Polysulfone thin film composite nanofiltration membranes for removal of textile dyes wastewater

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Abstract. This research was conducted to produce nanofiltration (NF) membranes, which have good performance in terms of removal of textile dye (Reactive Red 120, RR120) from simulated wastewater as one of several eco-engineering developments for sustainable water resource management. Phase inversion technique was utilized to fabricate the membrane with polysulfone (PSF) support, dissolved in N-methyl-2 pyrollidone (NMP) solvent, and diethylene glycol (DEG) as non-solvent additive. The fabricated membrane then modified with the additional of dopamine coating and further modified by interfacial polymerization (IP) to form a thin film composite (TFC)-NF membrane with PSF substrate. TFC was formed from interaction between amine monomer (2 %-weight of m-phenylenediamine (MPD) in deionized water) and acyl chloride (0.2 %-weight of trimesoyl chloride (TMC) in hexane). From this study, the fabricated PSF-TFC membrane could remove dyestuff from RR120 wastewater by 88% rejection at 120 psi. The result of this study is promising to be applied in Indonesia where researches on removal of dyes from textile wastewater by using membranes are still quite rare. Therefore, this paper may open new avenues for development of eco-engineering development in Indonesia.

Keywords: membrane, nanofiltration, textile, interfacial polymerization, polysulfone

1. Introduction
In textile industry, generally 10-15% dyes were lost during the dyeing process, where about 200-350 m³ waters required per 1 ton of finished products [1]. Some counties already strict their environmental regulation, disposing the wastewater directly will becomes more complicated [2]. In order to follow such stringent regulation, one of the important process is at least to decolorize the wastewater by some methods, such as destruction of dyes molecules and separation of dyes from waters [3]. To destruct or transform the dyes, conventional process is usually applied, such as chemical oxidation, photocatalysis and biodegradation [4]. However, this methods were found to be inadequate and required enormous energy to broke the dyes molecules which are stable to light, oxidizing agent, and microbiological degradation [5-7].

The overcome the limitation from the dyes molecules destruction method, separation process such as adsorption, coagulation, flocculation and membrane separation begins to develop [3]. Adsorption separation process using activated carbon is quite common, but not economically efficient since the
price of activated carbon is quite expensive and the performance decreases after several times of usage/regeneration [1, 8, 9].

On the other hand, coagulation and flocculation were commonly used due to process efficiency [9-11]. In this process, the dyestuff solution is destabilized to agglomerate and flock to form heavy and large molecules, which makes the clumps easily separated [12, 13]. However, either coagulation or flocculation process were found infective for some soluble dyes in water. Thus there will always be a challenge to determine the right coagulant to overcome the pollution caused by various dyestuff [1].

Besides conventional processes like coagulation and flocculation, there are also membrane technologies such as, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [5]. UF has been proven successful in separating insoluble dyes and large molecule dyes. However, UF unable to remove dissolved dyes with small molecule [5, 14]. Although perfect separation can be achieved using RO, but its required very high pressure (>50 bar) makes this separation unattractive due to high operational cost. With the limitation from UF and RO, NF has a promising performance to remove dyes from textile wastewater [3] and low operational cost [15]. NF membrane nominal molecular weight cut-off (MWCO) range between 100 until 1000 Da with 0.5-2.0 nm pore size [15, 16], with the right modification method, NF can remove as good as RO without requiring high pressure.

In the separations using membrane, there is a tendency of a membrane to form a fouling that may reduce the flux or the productivity of the membrane. This phenomenon could be reduced by applying surface modification, where one of the modification processes is interfacial polymerization (IP). It is a method for depositing a thin layer upon a porous membrane support, where a polymerization reaction occurs between two very reactive monomers at the interface of two immiscible solvents. The common precursors for IP are: (1) a reactive aqueous of amine solution (in this paper, we use m-phenylenediamine (MPD)) and (2) water-immiscible solvent solution consisting of acyl chloride (we use trimesoyl chloride (TMC)) that are reactive at the interface of the two immiscible solutions to form a thin film composite (TFC) membrane [17, 18]. The illustration of IP using TMC and MPD is to form TFC is shown in Figure 1a.

**Figure 1.** Interfacial polymerization between trimesoyl chloride (TMC) and m-phenylenediamine (MPD)
Today almost all NF membrane for textile dyes wastewater treatment in Asia are dominated by China or Singapore [16, 19-23], whereas in Indonesian literature about dyestuff degradation were still using bioreactor [24-28]. It is quite ironic as Indonesia have many textile industries around 2500 companies with total investment of more than 100 trillion dollars, and capacity of 6 million ton of textile products per year [29], but with limited number of research in this field. By assuming 200 m$^3$ of wastewater is produced per 1 ton textile product, then there is more than 100 trillion m$^3$ wastewater discharged to environment without adequate treatment. If Indonesia could master the membrane technology and eco-engineering development to treat the textile wastewater effluents, then it would be very beneficial for the national environmental sustainability. In this study, m-phenylenediamine (MPD) and trimesoyl chloride (TMC) was utilized to form TFC membrane on top of common polysulfone (PSF) membrane to treat simulated textile wastewater, and tested in laboratory scale using permeation scale illustrated in Figure 1b.

2. Methodology
This research was conducted to produce selective and productive membrane, which are capable to reducing the color concentration from textile wastewater. The membrane material used in this research was polysulfone (PSF) that can only be dissolved in a dipolar aprotic solvent, i.e. N-methyl pyrroldone (NMP) in this paper, and with diethylene glycol (DEG) as the non-solvent additive. The formulation of PSF/NMP/DEG 14/72/14, 16/70/14, and 18/68/14 %-weight were varied, with detailed membrane fabrication procedures and decision of membrane composition was taken according to the literatures [30, 31].

The various dope solutions obtained are then casted using flat sheet casting method, illustrated in Figure 2.

![Figure 2. Flat sheet membrane fabrication process](image)

Casted membrane was coated using dopamine then with MPD and TMC, with the molecular form listed in Figure 1 [30], and hereafter referred as PSF-TFC. Dopamine solution was made with a concentration of 0.02 grams in a 10 mM tris-HCl solution of 100 mL. The PSF membrane immersed in dopamine for 3 h. Dopamine-coated PSF membrane was immersed in 2 wt% MPD dissolved in deionized for 1 min and subsequently in 0.2 wt% TMC in hexane also for 1 min. The membrane is then heat treated in 70°C hot water for 2 min, and kept immersed in water until testing.

The permeation cell shown in Figure 1b was utilized to test PSF-TFC membrane performance by removing Reactive Red 120 (RR120), with the feed concentration of 100 ppm [32]. All condition for nanofiltration performance test will be maintained at room temperature. Pressure variation will be explained in the section of Result and Discussion. All chemicals are used as is without further purification.

The membrane productivity parameter (flux) of the membrane calculated using the following equation:
\[ J = \frac{V}{AtP} \]  

with \( J \) = flux (L m\(^{-2}\) s\(^{-1}\) psi\(^{-1}\)), \( V \) = permeate volume (L), \( A \) = membrane active surface area, \( t \) = time required to contain the permeate (s), and \( P \) = pressure input (atm). On the other hand, we also test the membrane quality parameter (Rejection) calculated using this following equation:

\[ \%R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \]

With \( \%R \) = Rejection, \( C_p \) = permeate concentration (ppm), \( C_f \) = feed concentration (ppm). The feed concentration and the permeate concentration was measured by using spectrophotometer to construct a standard curve for RR120 measured at maximum wavelength \( \lambda_{max} \) 515 nm.

3. Results and Discussion
In this section, we will discuss the effect of the PSF concentration in the dope solution towards the membrane performance. Modification of PSF with IP to form PSF-TFC and its performance in dye removal from wastewater will also be discussed.

3.1. Effect of PSF concentration towards the permeate flux (without dyes)
Flux of the pure water without textile dyes (pure water permeability, PWP) testing using permeation cell is shown in Table 1. It could be observed that PSF 18/68/14 is not sufficient since its flux is very slow, due to the tight PSF polymer content in the membrane, as well as sacrificing the economic value of a membrane. Therefore PSF 14/72/14 and 16/70/14 were continued for further testing.

| PSF membranes | PWP (L m\(^{-2}\) s\(^{-1}\) atm\(^{-1}\)) |
|---------------|----------------------------------|
| 14/72/14      | 0.358                            |
| 16/70/14      | 0.042                            |
| 18/68/14      | 0.012                            |

3.2. Effect of PSF concentration towards the permeate flux (with RR120 dye)
Two PSF membranes (without modification), PSF 14/72/14 and 16/70/14, were utilized to remove RR120 dye from simulated wastewater (100 ppm, various operating pressures). The filtration result is shown in Figure 3a. It could be seen that each membrane has tight pores where pressure <50 psi was not enough to pass through any liquid from the permeation cell. The pore radius of the fabricated PSF membrane is estimated by using the Laplace equation [17]

\[ r_{pore} = \frac{2\gamma}{\Delta P} \cos \theta \]

Pore radius \( r_{pore} \) of a membrane pore with a shape of capillary tube, that is completely wetted (contact angle \( \theta = 0^\circ \)) by water (surface tension \( \gamma = 72.3 \) mN/m), with operating pressure of 50 psi (~3.5 bar= 350000 Pa) is around 400 nm. Thus it is confirmed that the fabricated PSF membrane is in the nanometer range.

The PSF 14/72/14 could bring permeate with pressure of 40 psi only, but with upsetting quality (dye concentration in the output is still 100 ppm, similar to that of the input, \( \% \) rejection = 0%). Different to PSF 14/72/14, the PSF 16/70/14 is able to maintain quality at around 50 ppm (pressure >70 psi). This result delivered the PSF 16/70/14 to be further modified with IP to get PSF-TFC membrane. The performance of PSF-TFC compared to that of PSF 16/70/14 is shown in Figure 3b. It could be obviously seen that the performance of PSF-TFC (permeate concentration ~12 ppm, \( \% \) rejection = 88%) is much better that PSF 16/70/14 (permeate concentration 50%), although PSF-TFC 16/70/14 required much higher operation pressure (>80 psi), compared to that of unmodified PSF 16/70/14 (starts from 50 psi).
Figure 3. Dye concentration in the permeate (ppm) as the function of operating pressure (psi) for (a) unmodified PSF membranes, and (b) PSF-TFC membrane.

3.3. Membrane morphology

To describe how the membrane performance is delivered in such nature, we characterized the physical morphology of the membrane by using scanning electron microscopy (SEM). The structures of the membranes are shown in Figure 4 and 5. From these images, it can be judged that this membrane configuration was asymmetric membrane due to its pore distribution from the top until bottom layer; where the pores were bigger as it were closer to the bottom surface. However, the thin layer of TFC could not be detected from both the cross-sectional view and the top view (Figure 4) since it is too thin.

Figure 4. SEM images of membrane substrate cross-section; (a) PSF, (b) PSF-dopamine, (c) PSF-TFC ×500, and (d) PSF-TFC ×1000
4. Conclusions
In this study, we have successfully fabricated a PSF-based membrane that was modified with interfacial polymerization technique to produce PSF-TFC membrane that was able to remove 88% of RR120 dye, require pressure of 120 psi.

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