J. Applied Membrane Science & Technology, Vol. 26, No. 2, August 2022, 29–42

Removal of Organic Dye in Wastewater Using Polyethersulfone Hollow Fiber Membrane

Asyrine Abdullah[a], Prakash Peechmani[a], Mohd Hafiz Dzarfan Othman[a*], Mohd Hafiz Puteh[a,b], Juhana Jaafar[a], Muklis A. Rahman[a] & Ahmad Fauzi Ismail[a]

[a]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Department of Environmental Engineering, School of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

Submitted: 31/12/2021. Revised edition: 31/3/2022. Accepted: 4/4/2022. Available online: 25/7/2022

ABSTRACT

In this study, polyethersulfone (PES) hollow fiber membranes (HFM) were fabricated with different weight percentage (wt. %) of polymer at 16 wt. %, 18 wt. % and 20 wt. %, in order to study the impact of polymer weight percentages on membrane properties and its dye rejection performance. Microfiltration HFM were fabricated by using the laboratory dry-wet spinning method. In order to improve the pore structure of the polymer membrane, 3 wt. % of polyvinylpyrrolidone (PVP) of 8000 M.W. was added in the dope solution. All the fabricated PES hollow fiber membranes were characterized using the Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM), Fourier Transform Infrared Spectroscopy (FTIR) and the contact angle. The HFM's performance was evaluated in terms of dye rejection, by using Direct Red 80 dye as substitute of organic dye in wastewater. The results showed that the membrane with higher weight percentage of PES polymer (20 % PES) had thicker separation layer, smoother membrane surface and uniform like pore structures. The membrane with the higher weight percentage of polymer (20% PES) had higher dye rejection percentage (67.33%) and higher permeate flux (10.024 L/m^{2}h) compared to 16 wt. % and 18 wt. %. The results of this study revealed that the weight percentage of polymer in the membrane did affect the membrane properties and its performance.

Keywords: Polyethersulfone (PES), Polvinylpyrrolidone (PVP), dye rejection, Direct Red 80

1.0 INTRODUCTION

Over these past few years of rapid globalization, technology alongside development of economy had increased expeditiously. This includes the industrial sector, such as textile industry which utilizes organic waste such as dye, pharmaceutical industry which introduces unconsumable antibiotics as organic waste and other vast industries that produces large amount of organic waste into wastewater. One of the most prominent industries which practices the anthropogenic activities was the textile industry which has the reputation as one of that most water consuming and polluting water bodies [1]. The global total volume of wastewater had increased from 1500 km^3 in 1995 to 2212 km^3 in 2010 [2]. This also signifies the increase of water pollution caused by these untreated wastes. We often face industries that discharges untreated effluents or wastewater into the river or water sources and the textile industry is not well known for it.

In this study, the textile industry was being focused on as this industry excretes dye as organic waste which in

* Corresponding to: Mohd Hafiz Dzarfan Othman (email: hafiz@petroleum.utm.my)
DOI: https://doi.org/10.11113/amst.v26n2.238

accumulation had caused danger to the environment and very detrimental to health. Additionally, presence (even in small amount) of dye in water bodies could affect the aquatic life by blocking the sunlight beams [3]. During the process of dyeing, approximately 10-15 % of dyes has been released into the environment making the effluent highly colored and aesthetically unpleasant [4]. Untreated wastewater with high toxic content due to toxic dyes such as azo dyes and carcinogenic amaranth. Other harmful chemicals present in the water may be formaldehyde- based dye fixing agents, chlorinated stain removers, hydrocarbon-based softeners, non-biodegradable dyeing chemicals. These organic materials react with many disinfectants especially chlorine and form by-products that were often carcinogenic and therefore undesirable. Thus, had horrendously affected the ecosystem of marine life and caused a big harmful impact on the food chain in the long run. This was very concerning and kinds of research had been done in order to curb this problem [5].

Many decolorization methods have been explored by researchers in recent decades, such as physical separation, chemical and biological process. Among these three, physical separation particularly using membrane technologies are more forwarded as they are cost effective, low energy consumption, short duration, flexible, highly selective, smaller footprint and flexible to be combined with other procedures [6–8].

PES was frequently utilized polymer membrane that was commonly used for the preparation of microfiltration (MF), ultrafiltration (UF) and gas separation membranes. Apart from that, PES is convenient primarily due to the advantageous characteristics of wide temperature limits, wide pH tolerances, relatively good chlorine resistance, easy fabrication of membranes in a variety of configurations and modules, a wide range of pore sizes available for UF and MF applications, and good chemical resistance [9–12]. The preparation of hollow fiber membranes need to take into account different factors during membrane formations compared to the preparation of flat sheet membranes, that includes rapid phase inversion kinetics and interfacial mass transfer during the spinning process, as well as a large number of spinning parameters, such as the spinneret's inner and outer diameters, polymer dope viscosity, the bore fluid flow rate, dope extrusion rate, air-gap length, and take-up speed are all factors to consider.

One of the major variables utilized to maximize membrane function, particularly via membrane surface modification, is surface membrane properties. Cross-linking, grafting, and pre-adsorption of water-soluble polymers are some of the techniques used to modify membrane surfaces [13]. Surface-modified membranes can be casted in a single step using a modification process that involves blending surface modifying macromolecules (SMMs) into polymer casting solutions. This method has advantages over other methods since it can generate surface-modified membranes in a single step. The characteristics of the PES polymer membranes can be enhanced by adding non-solvent additives to the polymer solution according to several publications [14]. It was found that adding a second polymer like PVP into PES solutions resulted in highly porous membranes with well-connected pores and surface characteristics. PVP blending has proven to ‘hydrophilize' PES membrane while also tuning the pore

structures [15]. However, because a portion of the PVP is washed out during use, the PVP blending change is not permanent. PVP acts as a pore forming agent.

The main objective of this study was to fabricate dye removal microfiltration polymeric membranes made of PES with various polymer PES weight percentages. In this study, PES hollow fiber membranes with different weight percentages of 16 %, 18 %, 20 % were fabricated by using the laboratory dry-wet spinning technique and it went through characterization and performance test of dye rejection. The polymer weight percentage was varied to study the effect of different weight percentages of polymer on the membrane properties and the membrane performance on dye rejection.

Additive, PVP was added into the PES dope polymer solution to enhance the pore structure of the polymer membrane [16]. However, the weight percentage of PVP was fixed at 3 wt. %. Direct Red 80 was used to constitute the dyes in the wastewater. Direct Red 80 dye was chosen because of its molecular weight of 1373.07 g/mol which will ensure the dye removal to occur since Direct Red 80 molecules was bigger than the microfiltration PES membrane.

2.0 METHODS

2.1 Materials

Materials that were needed for the preparation of dope solution for PES hollow fiber membrane were PES in pellets form, N,N-Dimethylacetamide (DMAc, M.W. of 87.12 g/mol) and Direct Red 80 (M.W. of 1373.07 g/mol) were purchased from Sigma Aldrich.

2.2 Fabrication of Polyethersulfone (PES) Hollow Fiber Membrane

The fabrication of PES hollow fiber membranes was made by utilizing the laboratory dry-wet spinning method for hollow fiber membrane. The preparation for dope polymer solution was necessary prior to the spinning process. The polymer dope solutions were prepared by mixing the solvent DMAc and the additive PVP in a Teflon bottle that was stirred by magnetic stirrer under 450 rpm and 60 °C. After the solution had mixed well for 1 hour and 30 minutes, PES in pellets which have been dried in the oven overnight to remove moisture were added gradually under the same conditions, 450 rpm and 60 °C. In order to get a homogeneous solution, the mixture was stirred slowly at 60 °C for overnight. Prior to spinning, the solution was ultrasonicated for roughly 2 hours to remove the bubbles and left at room temperature for 24 hours [17]. The composition of the dope polymers was described in Table 1 below.

For the process of fabrication of membrane via spinning method, the membrane was spun using the laboratory dry-wet spinning method as shown in Figure 1. Two types of phase inversion can be distinguished in the membrane development process. Evaporation of the volatile solvent causes the dry phase inversion in the atmosphere. Wet phase inversion is accomplished by immersing the polymer solution membrane in a non-solvent coagulation bath which consists of water where the membrane was created. The spinneret outer diameter was 1.0 mm and the inner diameter was 0.4 mm. Meanwhile, the bore fluid and coagulation bath composition utilized throughout the experiment were Milli-Q water and ordinary tap water, respectively. At room temperature, the dope solution

and bore fluid were extruded through the spinneret to generate the hollow fiber. Before entering the coagulation bath at room temperature, the hollow fiber formed on the end of the spinneret passed through an air gap of 10 cm.

Table 1 The dope polymer concentration of Polyethersulfone (PES) hollow fiber membrane

Dope Composition			
Membrane	**PES** ***(wt. %)***	**PVP** ***(wt. %)***	**DMAc** ***(wt. %)***
16% PES	16	3	81
18% PES	18	3	79
20% PES	20	3	77

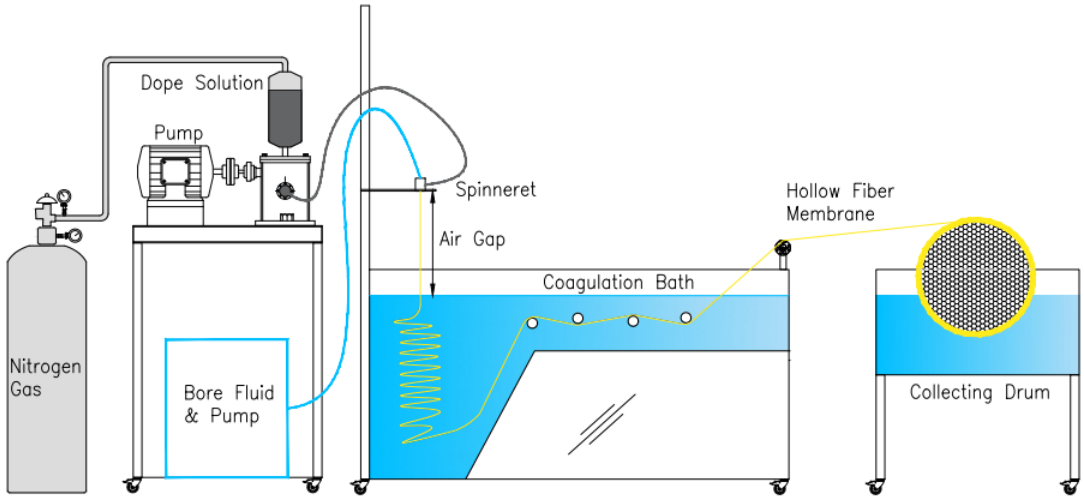

Figure 1 Schematic of laboratory dry-wet spinning apparatus

The hollow fiber was collected at a collection drum after passing through two coagulation baths. Due to the accumulation of solvent extruded from the fiber, the first coagulation bath will have a larger concentration of solvent (DMAc) after a period of dope extrusion. The second coagulation bath, on the other hand, aids in maintaining the fiber as it passes through more clean, uncontaminated water and promotes the solidification of the fiber when it reaches the collection drum. After the fabrication of the hollow fiber membrane, the membrane was collected from collecting drum and stored in water (25 °C) for 24 h to remove the residual solvent and water soluble additives from the membranes. Then, the membranes were post-treated with 30% glycerol solution for 24 h and dried prior to characterization. Table 2 shows the PES hollow fiber spinning conditions.

Table 1 PES hollow fiber spinning conditions

Spinning parameter	Value
Outer diameter of spinneret (mm)	1.0
Inner diameter of spinneret (mm)	0.4
Dope solution flow rate (mL/min)	7
Bore fluid flow rate (mL/min)	3
Air gap distance (cm)	10
External coagulant	Tap water
Coagulant bath temperature (°C)	25

2.3 Membrane Characterization

SEM was used to examine the outer surface and cross-sectional morphology of membranes (Model: TM 3000 Tabletop Scanning Electron Microscope, Hitachi, USA). The HFMs were submerged in liquid nitrogen for a few minutes before examination, then was snapped to obtain a precise and clean-cut structure. Under normal circumstances, all membrane samples that were going to go through SEM need to be sputtered by sputter coater by metal in order to obtain clearer and more precise image. This PES membrane however did not go through sputtering due to the structure of the membrane that was too thin. Two failed attempts at sputtering the membrane have resulted the membrane to be completely burned and defect.

AFM was carried out with a Park XE-100 AFM (Park Systems, CA). The morphology of the membrane surface was measured in terms of mean surface roughness (Ra). The mean surface roughness is the average roughness of the surface in relation to the center plane, which is the plane in which the volumes were encircled by an equal number of pictures above and below it. The roughness characteristics are dependent on how the collected surface data is processed. The membrane was cut into small pieces and attached to the sample holder for sample preparation.

FTIR analyses (Perkin Elmer Spectrum 100) were carried to determine the functional groups of the PES hollow fiber membrane. FTIR analysis is also applied to the hollow fiber membrane to ensure the existence of the PVP incorporated in the membrane after the blending and membrane fabrication procedure. FTIR results can display the change of the functional groups and elemental in the polymers and can characterize covalent bonding information.

Hydrophilicity of the fabricated membranes were measured using the OCA contact angle system (Dataphysics, USA). The sessile drop method was used to determine the membrane surface's static contact angles. The contact angle was measured after a continuous dosing volume of 0.2 μL of pure water was deposited onto a dry hollow fiber membrane in air with a dosing rate of 1.0 μL/s by using a microsyringe. For each PES hollow fiber's membrane contact angle, an average of five measurements was taken.

2.4 Dyes Rejection Test

The dye rejection test was carried out to examine the effectiveness of the dye rejection of microfiltration PES membrane. Direct Red 80, which has a

molecular weight of 1373.07 g/mol, was the only dye utilized. Using a basic dead-end permeation cell, the test was carried out at a 2 L constant dye feed concentration of 100 ppm (pH: 5.75) and a set working pressure of 1.0 bar. The permeated solution was measured every 10 minutes for the calculation of permeate flux and taken to be kept inside a vial for the permeate concentration measurement using a spectrophotometer for the rejection percentage calculation. The initial absorbance for the feed concentration recorded by the spectrophotometer was 0.502 the permeate concentration of Direct Red 80 was calculated spectrophotometrically at a maximum absorbance (max) of 526 nm. The average of five measurements was taken for each membrane as the permeate absorbance value was measured at the spectrophotometer. Water flux 'Jw' and rejection percentage (R) were evaluated using the following equations.

$$J_w = \frac{Q}{n\,A\,\Delta t} \qquad \textbf{Equation 1}$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad \textbf{Equation 2}$$

Where 'Q' is the filtrate volume (L) within the operation time, 'Δt' (h) and 'A' is the area of the membrane (m^2) and 'n' is the number of hollow-fibers in the module. 'C_f' and 'C_p' are the concentration of feed and permeate solution (gL^{-1}), respectively.

3.0 RESULTS AND DISCUSSION

3.1 Membrane Characterization

Cross section and surface morphology for the fabricated HFMs are shown in Figures 2, 3 and 4 for 16 wt.%, 18 wt.% and 20 wt.% respectively. From the cross sections, we can observe that at the outer and inner layers of the hollow fiber membranes, the finger-like structure has formed successfully, while the sponge-like structure has developed at the intermediate layer. Spongy and porous sublayers were sandwiched between the finger-like structures protruding from the inner and outer walls in the membranes. This is due to the polymer dope solution's liquid–liquid demixing with the bore fluid and non-solvent bath. For the surface morphologies, a number of uniformly distributed tiny pores were found on the surface of all the PES HFM. All the PES HFM have porous structures which helps the water flux and selectivity of the membrane.

Among the three hollow fiber membranes, it can be observed that 20% PES hollow fiber membrane has the desired morphology as the membrane has the thickest separation layer (129 μm) compared to the other two HFMs as shown in Table 3 below. From here, it can be concluded that the higher the PES wt. % of hollow fiber membrane was, the thicker of resultant microfiltration membrane surface was. This is very important to ensure the membrane has sufficient mechanical strength. It was found that all membrane's internal and external cross sections had skin layers on both inner and outer surfaces. However, 20 % PES HFM possess (Figure 4a) better three layers compared to other membranes; inner edge with narrow or small finger-like structure, middle layer which consist of bigger macrovoids structures, and an outer layer with perfect thin separation layer and longer finger like structures. From the surface images, it can be seen the formation of membrane pores are become smaller and increased in number as the polymer concentrations are increased. The increase in polymer concentrations encouraged the pore

plugging process during the phase separation process. Similar results were observed by Ahmad *et al.*, Jin *et al.*, and Dang *et al.*, [18–20].

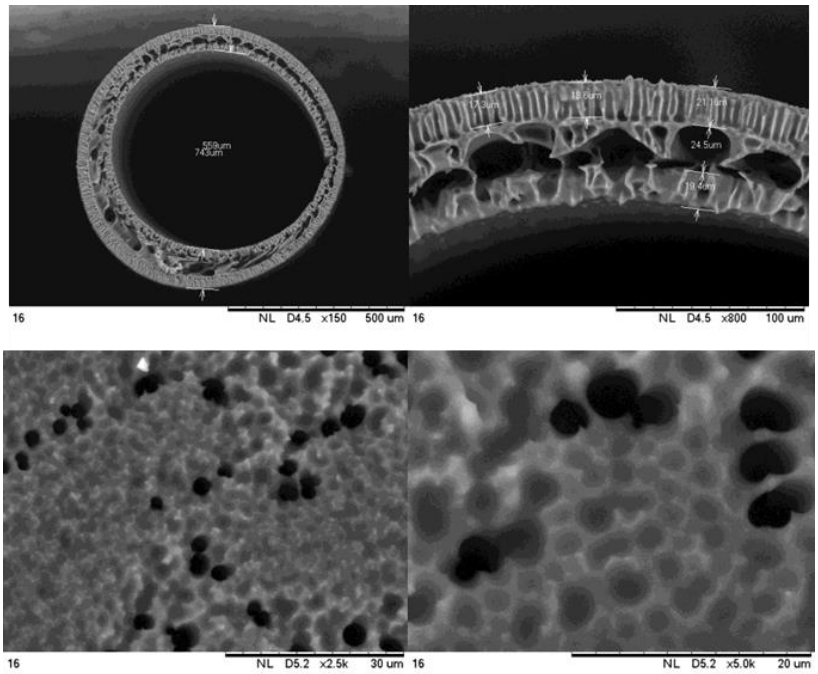

Figure 2 Cross section and surface morphology of 16 wt.% PES HFM at magnification of x150, x800, x2500 and x5000

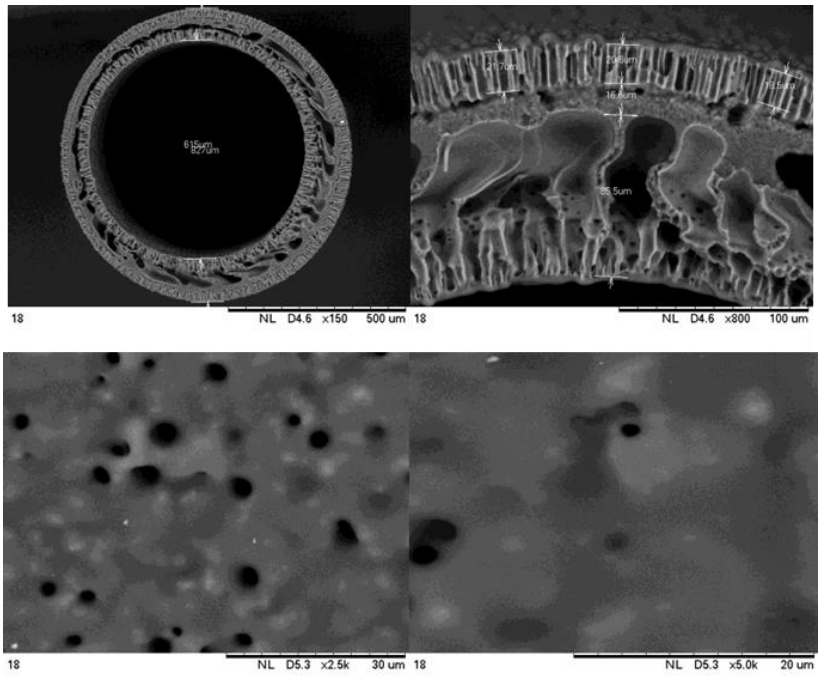

Figure 3 Cross section and surface morphology of 18 wt.% PES HFM at magnification of x150, x800, x2500 and x5000

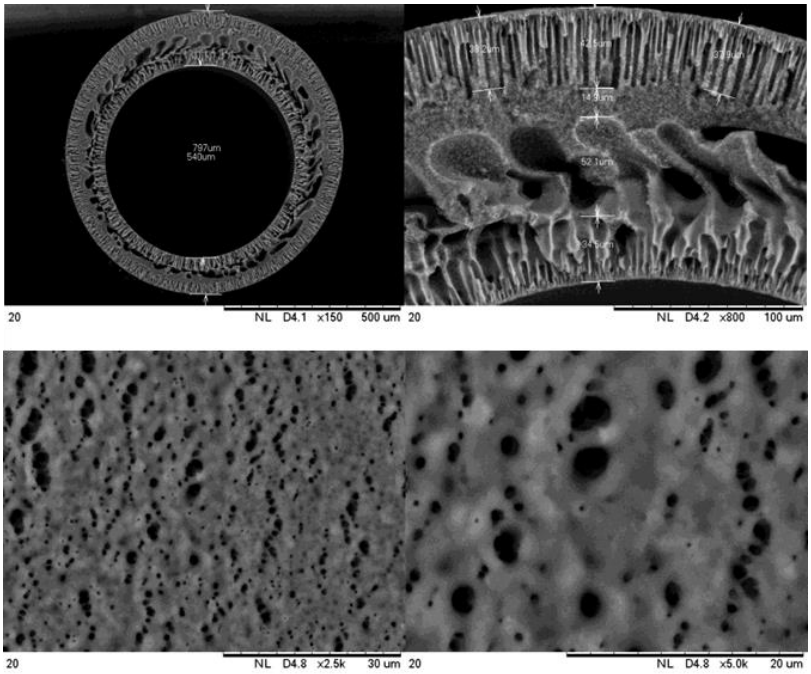

Figure 4 Cross section and surface morphology of 20 wt.% PES HFM at magnification of x150, x800, x2500 and x5000

Table 2 The thickness of all the hollow fiber membranes. (16 % PES, 18 % PES, 20 % PES)

Membrane	Outer diameter (µm)	Inner diameter (µm)	Thickness (µm)
16% PES	743	559	92
18% PES	827	615	106
20% PES	797	540	129

Figure 5 shows the surface roughness (Ra) and three-dimensional (3D) AFM images of the 16 % PES, 18 % PES, and 20 % PES hollow fiber membranes. The AFM images shows that the membrane surface roughness for the all three membranes has no prominent difference due to the fact that the PVP added loading in the dope solutions are at equal wt. % of 3 % in each membrane. The surface roughness (Ra) value is slightly dissimilar due to different wt% of PES that was used and this further proven that the higher the PES wt % of hollow fiber membrane was, the smoother the surface of resultant microfiltration membrane surface was. 20% PES had the lowest surface roughness at Ra=10.30 compared to 16 % PES and 18 % PES which had Ra=18.35 and Ra=11.94 respectively. Hence, 20% PES HFM had the smoothest surface among the three membranes. Barzin et. al., also observed similar Ra value for 18 % PES/3 % PVP membranes [21]. From the observed Ra values, we can conclude that reduction in the roughness of the membrane surface can improve antifouling properties of membranes [22].

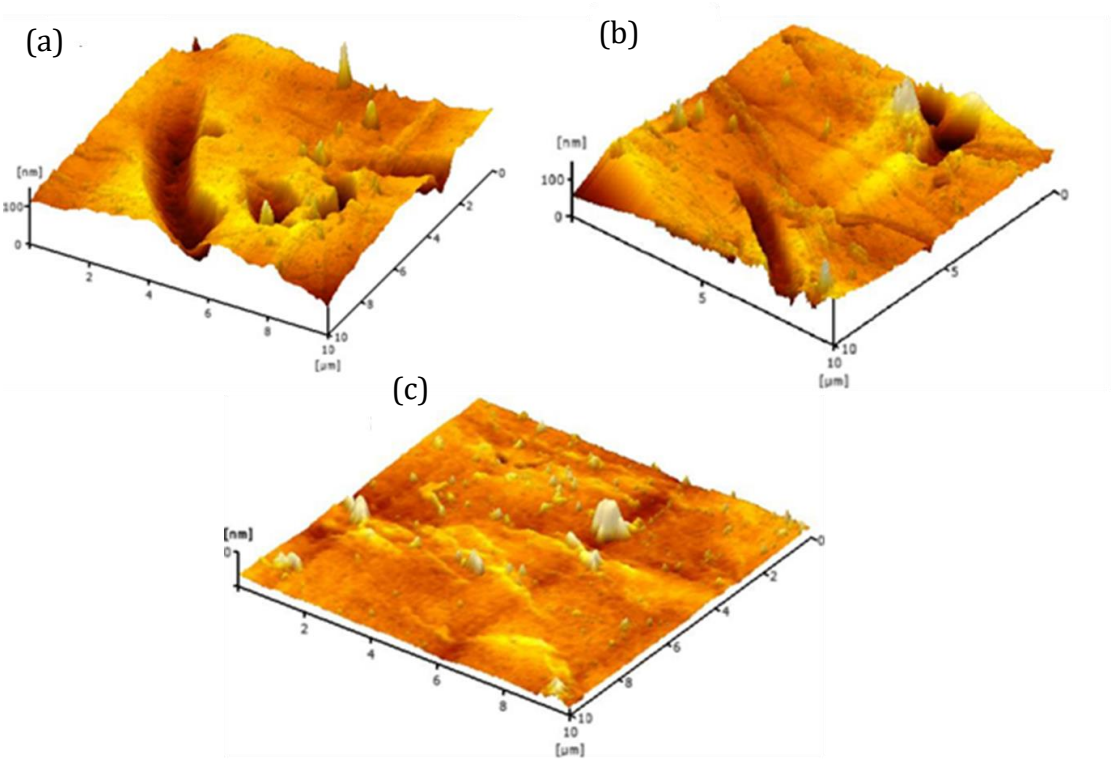

Figure 5 The image of surface roughness (Ra) of a) 16 % PES, b) 18 % PES, c) 20 % PES hol-low fiber membranes

Figure 6 shows the FTIR spectroscopy which was used to determine the presence of functional groups in the membrane. Characteristic peaks at 3395 cm^{-1} of the PES/DMAC/PVP/H_2O membrane correspond to –OH stretch shows the water presence in the dope solution as non-solvent while peaks at 2871 cm^{-1} referred to C-H stretch. Peaks corresponding to the polyethersulfone group were found at a wavenumber of 1100 cm^{-1} (S=O asymmetric stretch). The presence of band 717 cm^{-1}, which corresponds to PVP bending, can be used to identify and verify the presence of PVP as an addition in the dope solution. DMAc bands are not visible since all DMAc has leached out from the membrane matrix during the phase inversion process.

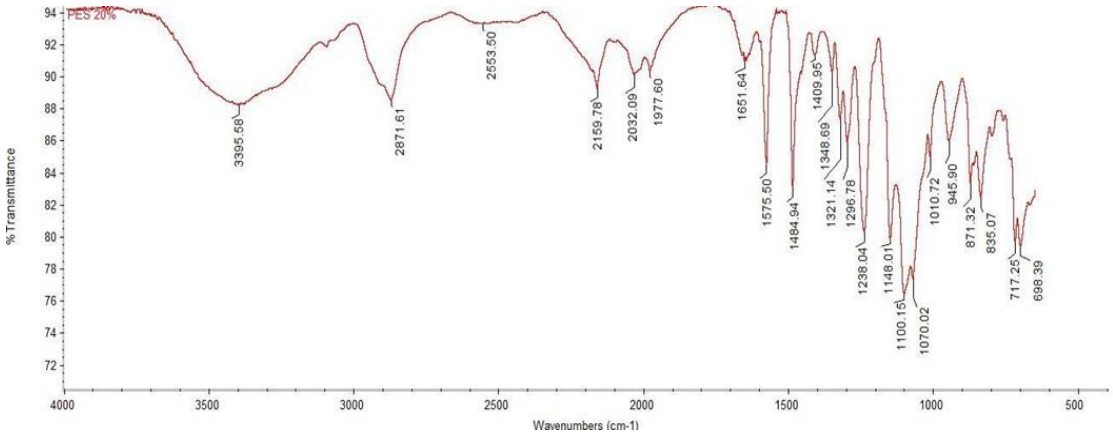

Figure 6 FTIR spectra of 20 % PES hollow fiber membrane

For the hydrophilicity of the membranes, water contact angle measurement was conducted. Five measurements were taken for all membranes and the value of the contact angle was taken at average. It can be seen from Table 4 that the 20 % PES hollow fiber membrane has the highest average water contact angle value at 78.85 °. This shows that this 20 % PES sample is the most hydrophobic compared to 16 % PES and 18 % PES. Meanwhile, 16 % PES hollow fiber membrane shows that it is the most hydrophilic membrane with the lowest contact angle at 70.66°. PVP was stated to increase the hydrophilicity of the PES membrane. This data shows that the wt. % of PES plays a role on the hydrophilicity of the PES membrane as the wt. % of PES in membrane varies in all the membranes while wt% of PVP was constant in all three membranes at 3 %. This can be justified as the high wt % of polymer in the membrane reduce the hydrophilicity of the membrane. However, the differences in the contact angle are not that drastic and prominent, hence, the contact angle of 20 % PES membrane is still acceptable.

Table 4 The contact angle measurement for all three hollow fiber membranes (16 % PES, 18 % PES, 20 % PES

Reading	**Contact Angle (°)**		
	16 % PES	**18% PES**	**20% PES**
1	68.77	73.35	80.91
2	71.70	72.69	84.00
3	73.74	74.30	77.29
4	68.93	72.74	82.68
5	70.18	72.82	78.85
Average	70.66	72.82	78.85
Standard error	+2.09	+0.68	+2.74

3.2 Water Flux and Dye Rejection

The performance of these HFMs were evaluated by the water flux and dye rejection test. Direct Red 80, was the dye used in this performance test. Figure 7 shows the graph of water flux and rejection percentage for 16 % PES, 18 % PES, and 20 % PES hollow fiber membranes. According to Figure 7, 20 % PES membrane has the highest permeation flow of 10.024 L/m^{2}h and also gave the highest rejection rate of 67.33% among all membranes in the rejection test. 16% PES membrane had the lowest water flux of 0.400 L/m^{2}h, which resulted in a rejection percentage of 22.19 %. Meanwhile 18 % PES is on the intermediate between the three membranes with the water flux of 3.800 L/m^{2}h and rejection percentage at 29.28 %. It can be observed that 20 % PES hollow fiber membrane serves the highest water flux permeation compared to other two membranes. The observed increment in the permeate water flux could be justified by referring the cross section and surface morphology which shown in Figure 2, 3 and 4 and surface roughness explained in earlier section**.** Compared to 16 wt. % and 18 wt.% PES HFMs, 20 wt. % PES HFM has smaller and well distributed pores on the surface of the membrane which enhanced the surface porosity and are

responsible for this high permeation [23]. In addition, the smooth surface of the 20 wt. % of PES HFM has enhanced the anti-fouling properties on the membrane's surface which also aids in the continuous permeation process [22]. Despite the fact that 20 % PES membrane has the highest contact angle, it still does not deter it from having high permeate flux. On the other hand, the rejection rate also increased as the polymer concentration are increased. These results are consistent with the surface roughness data obtained from the AFM result (Figure 5). The 20 wt. % PES HFM with lower porosity and smaller pores diameter and enhanced the rejection of the Direct Red 80, while other membranes with larger pore diameters leads to the higher permeation of Direct Red 80 particles into the HFMs. Furthermore, the rough surface of the 16 wt. % and 18 wt. % may have increased the clogging of the Direct Red 80 particles which again lead to the lower flux

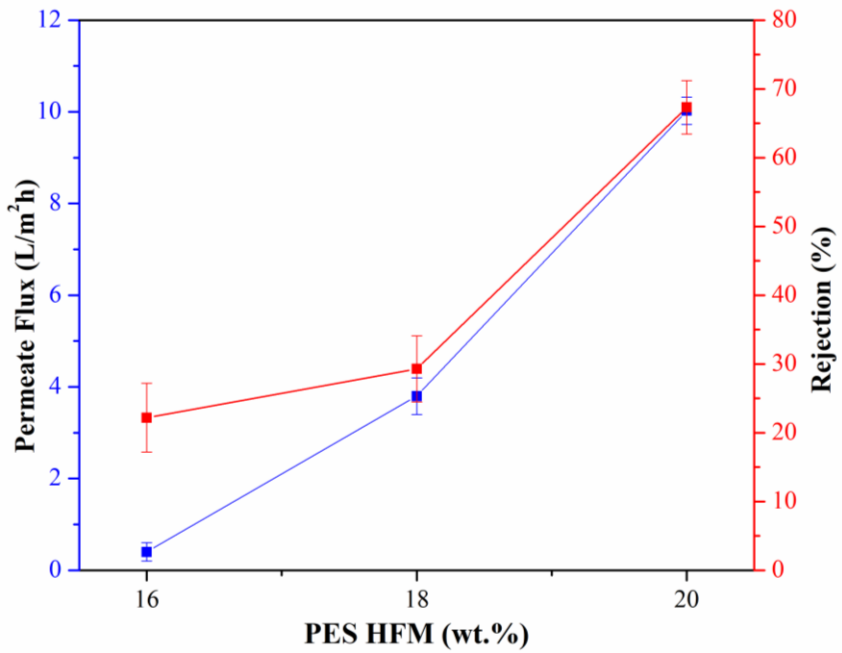

Figure 7 The permeate flux and the dye rejection percentage for each PES hollow fiber membranes (16 % PES, 18 % PES, 20 % PES)

4.0 CONCLUSION

In conclusion, among the three 16 wt.% 18 wt.% and 20 wt. % PES HFMs , it can be said as 20 % PES HFM is the best option of a membrane as it has the smoothest surface morphology and uniform porous structure as proven by Ra by AFM and the most uniform hollow fiber cross section as proven by SEM. The FTIR proves that the presence of the PES functional group in the membranes. The percentage of dye rejection (67.33 %) and the water flux (10.024 L/m^{2}h) of 20% PES hollow fiber membrane was also the highest among all the membranes. Granted that the contact angle is slightly defer, the difference between the other two membranes is not that significant. Thus, 20 % PES hollow fiber membrane is the most suitable membrane to further carry out this study.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to the Ministry of Higher Education Malaysia for financial support through the Higher Institution Centre of Excellence Scheme (Project Number: R.J090301.7809.4J430). Besides that, the authors wish to thank Universiti Teknologi Malaysia for funding this research through the Collaborative Research Grant (Project number: Q.J130000.2409.08G29) and the Matching Grant (Q.J130000.3009.02M25). Finally, the authors wish to express their gratitude to the Research Management Centre at Universiti Teknologi Malaysia for the technical assistance.

REFERENCES

[1] Lellis, B., Fávaro-Polonio, C. Z., Pamphile, J. A., Polonio, J. C. 2019. Effects of Textile Dyes on Health and the Environment and Bioremediation Potential of Living Organisms. *Biotechnology Research and Innovation*. (2): 275-290.

[2] Shen, X., Zhang, T., Xu, P., Zhang, L., Liu, J., Chen, Z. 2017. Growth of C3N4 Nanosheets on Carbon-fiber Cloth as Flexible and Macroscale Filter-Membrane-shaped Photocatalyst for Degrading the Flowing Wastewater. *Applied Catalysis B: Environmental*. 19: 425-431.

[3] Ali, M. E. A., Atta, A. H., Medhat, M., Shahat, A., Mohamed, S. K. 2022. Effective Removal of Methyl Blue and Crystal Violet Dyes Using Improved Polysulfone / Zif-8 Nanocomposite Ultrafiltration Membrane. *Biointerface Research in Applied Chemistry*. 12(6): 7942-7956.

[4] Martínez-Huitle, C. A., Brillas, E. 2009. Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods: A General Review. *Applied Catalysis B: Environmental*. 105-145.

[5] Kant, R. 2012. Textile Dyeing Industry an Environmental Hazard. *Natural Science*. 04(01): 22-26.

[6] Zheng, J., Zhao, R., Uliana, A. A., Liu, Y., de Donnea, D., Zhang, X., Xu, D., Gao, Q., Jin, P., Liu, Y., Volodine, A., Zhu, J., van der Bruggen, B. 2022. Separation of Textile Wastewater Using a Highly Permeable Resveratrol-based Loose Nanofiltration Membrane with Excellent Anti-fouling Performance. *Chemical Engineering Journal*. 434.

[7] Bao, X., Wang, F., Liu, Q., Yu, F., Yang, Y. 2022. Controlled Aggregation of Phytic Acid Metal Complex on Polysulfone Ultrafiltration Membrane toward Simultaneous Rejection of Highly Emulsified Oils and Dyes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 641.

[8] Qiao, L., Ye, H., Xin, Q., Huang, L., Zhang, Y., Li, H. 2022. An Adsorptive Sulfonated Polyethersulfone/Functionalized Graphene Ultrafiltration Membrane for Hardness Removal. *Separation and Purification Technology*. 287.

[9] Munir Cheryan. 1998. *Ultrafiltration and Microfiltration: Handbook*. CRC Press. 1-75.

[10] Poolachira, S.; Velmurugan, S. 2022. Efficient Removal of Lead Ions from Aqueous Solution by Graphene Oxide Modified

Polyethersulfone Adsorptive Mixed Matrix Membrane. Environmental Research. 210.

[11] Lin, Z., Liu, Y., Zhang, Z., Yao, J. 2022. Preparation and Characterization of OH/SiO2-TiO2/PES Composite Hollow Fiber Membrane Using Gas-Liquid Membrane Contactor for CO2/CH4 Separation. Separation and Purification Technology. 288.

[12] Ma, D., Zou, X., Zhao, Z., Zhou, J., Li, S., Yin, H., Wang, J. 2022. Hydrophilic PAA-g-MWCNT/TiO2@PES Nano-Matrix Composite Membranes: Anti-Fouling, Antibacterial and Photocatalytic. *European Polymer Journal*. 168: 111006.

[13] Rabiee, H., Seyedi, S. M., Rabiei, H., Alvandifar, N. 2016. Improvements in Permeation and Fouling Resistance of PVC Ultrafiltration Membranes via Addition of Tetronic-1107 and Triton X-100 as Two Non-Ionic and Hydrophilic Surfactants. Water Science and Technology. 74(6): 1469-1483.

[14] Ulbricht, M. 2006. Advanced Functional Polymer Membranes. Polymer. Elsevier BV. 2217-2262.

[15] Xu, Z.-L., Chung, T.-S., Huang, Y. U. 1999. Effect of Polyvinylpyrrolidone Molecular Weights on Morphology, Oil/Water Separation, Mechanical and Thermal Properties of Polyetherimide/Polyvinylpyrroli done Hollow Fiber Membranes. *Applied Polymer*. 74(9): 2220-2233.

[16] Febriasari, A., Ananto, A. H., Kartohardjono, S. 2021. Polysulfone Filtration Membranes with Polyvinilpirrolidone (PVP) Additive for Batik Wastewater Treatment. J. Applied Membrane Science & Technology. 25(1): 1-9.

[17] Fadaly, N. S., Aziz, F. 2020. Preparation and Characterization of Mixed Matrix Membrane Based on Polysulfone (PSF) and Lanthanum Orthoferrite (LaFeO3) for Gas Separation. *Journal of Applied Membrane Science & Technology*. 24(1).

[18] Jin, J., Du, X., Yu, J., Qin, S., He, M., Zhang, K., Chen, G. 2020. High Performance Nanofiltration Membrane Based on SMA-PEI Cross-linked Coating for Dye/Salt Separation. *Journal of Membrane Science*. 611.

[19] Ahmad, A. L., Abdulkarim, A. A., Mohd Shafie, Z. M. H., Ooi, B. S. 2017. Fouling Evaluation of PES/ZnO Mixed Matrix Hollow Fiber Membrane. *Desalination*. 403: 53-63.

[20] Cheng, J., Shi, W., Zhang, L., Zhang, R. 2017. A Novel Polyester Composite Nanofiltration Membrane Formed by Interfacial Polymerization of Pentaerythritol (PE) and Trimesoyl Chloride (TMC). *Applied Surface Science*. 416: 152-159.

[21] Barzin, J., Feng, C., Khulbe, K. C., Matsuura, T., Madaeni, S. S., Mirzadeh, H. 2004. Characterization of Polyethersulfone Hemodialysis Membrane by Ultrafiltration and Atomic Force Microscopy. *Journal of Membrane Science*. 237(1-2): 77-85.

[22] Alpatova, A., Kim, E. S., Sun, X., Hwang, G., Liu, Y., Gamal El-Din, M. 2013. Fabrication of Porous Polymeric Nanocomposite Membranes with Enhanced Anti-fouling

Properties: Effect of Casting Composition. *Journal of Membrane Science*. 444: 449-460.

[23] Li, P., Thankamony, R. L., Li, X., Li, Z., Liu, X., Lai, Z. 2021. Nanoporous Polyethersulfone Membranes Prepared by Mixed Solvent Phase Separation Method for Protein Separation. *Journal of Membrane Science*. 635.