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OPTIMIZATION AND CHARACTERIZATION OF POLYSULFONE MEMBRANES MADE OF ZINC OXIDE, POLYETHYLENE GLYCOL AND EUGENOL AS ADDITIVES

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Abstract

The aim of this study to investigate the effect of zinc oxide, polyethylene glycol (PEG) and eugenol on the properties of membranes made of polysulfone (PSf). Polysulfone membranes were prepared via phase inversion method using N-methyl-2-pyrolidone (NMP) as a solvent and water as non-solvent. The membranes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), porosity, tensile strength, permeability, rejection and antibacterial test. The results were designed and optimized through a statistical approach using response surface methodology (RSM). The results showed that the use of zinc oxide and eugenol could improve membrane rejection and anti-bacterial property. The membrane permeability was found to increase with addition of PEG. The optimized dope formulation for maximum membrane permeability and rejection was found at 13.14 wt.% PEG 5 wt.% zinc oxide and 0.17 wt.% eugenol. The permeability and rejection obtained for actual value is 866 L $m^{-2}h^{-1}$ and 91.0% respectively, which 1 and 2% difference compared to the predicted value.

Keywords: Additives, Membrane, Morphology, Response surface methodology.

1. Introduction

Membrane separation becomes an attractive alternative for most of separation unit in industrial and commercial use because of its low cost, scalability and low energy

consumption [1]. A highly separation technology of membrane can separate smaller particle as well as able to avoid dangerous contaminate of viruses, fungi and bacteria. Generally, the membrane with an asymmetric and symmetric structure consists of dense top layer which could act as separator and bottom layers that give mechanical strength and provide highly flux rate [2]. Modification of membrane via improvement of membrane structure, mechanical properties and performance has been intensively studied to enhance the membrane filtering process [3-5]. According to previous research works, the use of additive is one of the improvement methods which is frequently used to modify membrane structure such as to improve pore interconnectivity, enhancing pore structure, improving hydrophilicity and surface roughness [6, 7]. Furthermore the strong effect of additives could easily disturb and change the membrane structure formation during phase inversion process by influencing the inflow and outflow of the solvent and coagulant [8]. The changes of membrane structure strongly influence the membrane properties and performance as described previously by many researchers [9-11]. Generally speaking, the additive addition is the simplest and most economical technique to prevent fouling of most hydrophobic membrane.

Polysulfone (PSF) membrane is one of the polymeric materials that commonly used in ultrafiltration as well as nanofiltration membrane. It is of semi-hydrophobic in nature and is popularly used in the applications of pharmacy, biology and medicine due to its high stability on a variety of methods. The advantages of PSF are highly rigidity, stability and creep resistance. Besides, it also exhibits good thermal stability. Polysulfone is used as membrane material because of its stability for high chemical resistance and tolerance wide range of pH. One of the characteristics of PSF is able to acting as a good oxidizing substance on the variety of pH range. This good resistance of polymers in wide pH range also allows the process to operate at temperature up to 80ºC. However due to its hydrophobic nature, PSF membrane is highly susceptible to fouling problem. Thus, many works have been conducted on the PSF membrane modification to reduce the tendency of membrane foulants as well as improving other properties [12]. These studies involve on the additive addition, composition formulation, processing variables as well as the study of kinetic and thermodynamic phase inversion. Among these modification techniques, additive addition is widely used for membrane making. In this work, zinc oxide and eugenol are selected as additive that will be introduced into PSF to form mixed matrix membrane. The present effort focuses on the improvement of PSF-based membrane by incorporating ZnO and eugenol. It is expected that the addition of such materials will not only improve membrane separation performance but also will create synergetic effect of the antibacterial properties.

The used of eugenol is widely applied and known in various applications of medicine due its antibacterial properties and strong antioxidants. It is a natural phenolic constituent of clove oil. Eugenol is widely used as perfumeries, antiseptic, anesthetic and flavoring and also has a widely range of applications in medicine. Preliminary research has shown that eugenol has antibacterial, antifungal, antioxidants, anticancer and insect repellent activities [13,14]. Given its minimal side-effects, low toxicity and non-metabolized residue, eugenol has been widely accepted in many fields such as pharmaceuticals and cosmetics. Thus for antibacterial activity, eugenol will be used in this work to overcome PSF membrane that suffered from bacteria adhesion. The use of zinc oxide will also be

considered in this work since this small inorganic particle not only able to increase hydrophilicity but also offer photocatalytic activity as well as antibacterial resistance [15]. It was observed that antibacterial activity of zinc oxide is effective for several types of bacteria such as Gram-positive and Gram-negative bacteria. In fact, zinc oxide imbedded in solid matrix also can improve mechanical properties and increase membrane hydrophilicy [16].

Previous study has shown that the use of zinc oxide in PSF membrane can reduce the fouling activity, improve the thermal decomposition temperature, water flux and increase membrane porosity [17]. Thus, in order to increase membrane antibacterial resistance and performance, the prepared PSF membrane was integrated with the eugenol and zinc oxide. It is expected this Eugenol-zinc oxide polymer mixed matric membrane could exhibit a better properties, structure and membrane performance. Complex interaction between these two additives with polymer membrane structure would change not only the properties and membrane structure but also affect the rejection and permeability performance of the membrane. Therefore, the right composition of this membrane material with better properties and performance were optimized and studied through response surface methodology (RSM).

2. Materials and Methods

The following subsections will describe the membrane fabrication procedure as well as its surface and cross-sectional characterization using SEM and AFM. The procdure to study the effects of additives at different loading on membrane filtration performance with respect to permeability and solute rejection will also be provided in the section.

2.1. Membrane preparation

The membrane was fabricated using PSF as a base polymer, N-menthly-2-pyrrolidone (NMP) as a solvent and distilled water as nonsolvent. The zinc oxide, eugenol and poly (ethylene glycol) (PEG) were used as additive whereas PEG was used as a pore forming agent. PSF (UDEL P-1700) purchased from Solvay was dried at 100 °C for 1h before used. NMP from Merck was used as a solvent without further purification. PEG with molecular weight 400 g/mol was purchased from R& M chemical. PSF was first mixed with NMP under mechanism stirring for 4 h. Then, eugenol and zinc oxide additive at different concentration (Table 1) was subsequently added followed by continuous stirring and heating at 60°C until the solution was completely homogeneous. After that, the casting solution was ultrasonicated for 1 h to release the bubbles. The membrane solution was cast on the glass plate (support) with a knife and placed in coagulation bath (filled with 2.5 litters of distilled water). Then, the flat sheet membrane was removed and dried at room temperature for 24 h.

2.2. Experimental design

The validity of the second order model for optimizing the variables was tested and generated using Design Expert 7.0. The statistical significance of the second order

regression models was determined by F-value which is a measurement of variance of data about the mean, based on the ratio of mean square of group variance due to error. The analysis was done for two responses - permeability and rejection. In the data analysis, the mathematical model selected from centre cubic design (CCD) had the highest polynomial order with significant terms. The runs summarized in Table 1 shows the CCD of experiments with three input variables and two responses. In order to verify the model, five confirmation runs were conducted on the optimized dope formulation. The actual and predicted values were compared and the errors were calculated. In this study, the performance of membrane with respect to permeability and rejection properties will be evaluated and optimized using RSM. The morphology, surface roughness and antibacterial properties were also characterized to support the results.

Table 1. CCD of the experiments for membranes modified with ZnO/Eugenol/PEG.

Run	Zinc Oxide (wt.%)	Eugenol (wt.%)	PEG (wt.%)	Permeability (Lm^{-2} h^{-1})	Rejection (%)
1	0	0	7	81	85
2	5	0	14	855	86
3	2.5	2.5	10.5	716	85
4	5	0	7	86	87
5	2.5	2.5	10.5	715	88
6	5	5	14	133	95
7	0	5	14	517	81
8	0	5	7	126	89
9	2.5	2.5	10.5	613	83
10	5	5	7	78	97
11	0	0	14	817	75
12	0	2.5	10.5	332	80
13	6.7	2.5	10.5	516	97
14	2.5	0	10.5	768	87
15	2.5	6.7	4.61	512	96
16	2.5	2.5	16.39	159	89
17	2.5	2.5	10.5	817	90
18	2.5	2.5	10.5	615	87
19	2.5	2.5	10.5	546	88
20	2.5	2.5	10.5	517	85

2.3. SEM analysis

The cross section of membrane samples was characterized and examined using a JEOL JSM-6380LA scanning electron microscope (SEM). The cross sectional area of the membrane was prepared by immersing the membrane in liquid nitrogen followed by facturing. All the samples were coated with a thin layer of gold using JEOL FINE AUTO coater before scanning to improve sample conductivity. The scanning process was carried out at 15 kV under the scanning magnification ranging from 500 x to 2000 x. Meanwhile, the surface morphology of the membrane was analysed by using emission scanning electron microscope (FESEM JSM 7600F). The membrane samples were cut into pieces (3 mm width

and 10 mm length) and mounted on a metal plate with carbon paste and gold-coated prior to FESEM analysis.

2.4. Atomic force microscopy

The membranes surface roughness was characterized using the XE-100 Park system of atomic force microscopy (AFM) in a dynamic force. The membrane samples were dried at room temperature prior to surface measurement. The membrane was then cut into small pieces (1cm x 1cm) before placing on specific sample holder of the scanner tube. The outer surfaces of the membrane were determined within the scan size at 5 μm × 5 μm. The laser beam of AFM was focused on the spot area to characterize the value of the mean roughness parameter (R_a)

2.5. Membrane performance

The pure water flux, rejection and fouling test were measured using membrane permeation testing unit. The flat sheet membrane was cut to a circular disk before placing in membrane cell. The membrane was first compacted at 5 bar in order to achieve steady state condition before any measurement. Water flux and rejection of membrane were then evaluated at 2 bar. The value of water flux, J was recorded for every 10 min using the following equation.

$$J = \frac{Q}{A \times \Delta t} \quad (1)$$

where PWF is the pure water flux $\left(Lm^{-2}h^{-1}\right)$, Q is the permeate volume (L), A is the membrane area (m^2), and Δt is the time (h). The rejection measurement was carried out using humic acid (HA) solution with concentration of 0.2 g/L. The rejection result of UV_{254} and TOC was calculated using Eq. (2).

$$R(\%) = \left[1 - \left(\frac{C_p}{C_F}\right)\right] \text{ x } 100 \quad (2)$$

where C_p is solute concentration in permeate stream C_F is solute concentration in feed stream.

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2.6. Antibacterial activity

Disk diffusion technique was used to measure antibacterial performance of membrane against *E-coli*. The membrane sample was cut into circular disc and autoclaved. The samples were then put on bacteria culture before being incubated for 24 h at 37 ºC. The antibacterial activities were measured by examining the formation of inhibition ring around the disc.

3. Results and Discussion

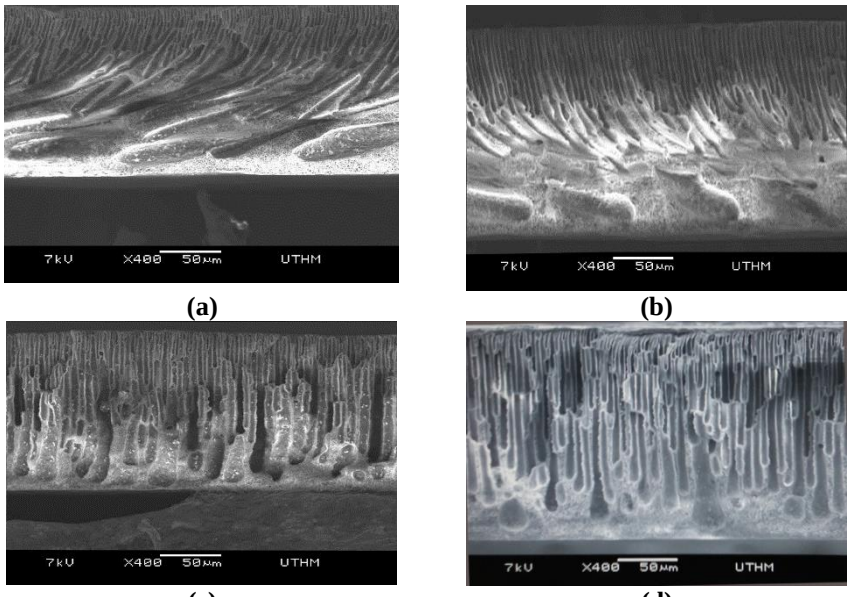
The findings of this work will be first discussed based on the membrane images obtained from SEM and AFM with respect to cross-sectional and surface morphology. It is followed by the discussion on the membrane filtration properties in terms of permeability, rejection and anti-fouling resistance. The in-depth analysis on the relationship between additives and membrane properties will be also carried out before final conclusion is made.

3.1. Scanning electron microscopy analysis

Observation was conducted on all samples with different composition of additive. Image for sample Run 1 shows the amounts of PEG is at higher concentration (Fig. 1(a)) at 7 wt% meanwhile images for sample Run 4 and Run 8 (Fig. 1(b) and (c)) show the addition of hydrophilic (zinc oxide at 5 wt%) and hydrophobic (eugenol at 5 wt%), respectively. Image for sample Run 10 (Fig. 1(d)) referred to the mixture between zinc oxide and eugenol. Comparison of SEM images between sample Run 1 and Run 4 shows hydrophilic zinc oxide is able to create smaller finger-like structure at top surface layer compared to the hydrophilic PEG.

Figure 1 also shows the asymmetric structure of membrane with smaller finger-like structure at top surface membrane and bigger porous structure at bottom layer. Similar result was reported by Hong and He [17] in which zinc oxide was used as additive in PEG membrane. Additive of zinc oxide with strong hydrophilic properties has tendency to attract more water during phase inversion and this results in faster demixing and better porous network compared to PEG additive alone. Whereas the hydrophobicity of eugenol tends to create a thick top dense and bottom layer owing to the delayed demixing process.

Mixture of both eugenol and zinc oxide has resulted in a homogenized structure by inhibiting slightly slim dense layers with more finger-like structure at top layer and higher porous network at bottom layer. This indicates relatively fast demixing process. In fact, the sample run 10 shows the combination effect of hydrophilic zinc oxide and hydrophobic eugenol along with PEG as pore forming agent.



(a) **(b)**

(c) **(d)**

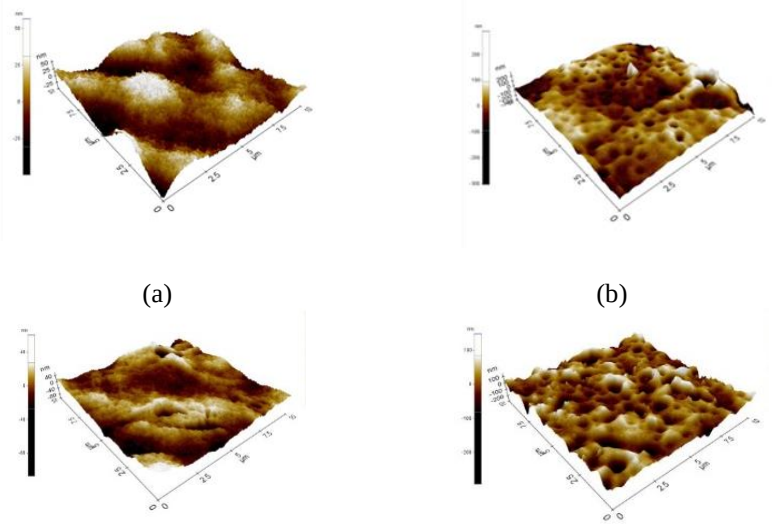
Fig. 1. SEM cross sectional images of PSF membrane made of different additives at different loading, (a) 7 wt.% PEG (Run 1), (b) 5 wt.% zinc oxide (Run 4), (c) 5 wt.% eugenol (Run 8) and (d) 5 wt.% zinc oxide and 5 wt.% eugenol (Run 10).

3.2. Surface roughness

AFM was used to identify the effect on surface roughness of the membrane made of various additives at different composition. The effect of hydrophilicity of zinc oxide and PEG is obviously shown in Fig. 2 with higher surface roughness observed in the sample Run 8, Run 10 and Run 1.

Sample Run 4 shows the highest surface roughness, revealing the strong hydrophilicity of zinc oxide that tends to create faster demixing. Sample Run 8 which consists of hydrophobic additive shows the existence of smoother surface area which can be related to the delayed demixing as discussed in previous section. Combination of the hydrophilic and hydrophobic properties has generated a homogenized structure that also slightly reduces the surface roughness value.

Overall, it is found that zinc oxide addition strongly influences the surface properties by increasing its roughness value. Furthermore, higher concentration of zinc oxide is able to agglomerate and sediment at the top layer, increasing the surface roughness value. Similar observation was also reported by Yunos *et al.* [16] when zinc oxide was used as additive in membrane.



(a) (b)

(c) (d)

Fig. 2. Surface roughness of PSF membrane made of different additives at different loading, (a) 7 wt.% PEG (Run 1) (R_a: 15.70 nm), (b) 5 wt.% zinc oxide (Run 4) (R_a: 36.25 nm), (c) 5 wt.% eugenol (Run 8) (R_a: 10.55 nm) and (d) 5 wt.% zinc oxide and 5 wt.% eugenol (Run 10) (R_a: 31.16 nm).

3.3. Antibacterial activity

Antibacterial test in this experiment was conducted based on three different values of PEG (7 wt%), zinc oxide (5 wt%) and Eugenol (5 wt%). The objective in conducting this experiment was to identify the antibacterial effect on the modified membrane specifically for E-*coli.* Figures 3(a) to (d) show the result of membrane made of 7 wt% PEG, 5 wt% zinc oxide, 5 wt% eugenol and 5 wt% zinc oxide/5

wt% eugenol, respectively. As a comparison, only the sample with PEG does not show any inhibition ring. Sample with combination of zinc oxide and eugenol has displayed a large inhibition ring. This observation revealed that zinc oxide and eugenol could act a good antibacterial agent for membrane separation.

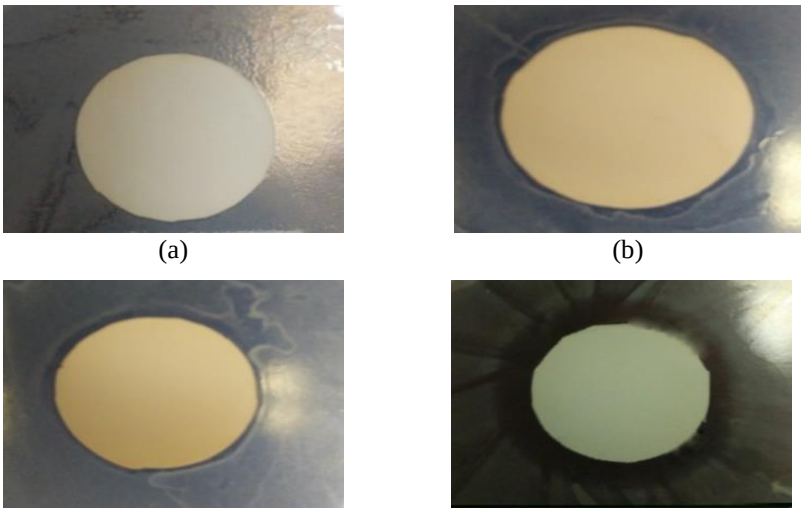


Fig. 3. Results of membrane for antibacterial activity using agar diffusion method, (a) 7 wt.% PEG (Run 1) (No thickness of inhibition ring), (b) 5 wt.% zinc oxide (Run 4) (2-mm thickness of inhibition ring), (c) 5 wt.% eugenol (Run 8) (2-mm thickness of inhibition ring) and (d) 5 wt.% zinc oxide and 5 wt.% eugenol (Run 10) (6-mm thickness of inhibition ring).

3.4. Membrane permeability and rejection

This study is investigated the interaction between PEG, zinc oxide and eugenol using response surface modelling on permeability and rejection. The ANOVA results for each response are shown in Tables 2 and 3. All ANOVA results were obtained after backward regression elimination at alpha of 0.1. Each table shows that PEG, zinc oxide, eugenol, all interaction factors and quadratic factor of PEG, zinc oxide and eugenol has significant model with probability values that associate with F values (Prob. >F) less than 0.5. It is worth to mention that the regression model is statistically significant if $p < 0.05$ at the 95% confidence level. The lack of fit for all response also shows not significant result. This indicates that the model is adequate for the goodness of fit.

The ANOVA result for permeability performance of the prepared membranes is shown in Table 2. As shown, after backward elimination, only interaction between PEG and eugenol is significant in this study. The quadratic regression model with actual factors variable for membrane permeability performance is expressed as follows:

Permeability = -2887.15648+ 90.87769*ZnO +72.34529*Eugenol + 574.9988* PEG -21.79162*Eugenol*PEG -17.25191* ZnO^2 +24.95767*$Eugenol^2$-22.01745*PEG

with subjected to : 7<PEG<14 wt.%, 0<ZnO<5 wt.% and 0< eugenol<5 wt.%.

Table 2. ANOVA results for membrane permeability.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1118101	7	159728.7	5.717564	0.0043	significant
A-ZnO	1404.344	1	1404.344	0.050269	0.8264	
B-Eugenol	60439.95	1	60439.95	2.163476	0.1671	
C-PEG	373868	1	373868	13.38278	0.0033	
BC	369349.8	1	369349.8	13.22105	0.0034	
A^2	97145.43	1	97145.43	3.477366	0.0868	
B^2	90046.3	1	90046.3	3.22325	0.0978	
C^2	480008.8	1	480008.8	17.18214	0.0014	
Residual	335238	12	27936.5			
Lack of Fit	267686.3	6	44614.38	3.962686	0.0591	not significant
Pure Error	67551.71	6	11258.62			

Table 3. ANOVA results for membrane rejection.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	519.2241	4	129.806	19.91381	< 0.0001	significant
A-ZnO	290.3999	1	290.3999	44.55085	< 0.0001	
B-Eugenol	122.8175	1	122.8175	18.84168	0.0006	
C-PEG	38.16382	1	38.16382	5.854791	0.0287	
AC	28.125	1	28.125	4.314715	0.0554	
Residual	97.77588	15	6.518392			
Lack of Fit	64.06159	9	7.117955	1.266755	0.3999	not significant
Pure Error	33.71429	6	5.619048			

The contour plot and interaction plot for PEG and eugenol at constant concentration of zinc oxide is shown in Figs. 4 and 5. At low concentration of PEG (7 wt%), permeability of membrane increases slightly as concentration eugenol increases. However, at high concentration of PEG (14 wt%), membrane permeability decreases significantly as eugenol concentration increases. The highest permeability could be obtained at low concentration of eugenol and high PEG

concentration as depicted in contour plot (Fig. 4). In this study, PEG is responsible to increase pore formation in membrane which provides a good path for permeability mechanism. On the other hand, eugenol is used to provide better interaction between hydrophilic zinc oxide and PSF. However, eugenol possess hydrophobic characteristic which will reduce water adsorption on membrane surface and decrease membrane permeability. Thus, optimizing amount of eugenol is necessary in order to obtain membrane with high permeability performance.

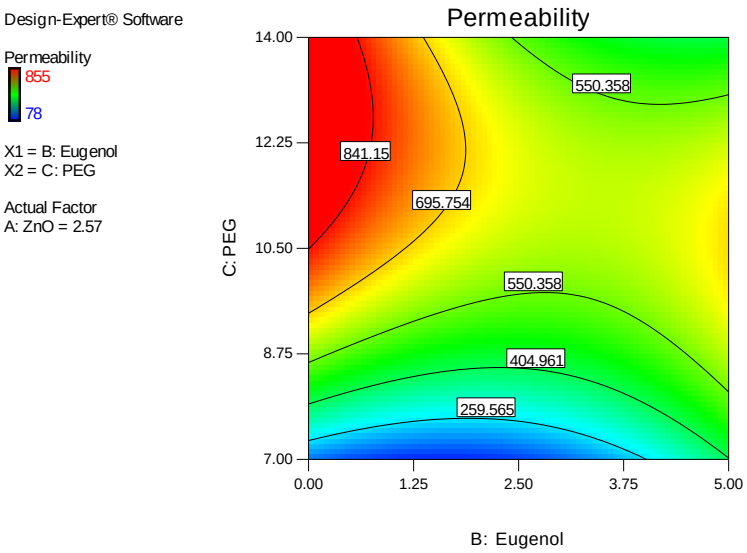


Fig. 4. Contour plot for interaction between eugenol and PEG.

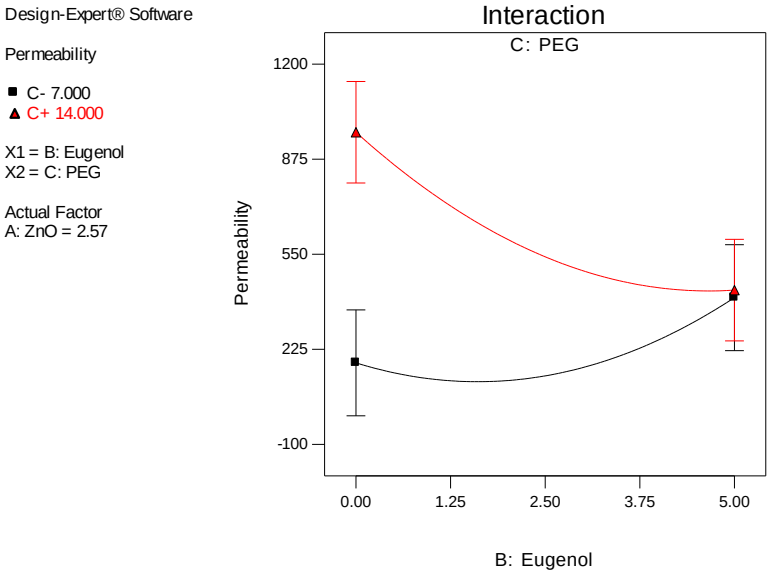


Fig. 5. Interaction plot between eugenol and PEG for membrane permeability.

Since zinc oxide does not have significant interaction between eugenol and PEG, the influence of zinc oxide on membrane permeability able to be observed on one factor analysis at constant concentration of eugenol and PEG as shown in Fig. 6. The result shows that membrane permeability increases quadratically as concentration of zinc oxide increases. Although zinc oxide is able to improve membrane hydrophilic and permeability, the high concentration of zinc oxide tends to block membrane pores, which result in reduction of membrane permeability. This result is in line with Yunos et al. [16] which used zinc oxide in PSF membrane.

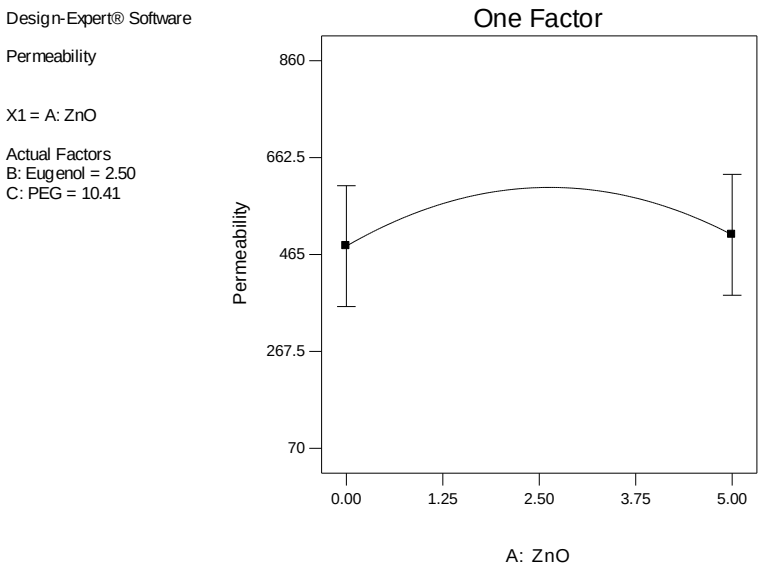


Fig. 6. Effect of zinc oxide on permeability of membrane.

The final ANOVA for humic acid rejection of prepared membrane is shown in Table 3. Interaction between zinc oxide-eugenol and PEG-eugenol were removed during backward elimination due to the p-value is higher than alpha 0.1. The following model with actual factors was developed for rejection of membrane within the limits of the experimental parameter:

Rejection=89.71622-0.26559*ZnO+1.32375*Eugenol*1.02550*PEG+0.21429* ZnO *PEG

with subjected to : 7<PEG<14 wt %, 0<ZnO<5 wt. % and 0< eugenol<5 wt. %.

The influence of PEG, zinc oxide and eugenol on rejection properties of membrane is shown in Figs. 7 and 8. As shown in Table 3, only zinc oxide and eugenol has interaction on rejection performance of membrane. Figure 8 shows the interaction between PEG and zinc oxide at constant concentration of eugenol. It can be observed that the rejection increases as concentration increases for both conditions of PEG (high and low concentration). The contour graph in Fig. 7 suggests that high rejection properties is able to be obtained at high concentration of zinc oxide (5 wt%) regardless of the concentration of PEG used (within the range of

7-14 wt%) in membrane solution. It is expected that zinc oxide is able to improve membrane rejection as reported in previous work [16]. According to Yunos et al. [16], the presence of zinc oxide in membrane will reduce membrane pore size which result in enhancement membrane rejection properties. This study found that although membrane pore is increased with the presence of PEG, the concentration of zinc oxide is dominant factor controlling membrane rejection performance.

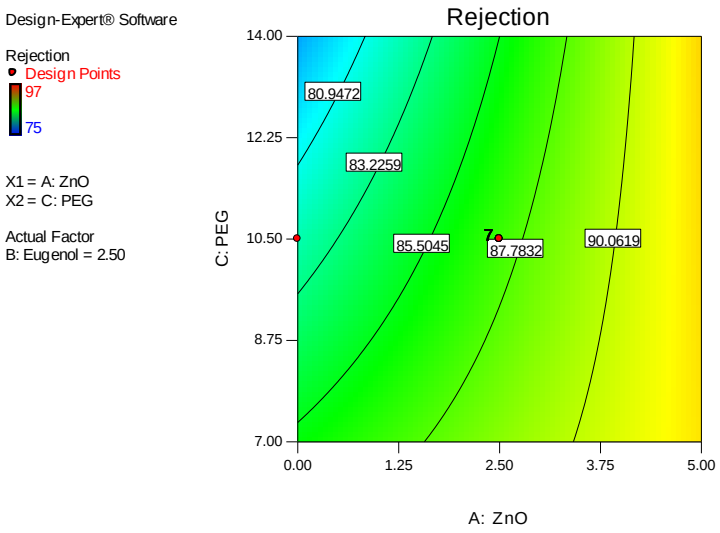


Fig. 7. Contour plot for interaction between zinc oxide and PEG on membrane rejection.

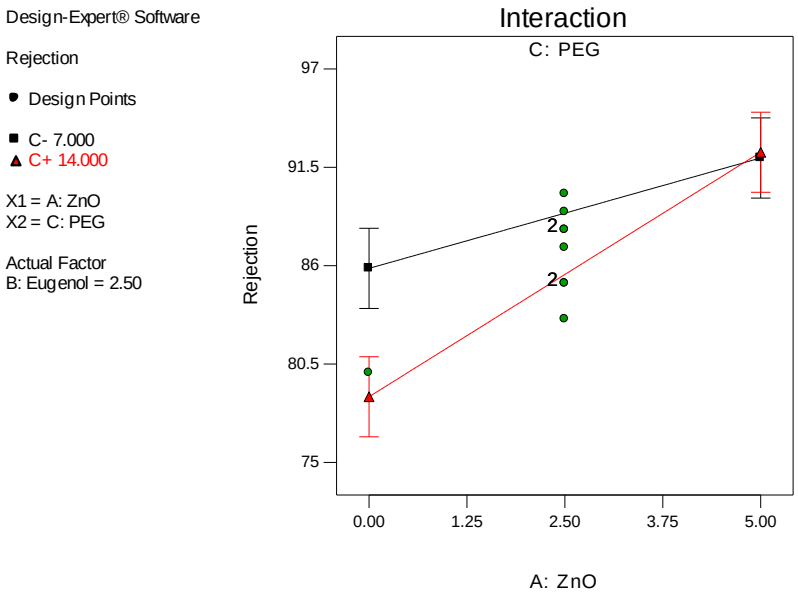


Fig. 8. Interaction plot between zinc oxide and PEG for membrane rejection.

The effect of eugenol on membrane performance is shown in Fig. 9. The rejection performance of membrane is highly increased in the presence of eugenol. As shown in SEM, the presence of eugenol tends to enhance dense layer of membrane. This behavior increases restriction of water transport through membrane and further improves rejection.

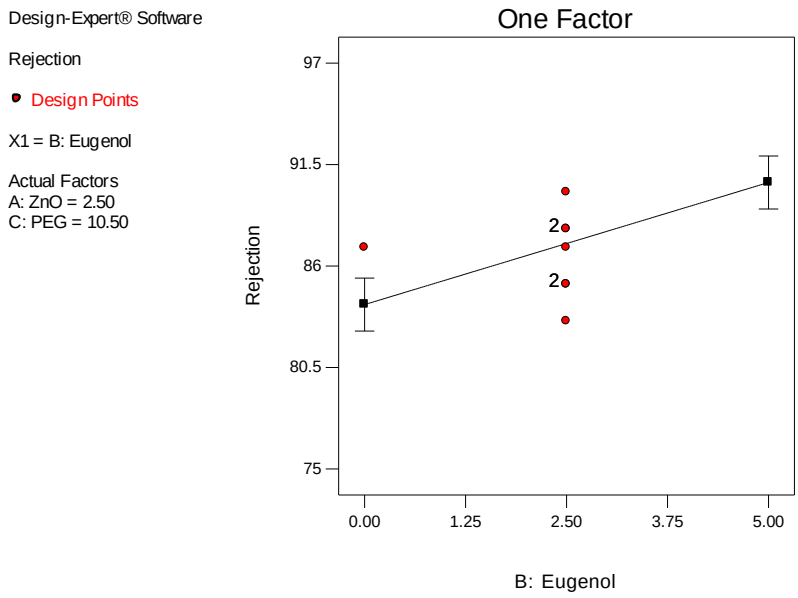


Fig. 9. Effect of eugenol on rejection properties of membrane.

3.5. Optimization of the membrane composition

The ultimate goal of optimization is to produce a membrane with the maximum permeability and highest rejection at given ranges. The local optimized formulation was conducted using Design Expert software for CCD which suggested that at 0.804 desirability, the optimum amount of additives should be designed at 5 wt% zinc oxide, 0.17 wt% eugenol and 13.14 wt% PEG. The desirability function reflects the desirability range for each response that is calculated by the software using function as shown in Eq. (3).

$$\text{Desirability} = (d_1 \times d_2 \times d_3 \ldots \times d_n)^{1/n} = \left(\prod_{i=1}^{n} d_i\right)^{1/n} \quad (3)$$

where d_i is desirability range of each responses and n is the number of response measured. The predicted values obtained after the confirmation run are shown in Table 4. The errors of the data were calculated on the basic of Eq. (4):

$$\text{Error (\%)} = \left(\frac{\text{Actual value} - \text{Predicted value}}{\text{Actual value}}\right) \times 100\% \quad (4)$$

Table 4 shows that the results are in agreement with predicted values with error below 5% for both permeability and rejection. These results verify the validity of model and indicated the existence of an optimal point.

Table 4. Confirmation runs for membrane rejection and permeability.

Run	Predicted Value	Actual Value	Error (%)
Permeability (L $m^{-2}h^{-1}$)	855.03	865.59	1.22
Rejection (%)	89.1	91.0	2.09

4. Conclusions

In this experiment, the right compositions in preparing PSF membrane were successfully determined. PSF membrane modification was conducted by adding different weight percentage of zinc oxide (0-2.5 wt%), eugenol (0-2.5 wt%) and PEG (7-16.39 wt%). The addition of these additives shows significant effect towards membrane permeability and rejection as well structure and anti-bacterial properties. Results from filtration experiments have been further analysed via empirical models that used statistical analysis to predict the optimum condition of the considered factor and response. The point of optimum composition obtained from CCD was PEG (13.14 wt%), zinc oxide (5 wt%) and eugenol (0.17 wt%). The permeability and rejection obtained for actual value is 866 L $m^{-2}h^{-1}$ and 91.0 %, respectively, which are 1 and 2 % off from the predicted values. In this study, the results from the response surface plots show that different weight percentage of additives tends to play different role in affecting membrane structure and filtration performance.

References

1. Asif Matin, Z.; Khan, S.M.J.; Zaidi, M.; and Boyce, C. (2011). Biofouling in reverse osmosis membrane for seawater desalination: Phenomena and prevention. *Desalination*, 281,1-16.
2. Arthanareeswaran, G.; Mohan, D.; and Raajenthiren, M. (2007). Preparation and performance of polysulfone-sulfonated poly(ether ether ketone) blend ultrafiltration membrane. Part I. *Applied Surface Science*, 253, 8705-8712.
3. Abdelrasoul, A.; Doan, H.; Lohi, A.; and Cheng, C.H. (2015). Morphology control of polysulfone membranes in filtration processes: A critical review. *ChemBioEng Reviews*, 2(1), 22-43.
4. Low, Z.X.; Wang, Z.; Leong, S.; Razmjou, A.; Dumée, L.F.; Zhang, X.; and Wang, H. (2015). Enhancement of the antifouling properties and filtration performance of poly(ethersulfone) ultrafiltration membranes by incorporation of nanoporous titania nanoparticles. *Industrial & Engineering Chemistry Research*, 54(44), 11188-11198.
5. Souza, V.C.; and Quadri, M.G.N. (2013). Organic-inorganic hybrid membranes in separation processes: a 10-year review. *Brazilian Journal of Chemical Engineering*, 30(4), 683-700.
6. Liu, F.; Hashim, N.A.; Liu, Y.; Abed, M.M.; and Li, K. (2011). Progress in the production and modification of PVDF membranes. *Journal of Membrane Science*, 375(1), 1-27.

7. Lau, W.J.; Ismail, A.F.; Misdan, N.; and Kassim, M.A. (2012). A recent progress in thin film composite membrane: a review. *Desalination, 287*, 190-199.
8. Mulder, M. (1996). *Basic Principles of Membrane Technology*. Springer Science & Business Media.
9. Vrijenhoek, E.M.; Hong, S.; and Elimelech, M. (2001). Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, 188, 115-128.
10. Rahimpour, A.; and Madaeni, S.S. (2007). Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: preparation, morphology, performance and antifouling properties. *Journal of Membrane Science*, 305, 299-312.
11. Susanto, H.; and Ulbricht, M. (2009). Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives. *Journal of Membrane Science*, 327, 125-135.
12. Harun, Z.; Jamalludin, M.R.; Basri, H.; Shohur, M.F.; Rosman, N.; and Yunos, M.Z. (2013). The effect of synthetic silica to the ultrafiltration PSf membrane. *Jurnal Teknologi (Sciences & Engineering*), 65(4), 121–125.
13. Kong, X.J.; Liu, X.W.; Li, J.Y.; and Yang, Y.J. (2014). Advances in pharmacological research of Eugenol. *Current Opinion in Complementary and Alternative Medicine*, 1(1), 8-11.
14. Li, Q.; Mahendra, S.; Lyon, D.Y.; Brunet, L.; Liga, M.V.; Li, D.; and Alvarez, P.J. (2008). Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. *Water Research*, 42(18), 4591-4602.
15. Yunos, M.Z.; Harun, Z.; Basri, H.; Shohur, M.F.; Jamalludin, M.R.; and Hassan, S. (2013). Effect of zinc oxide on performance of ultrafiltration membrane for humic acid separation. *Jurnal Teknologi*, 65(4), 111-115.
16. Ng, L.Y.; Mohammad, A.W.; Leo, C.P.; and Hilal, N. (2013). Polymeric membranes incorporated with metal/metal oxide nanoparticles: a comprehensive review. *Desalination*, 308, 15-33.
17. Hong, J.; and He, Y. (2014). Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning. *Desalination*, 332, 67-75.