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Optimizing a Novel Cement-Structured Zeolite Membrane for Electrodialysis Desalination System

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Water scarcity is one of the pressing challenges that we are facing as the demand for freshwater increases more than twice the rate of human population growth. As environmental stress of climate change and pollution of freshwater sources are exacerbated by rapid urbanization, there is also a growing interest in developing low-cost technologies to increase the water filtration and desalination capacity in water-scarce regions. For example, the inorganic filtration type of membranes is reported to be advantageous over the polymer-based filtration system in terms of high-temperature stability, low maintenance requirement, and fouling resistance. Thus, this study investigates the potential of cement-structured zeolite produced from corn stover ash to serve as the membrane for the electrodialysis (ED) desalination system. Response surface method was applied using the central composite design to determine the optimal value of sodium ion removal as a function of cement binder-zeolite ratio of 85:15, applied ED voltage of 15 V, and the number of stacked cell pairs of 3. The optimization of the ED desalination system indicates that utilizing synthetic zeolite A from corn stover ash into a zeolite composite membrane is effective at removing sodium ions from the prepared salt solution, yielding an 80.7 percent removal efficiency.

1. Introduction

Man's primary need is to have access to a clean and sufficient supply of water because water essentially serves a vital need in domestic, agricultural, and industrial activities. A consistent access to clean water is considered a core function of countries as they usher in public health, national security, and economic vitality. Despite the fact that three-fourths of the world is covered with water, the world now still considers freshwater shortage as one of the major global concerns that have to be solved. There is a major demand for low-saline water in industrial development and for supplies of safe drinking water, but present natural resources are not sufficient to address this need. This high demand for water and its decreasing supply birthed multiple solutions and alleviation plans like water conservation, water dam construction, among others. However, these solutions and plans proved to be insufficient for such a growing need; this current situation was taken into consideration in water treatment – a focus on the discovery and the development of new ways and techniques to get clean water from the abundant ever-present seawater is done.

Desalination as a water source is very potent and could be a major solution to this global dilemma, however, desalination technologies are very expensive and could cause mounting energy requirements for a given country where they are located (Cohen et al., 2018). One appropriate method for desalination is Electrodialysis (ED), it is one of the most important membrane filtration technologies these days. This process has been widely used in desalination as it removes electrically-charged particles in a given solution by utilizing ion-exchange membranes. More researches are focused on reducing operation cost of desalination plants and have been directed towards development of cost-effective membrane filtration: feed concentration (McGovern et al., 2014), membrane composition (Largier et al., 2017), among others.

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Recent advances on ion-exchange membranes (IEM) were done as these are applied broadly to many industrial applications. The preparations for IEMs proved to be challenging since desirable IEMs should possess high conductivity or low resistance, high-ion exchange capacity, permselectivity, among others. Although a lot of studies have been done before, high-ion exchange capacity is still very much interesting for the present study as one of the primary properties in the removal of sodium ions that is very important in desalination. A research on membranes was made using locally produced concrete as permeable membrane. The study's result showed that dissolved ions from water can move through concrete if there is a pressure gradient, or by diffusion due to a concentration gradient if pressure head is absent. With the aid of an electrical field, ion diffusion becomes accelerated, such as chloride into concrete. The diffusion rate of Cl^- ions is dependent on the applied voltage and the thickness of the concrete membrane. However, sodium ions were found to be less efficient (Abulencia, 2012). Further study needs to be conducted to improve the concrete membrane using natural ion-exchange materials such as zeolites. This study thus aims to develop an alternative IEM with synthesized zeolite A from corn stover ash to the conventional ion-exchange membranes and optimize the ED desalination system containing such membrane. Incorporation of such cement-structured zeolite membrane would serve also as an impetus for an inexpensive and environmentally sustainable membrane for ED desalination system.

2. Materials and Methods

2.1 Cement-Structured Zeolite Membrane

Cement-Structured Zeolite (CSZ) membranes were prepared from binder ratio of Portland cement (CEMEX Type IP) and synthesized zeolite A from corn stover ash in hydrogen form (Pangan et al., 2021) and fine aggregates with 0.50-1.00 mm diameter. A different ratio of binders of Portland cement and synthesized zeolite A (95:5, 90:10, and 85:15) was used. The mass ratio of fine aggregates-to-binder (F/B) of 4:1 and water-to-binder ratio (W/B) of 0.35 were fixed for all mixtures, similar to the study made by Vázquez-Rivera et al (2015) in developing pervious concrete. CSZ membrane specimens were manually mixed and cast using membrane molders. After casting to the membrane molders, the specimens were allowed to set undisturbed for 30 minutes and the specimens were placed in an airtight plastic bag. After 48 hours of curing at ambient temperature, specimens were demolded, and each specimen was further cured for 5 days in the same airtight plastic bag under ambient temperature. It should be noted that the specimens were not cured in water.

2.2 ED Desalination System Efficiency

The efficiency of the CSZ membranes was tested in the ED desalination system. The ED system used in this experiment was ED PCCell 64002 (Gonzalez-Vogel and Rojas, 2020) supplied by PCA GmBH, Germany. It comprises of an ED cell unit with a cell size 110 x 110 mm^2, an active membrane area of 64 cm^2 per membrane, and Pt/Ir MMO coated Ti-stretched metal for anode electrode and stainless steel for cathode electrode; liquid pumps; DC power supply; and containers for electrode rinse, concentrate and diluate. Note that the term "concentrate" and "diluate" are used here to differentiate the streams or solutions in each side of the membrane separation process. For example, a diluate can be a dilute solution or pure solvent which is on one side of the membrane whereas the concentrate is a solution with higher concentrations of salt solution on the other side of the membrane. The result of an ED process is an ion concentration increase in the side of concentrate stream with a depletion of ions in the side of the diluate stream. Figure 1 illustrates the actual set-up of the ED desalination system, respectively. The membrane stack was connected to a DC electric potential and consisted of normal cement-structured as an anodic membrane and cement-structured zeolite as the cathodic membrane, as illustrated in Figure 2. The ED system was controlled in a batch operation mode during the experiments and at room temperature. In this method the prepared salt solution (0.5 M NaCl) initially filled in both concentrate-labeled and diluate-labeled containers was recirculated throughout the concentrate and dilute solution streams for 2 h. A solution of 0.5 M sodium sulfate was used as the electrode rinse solution (Doornbusch et al., 2021) instead of sodium chloride solution, to avoid the production of chlorine or hypochlorite. Concentrate, dilute and electrode rinse solutions were fed into the ED desalination cell at a flow rate of 0.3 mL/s. Samples were taken every 30 min from both concentrate and diluate-labeled containers for testing of pH, temperature and sodium ion concentration. Concentration of sodium ion was determined by Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) method using SPS 7800 (SII).

2.3 Optimization Studies by Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a collection of mathematical and statistical methods that is used to explore the relationships between several explanatory variables and one or more response variables. RSM is widely used in the design of experiment for optimization (Mohd Nasir et al., 2021). Moreover, RSM aims to build an approximate regression model that is close to the real or true regression model wherein the true regression model is unknown (Karimi et al., 2018). In this study, three variable parameters, such as, binder ratio (95:5, 90:10, and 85:15), applied voltage (5, 10, and 15), and number of cell pairs stacked (1, 2, and 3), with three levels each were carried out to examine the % sodium ion rejection, as the experimental design response variable. The central composite method was designed, making 39 runs or samples and Design-Expert® Software V.13 was employed for the statistical analyses.

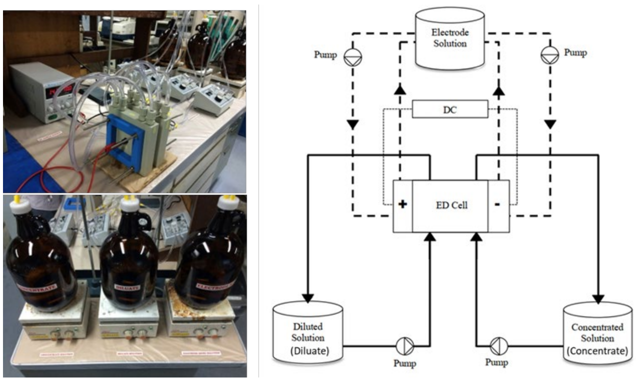


Figure 1: Set-up of the Electrodialysis (ED) desalination system

Figure 2: *Cement-Structured Zeolite (CSZ) membrane stacking in the ED desalination system*

3. Results and Discussion

3.1 Fabrication of Cement-Structured Zeolite (CSZ) Membrane

In the fabrication of cement structured zeolite (CSZ) membranes, a different ratio of binders of Portland cement and synthesized zeolite A (95:5, 90:10, and 85:15) was used. No coarse aggregates were employed because the CSZ membrane's thickness used in this study was 6.0 mm. Smaller fine aggregates of 0.5-1.0 mm are needed to fabricate these CSZ membranes. The presence of zeolite influenced the membrane durability positively in the case of 5-15 %, while a higher proportion of zeolite (20-30 %) significantly affected the durability of the CSZ membranes. The slight decrease in strength or durability due to the addition of zeolite as cement replacement may be explained by the following reasons: hydration reaction of cement is generally faster whereas the chemical reaction of pozzolanic materials is generally slower (Sicakova et al., 2017); and although the zeolite was already ground to higher fineness than cement, its chemical reactivity was still not high enough to compensate for the slower strength development caused by the reduced cement content (Rudzionis et al., 2021). This agrees with the study of Yehia et al. (2017), that an increase in zeolite as cement replacement will have a minor decrease in terms of its durability.

3.2 Central Composite Design Analysis under ED Desalination System

A total of 39 runs were generated using Central Composite Design by varying the three variables, specifically, binder ratio, applied voltage, and number of cell pair stacked. Table 1 illustrates the complete response of all the runs relating to the sodium ion removal (%). The range for the response for % sodium ion removal was between 7.74 % and 80.64 %. The responses were confirmed using a variety of models, including linear, two-factor interaction, quadratic, and cubic. This would establish the model that is most appropriate for the system. According to lack of fit test, a quadratic form is the most suitable for sodium ion removal responses. The proposed source is the model with the highest statistical significance and the least insignificant lack of fit when compared to other models. Based on the analysis of variance (ANOVA) for the response surface quadratic model, it is evident that variables A (binding ratios), B (applied voltages), and C (number of cell pairs stacked) are major factors affecting percent sodium ion removal, as are the interactions AB, and BC. Additionally, it can be established that A, B, C are highly significant ($p < 0.0001$) in terms of sodium ion removal.

R^2 was calculated to be 0.9829 using the quadratic regression model from ANOVA. The adjusted R^2 value of 0.9691 revealed that the model was extremely significant in terms of sodium ion removal. Additionally, the model was determined to be appropriate for prediction based on the range of experimental variables examined, since the predicted R^2 of 0.9149 is in reasonable agreement with the adjusted R^2. The F-value of 2.14 indicated that the lack of fit was not statistically significant in comparison to the pure error, and there is an 11.01 % chance that this value occurred due to noise. As a result, it can be inferred that this model is effective at navigating the design space and that additional optimization of the percent sodium ion removal can be performed.

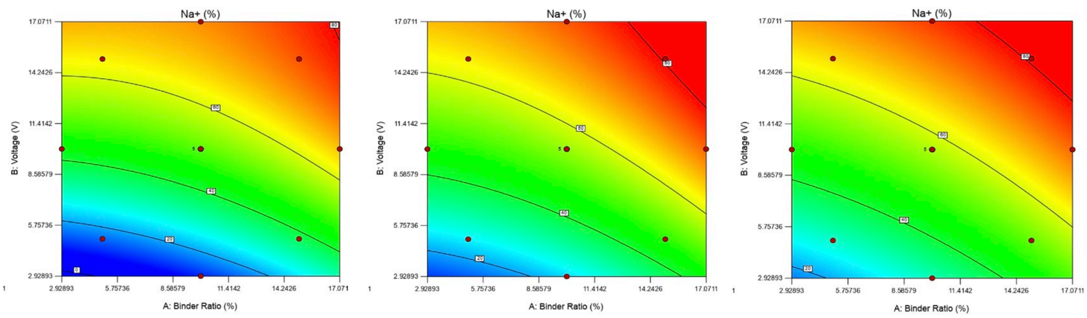
Table 1: Central Composite Design of Experiment for ED Desalination System

Run	Parameters			Sodium (Na^+) Ion Removal (%)
	Binder Ratio (%)	Applied Voltage (V)	Cell Pair Stacked (pair)	
1	17.07	10.00	1	67.78
2	17.07	10.00	2	73.62
3	10.00	10.00	2	52.24
4	15.00	15.00	3	80.64
5	10.00	10.00	1	45.59
6	5.00	15.00	1	62.72
7	5.00	5.00	1	18.75
8	10.00	17.07	1	72.57
9	15.00	5.00	1	38.62
10	10.00	17.07	2	74.43
11	10.00	10.00	1	51.97
12	2.93	10.00	1	41.92
13	5.00	15.00	3	66.89
14	10.00	10.00	3	53.65
15	10.00	10.00	1	52.28
16	10.00	10.00	2	54.38
17	15.00	5.00	2	49.15
18	5.00	15.00	2	65.49
19	2.93	10.00	3	44.01
20	15.00	15.00	2	79.34
21	10.00	10.00	2	58.62
22	10.00	10.00	3	58.52
23	10.00	2.93	3	30.66
24	10.00	2.93	1	7.74
25	10.00	2.93	2	19.72
26	10.00	10.00	2	54.85
27	10.00	10.00	2	55.99
28	10.00	10.00	3	58.12
29	10.00	10.00	1	53.17
30	17.07	10.00	3	73.84
31	5.00	5.00	2	30.70
32	10.00	10.00	1	51.20
33	15.00	15.00	1	71.91
34	10.00	10.00	3	56.78
35	5.00	5.00	3	31.03
36	2.93	10.00	2	41.57
37	10.00	17.07	3	75.44
38	15.00	5.00	3	51.01
39	10.00	10.00	3	57.89

Eq(1) illustrates a calculated equation for percent sodium ion removal using coded components derived from ANOVA. These coded factors can be used to forecast the system's actual response given a set of values.

$$\%\ Na^+\ removal = +\ 54.35 + 9.16 * A + 18.34 * B + 2.83 * C - 1.79 * AB - 2.51 * BC \tag{1}$$

The equation shows that raising a single or interacting component increases the percent sodium ion removal. A negative indication shows a reduction in percent sodium ion removal. The coefficient of the equation represents a factor's reaction sensitivity. The coefficient increases with the percent sodium ion elimination. The ANOVA analysis indicates that the interactions AC, ABC, A^2C, and B^2C are not significant in the reduction of sodium ion. This indicates that the interaction has little effect on the response. Additionally, these would have a negligible effect on the responsiveness of the ED desalination system when it comes to sodium ion removal. According to the model equation, an increase in A (binding ratios), B (applied voltage), and C (number of cell pairs stacked) will have a considerable increase in % Na^+ removal. The capacity of the zeolite /adsorbents for the removal of ions is directly proportional to the mass of the zeolite / adsorbents. This agrees with the conclusions of De Gisi et al. (2016), that there is a direct relationship between the removal of ions and mass of an adsorbents or zeolites. As the mass of zeolite increases in the binder ratio, the % Na^+ ion removal increases. Applied voltage (B), on the other hand, is one of the major or crucial factors for the ED to occur. It will have an extremely significant effect in the increment of the response since the coefficient is high. The dependence on applied voltage can be described by the Nernst-Planck Equation, which models the transport of ions in the membranes as a proportional function of the voltage. This explains how the electric field strength influences electromigration through membranes and demonstrates that in this study in which a voltage of 15V is applied, a higher removal of Na+ ions will be achieved. In terms of number of cell pairs stacked, the linear flow velocity and the limiting current density increases as the number of cell pairs increases. In this study, it was observed that cell pairs of 3 gave the highest % Na^+ removal. This conforms the findings of Jin Min et al. (2020) that the ion transfer rate increases leads to an increase in reaction rate and, in turn, an increase in % removal and reduction of the time required for separation. The AB and BC interaction are statistically significant and demonstrates effect on the result, as illustrated in Figure 3. AB is the binder ratio of synthesized zeolite A in the cathode membrane-applied voltage interaction that has a substantial effect on sodium ion removal. The trend as observed is a decrease in the response. There is a decrease in the ion-exchange membrane's selectivity and a drop in ion flux due to the fouling and scaling which will lead to the decrease in the percentage removal efficiency as the electrical resistance is increased (Ghyselbrecht et al., 2013). BC is the applied voltage-cell pair stacking interaction that has a substantial effect on sodium ion removal. The trend here, as observed, is that increasing the applied voltage and stacking the cell pairs maximizes sodium ion elimination. In principle, the fewer the cell pairs, the higher the efficiency of the current, because the ion separation performance decreases at each incremental step (pair). The efficiency of the current is a measure of the electric power used in the ion separation (Jin Min et al., 2020). The developed model in their research makes it possible to predict separation percent of an ED cell at different operating parameters, similar to the outcome of this study.



(a) Cell pair = 1 (b) Cell pair = 2 (c) Cell pair = 3

Figure 3: Generated contour plots of sodium ion (Na+) removal when binder ratio (in %) and voltage (in volts) were varied for (a) 1 cell pair, (b) 2 cell pairs, and (c) 3 cell pairs

The optimal conditions of binder ratio of 85:15, applied voltage of 15 V, and number of stacked cell pairs of 3 were established using Central Composite Design and the quadratic model for the response surface. The three confirmatory runs evaluated ranging from 78.13 % to 81.94 % were all within the acceptable range or confidence interval. This further establishes the validity of the model developed to simulate the reaction of the system's percent sodium ion elimination. After three tests, the maximum amount of sodium ion is removed around 80.7 %.

4. Conclusions

The optimization of ED desalination system revealed that utilizing synthetic zeolite A from corn stover ash into CSZ membrane is effective in removing sodium ions from the prepared salt solution, yielding an 80.7 % removal efficiency. The binder ratio of 85:15, applied voltage of 15 V, and number of stacked cell pairs of 3 were all found to have an effect on sodium ion reduction. In general, an ED desalination system using CSZ membranes proved to be a viable solution for treating saltwater or brackish water to produce fresh water in the end. Future work will investigate the characteristics of the membrane, to further optimize the ED desalination system.

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