Effect of Graphene Oxide on the Performance of Cellulose Acetate/ Polyethylene Glycol Membrane with Blending Method for Desalination of Brackish Water

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Abstract. Polymeric membrane must be strong during the reverse osmosis process. Carbon-based materials like carbon nanotubes (CNTs), graphene, and its derivative graphene oxide (GO) have strong mechanical strength, high resistance to strong acids/ alkaline and organic solvents, and easy in accessibility. In this study, GO were blendingd into Cellulose Acetate/ Polyethylene Glycol (CA/PEG) membranes prepared by phase inversion method. Performance of the membrane was evaluated from the water flux, salt rejection, and permeability. Morphology, hydrofilicity, tensile strength were investigated by using Scanning Electron Microscopy (SEM), Fourier-Transformed Infra-Red (FTIR) and contact angle analysis, and Dynamic Mechanical Analysis (DMA), respectively. The experiment results show that hydrophilicity and porosity increase with the addition of GO with the addition of 0.005% GO exhibits the highest value of them resulting membrane with better flux and salt rejection values as compared to the GO-free membrane. With the addition of 0.005 wt% GO resulted in salt rejection (%R) 83.3% and flux permeate (F) 2194 L/m2.h and tensile strength of 0.0148 Mpa. Membrane with CA/PEG/GO has more advantages, where GO affects the porosity of the membrane by increasing the pore size such as fingers and reducing the thickness of the wall which will result in increased membrane performance ability.

1. Introduction

The increasing human population combined with exploitation of water resources for domestic purposes, industry, and irrigation has resulted in a shortage of fresh water supply in many parts of the world. Only 0.5% of the 1.4 billion cubic kilometers of water in the world is accessible fresh water, which is furthermore poorly distributed across the globe [1]. Development of synthetich membranes opened up a new avenue to membrane separation tech- nology in the 1960s thus during the past 40 years, membrane separation technology has been widely applied in various fields of industries worldwide Nowadays membrane processes are needed for a wide spectrum of separations including supply of high-quality water for communities and industries (to remove surfactants, microparticles and macromolecules, organic colloidal, dissolved organic matters (DOM) etc. Food and pharmaceutical industries to obtain high-grade products, and removal or recovery of toxic or valuable components from various industrial effluents [2]. The phase inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric membranes. The phase inversion is the most widely used method in the process of membranes where phase inversion has asymmetrical membrane [3], both flat sheet and hollow fiber membrane type [4][5].
Recently, carbon-based materials like carbon nanotubes (CNTs) [6], graphene, and its derivative graphene oxide (GO) [7], have shown notable potential in membrane based separation fields because of their strong mechanical strength, high resistance to strong acids/alkaline and organic solvents, and easy accessibility. Among them, GO was served as one of the emerging nano-building materials for the fabrication of novel separation membrane owing to its distinct two-dimensional (2D) and single-atomic-thick structure, high mechanical strength, high chemical inertness, nearly frictionless surface, and good flexibility combined with large-scale and cost-effective production in solution. Based on these advantages as well as high surface-to-volume ratio structure of GO nanosheets, various GO-based membranes have been widely developed and exhibited great promise in many membrane separation fields such as gas separation, water purification, desalination, and pervaporation (PV) [8]. In recent years, rapid advances have been made in the study of nanoadditives in CA/PEG. These nanoparticles commonly include silica [9], titanium dioxide (TiO2) [10], Al2O3 [8][9], graphene oxide (GO) [13][14], and carbon nanotubes (CNTs) [15–17]. Among them, graphene oxide is a low-dimensional carbon nanomaterial and is widely used in traditional organic film preparations because of its large surface area, surface functional groups, and other characteristics.

GO as another promising type of nanomaterial, has been considered as a novel high efficiency membrane material [18]. Dai et al. [19] studied permeation and ion rejection in GO nanochannels layered by layer using molecular dynamics (MD) simulation and found that laminated GO membranes with reasonable interlayer spacing exhibited high ion rejection capabilities. Meanwhile, GO has also increased research hotspots in hybrid membranes [20]. Wang et al. [21] prepared GO-blended PVDF membranes, and the contact angel decreased from 79.2° to 60.7°, which implied an improved antifouling ability. Kabiri and Namazi [22] synthesized the CA–GO nanocomposite films with 63.88 and 61.92% increase in Young’s modulus and tensile strength, respectively. In a study conducted by Shi 2017 [23], the addition of GO could increase the % rejection value but the permeate flux value was still low.

In the present study, GO were introduced into Cellulose Acetate/ Polyethylene Glycol (CA/PEG) membranes for increased value of performance and characteristic of membrane. The water flux, salt rejection, Scanning Electron Microscopy (SEM), Fourier-Transformed Infra-Red (FTIR), contact angle analysis and Dynamic Mechanical Analysis (DMA) of membranes were investigated to characterize the effect of GO on the characterization and performance of CA/PEG membrane in the reverse osmosis.

2. Experimental

2.1 Material
Cellulose acetate (CA, 30.000 Da, with acetyl content 39.8 %), polyethylene glycol-400 (PEG, 400 Da) are purchased from Sigma Aldrich. Graphene oxide (GO) with bulk density of 1.8 g/cm³, was purchased from Sigma Aldrich. Aceton and Dimethylformamide (DMF) was used as solvent and water as nonsolvent

2.2 Membrane Preparation
Preparation of CA/PEG polymeric membrane was started by mixing 2 gram of CA and 0.5 gram of PEG in 17 mL of acetone-DMF. GO solution was made by dissolving GO in distilled CA/PEG membrane solution with variable GO composition, which are 0; 0.0025; 0.0050; 0.0075; 0.0100; 0.0125 wt% of membrane solvent. Then, the solution mixed using hotplate at 70°C for 12 hours. After that, membrane was casted and immersed in water resulting flat sheet membrane.

2.3 Membrane Characterization
Cross-sectional and surface morphologies of the membranes were observed by using scanning electron microscopy (SEM) observed by using scanning electron microscopy (SEM) (Hitachi, FlexSEM 1000, Japan) with 5 kVA. The membranes were frozen in liquid nitrogen, broken, and sputtered with gold before SEM analysis.

Fourier Transform Infrared (FTIR) spectra was performed at the wave number of 500 - 4,000 cm⁻¹ by using Thermo Scientific Nicolet iS10. The water contact angle between the water and the membranes was directly measured using a contact angle measuring by Camera [Sony a6000] and measuring by
Image J Application for evaluation of their hydrophilicity. De-ionized water was used as the probe liquid in all the measurements.

In terms of membrane’s performance, water permeate flux and salt rejection are measured. Water flux and salt rejection were characterized using cross-flow system. This experimental set-up consists of a reservoir, a pump, valves, pressure gauges, and flat sheet membrane module using Sterlitech CF042A membrane cell with an effective membrane area of 42 cm². The flat sheet membrane with a size of 13 x 15.5 cm was used to analyze membrane’s performance by using synthetic salt water with concentration of NaCl is 1000 ppm. Membrane flux was calculated using the following equations:

\[
\text{Permeate Flux} = \frac{Q}{A \Delta t}
\]  

(1)

Where Q is the quantity of permeate (L), A is the effective membrane area (m²) and \( \Delta t \) is the sampling time (h) [24]. Salt Rejection was calculated using the following equations [25]:

\[
\%R = \left( \frac{C_f - C_p}{C_f} \right) \times 100\%
\]  

(2)

Where R is the salt rejection, and \( C_f \) and \( C_p \) are the concentration of the feed and permeate (ppm).

3. Result and Discussion

3.1. Morphology of Membrane

The results of the FTIR analysis show the spectrum of the groups contained in the CA/PEG/GO membrane. The hydrophilicity character of a membrane can be analyzed from wavenumber at 3500 cm\(^{-1}\) as the -OH group in FTIR in Figure 1 and shows the difference in the character of CA/PEG membrane hydrophilicity by the addition of GO which varies from 0 wt% polymer to 0.0125 wt% polymer. The existence of groups in the FTIR results can be seen from the peak that appears at several wavenumber points.

![Figure 1. Results of FTIR spectroscopy membrane CA/ PEG/GO with blending method.](image-url)
Peak area of -OH of CA/PEG/GO membranes have been calculated from FTIR spectra as shown in Table 1. With the addition of 0.005 wt% GO, it shows the most significant increase in the peak area of the -OH group compared to other variables. Based on the peak area of the FTIR analysis graph, it is known that the addition of GO by using the blending method can increase the CA/PEG membrane hydrophilicity. This is indicated by an increase in peak area of -OH group with the addition of 0.005 %wt GO. Other evidence that can indicate changes due to the addition of GO can be explained by changes in functional groups that occur in the FTIR results, such as -OH and -COC groups [26].

| GO Content (%wt) | Area of -OH peak (area unit) |
|------------------|-----------------------------|
| 0                | 2335.33                     |
| 0.0025           | 1621.67                     |
| 0.005            | 2921.00                     |
| 0.0075           | 1197.33                     |
| 0.01             | 2607.33                     |
| 0.0125           | 1346.33                     |

The results of hydrophilicity analysis for the CA/ PEG membrane with the addition of GO using the blending method can be seen in Table 2. In Table 2, the addition of 0.005 %wt GO exhibit the lowest contact angle values. Lower contact angle leads to the conclusion that, the membrane surface is more hydrophilic in nature. The low contact angle value indicates that the membrane has good surface hydrophilicity because GO which is hydrophilic is spread on the upper surface of the membrane during the phase inversion. This indicates that the surfaces of GO doped membranes are relatively more hydrophilic in nature. This behavior can be explained by the mechanism of action involved during the phase inversion process. During membrane formation, the hydrophilic GO migrates towards the top surface of the membrane as the top layer is more exposed to water (non-solvent). This is also clear from the IR spectra of the membranes which confirmed the presence of -OH group [27].

| GO Content (%wt) | Contact Angle (°) |
|------------------|-------------------|
| 0                | 43.567            |
| 0.0025           | 44.095            |
| 0.005            | 39.517            |
| 0.0075           | 43.095            |
| 0.01             | 43.665            |
| 0.0125           | 43.895            |

SEM analysis was carried out with magnification of 2,000 times and 10,000 times to show the morphological structure of the membrane in the top surface and cross-section area. From the results of the SEM analysis, the morphological parameters observed were pore distribution, pore type, and pore diameter. Pore distribution in the blending method shows asymmetrical tendencies, where the membrane has finger-like structure and sponge-like pores. The existence of these pore variations due to the addition of GO affects the porosity of the membrane by increasing the finger-like pore size and reducing the thickness of the wall which will result in increased membrane permeability capability. The increase in porosity is also due to the nature of GO which is hydrophilic that helps form larger and wider pores. The addition of GO to the CA/ PEG membrane increases the viscosity of the membrane, causing a slower
demixing process. The slow demixing process makes changes to the pore structure of the CA/PEG membrane added with GO [28]. The results of SEM analysis for all CA/PEG/GO membrane variables by the blending method can be seen in Figure 2. The membrane is composed of a dense sponge-like pore in the outermost layer, then forms a finger-like pore in the middle layer separated by sponge-like pore walls.

| GO Content (%wt) | Fracture Surface (2000x) | Zoom in (10,000x) |
|------------------|------------------------|------------------|
| 0                | ![Image](image1.png)   | ![Image](image2.png) |
| 0.0025           | ![Image](image3.png)   | ![Image](image4.png) |
| 0.005            | ![Image](image5.png)   | ![Image](image6.png) |
| 0.0075           | ![Image](image7.png)   | ![Image](image8.png) |
| 0.01             | ![Image](image9.png)   | ![Image](image10.png) |
3.2. Performance of Membrane

The DMA analysis shows that the CA/PEG/GO membrane has the higher tensile strength. It can be seen from Figure 3 that the 0.0075 wt% GO membrane was able to handle more tensile stress before permanent deformation occurred. It could be assumed that a small concentration of GO perhaps did enhance the stress placed upon the membrane. However, a higher concentration had adverse effect on the membrane, thus causing it to fail under less stress [28].

The results of the analysis of salt rejection performance for the CA/PEG membrane with the addition of GO using the blending method can be seen in Figure 4. The best salt rejection performance is 83.3% with addition GO 0.005% wt. While the lowest salt rejection performance is in the addition GO 0.0025% and 0.01 %wt which have a salt rejection value of 33%. On Figure 4, we can see a decrease in salt rejection performance, which is due to the addition of GO causing an increase in pore size which causes more salt to escape. That is because the presence of GO can cause hydrophilic properties of non-solvent which can increase the unstable thermodynamic nature of the membrane, causing nucleation which will increase pore size [29]. The mass transport in Reverse Osmosis (RO) occurs due to the solution-diffusion phenomena. One of the characteristics of RO is dense structure [30]. Reverse osmosis (RO) is a filtration method able to set aside many types molecules and large ions from solution by giving pressure on the solution that is on one side of the membrane selective. External pressure applied on the solution to fight its osmotic pressure. So that the result is water displacement from hypertonic solution to solution hypotonic [31]. The resistance to mass transfer is determined by the thickness of the membrane, the membrane with a high thickness, the permeation will decrease, while if the thickness is thin, the permeation will increase. This asymmetric membrane consists of two layers, namely a pore support
layer with a thickness of 50 μm - 150 μm and a thin and dense layer on the membrane surface and has a thickness of 0.1 μm - 0.5 μm this layer is often called the active layer [31].

![Figure 4](image-url)

**Figure 4.** Salt rejection CA/PEG/GO membranes with blending method.

In the results of the analysis of permeate flux performance for CA/PEG/GO membranes using the blending method shows in **Figure 5**, the highest flux results obtained in the addition of GO 0.005 %wt where membrane variable has a larger macro-void size compared to other membranes. Therefore, the rate of water through a variable membrane with addition of GO 0.005 %wt is greater than that of other membranes. Meanwhile, the amount of GO addition to the CA/PEG membrane with blending method influences the tendency of permeating flux to increase on CA/PEG/GO membrane with blending method as shown on Figure 5. The best variable is the addition of GO 0.005% with Salt rejection is 82%, this is in accordance with research conducted by Shi, 2017 [23], where performance increases with added GO content 0.005%. In this study, it has an increasing of permeate flux value.

![Figure 5](image-url)

**Figure 5.** Permeate flux CA/PEG/GO membranes with blending method.
Conclusion
GO-blended with CA/PEG membranes were successfully prepared using Aceton-DMF as solvent. The prepared membranes displayed enhanced hydrophilicity and porosity, which improved their overall flux and salt rejection as compared to the GO-free membrane. The addition of GO by the blending method contributed to improving the performance of CA/PEG membrane with the best results on the addition of 0.005 wt% GO resulted in salt rejection (%R) 83.3% and flux permeate (F) 2194 L/m².h. The results from this study highlight the role of GO and Acetone-DMF in obtaining a highly porous membrane that provides improved flux and enhanced rejection of salt without compromising on membrane performance.

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