Removal of dyes from textile wastewater by using nanofiltration polyetherimide membrane

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Abstract. Followed by rapid development of the textile industries since 19th century the dyeing technology is thriving ever since. However, its progress is followed by lack of responsibility and knowledge in treating the dye-containing wastewater. There are some emerging technologies in treating such kind of wastewater, where membrane technology is one of those technologies that has uniqueness in the performance of separating dyes from wastewater, accompanied with small amount of energy. The development of membrane technology is one of several eco-engineering developments for sustainability in water resource management. However, there are a lot of rooms for improvement for this membrane technology, especially for the application in treating textile wastewater in Indonesia. Based on the demand in Indonesia for clean water and further treatment of dye-containing wastewater, the purpose of this research is to fabricate nanofiltration (NF) membranes to accommodate those problems. Furthermore, the fabricated NF membrane will be modified by interfacial polymerization to impart a new selective layer on top of NF membrane to improve the performance of the separation of the dyes from dye-containing wastewater. This research was conducted into two phases of experiments. In the first phase the formulation of polymeric dope solution of PEI/Acetone/NMP (N-methyl-pyrrolidone), using the variation of 15/65/20, 16/64/20, and 17/63/20. This research show that many areas still can be explored in textile wastewater treatment using membrane in Indonesia.

Keywords: Membrane, polyetherimide, nanofiltration, acetone, reactive red

1. Introduction

The global crisis of clean water is one of the challenges facing humankind today [1]. Textile industry consumed large amount of water [2], where each kilogram of fabrics consumes between 60-100 kg during dying and washing process [3]. This is why textile industry became one of the largest producers of wastewater. Unfortunately, most textile industries choose to dispose their wastewater to the surrounding environment, because it is quite difficult to handle this kind of waste. The amount of liquid waste generated from textile industry is reported to be about 2-180 liters wastewater per kg textile product [4]. Remazol black 5 (RB5), remazol red, remazol blue, and remazol yellow are some widely used dyes in the textile industry [5].
Until now, there are several methods have been developed to deal with waste from the textile industry and classified to biological treatment process (eg, activated sludge) and chemical-physical treatment (eg, coagulation-flocculation) [4, 6]. However, those methods still require further process. The output from those methods not clean enough to use for process water, still contain dyes and high COD (Chemical Oxygen Demand) [7].

Therefore, membrane technology has been developed which have a good ability to reduce COD, BOD (Biological Oxidation Demand), TSS (Total Suspended Solid), pH, conductivity and high dyes rejection [7]. Membrane separation process is called molecular level separation. Molecule transfer through membrane, caused or assisted by several driving force such as concentration gradient (∆C), temperature gradient (∆T), pressure gradient (∆P), and energy gradient (∆E) [8].

There are several types of membrane based on it pore size [8], such as: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF Membrane pore diameter ranged between 0.1 to 10 μm [9] and 10-150 μm for the thickness, whereas UF membrane pore diameter ranged between 0.1 to 1 nm, UF membrane give good result for separation of large molecule but not with small molecule. RO membrane has the better result for separation of small molecule until ionic molecule, caused it has smallest pore diameter compared with MF, UF and NF. Although efficient dye removal can be achieved by RO, the high-pressure requirement of RO process (50-70 bar, for some process can reach until 120 bar) jeopardizes its potential due to expensive cost of utilizing high pressure [10, 11]. NF is categorized between UF and RO, therefore NF provide significant advantages such as, lower osmotic pressure gradient, higher permeate flux, multivalent salt retention and can reject organic component with molecular weight 200 until 1000 Da such as dye and salt divalent [11, 12]. Furthermore, NF membrane operating pressure is not high as RO membrane, which is about 2-40 bar [10, 11]. Although NF retention is not good as RO, NF considered more advantageous because its operating cost are lower than RO; the higher the operating pressure, the higher the operating cost.

Industrial polymers are commonly used for NF membrane fabrication such as: polyacrylic acid (PAA), polyvinyl alcohol (PVA), agarose, alginate, chitosan [13], polyimide, polysulfone and polyetherimide [14, 15, 16]. Polyetherimide (PEI) is one of the polymers that can support and produced superior NF membrane. This paper is aiming to fabricate NF membranes from PEI to treat textile wastewater, especially to obtain sustainable water treatment that is complying eco-engineering development in Indonesia.

2. Experimental

This research was conducted with the objective of fabricating NF membrane from PEI, first by making dope solution of PEI. The PEI polymer could only be dissolved in a dipolar aprotic solvent only, in this case N-methyl pyrollidone (NMP). Furthermore, acetone is selected as a non-solvent additive for the polymeric dope solution of PEI/NMP/Acetone with compositions of 15/65/20, 16/64/20 and 17/63/20 wt% was utilized for this study. The concentration of PEI was chosen based on the previous researches where the best polyimide-based membranes are from those with concentration of 15-20 wt% in the special solvent NMP.

Polymeric dope was casted as a thin film through non-solvent induced phase separation process (NIPS). In the casting process, the dope solution is poured onto the glass plate, and spread evenly using casting knife of 250μm thick. NIPS process or called phase inversion happened when the dope solution submerged into water so that the dope solution become a solid membrane. Addition of non-solvent additive (in this case is acetone), will increasing the viscosity of the dope solution. With higher viscosity, the water cannot easily penetrate the dope solution, so the phase inversion will be delayed. The process illustrated at Figure 1. The effect of delayed demixing is the formation of sponge like pore [16, 17] which is make membrane more selective and higher retention.

After the membrane has been casted, then the membrane is immersed in flowing water. The excess of solvent that keep remains inside the membrane removed by solvent exchange. The
membranes are immersed in methanol for 3×30 minutes, with immersion in hexane for another 3×30 minutes. Finally, the membranes were stored at cool dry place.

Performance of the membrane tested using 100 ppm of Reactive Red 120 (RR120). The membrane expected to have good rejection for RR120 that contain in wastewater. Permeation cell (Figure 1) was utilized to testing the membrane performance. The parameter that will be tested are permeate flux (membrane quantity parameter) and the permeate concentration (membrane quality parameter).

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 effluent (s), and \( P \) = the pressure required feed to pass through the membrane (psi).

Furthermore, the color determination was conducted for the textile wastewater before and after treat using membrane. The purpose is held to know the color rejection achieved by membrane separation. In this determination, UV-Vis spectrophotometer was utilized to measure the absorbance of the effluent. The color rejection 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 \( \lambda_{max} = 515 \ nm \).

![Figure 1. Flat sheet membrane fabrication process, and the permeation cell](image-url)
3. Result and discussion

3.1. Effect of PEI membrane concentration on the pure water permeability (quantitative performance)

Before performing the main research, a preliminary research needs to be performed. The purpose for doing this preliminary research is to find the best dope formulation with the best permeate rate (flux). Flux (permeate rate) of pure water permeability (PWP) from different formulation is shown in Table 1. From Table 1, it is observed that the PWP from 17/63/20 formulation is too slow, the membrane will not be tested further. The very low flux of the 17/62/20 membrane came from too much polymer chain inside the membrane (17% PEI). Therefore, the other two membranes, with adequate amount of PEI (15/65/20 and 16/64/20 membranes) will be tested for quality determination.

| PEI dope formulation | PWP (mL m⁻² s⁻¹ psi⁻¹) |
|----------------------|-------------------------|
| 15/65/20             | 30.52                   |
| 16/64/20             | 6.44                    |
| 17/63/20             | 0.02                    |

3.2. Effect of PEI membrane concentration on the rejection (qualitative performance)

Permeate concentration measure using spectrophotometer. Standard curved was made (Figure 2) to determine the effect of RR120 concentration with absorbance.

![Figure 2. RR120 standard cuve (absorbance vs concentration)](image)

The main research carried out once the standard curved was obtained. The 15/65/20 and 16/64/20 PEI membrane will be tested. Membrane performance was tested by removing RR120 with 100 ppm initial concentration from textile wastewater at various operating pressure. Nanofiltration result was shown in Figure 3. Furthermore, the pore radius of the membrane is estimated by using the Laplace equation

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

Pore radius \(r_{pore}\) of a capillary shaped pore 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. Therefore, the nanofiltration feature of the fabricated NF membrane is confirmed to be in the nanometer range.
Figure 3. Permeate concentration at different nanofiltration operating pressure

From Figure 3, it can be assumed that each membrane has dense pore, where at <30 psi (2 atm) pressure none of liquid pass through permeation cell. 15/65/20 PEI membrane can be penetrated at 40 psi, but the permeate quality is not satisfactory because the concentration is almost same with the feed concentration, which is around 80 ppm.

On the other hand, 16/64/20 membrane has quite high threshold pressure (50 psi/3.5 atm), but the permeate concentration is lower than 30 ppm, so 16/64/20 membrane have good potential at dyes removal. The results in Figure 3 were requalified using the %R rejection parameter, and presented in Table 2.

Table 2. 15/65/20 and 16/64/20 PEI membrane performance from nanofiltration

| Pressure (psi) | PEI 15/65/20 | PEI 16/64/20 | PEI 15/65/20 | PEI 16/64/20 |
|---------------|---------------|---------------|---------------|---------------|
| 10            | -             | -             | -             | -             |
| 20            | -             | -             | -             | -             |
| 30            | -             | -             | -             | -             |
| 40            | 42.23         | -             | 57.76         | -             |
| 50            | 66.38         | 18.57         | 33.61         | 81.42         |
| 60            | 75.76         | 25.23         | 24.23         | 74.76         |
| 70            | 84.66         | 24.14         | 15.33         | 75.85         |
| 80            | -             | 23.81         | -             | 76.19         |

Referring to Table 2, shown that 16/64/20 membrane rejection reach until 81%, so that the textile wastewater with 100 ppm of RR120 can be reduce to 19 ppm. The different result is shown by 15/62/20 membrane, where it only reduces to 42 ppm (57% rejection).

4. Conclusion
This study success to made PEI-based membrane, which able to reduces until 81% of RR120 dyes with 50 psi pressure. The PEI membrane was fabricated from 16/64/20%-weight of PEI/NMP/Acetone formulation.

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References

[1] G. Han, S. Zhang, X. Li, N. Widjojo, TS. Chung, (2012), “Thin film composite forward osmosis membranes based on polydopamine modified polysulfone substrates with enhancements in both water flux and salt rejection”, Chemical Engineering Science, Vol. 80, pp. 219-231

[2] J. Sójka-Ledakowicz, T. Koprowski, W. Machnowski, HH. Knudsen, (1998). “Membrane filtration of textile dyehouse wastewater for technological water reuse”. Desalination, Vol. 119, pp. 1-9.

[3] T. Chidambaram, Y. Oren, M. Noel, M., (2015), “Fouling of nanofiltration membranes by dyes during brine recovery from textile dye bath wastewater”. Chemical Engineering Journal, Vol. 262, pp. 156-168.

[4] YK. Ong, FY. Li, SP. Sun, BW. Zhao, CZ. Liang, TS. Chung, (2014), “Nanofiltration Hollow Fibre Membranes for Textile Wastewater Treatment: Lab-scale and Pilot-scale Studies”, Chemical Engineering Science, Vol. 114, pp. 51-57.

[5] S. Meric, G. Lofrano, V. Belgiorno, (2005) “Treatment of reactive dyes and textile finishing wastewater using Fenton’s oxidation for reuse”. International Journal Environment and Pollution, Vol. 23, pp. 248-258

[6] MR. Templeton, D. Butler, (2011), An Introduction to Wastewater Treatment. Imperial College London and University of Exeter, United Kingdom.

[7] M. Marcucci, G. Nosenzo, G. Capannelli, I. Ciabatti, D. Corrieri, G. Ciardelli, (2001), Treatment and Reuse of Textile Effluents Based on New Ultrafiltration and Other Membranes Technologies. Desalination, Vol. 138, pp. 75-82

[8] M. Mulder, (1992). Basic Principles Of Membrane Technology. Netherland: Kluwer Academic Publishers.

[9] RW Baker, (2000), Membrane Separation, Membrane Technology & Research Inc. (MTR), Menlo Park, CA, USA.

[10] J. Pinnekamp, H. Friendrich (Eds). (2003). Membrane Technology for Waste Water Treatment.

[11] SP. Sun, (2011), Fabrication of Nanofiltration Hollow Fiber Membranes for Sustainable Pharmaceutical Manufacture. National University of Singapore, PhD thesis.

[12] M. Amini, M. Arami, NM. Mahmoodi, A. Akbari, (2011), “Dye removal from colored textile wastewater using acrylic grafted nanomembrane”. Desalination, Vol. 267, pp. 107-113.

[13] X. Qiao, T. Matsuura, TS. Chung, SH. Goh (2008), “Investigation of the fundamental differences between polyamide-imide (PAI) and polyetherimide (PEI) membranes for isopropanol dehydration via pervaporation”, Journal of Membrane Science, Vol. 318, pp. 217-226.

[14] DW. Mangindaan, GM. Shi, TS. Chung, (2014), “Pervaporation dehydration of acetone using P84 co-polyimide flat sheet membranes modified by vapor phase crosslinking”, Journal of Membrane Science, Vol.458, pp.76-85.

[15] DW. Mangindaan, NM. Woon, GM. Shi, TS. Chung, (2015), “P84 polyimide membranes modified by a tripodal amine for enhanced pervaporation dehydration of acetone”. Chemical Engineering Science, Vol. 122, pp. 14-23.