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Performance Study of Double Chamber Microbial Fuel Cell Operating with Dihydrogen Phyllosilicate Clay and Activated Carbon from Coconut Shells as Proton Exchange Membrane

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Bioelectrochemical system is one of the promising tools under the waste-energy nexus, a chief key in reducing the detrimental impact of global warming and wastewater problem. The upscale of microbial fuel cell (MFC) technology is hindered by the high cost of proton exchange membranes (PEM). In this study, a lower cost material than the commonly used Nafion membrane was investigated. Mixtures of activated carbon from coconut shells, ACCS, was incorporated in the *Manihot* starch- kaolin-clay composite as PEM. The ACCS/Clay membrane was characterized based on its swelling degree and proton transfer. Results showed that 2 % ACCS/Clay mixture has the lowest swelling degree and highest amount of proton transfer. The performance of the double chamber yeast-microalgal MFC is evaluated based on its operating voltage produced and % COD reduction within the 240-hour period. The MFC exhibited a maximum voltage of 0.339 V while obtaining an average % COD reduction of 51.27 %. Promising results were obtained in the upscale of this technology as this was around 3 times higher than the voltage generated by commercialized Nafion membranes.

1. Introduction

Microbial fuel cell (MFC) is a technology that associates the benefits of wastewater treatment and electricity generation (Chin et al., 2021). It offers a diverse solution to two of the greatest environmental concerns the world is facing: global warming brought about by fossil fuel energy generation and the alarming water pollution. In MFC, organic wastes found in waste water are converted into electricity. Anodophilic microorganisms which are attached to an anode decompose organic matter in wastewater into carbon dioxide, protons and electrons which are then transferred to a cathode. An electric current is generated due to the potential difference between the two electrodes. (Aboelela et al., 2020). The anode and the cathode are separated by a proton exchange membrane (PEM) which facilitates the proton transfer from anode to cathode while preventing diffusion of electron acceptor. Membrane materials to be selected must be conducive to proton transfer, low cost, and able to resist microbial migration. Membranes commonly used are perfluorinated polymers containing sulfonic acid groups on side chains. Nafion membranes have been the most predominantly used PEM in MFCs owing to its high proton conductivity (Neethu et al., 2018). The problem arises on the high cost of these membranes. Aside from its high cost, a higher oxygen diffusion, sulphide poisoning and substrate crossover do not make it an ideal material to be used for scaling up of MFC (Bhowmick et al., 2018). Its relatively high cost-to-power ratio has necessitated the yearning for a cheaper alternative. Among several membranes, ceramic and clay-based membranes have exhibited superior properties like good chemical, mechanical, and thermal stability, minimal cost, and availability over the polymer-based membrane (Yousefi et al., 2017). To enhance the characteristics of the ceramics membrane, some modifications are employed. *Manihot* starch kaolinite clay composite was developed and showed optimum results as PEM in the dual MFC by a study conducted by Obasi et al. (2012). Heating the kaolinite clay with its properties modified by *Manihot* starch showed higher cell performance, stability and durability. Activated carbon made from coconut shell, ACCS, has started its way in the MFC application. Activated carbon incorporated on the Nafion membrane gives dramatic enhancement in ionic conductivity at a

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minimal dimensional swelling (Chien et al., 2011). Neethu et al. (2019) developed a casted ACCS/Clay PEM which showed higher proton diffusion coefficient (36 x 10^6 cm^2/s) as compared with Nafion 117 membrane (4.64 x 10^6 cm^2/s). The superior specific surface area of activated carbon contributes to water retention for proton hopping, enhancing the proton transfer. ACCS-Clay PEM has an advantage of high density, high purity, virtually dust-free nature, harder structure and more resistant to attrition since the price of a one kg of activated carbon derived from coconut shell is approximately 1.97 USD/m^2 as compared to the high cost of Nafion membrane of 2,229 USD/m^2 (Neethu et al., 2019). This study evaluates the performance of ACCS/Clay with *Manihot* starch as PEM in the double chamber MFC.

2. Materials and Methods

2.1 Materials

Ceramic membrane was prepared from kaolin clay, 10 % v/v HNO_3 (Asteria Apothecary, Quezon City Phils), cassava starch (Signal, Calamba, Phils), sodium alginate (DKL Lab, Manila Phils) and activated carbon from coconut shells (ACSS), (Kemrad Incorporated, Quezon City, Phils.). Anolyte chamber was filled with NaCl, NaOH, deionized water (Yana Chemodities, Quezon City, Phils), dry yeast (Ferna Corp, Navotas City, Phils) and buffer solution (Nicolie Enterprises, Los Banos, Phils). *Chlorella sorokiniana* (SEAFDEC AQD, Iloilo City, Phils) was used as the microalgal catholyte. PET jars were used as anode and cathode chambers connected by 5.25 cm x 32 mm PVC pipe. The cathode chamber is equipped with air pump (YL, Beijing, China). Carbon electrodes, 30 cm x 30 cm, were obtained from Zibho Ouzheng Carbon Co Ltd, Northeast China.

2.2 Fabrication of Proton Exchange Membrane

The kaolinite clay was heated at 300 °C for 2 h, to transform the kaolin to meta-kaolinite to improve its performance as PEM (Obasi et al., 2012). Binding ability is provided by activated sodium alginate reinforced with *Mahinot* starch. Activation of sodium alginate was done by adding 70 % isopropyl alcohol to 12 mL of water mixed with 0.33 g of sodium alginate while constantly stirring using magnetic stirrer until a homogenized mixture is formed. PEM was fabricated by mixing the heated kaolinite clay, activated sodium alginate, *Mahinot* starch, NaCl, and ACCS. Four samples of ACCS/Clay membrane with varying amounts of activated carbon were fabricated as shown in Table 1.

Table 1: ACCS/Clay Membrane Composition

Membrane Composition	1 % ACCS	2 % ACCS	5 % ACCS	10 % ACCS
Kaolin Clay, g	10	10	10	10
Mahinot starch, g	6	6	6	6
ACCS, g	0.1	0.2	0.5	1.0

The components were mixed , kneaded until clay-like texture then molded into a circular form of 32 sq mm with a thickness of 4 mm. The ACCS/Clay membrane was air-dried for 3 d at room temperature prior to sintering process. Sintering temperature was setup at 300 °C for 2 h to ensure that the pore former starch would be burned off, before charging the membranes inside the pipe. Thermal sintering of kaolin clay changes its properties to obtain mullite ceramics with improved hydrophobicity, density, low apparent porosity, good optical properties, and electrical properties (Chandrasekhar et al., 2002).

2.3 Fabrication of Fuel Cell

A set of two 500 mL PET bottles served as the anode and cathode chamber connected by 5.25 cm length PVC pipe. The membrane was placed inside the pipe dividing the two chambers, Figure 1 (Hadiyanto et. al., 2022). The aeration in the cathode chamber would promote a cumulative biomass cultivation of *Chlorella sorokiniana*. The simulated wastewater contained 0.7 mg/mL of active dried *Saccharomyces cerevisiae* in yeast extract, 2.5 mg/mL of yeast nutrient, and 5 mg/mL of 0.1 MPBS buffer solution with pH of 7.4. The anode solution was rotated at approximately 250 rpm for 48 h and diluted by adding 250 mL of deionized water before feeding at the anode chamber. Carbon electrodes were immersed in nitric acid for 2 h , washed and air dried for 48 h. A multimeter is connected to the electrodes to record the voltage output.

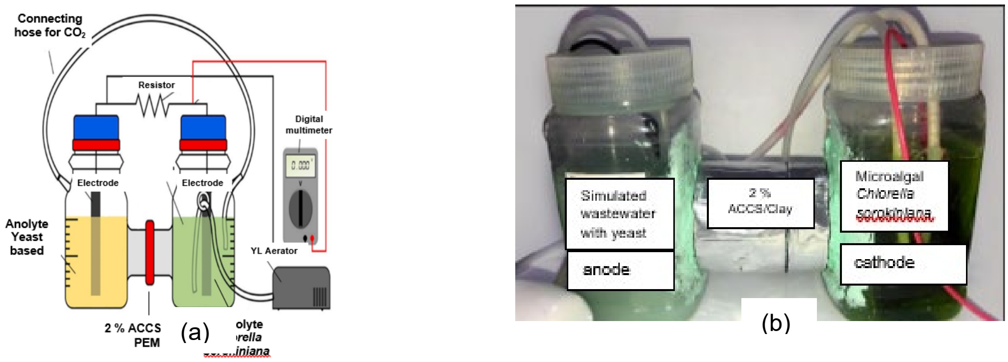

Figure 1: MFC Set-up: (a) Schematic diagram (Hadiyanto et. al., 2022) (b) Actual set-up

2.4 Data Treatment for Membrane Characterization

2.4.1 Swelling Degree

Dried ACCS/Clay membrane was immersed in water in a sealed vessel at room temperature for 1 h to observe its swelling degree. Then, the membrane was quickly removed from the water, wiped with tissue paper, then swelling was measured by comparing the weight of the membranes before, M_o and after immersion in water, M, (Truong et al, 2018). The swelling degree of the membrane is calculated using Eq(1).

$$SD\ (\%) = \frac{M - M_o}{M_o} \times 100\ \% \qquad (1)$$

2.4.2 Proton Transfer

The proton concentration transferred were calculated from similar tests using the double chamber MFC filled with DI water (pH, ~7, recorded for c1.0 calculation). NaOH solution was then added into the anode chamber to adjust the pH of anolyte to ~10.5, and the pH in anode chamber was continuously monitored using a pH meter. The proton concentration, $[H^+]$ was calculated using Eq(2).

$$[H^+] = 10^{-pH} \qquad (2)$$

2.5 Data Treatment for Performance Evaluation

The performance of the double chamber MFC was based on the maximum voltage produced by the ACCS/Clay membrane that has the lowest swelling degree and the highest proton transfer. The evaluation was performed in three trials with three replicates. The reduction of the water contaminants in the anode chamber was measured initially, COD_i, and was compared with the COD anode solution after 240 h, COD_f. The COD reduction was calculated using Eq(3).

$$\%\ COD = \frac{COD_i - COD_f}{COD_i} \times 100\% \qquad (3)$$

3. Results and Discussions

3.1 Swelling Degree

The swelling degree acquired after membranes were immersed for 1 h were 8.98 %, 2.79 %, 17.52 %, and 28.98 % for 1 %, 2 %, 5 % and 10 % ACCS/Clay, respectively as presented in Figure 2. Kaolin as a polar compound containing hydroxyl (-OH) groups tends to increase the swelling with its high-water retention ability. Also, the addition of activated carbon which is a highly porous adsorptive medium adds up to the amount of water captured by each membrane. High water content is desirable for easy proton transport. But there is a risk in membrane mechanical stability. This indicates that the lower the swelling degree of the membrane, the more advantageous it is in MFC applications since mechanical stability offers the same degree of factor to consider in order to act as separator in the proton exchange.

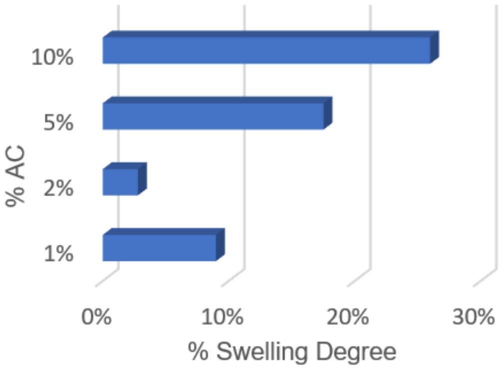

Figure 2: Swelling degree analysis of ACCS-Kaolin clay with different % AC composition

3.2 Proton Transfer

In this study, the proton transfer was calculated by getting the difference in the proton concentration as in Table 2. Among the four AC clay membranes, 2 % ACCS/Clay has the highest performance in terms proton transfer.

Table 2: Proton Transfer of the ACCS/Clay Membranes

% ACCS	Time, min	Average pH	$[H^+]$, x 10^{-11}	Difference in $[H^+]$
1 %	2	10.63	2.34	0.35
	120	10.57	2.69	
2 %	2	10.48	13.8	10.49
	120	9.86	3.24	
5 %	2	10.49	3.24	2.79
	120	10.22	6.03	
10 %	2	10.66	2.19	1.12
	120	10.48	3.31	

Normally, the addition of inorganic materials such as activated carbon would provide a magnitude improvement in the ionic conductivity of the membrane. The data indicate that 5 % activated carbon and above would decrease its proton transfer since kaolin clay has a threshold amount of activated carbon it can hold that would facilitate a high proton transfer. According to Neethu et al. (2019) increasing the amount of inorganic material incorporated on the ceramic membrane would decrease the proton transfer as excessive amount would hinder the vehicular mechanism to proceed.

3.3 Voltage Output

The performance of the three MFCs operating using 2 %ACCS/Clay membrane were evaluated. In the span of 240 h of operation, the maximum voltage generated is obtained at 0.339 V as presented in Figure 3.

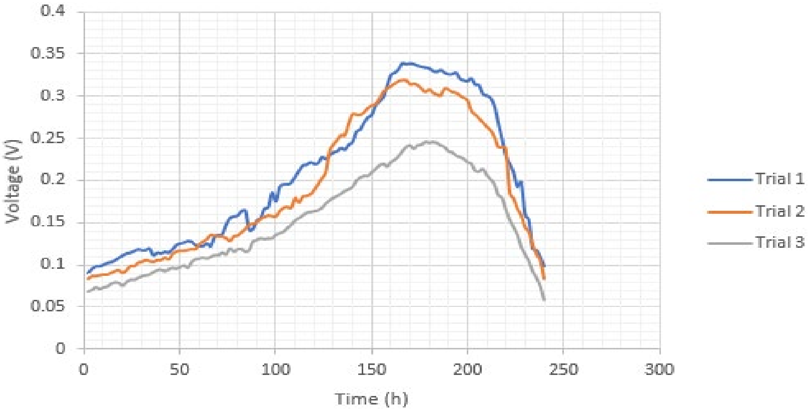

Figure 3: Voltage Output Measurement of 2 % ACCS/ Clay membrane

This value is slightly higher than the study of Neethu et al. (2019) which exhibited a maximum operating voltage of 0.290 V, significantly higher also on MFC empowered by Nafion Membrane (0.187 V) (see Table 3). A sharp decline in the voltage produced is observed after the maximum operating voltage was generated. This is due to the fact that the yeast population reached a concentration enough for forming the anodic biofilm to achieve a steady state voltage. The large decline of the voltage after its maximum peak is supported by the study of Winfield et al. (2010) that shows the impact on the internal resistance of the cell.

Table 3: Performance Comparison of ACCS/Clay with Nafion PEM

	Maximum Voltage Output, mV	References
2 % ACCS/Clay with *Mahinot starch*	339	This study
2 % ACCS/Clay	290	Neethu et. al. (2019)
Nafion 117	187	Neethu et. al. (2019)

3.4 COD Reduction

Chemical oxygen demand (COD) is the indicative measure of oxygen consumption in respect to the decomposition of organic matter and the oxidation of inorganic chemicals. In an anaerobic configuration, bacteria in the anode chamber convert organic compounds into biogas in an oxygen-free environment. Aerobic COD removal breaks down organic compounds present in the influent into carbon dioxide and water through microalgal or bacterial activities. Table 4 shows the COD reduction of the anode chamber before and after subjecting in the fuel cell. A maximum % COD reduction of 51.27 % was achieved and the trials were statistically tested for significant difference using one-way ANOVA presented in Table 5 concluding that there is significant difference among the means of each trial. The aeration of the biocathode contributed to the increased DO concentration accompanied with heterotrophic bacterial activity in the anode chamber which leads to improved COD reduction. A larger surface area of treated anode electrode with nitric acid allowed better attachment of electrochemically active bacteria onto the electrode surface. This promoted growth of microbes which performed the breakdown of organic materials and nutrients, therefore increasing COD reduction

Table 4: Percentage COD reduction

Run	Sample	Initial COD, mg/L	Final COD, mg/L	COD Difference	% COD Reduction
Trial 1	R1	7943.56	3962.51	3981.05	50.11
	R2	7845.65	3915.37	3930.28	50.10
	R3	7945.13	3974.27	3970.86	49.48
Trial 2	R1	7931.18	3887.20	4043.98	50.99
	R2	7845.40	3910.61	3934.79	50.15
	R3	7944.88	3872.49	4072.39	50.26
Trial 3	R1	7960.18	3920.06	4040.12	50.75
	R2	7874.40	3860.57	4013.83	50.97
	R3	7973.15	3884.99	4088.16	51.27

Table 5: ANOVA: One Way Analysis of % COD Reduction

Source of Variation	SS	df	MS	F stat	F critical	P-value
Between Groups	1.804689	2	0.902344	6.619203	5.143253	0.030335
Within Groups	0.817933	6				
Total	2.622622	8				

4. Conclusion

As presented in this study, ACCS/Clay reinforced with *Manihot* starch shows a potential PEM in the fabrication of MFC. The 2 % ACCS/Clay mixture shows the most ideal composition obtaining 2.79 % swelling degree and [10.49 x 10^{-11}] proton transfer as measured by the pH change after 240 min of operation. Maximum voltage output was generated at 0.339 V and % COD reduction of 51.27 % was obtained. Further investigations can be done to test the mechanical and morphological structure of the membrane.

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References

Aboelela D., Soliman M.A., Ashour I., 2020, A reduced model for microbial fuel cell, Chemical Engineering Transactions, 79, 43

Bhowmick G.D., Noori M.T., Das I., Neethu B., Ghangrekar M.M., Mitra A., 2018, Bismuth doped TiO_2 as an excellent photocathode catalyst to enhance the performance of microbial fuel cell, International Journal of Hydrogen Energy, 43, 7501 - 7510

Chakraborty I., Das S., Dubey B., Ghangrekar M.M., 2019, Novel low-cost proton exchange membrane made from sulphonated biochar for application in microbial fuel cells, Materials Chemistry and Physics, 239, 122025.

Chandrasekhar K., Mohan S.V, 2014, Bio-electrohydrolysis as a pretreatment strategy to catabolize complex food waste in closed circuitry: Function of electron flux to enhance acidogenic biohydrogen production, International Journal of Hydrogen Energy, 39, 11411 – 11422.

Chin M.Y., Phuang Z.X., Hanafiah M.M., Zhang Z., Woon K.S., 2021, Exploring the life cycle environmental performance of different microbial fuel cell configurations, Chemical Engineering Transactions, 89, 175

Chien H.C., Tsai L.D., Kelarakis A., Lai C.M., Lin J.N., Fang J., Zhu C.Y., Chang F.C., 2011, Highly hydrated nafion/ activated carbon hybrids, Polymer, 53, 22, 4927 – 4930.

Das I., Das S., Dixit R., Ghangrekar M.M., 2020, Geothite supplemented natural clay ceramic as an alternative proton exchange membrane and its application in microbial fuel cell, Ionics, 26, 3061 – 3072.

Dharmalingam S., Kugarajah V., Sugumar M., 2019, Membranes for microbial fuel cells. In Biomass, Biofuels and Biochemicals, Microbial Electrochemical Technology, Elsevier, 143 – 194.

Hadiyanto H., Christwardana M., Prawiti W.Z., Purwanto P., Sudarno S., Haryani K., Hoang A.T., 2022, Response surface optimization of microalgae microbial fuel cell (MMFC) enhanced by yeast immobilization for bioelectricity production, Chemosphere, 287: 3, 132275.

Neethu B., Bhowmick G.D., Ghangrekar M.M., 2018, Enhancement of bioelectricity generation and algal productivity in microbial carbon-capture cell using low cost coconut shell as membrane separator, Biochemical Engineering Journal, 133, 205 – 213.

Neethu B., Bhowmick G.D., Ghangrekar M.M., 2019, A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell, Biochemical Engineering Journal, 148, 170 - 177

Obada O.D, Doodo-Arhin D., Dauda M., Anafi F., Ahmed A., Ajayi O., 2017, The impact of kaolin dehydroxylation on the porosity and mechanical integrity of kaolin based ceramics using different pore formers, Result in Physics, 7, 2718 – 2727.,

Obasi L., Opara C., Oji A., 2012, Performance of cassava starch as a proton exchange membrane in a dual chambered microbial fuel cell, International Journal of Engineering Science and Technology, 4, 1

Suransh J., Tiwari A.K., Mungray A.K., 2020, Modification of clayware ceramic membrane for enhancing the performance of microbial fuel cell, Environmental Progress & Sustainable Energy, 39, 13427.

Truong T.C.T., Bui M.H., Nguyen A.K., Kobayashi T., 2018, Fabrication and characterization of chitosan/coconut fiber composite membranes for elimination Cu^{2+} and Pb^{2+} from aqueous solutions, Architecture, Civil Engineering Environment, 12:1, 163 – 169.

Winfield J., Greenman J., Huson D., Leporoulous I., 2013, Comparing terracotta and earthenware for multiple functionalities in microbial fuel cells, Bioprocess and Biosystems Engineering, 36:12, 1913 – 1921.

Yousefi V., Mohebbi-Kalhori D., Samimi A., 2017, Ceramic-based microbial fuel cells (MFCs): A review, International Journal of Hydrogen Energy, 42, 1672–1690.