Polyetherimide nanofiltration membranes modified by interfacial polymerization for treatment of textile dyes wastewater

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Abstract. Azo dyes are the major type of textile dye in the world, owing to their stability to light, microbial degradation, and physical degradation due to washing. However, these properties also lead to problematic removal or degradation of azo dyes that pollute the water body. In this research, nanofiltration (NF) thin film composite (TFC) membranes based on polyetherimide (PEI) polymer are utilized to remove an azo-based dye from a simulated textile wastewater, namely Reactive Black 5 (RB5). PEI is firstly dissolved by using N-methyl-2 pyrrolidone (NMP) as solvent, combined with acetone as a non-solvent, and converted to be membranes via phase inversion method. The created membrane will be further modified by interfacial polymerization (IP) method using trimesoyl chloride (TMC) and m-phenylene diamine (MPD) as precursors of acyl chloride and amine, immersed in two immiscible liquids of hexane and water, respectively. This method fabricates a new selective layer composed of tightly-packed nylon-like polyamide layer that might improve the separation performance. Membranes from polymeric dope solution of PEI/acetone/NMP 15/65/20 (w/w) were employed due to acceptable flux and rejection, compared to other formulations. They were then modified by using IP method (0.05% TMC in hexane and 1.5% MPD in water) to create PEI-TFC membranes. The PEI-TFC membranes exhibited fluxes around 0.01 L m⁻² h⁻¹ psi⁻¹, with rejection of RB5 dyes up to 90%, which suggested the successful IP method on the PEI membranes. SEM and FTIR were carried out for comprehending the reasons behind the improved separation performance, and they revealed that the TFC nylon-like selective layer was successfully developed, from both physical and chemical perspectives, respectively. The fabrication of NF TFC membranes might open some new roads for environmental application of membranes in Indonesia.

Keywords: membranes, nanofiltration, dyes, polyetherimide

1. Introduction
The global scarcity of clean potable water is one of the major challenge faced by the humanity these days [1]. One of the largest industry sector that plays a pivotal role in the society’s fundamental needs, and global economy as well as in the consumption of water is the textile industry [2]. This industry uses a huge amount of water for its dyeing process [3]. As an illustration, a kilogram of textile uses 60 to 100
kg of water during dyeing and washing [4]. As a big issue of supply and demand of water, it is absolutely necessary to have the wastewater treated and recycled. However, the textile wastewater treatment is relatively not a straightforward process. The textile wastewater definitely must be decolorized, via some meticulous process of destruction of dyes molecules, or by separation of dyes from waters [5]. In order to broken down the dyes (which is generally made up of resilient azo structures), some processes namely chemical oxidation, photo-catalysis and biodegradation [6] could be taken. On the contrary, these methods could only be employed to some extent, as there are limitations on the intensive energy consumption, and also long treatment duration, due to the common azo molecular structure of dyes [7-9].

As an alternative resolution for the dyes destruction processes, the separation of dyes from wastewater (e.g. adsorption, coagulation and flocculation, and membrane-based treatment) are developed [5]. The adsorption process utilizing activated carbon-based materials is not uncommon; however it is limited by the removal capacity which requires vast amount of adsorbents, rendering uneconomical process especially for the application in the treatment of textile dyes wastewater. Moreover, after several time and regeneration processes, the adsorbents may suffer some significant reduction of adsorption performance [10-12].

Besides adsorption process, the coagulation and flocculation were also utilized in the treatment of wastewater due to their efficiency [12-14]. Coagulation and flocculation process agglomerates some insoluble particles of dyes, causing the dyes to clump in large quantity, thus could be effortlessly separated from the wastewater [15, 16]. However, they are not applicable in separating the soluble dyes [11].

A separation process that could remove both soluble and insoluble dyes is the membrane-based process that might be classified as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [7]. UF successfully separated insoluble dyes and also soluble dyes with large molecule structure, but ineffective for removing dissolved dyes having small molecular weight [7, 17]. The absolute separation of dyes could be obtained by application of RO, but limited with the high operation pressure (>50 bar). Therefore, it would be a good strategy to develop the membranes with properties between these two boundaries, which is the NF membranes. It demonstrates a good separation performance of dyes removal from textile wastewater [5], balanced with affordable operational cost [18]. This study targets to have a good performance in separating soluble textile dyes from wastewater, with relatively low operational pressure. This target is planned to be accomplished via further improvement of the previously developed polyetherimide (PEI) membranes, by preparing thin film composite (TFC) NF membranes [19].

![Figure 1. An illustration of interfacial polymerization involving TMC and MPD resulting in polyamide TFC membranes](image-url)
To prepare TFC membranes, an unconventional polymerization processed called interfacial polymerization process was utilized. In brief, it is basically a polymerization reaction between two reactive precursors reacting at the border or interface of two immiscible solvents. Generally, the system comprises of amine dissolved in water, and acyl chloride in hexane, both in very low concentration to avoid rapid build of reaction temperature that may lead to explosion. The product of the interfacial reaction of the reactive precursors is a thin Nylon-like polyamide layer. In this study, m-phenylenediamine (MPD) and trimesoyl chloride (TMC) were used as the precursors [20, 21]. The illustration of interfacial polymerization to form TFC is shown in Figure 1.

2. Experimental methods

In this study, we prepared the membranes based on PEI materials (polyetherimide, Sigma-Aldrich, CAS 61128-46-9), using the previously developed formulation of polymeric dope solution [19]. The dope consists of using PEI polymer, acetone as non-solvent, and N-methyl pyrrolidone (NMP) solvent (PEI/acetone/NMP mixture), having the dope compositions of 15/20/65 and 16/20/64 w/w. Acetone and NMP (CAS 872-50-4) were obtained from Merck. After the dope solutions were successfully prepared, membranes were casted via flat sheet casting method. The details of flat sheet membrane casting process could be found in the previous work [19, 22].

Briefly, the polymeric dope solutions were mixed until visually homogeneous, and then went into stationary condition for about two days to ensure removal of micro gas bubbles from the dope solution. The dope solution was poured onto A4 glass plates and then casted with thickness of 250 μm at room temperature. The casted membranes were removed from solvent residues via copious immersion in methanol and hexane for 3×30 mins each.

The casted membranes were then proceed to the stage of interfacial polymerization, by being immersed in aqueous MPD solution for 2 mins, subsequently followed with immersion in TMC for also 2 mins to form PEI-TFC membranes. Aqueous MPD solution is dissolved in deionized water at concentration of 1.5 wt%, while the TMC is dissolved in hexane at 0.05 wt%, with the molecular form listed in Figure 1 [23]. After the interfacial polymerization processes, the membranes were dried 70°C for 30 min in an oven. MPD (CAS 108-45-2) and TMC (CAS 4422-95-1) were obtained from Sigma-Aldrich.

![Figure 2. Molecular structure of RB5](image)

![Figure 3. Standard curve of RB5 dyes at various concentration, with absorbance measured at λ<sub>max</sub> 590 nm](image)

The fabricated TFC membranes were objected to a test for separation performance, to assess both the quantity and quality of the separation performances. For the quantity aspect, the test was carried out by using a permeation cell combined with pressurized N₂ gas (pressure 40-80 psi). The separated object is Reactive Black 5 textile dye (RB5, CAS number 17095-24-8, Sigma-Aldrich, Figure 2) dissolved in water as a simulated wastewater, with concentration of 100 ppm and 150 ppm. The detailed procedure and illustration of the equipment for testing of the TFC membranes are shown elsewhere [19]. The assessment for the quality of the separation is obtained by using UV-Vis spectrophotometer. The
spectrophotometer was utilized to quantify the colour intensity of the permeate, at a certain wavelength, in this case for that of RB5 dyes is at the wavelength that provides maximum absorbance $\lambda_{\text{max}} = 590$ nm, and shown in Figure 3.

The quantity of the separation is demonstrated by the parameter of permeate flux, while for that of quality, the parameter of rejection is utilized. The permeate flux flow rate is written in Equation 1.

$$J = \frac{V}{AtP}$$

(1)

with $J = \text{flux (L m}^{-2} \text{s}^{-1} \text{psi}^{-1})$, $V= \text{volume of the permeate (L)}$, $A= \text{membrane surface area (m}^2)$, $t= \text{time required to contain the permeate (s)}$, and $P = \text{the pressure required for the feed to pass through the membrane (psi)}$.

The quality of the membrane separation is exhibited by using the parameter of color rejection, as shown in Equation 2, as follows:

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

(2)

with $%\text{R} = \text{Rejection}$, $C_p = \text{Concentration of the permeate (ppm)}$, and $C_f = \text{Concentration of feed solution (ppm)}$. Moreover, the pore radius of the fabricated membrane is estimated by using the Laplace equation, as follows [24]

$$r_{\text{pore}} = \frac{2\gamma}{\Delta P} \cos \theta$$

(3)

Pore radius $r_{\text{pore}}$ of a capillary shaped pore completely wetted (contact angle $\theta= 0^\circ$) by water (surface tension $\gamma = 72.3$ mN/m), with the highest operating pressure of ~80 psi (~5.44 bar = 545000 Pa) is around 267 nm. Therefore, the pore of the fabricated NF membrane is confirmed to be in the nanometer range. The physical morphology (cross-section) of the membranes were analyzed by using scanning electron microscopy (SEM, JEOL JSM-5600LV), while the chemical properties of the membranes were characterized by employing Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer FTIR Spectrum 2000, resolution of 2 cm$^{-1}$) [25, 26].

3. Results and discussion

As the PEI membranes have been prepared, the separation performances were then investigated from the perspectives of the quantity and quality. Similar to that of in the previous work [19] we firstly explored the permeate flux (quantitative parameter). Before any molecular separation were performed, we subjected the membranes to pure water first in order to comprehend the ability to pass the water molecules through the membranes, mentioned as PWP (pure water permeability). The PWP result is shown in Figure 4.

From Figure 4, it could be observed that the membrane casted from the PEI16 (from dope solution with concentration of PEI/acetone/NMP 16/20/64 w/w) delivered much slower PWP compared to that of PEI15 (15/20/65 w/w), i.e. only 0.25 vs up to 1.50 L m$^{-2}$ h$^{-1}$ psi$^{-1}$, respectively. The operating pressure requirement of PEI16 is also higher than that of PEI15, i.e. 50-80 psi vs. 40-70 psi, respectively. Based on this result we directed the PEI15 to be further processed to the interfacial polymerization stage, for additional attachment of polyamide selective layer on top of PEI15, thus creating the TFC membranes.

The separation performance of the PEI15-TFC membranes in separating RB5 dyes (100 ppm) is shown in Figure 5. It could be observed that there the flux is decreased significantly after the membranes were modified by TFC, which is from around 0.25-0.40 to be about 0.05 L m$^{-2}$ h$^{-1}$, respectively. It is quite common to obtain the reduction of flux for the membranes coated with additional layer, creating TFC membrane [21] or for membranes subjected to crosslinking processes [25, 26]. The reduction is
likely due to the addition of tighter layers or caused by polymer chain repacking in microscopic level [25]. The quality of the separation was improved slightly, from between 20-50% to 50%-67% (with varied operating pressure from 40-70 psi), for PEI15 and PEI15-TFC, respectively.

The low quality of rejection of RB5 dyes shown in Figure 5 might be a result of low concentration of dyes in the simulated wastewater containing RB5 dyes. Therefore, to corroborate this suggestion, addition experiments for testing the effect of the concentration of dyes were conducted. The nanofiltration process of RB5 dyes with initial dyes concentrations of 50, 100, and 150 ppm were conducted at uniform operating pressure of 40 psi, and the result is reported in Figure 6. It could be observed that the higher the concentration of RB5, then the higher the rejection, where it could achieve 92.2% rejection for initial dyes concentration of 150 ppm.

In order to understand the structure-performance relationship of the membranes, or how the membrane modification influenced the separation performance, the cross-sectional view of the membranes as captured via SEM is shown in Figure 7.

It could be observed that the top surface of PEI15 (Figure 7a) is still thin and has numerous voids in the structure. However, the PEI15-TFC (Figure 7b) exhibited a denser top surface than that of PEI15, having less voids and giving an impression of being stiffer than that of PEI15. This is the structure that is desired for a top selective layer.
The chemistry behind the fabrication of PEI-TFC membranes is discussed in Figure 8, based on the results from the FTIR characterizations, for PEI15 and PEI15-TFC, in Figure 8a, and 8b, respectively. The FTIR spectra of PEI15-TFC showed N-H deformation vibration and C=C stretching vibration [27] at around 1600-1640 cm⁻¹, and aromatic ring breathing [28] at as the indicator of polyimide groups.

4. Conclusion

It could be concluded that PEI-TFC membrane was successfully prepared via interfacial polymerization between MPD and TMC. The fabricated PEI-TFC membrane could separate textile dyes wastewater (RB5, 150 ppm) with 92% rejection, due to the additional TFC selective layer which was confirmed by SEM and FTIR characterizations.

Acknowledgement

The authors would like to thanks Indonesia Toray Science Foundation who has awarded the research grant at 21st Science and Technology Research Grant to the Principal Investigator (Ir. Dave Mangindaan, PhD, AMRSC, AMIChemE, IPM) for conducted this study.
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