chemistry proceedings

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Proceeding Paper

Evaluation of Chitosan-Derived Mixed-Matrix Membranes as Potential Separators in Bioelectrochemical Systems †

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† Presented at the 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-28), 15–30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: Bioelectrochemical systems are energy-efficient devices that transform chemical energy into electrical energy or synthesize products of interest. These technologies make use of Nafion membranes that function as proton exchangers; however, these separators have some problems, such as fouling. Therefore, this research explores mixed-matrix membranes of chitosan and chitosan derivatives to determine their antimicrobial, anti-fouling, chemical stability and high-water retention properties. The results showed that these membranes could be good candidates to be used as separators in bioelectrochemical systems.

Keywords: bioelectrochemical systems; Nafion membranes; chitosan; chitosan derivatives

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Citation: Alvear Méndez, S.; Bahamonde Soria, R.; Arboleda, D.; Cevallos, C.; Alcivar, C.; Pupiales, H.; Luis, P. Evaluation of Chitosan-Derived Mixed-Matrix Membranes as Potential Separators in Bioelectrochemical Systems. *Chem. Proc.* **2024**, *16*, 101. https://doi.org/10.3390/ecsoc-28-20245

Academic Editor: Julio A. Seijas

Published: 15 November 2024

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1. Introduction

The discharge of wastewater into rivers or seas causes a serious environmental impact, as it may contain organic pollutants, medical waste and bacteria [1]. The discharge of wastewater into rivers or seas causes a serious environmental impact, as it may contain organic pollutants, medical waste and bacteria [1]. Some ways to treat wastewater exist and among them are bioelectrochemical systems which are devices that transform chemical energy into electrical energy or require energy to obtain products of interest, such as hydrogen, methane, acetates, bioalcohols and bioplastics, by oxidizing organic matter in microbial fuel cells or microbial electrosynthesis cells, respectively [2]. These technologies use Nafion as membranes since they are good proton exchangers. However, Nafion membranes, which are the most used for these systems, are expensive, encourage gas leakage, substrate loss and fouling [3].

However, studies indicate that certain biopolymers may be candidates as potential materials for PEMs [4]. Therefore, the aim of this research was to evaluate chitosan and chitosan-derived mixed-matrix membranes (chitosan Schiff bases), as possible candidates for separators in bioelectrochemical systems.

2. Materials

Sulphury acid (H_2SO_4, 98%), hydrochloric acid (HCl, 37%), sodium chloride (NaCl, 99.99%), anhydrous sodium sulphate (Na2SO4, ≥99. 0%), bovine serum (BSA lyophilized powder ~66 kDa), ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.5%), hydrogen peroxide (H_2O_2, 30%), acetic acid (CH3COOH, 99.8%) and Mueller Hinton Agar Mueller Hinton were purchased from Merk KGaA. Chitosan (Q) and chitosan derivatives Q1

(chitosan + salicylaldehyde) and Q_2 (chitosan + methoxybenzaldehyde) were provided by [5]. The antibiotic discs of ciprofloxacin, and the strains *Escherichia coli* ATCC 25922 and Staphylococcus aureus ATCC 25923 were obtained from the microbiology laboratory of Chemical Sciences of the Central University of Ecuador. Finally, PZ-FSR-1-DRY ultrafiltration membranes were obtained from Synder Filtration.

3. Methodology

3.1. Preparation of Mixed-Matrix Membranes

The mixed-matrix membranes were prepared by the pour-on-ultrafiltration membrane method, following the methodology of [6]. Prepared membranes have the following abbreviations: chitosan membranes (MQ), Q1 membranes (MQ1) and Q2 membranes (MQ2).

3.2. Antimicrobial Capacity

The antibacterial tests were performed using the disc diffusion method, and 5 diameter samples of MQ, MQ1 and MQ2 were used. All materials, including Mueller Hinton agar and 0.9% saline, were sterilized. Subsequently, the inoculum was prepared in the saline solution to 0.5 on the McFarland scale with *S. aureus* and *E. coli* and then seeded in the Petri dishes containing the agar. Ciprofloxacin and 1% acetic acid were used as positive and negative control, respectively. Finally, incubation was carried out at 35 °C, and the inhibition halo was measured after 24 h [7].

3.3. Water Holding Capacity

This property was determined by gravimetry, based on the procedure of [8]. The following formula was used to determine the percentage of water retention:

$$W = \frac{W_f - W_0}{W_0} \cdot 100\%$$

where W is the percentage of water retention, W_f is the weight of the wetted membrane and W_0 is the weight of the dry membrane.

3.4. Chemical Stability

Chemical stability is the ability of a membrane to resist severe oxidative conditions, and this property was measured based on the methodology of [9].The following formula was used to determine the tolerance of hydroxyl radicals.

$$T = \frac{W_d - W_a}{W_d} \cdot 100\%$$

where T is the tolerance of hydroxyl radicals, W_a and W_d are the masses in g of the membranes when dry and after being attacked by hydroxyl radicals.

3.5. Fouling and Biofouling

For this procedure, the surface electrical resistance was measured using a four-compartment cell, filled with 0.2 M sodium sulphate and 0.1 M sodium chloride for fouling and with the addition of serum coil for biofouling. This test was based on the methodology of [7].

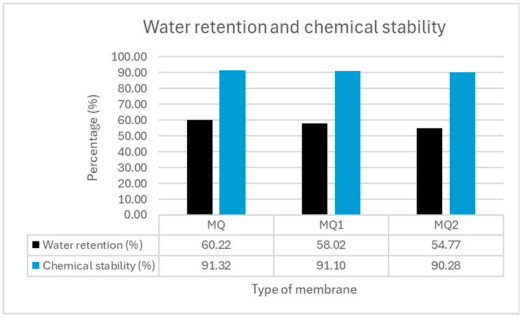
$$R_s = \left(\frac{V - V_0}{I}\right) \cdot A$$

where V is the voltage of the membrane to be studied, V_0 is the target voltage, I is the current (0.011 A) and A is the effective area (7.065 cm^2) of the membrane.

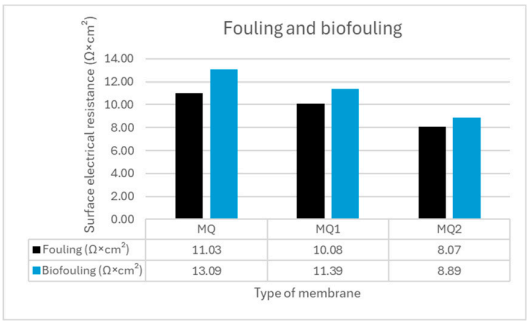
4. Results and Discussion

4.1. Water Retention Capacity

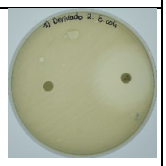
According to [10], Nafion membranes have a water holding capacity of 21.8%, and observing Figure 1a, it can be deduced that MQ, MQ1 and MQ2 retain more moisture than the Nafion separators. This could be because chitosan has hydroxyl and amine groups that can form hydrogen bridges with water and therefore absorb more water [11]. However, comparing chitosan membranes with chitosan-derivative membranes, the percentage decreases because the amount of hydrogen bonds decreases. In the case of the Q1 derivative, this is probably because the amine group is transformed to the imine group, and in the case of the Q2 derivative, this is because of the presence of the methoxy group.



(**a**)



(**b**)

Bacteria	MQ	MQ1	MQ2
E. coli			
S. aureus			

(**c**)

Figure 1. Results. (**a**) Water retention and chemical stability. (**b**) Fouling and biofouling. (**c**) Antimicrobial capacity of membranes.

4.2. Chemical Stability

Figure 1a shows that the membranes in general have a high percentage of hydroxyl tolerance, showing that they have a high tolerance of strong oxidizing conditions, as they withstood the Fenton reagent for a period of 7 days [9].Furthermore, compared to Nafion membranes, the membranes tested have a lower tolerance to hydroxyls; however, the membrane performance is close to that of Nafion membranes [10].

4.3. Fouling and Biofouling

Figure 1b shows that the surface electrical resistance of the membranes in the biofouling test is higher than the fouling test, suggesting that the ionic conductivity decreases with organic contaminants such as bovine serum [12].

According to [10] Nafion membranes, for the fouling test, have a surface electrical resistance of 5.31 $\Omega \times cm^2$ $\Omega \times cm^2$, with MQ1 and MQ2 membranes being comparable to Nafion membranes. However, in the biofouling test, the Nafion membranes foul up to 10.21 times more, while the tested membranes foul less than 2 times. This indicates that

membranes made from chitosan derivatives have better antibiofouling properties than Nafion membranes.

4.4. Antimicrobial Capacity

Figure 1c shows that MQ, MQ1 and MQ2 membranes have antibacterial properties for *E. coli* and *S. aureus*, as no growth of microorganisms is observed on their surface. This could be because the biopolymers form a film on the cell surface to cut off the passage of nutrients into the cell or also because they are positively charged and can attract the negative charges of the bacteria, causing bacterial lysis [13].

The Q1 derivative has no significant differences with the other membranes of *E. coli* bacteria; however, for *S. aureus*, an inhibition halo of 6 mm is observed. This could be explained by the fact that when a positive charge is formed on the imine carbon, it can be stabilized by resonance on the aromatic ring [13].

5. Conclusions

The mixed-matrix membranes of chitosan and chitosan derivatives were found to have good antibacterial activity. In addition, it was observed that the water retention is much better compared to Nafion separators. On the other hand, the chemical stability is good because it has more than 90% for all membranes. Therefore, the studied separators are an interesting candidate to be tested in bioelectrochemical systems.

Author Contributions: Conceptualization: S.A.M. and R.B.S.; Methodology: R.B.S., S.A.M. and H.P.; Software: S.A.M. and H.P.; Validation: S.A.M., R.B.S., and P.L.; Formal analysis: S.A.M.; Investigation: S.A.M., R.B.S., C.C., and C.A.; Resources: D.A.; Data curation: S.A.M.; Writing—original draft preparation: S.A.M.; Writing—review and editing: R.B.S., C.A. and C.C.; Visualization: S.A.M.; Supervision: R.B.S.; Project administration: D.A.; Funding acquisition: D.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

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

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