Pin nhiên liệu vi sinh sử dụng màng trao đổi Poly (vinyl alcohol) liên kết chéo ứng dụng xử lý nước thải bệnh viện

Đinh Kha Lil[1,*], Imee A. Saladag[2]

[1]Khoa Khoa học Tự nhiên, Trường Đại học Cần Thơ, Việt Nam
[2]Khoa Công nghệ, Đại học bang Eastern Visayas, Phi-líp-pin

TÓM TẮT

Bộ phận phân tách giữa cực dương và cực âm là một phần thiết yếu trong pin nhiên liệu vi sinh vật (Microbial fuel cells - MFCs) và nó ảnh hưởng đáng kể đến hiệu suất của hệ thống. Các loại màng được sử dụng hiện nay đa phần có giá thành cao là khó khăn lớn làm cho công nghệ MFC chưa được đưa vào ứng dụng thực tiễn. Trong nghiên cứu này tập trung vào việc sản xuất điện bằng cách sử dụng pin nhiên liệu vi sinh hai buồng sử dụng nước thải bệnh viện kết hợp sử dụng màng poly(vinyl alcohol) (PVA) liên kết chéo với glutaraldehyde (GA) với giá thành thấp. Mật độ công suất cao nhất 209,85 mW.m^{-2} và điện áp tối đa tạo ra là 652,75 mV khi sử dụng màng trao đổi 5% PVA. Các phát hiện chứng minh những ưu điểm của việc sử dụng thiết kế MFC dựa trên màng trao đổi thay thế Nafion chế độ tĩnh để xử lý nước thải bệnh viện là tiết kiệm chi phí vận hành, sản lượng điện cao. Các màng PVA liên kết chéo có thể là một giải pháp thay thế đầy hứa hẹn cho các vật liệu phân tách để xây dựng các hệ thống MFC thực tế.

Từ khóa: Pin nhiên liệu vi sinh, màng polyvinyl alcohol (PVA) liên kết chéo, xử lý nước thải, nước thải bệnh viện.

*Tác giả liên hệ chính.
Email: lildk93@gmail.com

Microbial Fuel Cells using crosslinked Poly (vinyl alcohol) membrane separator for hospital wastewater treatment

Kha Lil Dinh[1],*, Imee A. Saladag[2]

[1]*College of Natural Sciences, Can Tho University, Vietnam*
[2]*College of Engineering, Eastern Visayas State University, Philippines*

ABSTRACT

The anode and cathode separator is an essential part of microbial fuel cells (MFCs) and it significantly affects the system performance. Most of the membranes used today have a high cost, which is a big difficulty, making MFC technology not yet put into practice. The present study is focused on the production of electricity using double chambered microbial fuel cells (MFCs) to treat hospital wastewater treatment combined with poly (vinyl alcohol) (PVA) membrane cross-linked with glutaraldehyde (GA) with low cost. The highest power density of 209.85 mW.m^{-2} and the maximum voltage generated of 652.75 mV occur when using 5% PVA membrane. The findings demonstrate that the main advantages of using static mode Nafion alternative membrane based MFC configurations for hospital wastewater treatment are savings on operational cost, high power output, negligible crossover, and higher treatment efficiency. The crosslinked PVA membranes can be a promising alternative to separation materials for building practical MFC systems.

Keywords: *Microbial Fuel Cells, crosslinked polyvinyl alcohol (PVA) membrane, wastewater treatment, hospital wastewater.*

1. INTRODUCTION

Conventional wastewater treatment is an energy intensive process, with aeration accounting for 50% of the operating cost for removal of organic compounds.[1] Wastewaters are a source of large amount of potential energy in the form of pollutants.[2] Besides, anaerobic treatment of wastewater also produces biogas but the energy recovery is discouraging. With escalating energy demands, the necessity for low-energy wastewater treatment has never been greater.[3] Microbial fuel cells are an emerging, sustainable technology which enables the recovery of energy out of wastewater with the aid of bacteria, while limiting both the energy input and the excess sludge production. The most promising application is the energy-efficient treatment of wastewater.[4]

The function of the membrane is to separate the reaction between the anode and the cathode in the MFC system while allowing the selective transport of protons from the anode to the cathode and preventing oxygen transport into the anode chamber. MFC is classified as membrane or membrane-less, membrane acts as a barrier between the anode and cathode electrodes. Although membrane-less MFCs help

reduce design costs, diffusion of oxygen from the cathode to the anode side occurs, resulting in low power generation efficiency.[5] An ideal separative membrane should prevent the transfer of the substrate and oxygen between the cathode chamber and the anode chamber while allowing protons to pass.[6] Major challenges in the realization of MFC for practical applications are in terms of material costs and energy recovery efficiency. The commonly used membrane type for MFCs is Nafion. This is a persistent material due to the presence of fluorine in the structure that is harmful to the environment and also accounts for 38% of the total capital cost in investing in an MFC system.[7]

Hospitals play an important role in the human health. Their activities require large amounts of water and generate large amounts of wastewater. In general, the characteristics of hospital wastewater (HWW) are similar to those of domestic wastewater, but a part of HWW includes drugs, organic substances, toxic metals, radioactive tracer. They also carry microorganisms such as viruses, bacteria, fungi, protozoa and helminths. There is increasing evidence that HWW treatment systems contribute to the spread of antimicrobial resistant bacteria into the environment.[8]

Following our previous report on crosslinked PVA membrane with GA as separator in domestic wastewater fed MFCs which exhibited high power density and Chemical oxygen demand (COD) removal with antibacterial property, thermo-mechanical stability and negligible fuel crossover. In this study, GA-linked biodegradable PVA was used as a low-cost in a dual-chamber MFC separator fed hospital wastewater that was evaluated for practical application. The microbiota in wastewater acts as a biological catalyst while wastewater is used as a substrate.

2. MATERIALS AND METHODS

2.1. Synthesis of PVA membranes

The membranes were synthesized using solution casting and solvent evaporation. After the synthesis, all films were stored at room temperature. The synthesis of each membrane is described below:

The neat PVA (nPVA) membrane: 2 g (95 wt.%) of PVA powder was added to 100 mL of deionized water to obtain a film of about 100 μm thick. The mixture was continuously stirred at 650 rpm at 85 °C. Then, 60 mL of homogeneous PVA solution was placed on Teflon plates and airdried at room temperature. The neat sample is, here onwards, called the nPVA membrane.[9]

5% PVA membrane: The steps for preparation of the membrane are followed as reported earlier.[9] To achieve a thickness of about 100 μm, the film was synthesized using 2 g (95 wt.%) of PVA dissolved in 100 mL deionized water with continuous stirring (650 rpm) at 85 °C (the temperature at which PVA readily dissolves in water). To crosslink the polymer, 5 wt.% GA was mixed drop by drop to the PVA solution and was stirred further for 15 min. Attached to its backbone, neat PVA consists of hydroxyl groups. The addition of the crosslinker causes the acetal linkages and aldehyde side chain formations. 5 wt.% GA was selected based on the % swelling in puffiness.[9]

2.2. Reactor design, setup, and operation

2.2.1. MFC setup and operation

The shape of double chamber H-cell membrane reactor for MFCs is illustrated in Figure 1. Three identical H-cell MFC were composed of two glass chambers with a volume of 250 mL each separated by a proton exchange membrane in between the two chambers. The anode and cathode are composed of graphite felts with dimensions of 5 cm × 5 cm with nPVA and 5% PVA membranes of size 3 cm in diameter in the experimental case. Another MFCs using Nafion-117, Dupont Co., USA (with similar size) was considered as the control case.

Meanwhile, the Nafion-117 membrane were treated in 5% H_2O_2 solution at 70 °C for 1 h,

repeatedly rinsed with deionized water (DI), and then treated in 0.5 M H_2SO_4 at 90 ºC for 1 h. These were rinsed repeatedly and stored in DI water for later use. Graphite felt electrodes were used as the cathode and anode. The electrodes were pretreated in 10% H_2O_2 solution for 3 h at 90 ºC followed by airdrying at ambient temperature for at least two days before use.
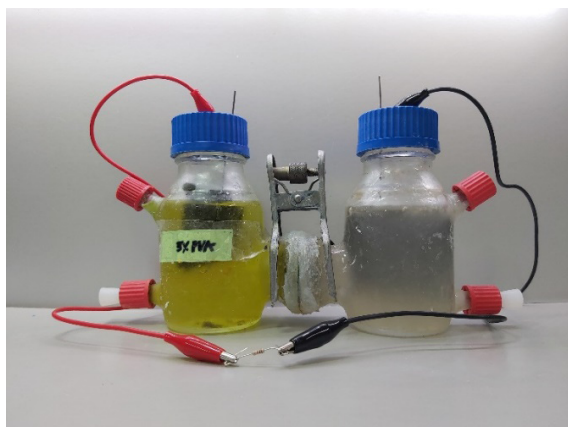

Figure 1. The schematic representation of the MFCs fed with hospital wastewater.

According to the Proton exchange membrane (PEM) applied, three MFCs were used in this study labelled as Nafion-117, nPVA and 5% PVA. All were operated batch-wise and tested at 25 °C. A steady voltage was achieved for at least three consecutive cycles before output measurements were performed.

2.2.2. Anode biofilm acclimation

A mixed culture of bacteria had the source of hospital wastewater, obtained from the National Yang Ming Chiao Tung University Hospital Xinmin Branch, Yilan City, Taiwan, used as anode inoculum. Mixture hospital wastewater containing mixed culture of bacteria and 50 mM phosphate buffer nutrient solution (1:1 ratio) as the inoculum in the anode chamber. Phosphate buffer nutrient solution (PBS) was composed of Na_2HPO_4, 9.16 g L^{-1}; $NaH_2PO_4 \cdot 2H_2O$, 5.56 g L^{-1}; NH_4Cl, 0.638 g L^{-1}; and KCl, 0.278 g L^{-1}. Sodium acetate (1 g) was added per liter of the solution as the electroactive bacteria (EAB) substrate.

During the EAB acclimation, a 1:1 solution of 100 mM $K_3[Fe(CN)_6]$ (32.924 g L^{-1}) and 100 mM PBS solution served as the catholyte. The anolyte and catholyte were replaced with new solutions when the voltage production declined to 10% of the maximum voltage produced, which indicates the end of each fed-batch cycle. A titanium wire was inserted in each electrode and then connected to a 1,000-Ω external resistance using copper wire to reduce the biofilms' acclimation time.[10] The MFCs were operated on for 3 months to obtain a robust bacterial biofilm.

2.3. Biofilm characterizations

After MFCs operations, electrode samples were microanalysis by scanning electron microscopy (SEM) (JEOL JSM-6500F, JEOL Ltd., Tokyo, Japan). To characterize the bacterial anode and structure biofilms.

2.4. Electrochemical measurements

MFCs voltage was measured every 2 h during the operations. Open circuit condition of the HMFCs was maintained for 4 h before polarization and electrochemical impedance spectroscopy (EIS) tests. Linear sweep voltammetry (LSV) was done three times at a scan rate of 10 mV s^{-1} starting from the measured open-circuit voltage (OCV) to zero. Data were acquired at 10 points per second using a multifunctional electrochemical analyzer (JIEHAN 5640, JIEHAN Technology Group, Taiwan).

The current was calculated from Ohm's Law, $I = V/R$, where I is the current (mA) and V is the output voltage (mV) through a resistance, R (Ω). Power (P, mW) was calculated from $P = V \times I$. Current density (I_D, mA.m^{-2}) and power density (P_D, mW.m^{-2}) were calculated using the total anode surface area (0.005 m^2).[11]

Electrochemical impedance spectroscopy (EIS) was carried out using HIOKY 3522-50 LCR Hi-TESTER (Japan) by applying a 10-mV AC signal within 100 kHz to 0.1 Hz frequency range. An equivalent circuit was used to fit the

EIS spectra and calculate internal resistance values in EC Lab software.[12]

3. RESULTS AND DISCUSSION

Crosslinking of PVA with GA improves the properties of the pristine PVA membrane making it suitable for real wastewater treatment which has been reported below. The continuous operation of the MFC condition with crosslinked membrane as separator is analyzed in the latter section.

3.1. Bioelectricity production in the double chambered MFC

Under the mode of fed-batch operation, the MFCs investigated took a period of 1 month to reach stable conditions. A gradual increase in voltage under an external load of 1000 Ω was observed. No significant lag in the voltage generation was observed during start-up which is indication of the microbial cell to anode adhesion efficiency. In order to inoculate the graphite electrode with mixed culture of bacteria present in HWW, three successive acclimation cycles were carried out with acetate as the carbon source.

The current and power density curves are shown in Figure 2. Among the three MFCs, the highest power density was achieved by Nafion-117 membrane MFC at 316.17 mW.m^{-2}. It also obtained the maximum voltage generated

of 736.83 mV. The 5% PVA membrane MFC followed with respective power current and maximum voltage generated: 209.85 mW.m^{-2} and 652.75 mV while nPVA membrane MFC achieved 116.46 mW.m^{-2} and 522.24 mV. The enhanced performance of the crosslinked membrane can be ascribed to the crosslinking and branching with GA as it successfully altered the undesirable properties of the nPVA membrane with enhanced stability in terms of chemical, thermal, and mechanical properties, and controlled water uptake and degree of swelling, which has been reported in the previous study by our research group.[13] It is known that the water uptake capacity with the optimum swelling ratio is desirable for the transport of protons across the polymeric membrane since it aids the proton transfer across the membrane in MFCs. However, higher water content with high swelling has a negative impact on its mechanical integrity. The nPVA being a straight-chain polymer, forms intramolecular and intermolecular hydrogen bonding with water. On crosslinking with GA, acetal ring linkage is formed with a reduction in available hydroxyl groups in PVA. The nPVA demonstrated water uptake up to 250%, which was reduced to 50% for the crosslinked membrane. Similarly, the swelling percentage reduced from 50% for the neat PVA membrane to 20% for the crosslinked membrane.[13]
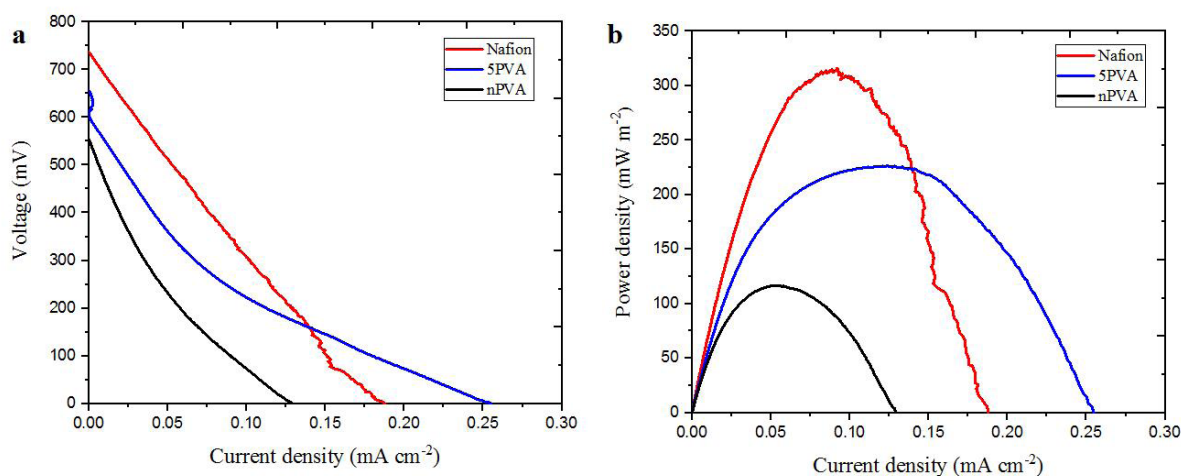

Figure 2. Polarization curves (a) and power density generated (b) by MFCs equipped with different types of membranes.

Table 1. Power density reported of different exchange membrane in MFCs.

Electrode material	Anode volume (mL)	Exchange membrane	Power density (mW m^{-2})	Ref.
Graphite granules	390	UltrexeCMI7000, Membranes International Inc., USA	8 ± 5	Rabaey et al.[14]
Graphite granules	60	UltrexeCMI7000, Membranes International Inc., USA	14 ± 1	Aelterman et al.[15]
Aluminium	2,000	Gar-salt bridge	∼ 0.25	Shakunthala et al.[16]
Carbon cloth	100	Ceramic-separator	168.91±3.89	Chaijak et al.[17]
Graphite felts	250	Nafion-117, Dupont Co., USA	316.17	This work
Graphite felts	250	nPVA	116.46	This work
Graphite felts	250	5%PVA	209.85	This work

Hospital wastewater is not a common source of substrate tested for electricity production by MFCs technology. The production of bioelectricity from these wastewaters depends on the type of organic compounds present in the effluent. Especially, particulate organic matters that have complex chemical structures must be converted into low molecular weight substrates, and then these substrates can then be used by microbes. Table 1 provides a series of characteristics ability to generate electricity of hospital wastewater as substrate for bioelectricity formation with MFCs in our study in comparison with other reports. MFCs is improving and power density of 209.85 mW.m^{-2} and maximum voltage generated of 652.75 mV using a crosslinked 5% PVA membrane. The results showed that hospital wastewater can be successfully employed as a cheap substrate for electricity production in MFC. However, the challenges due to the hazardous compounds in the effluents, for example, dialysis hospital wastewater has a high content of organic load and salt concentration.

3.2. Biofilm analysis

A mixed consortium is preferred for performance enhancement in MFCs fed with wastewater compared to the pure culture. The reason is it exhibits a "nutrient cycle ecosystem" in which some species degrade the organic matter, while some species act against harmful pollutants present in wastewater.[18]

The bacterial mixture in hospital wastewater has grown a biofilm on the anode, as shown in the SEM images in Figure 3. Variations on the biofilm can be observed with uniform growth and clumps as well as undeveloped areas. In previous studies, clumping growth has been associated with detrimental effects on power output as it can inhibit electron transfer.[19] As can be seen, biofilms are dominated by growth uniform growth, which is a good indication of a good bacterial colonization.[20] The combination of bacteria contributes to the diversity of biofilms. It produces a higher specific capacity than MFCs operating with monocultures in the anode compartment. The stable biofilm developed favored low resistance to the electrochemical reaction at the anode surface, as demonstrated by the low R_1 value in EIS analysis.
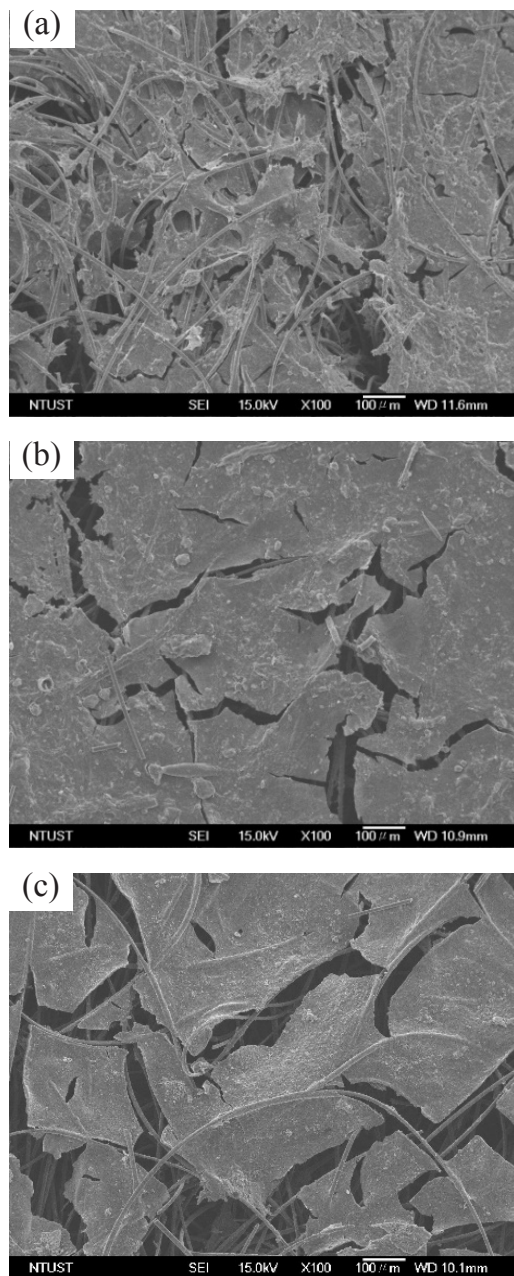
Figure 3. SEM images of anodes with electroactive bacteria biofilm were grown with: (a) Nafion membrane, (b) nPVA membrane and (c) 5% PVA membrane.
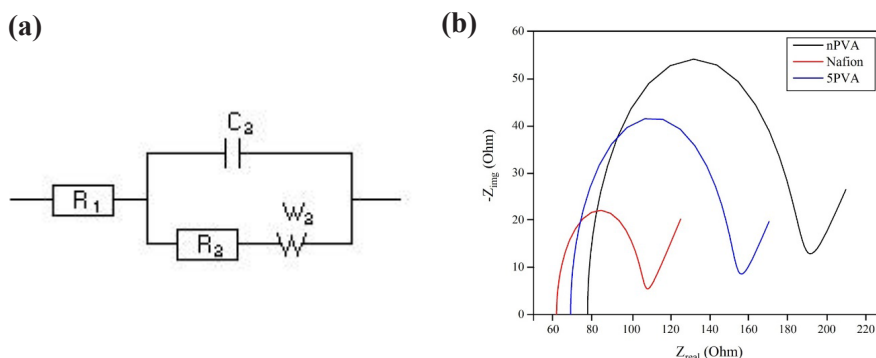
3.3. Internal resistance of the MFC with crosslinked membrane

The proton exchange membrane is one of the most critical components in the fuel cell configuration. It not only provides a separation between the two electrolytes, but also provides electroneutrality by facilitating transport of H^+ to compensate for transport of electrons. In order to assess the internal resistance of the MFCs equipped with the membranes, the EIS results were interpreted according to the Randles equivalent circuit shown in Figure 4 (a). R_1, R_2, C_2 and W_2 represent the ohmic resistance, charge transfer resistance, double layer capacitance, and Warburg impedance, respectively which are components of the internal resistances. The diameter of the semicircle in the low frequency side of the Nyquist plot as seen from Figure 4 (b) represents the charge transfer resistance while the linear portion in low frequency side represents diffusion resistance. The difference between origin to the initial start of the semicircle gives the ohmic resistance.[21] Nafion exhibited lower ohmic resistance compared to the crosslinked membrane, which is mainly due to the presence of sulphonic acid groups in its polymer chain.[22] Although PVA is an insulation material with no polar groups,[23] the charge transfer resistance was found to be lower in case of the PVA based MFCs and comparable to the charge transfer resistance observed in the Nafion based MFCs. This can be attributed to crosslinking with GA which resulted in low value of charge transfer indicating better charge transport through the crosslinked membrane due to optimum water content facilitating proton transfer through vehicular mechanism.[24]

(a)

(b)

Figure 4. (a) Equivalent circuit of MFC, (b) Nyquist plot of MFC fit: Nyquist diagram from Z-fit by EC Lab software.

Table 2. Internal resistance of MFCs and other circuit parameter values.

Membrane	R_1 (Ω)	R_2 (Ω)	C_2 (F)	$W_2 \left(\dfrac{\text{Ohm}}{\sqrt{s}} \right)$
Nafion	62.58	41.53	43.14×10^{-6}	15.93
5%PVA	68.97	82.31	51.98×10^{-6}	15.35
nPVA	84.14	105.26	58.46×10^{-6}	15.64

The individual resistance components in the reactors used in this research are listed in Table 2. The least ohmic resistance was observed for the 5% PVA based MFC 68.97 Ω, followed by Nafion with 62.58 Ω, while nPVA showed the highest ohmic resistance 84.14 Ω. The ohmic loss in the crosslinked membrane is comparable with Nafion and relatively lesser than its neat counterpart. Nafion has sulphonic acid groups attached to its polymer chain, which explains its low resistance. nPVA is an insulation material without polar groups. However, due to crosslinking, proton transfer is facilitated, resulting in its low resistance and higher power performance.[13] Also, due to the recirculation mode, homogenous mass and ion transfer rendered by the flow straighteners contributed in reducing the ohmic and concentration losses.[25] Thus, this study has confirmed the fact that resistance in MFCs strongly influences power performance.

EIS can be used to obtain information on the electronic and ionic conductivity in the charging and discharging process. The semicircle portion of the Nyquist plot at a higher frequency corresponds to the electronic transition, which controls the electron transfer kinetics of the redox reaction at the interfacing electrode. Simultaneously, the straight line in the low-frequency region is due to the diffusion process corresponding to a diffuse resistance. The magnitude of the Nyquist arc gives the electrode's electrochemical polarization resistance quality that works in the anode configuration. At the same time, quantitative values can be obtained by mounting the equivalent circuit (EC) of the data. The MFC anode's impedance spectrum was analyzed by matching the EC, as shown in Figure 4a. The internal resistance of the HMFCs was composed of ohmic losses, charge transfer losses of cathode and anode, and concentration losses.

4. CONCLUSIONS

In this work, crosslinked PVA membrane as separators with hospital wastewater has been successfully demonstrated in MFCs. Using the low-cost membranes with hospital wastewater as a substrate not only drastically reduces its capital and operational costs but also allows to treat hospital wastewater eco-friendly, which is a competitive advantage for the practical application of MFCs in the future.

REFERENCES

1. Y. Chen, H. Zhang, Y. Yin, F. Zeng, Z. Cui. Smart energy savings for aeration control in wastewater treatment, *Energy Reports,* **2022**, *8*, 1711-1721.

2. K. M. Khalid. Correlation between air quality and Wastewater pollution, In *Environmental Sustainability-Preparing for Tomorrow*, Intech Open, 2021.

3. R. A. Rozendal, H. V. Hamelers, K. Rabaey, J. Keller, C. J. Buisman. Towards practical implementation of bioelectrochemical wastewater treatment, *Trends in Biotechnology,* **2008**, *26*(8), 450-459.

4. A. Nawaz, I. ul Haq, K. Qaisar, B. Gunes, S. I. Raja, K. Mohyuddin, H. Amin. Microbial fuel cells: Insight into simultaneous wastewater treatment and bioelectricity generation, *Process Safety and Environmental Protection,* **2022**, *161*, 357-373.

5. M. Zhou, H. Wang, D. J. Hassett, T. Gu. Recent advances in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) for wastewater treatment, bioenergy and bioproducts, *Journal of Chemical Technology & Biotechnology,* **2013**, *88*(4), 508-518.

6. D. R. Lovley. Bug juice: harvesting electricity with microorganisms, *Nature Reviews Microbiology,* **2006**, *4*(7), 497-508.

7. M. J. González-Pabón, F. Figueredo, D. C. Martínez-Casillas, E. Corton. Characterization of a new composite membrane for point of need paper-based micro-scale microbial fuel cell analytical devices, *PloS One,* **2019**, *14*(9), e0222538.

8. A. Kumari, N. S. Maurya, B. Tiwari. Hospital wastewater treatment scenario around the globe, *Current Developments in Biotechnology and Bioengineering*, **2020**, 549-570.

9. B. Das, S. S. Gaur, A. R. Katha, C.-T. Wang, V. Katiyar. Crosslinked poly (vinyl alcohol) membrane as separator for domestic wastewater fed dual chambered microbial fuel cells, *International Journal of Hydrogen Energy,* **2021**, *46*(10), 7073-7086.

10. G. Buitrón, I. López-Prieto, I. T. Zúñiga, A. Vargas. Reduction of start-up time in a microbial fuel cell through the variation of external resistance, *Energy Procedia,* **2017**, *142*, 694-699.

11. B. E. Logan, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey. Microbial fuel cells: methodology and technology, *Environmental Science & Technology,* **2006**, *40* (17), 5181-5192.

12. A. J. Hutchinson, J. C. Tokash, B. E. Logan. Analysis of carbon fiber brush loading in anodes on startup and performance of microbial fuel cells, *Journal of Power Sources,* **2011**, *196*(22), 9213-9219.

13. B. Das, S. S. Gaur, A. R. Katha, C. T. Wang, V. Katiyar. Crosslinked poly (vinyl alcohol) membrane as separator for domestic wastewater fed dual chambered microbial fuel cells, *International Journal of Hydrogen Energy,* **2021**, *46*(10), 7073-7086.

14. K. Rabaey, P. Clauwaert, P. Aelterman, W. Verstraete. Tubular microbial fuel cells for efficient electricity generation, *Environmental Science & Technology,* **2005**, *39* (20), 8077-8082.

15. P. Aelterman, K. Rabaey, P. Clauwaert, W. Verstraete. Microbial fuel cells for wastewater treatment, *Water Science and Technology,* **2006**, *54*(8), 9-15.

16. C. Shakunthala, S. Manoj. Energy Harvesting from Dairy and Hospital Wastewater Using Microbial Fuel Cell (MFC), *International Conference on Cognitive Computing and Information Processing*, **2017**, 440-446.

17. P. Chaijak, M. Lertworapreecha, N. Changkit, P. Sola. Electricity generation from hospital wastewater in microbial fuel cell using radiation tolerant bacteria, *Biointerface Research in Applied Chemistry,* **2022**, *12*(4), 5601.

18. M. Li, M. Zhou, X. Tian, C. Tan, C. T. McDaniel, D. J. Hassett, T. Gu. Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity, *Biotechnology Advances,* **2018**, *36*(4), 1316-1327.

19. X. Zhou, Y. Qu, B. H. Kim, P. Y. Choo, J. Liu, Y. Du, W. He, I. S. Chang, N. Ren, Y. Feng. Effects of azide on electron transport of exoelectrogens in air-cathode microbial fuel cells, *Bioresource Technology,* **2014**, *169*, 265-270.

20. Y. Cao, H. Mu, W. Liu, R. Zhang, J. Guo, M. Xian, H. Liu. Electricigens in the anode of microbial fuel cells: pure cultures versus mixed communities, *Microbial Cell Factories,* **2019**, *18*(1), 1-14.

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

22. C. Y. Wong, W. Y. Wong, K. S. Loh, R. W. Daud, K. L. Lim, M. Khalid, R. Walvekar. Development of poly (vinyl alcohol)-based polymers as proton exchange membranes and challenges in fuel cell application: A review, *Polymer Reviews,* **2020**, *60*(1), 171-202.

23. R. Rudra, V. Kumar, P. P. Kundu. Acid catalysed cross-linking of poly vinyl alcohol (PVA) by glutaraldehyde: effect of crosslink density on the characteristics of PVA membranes used in single chambered microbial fuel cells, *RSC Advances,* **2015**, *5*(101), 83436-83447.

24. S. Zinadini, A. Zinatizadeh, M. Rahimi, V. Vatanpour, Z. Rahimi. High power generation and COD removal in a microbial fuel cell operated by a novel sulfonated PES/PES blend proton exchange membrane, *Energy,* **2017**, *125*, 427-438.

25. T. Sangeetha, I.-T. Li, T.-H. Lan, C.-T. Wang, W.-M. Yan. A fluid dynamics perspective on the flow dependent performance of honey comb microbial fuel cells, *Energy,* **2021**, *214*, 118928.