

Figure 1. (**a**): COD removal from anodic chamber. (**b**): COD removal from cathodic chamber.

Columbic efficiency basically tells us the amount of COD removed that was utilized into electricity. As shown in Figure 2, in batch mode the COD removal was 67.2% while the columbic efficiency (CE) was around 5.8%. In continuous flow mode the COD removal was 54% while the columbic efficiency was around 7.7%. A difference of 1.9% was noted and MFC-C had more columbic efficiency despite having less removal efficiency. It is worth noting that the values of CE is quite low in comparison to the values of COD removal for both systems which indicates that a significant amount of electrons were lost.

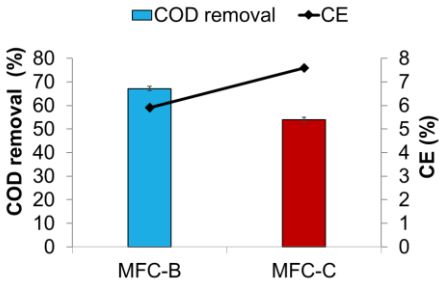
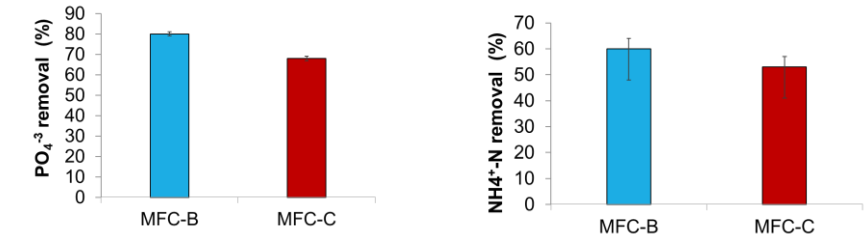


Figure 2. Columbic Efficiency in MFC-B and MFC-C.

Figure 3a shows that the orthophosphate removal of MFC-B was 80% while for MFC-C it was 68%. MFC-B was able to achieve a 12% high orthophosphate removal as compared to MFC-C. Figure 3b shows that ammonium nitrogen removal percentage of 60% was achieved in batch mode and in continuous flow mode it was around 57%.



(**a**) (**b**)

Figure 3. (**a**): Orthophosphate removal in cathodic chamber. (**b**): Ammonium-N Removal in cathodic chamber.

In Figure 4, an increasing trend can be seen in algal growth. The dotted line shows algal growth in MFC-B and the solid line show algal growth in MFC-C. There was a similar trend in both mMFCs with both starting at around 4900 mg/L and growing to about 5700 mg/L in a span of four days.

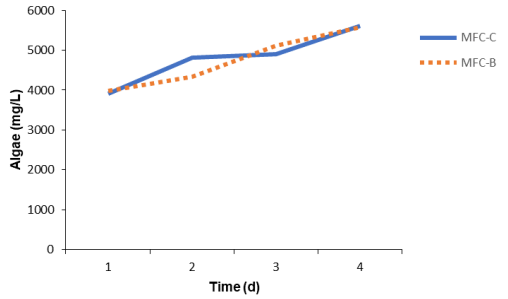


Figure 4. Algal growth in cathodic chamber.

Figure 5 shows the polarization and power curves for MFC-B and MFC-C. The maximum current density was 375 mA/m² in MFC-C and 272.2 mA/m² in MFC-B. The maximum power density was 42 mW/m² in MFC-C and 25.9 mW/m² in MFC-B. The internal resistance was found by calculating the slopes of the polarization curves which was calculated to be 867.875 Ω in MFC-C and 847.250 Ω in MFC-B. In continuous mode although the internal resistance is more than the batch mode, but the values of power density and current density are greater as well. This may be due to the microbial configuration of the continuous flow mode sludge, it may be possible that the number of current producing bacteria is greater in continuous flow mode than in batch mode.

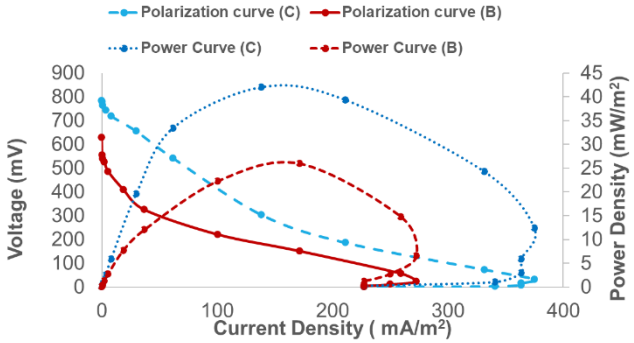


Figure 5. Polarization and Power Curves.

As shown in Figure 6, The voltage of the continuous flow mode is greater than the batch mode. In the batch mode graph, there are dips in the values of voltage after every 24 h indicating that batch has ended and most of the COD has been consumed. Also, in the batch mode maximum value is seen to be achieved in the middle of the batch and the value steadily decreases towards the end of the batch after every 24 h. The continuous flow mode graph is relatively steady because of the continuous feed that is being provided thus COD is always available to the microorganisms and voltage is constantly being produced.

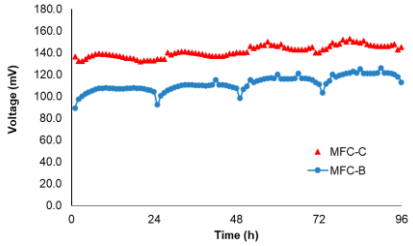


Figure 6. Voltage vs. time graph of MFC-B and MFC-C with a resistor of 470 Ω.

3.3. Results of MEC

Figure 7 shows a decrease in the value of COD of wastewater in MEC. The initial COD of the wastewater was 10,000 mg/L and after running a batch of 10 days the value had decreased to 2700 mg/L indicating a removal efficiency of 73%. The voltage provided by the mMFCs initiates a forceful current and is utilized to reduce the protons into hydrogen [6]. The average hydrogen production rate at the same time was 9.8 ± 0.2 mL L^{-1} d^{-1}.

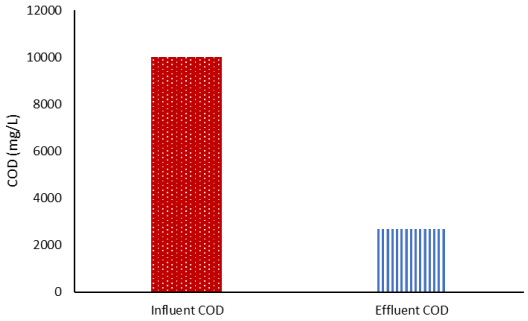


Figure 7. COD Removal in MEC.

4. Conclusions

In this work three mMFCs, each of 1.7 L working volume, were run, and compared in batch mode and continuous flow mode. The system could be applied for both secondary and tertiary treatment as depicted by the results. The secondary treatment was performed as the organics were removed; tertiary treatment was performed as nutrients removal was achieved using algae. The COD removal was greater in MFC-B, but MFC-C had a greater columbic efficiency. OCV was similar in both the systems. But in a closed circuit MFC-C had a greater voltage output. The combined voltage was enough to power up the MEC and results shows that the voltage supplied overcame its potential barrier and thus the hydrogen was produced along with the treatment of wastewater.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ritchie, H. Max Roser and Pablo Rosado—"Energy". 2022. Available online: https://ourworldindata.org/energy (accessed on).
2. Yu, J.; Cho, S.; Kim, S.; Cho, H.; Lee, T. Comparison of Exoelectrogenic Bacteria Detected Using Two Different Methods: U-tube Microbial Fuel Cell and Plating Method. *Microbes Environ.* **2012**, *27*, 49–53.
3. Logan, B.E.; Hamelers, B.; Rozendal, R.; Schröder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K. Microbial Fuel Cells: Methodology and Technology. *Environ. Sci. Technol.* **2006**, *40*, 5181–5192.
4. Arun, S.; Sinharoy, A.; Pakshirajan, K.; Lens, P.N. Algae based microbial fuel cells for wastewater treatment and recovery of value-added products. *Renew. Sustain. Energy Rev.* **2020**, *132*, 110041.
5. Aboelela, D.; Soliman, M.A. Hydrogen production from microbial electrolysis cells powered with microbial fuel cells. *J. King Saud Univ. Eng. Sci.* **2022**.

6. Sun, M.; Sheng, G.-P.; Zhang, L.; Xia, C.; Mu, Z.-X.; Liu, X.-W.; Wang, H.-L.; Yu, H.-Q.; Qi, R.; Yu, T.; et al. An MEC-MFC-Coupled System for Biohydrogen Production from Acetate. *Environ. Sci. Technol.* **2008**, *42*, 8095–8100.
7. Saleem, S.; Zeshan; Iftikhar, R.; Zafar, M.I.; Sohail, N.F. Growth kinetics of microalgae cultivated in different dilutions of fresh leachate for sustainable nutrient recovery and carbon fixation. *Biochem. Eng. J.* **2022**, *178*, 108299.
8. Ullah, Z.; Zeshan, S. Effect of substrate type and concentration on the performance of a double chamber microbial fuel cell. *Water Sci. Technol.* **2019**, *81*, 1336–1344. https://doi.org/10.2166/wst.2019.387.