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Fabrication and Characterisation of Polyethersulfone/Chitosan/Non-ionic Nanofiltration Membrane for Dyes Removal

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Abstract. Recently, dyes are generally used in various industries and release of these dyes into streams will pose a serious threat to the environment. In this research, a nanofiltration membrane was fabricated via phase inversion as it is one of the most convenient methods for membrane fabrication. It is used in removing dyes by using pluronic as a surfactant and chitosan as an additive. By varying the concentration of pluronic as a surfactant at 1 wt%, 2 wt%, and 3 wt%, and a constant amount of chitosan as an additive, three newly dope solutions were formulated. The fabricated membranes were analyzed by evaluating the membrane in terms of pure water permeation (PWP), permeation flux, salts rejection and dyes rejection. The introduction of pluronic as a surfactant and chitosan as an additive to the nanofiltration membrane produced high PWP and presented high salts rejection and dyes removal. Generally, high dyes rejections were achieved by M3 which contained high weight percentage (wt%) of pluronic as it showed highest percentage rejection for acid red, methyl blue and reactive black 5. The functional groups of the membranes were characterized and verified by using Fourier transform infrared spectroscopy (FTIR).

INTRODUCTION

Dye effluents from dye manufacturing and dye consuming industries such as food, paper, plastic and textile can cause problematic water pollution [1]. Dye production and dyeing stages containing high chemical oxygen demand (COD) and poor biochemical purification produce effluents that contains a variety of organic matter with biological toxicity such as carcinogenic, teratogenicity and mutagenicity [2].There are numerous available methods to remove the dye from wastewater such as biodegradation, flocculation-coagulation, oxidation and adsorption. However, membrane separation technology was introduced for dyes removal and nanofiltration membrane is the most suitable for the separation [3].

Nanofiltration can be considered closely related to reverse osmosis as it is also known as loose reverse osmosis due to its larger pores. However, it actually intersects the characteristic between ultrafiltration membranes and reverse osmosis ranging from 200 to 2000 Da [4]. Nanofiltration membrane fabrication by using the phase inversion technique is usually accompanied by the presence of large elongated pores known as macrovoids. These macrovoids allow the passage of dye molecules, therefore reducing the retention properties of the membranes [5].

To enhance asymmetric nanofiltration membranes performance, manipulation of the membrane formation process, by introducing additive and surfactant in the casting solution, is an effective and efficient method. Chitosan

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is a good additive as it has a high potential of sorption of toxic metal ions, dyes and phenol due to their lone pair of electron on amino group enables it to act as active sites for the toxic ion adsorption, hence, demonstrate chitosan capabilities for adsorption of high and low concentrations of dyes [6]. A membrane is an interphase between two adjacent phases and acts as a selective barrier, which regulate the transport of substances between the two compartments. Hence, the different concentrations of pluronic as non-ionic surfactants was used in the formulation of nanofiltration membrane to solve the problem with a potential breakthrough advancement in industrial and analytical separations. Pluronic was used in membrane formation as it is a good pore forming agent and surface modifier because of its chemical stability. Hence, it can reduce interfacial free energy occurrence [7]. Thus, in this study, several pluronic concentrations were used to determine the most suitable membrane formulation for dyes rejection. The addition of pluronic to a polymer solution strongly enhances the permeability of the membrane to a specific point because of the increasing hydrophilicity of the membrane. Therefore, the main goal of this proposed project is to study the effect of different concentrations of surfactants on dyes removal. Fourier transform infrared spectroscopy (FTIR) was used to characterize the functional groups presence in the nanofiltration membrane.

MATERIALS AND METHOD

Preparation of Chitosan

The solid chitosan (Chitotech) was diluted with organic solvent acetic acid before it was added into a dope solution. 1.0 wt.% of aqueous acetic acid was obtained by mixing with 100 mL distilled water and 1.0 mL of glacial acetic acid. 100 mL of 1.0 wt.% of aqueous acetic acid was used to dissolve 1.0 g of medium molecular weight of chitosan. The mixed solution was then stirred vigorously overnight by using a magnetic stirrer.

Dope Formulation and Preparation

In this study, nanofiltration membrane dopes were formulated by using polyethersulfone (PES) from SOLVAY as polymer, N-methyl-2-pyrillidone (NMP) from Merck Millipore as the solvent, chitosan (Cs) (Chitotech) and polyethylene glycol (PEG) (Sigma Aldrich) as additives and pluronic F108 (Sigma Aldrich) as surfactant. The non-solvent used in this research was water. This is called as multi-component casting formulation. PES polymer was dried at room temperature (30±2 ºC) for 24 hours to remove all absorbed water vapor. The presence of water vapor in polymer solution was influenced by the quality of the dope solution. The polymer, PES, was gradually added into the flask that contained a desired amount of solvent, namely N-methyl-2-pyrrolidone (NMP), under a controlled temperature until it reached to 50-60 ºC throughout the mixing process. After all the polymer dissolved, PEG and chitosan (Cs) were gradually added into the flask followed by the pluronic as the surfactant. The mixing temperature was controlled and maintained as not to exceed the boiling point of the solvents (100 ºC) because they tend to vaporize. However, a low temperature was not encouraged during the mixing process. The dope solution was stirred until it became homogeneous, which typically took about 6-8 hours. The solution was then poured into a clean bottle after it had fully dissolved.

TABLE 1. Dope Formulation

Dopes	PES (wt. %)	NMP (wt. %)	PEG (wt. %)	Pluronic (wt. %)	Chitosan (wt. %)
M1	21	73	3	1	2
M2	21	72	3	2	2
M3	21	71	3	3	2

Membrane Casting

The membrane was fabricated by using dry/wet phase inversion via the immersion precipitation technique. The newly formulated dope solution was casted onto a glass plate as support layer with casting knife setting at 150 µm. Then, the glass plate, together with the membrane, was immersed in a water bath for 24 hours until coagulation was completed. The immersed membrane was soaked in ethanol for another 24 hours and followed by an n-hexane immersion for about 2-3 hours before it was dried at room temperature for at least 24 hours.

Membrane Permeation Performance

Pure Water Permeation

The NF membrane performance was evaluated by analyzing its stability in terms of pure water flux. This experiment was conducted with pure water which was about 5 bar under pressure to ensure it was stable. The membrane permeability was calculated by using the following equation:

$$\text{Permeation flux, } J_W = Q/(A.\Delta T)$$

Where,
J_W = the permeate flux (L/m^2h)
Q = volume of permeate solution collected (L)
A = area of membrane (m^2)
ΔT = permeation time of membrane (h)

Salt Rejection Test

The rejection of monovalent (NaCl) and multivalent salt ($MgSO_4$, $MgCl_2$, and Na_2SO_4) were used as a feed solution. The conductivity meter was used to measure the feed, permeate and retentate concentrations for each membrane. The following expression was used to calculate the percentage of salts rejection:

$$\text{Retention of rejection, R (\%)} = (1-C_p/C_f) \times 100$$

Where,
R = retention of rejection (%)
C_P = ion concentration of solute permeation (mg/L)
C_f = ion concentration of solute feed (mg/L)

Dyes Rejection

The dyes rejection test was carried out to determine the effectiveness of NF membrane fabricated for the dye removal. Three types of dyes were used, namely acid dye (Acid Red), basic dye (methyl blue) and reactive dye (Reactive Black 5). The test was conducted at a constant 100 ppm feed concentration of dyes and at a fixed operating pressure of 4.5 bar by using a simple dead-end permeation cell.

Membrane Characterization

The membrane sample was tested by using FTIR spectroscopy to analyze and verify the functional groups that presence in the membranes. IR spectrum determines the vibrational frequencies and transition intensities of most molecules (with the exception of diatomics, such as N_2 and O_2) including characteristic functional group frequencies.

RESULTS AND DISCUSSION

Pure Water Permeation Test

In this research, the measurement of water flux as a function of applied pressure was implemented to evaluate the stability and hydraulic properties of NF membrane. After about 15 – 20 minutes compaction process, the pure water permeability for each membrane samples were verified at five different pressures (3, 3.5, 4, 4.5 and 5 bar). Permeate was then collected at a steady state condition. The NF membranes permeability coefficient data were calculated and illustrated in Fig. 1.

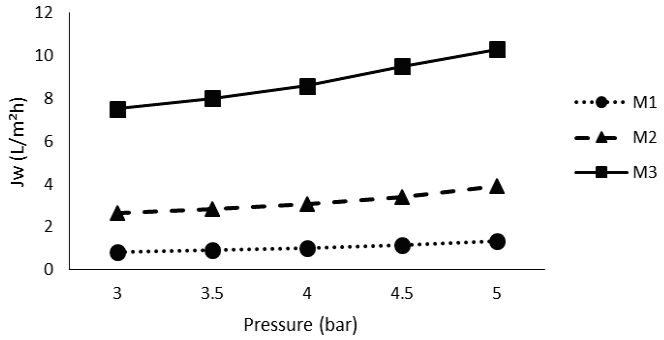

FIGURE 1. The flux value of PWP for NF membrane at different operating pressure

Generally, the incorporation of pluronic surfactant resulted in a better PWP and good porosity of NF membranes. The graph above states that the flux value trend, in general, is M3 > M2 > M1, whereby the lowest flux obtained was 0.81 L/m²h by M1 where the pressure at 3 bar and the highest pure water permeation achieved was 10.31 L/m²h by M3 at pressure of 5 bar. In general, it can be seen that the PWP flux value increases with the applied increasing pressure (bar). These results were supported by Amirilargani and co-worker [8] where it was stated that membranes with the inclusion of surfactant were found to produce a higher flux permeation with the increased porosity of the membranes support layer, thus resulting in high flux membranes. By using non-ionic surfactant, these hydrophilic membranes usually display good wettability, thus produce high fluxes [9]. According to Nguyen [10], non-ionic surfactant was stated to have a larger micelles size due to its low values of critical micelle concentration (cmc) hence, a higher flux can be obtained.

Flux and Salt Rejection Test

Practically, NaCl, $MgCl_2$, $MgSO_4$, and Na_2SO_4 are commonly used in the flux and rejection test in many salts and dyes rejection studies. In this research, 0.01 M of salt solution was used under the operating pressure of 4.5 bar. Based on Fig. 2 and 3, it can be concluded that by increasing the percentage of non-ionic surfactant, the permeation flux and salt rejection percentage increased. Azarteimour et al. [11] reported that adding more non-ionic surfactant increased the rejection of salt solution. The results from this research indicated that $MgSO_4$, Na_2SO_4, NaCl and $MgCl_2$ permeation flux showed respective increment by enhancing the non-ionic surfactant percentage in the membrane. All salts showed an increment in the permeation flux due to the increase of non-ionic surfactant concentration in the membrane matrix since pluronic enhanced the porosity of the membrane support layer, thus resulted in high flux membranes [8]. As shown in Fig. 2, $MgSO_4$ has the highest flux for M3, which is 8.39 L/m²h, followed by Na_2SO_4 (7.84 L/m²h), NaCl (7.22 L/m²h), and $MgCl_2$ (4.01 L/m²h), respectively. The hydration radius has influenced the result because Mg^{2+} has the largest radius as compared to others. For Na_2SO_4 at M2, it was slightly decreased from 3.08 L/m²h to 2.58 L/m²h due to cation accumulation during the test and the operating temperature might also be one of the causing factors [12].

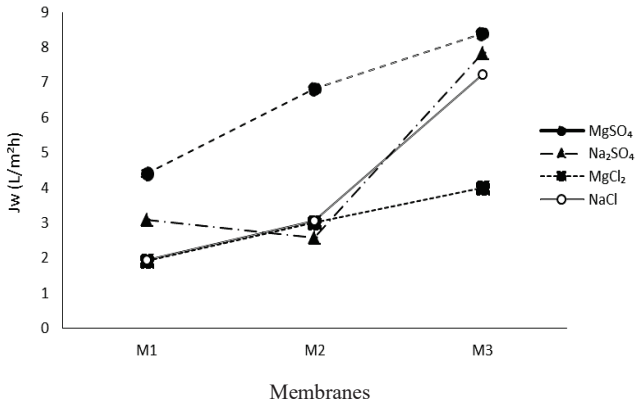

FIGURE 2. Permeation flux of salts of NF membrane

Generally, the rejection percentage results of M1 showed the highest result, especially with $MgSO_4$ as it has the largest hydration radius as compared to others, hence will result in low mobility and diffusion [11]. Steric effect on neutral surface membrane also plays a crucial role in salt rejection and typically shows low salt rejection. Size of exclusion and Donna exclusion effect influenced the result as $MgSO_4$ has a higher static electric action between the ion in the solution and membrane surface [12]. As for the rejection test shown in Fig. 3, these salts had resulted in the following manner, M1 > M2 > M3. M3, with the highest concentration of pluronic surfactant showing the lowest salt rejection values of 93.27% ($MgSO_4$), 93.0% (NaCl), 92.8% (Na_2SO_4), and 89.85% ($MgCl_2$) as compared to other membranes. It can also be concluded that M1, with the lowest concentration of pluronic surfactant, showed the highest salt rejection value for all four salts.

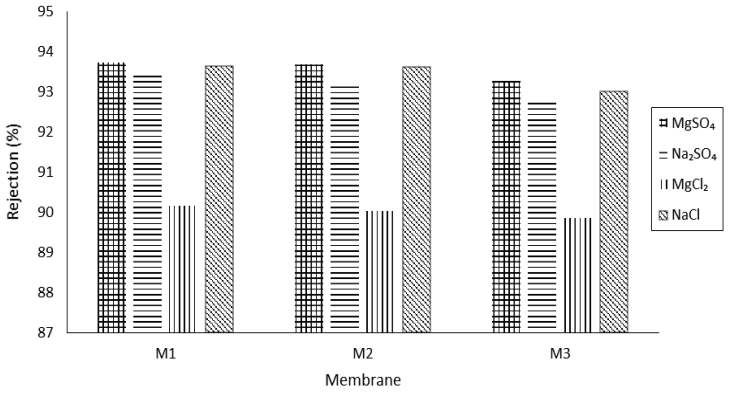

FIGURE 3. Percentage of multivalent salts rejection (%) of NF membrane

Flux and Dyes Rejection Test

Three different types of dyes, such as acid dye (Acid Red), basic dye (methyl blue), and reactive dye (Reactive Black 5) at a constant feed concentration of 100 ppm and fixed operating pressure of 4.5 bar were used to test flux and rejection. The permeate concentration of Acid Red was spectrophotometrically determined at maximum absorbance (λ_{max}) of 506 nm, methyl blue at maximum absorbance (λ_{max}) of 663 nm and Reactive Black 5 at maximum absorbance (λ_{max}) of 597 nm. Figure 4 shows the effect of NF membrane in different concentration of surfactant towards Acid Red, Methyl Blue, and Reactive Black 5 permeation flux and percentage of dyes rejection.

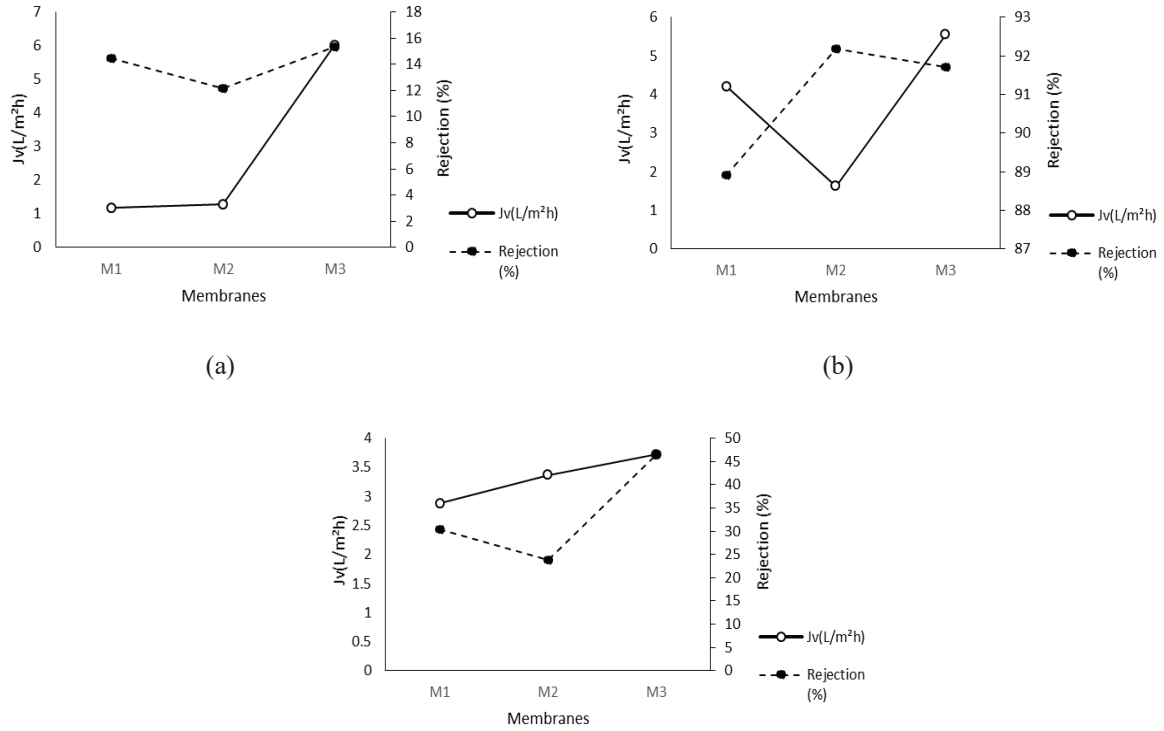

FIGURE 4. Flux and rejection of a) acid red permeation, b) methyl blue permeation and c) reactive black 5 permeation

From Fig. 4(a), it can be stated that M3 has the highest permeation flux at 6.01 L/m²h and also gave the highest percentage in the rejection test among all membranes, which was 15.35%. The lowest permeation flux was M1 with 1.19 L/m²h and gave the rejection test at 14.44%. While M2 has a permeation flux at 1.28 L/m²h but has the lowest percentage in rejection test among other membranes, which was only 12.19%. This revealed that the higher the concentration of pluronic caused a higher dyes rejection, except for M2. This might be due to the role of high pluronic percentage concentration in the membrane formulation. The overall dyes rejection might be due to the role of pluronic surfactant, chitosan and PEG where act as an additive and a denser polymeric membrane produced as they can increase porosity. The result from high concentration of polymer PES (21 wt %) in the dope formulations may change the membrane morphology and performance which can lead to a better dye removal [13]. The rejection change in the following manner, M3 > M1 > M2 at 15.35% > 14.44% > 12.18%, respectively. The decreasing rejection at M2 might be caused by fouling of membrane due to dye adsorption on membrane surfaces [14].

Meanwhile as for methyl blue permeation from Fig. 4(b) shows the highest flux permeation was at 5.55 L/m²h by M3 and the rejection was 91.7% which is the second highest after M2, in which the rejection was at 92.19%. Even though M2 shows the highest rejection at 92.19%, it has the lowest flux permeation value at 1.62 L/m²h. The experimental data shows that the higher the concentration of pluronic caused a higher dyes rejection, except for M2. This shows that M2 reacted well to methyl blue dye, which is a basic dye, as M2 gives only high rejection with methyl blue dye. As seen from Fig. 4(b), rejection percentage of methyl blue is dropped, might be due to the cake layer formed on the membrane surface [15].

The highest permeation flux for Reactant Black 5 from Fig. 4(c) is at 3.72 L/m²h and also gave the highest percentage of rejection test among all membranes, which was 46.64%. The lowest permeation flux goes to M1 at 2.89 L/m²h but gives a higher percentage in rejection at 30.32% than M2 which is only at 23.89%, even though M2 have the highest permeation flux at 3.37 L/m²h than M1. This revealed that a higher Pluronic concentration caused a higher dye rejection, except for M2. The rejection changed in the following sequences, M3 > M1 > M2 at 46.64% > 30.32% > 23.89%. The decreasing rejection at M2 may be caused by fouling of membrane by operational condition such as temperature, which might affect the rejection [16].

From Fig. 4, methyl blue indicates the highest percentage of rejection in the range of 85% to 93% while the lowest percentage rejection is shown at acid red about 10% to 16% rejection. As methylene blue is cationic soluble in water, there is an ionic interactions between the membrane and solute play a major role in the transport of ion across the membrane in term of diffusion and migration resulting in the highest permeate flux and also induced the highest percentage of rejection [11].

Characterisation of Nanofiltration Membrane

Nanofiltration membrane was characterized by using FTIR spectroscopy to distinguish functional groups presence in the membrane. Figure 5 shows the combination of the three spectra that consist of different concentrations of pluronic surfactant of the prepared membranes. The combined spectrum showed that all of the membranes exhibited a similar pattern of spectrum. A characteristics peaks at 3200 – 3550 cm^{-1} of the PES/NMP/H_2O/PEG/Cs/pluronic membrane correspond to –OH stretch shows the water presence in the dope solution as non-solvent while peaks at 2850-2950 cm^{-1} referred to C-H stretch. The presence of peaks that corresponds to polyethersulfone group were positioned at 1296 cm^{-1} (S=O asymmetric stretch), 1151 cm^{-1} (S=O asymmetric stretch), 1243 cm^{-1} (C-O stretch) and 1585 cm^{-1} (aromatic stretch). Since all the membranes used the same materials, thus, the FTIR results showed almost the same bands of polyethersulfone that appeared. There is no sign of NMP bands as NMP is a good solvent and already been dissolved during dope formulation process. On the other hand, the strong peak of C-O-C at 1101 cm^{-1} is due to the presence of pluronic in the membranes. The inclusion of PEG as additive in the dope solution can be identified and verified by the presence of band 843 cm^{-1} which correspond to the methyl group (-CH) bending of PEG.

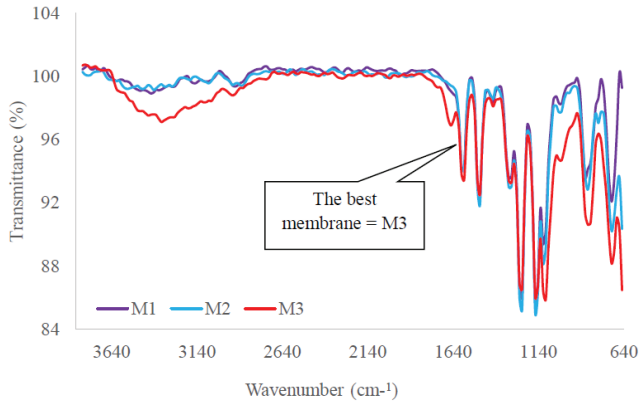

FIGURE 5. Functional group of the combined spectrum of NF membrane

CONCLUSIONS

Generally, increasing the concentration of pluronic (surfactant) enhanced the performance of nanofiltration membrane. In this study, it was found that M3 was the best membrane in terms of different concentrations between pluronic surfactant on the performance of NF membrane for dyes wastewater treatment. The membrane rejection rate and permeation flux for salts and dyes were high as the concentration of pluronic surfactant increased. The NF membranes also were successfully characterized and verified by using FTIR spectroscopy. In conclusion, polyethersulfone/surfactant/chitosan membrane prepared should be ready for use in practical applications, particularly in dye wastewater treatment process.

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