Removal of direct red dye using polysulfone-chitosan ultrafiltration membrane

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Abstract. Textile industries are one of the largest pollution contributor to the environment through high amount of wastewater discharge that contain high concentration dyes. The present state of application of using membrane technology in the removal of dyes from textile wastewater has shown positive pathway for this research. Chitosan are biopolymer that are naturally occurring. It is used as a hydrophilic additive in the fabrication of polysulfone (PSF) and chitosan (CS) membrane. Different loadings of CS at 0.1, 0.3, 0.5, 0.7 and 1.0 wt% were used. The fabricated PSF-CS membrane by phase inversion method were characterized using SEM for its morphology, FTIR for its functional group and contact angle for membrane hydrophilicity. As the addition of CS increase the hydrophilicity of the PSF-CS membrane, excessive CS precipitation was observed at chitosan loading at 1.0wt% creating a large macro void causing lower permeation performance. It is found that PSF-CS membrane with 0.7wt% has the best contact angle and dye rejection performance of 65.49º and 99.78%.

1. Introduction

Textile industry is one of the vital and vast emerging industry worldwide including Malaysia. Despite being a contributor to the economic growth, textile industry has been categorized as one of the industry that produces massive pollution problem especially with respect to liquid effluent. Wastewater effluent produced from textile factory have high possibility to cause environmental pollution and health-risk issues to rise due to the large scale production and extensive dye usage in dyeing and finishing involved[1]. Textile wastewater effluent that contain dyes has high intensity in color even in low concentration and removing dye itself is a challenging problem [2]. When wastewater contain untreated dye is released into the sewer, the high intensity color will affect the aquatic life because dye particles will block sunlight from penetrating through causing the photosynthetic activity to decrease [3]. Existing techniques that currently applied by the industry is either ineffective in removing dye as they pass through the municipal wastewater treatment facilities or they are very expensive such as activated sludge adsorbent.
Therefore, other alternative such as membrane technology could be a promising technique in treating textile effluent, effectively. Several studies have been conducted in matter of removing, treating or purifying textile wastewater effluent through membrane technology. In 2012, Abid [4] uses reverse osmosis and nanolfiltration to treat several synthetic dye which are acid red, reactive black and reactive blue. They achieved up to 99% for reverse osmosis technique while the nanolfiltration achieved up to 97% rejection with all the synthetic dye. Karisma [5] studied nanolfiltration polyetherimide membrane for the removal of reactive red (RR120), obtained 81% rejection performance operating at 50 psi and Gholami [6] also studied nanolfiltration polyamid and cellulose acetate blend running pressure at 0.5-3 bar, were able to achieved 92.5% rejection for disperse dye. Recently, Kadhim [7] studied ultrafiltration of the removal of two toxic dye which are acid black and rose bengal using graphene oxide mixed matrix membrane. As a result, the membrane displayed high rejection rate of 99% for both dyes. Therefore, membrane technology is an efficient way in the treatment of textile wastewater in order to tackle the existing challenges.

Polymeric membrane used in this study is polysulfone (PSF) where it exhibits high mechanical strength, good chemical resistance, thermal stability and excellent aging resistance making it a suitable material for the application in textile wastewater effluent treatment [8]. However, for the application of PSF in the industry comes down to a few major downsides which are PSF is naturally hydrophobic [9] and over a period of time protein or particles presence in the wastewater effluent got absorbed onto the membrane surface can block the surface pores and causes serious fluctuation in flux and low rejection performance [10]. Therefore, hydrophilic additive or nanoparticles can be included with the PSF membrane to produce a hydrophilic membrane. In this study, chitosan is used as an additive to be incorporated inside the PSF polymer to formed a mixed matrix membrane for the removal of direct red (DR80) dye.

Chitosan originated from chitin through deacetylation process. It is a hydrophilic material due to presence of two crosslinkable groups of hydroxyl (-OH) and amine (-NH₂) [11]. It became soluble in aqueous acidic solution when the degree of deacetylation of chitin reaches 50% and it is widely used in different field used for removing pollutants through coagulation, flocculation, filtration and membrane filtration [12]. Chitosan is a pseudonatural cationic polymer and is unique enough to be used in different applications mainly as solutions, gels, films or fibres [13]. Furthermore, chitosan has been used in other previous studies such as PVDF [14], PES [15], films [16] and coatings [17]. The preparation of the PSF-CS mixed matrix membrane using phase inversion which is relatively simple process. The produce membrane was thoroughly characterized and tested for DR80 removal performance.

2. Materials and Methods

2.1. Chemicals
Polysulfone pellet (PSF, Udell1700) with average molecular weight of 69 500 g mol⁻¹ was purchased from Solvay Advanced Polymers. Other following chemicals were directly supplied by Sigma Aldrich, USA, such as chitosan low molecular weight (degree of deacetylation > 75%), polyvinylpyrrolidone (PVP, K40) with average molecular weight of ~40,000 g mol⁻¹ was used as an additive for the dope solution, while 1-methyl-2-pyrrolidone (NMP, Purity = 99.5%) was used as the organic solvent to dissolve dope solution. The soluble dye used for the filtration performance was Direct Red 80 (DR80) with average molecular of 1373.07 g mol⁻¹. Tap water was used as the coagulation bath.

2.2. Membrane fabrication
Prior to the fabrication of PSF-CS dope solution, PSF pellet need to be oven-dried for 24 hours at 80°C to remove any moisture present. The method of blending chitosan inside polymeric dope solution consist of suspending chitosan powder in N-methyl-1-pyrrolidone solution together with polyvinylpyrrolidone as the pore former at 50°C until homogenous solution was formed. Fix amount of PSF pellet was slowly added into the solution forming a homogenous dope solution. Dope solutions were mixed using a magnetic stirrer and sonicated for 1 hour to remove any air bubbles formed during mixing. The
membranes were prepared using phase inversion method. Flat sheet membranes with thickness approximately ~200µm were casted onto a glass plate and was immersed into the coagulation bath at 24 °C. The prepared PSF-CS membrane was kept in the coagulation bath for two (2) days to remove any excess solvent and let dried in the oven at 35 °C. The prepared membrane was kept sealed in an air tight container until further used.

2.3. Membrane characterization
The functional group of the membrane was examined using a ATR-Fourier Transform Infrared Spectroscopy (ATR-FTIR, Nicole 5700 Thermo Electron) to analyse the chemical structure of pristine PSF membrane and modified PSF-CS membrane. The morphology for the surface and cross section of the membrane was characterize using Scanning Electron Microscopy (SEM, Hitachi TM3000). The membrane sample was fractured in liquid nitrogen and spurred coated with gold before carrying out the analysis. The hydrophilicity of the membrane was determined using water contact angle which was measured with Contact Angle System OCA. Approximately 1µl of deionized water was carefully dropped on the membrane surface at 5 different points and the average of measured values are recorded as the final water contact angle.

2.4. Permeation performance
All permeation performance for pristine and modified membrane including pure water flux and rejection performance were carried out using crossflow filtration system. The effective membrane area was 2.46×10⁻³ m² at 25 °C and pressure of 1 bar. The membrane was soaked in deionized water for 24-hour prior for testing to ensure even water distribution before being placed in the cell holder. Feed tank was filled with deionized water and permeate sample collection started after 30 minutes of membrane compaction time at pressure of 2 bar. Sample collection continued at every 10-minute interval. The pure water flux (PWF) was calculated using the following equation:

\[ J_W (L/m^2h) = \frac{Q}{\Delta t A} \]

Where \( J_W \) is the pure water flux expressed as L/m²h, while \( Q \) is the volume of permeate sample in Litre (L), \( t \) is the time interval in hour and \( A \) is the total membrane area in m².

The permeate sample concentration was measured using UV-Spectrophotometer (HACH DR5000). For direct red dye rejection, 50 ppm of direct red dye solution was prepared and maximum wavelength was 532nm. The permeate sample was collected every 30 minutes under the pressure of 1 bar. The system was allowed to run for total of 180 minutes. The rejection (R%) was calculated using the following equation:

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

Where R is the rejection in percent (%), while \( C_P \) and \( C_F \) is the concentration of permeate and feed sample in ppm, respectively.

3. Results and Discussions
3.1. ATR-FTIR analysis
The ATR-FTIR analysis was carried out on the prepared membrane to confirm the presence of chitosan on the surface of the PSF membrane. Different loadings of chitosan (0.1, 0.3, 0.5, 0.7 and 1.0wt%) were prepared. Excessive precipitation chitosan loadings above 1.0wt% in the dope solution can be observed. Figure 1 shows the FTIR spectra for pure chitosan, pristine PSF and PSF-CS membrane. All different loadings of chitosan showed similar FTIR peaks. In Region I, it can indicate the presence of O-H stretching at 3345 cm⁻¹, that belongs to hydroxyl group of chitosan that contribute to the hydrophilicity...
of the PSF-CS membrane. Region II, peaks at 2970 cm\(^{-1}\) and 2872 cm\(^{-1}\) that belongs to aromatic C-H stretch and aliphatic C-H stretch, respectively proving that chitosan has been successfully incorporated inside the PSF membrane. In Region III, at peak 1659 cm\(^{-1}\) depicts the presence of amine group \(-\text{NH}_3\) originated from chitosan [18].

*Figure 1.* ATR-FTIR spectra for CS, PSF-CS and PSF membrane.

3.2. Morphology analysis

The difference on the morphology of PSF-CS membrane were studied by SEM. Figure 2 shows the cross-sectional and surface images of pristine PSF and PSF-CS membrane. From the SEM images, the pristine PSF membrane and PSF-CS membrane have a typical asymmetric structure with top and support layer with finger-like channel [19]. Upon the addition of chitosan, the finger-like channel became wider and short in length. This phenomenon may be cause by the intrusion of non-solvent (water) through the membrane as the chitosan loadings increases therefore, bigger pore can be observed [20]. At the same time, bigger macro void can be observed in all PSF-CS membrane as the chitosan loadings increase from 0.1wt\% to 1.0wt\%. The pore size of the membrane upon the addition of chitosan was approximately 100nm. As higher loadings chitosan is blend directly with the dope solution, excessive chitosan precipitation can be observed inside the dope solution. This can also be proved from its cross-section where a large “lump” of chitosan can be observed where it settles under the surface of the membrane. Initially, the addition of chitosan was to increase the membrane hydrophilicity but due to this behavior, excessive present chitosan has eventually decreases its hydrophilicity and its rejection performance. Figure 2 also shows that as the chitosan loadings increases, more porous surface can be observed but even more chitosan particles can be seen which will lead to pore blocking.
Figure 2. SEM images of cross-sectional and surface morphology of pristine PSF and PSF-CS membrane.

3.3. Water contact angle analysis
Water contact angle analysis is carried out to determine the membrane hydrophilicity. Table 1 represents the water contact angle analysis of the PSF and PSF-CS membrane. It is generally known that any membrane that has a contact angle <90º is considered hydrophilic [21]. Pristine membrane is hydrophobic but upon the addition of chitosan, the PSF-CS membrane gradually became hydrophilic. PSF-CS membrane with chitosan loading of 0.7wt% was the most hydrophilic in comparison with the other PSF-CS membrane. As for PSF-CS membrane with chitosan loading of 1.0wt%, the membrane started to become hydrophobic due to the fact that the chitosan particles have started to clog the pores of the membrane.

Table 1. Water contact angle analysis for pristine PSF and PSF-CS membrane.

| Membrane | PSF  | CS0.1 | CS0.3 | CS0.5 | CS0.7 | CS1.0 |
|-----------|------|-------|-------|-------|-------|-------|
| WCA (°)   | 95.40| 92.90 | 81.79 | 78.09 | 65.49 | 82.57 |

3.4. Permeation performance
The pure water flux performance of the membrane was carried out using cross-flow filtration system. As expected, all PSF-CS membrane have higher pure water flux in comparison with pristine PSF membrane. Previously, it is proven that the addition of chitosan increases the membrane hydrophilicity [22]. As the hydrophilicity increases, the pure water flux will also increase. Figure 3 shows the pure water flux analysis, where PSF-CS membrane with chitosan loading of 0.7wt% has the highest amount at 160.249 L/m²h. The pure water flux started to decrease when chitosan loading is at 1.0wt%. This may due to the fact that excessive loading of chitosan has blocked the pore surface of the PSF-CS membrane which reduce the surface area of the membrane and the formation of large macro void that was formed during the fabrication of the membrane.
3.5. Dye rejection analysis

Pristine PSF and PSF-CS membrane that was developed could be used to remove textile effluents that is usually charged. Direct red (DR80) dye (MW = 1373.07 g/mol) is anionic charged dye which is suitable for this developed PSF-CS membrane. The developed PSF-CS membrane has been analyzed to be negatively charged upon the addition of chitosan. Since, both the membrane and DR80 dye particles are both negatively charged, the membrane is able to repel the DR80 dye particles as DR80 is relatively a large dye particle. Since the pore size of the PSF-CS membrane is larger (~100nm) than the size of the dye particles, the dye particles can be removed through charge repulsion mechanism [23]. From Figure 4, PSF-CS with chitosan loading of 0.7wt% has the best DR80 rejection of 99.78% followed by membrane with loading of 0.3wt% with DR80 rejection of 99.56%. From these results, it is worth to note that the removal of dye does not only depend on sieving mechanism [24]. From the high rejection observed, it is believed that the charged repulsion mechanism between the PSF-CS membrane and DR80 dye, together with the morphological structure of the PSF-CS membrane, DR80 can be successfully removed without any further treatment such as backwash or even using polyelectrolyte or micellar assisted ultrafiltration.

Figure 3. Pure water flux performance for PSF-CS membrane.
4. Conclusion
In this study, chitosan has been successfully incorporated with PSF membrane producing a PSF-CS membrane. Blending of chitosan inside the dope solution has turned PSF membrane that is naturally hydrophobic into a hydrophilic membrane due to the presence of hydroxyl groups of chitosan. The presence of chitosan also increases the membrane permeation. However, the amount of chitosan used affect the morphological structure of the membrane due to the formation of large macro void and excessive amount of chitosan will eventually reduce the pure water flux performance and its hydrophilicity due to pore blockage. Filtration test performance of direct red (DR80) was performed on the PSF-CS membrane with chitosan loading of 0.7wt% has the highest rejection of 99.78%.

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