

Forward Osmosis-*Nata-de-Coco* Membrane Reinforced with Nano-silica for Desalination

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Forward Osmosis (FO) is a process that can be used for water treatment with less energy requirement. Previous study has been successful in synthesizing FO membrane from *nata-de-coco* (NDC). Its strength still needs to be improved. This study explored the modification of FO-NDC membrane to improve its strength and durability. Composite of NDC/sodium alginate membranes were reinforced with nano-silica powder. Initial modification of the bacterial cellulose (BC) film was done using Sodium alginate (SA) to fill the voids. The cross-linking between the composite layers was induced using two varied concentrations (10 % and 15 %) of calcium chloride (CaCl₂). Results revealed that the most appropriate membranes are the ones prepared by adding 2 % nano-silica powder in the medium for the cultivation of BC film forming a composite with 1 % alginate solution and using 10 % CaCl₂ cross-linking agent. Characterization of the modified FO-NDC membrane yielded an average contact angle of 19.41° proving that the membrane is hydrophilic. The performance of the modified FO-NDC membrane was evaluated in terms of the water flux, salt flux, and percent salt rejection. The laboratory scale FO system used 0.6 M NaCl feed and 2.0 M MgCl₂ draw solutions. A water flux of 3.88 LMH with 89.51 % salt rejection was obtained in the FO experiment.

1. Introduction

The Forward Osmosis (FO) process has several applications, including wastewater reclamation, desalination, energy production, fertigation, and food and pharmaceutical processing. It is gaining attention due to its potential of decreasing energy costs compared to RO and other energy-intensive thermal processes for desalination. This was supported by Shahzad et al. (2017) by presenting a state-of-the-art review on the nexus of water-energy-environment towards an energy-efficient desalination. According to Chun et al. (2017), there are inherent disadvantages to using FO such as lower permeate water flux compared to pressure-driven membrane processes, concentration polarization, reverse salt diffusion, the energy consumption of draw solution recovery, and problems with membrane fouling, which have suppressed its industrial applications.

The present development of nanotechnology led to the exploration of numerous novel nanomaterials to improve the performance of membranes. Cellulosic materials were developed for the manufacture of 'green' nanocomposite materials (Park et al., 2004) and modification is necessary to enhance the separation performance. Organic-inorganic hybrid nanocomposite membranes have significantly higher water flux, mechanical strength, selectivity, stability, and hydrophilicity compared with conventional polymeric FO membranes (Li et al., 2016). An effective combination of nanofibers and nanocomposite materials to procure highly functional hybrid materials with fused organic and inorganic components has been observed in other studies (Ashori et al., 2012). Another potential material that could be utilized for the FO process is bacterial cellulose (BC). It consists of nano-sized fibers free from unwanted components, such as lignin, which occur naturally in the majority of plant-based cellulosic materials. BC manifests superior properties over plant-derived cellulose in terms of surface area, degree of polymerization, wet tensile strength, purity, crystallinity, and nano-structured fiber (Hakam et al., 2013). *Nata-de-coco* (NDC) is a traditional sweet dessert in the Philippines produced by oxidative fermentation by *Acetobacter xylinum*. The potential of NDC as a membrane for

desalination has been explored by Dang et al. (2017), which is attributable to its nano-fiber network structure, tensile strength, moldability, and ability as a separation membrane. They made modifications using SA solution to fill the voids in the BC sheet to create a dense membrane. Though they have successfully fabricated the NDC membrane they did not investigate the strength of the membrane. According to Xie et al. (2009), nanofibers and nanocomposite can be effectively combined to achieve organic–inorganic hybrid materials. Due to the established strengthening power of silica, this study utilized nano-silica to improve the tensile strength and durability of the previously synthesized NDC membrane through the solution impregnation method. The main objective of this study is to fabricate a composite nano-silica/NDC-FO membrane to improve the performance of a previously modified NDC-FO membrane for desalination.

2. Methodology

2.1 Fabrication of FO-NDC Membrane

The BC film was formed following the procedure used in a previous study (Bautista-Patacsil et al., 2020) as shown in Figure 1 with the following modifications: neutralization is usually done by washing the harvested BC with water several times to remove the traces of acetic acid, this time after soaking in water, the BC film was pressed using a 5 kg weight. This process of soaking in water and then pressing was repeated several times until the pH reached 7.

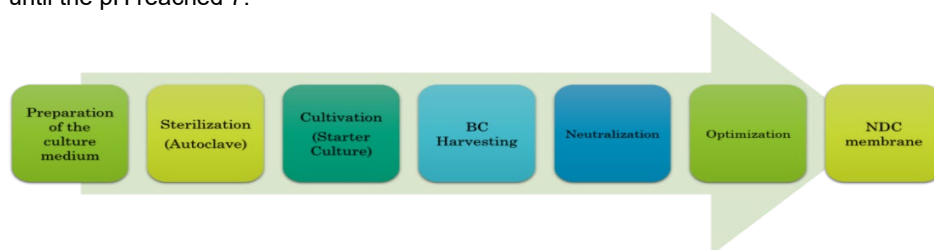


Figure 1: Process flow diagram for the fabrication of FO-NDC membrane

2.2 Modifications of the FO-NDC Membrane Produced

The harvested NDC was transformed into a suitable FO membrane by subjecting it to SA solution and with the application of a cross-linking agent, calcium chloride (CaCl_2). Effects of the amount of CaCl_2 (10 % or 15 % concentration) as well as the addition of nano-silica in 2 different ways are explored as part of the modifications in the fabrication of FO membrane. Impregnation of nano-silica was accomplished in 2 ways: Simultaneous Treatment Method and Integrated Treatment Method. The schematic diagram is shown in Figure 2.

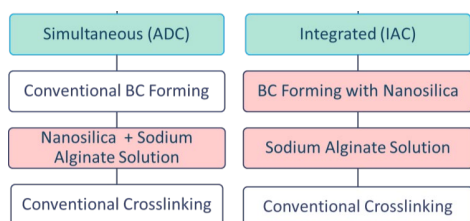


Figure 2: Schematic diagram of the 2 ways of nano-silica impregnation

For the Simultaneous Treatment Method, standard fabrication of NDC was done followed by impregnation of nano-silica dissolved in 1 % SA solution, then cross-linked for 2 h. The sampling labels used in Table 1 are A – 1 % SA, B2, B4, B6 – refers to nano-silica powder (0.2 %, 0.4 %, 0.6 %), C10, C15 – refer to CaCl_2 (10 %, 15 %). In the Integrated Treatment Method, nano-silica powder was incorporated during the formation of NDC. The sampling labels used in Table 2 are A – 1 % SA, C – CaCl_2 (10 %, 15 %) I–Integrated Nanosilica Powder (0.2 %, 0.4 %, 0.6 %).

In choosing the most appropriate membrane from the 2 methods used, the employed method of comparison used ratio and summations. If maximum value is desired (Water Flux and Salt rejection), all values per criterion was divided by the highest value. In such a way, the highest value gets 1, while others get a fraction. On the other hand, if the minimum value is desired (Reverse Salt Flux), the lowest value was multiplied by the inverse of all values. The lowest value gets 1, while others get a value less than 1. If the 2 criteria have equal weights, the results are simply added and compared. This was done per batch (Separate and Integrated) and the highest-ranking membrane for each batch was compared in a similar manner.

2.3 Evaluation of the FO-NDC Performance

The fabricated FO-NDC membrane is tested using a laboratory-scale FO system as shown in Figure 3. The feed consists of synthetic seawater simulating a salinity of 35 ppt using 0.6 M NaCl while the draw solution consists of 2.0 M MgCl₂. The feed solution is placed on a top loading balance to determine the change in weight during the full experimental run and the draw solution is placed on a magnetic stirrer to maintain its homogeneity. The solutions were pumped into the FO cell module in a counter-current direction at 200 cm³/min.

The membrane performance is evaluated in terms of water flux, salt rejection, and solute flux. Water flux refers to the transfer of water from the feed to the draw solution. Percent salt rejection refers to the fraction of salt in the feed solution (brine) rejected from passing through the membrane to the draw solution and reverse salt flux refers to the transfer of salt in the draw solution to the feed across the membrane.

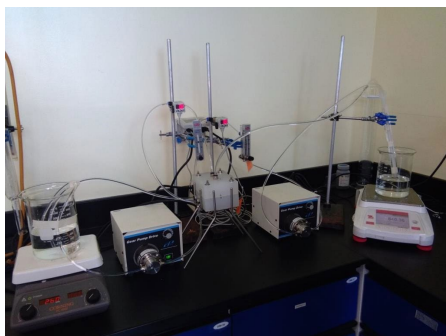


Figure 3: Laboratory-scale setup of the FO system

2.4 Characterization of the FO-NDC Membrane

The hydrophilicity of the membrane is determined using a DinoCapture 2.0 Microscope Imaging Software. Surface wettability conditions can be represented by the contact angle or the wetting angle – the angle formed by the line tangent to the contact point and the horizontal solid surface. Surface morphologies of the membranes are determined using a Generation 5 Phenom ProX Scanning Electron Microscope (SEM) coupled with Elemental Mapping and Line Scan. Chemical functional groups of the FO-NDC membranes are determined using Nicolet 6700 Fourier-transform Infrared (FTIR) spectrometer.

The selected membranes were tested for mechanical strength. Test specimens of varying thickness are prepared. The strips from the composite sheets subjected to the test have a uniform width of 10 mm and a gauge length of 40 mm. The tensile strength of the surface-modified membrane and nanocomposite membrane was measured using Shimadzu Autograph AGS-X, a universal testing machine (UTM), with the following settings: tensile test type; plate shape; and 2 mm/min speed. The pore size and pore distribution of the membrane were examined using a Porolux™ 1000 porometer. The test determined the mean, maximum, and minimum diameters, as well as pore size distribution.

To analyze the FO membrane performance, water flux (Eq(1)), Percent salt rejection (Eq(2)) and Solute Flux (Eq(3)) were determined using the following equations:

$$J_w = \frac{\Delta \text{weight of feed solution}}{\text{water density} \times \text{membrane surface area} \times \Delta \text{time}} \quad (1)$$

$$r = 100 \times \left(1 - \frac{\text{salt concentration in draw}}{\text{initial salt concentration in feed}} \right) \quad (2)$$

$$J_s = \text{solute permeability coefficient}_{\text{membrane}} \Delta \text{concentration} \quad (3)$$

3. Results and Discussion

3.1 Fabrication and Modification of FO-NDC Membrane

The harvested NDC contains lots of water. The application of pressure using a 5 kg weight to the BC film helped in the efficient removal of water during the neutralization process, which easily removed the traces of acetic acid even without the use of NaOH solution. This lessens the use of water for washing and decreases the time dedicated to neutralization as well as removing the use of NaOH to bring the pH to 7.

Modification of the BC film is done using SA and CaCl₂. Sodium alginate consists of α-L-guluronic acid and β-D-mannuronic acid substituent and is an anionic polysaccharide, which contains a carboxylate group (-COO) in its backbone. This fills the voids of the cellulose by forming a hydrogen bond with the free hydroxyl group of the

cellulose. The addition of CaCl_2 causes an electrostatic crosslink between the carboxylic group of the cellulose and CaCl_2 in which the carboxylate group ($-\text{COO}^-$) of the SA form complexes with cations such as Ca^{2+} by ionic bonding as shown in Figure 4. The crosslinking caused the BC film to become dense and to be a suitable membrane while the addition of silica nanoparticles in the BC can make it strong and durable. At higher concentrations of CaCl_2 , higher amounts of Ca^{2+} are present thus more voids are filled by the alginate generating smaller pore size.

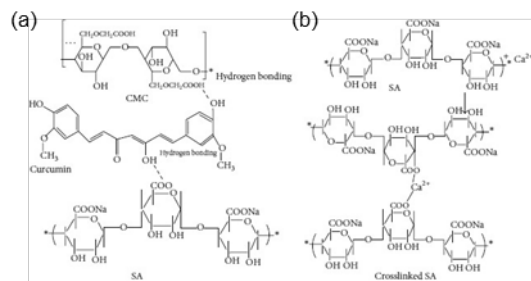


Figure 4: (a) Hydrogen bonding between Cellulose and SA and (b) interaction between Ca^{2+} and SA/Cellulose blend (Riyajan and Nuim, 2013)

The results obtained using the simultaneous treatment batch are summarized in Table 1. The membranes treated with 10 % CaCl_2 produced a higher water flux and percent salt rejection, while in the membranes treated with 15 % CaCl_2 , a lower reverse salt flux was observed. The most appropriate membrane was found to be the fabricated NDC optimized by impregnation of 2 % nano-silica powder in 1 % alginate solution and a standard 15 % CaCl_2 solution. Increased concentration of CaCl_2 allowed for more voids to be filled, hindering the transfer of salt, but not enough to significantly affect the average water flux. The percent salt rejection exceeded 80 %.

Table 1: Summary of membrane performance for simultaneous treatment batch analysis.

BATCH	Ave Water Flux, LMH	% Salt Rejection	Rev Salt Flux, GMH	Max. Stress N/mm ²
AB2C10	4.9205	80.11	26.7324	6.16292
AB4C10	5.1383	80.38	40.6895	4.15939
AB6C10	4.5298	81.06	28.6792	4.30051
AB2C15	3.2422	76.12	15.2244	3.51648
AB4C15	1.8656	68.69	17.2605	4.65483
AB6C15	4.5767	77.40	28.0961	0.73805

In terms of tensile strength, higher stress can be tolerated by the membrane with the least amount of nano-silica reinforcement – AB2C10. This supported the study conducted by Yang et al. (2000) that a higher concentration of silica affects its physical property. Noticed that the tensile strength of membranes fluctuated with the addition of nano-silica reinforcement. The higher the % nanosilica added the lower the maximum stress it can withstand. These suggest that given the right amount, nano-silica is an effective reinforcement. Across the batch, higher stress was tolerated by the membrane with the least amount of nano-silica reinforcement paired with the lesser amount of CaCl_2 . For the Integrated Treatment batch, the results are summarized in Table 2.

Table 2: Summary of membrane performance for integrated treatment batch analysis

BATCH	Ave Water Flux, LMH	% Salt Rejection	Rev Salt Flux, GMH	Max. Stress N/mm ²
I2AC10	3.8841	89.51	13.5767	2.6496
I4AC10	4.8457	85.45	27.0523	3.80407
I6AC10	7.4620	86.20	36.6672	7.56209
I2AC15	8.4535	60.35	162.2705	7.01295
I4AC15	4.7599	56.97	92.2839	5.20712
I6AC15	12.1797	59.88	103.5781	9.22543

The membranes treated with 10 % CaCl_2 produced a higher % salt rejection and gave a lower reverse salt flux. The membranes treated with 15 % CaCl_2 give higher water flux. The most appropriate membrane is that in which 2 % nano-silica powder was added in the medium during the fabrication of NDC, and further modified using 1

% SA and 10 % CaCl₂. The membranes treated with nano-silica upon formation of BC sheets with 10 % CaCl₂ showed >80 % salt rejection.

After analyzing the performance of the tested membrane, though AB2C10 can withstand higher stress, in the FO system, the higher % salt rejection is much desired than the strength of the membrane. Using the method of ratio and summations to compare the 2 methods used, the most appropriate membrane is I2AC10, with 89.51 % salt rejection, 13.5767 GMH reverse salt flux, and 3.8841 LMH average water flux.

3.2 Characterization of FO-NDC Membrane

Only selected samples are characterized. For the Simultaneous Treatment membranes, different nano-silica powder concentrations (0.2 % and 0.4 %) under 10 % CaCl₂ are compared. The bubble point pore size or the maximum pore diameter increased with the addition of nano-silica (38.1 μm vs 38.5 μm), allowing a slight increase in average water flux. The contact angle also increased from 27.40° to 29.34° creating the increase in hydrophobicity of the membrane, which is an effect of nano-silica reinforcement, as observed in several studies in membranes coated by nanoparticles (Rezaei and Samhaber, 2016) and in polymer composites by Gun'ko (2019). It was observed that for different nano-silica powder concentrations (0.4 % and 0.6 %) under the same cross-linking treatment (15 %), additional nano-silica increased the percent salt rejection and average water flux. This scenario recognized the balance between the effects of the nano-silica: increased porosity for water flux and altered hydrophilicity for salt rejection.

The surface morphology of the most appropriate membrane, I2AC10, was analyzed using SEM at 15500x and 40000x magnifications, and the images taken are shown in Figure 5. The white spots shown in Figure 5a indicate that silica is successfully embedded in the membrane while the dark spots as shown in Figure 5b suggest trenches that indicate weave formation. This indicates that the method of surface modification can be used to manufacture the FO-NDC membrane.

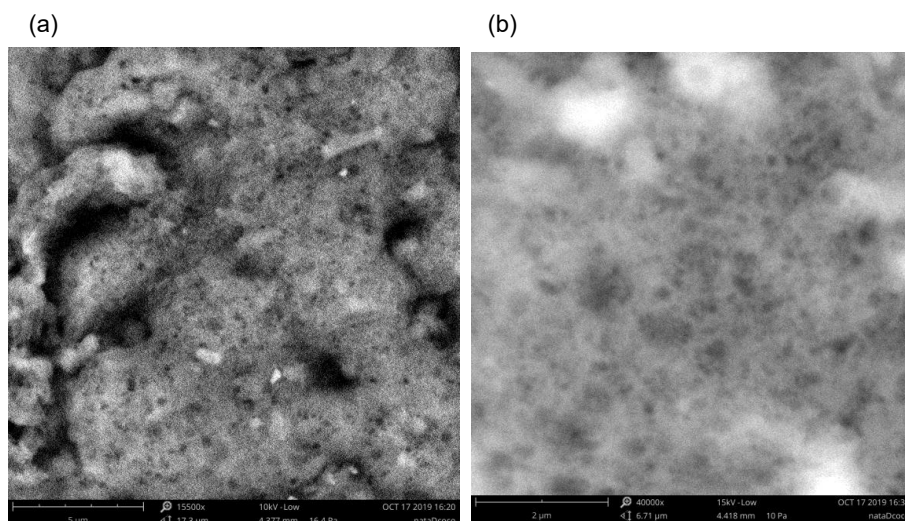


Figure 5: SEM images of I2AC10 at (a) 15500x, and (b) 40000x magnifications

The weave-like formation from fiber cross-linkages of the modified BC membrane is evident at the highest magnification, which suggests that the fabricated NDC membrane is dense – a characteristic of the FO membrane. The embedded silica proved that the addition of reinforcement during the BC forming stage yielded favorable results as represented by the results obtained in the water flux and % salt rejection shown in Table 2. The I2AC10 has an average contact angle of 19.41°, which proves that it is hydrophilic. FO membranes are desired to be hydrophilic since according to Mecha (2018), a hydrophilic membrane has high resistance to fouling, has low roughness, and neutral-charged. It was observed that by increasing the amount of silica added the contact angle increased making the membrane less hydrophilic, which is not desirable.

The fabricated membrane was subjected to FT-IR and results revealed several functional groups formed with Si. These are (RO)₃Si—CH₂CH₂CH₂NH₂, Si—CH₃, Si—CH₂CHCH₂, Si—OR (the identity of the R group was not confirmed), Si—OCH₂CH₃, Si—OCH(CH₃)₂ and CH₃SiO₃. These suggest that the process of impregnation was successful in reinforcing the membrane with nano-silica. Compared with the previous study, the nano-silica reinforced membrane is stronger as it was observed to last longer. Though it was not tested until it starts to break. This can be explored further.

4. Conclusions

This study explored the modification of NDC film and measured its tensile strength to address the gap from previous research on FO-NDC membrane fabrication. Nanosilica powder is used as reinforcements and sodium alginate is used to fill the voids and to form composites with the BC film. Two concentrations of cross-linking agent, CaCl_2 , are used. The performance of the membrane in FO desalination is evaluated in terms of water flux, salt flux, and % salt rejection. Based on the results, a higher concentration of CaCl_2 resulted in lower reverse salt flux and higher % salt rejection. The most appropriate membrane is I2AC10, which is treated with 2 % nano-silica during the formation of BC film and then treated with SA solution and 10 % CaCl_2 . The results showed that I2AC10 has an average contact angle of 19.41° , a water flux of 3.88 LMH with 89.51 % salt rejection. In terms of strength and durability, it was proven that the membrane fabricated could withstand a maximum stress of 2.65 N/mm^2 . The silica-reinforced membrane achieved higher % salt rejection compared to that obtained from previous study with no significant decrease in the water flux. The strength of the membrane was also improved.

Acknowledgments

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