Filtration performance of polyethersulfone (PES) composite membrane incorporated with organic and inorganic additives

A Fathurrahman¹, R Arisandi¹, A Fahrina¹², N Arahman¹³⁴⁵, F Razi¹
¹Department of Chemical Engineering, Universitas Syiah Kuala, Jl. Syeh A. Rauf, No. 7, Banda Aceh, 23111 Indonesia
²Doctoral Program, School of Engineering, Universitas Syiah Kuala, Jl. Syeh A. Rauf, No. 7, Banda Aceh, 23111 Indonesia
³Graduate School of Environmental Management, Universitas Syiah Kuala, Jl. Tgk Chik Pante Kulu No. 5, Banda Aceh, 23111, Indonesia
⁴Research Center for Environmental and Natural Resources, Universitas Syiah Kuala, Jl. Hamzah Fansuri, No. 4, Darussalam, Banda Aceh, 23111 Indonesia
⁵Atsiri Research Center, Universitas Syiah Kuala, Jl. Syeh A. Rauf, No. 7, Banda Aceh, 23111 Indonesia

*E-mail: nasrular@unsyiah.ac.id

Abstract. Membrane separation technology has been extensively applied in separation processes. Improving membrane hydrophilicity plays a significant role in mitigating fouling phenomena and maintain membrane filtration performance. Fouling is a pore blockage of the membrane due to the interaction between hydrophobic molecules and membrane surface that cause membrane flux declining, shorter membrane durability, and increasing energy consumption. Incorporating inorganic particles to enhance membrane hydrophilicity is very attractive nowadays. Inorganic particles have unique characters due to their small size, excellent mechanical properties, and hydrophilic nature. This research aims to improve PES membrane filtration performances by employing nanocarbon and Fe₂O₃ as an inorganic additive. The membrane manufacturing process was carried out using a phase-inversion method, especially non-solvent induced phase separation (NIPS). The resulted membranes were analyzed by filtration soy protein solution to evaluate protein permeation flux and flux recovery ratio (FRR). The result experiments showed that PES/Nanocarbon could provide the highest FRR of up to 76.46%.

1. Introduction
Among a large number of separation technology, membrane filtration is one of the most frequently applied technology for water purification, wastewater treatment, and protein concentration. The advantages of using membrane are high solid retention, high volumetric rate, flexible in process, environmentally friendly, and small footprints [1,2]. Membrane technology classified in different types, including micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), and reverse osmosis (RO) [2,3]. Ultra-filtration (UF) is currently used due to its performance in separating colloids, macromolecules, and particles. The UF membrane should provide better anti-fouling property to maintain permeation stability and energy consumption.

Polyethersulfone (PES) is a polymer that extensively used as membrane materials due to its mechanical and environmental endurance, chemical resistance, and secure processing [4][5]. However,
the character of PES significantly affects on the performance of the resulted membrane. Membrane fouling such as protein adsorption, denaturation, and aggregation occurs due to the hydrophobic nature of the PES membrane surface that caused water flux decline, increase energy consumption, and high maintenance required. Therefore, an anti-fouling should be added into membrane matrices to increase hydrophilicity and reduce membrane fouling. Some methods to modify membrane surfaces are coating, surface grafting, and blending. Among this modification, the blending technique is the most straightforward way to improve membrane hydrophilicity.

Nowadays, inorganic particles are extensively used in membrane preparation through the blending method. The advantages of inorganic application materials provide uniform pores in the membrane surface due to their small sizes, have mechanical and chemical stable properties, and excellent hydrophilicity [6]. Furthermore, the material could enhance the mass transfer, increase selectivity in separation applications, and mitigate fouling phenomena [7,8]. The most common inorganic particles applied in the membrane are TiO$_2$, SiO$_2$, CNT, HNTs, and Al$_2$O$_3$[6,7]. The increasing membrane hydrophilicity can be evaluated by the calculated flux recovery percentage of filtration. In this study, nanocarbon and Fe$_2$O$_3$ was employed to enhance membrane hydrophilicity analyzed by calculating membrane flux recovery of soy protein concentrate.

2. Materials and methods

2.1. Materials

PES with an average molecular weight of 65,000 Da (BASF, Ludwigshafen, Germany) was used as the primary polymer to prepare a flat sheet membrane. Dimethylformamide purchased from Merck KgaA, Germany, was supplied as a solvent to dissolve the polymer. Fe$_2$O$_3$ and nanocarbon were kindly provided by the Physic Science Laboratory and Energy laboratory of Syiah Kuala University, respectively.

2.2. Membrane preparation

For the original membrane, the dope solution is prepared by mixing 16wt% of PES in DMF. In other dope solution, nanocarbon and Fe$_2$O$_3$ of 0.05 wt% was added separately to prepare the modified PES membrane. The detailed composition of the membrane solution is summarized in Table 1. All dope sample is stirred for about 24 hours to obtain the homogeneous solution. After releasing the air bubble, the solution is poured onto a glass plate using an applicator knife with a thickness of 300 μm. The casted solution and the glass plate then dipped in a coagulation bath containing pure water for solidification of the membrane.

| Table 1. Membrane composition. |
|-----------------------------|
| **Concentration (wt%)**     | Code    |
| PES  | DMF | Fe$_2$O$_3$ | Nanocarbon |
| 16   | 84  | -           | -          | M1          |
| 16   | 83.95 | 0.05      | -          | M2          |
| 16   | 83.95 | -           | 0.05      | M3          |

2.3. Membrane filtration performance

Filtration performance of the fabricated membrane was analyzed in terms of water flux and flux recovery ratio (FRR). Soy protein solution with 5000 ppm concentration was filtrated by the formed membranes using a cross-flow module for 190 minutes. The filtration experiment was carried out at constant pressure (1 bar), and the permeate was collected every 10 minutes. Every 60 minutes of filtration, the membrane inside the module was washed using distilled water for 5 mins, then soy protein filtration was continued, and the permeation was measured again. Soy protein flux was calculated by measuring the volume of permeate that passes through the active area of the membrane during a certain time, as shown in Equation (1). Flux recovery ratio (FRR) of the membrane was determined by using Equation (2).
\[ J_p = \frac{V_p}{A \times \Delta t} \]  

(1)

\[ \text{FRR} \, (\%) = \frac{J_w_1}{J_w_2} \times 100 \]  

(2)

Where:
- \( J_p \) = flux of soy protein (L/m².hour)
- \( V_p \) = permeate volume (L)
- \( A \) = membrane effective surface area (m²)
- \( \Delta t \) = permeation Time (hour)
- \( \text{FRR} \) = Flux Recovery Ratio (%)
- \( J_w_1 \) = protein flux before washing (L/m².hour)
- \( J_w_2 \) = protein flux after washing (L/m².hour)

3. Result and discussion

3.1. Soy protein permeability

The soy protein flux test was carried out to determine the rate of separation of soy protein using the PES membrane. Flux is a standard that can be used in evaluating membrane performance before and after use. The membrane is tested on the cross-flow module for 190 minutes, and the permeate rate is recorded every 10 minutes then backwashing every 60 minutes. The PES membranes flux rate of soy protein is presented in Figure 1.

![Figure 1. Soy protein permeation flux of all membranes.](image)

Based on Figure 1, soy protein flux tends to decrease significantly in the first cycle (0-60 minutes) and falls stably in the second and third cycles. It is due to membrane fouling phenomena in the initial filtration caused by adsorption of protein onto the membrane surface. Moreover, the protein molecules blockage membrane pores and consequently decline membrane flux. Backwashing helps to decrease membrane fouling and increase membrane flux. As shown in Figure 1, the pristine membrane (M1) without the addition of additives have a more stable flux, but also have the lowest flux compared to the other membranes while the PES membrane with the presence of inorganic particles; nanocarbon and Fe₂O₃ particles showed higher flux. Inorganic particles are containing oxygen-functional groups promising hydrophilic properties because of high interaction with water molecules [9]–[11]. The addition of hydrophilic particles in membrane solution leads to rapid solidification in the coagulation bath resulting in higher porosity [7], [12]–[15]. As confirmed in our previous research, PES/Fe₂O₃ membrane has longer finger-like structure in membrane sub-layer due to its hydrophilic
nature compared with the nascent PES and PES/nanocarbon membranes [16]. Therefore, in this study M2 and M3 membranes produce higher protein flux than the M1 as a pristine membrane.

3.2. Flux recovery ratio (FRR)

The determination of the flux recovery ratio aims to find out the effectiveness of the reused membrane after filtration. The backwash process is carried out to normalize membrane performance from reversible fouling [16]. In this study, fouling was occurred due to the interaction between soy protein and PES membrane surface that has the same hydrophobic nature. Therefore, flux recovery ratio (FRR) should be evaluated to determine the impact of anti-fouling additives, nanocarbon, and Fe₂O₃ used in this experiment.

Figure 2 displays the flux recovery ratio of all membranes. As shown in Figure 2, the PES membrane, with the addition of 0.05% carbon (M3), has the highest FRR value of 76 %, followed by the PES membrane with the addition of 0.05% Fe₂O₃ (M2) of 66 % while the PES pristine membrane showed the lowest value of FRR. From this study, nanocarbon and Fe₂O₃ given the positive impact to increase membrane anti-fouling property. More hydrophilic surfaces of membrane lowered the interaction between protein molecules and membrane surface, resulting in reversible fouling that easier to clean up by physical cleaning [17,18].

![Figure 2. The flux recovery ratio of PES membranes.](image)

4. Conclusion

Based on the research, the addition of nanocarbon and Fe₂O₃ increases the anti-fouling property of the PES membrane indicated by producing higher protein permeation and flux recovery ratio (FRR). PES/nanocarbon reach the highest value FRR of 76 %; PES/Fe₂O₃ provides FRR of 66 %, while PES pristine membrane showed the lowest FRR of 55.39%.

References

[1] Saleem M, Alibardi L, Cossu R, Cristina M, Spagni A 2017 Chem. Eng. J., 312 136–143.
[2] Saraswathi M S A, Kausalya R, Kaleekkal J N, Rana D, Nagendran A 2017 J. Environ. Chem. Eng., 5 2937–43.
[3] Lin J, Ye W, Zhong K, Shen J, Jullok N, Sotto A, Van der Bruggen B 2016 Chem. Eng. Proc., 107 194-205.
[4] Wang Z, Wang H, Liu J, Zhang Y 2014 Desalination, 344 313–320.
[5] Liu F, Hashim N A, Liu Y, Abed M R M, Li K 2011 J. Membr. Sci., 375 1–27.
[6] Wang X, Wang X, Xiao P, Li J, Tian E, Zhao Y, Ren Y 2016 Colloids Surfaces A: Physicochem. Eng. Asp., 508 327–335.

[7] Arahman N, Mulyati S, Fahrina A, Muchtar S. 2019 Molecules, 24 1-13.

[8] Arahman N, Mukramah, Syawaliah, Maimun T, Bilad M R 2018 Int. J. GEOMATE, 15 50-57.

[9] Shi H, He Y, Pan Y, Haihui D, Zeng G, Zhang L, Zhang C 2016 J. Membr. Sci., 506 60-70.

[10] Rahimi Z, Zinatizadeh A A L, Zinadini S 2015 J. Ind. Eng. Chem., 29 366–374.

[11] Arahman N, Mulyati S, Fahrina A 2019. Mater. Res. Express, 6 (66419) 1-8.

[12] Mavukkandy M O, Bilad M R, Kujawa J, Al-Gharabli S, Arafat H A. 2017. Sep.Purif. Technol., 187 365–373.

[13] Chang J, Zuo J, Zhang L, O’Brien G S O, Chung T S. 2017 J. Membr. Sci., 539 295–304.

[14] Yeow M L, Liu Y T, Li K 2004 J. Appl. Polym. Sci. 92 1782–89.

[15] Arisandi R, Fathurrahman A, Fahrina A, Razi F, Jalil Z, Arahman N. 2020. IOP Conf. Series: Mater. Sci. Eng., 845 1-6.

[16] Zuthi F M R, Guo W, Ngo H H, Nghiem D L, Xia S, Li J, Li J, Liu Y 2017. Bioresour. Technol., 238 86–94.

[17] Jamal S, Chang S, Zhou H 2014 Membranes, 4 319–332.