

ASSESSMENT THE PERFORMANCE AND MORPHOLOGICAL STRUCTURES OF ASYMMETRIC PES/SURFACTANT MEMBRANES FOR NANOFILTRATION OF DYES WASTEWATER

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ABSTRACT

In this study, an asymmetric PES/surfactant based nanofiltration membrane was prepared via simple dry/wet phase inversion technique. A newly dope formulations consisting of different surfactants and polymer concentrations ranging from 17wt% to 21wt% were developed. The effect of these parameters on dyes performance in terms of dyes flux, rejection and morphological structure were examined. Experimental data showed that at different ranges of polymer concentration, NFS membranes results low permeation flux of dyes ranging from 9.256 L/m²h to 14.315 L/m²h at 4 bars of operating pressure. Significantly, the addition of surfactant as additives into the membranes was found to cause the increasing of dyes flux and rejection up to 79.698 L/m²h and 99.5% respectively. Moreover, morphological study shows that the fabricated membranes were having of fine morphological structures.

Keywords: nanofiltration; surfactant; flux; rejection; morphological structure.

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1. INTRODUCTION

Nanofiltration (NF) membrane is the one promising technologies which has been largely developed and commercialized for the separation of neutral and charged solutes in aqueous solutions. NF membranes has two remarkable features which are has molecular weight cut-off (MWCO) between reverse osmosis (RO) membranes and ultrafiltration (UF) membranes ranges from 200 to 2000 Da. The other is NF can do separation electrolytes due to the materials containing charged groups [1]. According to these features, the separation mechanisms involve both steric and electrostatic partitioning effects between the membrane and external solutions. The combination between steric and electrostatic allows NF membranes more effective for the separations of mixtures of organic molecules and salts. An NF membranes main feature is that most of them are charged either positively or negatively depends on their materials [2-3].

In this study, asymmetric nanofiltration membranes were prepared via dry/wet phase inversion techniques. This technique has been introduced by [12] where is the most extensively used technique for the preparation of asymmetric membranes. In this technique, the solution is cast on a substrate/glass and immersed and precipitated in a water bath. Solvent in the casting solution was exchanged with non-solvent and phase separation will occurs in the film. This will resulted to the morphology of asymmetric membranes showing a dense top layer and porous sub-layer membranes [4]. Addition of surfactant as additive is the new materials used in formulating newly NF membranes. Surfactant has been used in soaps, laundry detergents, dishwashing liquids and shampoos are organic chemicals that reduce surface tension in water and other liquids. Surfactant also can be considered as amphiphilic due to the two parts which are hydrophilic part and hydrophobic part [5-6].

Addition of surfactant has been studied by several researchers which gives high membrane performance [7]. However, addition of surfactant in nanofiltration membranes and the interaction between surfactants and dyes is not been studied yet. According to [8], addition of surfactants in the casting solution can influence the formation process of macrovoids. Moreover, the size of macrovoids decreases with increasing the surfactant content [8]. In [9] in their studies discovered that addition of non-ionic surfactant in the casting solutions shows

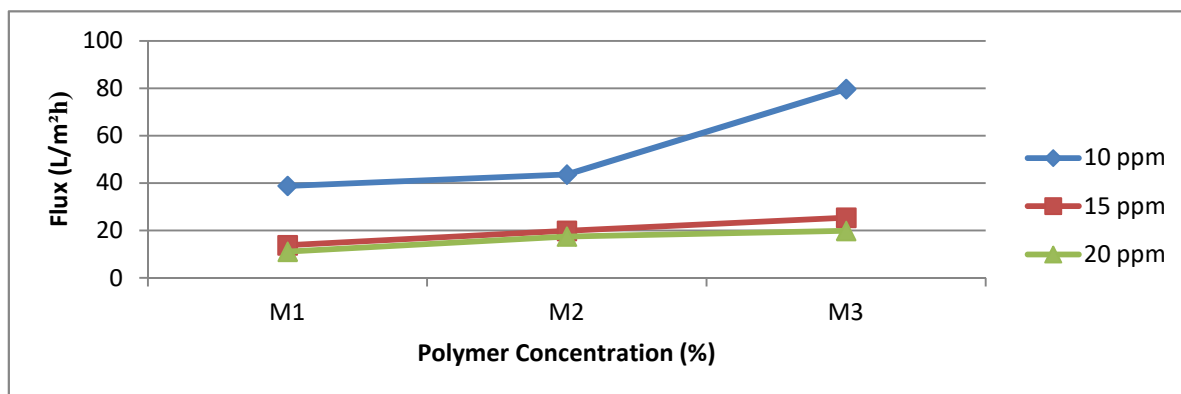
that the macrovoids and finger-like pores in the sub-layer can be induced or suppressed depending on their miscibility. Besides, they also discovered that addition of small amount surfactant will increase the water content, porosity and thickness of the prepared membranes.

2. RESULTS AND DISCUSSION

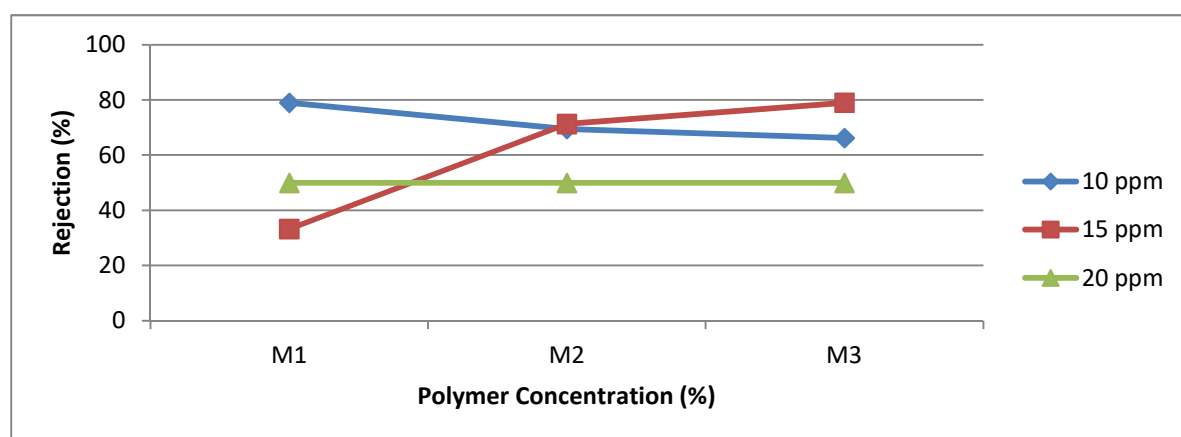
2.1. Dyes Flux and Rejection

In this study, three different dyes were used (Methyl Violet, Methyl Blue and Acid Orange) in order to determine the membrane performance in terms of permeation flux and dye rejection. Three different concentration of Methyl violet has been tested in order to see the significance difference of each prepared membrane tested where each concentration will give difference permeation flux and rejection.

Fig. 1(a) shows the permeation flux of Methyl violet at three different dye concentration of membrane with SDS as surfactant. Since 10ppm is the lowest dye concentration, it shows highest flux among other concentration of about, 38.8363 L/m²h. However, the permeate flux keep increasing as polymer concentration increase up to 79.6979 L/m²h. The rejection of 10ppm concentration of Methyl violet shows that as polymer concentration increase, the rejection will decrease from 79% to 66.2%. Unlike the lower dye concentration, at 13.7760 L/m²h, the membrane can reject dye only 33.3% at 15ppm dye concentration. Since polymer concentration also plays an important role in this study, the colour rejection of Methyl violet increased up to 79% at higher polymer concentration. As dye concentration increase, the permeate flux keep decreasing to 11.0843 L/m²h. However, for 20ppm of dye concentration, the three different polymer concentrations resulted to the same rejection. Study has been made revealed that addition of surfactants in casting solution will influence the formation of macrovoids [8].



(a)

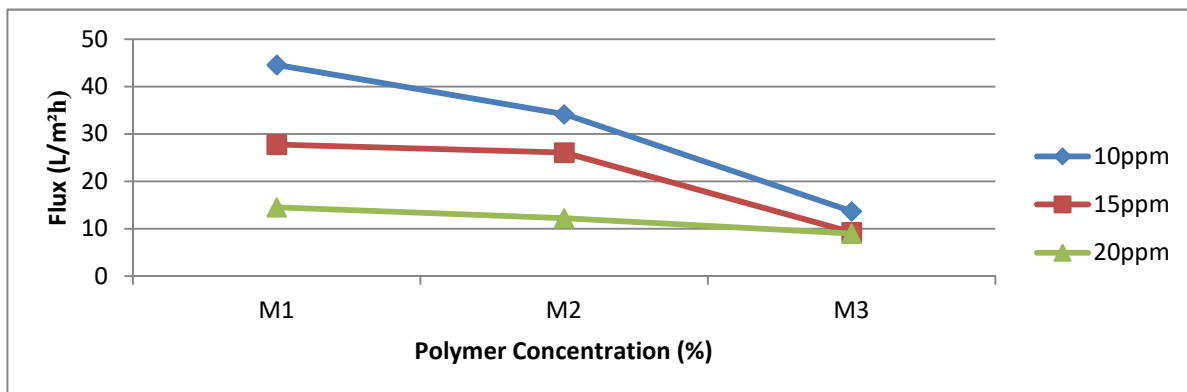


(b)

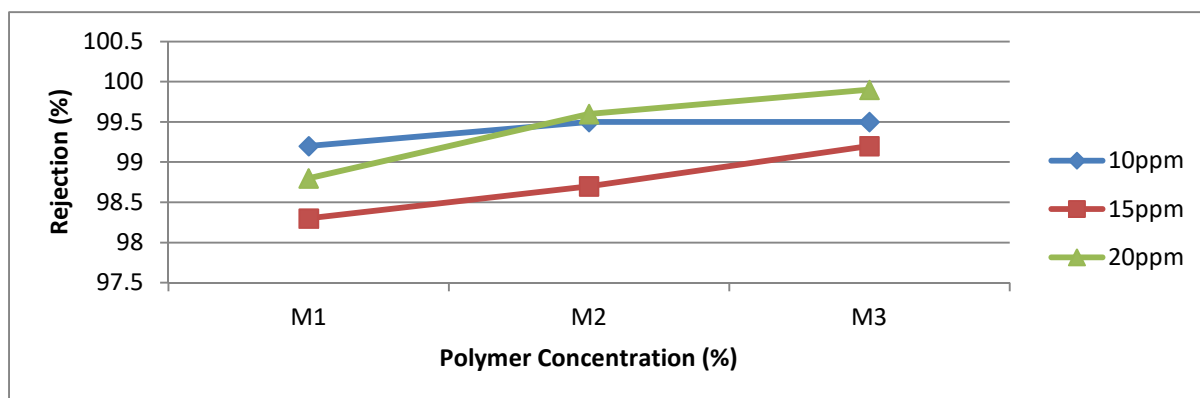
Fig.1. (a) Permeate flux (b) Percentage rejection of Methyl Violet

Experiment has been done shows that addition of SDS in polymer solution is not quite good for dyes rejection. Fig. 2(a) and 2(b) shows permeation flux and percentage rejection of Methyl blue using the membrane with CTAB as surfactant. The highest permeate flux were obtained from the lowest polymer concentration at the lowest dye concentration. At 44.565 L/m²h, M1 can remove dye of about 99.2% at 10ppm dye concentration. The results also shows that, as polymer concentration increase, the permeate flux decreased up to 13.682 L/m²h and increase the rejection to 99.5% for M3. According to [10], addition of CTAB surfactant in polymer solution will gives membrane with large pores that formed in the sub-layer of the membrane. Moreover, addition of CTAB said to be capable to increase the porosity of membrane support layer and result in high rejection of Methyl blue [10]. At 15ppm of dye concentration, the permeate flux shows the same results where the flux decrease when polymer concentration increase from 27.758 L/m²h to 9.272 L/m²h. Moreover,

the rejection of Methyl blue at 15ppm dye concentration increasing up to 99.1% for M3. Highest polymer concentration shows 8.972 L/m²h of permeation flux and can reject dye up to 99.9% at 20ppm of dye concentration.



(a)



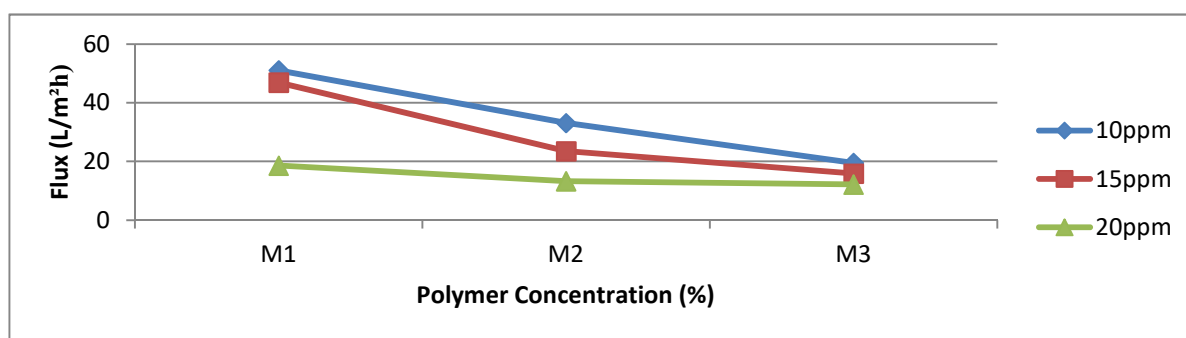
(b)

Fig.2. (a) Permeate flux (b) Percentage rejection of Methyl Blue

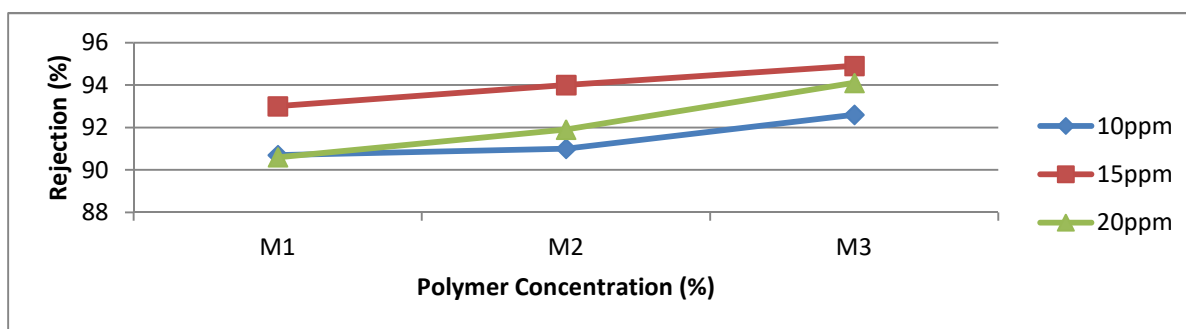
This study has covered three different types of dyes in order to see the significance difference tested using prepared membrane. In order to complete the experimental data, In addition, further test on the performance of the PES/CTAB membrane was conducted by using the acid orange dye. The same trends shown by Methyl blue and Acid orange permeation flux where the permeation flux decreased as polymer concentration increased with increasing of dye concentration as showed in Fig. 3. At 51.044 L/m²h, M1 gives dye rejection of 90.7% at 10ppm dye concentration. Research has been made to show that concentration of feed solutions is one of parameters that affects the membrane performance [11].

Acid orange resulted to decreasing of permeate flux when dye concentration increase and increasing of rejection as dye concentration increase. For 15ppm dye concentration, M1 gives

46.898 L/m²h of permeation flux and decrease to 15.871 L/m²h indicate M3 as the highest polymer concentration. Decreasing of permeation flux has increase the rejection up to 94.9%. Other than that, morphological structures of prepared membrane also is the most important parameters that gives high or low rejection towards dye solutions. At the lowest permeation flux of acid orange of about 12.175 L/m²h, 20ppm of dye concentration gives 94.1% dye rejection. Thus, this can be conclude that for acid orange with lower molecular weight, it will decrease the permeation flux and increase the rejection as polymer concentration increase as well as dye concentration increased.



(a)



(b)

Fig.3. (a) Permeate flux (b) Percentage rejection of acid orange

2.2. Morphological Structures Analysis

Fig. 4(a) shows the image of normal nanofiltration membrane without any surfactants. It can be seen that the resultant asymmetric membranes consists of dense top-layer and finger-like substructure. The cross-sectional image revealed that increasing of polymer concentration will increase the number of pores on the top-layer of the membranes. The long finger-like substructure is the key towards the performance of membranes. The support layer is not too thick that make the solutions harder too pass through the membranes.

The effects of the addition of small amount SDS additive is shown by Fig. 4(b) where

different morphological structure produced. SDS makes the membrane structure more porous in terms of formation of larger macrovoids. Moreover, the support layer of membranes also containing microvoids that leads to the lower mechanical strength of the membrane. In order to study the effect of different type of surfactant on membrane performance, Fig. 4(c) shows SEM image of membrane with CTAB. Addition of CTAB on polymer solution shows the formation of long finger-like structure across the substructure of the membrane.

From the previous study, the SEM images shows the formation of large pores in the sub-layer of membrane with addition of CTAB. This phenomenon is due to the miscibility of the surfactant and coagulant. Other than that, addition of CTAB revealed that it will become induces and extends the formation of macrovoids as well as finger-like pores in the support layer of membranes [10]. From the experimental data, membrane with CTAB shows lower flux and high rejection of dyes. This can be conclude that, the structure of membrane containing CTAB as surfactant is more fine and high mechanical strength than membrane with SDS.

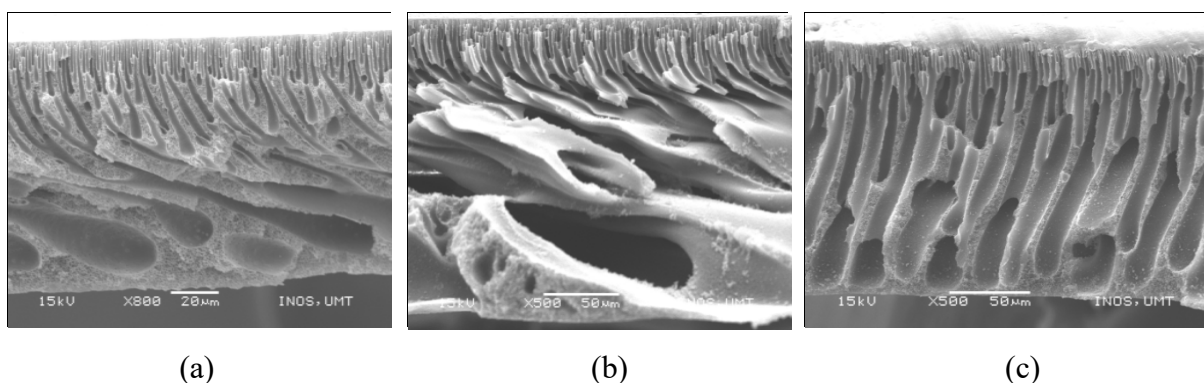


Fig.4. SEM images (a) NF membrane (b) NF membrane with SDS (c) NF membrane with CTAB

3. EXPERIMENTAL

3.1. Chemicals and Raw Materials

In making nanofiltration-surfactant membranes, polyethersulfone (PES) is used as polymer materials. This polymer was purchased from SOLVAY Advanced Polymers Company (RADEL A-300). 1-Methyl-2-Pyrrolidone (NMP) with analytical purity of 99.5% was purchased from Merck, ethanol and n-hexane both are from Merck was used as pre-treatment solutions in membrane fabrication. Polyethylene glycol (PEG) with average molecular weight

600g/mol was purchased from Merck used as additive. Cetyltrimethylammonium bromide (CTAB) with molecular weight 364.5g/mol from EMD Chemicals and Sodium dodecyl sulfate (SDS) with molecular weight 288.37g/mol from Merck were used as surfactant addition in the polymer solution. Methyl violet from Blulux Laboratory Reagents and Methyl blue from Merck were used as synthetic dyes.

3.2. Membrane Preparation and Fabrication

NMP was used to dissolve polymer in polymer solution method. NMP was heated at about 50°C and PES was dissolved. PEG 600 was added when the entire polymer has been dissolved. The solution must be stirred for 8 hours to get homogenous solution. Then, 2 wt% of surfactants (SDS and CTAB) were added 3 hours before the polymer solution was completed. Asymmetric PES/surfactant membrane was fabricated according to dry/wet phase separation process. The casting process was conducted at room temperature (30±2°C). Small amount of polymer solution was poured onto glass plate as support layer with casting knife setting at 150µm. After the membrane has been casted, the glass plate support together with membrane was immersed into the coagulation bath. When coagulation was completed, the membrane was immersed in water bath for 24 hours. Then, it will immerse in ethanol for another 24 hours. Finally, membrane will soak in n-hexane for 2-3 hours before dried at room temperature at least for 24 hours.

3.3. Membrane Performance Evaluation

The permeation test was conducted by using a simple dead-end permeation cell. Prior to the testing, each membrane was subjected for the passages of the first 10ml permeate and it was collected for concentration analysis. The volume flux was calculated as follows;

$$\text{Pure Water Permeation} = \frac{\text{Volume of permeate solution collected}}{\text{Effective membrane area} \times \text{Time}} \quad (1)$$

To study the effect of dyes rejection, operating pressure at 4 bars were used to obtain respective flux. Permeation flux test of dyes was carried out using two types of dyes (methyl violet and methyl blue) at 3 different concentrations (10ppm, 15ppm, 20ppm). The volume flux and rejection was calculated as follows:

$$\text{Flux} = \frac{\text{Volume of permeate solution collected}}{\text{Effective area of membrane} \times \text{Time}} \quad (2)$$

$$\text{Percentage of Rejection} = 1 - \left[\frac{\text{Concentration permeate} \times 100\%}{\text{Concentration Feed}} \right] \quad (3)$$

4. CONCLUSION

Experimental data shows the highest rejection of dyes was obtained by membrane with CTAB as surfactant. Up to 99.9% dyes rejection could be comparable to commercial membrane in the industry. With fine morphological structure consists of dense top-layer, long finger-like structure and high mechanical strength of support layer, membrane with CTAB is the best membranes to be used in textile industries in Malaysia. Mechanical strength of the membranes is the most important things in order to determine the continuous of membrane used. Besides, CTAB is readily available and very economical to use in making membrane.

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