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*Proceeding Paper*

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

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**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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## 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 (Sun et al., 2022).

The discharge of wastewater into rivers or seas causes a serious environmental impact, as it may contain organic pollutants, medical waste and bacteria (Sun et al., 2022). 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 oxidising organic matter in microbial fuel cells or microbial electrosynthesis cells, respectively (Al-Sahari et al., 2021). 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 (Borja-Maldonado & López Zavala, 2022).

However, studies indicate that certain biopolymers may be candidates as potential materials for PEMs (Jenani et al., 2024). 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 ($FeSO_4.7H_2O$, 99.5%), hydrogen peroxide ($H_2O_2$, 30%), acetic acid ($CH_3COOH$, 99.8%) and Mueller Hinton Agar Mueller Hinton were purchased from Merk KGaA. Chitosan (Q) and chitosan derivatives Q1 (chitosan + Salicylaldehyde) and Q2 (chitosan + methoxybenzaldehyde) were provided by (Caisapanta, 2023). 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 (Xu et al., 2022). 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 (Bahamonde Soria et al., 2020).

### *3.3. Water Holding Capacity*

This property was determined by gravimetry, based on the procedure of (Xin et al., 2023). The following formula was used to determine the percentage of water retention:

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

where X 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 (Madih et al., 2022). 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 (Bahamonde Soria et al., 2020).

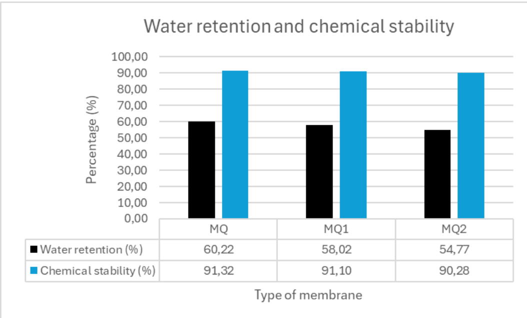
$$R_s = \left(\frac{V - V_0}{I}\right) \cdot A$$

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.

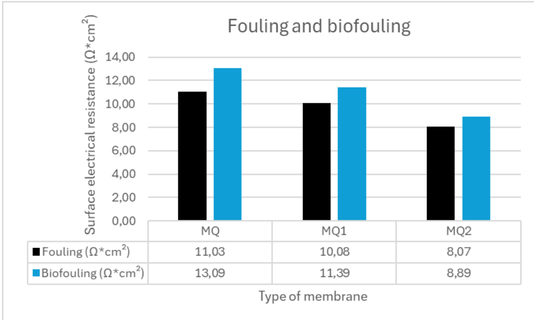
## 4. Results and Discussion

### *4.1. Water retention capacity*

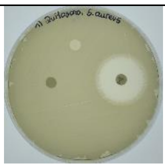
According to (Pupiales, 2023), Nafion membranes have a water holding capacity of 21.8%, and observing Figure 1a it can be deduced that MQ, MQ1 and MQ2 retain more moisture than the Nafion separators. This could be because chitosan has hydroxyl and amine groups that can form hydrogen bridges with water and therefore absorb more water (Wu et al., 2022). 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 because probably the amine group is transformed to imine group and in the case of the Q2 derivative 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 to strong oxidizing conditions as they withstood the Fenton reagent for a period of 7 days (Madih et al., 2022). 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 (Pupiales, 2023).

### 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 (Bahamonde Soria et al., 2022).

According to (Pupiales, 2023) Nafion membranes, for the fouling test, have a surface electrical resistance of 5.31 $\Omega$*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 (Chen et al., 2022).

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 (Chen et al., 2022).

## 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.

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**Data Availability Statement:**

**Conflicts of Interest:**

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