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Fouling Analysis on Polysulfone/PEG400/ZnO Membrane during Textile Wastewater Treatment

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Abstract

Fouling has become the main problem in long-term application of ultrafiltration (UF) membrane for water and wastewater treatment, significantly reducing membrane productivity. In this paper, fouling on polysulfone-based membrane was analyzed using Hermia's model during textile wastewater treatment. The UF membrane has been prepared by blending polysulfone (PSf), acetone, and PEG400 in DMAc, with ZnO nanoparticles at a concentration of 1% by weight of polymers (PSf and PEG400). The influence of polysulfone concentration (18 and 20 wt.%) and PEG400 (0 - 25 wt.%) on fouling mechanisms was investigated. It was found that the increase of polysulfone from 18 to 20 wt.% reduced permeate flux from 54 to 25 L.m^{-2}.h^{-1}. Vise versa, the increase of PEG400 concentration enhanced the permeate flux. More stable flux was achieved when 18 wt.% of polysulfone was used to prepare the UF membrane. The fouling type in the UF membrane depends on the characteristics of the membrane. A significant flux decline occurred when used 20 wt.% of polysulfone without the addition of PEG400. Smaller membrane pore and higher hydrophobicity due to high polysulfone concentration induced cake layer of fouling on the membrane surface at the first 40 minutes of ultrafiltration. Further increase of operating time, internal fouling was formed due to the movement of pollutants to the permeate side caused by different concentrations. The highest color rejection (86%) was achieved when 25 wt.% of PEG400 was added in 20 wt.% of polysulfone solution.

Keywords: *fouling, Hermia model, ultrafiltration, wastewater treatment.*

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INTRODUCTION

Ultrafiltration (UF) membrane has extensively been used in water and wastewater treatment due to its high effluent quality compared other separation processes as well as low energy requirement (Wenten *et al.*, 2016). Most of the UF membranes are polymeric, which have been modified to produce a membrane with low fouling characteristics and high productivity and selectivity (Ariono *et al.*, 2017). It has been known that fouling is the main problem in the long-term application of UF membrane for water and wastewater treatment (Yu *et al.*, 2021). The accumulation of pollutants on the membrane surface or in the membrane structure results in flux decline and low productivity (Yin *et al.*, 2020). The fouling mechanisms on UF membrane are continuously investigated, particularly for water and wastewater treatment.

Fouling on UF membrane is mainly attributed to the interaction between pollutants (solutes) and the membrane surface (Shen *et al.*, 2017). As the operating time increases, the concentration of pollutants on the membrane surface rapidly increases, which inhibits the solvent to the permeate side and attributes to flux decline (Ariono *et al.*, 2018). It is known as the concentration polarization phenomenon (Scutariu *et al.*, 2020). The Concentration polarization is categorized as reversible and can be easily cleaned by a simple method, such as flushing and backwash. On the contrary, irreversible fouling remains in the membrane structure even after the cleaning process. The irreversible fouling could be induced by large pores in the membrane structure (Alresheedi *et al.*, 2019). Pore blocking or cake/gel layer of fouling has rapidly occurred on the membrane surface when the pollutant molecular size is larger than the membrane pore (Doan and Lai, 2021).

Hermia developed four empirical models to define fouling mechanisms in a constant pressure dead-end filtration and then adapted to crossflow filtration (de Barros *et al.*, 2003, Vela *et al.*, 2009). There are 4 (four) types of fouling in the membrane structure, i.e., (a) cake layer formation, (b) standard/internal blocking, (c) intermediate blocking, and (d) complete blocking (Figure 1). The Hermia's model could be used to predict the dominant fouling occurred

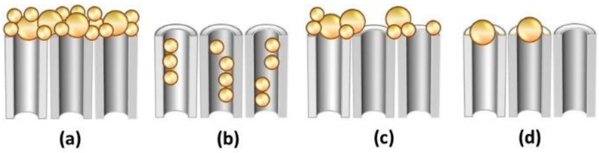

Figure 1. Fouling mechanisms on UF membrane: (a) cake layer formation, (b) standard blocking, (c) intermediate blocking, and (d) complete blocking.

Several studies on composite UF membranes based on polysulfone (PSf), polyethylene glycol (PEG400), ZnO nanoparticles (ZnO-Np) have been conducted. Sarihan and Eren (2017) found that the presence of ZnO in the membrane solution increased the skin membrane thickness while maintaining membrane hydrophilicity. Wenten *et al*. (2019) blended PSf with PEG400, ZnO-NP, and eugenol as additives. The membrane solution was coated on polypropylene (PP) membrane support. The composite UF membrane provided high rejection of humic substances (>95%) with permeate flux of 83 $L.m^{-2}.h^{-1}$ and a relative flux reduction ratio (RFR) of 30.2%. The previous research only studied the effect of additives on membrane performances, but not on the fouling phenomenon formed during ultrafiltration. In this paper, the fouling phenomenon on the UF membrane prepared by blending PSf, PEG400, and ZnO-Np was investigated. The UF membrane was used for textile wastewater treatment. The influence of UF membrane characteristics at different concentrations of polymers (PSf and PEG400) on permeate flux and color rejection was also investigated. The fouling phenomenon was analyzed using Hermia's model based on the permeate flux decline during the textile wastewater treatment.

MATERIAL AND METHOD

Materials

PSf (UDEL-P3500 MB7) was provided by Solvay Advanced polymer, while the DMAC (purity 99.9%) was from Shanghai Jingsan Jingwei Chemical Co. Ltd. The PEG400, acetone, and ZnO nanoparticles were obtained from local suppliers. The particle size of ZnO nanoparticle was 20 - 30 nm. The textile wastewater was obtained from one of the local textile industries in Cimahi, West-Java, Indonesia. The color concentration of the textile wastewater was between 230 – 250 PCU.

Preparation of the flat-sheet UF membrane

The UF membrane was prepared by blending PSf in DMAc as solvent. PEG400 and ZnO nanoparticles were added to the solution as additives to improve membrane hydrophilicity. A small acetone concentration (4 wt.%) was also added to the membrane solution, with a fixed ratio to DMAc of 1:15. Meanwhile, the concentration of ZnO in the membrane solution was 1 (one) wt.% of the total weight of polymers (PSf and PEG400). Concentrations of PSf were varied by 18 and 20 wt.%, while the concentration of PEG400 was from 0 to 25 wt.%. The membrane solution was stirred until homogenous and then left without stirring until no bubbles were observed in the solution. The homogenous membrane solution was cast on the glass plate with a thickness of 200 µm. The casted membrane was immediately immersed in the coagulation bath, which was filled with demineralized water at room temperature. After 12 hours, the membrane was cut into a circle shape with a diameter of 7.5 cm and then placed in a membrane module.

Flux and rejection measurement

The experimental apparatus to measure flux and rejection of the membrane is shown in Figure 2. The UF membrane was operated in crossflow mode and constant operating pressure of 15 psig. The feed wastewater was placed in a cylindrical tank with a volume of 5 L.

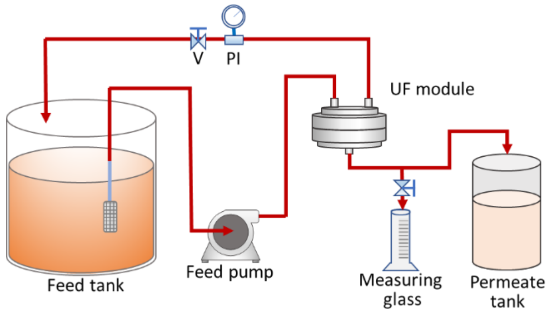

Figure 2. Experimental set up of UF membrane system for wastewater treatment

Then, the feed wastewater was delivered to the membrane module using a centrifugal pump. The operating pressure was set by adjusting the valve (V) attached to the concentrate stream. The permeate flux was measured every 20 minutes during 2 hours of ultrafiltration and then calculated using Equation (1).

$$J = {}^{V}\!/_{A.t} \qquad (1)$$

where J is permeate flux (L.m-2.h-1). V and A are permeate volume (L) and effective membrane area (m^2), respectively. Meanwhile, t is the time required to achieve a specified permeate volume (V).

The selectivity of the resulted UF membrane was characterized by color rejection (Equation 2). The color of feed (C_f) and permeate (C_p) was measured using color checker HI727 Hanna Instruments.

$$Color\ rejection\ (\%) = \left(1 - {}^{C_p}\!/_{C_f}\right) x\ 100\% \qquad (2)$$

Table 1. Linear equations for fouling analysis during textile wastewater treatment.

Code	Fouling mechanisms	Linear equations	Eq no.
Model 1	Cake layer formation (code: c_f)	$\frac{1}{J^2} = \frac{1}{J_o^2} + K_{cf}t$	(3)
Model 2	Intermediate blocking (code: ib)	$\frac{1}{J} = \frac{1}{J_o} + K_{ib}A\ t$	(4)
Model 3	Standard blocking (code: sb)	$\frac{1}{J^{1/2}} = \frac{1}{J^{1/2}} + K_{sb}t$	(5)
Model 4	Complete blocking (code: cb)	$\ln(J) = \ln(J_o) + K_{cb}t$	(6)

Notes: Jo is initial flux at t = 0 min.($L.m^{-2}.h^{-1}$),
A is membrane area (m^2),
t is operating time (h), and
K is fouling parameter of each fouling mechanism.

Fouling analysis method

In this work, the fouling analysis method refers to the previous work (Aryanti *et al.*, 2015) The dominant fouling mechanisms during textile wastewater treatment were determined by using Hermia's model, as presented in Equation (3) to (5). The experimental results were fitted to these Hermia's model for up to 500 minutes. The fitted data with the highest R^2 value was defined as the dominant fouling that occurred in the membrane system. In addition, the influence of PSf and PEG400 concentration in the membrane solution on fouling types formed in UF membrane was analyzed.

RESULT AND DISCUSSION

Profile of permeate flux during textile wastewater treatment

Profile of permeate flux of the resulted UF membrane was analyzed at different concentrations of PSf and PEG400, with a fixed ratio of acetone and DMAc of 1:15 (Figure 3a). The operating pressure was kept at 15 psig during 2 hours of textile wastewater treatment.

The experimental results showed that the addition of PEG400 increased the permeate flux. The lowest permeate flux was achieved when 20 wt.% of PSf without the presence of PEG400. A high concentration of PSf inhibited the formation of macrovoids in the membrane structure and reduced the growth of the membrane pore (Ariono *et al.*, 2017). The smaller pores enhanced the intrinsic resistance of the membrane and reduced mass transfer of the solvent through the membrane, and therefore, a smaller permeate flux was obtained. When the PSf concentration was reduced to 18 wt.%, the permeate flux increased up to 2 times (from 25 to 54 $L.m^{-2}.h^{-1}$). By lowering the PSf concentration, the lower viscosity allowed the formation of larger membrane pores, which reduced the membrane resistance and enhanced the mass transfer (Ariono *et al.*, 2017, Borisov *et al.*, 2019).

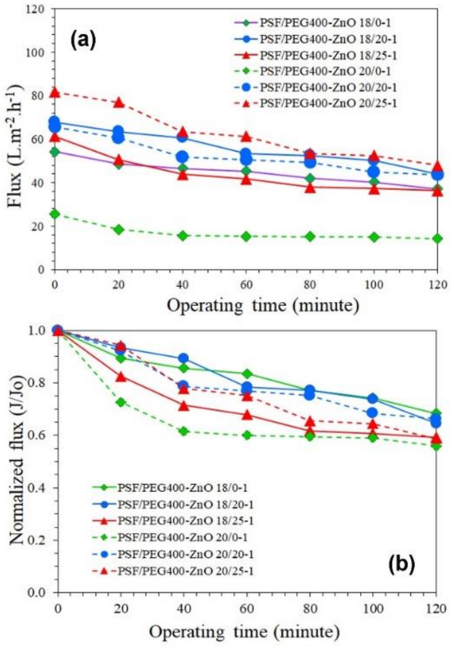

Figure 3. Profile of permeate flux (a) and normalized flux (b) during 2 hours of textile wastewater treatment at 15 psig.

The stability of permeate flux in each UF membrane was observed based on normalized flux, i.e., the ratio between the flux at a certain time to the initial flux (J/J_o) (Figure 3b). More stable flux was obtained when 18 wt.% of PSf and 1 wt.% of ZnO nanoparticles were used and then blended in a solvent with Acetone:DMAc ratio of 1:15. The flux decline was 32% (from 54 to 37 $L.m^{-2}.h^{-1}$). Further increase the PSf concentration to 20 wt.%, the flux decline got worse to 44%. The hydrophobicity of the membrane increased with the increase of PSf concentration in the membrane solution. Hydrophobic interaction enhanced the fouling formation on the membrane surface, which enhanced the resistance of the solvent to pass through the membrane (Shen *et al.*, 2017).

Fouling analysis of the UF membrane during textile wastewater treatment

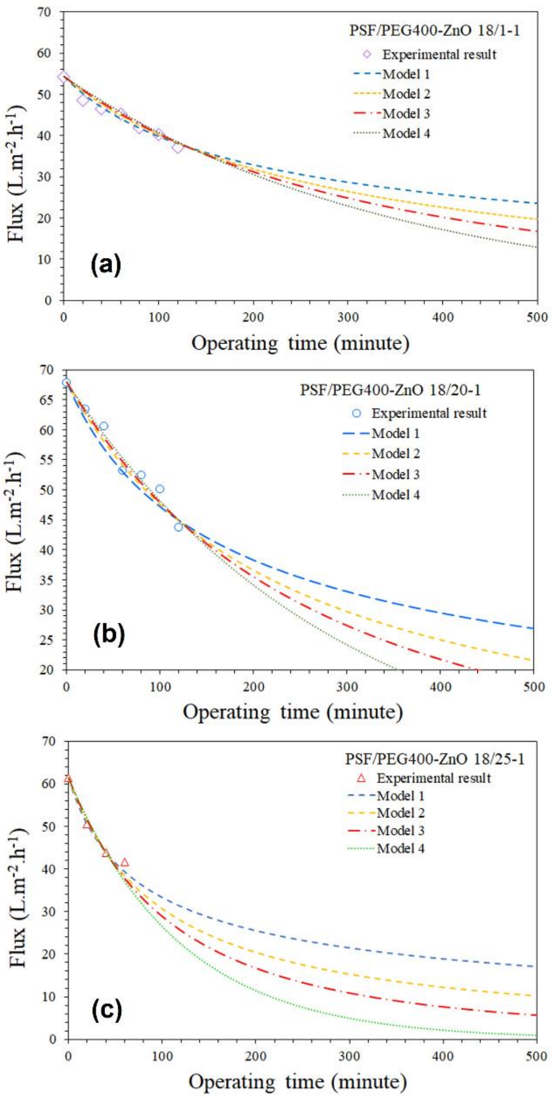

Figure 4. Prediction of fouling formation at PSf concentration of 18 wt.%, ZnO of 1 wt.% of polymer, and various concentration of PEG400: (a) 0 wt.%, (b) 20 wt.%, and (c) 25 wt.%.

The addition of PEG400 to the membrane solution reduced the hydrophobicity of the UF membrane, which minimized hydrophobic interaction between the pollutant and membrane surface (Lin *et al.*, 2021). Therefore, flux decline due to fouling formation could be minimized.

It has been known that the flux decline in UF membrane is strongly associated with the formation of fouling (Zhang and Fu, 2018). Fouling formation was analyzed for up to 500 minutes using Hermia's model, based on the experimental data. The predicted fouling formation on the resulting UF membranes with different PSf and PEG400 was presented in Figures 4 and 5. To estimate the dominant fouling mechanism on membrane during the textile wastewater treatment, the flux (J) was plotted in a J-t curve referred to linear Equation (3) to (6). The fouling parameters of each fouling mechanism are shown in Table 2, while the R^2 values are presented in Table 3. The highest R^2 value defined the fouling mechanism in each resulted UF membrane.

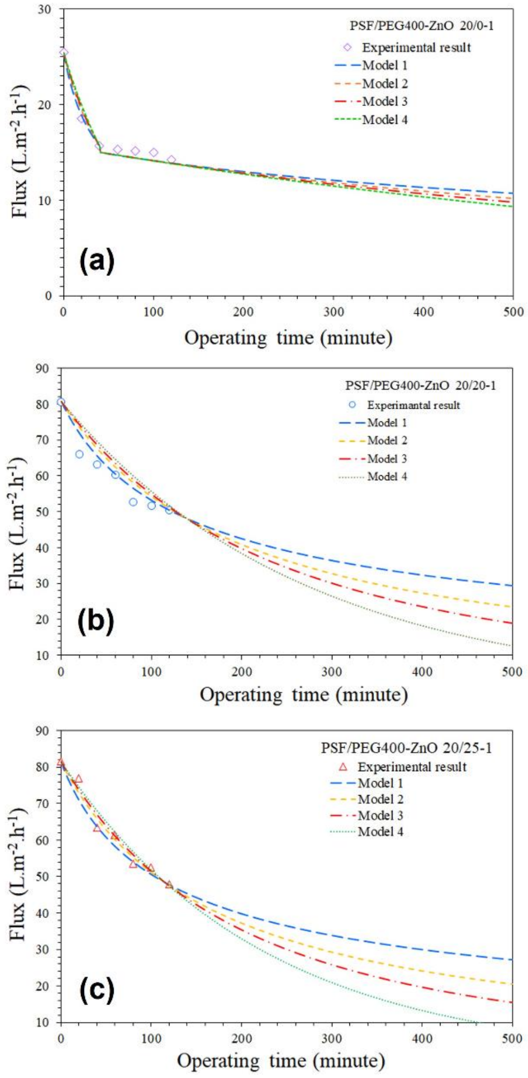

Figure 5. Prediction of fouling formation at PSf concentration of 20 wt.%, ZnO 1 wt.% of polymer, and various concentrations of PEG400: (a) 0 wt.%, (b) 20 wt.%, and (c) 25 wt.%.

The case of UF membrane that prepared by 20 wt% of PSf with a little concentration of ZnO nanoparticles (1 wt.% from the total polymers) generated two types of fouling mechanism. In the first 40 minutes, a significant flux decline has occurred (Figure 5a). The initial flux decline that was occurred at the earlier ultrafiltration process may be attributed to concentration phenomena (Kanani and Ghosh, 2007). Pore blocking was generated for the next fouling step in the membrane structure prior to the cake layer formation on the membrane surface (Wang and Tarabara, 2008). In textile wastewater, several pollutants, both organic and inorganic compounds, could form fouling on the membrane surface or inside the membrane structure. Some of the pollutants include fibers, organic dyes, inorganic salts, supplementary chemicals, etc. (Mani *et al*., 2019). The low molecular weight of pollutants, such as dyes and salt, could easily enter the larger membrane pore and then induces a pore blocking mechanism. The high concentration of pollutants enhanced the hydraulic resistance of the ultrafiltration and then significantly – reduced the permeate flux. Due to the small pore size and higher hydrophobicity of the UF membrane at high PSf concentrations, a layer of cake is easily formed on the membrane surface.

Table 2. Fouling parameters in Hermia’s model for each fouling mechanism.

Membrane formulation	K_{cf}	K_{ib}	K_{sb}	K_{cb}
PSF/PEG 18/0	2.94E-06	6.48E-05	2.16E-04	-2.88E-03
PSF/PEG 18/20	2.33E-06	6.29E-05	2.33E-04	-3.45E-03
PSF/PEG 18/25	6.37E-06	1.63E-04	5.84E-04	-8.40E-03
PSF/PEG 20/0				
0-40 min.	6.32E-05	6.13E-04	1.36E-03	-1.21E-02
40-120 min.	9.29E-06	6.94E-05	1.34E-04	-1.04E-03
PSF/PEG 20/20	2.00E-06	6.05E-05	2.37E-04	-3.72E-03
PSF/PEG 20/25	2.45E-06	8.74E-05	3.70E-04	-6.27E-03

Fouling parameters: K_{cf} = cake formation; K_{ib} = intermediate blocking; K_{sb} = standard blocking; K_{cb} = complete blocking

Table 3. R^2 values of Hermia’s model for each fouling mechanisms

Membrane formulation	R^2			
	Cake formation	Intermediate blocking	Standard blocking	Complete blocking
PSF/PEG 18/0	0.9702	0.9771	0.9775	0.9758
PSF/PEG 18/20	0.9333	0.9533	0.9628	0.9680
PSF/PEG 18/25	0.9501	0.9225	0.9053	0.8858
PSF/PEG 20/0				
0 - 40 min.	0.9976	0.9868	0.9786	0.9686
40 - 120 min.	0.8617	0.8695	0.8733	0.8770
PSF/PEG 20/20	0.9555	0.9414	0.9305	0.9169
PSF/PEG 20/25	0.9741	0.9754	0.9695	0.9625

Over 40 minutes of ultrafiltration, a stable permeate flux was achieved, with no significant change in permeate flux. When the accumulation of pollutants on the membrane surface reached the maximum concentration, it led to a higher diffusive backflow of the pollutants to the bulk solution (Virtanen *et al*., 2019). Therefore, a stable permeate flux was obtained.

Color rejection of the UF membrane in textile wastewater treatment

The color rejection of the resulted UF membranes is shown in Figure 6. When the PSf in membrane solution was 18 wt.%, the color rejection was slightly changed during 2 hours of ultrafiltration textile wastewater. The color rejection was between 73 – 86%. The highest color rejection was achieved when 25 wt.% of PEG400 was added in 20 wt.% of PSf solution, followed with UF membrane that was prepared by blending 18 wt.% of PSf without the addition of PEG400. The color rejection of each membrane was 81 and 86%, respectively. Based on fouling prediction and the experimental results, it could be predicted that the intermediate and standard fouling formation on the membrane surface attribute to higher color rejection than complete and cake fouling. When the concentration of pollutants on the membrane surface is high and forms cake layer on the membrane surface, mass transfer of pollutants to the permeate side increases due to the high osmotic pressure and concentration difference.

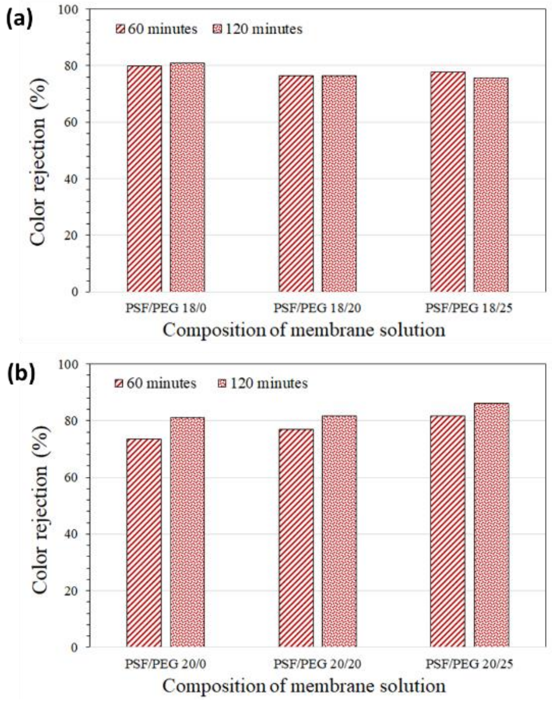

Figure 6. Color rejection of the UF membranes at PSf concentration of: (a) 18 wt.% and (b) 20 wt.%.

CONCLUSION

Ultrafiltration (UF) membranes are prepared by blending polysulfone (PSf), acetone, and PEG400 in DMAc, with ZnO nanoparticles at a concentration of 1% by weight of polymers (PSf and PEG400). The influence of PSf concentration (18 and 20 wt.%) and PEG400 (0 - 25 wt.%) on fouling mechanisms is investigated. The fouling mechanisms are analyzed using Hermia's model during textile wastewater treatment. It is found that the increase of PEG400 concentration enhanced the permeate flux. More stable flux was achieved when 18 wt.% of PSf was used to prepare the UF membrane. The fouling type in the UF membrane depends on the characteristics of the membrane. A significant flux decline occurred when used 20 wt.% of PSf without the addition of PEG400. Smaller membrane pore and higher hydrophobicity due to high PSf concentration induced cake layer of fouling on the membrane surface at the first 40 minutes of ultrafiltration. Further increase of operating time, internal fouling was formed due to the movement of pollutants to the permeate side caused by different concentrations. The highest color rejection (86%) was achieved when 25 wt.% of PEG400 was added in 20 wt.% of PSf solution.

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