Optimization of Polysulfone / Graphene Oxide / Polyethylene Glycol/ Triaminopyrimidine by Using Response Surface Methodology

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Abstract. The addition of polyethylene glycol (PEG), graphene oxide (GO) and triaminopyrimidine (TAP) into polysulfone membranes was used to modify the membrane morphology and increase membrane performance. The central composite design of the response surface methodology was used to predict the maximum permeability and rejection of the PSf membrane. The parameter chosen for this study were PEG (7-14 wt%), GO (0-2.5wt%) and TAP (0-0.5 wt%) concentration. The flat sheet membrane was prepared via phase inversion technique where polysulfone (PSf) was used as base polymer. Various concentration of GO, PEG and TAP were added into the casting solution to produce different membrane composition. PEG was added as pore forming agent for the PSf membrane while inorganic additive such as GO was used to increase the hydrophilicity of the membrane. Besides that, the addition of TAP as a compatibilizer to enhance the physical interaction between GO and PEG. The characterization and surface morphology of produced membrane were analysed via scanning electron microscope, SEM and X-ray diffraction, XRD. The optimization of membrane performance was carried out by using response surface methodology (RSM). The performance of the membrane was analysed by using distilled water for pure water flux test and humic acid for rejection test. The optimized responses, membrane permeability and rejection obtained experimentally were 301.562 Lm⁻²h⁻¹ and 91.562% respectively, with deviation from the predicted value of 7.884 and 0.4381 %, respectively.

1. Introduction
Membrane separation process for water treatment plays an important role to provide a clean and quality water system. Membrane technology are currently being applied to all sorts of fields including energy production, medical, industry, agriculture and food processing. In fact, membrane technology can be considered as the backbone in our industry and human life. As for example, the demand for high quality water has increased from time to time. To meet this demand, manufacturer and developer has manage to come out with a lot of techniques to produce high quality water. However, the most promising technique that has been studied by a lot of researcher is membrane technology process [1]. This process has found to be most suitable in water separation compared to other process such as halogen disinfection, radiation and chlorination. Membrane technology has become quite popular because of they are cheap and fast to fabricate, highly selective, flexible to be integrated with other process, required small space and its separation process will not change the water
phase [1]. Briefly, membrane is a selective barrier that allows the passage of certain constituents and retains other constituents to pass through it. In other word, it acts as a filter. Separation is achieved when the membrane successfully permeating the passing of selective one or more components of a stream while retarding or restricted the passing of one or more other components. Polysulfone (PSf) are the most popular polymer to be used in membrane fabrication due to its good mechanical, thermal and chemical stability [2]. Even though it has good properties, PSf has a hydrophobic nature which make it prone to membrane fouling by the absorption of protein and other biomolecules from the feed stream [3]. Many researchers has studies a lot of alternatives to overcome this weakness. One alternative is via membrane modification. This technique require the incorporation of additive into the membrane formulation which may cause alteration in membrane morphology structure, pore size and its separation layer [1,2]. Additive has shown significant effect on the enhancement of protein rejection and antifouling properties of PSf membrane [4]. Even though a lot of additive studies and achievement in membrane properties is well published in various journals, however the selection of best additive for membrane has yet to be determine.

2. Experimental

2.1 Materials
Membrane were prepared from PSf was supplied from Udel P1700, N-methyl-2- pyrrolidone (NMP) was manufactured from Emplura®; Merck Schuchardt OHG. PEG was supplied from R&M Marketing, ESSEX, U.K. Graphene oxide was prepared via modified Hummers method and TAP was manufactured from Alfa Aesar, Johnson Mothey Company.

2.2 Preparation of graphene Oxide (GO)
Graphene oxide was synthesized from commercial graphite via modified Hummers method. 4g of commercial graphite powder was put into 230 mL concentrated of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) under ice bath. Then, 30g of potassium permanganate (KMnO\textsubscript{4}) was added slowly with stirring for 1 1/2 hours. After that, the temperature of the reaction was increased to 40°C and the stirring continued for another 1 hour. Then 500mL of de-ionized water was added to the mixture and temperature were brought up to 100°C for 45 minutes. 7 mL of hydrogen pyroxide (H\textsubscript{2}O\textsubscript{2}) 30 wt % was slowly added to the mixture with additional of 500mL de-ionized water. The mixture was then diluted with 1:10 HCl solution (200mL) in order to remove metal ions by filter paper and vacuum pump. The suspension was washed several times with distilled water until the filtrate became neutral to remove remaining salt impurities. The final GO was sonicated for 1 hour and drying in vacuum oven at 40°C for 24 hours.

2.3 Membrane preparation
All membrane were prepared by using phased inversion method. PSf weighted at 18 wt% are stirred with 82 wt% solvent NMP for 4 hour with 500 rpm with 60 °C using a mechanical stirrer. After the solution has dissolved completely, additive such as Graphene Oxide (GO) and Polyethylene glycol 400 (PEG) were added into the solution and stirring continued for 30 minutes or until the additive has completely dissolved. The flat sheet membrane were fabricated by pouring dope solution on a glass plate with thickness of 120 μm. Distilled water was used as non-solvent in a coagulation bath. The produced flat sheet membranes were then left to dry for 24 hours in room temperature.

2.4 Characterization of membrane
2.4.1 Scanning electron microscope (SEM)
The surface and cross sectional structures of a few membranes were examine by SEM. The equipment used was a model JEOL JSM6380LA. The cross section of the membrane were prepared by immersed and fracturing the membranes at the temperature of liquid nitrogen manufactured by MOX. All the specimens were coated with a thin layer of gold before scanned with SEM.
2.4.2 X-ray diffraction (XRD)
XRD technique to determine the phase of crystalline material and provide the information on unit cell dimension. The machine used was XRD Bruker D8 Advance.

2.4.3 Permeation flux (PWF)
The pure water flux is a measure of permeability of a membrane and from the knowledge of pure water flux can predict the permeability of the membrane. The formulas to calculate pure water flux are mention as below:

\[ PWF = \frac{Q}{[A \cdot V \cdot t]} \] (1)

2.4.4 Rejection (R)
In this study humic acid was prepared as water rejection. The percentage of humic acid are by using 0.2 g/l of humic acid, 2 liter distilled water and stir by using a magnetic stirrer. The equation solute separation of the membrane:

\[ R (\%) = [1 - (C_p / C_0)] \times 100 \] (2)

2.4.5 Porosity
Membrane was immersed into distilled water for 24 hours at 25°C in order to determine the membrane surface porosity in a dimension of 2cm x2cm. The membrane in wet state was weight, \( W_w \) by using an electronic balance after carefully wiping the entire surface with clean tissue. Then the wet membrane dried in an oven for 50 to 60°C for 24 h. Then, membrane is weighed again in dry state. The membrane surface porosity was calculated using the following equation below:

2.4.6 Tensile strength
Tensile strength was determined by a universal electronic strength measurement (ABC machine). The standard tensile test was referred from American Society of Testing Method (ASTM) designation code of D882-12. In order to measure membrane tensile strength, each type were cut into strips 5 cm long and 1 cm wide. Five specimens were taken from each sample for the measurement and their average value are calculated.

3. Result and Discussion
3.1 X-ray Diffraction (XRD)
The characterization of GO was carried out by using XRD Bruker D8 Advance. Figure 3.1 shows the XRD pattern of natural graphite. From the pattern presented, natural graphite shows a peak at 26.22°. After the synthesization process, GO the obtained XRD pattern was showed the existence of GO as the peak has shifted to 10.9°. This pattern is similar to the GO obtained by Ganesh et al.

3.2 Scanning Electron Microscopy Analysis (SEM)
The Figure. 3.2 shows cross sections of flat sheet membrane containing PEG, GO and TAP. From the figure, it is found that all membranes are having asymmetric structure consisting of a dense top surface layer, porous sublayer and a small portion of sponge-like structure of bottom surface layer. Figure 2 demonstrated that the pore at the top and bottom layer increase with increasing of PEG concentration. The Figure 2 also shows the finger-like structure is shorten with the increasing of PEG concentration as the bigger porous started to growth. This is due hydrophilicity of PEG properties that increased the inflow of water diffusion rate in the polymer solution during phase inversion process and leads to the formation of larger finger-like pores. Similar result was found by Ma et al. Meanwhile, the cross sectional morphology of prepared membrane at different GO concentration. The result shows that the number of finger-like pore at the top layer increases as the GO concentration increased. The membrane bottom layer was noticed to become more porous due to the increased of hydrophilic of GO
content. This condition might be due to the hydrophilic effect of GO that attracted more water and responsible for the fast exchange of solvent and non-solvent during the phase inversion phase which leads to this porous structure at both layers [4]. Figure 2 (c) shows the result of TAP with concentration of 0 wt%, 0.25 wt% and 0.67 wt% with the fixed value of PEG and GO. The cross-sectional and morphology analysis of the effect TAP crystalline characteristic revealed that the finger-like structure at top surface increases and macrovoid start to expand more that restrict the smaller finger-like formation as increases TAP concentration. Similar result was found by Basri et al that using TAP in PES-AgNO₃ [3]. This observation proved that TAP is functioned as a good compatibilizer between GO and PEG.

Figure 1. XRD pattern of graphene oxide
3.3 Response Surface Methodology (RSM) and Analysis of Variance (ANOVA)

3.3.1 Permeability
Figure 3 shows the three-dimensional graph for membrane performance in term of permeability response. Figure 3 (a) shows an effect of PEG and GO weight percentage with fixed TAP concentration of 0.25 wt% and Figure 3 (b) shows an effect of GO and TAP weight percentage with fixed PEG concentration at 10.50 wt% meanwhile Figure 3 (c) shows an effect of TAP and PEG at fixed GO concentration of 1.25 wt%. The result shows that PEG has significant effect to permeability compared to GO at fixed TAP value. The addition of TAP into membrane structure shows that when this concentration increases, the membrane permeability will also increase for both composition of fixed PEG and GO. This proved that TAP was a good compatibilizer of GO and PEG to enhance the physical interaction between polymer membrane and additives that would brings to good performance. Similar result was obtained by Basri et al., that using the additive and TAP as compatibilizer was increased the membrane performance [3,4].

3.3.2 Rejection
Figure 4 shows the three-dimensional graph of membrane rejection performance based on two selected factor. In this study, the effect of PEG and GO weight percentage with fixed TAP concentration of 0.25 wt% was shown in Figure 4 (a). Figure 4 (b) shows the effect of GO and TAP weight percentage with fixed PEG concentration at 10.50 wt% meanwhile Figure 4 (c) shows the effect of TAP and PEG with fixed GO concentration at 1.25 wt%. Both Figure 4 (a) and (c) that demonstrated by increasing PEG concentration reduced the rejection performance of membrane [5]. This is due to PEG function as pore forming agent that definitely increase the pore structure. Therefore, as the concentration of PEG increased, the number of pore and size also increased and thus promotes better permeation and reduce rejection. Meanwhile, in Figure 4 (a) and (b) the present of GO as additives promotes better rejection percentage for a certain range. As shown in Figure 3 (a) and (b), the increase of GO increase slightly the permeability value [6,7]. This result proved that GO has ability to increase the permeability with at the same time maintaining the rejection value which contradict to the PEG effect [8,9]. Thus, GO is a good additive to enhance the membrane performance. Figure 4 (b) and (c), shows the effect of increasing TAP concentration show an increase in rejection value. TAP as compatibilizer able to mix
GO and PEG and that result in good dispersion of GO. These will leads to formation of barrier on membrane and helps increase the rejection percentage [10,11,12].

![Figure 3. 3-D results of permeability](image1)

![Figure 4. 3-D results of Rejection](image2)

### 3.3.3 Optimization of the Membrane Composition

The optimal prediction of the response obtained was at 0.890 desirability. Thus, it can be conducted with PEG (8.74 wt %), GO (2.50 wt %) and TAP (0.50 wt %). The result shows that the most desirable operating condition is 0.890. The desirability value that is closer to 1 is the ideal response [13]. Table 1 shows the prediction and actual obtained. The results presented that the predicted value for permeability was 293.678 and rejection 92.0001. Meanwhile, the actual membrane permeability was at 301.562 and the rejection was at 91.562. The error for permeability was 7.884% and for rejection 0.4381%.

|                | Permeability | Rejection  |
|----------------|--------------|------------|
| Predicted value| 293.678      | 92.0001    |
| Actual value   | 301.562      | 91.562     |
| Error          | 7.884%       | 0.4381%    |

### 4. Conclusion

Flat sheet polysulfone membrane with containing Polyethlene Glycol (PEG), Graphene Oxide (GO) and Triaminopyrimidine (TAP) was successfully prepared via phase inversion technique. The performance of PSf membrane were evaluated and optimized by using RSM approach. The effect of
additive GO in membrane were carefully observed with interaction of other two parameter as it is the main factor in this study. The result found that the optimum composition of GO/PEG/TAP for membrane performance was 2.50 wt %, 8.74 wt %, and 0.50 wt % respectively with desirability at 0.89. The result also obtained that presences of GO/PEG/TAP in polysulfone membrane was changes the microstructure of membrane, enhanced hydrophilicity, water flux, and rejection property of membrane.

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