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Fabrication and Characterization of GO-Fe_3O_4/PSF Membrane with Phase Inversion Method

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Abstract
Polysulfones (PSF) are hydrophobic, which can reduce membrane permeability. Permeability can be increase by applying hydrophilic materials such as GO-Fe_3O_4 to the polysulfone membrane so that the membrane is hydrophilic. The research aims to determine the effect of the percentage weight of different material compositions on the hydrophilicity properties of the polysulfone membrane. Membrane fabrication carried out using the phase inversion method where the polymer solution is moulded in a place and immersed in a coagulation bath containing non-solvent. This solvent exchange causes the polymer to form a solid matrix and become a membrane. The results showed that graphene oxide (GO) particles successfully doped with Fe_3O_4 material as shown by X-Ray Diffraction (XRD) analysis at the peak of 35.61° with a magnetite phase. In contrast, Fourier Transform Infrared (FTIR) spectroscopy analysis showed an absorption band characteristic of Fe-O stretching vibrations. The results of the contact angle test on the GO-Fe_3O_4/PSF membrane 0.75 wt% were around 73.17°. The results showed the smallest hydrophobic value and the membrane surface morphology had an average pore size of 333.61 nm so that the addition of GO-Fe_3O_4 composites could increase membrane hydrophilicity.
Keywords: Graphene oxide, GO-Fe_3O_4/PSF membrane, phase inversion method.

1. Introduction

Indonesia has 81,000 kilometres of coastline and a sea area of 5.8 million square kilometres. Indonesia can utilize large quantities of seawater as an alternative raw material to meet the community's clean water needs. One process of processing seawater into freshwater is called the desalination process [1]. Desalination is a technique for reducing salt ions and other ions to the desired level to utilize water according to human needs [2]. The results of desalination can produce freshwater for households and industry [3]. The development of traditional to conventional desalination techniques relies heavily on thermal [4], [5] in separating water from its salts [5]. The desalination technique with lower production costs is membrane desalination because it does not use thermal energy in the process [5].

Membrane desalination utilizes selective properties that depend on the membrane's pore size so that only molecules such as H_2O, which are smaller than the membrane pores, escape the filtration process [6]. At the same time, the particles that do not pass through the desalination filter are hydrate ions with a size of 0.21–2.58 nm [7], [8]. In this case, the hydrophilicity of the membrane and its porous structure plays an essential role in the membrane filtration process. Adding composites into polysulfone membranes through the phase inversion method has shown another strategy to increase the hydrophilicity of the membrane. However, polysulfone is hydrophobic, which can reduce membrane permeability. Permeability can be increase by applying a hydrophilic material to the polysulfone [9], [10] membrane, which causes the hydrophilic ability of the membrane to increase in proportion to the increased material concentration [11].

The addition of hydrophilic materials and adsorbents such as graphene oxide (GO) [9] can reject salt compounds [12] and antibacterial abilities [13]. GO oxide compounds reported to be able to absorb heavy metal ions [14]. The combination of GO with magnetite Fe_3O_4 material ensures that its hydrophilic properties can be maintained [15] to be more effective as an adsorbent material. Fe_3O_4

material also has excellent thermal and chemical stability, which is advantageous in the fabrication of polysulfone membranes [16].

Polysulfone membranes are hydrophobic [9] if modified with hydrophilic materials, which cause the membrane to be hydrophilic [10]. In this study, GO-Fe_3O_4/PSF membrane fabricated using the phase inversion method. Phase inversion is a technique widely used in the manufacture of membranes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis [17]. This membrane shows good hydrophilicity with the permeability in absorbing water can increase along with the increase in the adsorbent properties. Chai *et al*. [18] reported incorporating GO-Fe_3O_4 composites into polysulfone membranes showed a higher hydrophilicity increase than membranes without the composite. Based on some of the previous research has described, this research will discuss the effect of different weight percentages of GO-Fe_3O_4 composites on the hydrophilicity properties of GO-Fe_3O_4/PSF membranes.

2. Method

2.1. Fabrication of GO-Fe_3O_4/PSF Membrane

The synthesis of GO using the hummer method. Five grams of graphite powder and 2.5 grams of sodium nitrate powder dissolved in 120 mL of 97% sulfuric acid under ice bath conditions (freezing point of water), stirring for 30 minutes using a magnetic stirrer. Fifteen grams of potassium permanganate added slowly, then continued with stirring under 20 °C for 30 minutes so that it turned into a purple solution, then continued stirring for 3 hours at room temperature. A brown solution formed at this stage, then 150 mL of distilled water was added at 95 °C and kept stirring for 3 hours. In the next step, a brownish-yellow (light brown) solution added 50 mL of 30% peroxide slowly to remove the manganate compound. In the final stage, solution washed with 1 M HCL and distilled water until neutral (pH≈7), then continued drying at 60 °C for 6 hours.

The GO-Fe_3O_4 composite synthesized using the in-situ method in which the GO powder was sonified in 100 mL distilled water for 30 minutes and added 0.002 mol $FeSO_4.7H_2O$ and 0.004 mol $FeCl_3.6H_2O$ which is an iron salt compound, then stirred until dissolved. The formation of Fe_3O_4 took place simultaneously with the appearance of the GO-Fe_3O_4 composite. The blackish-brown solution formed was sonicated for one hour, and 50 mL of 1.65 M ammonia added, then washed with distilled water three times, followed by drying at 60 °C for three hours.

The GO-Fe_3O_4/PSF membrane fabricate using the phase inversion method (Figure 1). The 15 wt% polysulfones disolve using 85 wt% N-methyl-2-pyrrolidone (NMP) for three hours until homogeneously dissolved. The next step was adding GO-Fe_3O_4 composite particle powder with various compositions (0.25, 0.50, and 0.75 wt%) and sonicated for 15 minutes to form a black homogeneous solution. The resulting solution then printed on a glass plate with a thickness of 0.2 mm rolled using an aluminium rod. The final stage was soaked in distilled water for 24 hours and continued drying for 24 hours at room temperature.

2.2. Characterization of Samples

GO materials and GO-Fe3O4 composites characterized using XRD (Philips type X'pert Analytical XRD with CuK α radiation source) to determine the phase formed and using Fourier-Transform Infrared Spectroscopy (FTIR) (Shimadzu type IR One 8400S) to determine functional groups or chemical compounds bonds. Membrane testing carried out using SEM (FEI Inspect-S50 type) to determine surface morphology, pore diameter, and porosity. The contact angle measurement used the sessile drop method (Goniometer type LSB-1800B). The membrane sample was cut into appropriate sizes (2.0 × 0.5 cm) and affixed to a glass plate with the hydrophilic side facing up.

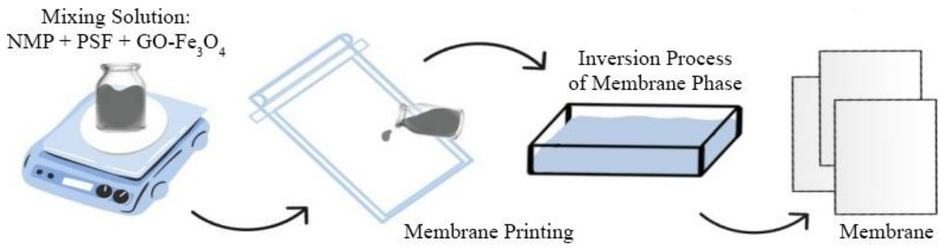


Figure 1. Schematic of phase invertion method.

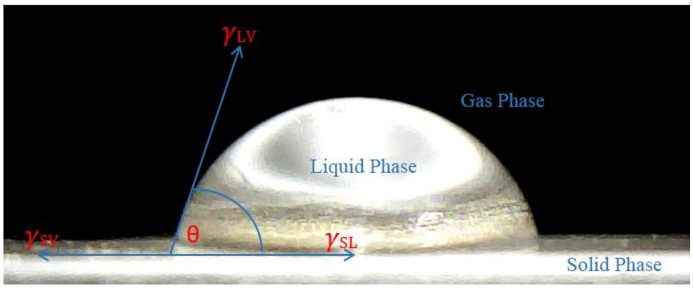


Figure 2. Contact angle of the GO-Fe_3O_4/PSF membrane.

Drops of distilled water (10 ml) were dropped onto the surface of the membrane with a micropipette to produce convex water. The micrograph of the contact angle viewed and analyzed using the Contact Angle Analyzer software to determine the angle value formed from water droplets on the sample surface. The value of the contact angle is a value created from the geometric angle of the liquid by the phase boundary where the liquid, solid, and gas intersect each other, and it is determine by the surface tension between the three phases [19]. The contact angle is expressed by Young's equation as shown in Equation 1,

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}, \tag{1}$$

where γ is the surface tension and S, V, and L refer to the solid, gas, and liquid phases, respectively. The measurement of the contact angle on a plane surface used to determine the hydrophobic or hydrophilic properties of a plane surface. The contact angle of the GO-Fe3O4/PSF membrane shown in Figure 2.

3. Result and Discussion

X-Ray diffraction (XRD) measurements carried out to confirm the crystal structure of GO and GO-Fe_3O_4 composite, as shown in Figure 3a. The results obtained from the XRD analysis were the diffraction pattern of the relationship between the 2θ angle and the scattering intensity. Based on XRD analysis, the position and intensity of all GO-Fe_3O_4 diffraction peaks at an angle of 2θ is 26.52°, 30.17°, 35.61°, 43.20°, and 57.04° can be assigned to the crystal planes of (002), (220), (311), (400), and (442). So, the cubic crystal structure of Fe_3O_4 is confirmed. When GO-Fe3O4 generated, the characteristic peak of Fe_3O_4 remained unchanged, but the diffraction peak for graphene oxide increased to 2θ = 26.52°, which indicates the formation of graphene oxide from graphite after ultrasonication. Furthermore, the diffraction pattern confirmed the appearance of the GO-Fe_3O_4 composite. These results appropriate with the research [20], where the characteristic peak of the GO-Fe_3O_4 composite can be found at the angle of 26°.

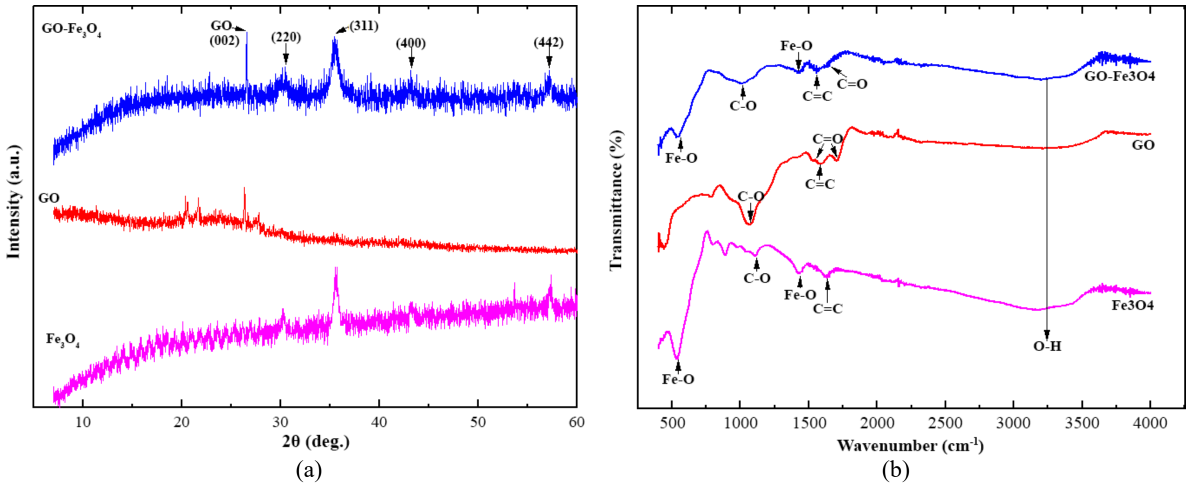
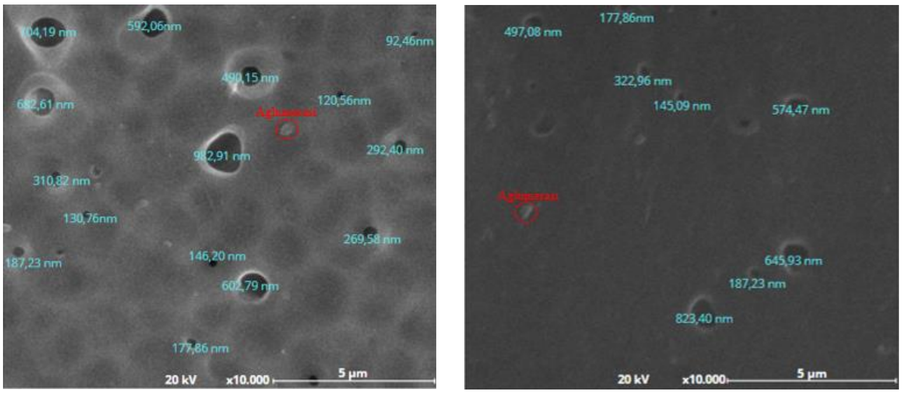


Figure 3. (a) XRD analysis and (b) FTIR spectrum of Fe_3O_4, GO, GO-Fe_3O_4.

FTIR instrument Characterization used to confirm the binding or type of molecular functional groups present in GO and GO-Fe_3O_4 composites. FTIR analysis carried out in the wavenumber of 500–4000 cm^{-1}, wherein that wave range we could identify the characteristic absorption numbers of the functional vibration groups belonging to GO and GO-Fe_3O_4 composites. Spectral data from the FTIR analysis for GO and GO-Fe_3O_4 composites as shown in Figure 3b. In the spectrum of GO-Fe_3O_4 composites, a peak with a wavenumber of 3257 cm^{-1} shows the absorption characteristics of stretching vibrations from the O–H group [21]. Absorption with a wavenumber of 1713 cm^{-1} indicates the stretching properties of the C=O group. A peak indicates the vibration absorption of the C=C aromatic binder at a wavenumber of 1559 cm^{-1}. The stretching of the C-O aromatic group or the epoxide group shown by vibrations that occur at a wavelength of 1111 cm^{-1}. The presence of C=O and C-O functional groups is evidence that the system has the characteristics of reduced graphene oxide [21]. The range of vibrations in the Fe-O bond indicates that iron oxide (Fe2+) is present at a wavenumber of 543 cm^{-1}. The presence of Fe2+ ions as a reducing agent is an essential factor in the redox reaction of the formation of GO-Fe_3O_4. The presence of the Fe-O functional group is evidence that the Fe_3O_4 material successfully mixed in the GO-Fe_3O_4 composite.

Figure 4 shows the SEM results for the surface morphology of the GO/PSF membrane (Figure 4a) and GO-Fe_3O_4/PSF membrane (Figure 4b) at a magnification of 10,000×. These results were used to analyze the size of the membrane pores using Image-J software and showed that the pore diameter sizes of GO and GO-Fe_3O_4 membranes ranged from 87.72–982.91 nm and 145.09–823.40 nm, respectively. In general, the size of the membrane pores depends on the mass transfer rate between the solvent (NMP) and non-solvent (water) phases during the phase inversion process. The addition of the GO-Fe_3O_4 composite causes the size and distribution of pores to increase. This increase is due to the presence of a hydrophilic functional group in the GO-Fe_3O_4 composite, which accelerates the formation of the membrane by accelerating the rate of exchange between the solvent and non-solvent phases, thereby encouraging the appearance of pores [22].

The size of the angle can determine the nature of the material in the form of hydrophilic or hydrophobic. Hydrophilic materials have a contact angle of less than 90°, while the contact angle of hydrophobic materials can found at more than 90°. The results of the membrane contact angle test based on the above description shown in Figure 5. Generally, the lower the contact angle value, the higher the hydrophilicity of the membrane [19]. The average value of the contact angle with the highest value of 80.25° on the PSF membrane continued to decrease as the concentration of the GO-Fe_3O_4 composite increased. The reduced interfacial energy can explain the decrease in contact angle during the phase inversion process due to the exchange of hydrophilic GO-Fe_3O_4 composite solution to the membrane/water interface [22]. This phenomenon due to the weight per cent of GO-Fe_3O_4 composites increases, allowing some composites to move towards the membrane surface to attract water than PSF membranes better. However, there was no significant decrease in the contact angle at higher concentrations indicating that agglomeration may occur at high composite concentrations [23].



(a) (b)

Figure 4. SEM of a) GO/PSF, b)GO-Fe_3O_4/PSF membrane.

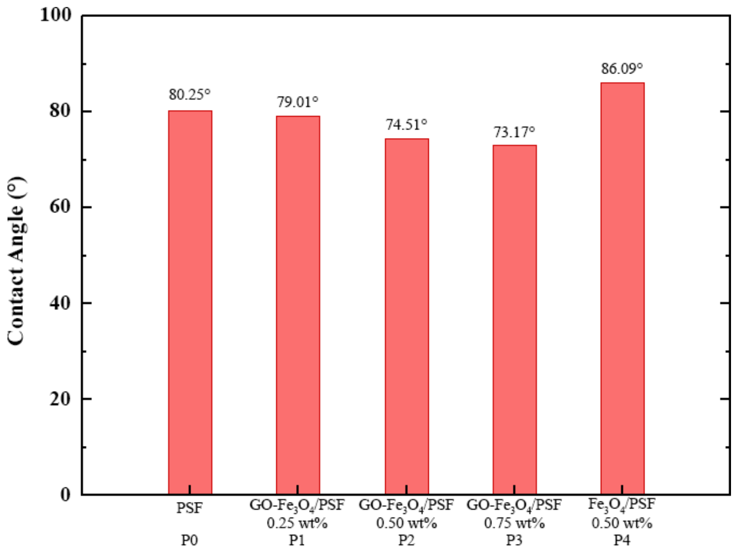


Figure 5. Contact angle of PSF, GO-Fe_3O_4/PSF (0.25, 0.50, and 0.75 wt%), and Fe_3O_4/PSF (0.50 wt%) membranes.

4. Conclusion

The GO-Fe_3O_4/PSF membrane successfully fabricated using the phase inversion method. This study indicates that the GO particles were successfully combined with Fe_3O_4 material, as shown in the XRD and FTIR results. The membrane morphology from the SEM analysis indicates the presence of pores on the surface of 333.61 nm. The addition of a composite concentration with a weight of 0.75 wt % will produce higher hydrophilicity compared to the membrane with a low concentration. So the GO-Fe_3O_4/PSF 0.75 wt % membrane can be a candidate in the water desalination process.

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