Preparation and application of thin film membranes incorporated with nanocomposite for water treatment

A Thesis

Submitted by

Eman Sobhy Abdel Wahed Mansour

Water Pollution Research Department
National Research Centre
M. Sc. (Chemistry) 2014

In the Partial Fulfillment of the Requirements
For
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To
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Ph.D. Thesis

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PUBLICATIONS

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Influence of the polyacrylonitrile proportion on the fabricated UF blend membranes' performance for humic acid removal

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Abstract: Asymmetric blend membranes of polyethersulfone (PES)/polyacrylonitrile (PAN) were prepared and developed for ultrafiltration applications. The membranes were prepared by dissolving two polymers in N-methyl-2-pyrrolidone (NMP) as a solvent with diethylene glycol (DEG) and polyvinylpyrrolidone (PVP) as non-solvent and pore former, respectively. The produced membranes were characterized by scanning electron microscopy (SEM) and fourier transform infrared (FTIR) spectroscopy, and the hydrophilicity of membranes was tested by contact angle measurements. The performance of prepared membranes was carried out by an ultrafiltration testing unit, where the efficiency of membranes was determined according to the humic acid separation and treated water permeate flux. The results indicated that using 1 wt.% of PAN in polymer mixture provided a blending membrane with high mechanical properties and high performance; the humic acid rejection reached 92.47% with treated water permeate flux 70 l/m^2·h at feed pressure 6 bar.

Keywords: blend ultrafiltration membranes; humic acid; polyethersulfone; polyacrylonitrile; preparation.

1 Introduction

The production of novel polymeric materials with favorable characteristics using the blending process is now under the spotlight since it is easier and cost effective than suggesting new polymerization [1]. Blending can be carried out between two polymers like polyacrylonitrile (PAN) with polyvinylidene fluoride [2], cellulose acetate with sulfonated polysulfone [3], etc. or blending between polymeric additives such as pore formers like polyethylene glycol and polyvinylpyrrolidone (PVP) [4, 5].

Polyethersulfone (PES) is one of the distinguished materials for membrane fabrication due to chemical stability and high mechanical characteristics, which is used in several industries such as food industries, pharmaceutical, hemodialysis, filtration of fine particles, bacteria, viruses, and desalination after membrane surface treatment by interfacial polymerization [6].

PAN has high hydrophilicity in addition to thermal and chemical stability, so it can be used in membrane fabrication for water treatment [7]. The brittleness and the aggregation of PAN membrane after drying oppose its application [8].

The phase inversion process is the most popular technique for preparation of asymmetric membranes, where the solvent can be exchanged in casting solution by a non-solvent, causing phase separation and membrane formation [9–11].

However, an ultrafiltration (UF) membrane is powerful pressure drove membrane that can be used in protein solutions separation, but adsorption of molecules on membrane pores, causing membrane fouling that decreases the permeate flux and consumes energy. Many studies have investigated whether increasing the hydrophilicity of the membrane leads to a reduction of membrane fouling [12, 13].

Membrane surface modification can be applied by several techniques including blending, coating, chemical grafting and radiation-induced grafting [14].

Membrane modification through polymer blending is a successful way to achieve membranes with high selectivity and permeability [15–17]. Abdallah et al. [17] prepared asymmetric PES/Mn(acac)^3 blend membranes by implementing metal organic compound Mn(acac)^3 in the polymer solution mixture, where the addition of Mn(acac)^3 resulted in a decrease in the pores size, porosity, and low contact angle due to improving hydrophilicity compared with bare PES [18]. In addition, Abdallah et al. [18] prepared PES/titanium dioxide

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nanotubes blend membranes by blending with titanium dioxide nanotubes and the membranes were applied in membrane distillation, where the selectivity of water vapor reached 99% and the average flux was 18.2 kg/m^2.h [19]. Ali and Abdallah [19] studied the effect of cellulose acetate blending with PES on membrane hydrophilicity [20].

The novelty of this work is the study of the effect of PAN ratio on fabricated blend membrane performance, where the blend membranes were prepared using blending between both PES and PAN in solvent with pore formers PVP and hygroscopic liquid diethylene glycol (DEG) as non-solvent to increase the hydrophilicity of prepared membranes.

Humic acid (HA) can be demonstrated in several sources such as water, soils, and bottom deposits. Total organic carbon of surface water contains 71.4–82.5% humic acid [21]. In addition, it is considered as a house for microbes in water pipes which is the source of carbon and energy [22]. HA is the main membrane foulant because of its carboxylic, phenolic, hydroxyl and quinine functional groups [23]. It is also the main source of disinfection by-products which are reported as carcinogenic and mutagenic compounds [24, 25].

Several chemical treatment technologies were reported for HA removal such as coagulation [26], Fenton oxidation [27], anoxic and oxic removal [28] and heterogeneous photocatalysts [26]. Nowadays, physical separation of HA by membrane is of high interest [29–33].

The objective of the present work is development of the preparation of blend membranes based on PES/PAN with a different composition, where PES was considered as the main polymer for the membrane backbone in the presence of DEG and PVP as non-solvent and pore former additives, respectively. In addition, the full membrane characterization in terms of morphology, hydrophilicity, mechanical properties, water flux, and humic acid separation percentage was investigated.

2 Materials and methods

2.1 Materials

PES (MW = 58,000 g/mol) and N-methyl-2-pyrrolidone (NMP) were supplied by BASF Company (Germany). PAN (MW = 150,000 g/mol), DEG, PVP (MW = 360,000 g/mol) and commercial humic acid were purchased from agent of Sigma-Aldrich (Egypt).

2.2 Preparation of PES/PAN membranes

PES/PAN blend membranes were fabricated by the immersion precipitation method. PVP was added into a solution consisting of DEG and NMP and the mixture was stirred until complete solubility. PAN was added slowly to the mixture with mechanical stirring until beads were dissolved, then PES was added. The mixture was stirred for 6 h to get a homogeneous casting solution. The composition of casting solutions is illustrated in Table 1. The polymer mixture solution was left in the refrigerator for 24 h to remove air bubbles. After that, the casting solution was cast onto a clean glass plate with 200 μm wet thickness. Subsequently, the glass plate was horizontally immersed into distilled water at room temperature until phase separation occurred. Finally, the membranes were preserved at room temperature for drying.

2.3 Membrane characterization

2.3.1 Morphology determination

The morphology of the prepared membranes was determined after being frozen in liquid N_2 for cross-sectional images and the samples were coated with gold to provide electrical conductivity. The cross-sectional images of membranes were taken on a QUANTA FEG250 scanning electron microscope (SEM).

2.3.2 Mechanical properties

Mechanical properties at break measurements of the prepared membranes were expressed in terms of tensile stress and elongation; the samples were measured using the H5KS universal tensile testing machine. The initial

Table 1: The polymer mixture casting composition for the blended membranes polyethersulfone/polyacrylonitrile (PES/PAN).

Membrane	PES (%)	PAN (%)	PVP (%)	DEG (%)	NMP (%)
PES-M1	18	0	0	0	82
PES-M2	14	0	4	2	80
PES-M3	0	14	4	0	82
PES-M4	13.5	0.5	4	2	80
PES-M5	13	1	4	2	80
PES-M6	12.5	1.5	4	2	80
PES-M7	12	2	4	2	80

DEG, diethylene glycol; NMP, N-methyl-2-pyrrolidone; PAN, polyacrylonitrile; PES, polyethersulfone; PVP, polyvinylpyrrolidone.

distance between grips was adjusted to 180 mm and width of the tested membranes was 50 mm. Samples were extended at a constant elongation rate of 30 mm/min. A set of five samples was analyzed and the average reading was calculated.

2.3.3 Membrane porosity

Variations in porosity and water content were studied as compact properties of the prepared membranes by impregnation of the samples in distilled water, then dryness at 80°C using an air circulating oven for 24 h. The porosity and the equilibrium water content (EWC) of the prepared membrane were determined using Eqs. (1) and (2) [32, 33]:

$$\text{Porosity } (\%) = \frac{\text{Wet membrane weight (g)} - \text{Dry membrane weight (g)}}{\text{Membrane area} * \text{Membrane thickness}} \times 100\% \quad (1)$$

$$W_{H_2O} (\%) = \frac{\text{Wet membrane weight (g)} - \text{Dry membrane weight (g)}}{\text{Dry membrane weight (g)}} \times 100\% \quad (2)$$

where W_{H_2O} is the EWC for the prepared membranes.

2.3.4 Hydrophilicity measurement

Contact angle measurement is used to characterize the hydrophilic property of polymeric surfaces. The contact angle of membranes was measured using a Compact video microscope (CVM) manufactured by SDL-UK; the contact time was 10 s with average drop volume 10 µl and each value was averaged from 10 measurements. The technique used was horizontal plate camera perpendicular to liquid droplet plane. The test method was according to ASTM D724-99 standard test method for surface wettability of paper (angle of contact method) and ASTM D5946-96 standard test method for corona-treated polymer films using water contact angle measurements.

2.3.5 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) analysis of 16 scans/min with a resolution of 4 cm^{-1} was carried out on a JASCO FTIR spectroscopy model: 6100 that was used to confirm the presence of functional groups on the surface of the prepared membranes.

2.3.6 Analytical methods

A humic acid solution of 150 mg/l was prepared and tested by a membrane filtration unit. The concentration of aqueous humic acid in the reject and permeate were measured by UV absorbance at 254 nm (UVA) using UV/Vis spectrophotometer (Agilent Carry 100).

2.3.7 Permeation experiment and rejection performances

A laboratory scale dead end UF cell consisting of a reservoir, a pump, valves, pressure regulators, and a membrane cell, was used to check the efficiency of the prepared membranes as shown in Figure 1. The effective area of the membrane in the test cell was 12.57 cm^2. Rejection of 150 mg/l HA aqueous solution was used for determination of membrane performance. In addition, the flux of pure water was tested prior to the HA separation tests. The flux was calculated from Eq. (3) [30]:

$$J(W) = \frac{Q}{\Delta T * A} \quad (3)$$

where Q is the permeate volume (l), A is the effective membrane area (m^2) and ΔT is the permeation time (h).

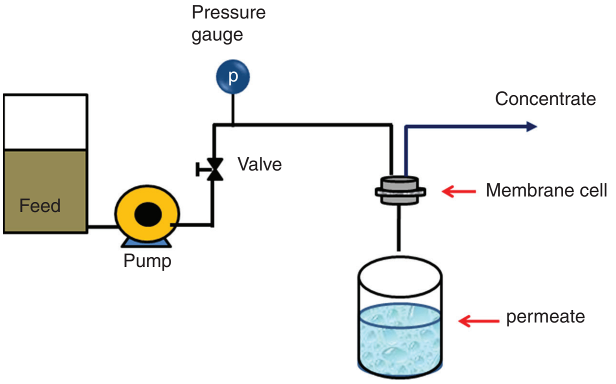

Figure 1: Schematic of membrane testing experimental laboratory setup.

Rejection of HA was calculated using Eq. 4 [32]:

$$R = \left(1 - \frac{HA_p}{HA_f}\right) * 100 \qquad (4)$$

where HA_p and HA_f are the concentrations of HA in permeate and feed, respectively.

3 Results and discussion

3.1 Membrane characterization

3.1.1 SEM images of the prepared membranes

Figure 2 shows the cross sections of prepared membranes. An asymmetric structure was exhibited in all prepared membranes. The dense top layer was observed in PES-M1 to PES-M3 membranes as shown in Figures 2A–C-ii. PES-M1was prepared without any pore former additives and without hydrophilic polymer (PAN); it has a sponge-like structure as shown in Figure 2A-i. The addition of DEG and/or PVP to the casting solutions leads to pore formation on the sublayer with a sponge-like structure, as shown in (PES-M2) in Figure 2B-i,iii. The dense skin layer is responsible for the permeation and retention of solutes, whereas the porous sublayer acts as a mechanical support [7–9]. Increasing PAN concentration from 0.5 wt.% to 2 wt.% in the casting solution provided the formation of larger pores on the surface, as shown in Figures 2D–G-ii,iii for PES-M4, PES-M5, PES-M6, and PES-M7 membranes, respectively. A finger-like structure gradually appeared in the cross-section which was clearly exhibited at PES-M7, as shown in Figure 2G-i. Meanwhile, an obvious finger-like structure appeared at PES-M3, as shown in Figure 2C-i, where a concentration of 14 wt.% PAN was used. The morphology of the prepared membranes is prominently influenced by the phase inversion kinetics and interactions between components. During the coagulation step at instantaneous demixing, the phase inversion occurs when the top surface of the film contacts with the nonsolvent (water). With time, the phase inversion rate decreases due to the reduction in the exchange rate between the solvent in the polymeric mixture film and water in delayed demixing [17]. Figures 2A–C-ii,iii indicate that a dense structure formed, due to slow demixing [8]. Accordingly, the porosity of the membrane is highly

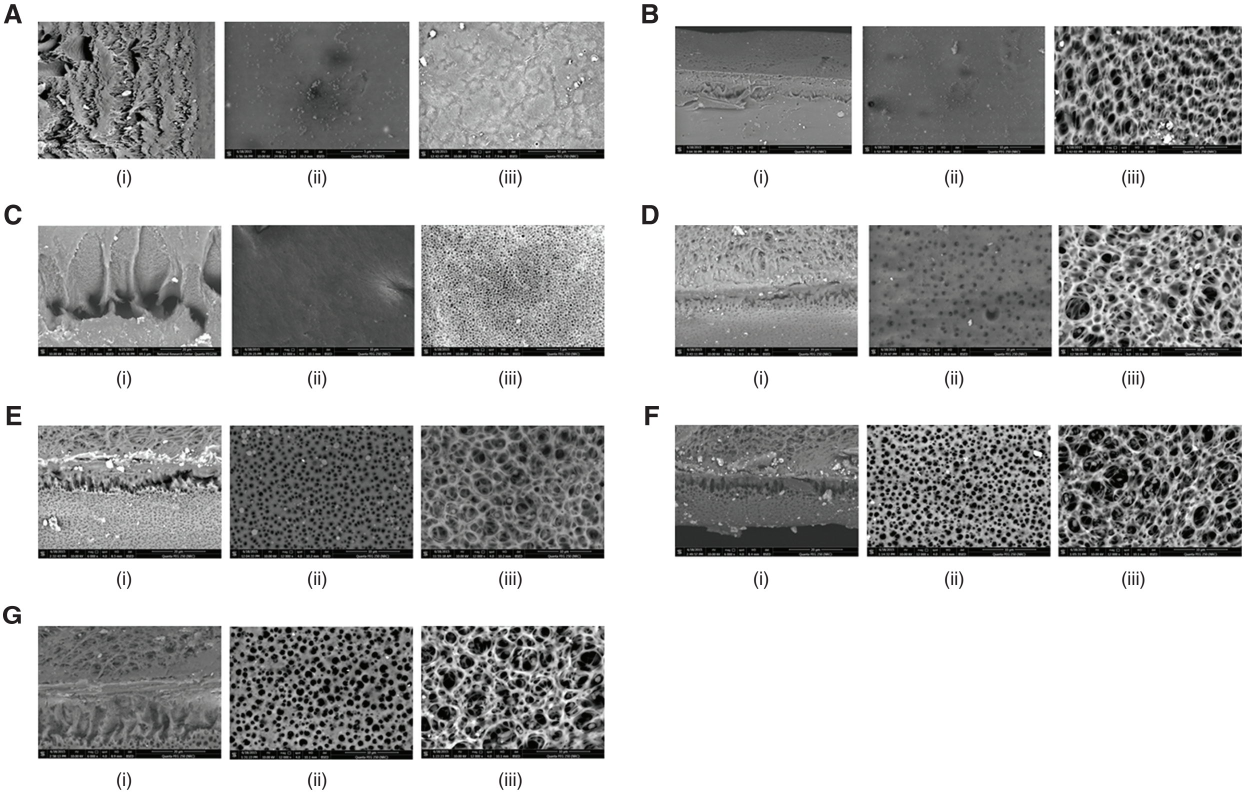

Figure 2: Scanning electron microscopy (SEM) images of polyethersulfone/polyacrylonitrile (PES/PAN) blend membranes. (A) PES-M1; (B) PES-M2; (C) PES-M3; (D) PES-M4; (E) PES-M5; (F) PES-M6; (G) PES-M7. Note: (i) cross section; (ii) top and (iii) bottom.

influenced by the rate of demixing in the coagulation bath [8]. Instantaneous demixing leads to the formation of a more porous structure and consequently the formation of membranes with higher porosities, as shown in Figures 2D–G-ii,iii. Also, during the membrane solidification process, PAN has more hydrophilic characters than PES. Accordingly, it is the dispersed phase that can be separated firstly in the membrane coagulation step. That is in accordance with interface microvoids structure formation which has a positive effect on the permeability of the PES membrane. Increasing the PAN content is more favorable for blend membrane preparation, since it leads to greater porosity and obvious microsphere separation, as shown in Figures 2D–G-ii,iii, which is in accordance with the change in water flux [34].

By contrast, PVP is reported as an important additive in the blending membrane preparation, since it suppresses macrovoids formation in PES membranes with NMP solvent [35] and PAN membranes [36]. Also, it enhances the permeability of PES membranes and increases the molecular weight cut-off [37]. PVP affects the thermodynamic and rheological characteristics of the PES casting solution [38].

Membrane porosity is directly proportional to PAN% and weight of PVP. The addition of PVP leads to easing phase separation by reduction of the miscibility of the casting solution with water or hinders phase separation by increasing the viscosity of the casting solution (rheological effect), which depends on the molecular weight of the added PVP. SEM images of PES-M4, PES-M5, PES-M6, and PES-M7, which have increased in pore formation, are shown in Figures 2D–G.

In this study, the rheological factor possibly becomes more significant than the thermodynamic one because of the use of high molecular weight PVP (360 kDa) increases the ratio of non-solvent in flow to solvent outflow, due to increasing the viscosity of the casting solution, which leads to the formation of more porous membranes [39]. In addition, according to the thermodynamic behavior, spinodal demixing may be the reason for the top layer formation in the prepared membrane due to a fast diffusion process; better pores interconnectivity in the membrane is due to spinodal decomposition forming in the membrane matrix, since interconnected pores can be deemed as a continuous PES lean (i.e. PVP rich) phase engaged by a continuous PES rich (i.e. PVP lean) phase [40].

3.1.2 Mechanical properties

The correlation between tensile strength and elongation of the prepared blended membranes is investigated in Figure 3. The results indicate that blending between PES and PAN improved the membrane mechanical properties, where the tensile strength improved gradually from 0.2 kg_f/mm^2 for PES-M1 to 1.167 kg_f/mm^2 for PES-M6. Also, the elongation improved from 1.16% for PES-M1 to 3.98% for PES-M6. Increasing the percentage of PAN, up to 2%, leads to failure in the membrane mechanical properties due to the delayed exchange between NMP and water in membrane formation step at coagulation bath, accordingly, initiation of microcracks number can take a place due to the delay time in solid-liquid demixing during membrane formation [41, 42].

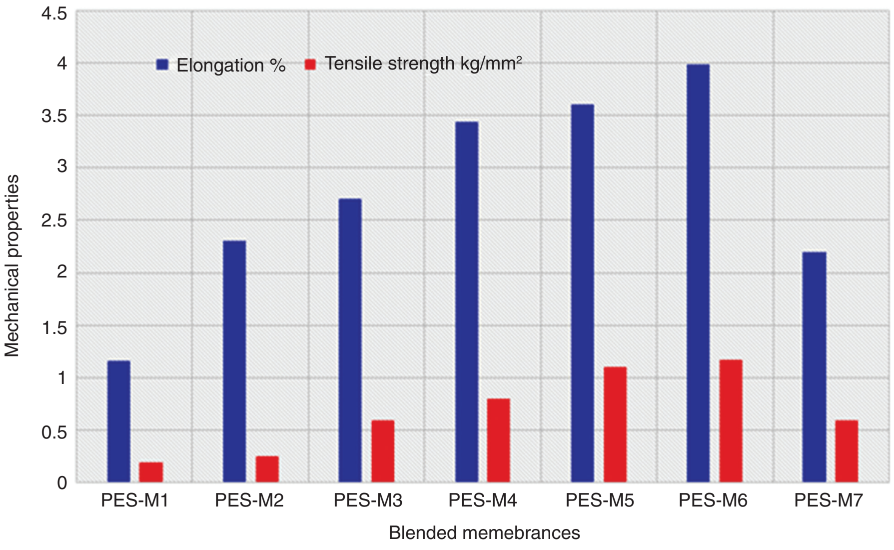

Figure 3: Mechanical properties of the blended membranes.

3.1.3 Membrane porosity

The EWC of the prepared membranes and porosity are shown in Table 2. Increasing PAN content leads to increased EWC and porosity, which indicates that hydrophilicity of the membranes improved as PAN blended with PES. The blend membranes (PES-M4, PES-M5, PES-M6, and PES-M7) have a sharp change in EWC and porosity compared with the PES membrane. Moreover, the interface microvoid structure formation in the PES/PAN blends during the phase separation step can effectively promote the membrane permeability [34].

3.1.4 Contact angle of the prepared membranes

Contact angle measurement is the common method for surface nature determination. Hydrophilicity of the membrane surface is one of the most important properties of membranes, and has a great influence on their flux, as well as their antifouling ability. Contact angles of the prepared membranes can be used for evaluation of PES/PAN composition effects on their hydrophilicity and surface properties, as shown in Figure 4. The naked PES membrane (PAN free) in the casting solution showed the highest contact angle indicating the lowest hydrophilicity of such a membrane [43]. By increasing the PAN concentration in the casting solution, the contact angle of the prepared membranes was reduced, referring to the increasing hydrophilic nature of the prepared membranes, where the lowest contact angle appeared at PES-M7 at 2 wt.% PAN.

3.1.5 FTIR spectroscopy

The changes in chemical structure of the membrane surface can be employed by FTIR as shown in Figure 5. The spectrum for PAN membrane (PES-M3) shows absorption band peaks at 3300 cm^{-1} and 2243.77 cm^{-1}, which refers to CH stretch and the symmetrical stretching vibration of a nitrile bond (CN), respectively [44]. By contrast, the spectrum for naked PES membrane (PES-M1), shows absorption band peaks at 1150 cm^{-1},1550 cm^{-1} and 1750 cm^{-1}, which are related to the (O=S=O), (C=C) and C=O bands, respectively [45]. Meanwhile, the spectrum of the prepared blend membranes, like PES-M7, indicates combination between naked PES and PAN membranes.

Table 2: Porosity and equilibrium water content of the membranes.

Membrane	Porosity (%)	Equilibrium water content (%)
PES-M1	23	25
PES-M2	39	39
PES-M3	55	48
PES-M4	67	68
PES-M5	78	76
PES-M6	81	78
PES-M7	88	84

PES, polyethersulfone.

3.1.6 Effect of pressure

Various pressures of 2 bar, 4 bar and 6 bar were studied to indicate the effect of pressure on the blend membrane performance. Figure 6 illustrates the evolution of permeate flux versus filtration time at different pressures for each prepared membrane. The results indicate that the permeate flux increases gradually by increasing the feeding pressure for all tested membranes. Figure 6A indicates that both PES-M1 and PES-M2 (the neat PES and PES with PVP K-90) have the lowest flux, while PES-M3 (pure PAN)

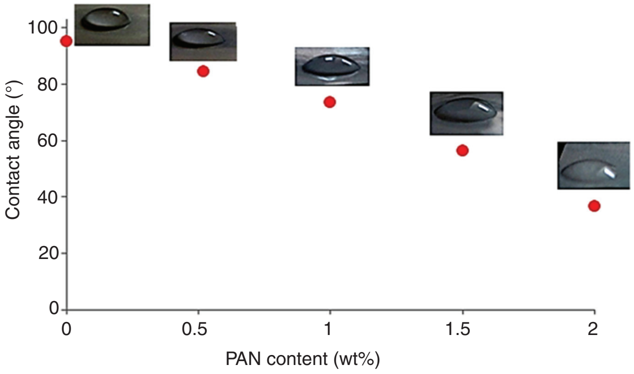

Figure 4: Hydrophilicity for the polyethersulfone/polyacrylonitrile (PES/PAN) blend membranes.

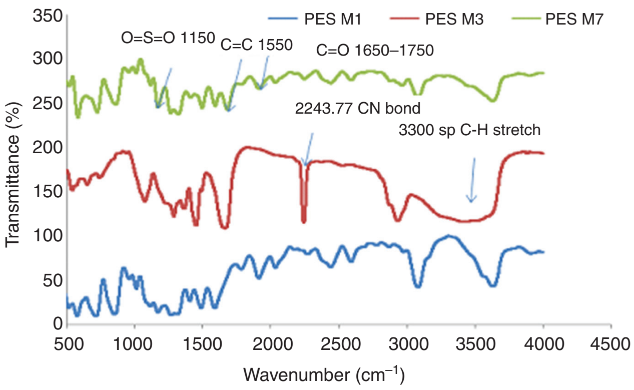

Figure 5: Fourier transform infrared (FTIR) spectra of polyethersulfone (PES), polyacrylonitrile (PAN), and PES/PAN blend membranes.

has the highest flux due to highest porosity and hydrophilicity of the PAN membrane.

By contrast, Figure 6B indicates that the water flux gradually increases with the addition of PAN under different pressures, where the hydrophilicity of the blend membranes improved and the driving force of the water permeation is enhanced by increasing applied pressures [1]. However, the addition of PAN leads to a change in the membrane morphology; the microvoids with a finger-like structure lead to improved membrane porosity, as shown in Figure 2 and Table 2. In addition, compared to PES-M4~PES-M7, the membrane PES-M3 exhibited low porosity and low EWC, but its permeate flux was higher than others; this can be attributed to the finger morphology structure of PES-M3 rather than PES-M4~PES-M7 which have a sponge-like structure (Figure 2C). Accordingly, PES-M3 had a faster water diffusion rate within the finger structure of this membrane [8].

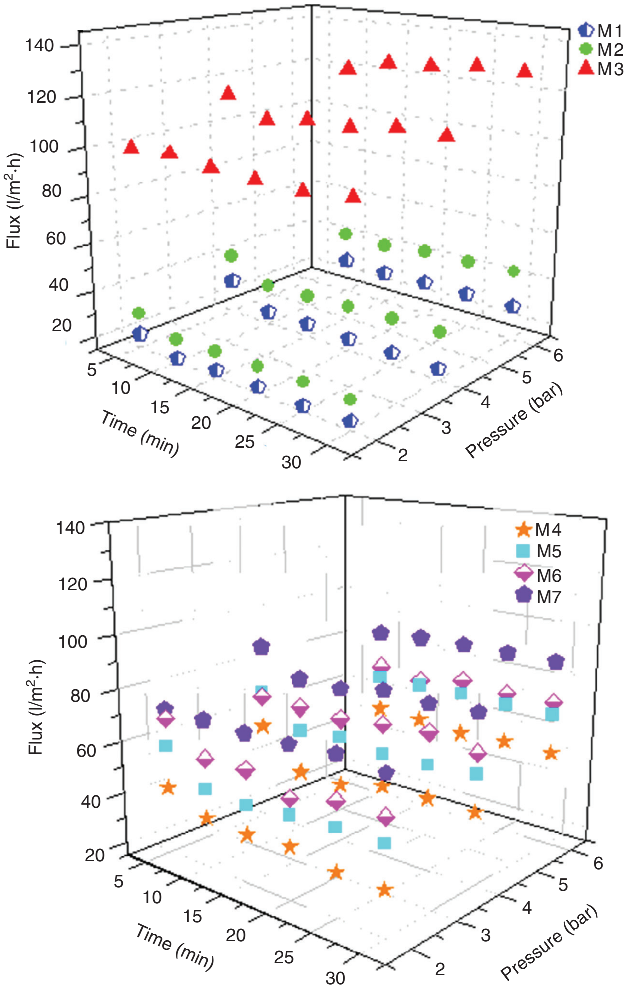

Figure 6: Effect of pressure on the prepared membranes in terms of flux at time intervals.

3.1.7 Permeation experiment and rejection performance

The prepared blend PES/PAN membranes were tested using a dead end UF membrane cell. Separation of 150 mg/l HA as a model compound at different pressures was investigated at a fixed process time of 30 min. Figure 7 illustrates the permeate flux and rejection percent for all prepared blend membranes. Figure 7A indicates that the PAN (PES-M3) provides highest permeate flux from 100 $l/m^2\cdot h$ to 120 $l/m^2\cdot h$ under applied pressure from 2 bar to 6 bar, respectively, while the lowest permeate flux appears at the naked PES membrane (PES-M1) to be 15–30 $l/m^2\cdot h$ at the same pressures. Prepared blending membranes provides enhancement in permeate flux according to the addition of PAN %. The flux increases from 57 $l/m^2\cdot h$ using PES-M4 (0.5% PAN) under pressure of 6 bar to 80 $l/m^2\cdot h$ using PES-M7 at the same pressure. These results can be attributed to the improvement of the porosity, water uptake and hydrophilicity of membranes, as well as changing the morphology of the membranes. By contrast, Figure 7B indicates that the rejection of blend membranes increases with increasing PAN % from 0.5% to 1% in blend membranes; PES-M4 and PES-M5 to be 81.3% and 92.47%, respectively, at low feed pressure of 2 bar. Using excess percent of PAN leads to increase in the porosity, pores in the sublayer of membranes, and thus the selectivity should be decreased. Furthermore, the influence of

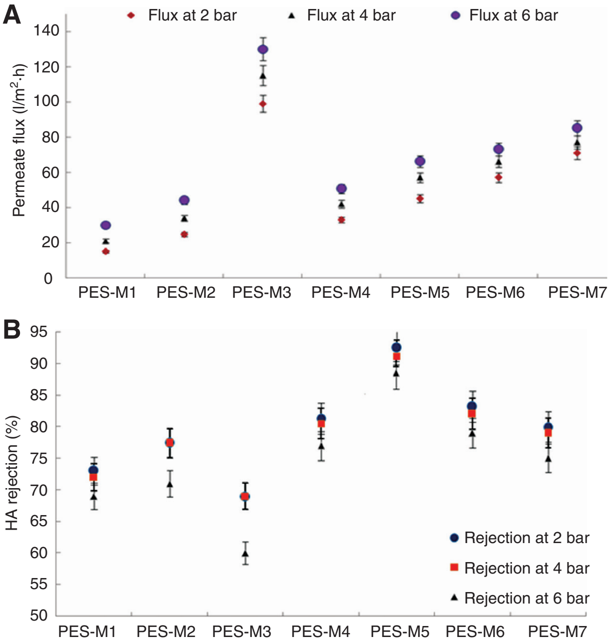

Figure 7: Effect of applied pressure on (A) permeate flux and (B) rejection.

Table 3: Influence of polyacrylonitrile (PAN) proportion on the rejection and permeate flux at pressure 2 bar.

Membrane	PAN proportion (%)	Rejection (%)	Permeate flux ($l/m^2 \cdot h$)
PES-M1	0	74	15
PES-M2	0	76	22
PES-M3	14	68	100
PES-M4	0.5	81.3	34
PES-M5	1	92.47	45
PES-M6	1.5	82	57
PES-M7	2	80	63

PAN, polyacrylonitrile.

PAN proportion of the blend membranes is presented in Table 3 which confirmed the positive effect of the use of hydrophilic polymer in the casting mixture. PES-M5 (1% PAN) can be considered to be the best membrane due to the high rejection percent (92.47%) with flux 45 $l/m^2 \cdot h$ at 2 bar, good mechanical properties and permeate flux.

4 Conclusion

Blend PES/PAN membranes were prepared and developed for ultrafiltration applications. The characterization of blend membranes was studied and indicated that increasing PAN percent can improve the membrane hydrophilicity, porosity, and water uptake. The UF testing for the blended membranes was performed at different pressures (2 bar, 4 bar and 6 bar) using HA 150 mg/l as a model compound. The best performance was at PES-M5 (1% PAN addition), where the rejection of HA reached 92.47% with good permeate flux of 70 $l/m^2 \cdot h$.

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