Diaminoethane-crosslinked polyetherimide nanofiltration membrane for textile wastewater dye removal

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Abstract. In this work, diaminoethane (DAE) is applied to improve the properties of polyetherimide (PEI) nanofiltration (NF) membranes via crosslinking process with the core objective of removal of textile dye from wastewater. The membranes were fabricated by phase inversion thin film casting technique, from PEI/acetone/NMP (n-methyl pyrrolidone) dope solution, crosslinked with DAE 2.5 % v/v in methanol. The novelty of this study is that DAE has never been utilized to crosslink PEI NF membrane for removal of dye from textile wastewater. In this study, the parameters of composition of polyetherimide dope solution having acetone as non-solvent content are investigated to obtain a potential membrane for clarifying wastewater, which is one of major problems in Indonesia. A model dye was utilized, namely Reactive Red 120 (RR120) as a synthetic wastewater. It is found that the rejection of dye is increased along with the acetone content, and also by the crosslinking duration. The crosslinking between PEI and DAE is analyzed from the physical and chemical aspects, by using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), respectively. A good performance in nanofiltration of RR120 synthetic dye wastewater is demonstrated with 92-98% dye rejection, which is quite reasonable compared to previous researches. This PEI-DAE NF is therefore promising not just for sustainable waste management, but also for the innovation and development in the ecology and environment of Indonesia.

Keywords: membrane; nanofiltration; polyetherimide; diaminobenzene; acetone.

1. Introduction
Textile industries have played a big role in contaminating clean water because of the waste produced. These industries are characterized by their high consumption of water and chemical, which is caused by dyeing, finishing, sizing processes, and multiple washing and rinsing cycles [1]. The produced effluents exhibits indication of contamination, such as conductivity, chemical oxidation demand (COD), turbidity, suspended solids, and color [2], with the aforementioned parameters of quality standards for textile wastewater effluent are shown in Table 1. Furthermore, they also contain organic compounds such as phenols, dyes, and so on, which some of them are very toxic and may damage the living things [3].
Table 1. Quality standard for wastewater from textile industries in Europe [2]

| Parameters                          | Criteria          |
|-------------------------------------|-------------------|
| Chemical oxygen demand (COD, mg/L)  | 60-80             |
| Conductivity (µS/cm)                | 1000              |
| pH                                  | 6.0-8.0           |
| Turbidity (NTU)                     | 1                 |
| Color (Pt-Co)                       | None              |
| Suspended solids (mg/L)             | 5                 |
| Dissolved solids (mg/L)             | 500               |
| Total Hardness (mg/L as CaCO$_3$)   | 25-50             |

It could be clearly observed from Table 1 that one of the hardest quality parameter that must be obtained is the removal of the color of textile dyes. Membrane technology, especially nanofiltration (NF), is an emerging strategy to overcome this problem [4] especially when several conventional methods are not satisfactorily address the issue. Some conventional methods are destruction of dyes [5] via chemical oxidation, photo-catalysis or biodegradation [6] which requires high energy demand; adsorption [7-9] that is limited to the regeneration of adsorbent; and coagulation and flocculation that capable only on agglomerating insoluble dyes, but not suitable for soluble dyes or reactive dyes [9-11]. NF membrane process has a promising performance to treat textile wastewater having reactive dyes [5, 12-14]. Furthermore, successful removal of color via NF process is followed by simultaneous reduction of COD, as demonstrated by Chakraborty and coworkers [15]. They effectively removed reactive dyes (Cibacron Black B and Cibacron Red RB) from wastewater by 74-96%, and at the same time reduced COD by similar trend 72-92%.

From the aforementioned descriptions, NF membrane process is a promising process for textile dyes removal from wastewater. However, its performance must be improved in order to tackle the removal efficiency of dyes from wastewater. There are some modifications for membranes in the literature such as interfacial polymerization [13, 16] and crosslinking [17], with crosslinking as one of the simplest method for membrane modification as it combines the polymeric chain of membranes, tightens loose structures of the membranes and then transforms them into tightly packed membranes that could separate small molecules. One of the commonly used chemical to enhance the performance of membranes is diaminooethane (DAE) [17]. Its vapor could even successfully crosslink pervaporation membranes [18], and imbues hydrophilic amine functionality that facilitates water transport [19]. It is also worth noting that the surface incorporation of hydrophilic amine group is favorable for biomedical applications [20].

To the best of our knowledge there is no NF membrane in the literature that is crosslinked by DAE and applied for the improved nanofiltration separation of textile dyes, especially the reactive dyes. Most of the reports from Indonesia are about dye degradation by using bioreactors [21-25]. It is quite ironic, because Indonesia has numerous textile industries, of more than 2500 companies, drawing investment of more than 100 billion dollars, with production capacity of 6.1 million ton per year [26] with estimated more than 1 billion m$^3$ wastewater generated every year (assuming 200 m$^3$ wastewater generated per ton product), with very minimum treatment taken for the wastewater. Therefore, this study aims to achieve this target by using polyetherimide (PEI) polymer as the building block of the membranes, having adequate chemical resistance properties [12]. The reactive dye to be separated from wastewater was Reactive Red 120 (RR120). To comprehend the effects of crosslinking to the membrane, SEM (scanning electron microscopy) was employed to examine the morphology of PEI after crosslinked by DAE. Moreover, the chemistry of crosslinking of PEI by DAE was evaluated by FTIR (Fourier transform infrared spectroscopy).
2. Methodology

The membrane material used in this research was PEI, dissolved in N-methyl pyrrolidone (NMP) and acetone (non-solvent additive) with concentration of PEI/NMP/acetone of 15/65/20, 16/64/20, 17/63/20 w/w, with total mass of 40 g each of polymeric dope solution. The detailed fabrication procedures of flat sheet PEI membranes could be found elsewhere [12]. In brief, the dope solutions were prepared by mixing PEI, NMP, and acetone until they form homogeneous mixture. The dope solution were then poured onto a clean glass plate and then casted with casting knife maintaining the thickness of 250 µm. The casted dope solution and the glass plate were directly immersed into a water bath, and transformed to be a solid membrane via the phase inversion process [27].

The prepared membranes were then tested for its ability to pass pure water using a permeate cell [12, 13, 28], being pressurized by gas at 40 to 80 psi (equals to 2.7 to 5.4 atm, respectively). This test to estimate the parameter of quantity (flux) of the membranes is called pure water permeability (PWP) test. Some selected membranes were further improved for the dye rejection performance via crosslinking modification. The membranes were crosslinked by using DAE dissolved in methanol, with concentration of 2.5 % v/v for 30 minutes. Membranes were washed by using methanol for three times to remove the residual crosslinking agent continued with heating in oven at 70 °C for 3 hours (following a modified procedure of [29]). The molecular structure of DAE is shown in Figure 1. The mechanism of the crosslinking process is happened when the imide ring of PEI is experienced nucleophilic attack by DAE that causes the scission of PEI chains and also opening the imide ring that is converted into amide groups [18].

![Figure 1. Molecular structure of DAE](image)

The membrane productivity parameter (flux) is calculated using the following equation:

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

(1)

with \( J \) = flux (L m\(^{-2}\) h\(^{-1}\)), \( V \) = permeate volume (L), \( A \) = membrane active surface area, \( t \) = time required to contain the permeate (s). The quality parameter (rejection) of the membrane is calculated using this following equation:

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

(2)

with \( %R \) = Rejection, \( C_p \) = permeate concentration (ppm), \( C_f \) = feed concentration (ppm).

The concentration of permeate and feed was analyzed by using spectroscopy analysis [12]. Spectroscopy was utilized to determine the evolution of concentration of RR120 in wastewater (initial concentration= 100 ppm, maximum absorption occurred at wavelength \( \lambda_{max} \) = 515 nm) after being filtrated through PEI NF membranes with and without crosslinking modification.

3. Results and Discussion

The fabricated membranes were assessed for their PWP performance, demonstrated in Table 2. It could be observed that the PEI 17/63/20 membrane is not suitable for further development since there is no flux produced. It is suggested that the concentration of dope solution of PEI 17/63/20 is too high and resulting in pores that are too tight or too small, hence no water could pass through. This result is not beneficial, and therefore further study will employ the membranes from PEI 15/65/20 and PEI 16/64/20 that could permeate pure water.
Table 2. PWP of PEI membranes

| Types    | Composition (w/w) | 40 psi | 50 psi | 60 psi | 70 psi | 80 psi |
|----------|-------------------|--------|--------|--------|--------|--------|
| Unmodified | 15/65/20         | 0.2676 | 1.1383 | 1.4042 | 1.6702 | 2.0585 |
|          | 16/64/20         | 0.1686 | 0.1986 | 0.2286 | 0.2534 | 0.2781 |
|          | 17/63/20         | 0      | 0      | 0      | 0      | 0      |
| Modified  | 15/65/20         | 0.2011 | 0.2514 | 0.2798 | 0.3143 | 0.3423 |
|          | 16/64/20         | 0.0947 | 0.1320 | 0.2399 | 0.2095 | 0.2127 |
|          | 17/63/20         | 0      | 0      | 0      | 0      | 0      |

The effect of operation pressure to the flux and rejection to the membranes PEI 15/65/20 and PEI 16/64/20 was investigated at variation of 40, 50, 60, 70, and 80 psi for treating RR120 solution with concentration of 100 ppm. The result is shown in Table 3. It could be observed that under same operation pressure of 40-80 psi, the membranes PEI 15/65/20 without crosslinking modification demonstrated higher permeate concentration, which correlated with lower rejection (less than 60%), compared to that of PEI 16/64/20 (rejection 76-84%). Based on the aforementioned result, it is suggested that PEI 16/64/20 is quite promising for further study employing DAE crosslinking. The separation performance of membranes crosslinked by DAE at 40, 50, 60, 70, and 80 psi is shown in Table 4. It could be observed that there are significant improvements of rejection (ranged from 92 to 98%) for the membranes crosslinked with DAE, which is better than the previous researches (PEI without modification [12], PEI with interfacial polymerization modifications [30, 31], and almost similar to PEI crosslinked with m-phenylenediamine [28]. In order to give better comprehension on the result, the separation performance of PEI membranes, with and without DAE modification is shown in Figure 2.

Table 3. Separation performance of PEI membranes, without DAE crosslinking modification

| Pressure (psi) | Permeate concentration (ppm) | Rejection (%) | Flux (L.m⁻².h⁻¹) | Permeate concentration (ppm) | Rejection (%) | Flux (L.m⁻².h⁻¹) |
|----------------|------------------------------|---------------|------------------|------------------------------|---------------|------------------|
| 40             | 40.6881                      | 59.3%         | 0.2514           | 15.3694                      | 84.6%         | 0.0541           |
| 50             | 63.9450                      | 36.1%         | 0.2606           | 17.8889                      | 82.1%         | 0.0566           |
| 60             | 72.9817                      | 27.0%         | 0.2892           | 20.4085                      | 79.6%         | 0.0590           |
| 70             | 81.5596                      | 18.4%         | 0.3374           | 22.8872                      | 77.1%         | 0.0616           |
| 80             | 90.1376                      | 9.9%          | 0.3856           | 23.3320                      | 76.7%         | 0.0651           |

Table 4. Separation performance of PEI membranes, with DAE crosslinking modification

| Pressure (psi) | Permeate concentration (ppm) | Rejection (%) | Flux (L.m⁻².h⁻¹) | Permeate concentration (ppm) | Rejection (%) | Flux (L.m⁻².h⁻¹) |
|----------------|------------------------------|---------------|------------------|------------------------------|---------------|------------------|
| 40             | 2.3853                       | 97.6%         | 0.0125           | 1.7045                       | 98.3%         | 0.0110           |
| 50             | 3.2142                       | 96.8%         | 0.0133           | 2.8169                       | 97.2%         | 0.0122           |
| 60             | 5.4149                       | 94.6%         | 0.0164           | 3.9292                       | 96.1%         | 0.0145           |
| 70             | 9.7495                       | 90.3%         | 0.0282           | 5.5724                       | 94.4%         | 0.0185           |
| 80             | 11.694                       | 88.3%         | 0.0366           | 7.1912                       | 92.8%         | 0.0268           |
From the result in Figure 2, it is clearly shown that the best membrane is PEI 16/64/20 membrane crosslinked with DAE 2.5 % v/v for 30 minutes, heated for 70 °C, giving high rejection ranged from 92 to 98%. In order to understand how the DAE crosslinking modification successfully improved the rejection performance of PEI membranes, SEM and FTIR characterizations were performed, in Figure 3 and Figure 4, respectively.

**Figure 3.** SEM cross section of (a) PEI 15/65/20 without modification, (b) PEI 15/65/20 with DAE crosslinking, (c) PEI 16/64/20 without modification, and (d) PEI 16/64/20 with DAE crosslinking modification.

From the SEM result in Figure 3, the morphology of membranes under SEM characterization was shown, having identical magnification of 1000×. The cross-sectional structures of crosslinked PEI 15/65/20 and PEI 16/64/20 membranes are thicker, tighter and have more homogeneous structure than
that of unmodified membranes. These structures are desired to obtain optimum filtration performance. In order to confirm the structure-performance relationship, these membranes were subjected to FTIR characterization, shown in Figure 4.

![Figure 4. FTIR characterization of PEI membranes (a) without modification, and (b) with DAE crosslinking](image)

From Figure 4, the FTIR chemical characterization of membranes (a) without, and (b) with DAE crosslinking modification showed that there are new peaks emerged, and therefore the crosslinking modification process was successfully carried out. In the Figure 4a there are fingerprint peak of PEI, from the C=O group for the asymmetric stretch at 1776.44 cm\(^{-1}\), C=O group for symmetric stretch at 1720.5 cm\(^{-1}\) and C-N group at 1352.1 cm\(^{-1}\). In Figure 4b, the successful modification brought the fingerprint of amide group (C=O stretching at 1641.42 cm\(^{-1}\) and C-N stretch at 1527.62 cm\(^{-1}\)) while simultaneously reduce the imide profile of PEI at 1352 cm\(^{-1}\) [18, 27].

4. Conclusions
In this study, we have successfully fabricated PEI-based membranes and improved the separation performance by DAE crosslinking. The crosslinked NF membrane PEI/NMP/acetone 16/64/20 %-wt crosslinked 30 mins) exhibited good performance in filtration of synthetic dye wastewater (RR120, 100 ppm) with 98% dye rejection and 0.011 L m\(^{-2}\) h\(^{-1}\) of flux at relatively low operating pressure (40 psi).

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