Polyetherimide thin film composite (PEI-TFC) membranes for nanofiltration treatment of dyes wastewater

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Abstract. In our previous work, a series of polyetherimide (PEI) nanofiltration membranes has been developed for removal of textile dyes from wastewater. Based on that previous study, another class of PEI-based membrane was developed for sustainable eco-engineering development in Indonesia, namely polyetherimide thin film composite (PEI-TFC) membranes. These PEI-TFC membranes were fabricated from dope solution consists of PEI dissolved in N-methyl pyrrolidone (NMP) solvent and acetone as a non-solvent. The dope solutions were then continued to the membrane casting process, followed by solvent exchange process to remove the residual NMP in the pores of the membranes. The cast membranes were then immersed in 1.5% w/w m-phenylenediamine (MPD) in deionized water, followed by immersion in (0.05% w/w trimesoyl chloride in hexane). Those chemicals act as precursor to form a polymeric thin film in a process called interfacial polymerization to attach TFC layer on top of the PEI-TFC membranes. The fabricated PEI-TFC membranes were employed to treat synthetic wastewater containing Reactive Red 120 dye (RR120), with good rejection of 90%. The membranes could be further explored for the improvement of environmental sustainability of Indonesia, especially for the water ecology system.

Keywords: membrane, polyetherimide, thin film composite, dyes, nanofiltration,

1. Introduction
Nowadays, the demand for high quality water for industrial and national usage is increasing. However, environment pollution keeps growing as most industries still discharge their wastewater directly to the surrounding water body. One of the major problems to the water body is the pollution caused by textile dyes. In order to overcome this environmental and ecology issue, there are several alternatives of commonly employed solutions, such as destructing the molecules of the dyes, or separate the dyes from wastewater [1]. Common routes for dyes destruction are chemical oxidation, photocatalysis, or biodegradation [2]. Unfortunately, they might not be feasible enough to break dyes which molecules are stable to light, microbial biodegradation, or oxidizers, and not to mention the requirement for high energy consumption [3-5].
As the approach of dyes destruction is quite limited, then the separation processes are emerged, namely adsorption, coagulation, and membrane-based separation [1]. Utilization of activated carbon is acceptable in terms of quality of separation, but sacrificed after being used or regenerated for few times, hence not economically viable [6-9], especially its effectiveness is limited only for acid and cationic dyes [10]. Similar limitation is also exhibited by coagulation and flocculation process [8, 11-14], where they are not effective for separating soluble dyes in water.

Besides those separation processes, membrane technologies for treatment of textile dyes wastewater have also been developed [3]. They are ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), which could be reviewed in detail in a particular literature [15]. With large pore diameter, hence large molecular cut-off, UF membranes are suitable for separating large molecule dyes and insoluble dyes, but not for separating small molecules [3, 16]. On the contrary, RO process is a high quality separation process, which it even can remove salt from seawater. However, RO is plagued with its requirement of high pressure (50 bar or more), thus rendering exorbitant operational cost [17]. In between those extremes, NF process come with a balance between adequate quality of separation of dyes [1] and low operational pressure [18]. With pore size between 0.5-2.0 nm, NF possesses molecular weight cut-off (MWCO) of 100 to 1000 Da [18, 19]. In this study we aim to approach the performance of RO in separating textile dyes, under lower operating pressure, by fabricating thin film composite (TFC) nanofiltration membranes, based on a previous development on polyetherimide (PEI) nanofiltration membranes [20].

The TFC membranes were prepared by interfacial polymerization process, described by a polymerization reaction which involves a system comprises of two reactive precursors (e.g. amine in water, and acyl chloride in hexane, which are both immiscible) reacting at the interface of those immiscible solvents, to create thin polyamide layer. In this study we employed m-phenylenediamine (MPD) and trimesoyl chloride (TMC) as the monomers [21, 22]. The illustration of interfacial polymerization to form TFC is shown in Figure 1.

![Interfacial polymerization between TMC and MPD to create polyamide thin film composite membranes (TFC)](image)

**2. Methodology**

Firstly, the membranes were prepared by modifying the previously fabricated and optimized formulation [20] using PEI/acetone/NMP (N-methyl pyrrolidone solvent) with compositions of 15/20/65 and 16/20/64 w/w. Secondly, the casted membranes were coated with MPD, followed with and TMC, with the molecular form listed in Figure 1 [23], and to be labelled as PEI-TFC. PEI membranes were then immersed in 1.5 wt% MPD dissolved in deionized water for 2 min, and subsequently immersed in 0.05 wt% TMC in hexane also for 2 min. The membranes were dried in oven at 70°C for 30 min. Thirdly, the separation performance of the membranes, in terms of quantity, was tested by using a permeation cell combined with pressurized N₂ gas (pressure 40-70 psi). The separated object is Reactive Red 120 (RR120) textile dye dissolved in water as a simulated wastewater, with concentration of 100 ppm. The procedure, apparatus for testing the membranes, the standard curve for quantifying the color of the permeate are detailed in the previous study [20].
The aspect of quantity in the separation performance of the membranes is demonstrated by the parameter of permeate flux, while the aspect of quality is illustrated by the parameter of the rejection. The following equation was used to determine the permeate flux flow rate.

\[ J = \frac{V}{A \times t \times P} \]  

with \( J \) = Flux (L m\(^{-2}\) s\(^{-1}\) psi\(^{-1}\)), \( V \) = Effluent volume (L), \( A \) = Membrane Surface Area, \( t \) = Time required to contain the permeate (s), and \( P \) = the pressure required feed to pass through the membrane (psi).

To determine the quality of the separation, UV-Vis spectrophotometer was utilized to measure the absorbance of the permeate flow. A typical series of results may varied from pale pink to transparent water (i.e. close to clean water). The quality of the membrane separation is illustrated as color rejection, which is determined by using following equation:

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

with \( \%R \) = Rejection, \( C_p \) = Concentration of the permeate (ppm), and \( C_f \) = Concentration of feed solution (ppm). Standard curve for RR120 was prepared beforehand and was measured at maximum wavelength \( \lambda_{\text{max}} = 515 \text{ nm} \). Furthermore, the pore radius of the fabricated membrane is estimated by using the Laplace equation, as follows [15]

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

Pore radius \( r_{\text{pore}} \) of a capillary shaped pore completely wetted (contact angle \( \theta = 0^\circ \)) by water (surface tension \( \gamma = 72.3 \text{ mN/m} \), with typical operating pressure of around 50 psi (~3.4 bar = 340000 Pa) is around 425 nm. Therefore, the pore of the fabricated NF membrane is confirmed to be in the nanometer range.

3. Results and Discussion

Firstly, the findings from the previous work [20] about the quantitative parameter (permeate flux) were reviewed. The previous work found that the suitable membranes are that of PEI16 (from the dope PEI/acetone/NMP concentration of 16/20/64 w/w). However, when subjected to filtration of pure water (without dyes), the pure water permeability (PWP) of PEI16 demonstrated low flux, less than 0.25 L m\(^{-2}\) h\(^{-1}\) psi\(^{-1}\), can only flow if the operating pressure is 50-80 psi, as shown in Figure 2. If PEI16 membranes are to be subjected to interfacial polymerization, it would not be recommended as the flux might be virtually nothing. Therefore, it was decided to make membranes with larger pore size by reducing the polymer concentration in the dope solution, resulting in PEI15 (PEI/acetone/NMP concentration of 15/20/65 w/w). This strategy worked out quite well as the PWP of PEI15 is around 0.40-1.50 L m\(^{-2}\) h\(^{-1}\) psi\(^{-1}\), with lower operating pressure of 40-70 psi. Therefore, the PEI15 membranes were utilized in this study.

![Figure 2. PWP of PEI15 (PEI/acetone/NMP concentration of 15/20/65) and PEI16 (16/20/64) membranes as function of operating pressure](image-url)
After the decision to use PEI15 (PEI/acetone/NMP concentration of 15/20/65) was taken, then the PEI15 membranes were modified by interfacial polymerization to obtain PEI-TFC. The separation performance of the PEI-TFC in separating RR120 dyes (100 ppm) is shown in Figure 3. It was observed that there is a significant decrease of flux after membranes were modified by TFC, from around 0.25-0.40 to be about 0.05 L m^{-2} h^{-1}. The reduction of flux is quite normal for the membranes modified with TFC [22] or crosslinking processes [24, 25] due to the addition of tighter layers or due to microscopic polymer chain repacking. The quality of the separation was not all encouraging, as the separation result for those under operating pressure 60-70 psi is not changed much. However, for those separated at 50 psi, there is an improvement of color rejection from 38% to 60%. In addition, the best result so far is for the separation using PEI16-TFC under 40 psi, that achieved rejection of 88%, which is also an improvement from the result from the previous work, which was only 81% rejection [20].

Figure 3. Separation performance of PEI15-TFC membranes for separating RR120 dyes (100 ppm) at operating pressure 40-70 psi

To comprehend how the membrane modification affected the separation performance, we conducted a characterization for physical morphology by using SEM. The cross-sectional views of the membranes are shown in Figure 4. It could be seen that PEI-TFC (Figure 4, right) exhibited an additional thin layer on top of the membrane, estimated at 3 μm, which came from the interfacial polymerization between MPD and TMC on the PEI15 (Figure 4, left).

Figure 4. Cross-sectional view of membranes, (left) PEI15, and (right) PEI15-TFC
4. Conclusions
Based on the results shown in this study, 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 (RR120, 100 ppm) with performance close to 90% rejection, at 0.17 L m$^{-2}$ h$^{-1}$ psi$^{-1}$, owing to the additional TFC selective layer which was confirmed by SEM characterizations. This study may open new avenues for the eco-engineering development in Indonesia, especially for the sustainable water ecology system.

5. Acknowledgement
The authors would like to thanks Indonesia Toray Science Foundation for research grant in this study.

References

[1] A.Y. Zahrim and N. Hilal, (2013), "Treatment of highly concentrated dye solution by coagulation/flocculation–sand filtration and nanofiltration", Water Resour. Ind. Vol. 3 pp. 23-34
[2] O.J. Hao, H. Kim and P.C. Chiang, (2000), "Decolorization of Wastewater", Crit. Rev. Env. Sci.Technol. Vol. 30 pp. 449-505
[3] A. Akbari, J.C. Remigy and P. Apte, (2002), "Treatment of textile dye effluent using a polyamide-based nanofiltration membrane", Chem. Eng. Process. Vol. 41 pp. 601-609
[4] E. Forgacs, T. Cserhati and G. Oros, (2004), "Removal of synthetic dyes from wastewaters: a review", Environ. Int. Vol. 30 pp. 953-971
[5] O. Tünün, I. Kabdasli, G. Erememktar and D. Orhon, (1996), "Color removal from textile wastewaters", Water Sci. Technol. Vol. 34 pp. 9-16
[6] T. Robinson, G. McMullan, R. Marchant and P. Nigam, (2001), "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative", Bioresour. Technol. Vol. pp. 247-255
[7] A.K. Verma, R.R. Dash and P. Bhunia, (2012), "A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters", J. Environ. Manage. Vol. 93 pp. 154-168
[8] M. Riera-Torres, C. Gutiérrez-Bouzán and M. Crespi, (2010), "Combination of coagulation–flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents", Desalination Vol. 252 pp. 53-59
[9] C.Z. Liang, S.P. Sun, F.Y. Li, Y.K. Ong and T.S. Chung, (2014), "Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration", Journal of Membrane Science Vol. 469 pp. 306-315
[10] W.-J. Lau and A.F. Ismail, (2009), "Polymeric nanofiltration membranes for textile dye wastewater treatment: Preparation, performance evaluation, transport modelling, and fouling control — a review", Desalination Vol. 245 pp. 321-348
[11] A. Bes-Piá, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, B. Cuartas-Uribe and M.I. Alcaina-Miranda, (2005), "Nanofiltration of textile industry wastewater using a physicochemical process as a pre-treatment", Desalination Vol. 178 pp. 343-349
[12] T. Chen, B. Gao and Q. Yue, (2010), "Effect of dosing method and pH on color removal performance and floc aggregation of polyferric chloride–polyamine dual-coagulant in synthetic dyeing wastewater treatment", Colloid Surf. A-Physicochem. Eng. Asp. Vol. 355 pp. 121-129
[13] A.Y. Zahrim, C. Tizaoui and N. Hilal, (2011), "Coagulation with polymers for nanofiltration pretreatment of highly concentrated dyes: A review", Desalination Vol. pp. 1-16
[14] K.E. Lee, N. Morad, T.T. Teng and B.T. Poh, (2012), "Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review", Chem. Eng. J. Vol. 203 pp. 370-386
[15] M. Mulder 1992 Basic Principles of Membrane Technology (Netherlands: Kluwer Academic Publishers)
[16] K. Majewska-Nowak, (1989), "Synthesis and properties of polysulfone membranes", Desalination Vol. 71 pp. 83-95
[17] T. Wang, L. Dai, Q. Zhang, A. Li and S. Zhang, (2013), "Effects of acyl chloride monomer functionality on the properties of polyamide reverse osmosis (RO) membrane", J. Membr. Sci. Vol. 440 pp. 48
[18] S. Cheng, D.L. Oatley, P.M. Williams and C.J. Wright, (2011), "Positively charged nanofiltration membranes: review of current fabrication methods and introduction of a novel approach", Adv. Coll. Interf. Sci. Vol. 164 pp. 12-20
[19] S.P. Sun, T.A. Hatton and T.S. Chung, (2011), "Hyperbranched polyethyleneimine induced cross-linking of polyamide-imide nanofiltration hollow fiber membranes for effective removal of ciprofloxacin", Environ. Sci. Technol. Vol. 45 pp. 4003-4009
[20] D. Karisma, G. Febrianto and D. Mangindaan, (2017), "Removal of dyes from textile wastewater by using nanofiltration polyetherimide membrane", IOP Conf. Ser.: Earth Environ. Sci. Vol. 109 pp. 012012
[21] K.C. Khulbe, C. Feng and T. Matsuura, (2010), "The Art of Surface Modification of Synthetic Polymeric Membranes", J. Appl. Polym. Sci. Vol. 115 pp. 855-895
[22] A. Sutedja, C.A. Josephine and D. Mangindaan, (2017), "Polysulfone thin film composite nanofiltration membranes for removal of textile dyes wastewater", IOP Conf. Ser.: Earth Environ. Sci. Vol. 109 pp. 012042
[23] G. Han, S. Zhang, X. Li, N. Widjojo and T.S. Chung, (2012), "Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection", Chem. Eng. Sci. Vol. 80 pp. 219-231
[24] D.W. Mangindaan, N.M. Woon, G.M. Shi and T.S. Chung, (2015), "P84 polyimide membranes modified by a tripodal amine for enhanced pervaporation dehydration of acetone", Chem. Eng. Sci. Vol. 122 pp. 14-23
[25] D.W. Mangindaan, G.M. Shi and T.S. Chung, (2014), "Pervaporation dehydration of acetone using P84 co-polyimide flat sheet membranes modified by vapor phase crosslinking", J. Membr. Sci. Vol. 458 pp. 76-85