



Implementation of Chitosan Modified Ultrafiltration Hollow Fiber as Proton Exchange Membrane of MI-Scale Microbial Fuel Cells

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Abstract

The study investigated the modification of polyethersulfone (PES), polyvinylidene fluoride (PVDF), and polyacrylonitrile (PAN) hollow fiber membranes using a chitosan solution as the proton exchange membrane for microbial fuel cells (MFCs). Firstly, the performance of the modified PES membrane using 1, 2, and 3% of chitosan in 0.1 M acetic acid coating was inspected. Chitosan coating decreased the internal resistance and enhanced the electricity generation of the MFCs. The maximum power and current densities of 755.202 mW/m², and 5525.42 mA/m² were achieved for 3% chitosan-coated PES (PES-3%chi) compared to 629.533 mW/m² and 3237.79 mA/m² for pristine PES membrane. Thereafter, application of a 3% chitosan coating over the PAN and PVDF membranes exhibited excessive improvement in the bioelectricity generation and wastewater treatment efficiency of the MFCs. The PAN-3%chi achieved the uppermost power and current densities of 765.147 mW/m² and 8297.46 mA/m², which were 1.7 and 2.6 higher than the PAN membrane (450.675 mW/m² and 3216.56 mA/m²). The electricity generation of the PVDF membrane was enhanced by 5.3 times (337.134 mW/m² and 2720.16 mA/m²) after the addition of 3% chitosan, likely due to the improvement in hydrophilicity and proton conductivity. The COD removal efficiencies of 42.41, 40.55, and 36.11% were obtained by PAN-3%chi, PES-3%chi, and PVDF-3%chi membranes, respectively, which were 3.53, 4.01, and 5.53 times higher than the values obtained by their pristine unmodified samples.

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1. Introduction

Over the last few decades, the most pressing challenges confronting the globe have been the lack of clean water and renewable energy sources. Further, one of the most appropriate ways to solve this significant problem and meet our residential and industrial needs is to reuse water and wastewater as a potential source of drinking water through advanced treatment technologies. Microbial fuel cells (MFCs) are innovative approaches that can generate bioelectricity and treat wastewater simultaneously [1, 2]. MFCs are typically composed of anode and cathode compartments separated by a proton exchange membrane (PEM) [3-5]. Implementing the right PEM is crucial for the practical use of MFCs. In fact, choosing a membrane for MFCs involves trade-offs between numerous factors, including cost, selectivity, proton conductivity, and fouling resistance. Researchers are still working to find the best membrane materials to enhance MFC performance and longevity [6].

Several types of materials have been explored as PEM for MFCs, each with distinct advantages and disadvantages [7]. Ion exchange membranes (IEMs), such as Nafion, are the predominant form of PEMs. They possess excellent ion conductivity, but their high cost and susceptibility to pH splitting and biofouling are notable drawbacks [8]. In the process of discovering an adequate alternative membrane, inexpensive fabric-based membranes are gaining attention for their affordability. Nevertheless, they might not possess the selectivity and durability required for the long-term operation of MFCs [9, 10]. Furthermore, ceramic membranes are being assessed for their cost-effectiveness, chemical and mechanical resilience, and resistance to fouling. These qualities make them particularly beneficial for scaling up wastewater treatment processes [11-17].

Ultrafiltration membranes have shown potential as a promising candidate for PEM in MFCs [18]. These

membranes facilitate the selective transport of ions, preventing the crossover of bacteria and other contaminants. While these membranes offer several advantages, such as affordability, high permeability, robustness, and chemical resistance, they are not explicitly tailored for use in MFC systems. They must be modified for real-world implementation in MFC systems. The process of selecting a membrane for MFCs requires balancing many criteria, including cost, selectivity, proton conductivity, and fouling resistance. Ongoing research focused on improving membrane materials to boost the performance and lifespan of MFCs.

Chitosan, a highly adaptable and versatile biopolymer, has been the subject of numerous investigations due to its potential applications in microbe-powered energy storage systems [19-21]. Because of its distinctive characteristics, such as its extensive surface area, biocompatibility, abundance, and antibacterial activity, it is well-suited for use in MFCs as a modification to the membrane or as a material for coating the electrodes [14, 16, 22]. The incorporation of chitosan can improve the mechanical properties, stability, ion selectivity, and longevity of the membrane. Moreover, chitosan can serve as an electron transfer mediator, promoting the transfer of electrons to the anode and enhancing the effectiveness and power output of the MFC.

Previously, the utilization of three different polymeric hollow fiber membranes has been explored in a novel-designed small MFC. The PES membrane exhibited superior power generation capability in comparison to PAN and PVDF due to its elevated hydrophilicity and enhanced proton conductivity [23]. The current investigation focuses on the alteration of these membranes by the utilization of varying concentrations of chitosan coating layer. The objective is to improve the performance of the microbial fuel cells (MFCs) in terms of electricity generation and efficiency in treating wastewater.

2. Experimental

2.1. MFC structure

In this study, a microbial fuel cell was constructed using a two-chamber cylindrical configuration, as documented in the previous publication [23]. Three distinct polymeric hollow-fiber membranes, namely PES, PAN, and PVDF, were employed as the base proton exchange membrane. The cathode chamber encompasses the inside region of the membranes where oxygen reclamation reactions take place, whereas the anode chamber comprises the exterior side of the membranes. The PES, PAN, and PVDF hollow-fiber membranes possess an inner diameter of 1, 0.9, and 1.3 mm, and a thickness of 0.1, 0.175, and 0.28 mm, respectively.

The cathode chamber has a length of 0.11 m and a diameter of 0.001 m, allowing water to enter and exit through connectors at both ends. The cathodic electron acceptor is oxygen from the air, which is introduced into the cathode chamber through the use of an

aeration aquarium pump. A single copper wire serves as the cathode electrode within the cathode chamber. The anode chamber, which refers to the area around the membrane, provides a site for bacterial electrochemical processes that generate electrons and protons. The anodic cylindrical container, measuring 0.11 m in length and 0.006 m in diameter, is fabricated using CNC cutting on plexiglass. It is fitted with an inlet and outlet for sewage. The anodic electrode, made of carbon cloth (Panex35, Zoltek Company) with a fiber diameter of 5×10^{-7} m and a surface area of 1.82×10^{-3} m², is used to transmit electrons to external circuits. Copper wire is utilized as the current collector for this purpose. The membrane is encased in carbon fabric using a pristine copper wire. Anodic bacteria that have been cultivated on the carbon cloth generate protons and electrons through the degradation of waste elements in the substrate. The electrons are conveyed to the electrical circuit by means of making contact with copper wire. Figure 1 displays a three-dimensional representation of the MFC structure, as well as a schematic of the whole process and an image of the three MFCs positioned inside the temperature control box.

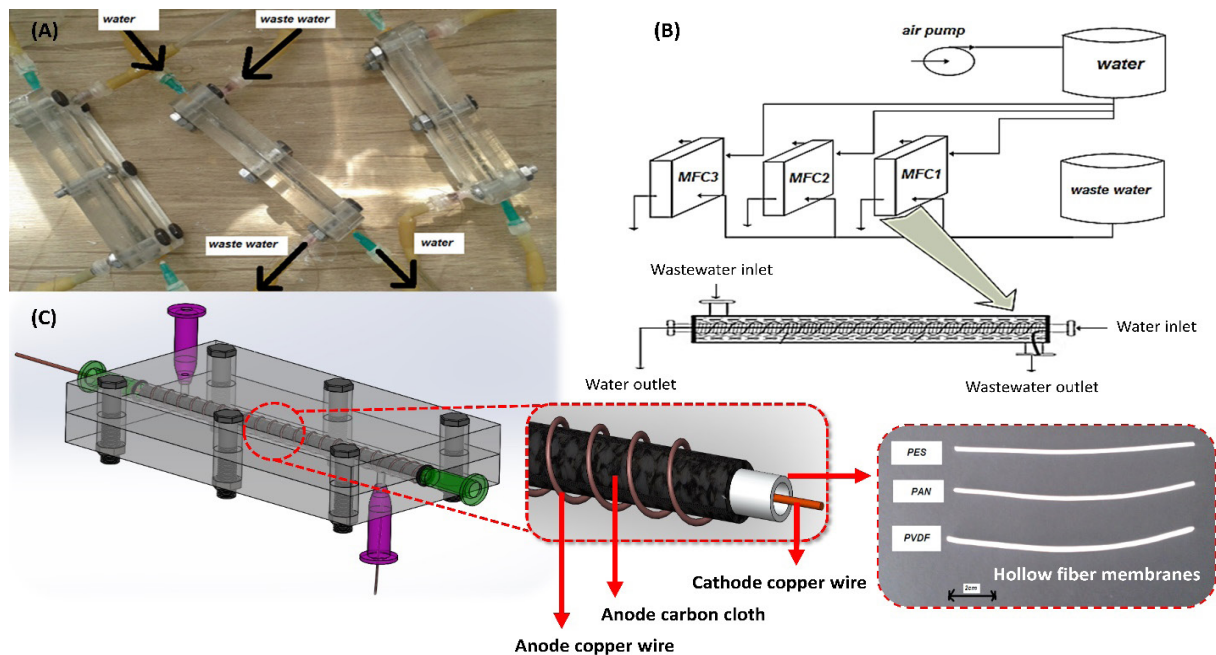


Fig. 1. (A) A photograph of microbial fuel cells located in the temperature control chamber; (B) A diagram illustrating the overall process and its connections; and (C) A three-dimensional representation of the microbial fuel cell constructed with hollow fiber membranes [23].

Following each experiment, the carbon cloth underwent a thorough washing process consisting of several steps to ensure the total elimination of contaminants and microorganisms. Initially, immerse it in a solution of 1 M hydrochloric acid (HCl) for a duration of one hour. Subsequently, rinse it multiple times with deionized water. Next, soak it in a solution of NaOH for one hour and proceed to rinse it thoroughly with DI water before commencing the subsequent experiment.

In this study, wastewater from the septic plant of Sistan and Baluchestan University was continuously fed (3.5 mL/min) as the substrate of MFCs without the addition of any nutrients. The pH of the influent wastewater was about 7.2. The MFC systems were placed in the temperature control chamber at 37 °C. Each test was repeated three times, and its mean value and standard deviation were reported as an outcome.

The investigation involved the continuous feeding (at a rate of 3.5 mL/min) of wastewater from the septic plant of Sistan and Baluchestan University into the MFCs, without the inclusion of any additional nutrients. The initial pH of the influent wastewater was approximately 7.2. The MFC systems were positioned within the temperature-controlled chamber at a temperature of 37 °C. The experiments were conducted in triplicate and the resulting mean value and standard deviation were reported.

2.2. Application of Coating on Hollow Fiber Polymeric Membranes

Three distinct concentrations of chitosan (1%, 2%, and 3%) in a solution of 0.1 M acetic acid were prepared for coating of the hollow-fiber membranes. During the coating process, the openings at the beginning and end of the hollow-fibers were sealed to ensure that the inner diameter of the membrane remained unchanged. The membranes were immersed in the chitosan solution for a duration of 72 hours. The PES hollow-fiber was coated with three concentrations of chitosan, and nominated as PES-1%chi, PES-2%chi, and PES-

3%chi. The remaining two hollow fibers were coated only with a 3% chitosan solution and were identified as PAN-3%chi and PVDF-3%chi.

2.3. Electrochemical Measurement

A digital multimeter (VC 9805, Zhangzhou Weihua Electronic Co., Ltd.) was used to measure both the open circuit potential (OCV, mV) and closed circuit potential (CCV, mV) of MFCs at regular intervals. External resistance (R_{ext} , Ω) of 1000 ohms was used to determine the current output (I, mA) via the Ohm law ($I = CCV/R_{ext}$). To obtain the polarization curve, the output voltage was measured by changing the external resistance in the range of 5–46000 ohms. Current density (CD, mA/m²) and power density (PD, mW/m²) were calculated using 1 and 2 relationships based on the lateral surface of the membrane (A, m²).

$$CD = V / AR_{ext} \quad (1)$$

$$PD = V^2 / AR_{ext} \quad (2)$$

The COD and BOD were measured using a Photometer (AL250 and CSB/COD-Reaktor AL 38) and a manometric device (OxiTop®IS, USA).

3. Results and Discussion

3.1. Determination of the Optimal Chitosan Concentration for PES Membrane

The proton conductivity of the PEM is a significant factor in determining the performance of MFC. The membrane should possess characteristics that facilitate efficient proton transport. Applying a suitable coating can effectively inhibit the unnecessary transport of oxygen from the cathode chamber to the anode compartment. Because the typical anodophilic bacteria such as *Geobacter* sp. are strongly anaerobes

[24, 25], the presence of oxygen in the anode chamber could prevent the growth and propagation of anoxic exo-electrogenic bacteria [26, 27]. In the present study, chitosan has been utilized as the coating layer because of its hydrophilic characteristics.

Figure 2A depicts the time-dependent open-circuit voltage curve for three different coatings of chitosan (1%, 2%, and 3%) applied on PES hollow fiber. More-

over, the highest achievable OCV values are provided in Table 1. It is evident that the membranes' final OCV nearly approached the identical values after a duration of 25 hours. The PES-3%chi sample achieved the maximum OCV of 859.50 mV, followed by PES-2%chi with 826.82 mV, PES with 813 mV, and the lowest value of 796.65 mV was seen for PES-1%chi.

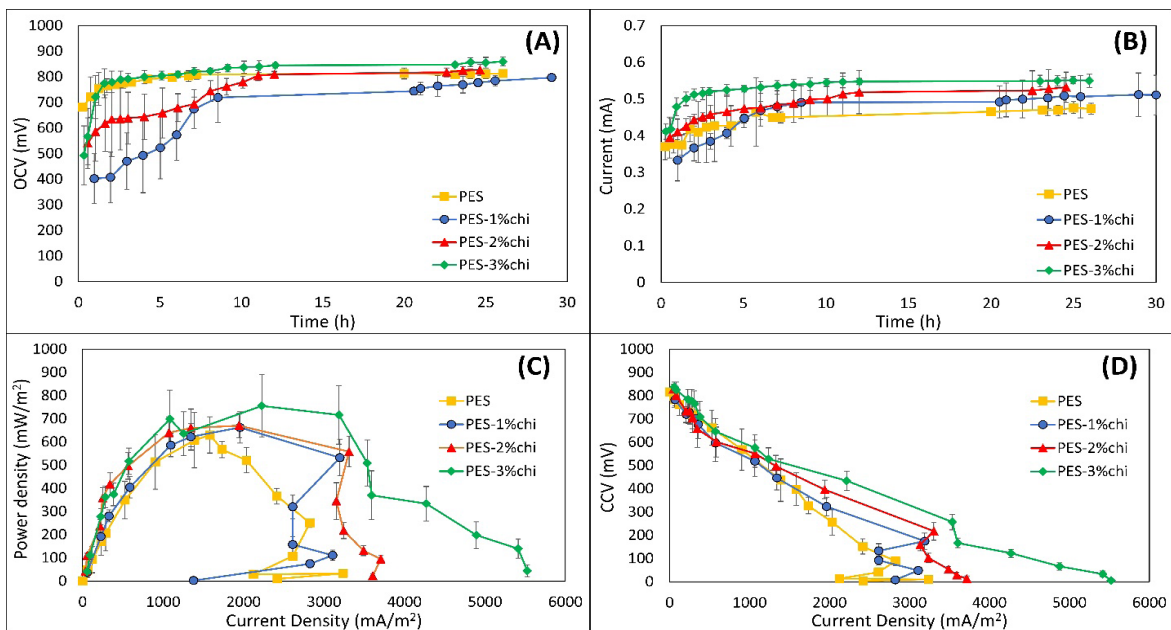


Fig.2. The effect of different concentrations of chitosan coating on the (A) open circuit voltage, (B) current, (C) power density, and (D) closed circuit voltage of the PES membrane.

The current generation trends of the MFCs containing plain and modified PES membranes are illustrated in Figure 2B and outlined in Table 1. Increasing the concentration of the chitosan coating layer on PES hollow fiber enhances the electric current magnitude. The maximum current of 0.501 mA achieved by PES-3% chi, which was 7.74% greater than the maximum current obtained by the plain PES membrane. The PES-2%chi, with a current of 0.482 mA, ranks second. Meanwhile, PES-1%chi generates a current that is nearly identical to the plain.

The polarization test results are displayed in Fig-

ures 2C and 2D, while the maximum power density (MPD) and maximum current density (MCD) values are compared in Table 1. The Figure 2C demonstrates that the MPD and MCD of the MFCs are improved when the chitosan content increases. PES-3%chi gained the greatest MPD value of 755.202 mW/m², which is 19.96% higher than the MPD value of PES (629.533 mW/m²). The current generation exhibits a notable enhancement of 70.65% for PES-3%chi (5525.42 mA/m²) compared to PES (3237.79 mA/m²). The PES-2%chi produced a MPD of 670.116 mW/m² and a MCD of 3706.21 mA/m², which are 6.44% and

14.47% greater than the respective values obtained from the PES.

Moreover, the internal resistance (R_{in} , Ω) of the MFCs is calculated based on the slope of CCV curves versus current density (Figure 2D) and summarized in Table 1. Noticeably, the lowest R_{in} was estimated for PES-3%chi (431.45 Ω), which was approximately half of the R_{in} value for PES (804.17 Ω). The incorporation of the chitosan layer onto the PES hollow fiber resulted in a reduction in the slope of the middle portion of the polarization curves (Figure 2D), mostly due to the decline in ohmic impedance. Additionally, the chitosan layer also decreased the mass transport impedance in the high current density region of the curves.

Overall, the modification of the PES hollow fiber membrane by the chitosan coating layer could obviously boost the electricity generation performance of the MFCs. This is probably due to the filling of membrane cavities and decreasing the porosity of the membrane. Thereby, excessive oxygen transportation between the chambers is prevented, which provides better condition for the propagation of exoelectrogenic anodic bacteria. Moreover, the greater power generation can be attributed to the improved hydrophilicity and water absorption capacities of the membrane due to the implementation of the chitosan layer. As a result, this can notably enhance the membrane's proton conductivity.

In this context, Ghaemi et al. (2018) examined how the presence of chitosan nanoparticles within the PES framework affects the membrane's ability to remove nitrates. They found that including chitosan nanoparticles, up to a concentration of 0.2 wt.%, resulted in a significant 70% increase in the water permeability of the PES membrane [28]. Similarly, Abriyanto et al. (2022) observed an increase in PES ultrafiltration membrane hydrophilicity as a result of chitosan and metal oxide additions. They also discovered a sub-

stantial upgrading in antifouling feature of the membrane by implementation of chitosan into PES framework [29].

In a related study, Gafri et al. (2019) characterized the PES membrane which was modified by chitosan or chitosan powder activated carbon (PAC). The membrane water flux was boosted by 29% when chitosan concentration increased from 0.1 to 1.0% (w/v), but it was decreased by further the chitosan concentration to 2.0 w/v. Furthermore, the implementation of chitosan enhanced the anti-biofouling feature of PES membrane (28% reduction in total coliform bacteria) [30]. Hence, the incorporation of a chitosan coating layer enhanced both the water permeability and the proton conductivity of the PES membrane. Additionally, it could mitigate the ohmic resistance of the MFC by diminishing the biofilm formation over the membrane. Although biofouling is not a short-time issue and may not be vital in this special MFC, it could be important in subsequent studies or might have an impact on the sensitivity and precision of MFC-based biosensors [31].

3.2. Coating of Chitosan Over Different Hollow Fiber Membranes

3.2.1. The Electricity Generation Performance

Given that the PES membrane exhibited the most favorable power production performance at a chitosan concentration of 3%, the subsequent phase of this study involved applying this optimal coating to PVDF and PAN membranes.

Figure 3A illustrates the OCV generation of all three original hollow fiber membranes with their modified counterparts. The OCV values of the chitosan-modified membranes showed no noticeable enhancement. As summarized in Table 1, the maximum OCV of

PAN-3%chi has a slight increase of 0.88% compared to the plain PAN membrane, and the final OCV of PVDF-3%chi has an even smaller value compared to the bare PVDF membrane. Nevertheless, the differences between the OCV of the modified and the bare membranes are not statistically significant (p -value > 0.05) based on the Tukey post hoc investigation.

Figure 3B represents the current generation of the modified and plain hollow fiber membranes versus time. In an obvious contradiction to OCV results, the current generation of the 3% chitosan-modified membranes exhibits significant enhancement compared to the unmodified ones. The PAN-3%chi and PVDF-3%chi membranes exhibit 23.18% and 26.20% increments of maximum current generation compared to PAN and PVDF membranes, respectively (Table 1).

The polarization results of the modified 3% chitosan membranes are depicted in Figures 3C and 3D. The slope of the CCV curve versus current density, which represents the internal resistance of MFCs, exhibits considerable declines for all the modified hollow fiber membranes. The PAN-3%chi shows the lowest internal resistance of 296.89 Ω , representing a 64.44% reduction compared to the pristine PAN membrane (Table 1). Similarly, the internal impedance of PVDF has decreased markedly from 2767.74 Ω to 548.25 Ω after the deposition of the 3% chitosan layer. Moreover, the maximum power and current densities of PAN and PVDF have been greatly enhanced after the chitosan modification. PAN-3%chi has achieved the uppermost MPD of 765.147 mW/m^2 , surpassing the value of bare PAN (450.675 mW/m^2) by nearly 70%.

The MPD of PVDF membrane has experienced a significant increase of 431.2%, rising from 63.468 mW/m^2 to 337.134 mW/m^2 for PVDF-3%chi sample. The current density values of the hollow fiber membranes have more evident enhancement in comparison to their power density. The extremely high MCD of 8297.46

mA/m^2 have been obtained for PAN-3%chi, which is 157.9% higher than the value of bare PAN membrane (3216.56 mA/m^2). The modification of PVDF resulted in an even greater augmentation of MCD by 424.6% from 518.52 mA/m^2 to 2720.16 mA/m^2 for PVDF-3%chi.

In total, the current and power generation of all the hollow fiber membranes of PES, PAN, and PVDF were enhanced by the addition of a chitosan coating over them. Nevertheless, the degrees of enhancement were different for them. The MPD and MCD of the PVDF membrane were boosted by approximately 4.5 times as a result of deposition of a 3% chitosan layer. Afterward, the power and current density of the PAN membrane underwent a significant increase of 70% and 157.9%, respectively. Finally, the PES membrane exhibits almost 20% and 70% increment of MPD and MCD after the modification by a 3% chitosan layer. The variations in the extent of enhancement are probably attributable to the discrepancies in the physical and chemical characteristics of the base hollow fiber membranes. The contact angles of 43.5, 66, and 87 degrees were respectively obtained for PES, PAN, and PVDF membranes during the hydrophilicity test [23]. As discussed previously, the inclusion of chitosan enhanced the hydrophilicity of membranes, resulting in improved conductivity of protons. This, in turn, directly impacts the overall efficiency of the MFCs. Hence, the more hydrophobic was the base membrane, the greater the improvement in proton conductivity and electricity generation performance after the modification by chitosan was achieved. Moreover, the chitosan amendment could have a decisive effect on the prevention of biofilm deposition over the membranes in long-term implementations.

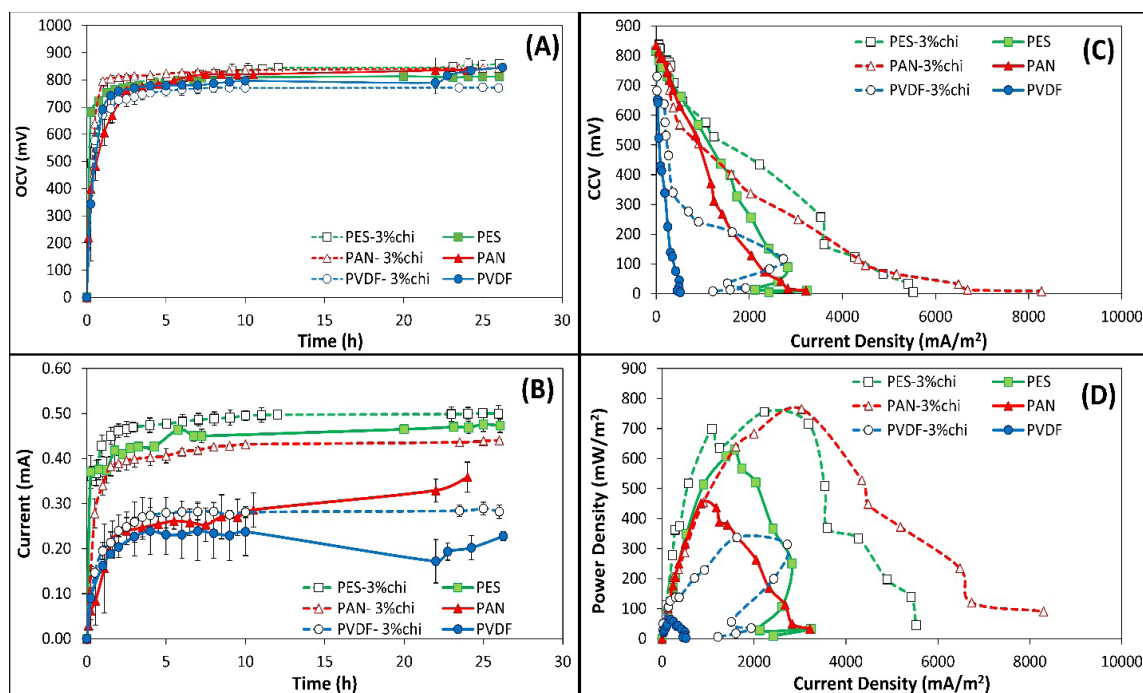


Fig. 3. The effect of the 3% chitosan deposition over different hollow fiber membranes with different materials; (A) open circuit voltage versus time, (B) current versus time, (C) closed circuit voltage in terms of current density, (D) power density in terms of current density.

3.2.2. Wastewater treatment efficiency

The influent wastewater for the microbial fuel cells has an average pH of 7.2, with BOD and COD values of 120 mg/L and 540 mg/L, respectively. Table 1 compares the outlet COD and the COD removal efficiency of each experiment. As can be seen, there is a significant disparity between the wastewater treatment capabilities of the MFCs containing the bare and the chitosan-modified hollow fiber membranes. The COD removal efficiencies of PES-3%chi, PAN-3%chi, and PVDF-3%chi are 3.53, 4.01, and 5.57 times greater than the unmodified PES, PAN, and PVDF membranes, respectively.

Presumably, putting a chitosan layer on top of hollow fiber ultrafiltration membranes restricts excessive oxygen passage between the anode and cathode chambers, creating a more favorable environment for bacterial proliferation. Furthermore, the inclusion of chitosan coating has particularly improved the overall performance of hydrophobic PVDF and PAN membranes by increasing their hydrophilicity and consequently improving the rate of proton exchange inside these membranes.

Moreover, the coulombic efficiency (CE) of the MFCs is calculated and compared in Table 1. The CE of PES demonstrates a significant enhancement of 30 percent following the application of chitosan coating. Nonetheless, the CE of PAN membrane remained almost unchanged, whereas the CE of PVDF experienced a little decline, probably attributable to the constraints imposed by MFC design and the extremely confined chamber conditions. In conclusion, it must be considered that such small MFCs are not intended for wastewater treatment purposes; instead, they could be very beneficial for bio-sensing applications.

Furthermore, the overall performance of the present modified hollow-fiber membranes has been compared to similar polymeric membranes as well as well-known commercial membranes. Nevertheless, it is important to acknowledge that MFCs are complicated systems, and numerous factors, including their configuration, size, electrodes, catalysts, and substrate specifications, can significantly influence their efficiency. However, the evaluation of the outcomes from our low-cost modified hollow-fiber membranes demonstrates their promising potential for utilization as the MFC membrane.

Table 1- Comparison of the performance of hollow fiber membranes investigated in this study regarding the amount of electricity produced and wastewater treatment efficiency

PEM membrane	OCV (mV)	I (mA)	R _{in} (Ω)	MCD (mA/m ²)	MPD (mW/m ²)	COD-in (mg/L)	COD-out (mg/L)	COD removal (%)	CE (%)	Cost (US \$/m ²)	Ref.
PES-1%chi	796.65	0.462	674.82	3197.74	662.023	540	----	----	----		This study
PES-2%chi	826.82	0.482	579.90	3706.21	670.116	540	----	----	----		This study
PES-3%chi	859.50	0.501	431.45	5525.42	755.202	540	321	40.55	5.49		This study
PAN-3%chi	843.33	0.441	296.89	8297.46	765.147	540	311	42.41	3.62		This study
PVDF-3%chi	772.34	0.289	548.25	2720.16	337.134	540	345	36.11	2.95		This study
PES	813	0.465	804.17 ^a	3237.79	629.533	540	478	11.48	4.22	40	[23]
PAN	836	0.358	834.84 ^a	3216.56	450.675	540	483	10.55	3.49	33	[23]
PVDF	845	0.229	2767.74 ^a	518.52	63.468	540	505	6.48	3.12	33	[23]
Nafion 117	856	5.03 ± 16	20	1750	602	1200	180	85	53.0	2300	[32]
PES	---	---	---	65.133	4.161	---	---	87	---	8	[33] ^b
PES/SPES	---	---	---	317.111	58.726	---	---	85	---	22	[33] ^b
Nafion 117	---	---	---	228.673	45.512	---	---	72	---	18	[33] ^b
PES-15% Fe ₃ O ₄	656	---	---	148	20	---	---	---	---	---	[34] ^c
Nafion 117	610	---	---	---	15.4	---	---	---	---	---	[34] ^c
Nafion 117	612.5	---	5790 ^d	69.27	17.68	---	---	75 ^f	23	---	[35]
CMI-7000	580.0	---	6130 ^d	49.30	12.58	---	---	74 ^f	15.5	---	[35]
PES 0	139.5	---	72930 ^d	1.12	.008	---	---	72 ^f	0.5	---	[35]
PES 5 ^e	485.0	---	46280 ^d	6.65	1.66	---	---	74 ^f	2.5	---	[35]
PES 20 ^e	552.5	---	8880 ^d	38.38	9.59	---	---	75 ^f	11.36	---	[35]

a. The values of internal resistance in this table are calculated based on the slope of polarization chart and in the previous paper were estimated based on the EIS results.

b. In this research synthetic wastewater and mediator (200 μmol/L Methylene blue) was used in the anode chamber of a double chamber MFC.

c. In this study, *Saccharomyces cerevisiae* was used as an active biocatalyst and neutral red with low concentration (200 μmol l⁻¹) was selected as electron shuttle in anode chamber.

d. membrane resistance

e. 5 wt% to 20 wt% of Fe₃O₄ nanoparticles

f. Total organic carbon (TOC) removal

Conclusion

The modification process involved coating the PES, PVDF, and PAN hollow fiber membranes with different concentrations of chitosan solution. The investiga-

tion of the modified PES membrane using 1, 2, and 3% chitosan concentrations demonstrated a substantial reduction in internal resistance and a notable enhancement in current and power generation of the MFCs. The subsequent application of a 3% chitosan coating over PAN and PVDF membranes exhibited consider-

able improvements in bioelectricity generation performance and wastewater treatment efficiency, indicating the potential of chitosan-modified membranes in enhancing MFC performance. The study's findings may contribute to the advancement of efficient and sustainable proton exchange membranes for microbial fuel cells, with potential implications for renewable energy generation and environmental remediation.

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