



Treatment of dyed saline water using developed polyethersulfone/cellulose acetate nanofiltration blend membranes

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ABSTRACT

Nanofiltration membranes of polyethersulfone/cellulose acetate (PES/CA) were fabricated by casting technique and characterized. Cationic dye removal (methylene blue dye) was used in the membrane performance test with the solution of pH 5.5, initial dye concentration of 100 mg/L and NaCl salt concentration of 2,000 mg/L. The membrane performance was improved by annealing of the blend membrane at 60°C (PES/CAt), where the dye removal reached 99.8% and salt rejection reached 99% with permeate flux of 22 L/m² h. This study demonstrated that annealed blend PES/CAt membrane has an enormous applicable potential in dye removal from aqueous saline solutions.

Keywords: Membrane; Polymer blend; Fabrication; Nanofiltration; Dye removal

1. Introduction

Recently, membranes separation techniques like reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) play a very important role in different industries and water treatment [1–6].

Drinking water production, dairy industry, paper industry, and the textile industry need nanofiltration membranes technology because it is the most important technology that can remove di and trivalent salts and small molecules for compounds that produced from these industries in water during treatment [7–11].

Textiles industries wastewater have many environmental problems one of these problems is the removal of dye from saline wastewater. The colored water can't be easily treated using conventional or biological processes. The most techniques which can be used to remove color depends on the physical adsorption, membrane separation, precipitation, photo and bio-degradation, and electrolytic chemical treatment [12–16].

Dye pollution is an organic compound that can block light and highly toxic so it should be treated before throwing it in the effluents [17]. In this field of research, a synthetic saline dye solution can be separated by the nanofiltration membrane [18–20].

Nanofiltration is a kind of membrane has properties between reverse osmosis membrane and ultrafiltration membrane [21].

NF pores size are ranged from 1 to 10 nm and it can separate materials that have a molecular weight from 200 to 1,000 Da [22]. The NF membrane can operate under pressure from 5 to 25 bar [23,24]. Most prepared NF membranes depend on surface charges to produce electrostatic interaction between surface and pollutants in water. To perform a charged surface that requires many surface modifications. Different modification methods like (1) coating, (2) blending, (3) composite, (4) chemical, (5) grafting, or (6) a combination of these methods could be used to improve surface charges, hydrophilicity, and roughness [25,26]. NF membranes can be prepared using various kinds of polymers

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such as polyamide (PA), polyimide (PI), polycarbonate (PC), polysulfone (PSf), polyethersulfone (PES), cellulose acetate (CA). PSf and PES have good mechanical properties, chemical, biological stability, and can be operated in the temperature range over 80°C [27].

The blending technique between two polymers can improve the hydrophilicity of PES. However, the blending of different percentages of cellulose acetate with PES provided hydrophilic membrane surface, which led to enhance membrane performance. Also, polar groups such as $-\text{SO}_3\text{H}$ and $-\text{COOH}$ can be introduced in the membrane by blending PES with other commercial polymers to improve the membrane hydrophilicity or surface charge [27–29].

The advantages of using PES are owing to its thermal and chemical stability and good mechanical properties. But the disadvantage of PES is low hydrophilic nature, which can increase the ability of membrane surface to fouling, according to that the modification of PES to improve the hydrophilicity of the membrane surface is required to reduce the membrane fouling [30]. The addition of hydrophilic polymers like cellulose acetate which rich with hydrophilic hydroxyl group and the carbonyl group of acetate can enhance the hydrophilic nature of the membrane [31]. The most advantageous for the preparation of hydrophilic polyethersulfone/cellulose acetate (PES/CA) surface is increasing interaction of water molecules to the surface and preventing interaction of the foulants to the surface [32].

Methylene blue (MB) is a cationic dye, and it is one of the dyes which is used in dyeing cotton, wool, and silk [33]. This kind of dye act as bases and after soluble in water, it produces a colored cationic salt which can react with the anionic sites on the membrane surface. Methylene blue is a basic dye as indicated by the presence of a nitrogen ion in its structural formula. However, the cationic charge is attracted by hydroxyl groups and carbonyl group on the PES/CA surface, which provide a good indication in produced water from the membrane for dye separation from water. The mechanism of polymer blend formation depends on the hydrogen bond formation between the ether of PES and the hydroxyl group or carbonyl group of cellulose acetate as shown in Fig. 1.

In the case of methylene blue, adsorption of dye onto the surface of the membrane was observed due to the dissociation of a cationic dye in the aqueous solution into a cation (the chromophore) and an anion, Cl^- . Also, methylene blue can represent $\text{MB}^+ \text{Cl}^-$ [34,35]. Accordingly, the negative charge of the membrane surface and the MB^+ produces electrostatic attraction and that facilitates adsorption of methylene blue to the membrane surface as shown in Fig. 1.

The motivation of this study is to produce a new type of membranes that have good characteristics to improve nanofiltration membrane performance, which can be used to treat the disposal from textile effluent streams that contain different kinds of dyes with salt. Blending between two polymeric materials can provide membrane gains the most characteristic of two polymers which can lead to improvement of membrane performance.

The main objective of this study is to fabricate polymeric nanofiltration membranes by blending techniques to treat the effluent wastewater of textiles. In this work, NF membranes are prepared by blending between PES and CA.

The membranes are characterized and the membrane performance in terms of dye removal and salt rejection from dyed saline water is investigated. The application of prepared NF blend membranes on dye separation from real sample of textile waste water is studied for long time.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES Ultrason E6020P with MW = 58,000 g/mol) was supplied by BASF Company (Germany). Cellulose acetate was purchased from Sigma-Aldrich (Germany Company). *N*-methyl-2-pyrrolidone was used as solvent and polyethylene glycol (PEG 400) was used as non-solvent where they purchased from Fluka (Swiss Chemicals Manufacturer). Tap water was used as a coagulant bath. Synthetic solutions of saline dye water were prepared for membrane performance tests. Methylene blue was purchased from Sigma-Aldrich (Germany Company) (purity $\geq 82\%$).

2.2. Methods

2.2.1. Membrane casting procedure

Three membranes were prepared using PES and cellulose acetate, where the content of the total polymer was 17.5 wt.%. The polymers were mixed with *N*-methyl 2-pyrrolidone in a glass bottle in the presence of 1 wt.% PEG as a non-solvent. The mixing time was 7 h for complete homogeneity.

The homogeneous solutions of the blended polymers (PES and CA) were cast on the glass plate at room temperature employing the dry/wet phase inversion method. The coagulation bath was maintained at room temperature. The fabricated flat sheet membranes were stored in a water bath for 24 h to remove the solvent. After that, membranes sheets were kept in a 50 wt.% glycerol aqueous solution for 24 h to prevent the collapse of the porous structure. Finally,

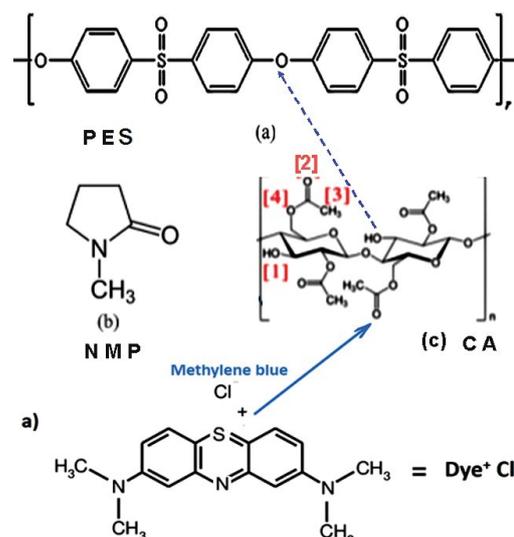


Fig. 1. Mechanism of adsorption of methylene blue dye on the membrane surface.

the membranes were dried in air at room temperature. The membranes sheets were immersed in distilled water for one day to eliminate the effect of glycerol before membrane performance testing. Annealing process was applied on the prepared membrane to study the effect of annealing temperature on prepared membranes at annealing time 2 and 30 min. Table 1 indicates that the percentage of polymer compositions and annealing temperatures.

2.3. Membrane characterization

2.3.1. Morphological surface analysis

Membrane polymer blend cross-section was examined by scanning electron microscopy (SEM) which was used to observe the microstructures of the dried membranes samples. The samples were cryogenically fractured in liquid nitrogen and after carrying out sputtering with gold to provide electrical conductivity. The cross-sections of membranes were taken by a JEOL 5410 SEM (Made in Japan) which was operating at 10 kV, where the significant views of surfaces were recorded.

2.3.2. Membrane surface roughness using the atomic force microscopy

Atomic force microscopy (AFM) topography images for pure PES, blend PES/CA, and annealed blend PES/CAt blend membrane were obtained using AFM, model Wet – scanning probe microscope (SPM) Shimadzu made in Japan. The mean pores radius, surface area, and roughness were measured in scan areas of $2\ \mu\text{m} \times 2\ \mu\text{m}$. The contacting imaging mode in the air was selected to study the membranes at room temperature. The membranes samples were attached to a steel disc with double-sided adhesive tape. The standard deviation of the various measurements was small, ranging from $0.9\ \text{\AA}$ on the smooth surfaces to $7.2\ \text{\AA}$ on the rough surfaces [30,31].

2.3.3. Thermal gravimetric analysis

The thermal stability was examined, under nitrogen, using a Perkin-Elmer, Made in USA (thermogravimetric analysis–differential thermal analysis) thermogravimetric analyzer from room temperature to 600°C .

2.3.4. Membrane contact angle measurements, porosity, and thickness measurements

The contact angle measurement was measured by a compact video microscopy. The testing method was according to the ASTM D724-99 (ASTM – American Society for

Testing and Materials) standard test method for the surface wet ability of paper [36]. The thickness of the membranes was measured by a micrometer measurement device. The porosity of membranes was measured using densometer device, which was operated using air pressure on the membrane area of $25\ \text{cm}^2$ [36].

2.3.5. Fourier transform infrared characterization

For the confirmation of the blend membranes, Fourier transform infrared spectroscopy (FTIR; JASCO FTIR-6100, Made in USA) spectrophotometer over the range of $700\text{--}4,000\ \text{cm}^{-1}$ was used for chemical characterization.

2.4. Membrane performance

A dead-end stirred cell filtration system was connected to a high-pressure pump and was applied to perform the permeate flux and rejection percentage as shown in Fig. 2. The system has a flat sheet membrane module of three openings for feeding, retentate, and permeate. The feed was continuously fed to the membrane module from a closed feeding tank (20 L) under pressure 15 bar. The product was collected from downstream of the membrane module. The prepared PES/CA blend, PES/Cat, and PES membranes were sandwiched in stainless steel plate module of 9 cm in diameter. In all experiments, synthetic methylene blue dye of concentration 100 mg/L and 2,000 NaCl mg/L solution was continuously fed to the membrane module, at pressure 15 bar and a temperature of 25°C . Distilled water was used to prepare a synthetic solution of salt and dye, where 2,000 mg/L of NaCl was added to the distilled water first and after complete solubility of the salt, the 100 mg/L of dye was added to the saline water and mixed for complete dispersion of dye in the solution.

2.4.1. Application of the prepared membranes on long term experiments

Long term experiment was carried out using the same apparatus of the membrane performance for 5 d. The feeding solution was the real wastewater from the textile factory placed in El-Asher of Ramadan city. The analysis of wastewater effluents was illustrated in Table 2. The surface wash for the membrane was applied every 1 h. The average data of permeate flux and dye separation were recorded every hour. Table 2 indicates the analysis of wastewater effluent from the textile factory after biological treatment using activated sludge, which indicates the color is considered a major pollutant that leads to increase the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) above law limits.

3. Results and discussions

3.1. Membrane characterization

3.1.1. Scan electron microscope

Fig. 3a illustrates PES, which indicates the porous top surface, highly porous bottom layer and finger-like structure in the sub-layer of the membrane. The finger-like

Table 1
Polymeric solution composition for prepared membranes

Membrane symbol	Composition weight %				Annealing temperature ($^\circ\text{C}$)
	PES	CA	PEG	NMP	
PES	17.5	0	1	81.5	–
PES/CA	15	2.5	1	81.5	–
PES/CAt	15	2.5	1	81.5	60°C , 80°C , and 100°C

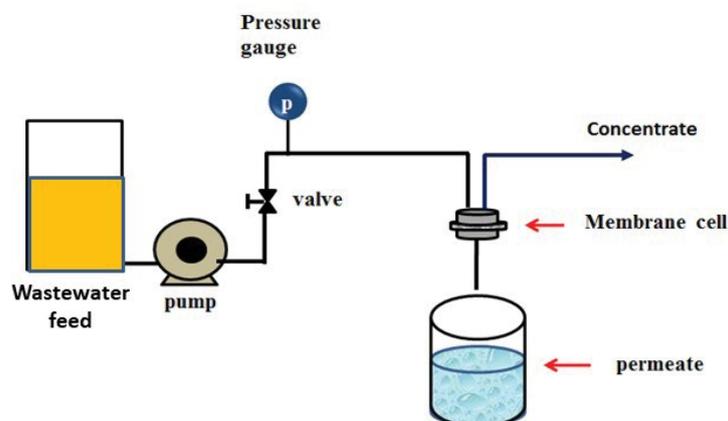


Fig. 2. Laboratory filtration testing unit.

Table 2
Analysis of textile wastewater after biological treatment in the factory

Parameters	Average results	Reference range according to 93/1963 (modified by executive law (44/2000))
Temperature (°C)	32	43
Color	Faint blue	
TSS (mg/L)	188	<800
pH	6.7	6–9.5
TDS (mg/L)	1,090	<2,000
BOD (mg/L)	240	<600
COD (mg/L)	380	<1,100
Nitrates [NO ₃] (mg/L)	2.7	100
Phosphate [PO ₄] ⁻³ (mg/L)	0.4	25
Sulfides [S ⁻²] (mg/L)	0.3	10

structure is due to the addition of PEG as a pore former [37,38]. Fig. 3b indicates the SEM snapshots of the top and bottom surfaces of blend PES/CA membrane, where the bottom surface is porous, while the top surface has a reduction in the size of the pores due to addition of cellulose acetate. However, the cross-section of the blend PES/CA membrane indicates that the blend membrane is asymmetric, and gains the spongy structure with a little bit finger-like structure. Fig. 3c illustrates a top, bottom, and the cross-section of annealed blend PES/CA at 60°C for 2 min. The cross-section indicates a relatively dense top surface, and the membrane structure is asymmetric spongy structure. The image of the cross-section of PES/CA exhibits asymmetric membrane with spongy structure, maybe that due to excessive polymers crosslinking during the heat-treatment process. This structure provides good mechanical properties and less void formation. However, the heat treatment of the prepared membrane leads to a reduction in the size of the pores and formation of the dense top layer [38,39].

3.1.2. Membrane surface roughness using atomic force microscope AFM

The surface roughness of the prepared membranes was studied; blank PES, PES/CA, and PES/CA at as shown in

Figs. 4a–c, respectively. Table 3 indicates the results of the average roughness and mean pore diameter of the PES membrane, PES/CA membrane, and annealed PES/CA at 60°C. The addition of CA to PES polymeric solution leads to the formation of the membrane with the rougher surface than blank PES as shown in Figs. 4a–c. Also, it has been previously reported that adhesive force for the membrane with high roughness surface is large compared with the smooth membrane [17]. It is shown from Table 3, the PES/CA has the highest value of the roughness compared with the blank PES and annealed PES/CA blend membrane. This observation was due to the addition of cellulose acetate to enhance the adhesive force of the PES membrane which is the ionic polymer and contains nonpolar regions that can bind with methylene blue dye by hydrophobic interaction. This result is agreed with the relative flux reduction, where the PES/CA blend membrane results indicate that 5%–10% reduction of flux compared with 75% of the PES membrane. AFM result indicates that the prepared blend membrane which was subjected to heat treatment exhibits its small pores size and the formation of nodules on the membrane surface was nearly reduced [40,41]. The membrane surface pores density of this membrane is very low. In contrast, the PES membrane has large pores size which was larger than the PES/CA membrane without thermal

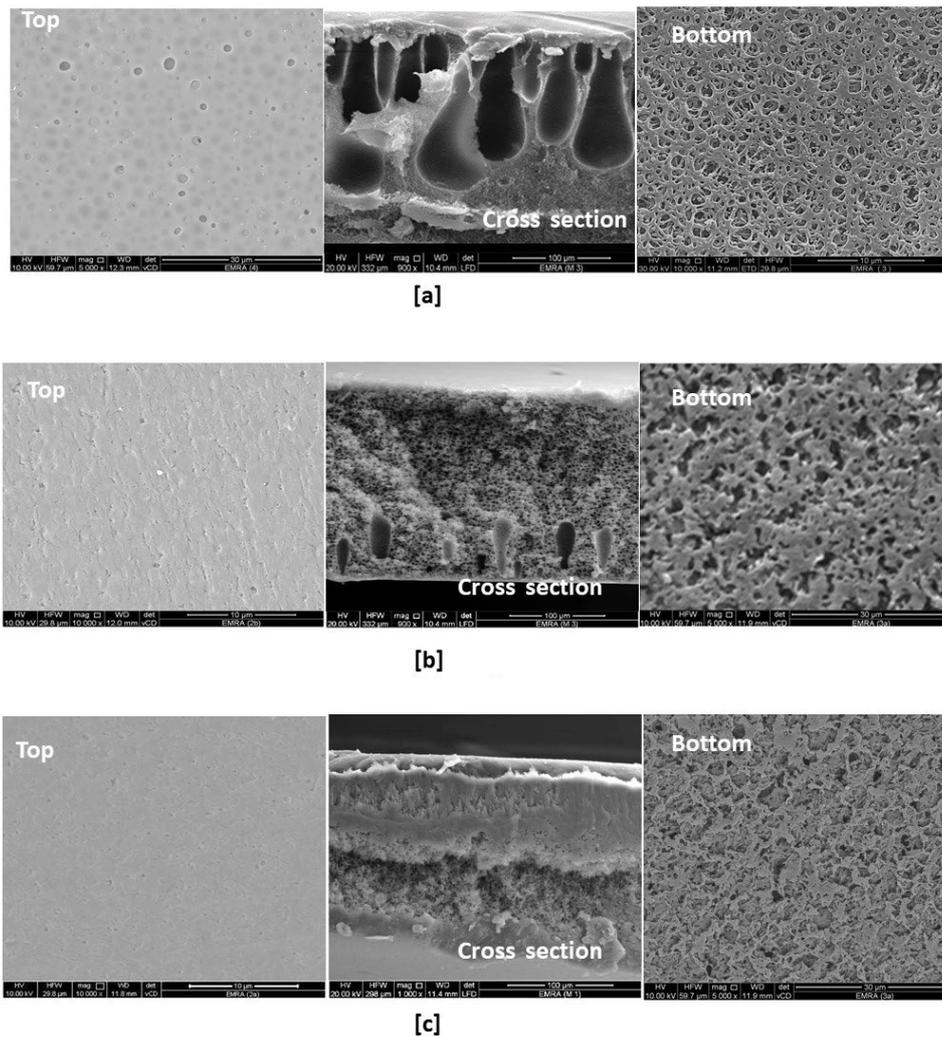


Fig. 3. SEM image of top, bottom, and cross-section of (a) pure PES, (b) PES/CA membrane, and (c) annealed blend membrane PES/CA.

treatment [40,41]. Table 3 shows the mean diameter and the average roughness of different membranes types.

3.2.2. Thermal gravimetric analysis

Fig. 5. shows that the PES/CA membrane exhibits a slight decrease in weight loss through four stages. The first one, from 30°C to 147.9°C, where the weight loss was 5.55% due to the evaporation of remaining absorbed water. The further degradation temperature occurred at 323°C–327°C due to the deacetylation in the second stage [42]. The decomposition of the pyranose ring in CA was initiated due to the elimination of the secondary acetate group leading to un-stability for the two olefinic bonds in carbohydrate derivatives. In the third stage, according to the volatility of volatile matter, the weight loss started from 451.5°C and ended at 558°C, that due to the $-O-$ bond of PES scission. This degradation of the prepared membrane was considered the major one. However, the wide loss of acetic acid and oxides of carbon were occurred due to this drastic decomposition,

which represents 38.93% of the weight loss. Blending PES with CA led to retard in the thermal decomposition of CA, so the thermal stability of PES decreased while the thermal stability of CA increased due to the sulfonic group effectiveness which can act as a physical barrier and hinder the volatile compound decomposition. The final stage began at 558.01 and ended at 627°C. The ash of the degraded product (degradation of the membrane) was due to the weight loss of 45.785 [43,44]. Table 4 shows the main differences between different types of membrane matrix CA, PES, PES/CA, and annealed PES/CA blend membranes.

3.2.3. Membrane contact angle measurements, porosity, and thickness measurements

Table 4. indicates the contact angle for prepared membranes, where the contact angle for PES was the highest one 68° and annealed PES/CA was the lowest one 45.5°, while PES/CA was 50° which means the hydrophilicity was enhanced after addition of CA and has more enhanced after

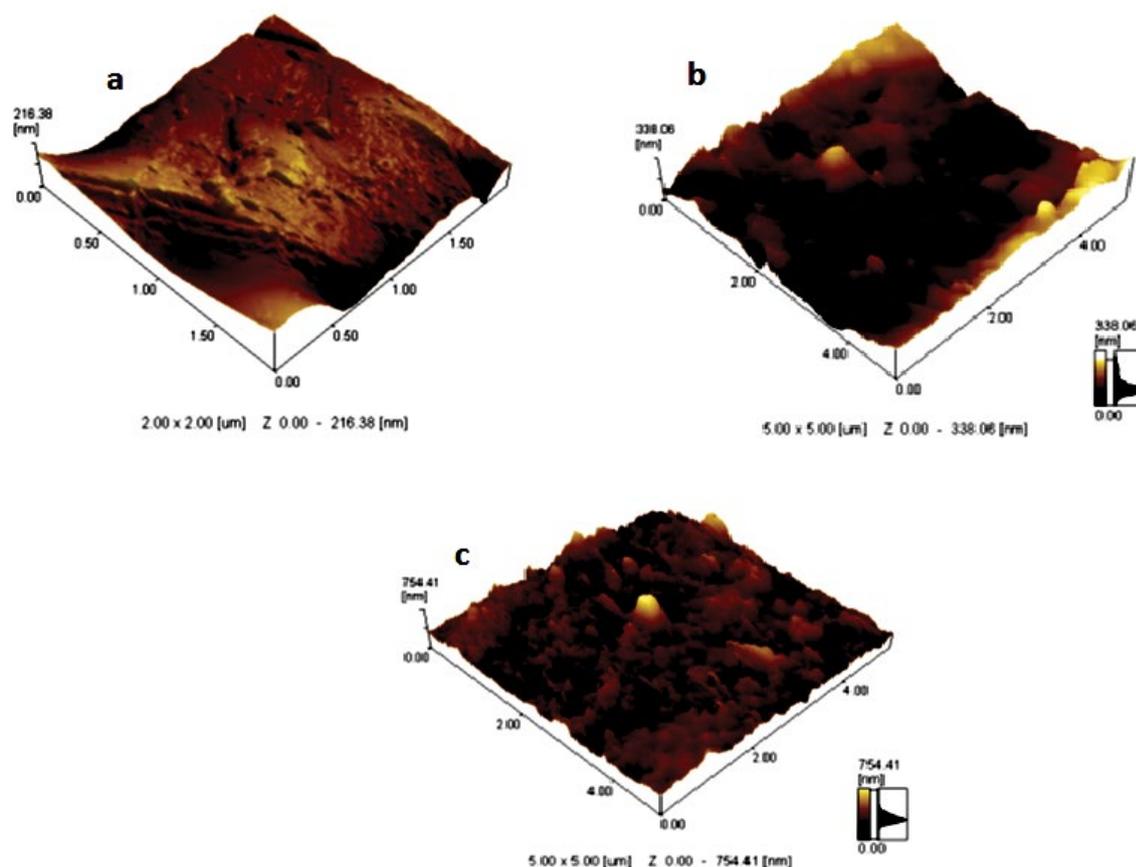


Fig. 4. Three-dimensional AFM surface images of prepared membranes, (a) pure PES, (b) PES/CA, and (c) PES/CAt.

Table 3

Parameters of surface morphology of prepared membranes were obtained from AFM images

Membrane types	Mean pore diameter (nm)	Average surface roughness (nm)
PES	34	1.043
PES/CA	20	1.3
PES/CAt	4.9	1.15

annealing to 60°C. Rising the annealing temperature to 80°C and 100°C provides a contact angle close to the contact angle of annealing temperature 60°C. The porosity of prepared membranes was illustrated in Table 4. The porosity results indicate that the porosity of annealed membrane was low, where the annealed membrane at 60°C was 51.2%, at 80°C was 48.6% and at 100°C was 45.5%. However, the thickness of the membrane was measured as shown in Table 4, where the annealed membrane to 100°C provides the highest thickness 102 μm, while the thickness of annealed membrane at 80°C was 98 μm and the lowest one was annealed membrane at 60°C, which was 92 μm. The further rising in annealing temperature can lead to shrinkage of pores size due to more polymerization crosslinking, which provides thicker membrane and reduces the membrane porosity, which can

lead to a decline in the permeate flux and fast clogging at dye separation. Annealing time was studied for 2 min and for 30 min, which has no effect on the membrane porosity or thickness, which means it is not necessary to increase the annealing time [40–43].

3.3. Fourier transform infrared characterization

From spectrum CA (1): the band in the range of 3,200–3,600 cm^{-1} is related to the hydration due to the stretching of OH vibration, which increases the intensity with a wide overlapping band combined with OH stretching vibrations from water molecules which were sorbed. Different bands indicate the cellulose acetate characteristics, where CH stretching at 2,903 cm^{-1} , the CH_2 bending at 3,429 cm^{-1} and the CH_2 bending at 1,370 cm^{-1} . Spectra at 1,744 cm^{-1} ($-\text{C}=\text{O}$), 1,368 cm^{-1} (CH_3), and 1,228 cm^{-1} ($\text{C}-\text{O}$) indicates acetyl groups in CA structure [38,39].

Spectrum PES (2): The peak at 3,097 cm^{-1} is related to the benzene ring in the PES structure. However, the peaks between 1,600 and 1,400 cm^{-1} are an indication of the vibration of aromatic skeletal. Stretching peaks at 1,324 and 1,239 cm^{-1} are related to $\text{C}-\text{O}-\text{C}$, while peaks at 1,151 and 1,105 cm^{-1} is an indication for ($-\text{S}=\text{O}$) appearance.

The chemical structure of the PES/CA blend membrane is shown in the spectrum 3. From the spectra 2 and 3, it is obvious that the characteristic peaks of pure PES group

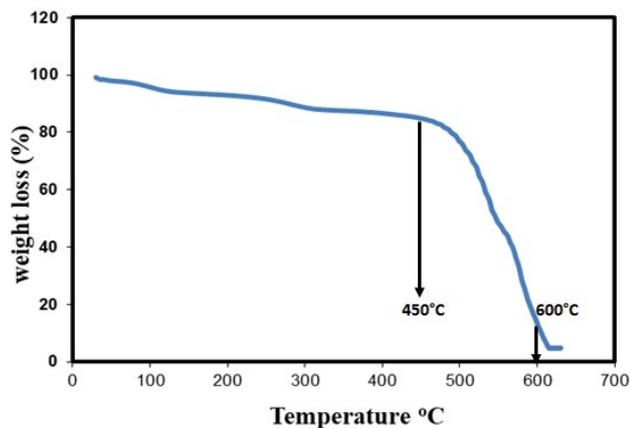


Fig. 5. Thermal gravimetric analysis of prepared blend membrane.

were displayed. For example: the peaks at $3,097\text{cm}^{-1}$ is due to the benzene ring of CH. Aromatic skeletal vibration provides three peaks between $1,579$; $1,475$; and $1,400\text{ cm}^{-1}$. The peaks at $1,324$ and $1,239\text{ cm}^{-1}$ and $1,151$ and $1,105\text{ cm}^{-1}$ are related to C–O–C and –S=O appearance [38,44].

Also, by comparison of spectra 1 and 2 it is the appearance of OH stretching peaks at $3,200$ – $3,600\text{ cm}^{-1}$ regions this is maybe due to the formation of the hydrogen bond between the oxygen in ether with OH group in cellulose acetate and OH groups of cellulose acetate and the oxygen atoms of ether and sulfone groups as shown in spectrum 2. From Fig. 6, we found that there are not new characteristic peaks that were found at spectrum 3 of the blend membrane. This evidence that the blend of PES and cellulose

acetate did not form new functional groups during the PES/CA membrane polymer blend [38,39].

3.4. Membrane performance measurements

The performance of prepared membranes was studied, pure water permeates flux, average dye rejection %, and salt rejection % were determined. The feed solution was synthetic saline dye solution of 100 mg/L , pH 5.5 and $2,000\text{ mg/L NaCl}$.

Comparison between various membranes (PES, PES/CA, and PES/CAt) according to permeate flux and dye rejection % are shown in Figs. 7 and 8, respectively. The average flux of PES/CAt reached to $22\text{ L/m}^2\text{ h}$, while the blank PES maximum average flux reached to $15\text{ L/m}^2\text{ h}$. Fig. 8 indicates that the average dye rejection% of annealing blend membrane PES/CAt reached 99.8% while the average dye rejection of PES was 98% . However, the salt rejection is highest using PES/CAt which was 99% , while the blank PES was 66% as shown in Fig. 9. The results indicate that the addition of cellulose acetate increases the hydrophilicity of the membrane and form the dense selective layer which can improve the performance of blend membranes according to permeate flux and rejection of dye and salt [24,45].

3.4.1. Long term experiments

The membrane separation performance was carried out for the treatment of synthetic wastewater effluent resulted from the textile industry, aiming to remove dyes and salts. Two membranes PES/CA and PES/CAt were used for this experiment. Table 5 indicates the results after using NF membranes. The experiments were carried out for 5 d and the average of samples analysis were taken.

Table 4
Comparison between different membranes matrix

Parameters	Cellulose acetate membrane (CA)*	Polyethersulfone membrane PES	Polyethersulfone/cellulose acetate membrane blend	Annealed polyethersulfone/cellulose acetate membrane blend
Tensile strength MPa	2.05	12	13.2	14.6 at 60°C
Elongation %	8.14	3	13	12.8 at 60°C
Cross-sectional view	Symmetric	Asymmetric	Asymmetric	Asymmetric
Decomposition temperature ($^\circ\text{C}$)	300	550**	450–600	–
Glass transition temperature, T_g ($^\circ\text{C}$)	182	220–230**	200	200 at 60°C
Water content %	76.59	69	77.6	83 at 60°C
Contact angle ($^\circ\text{C}$)	49	68	50	45.5° at 60°C 45.2° at 80°C 45.4° at 100°C
Thickness (μm)	55 μm	85 μm	89 μm	92 μm at 60°C 98 μm at 80°C 102 μm at 100°C
Porosity	75.4%	65.5%	54.6%	51.2% at 60°C 48.6% at 80°C 45.4% at 100°C

*Results of CA are from previous work [40] and **PES thermal analysis are from previous work [39].

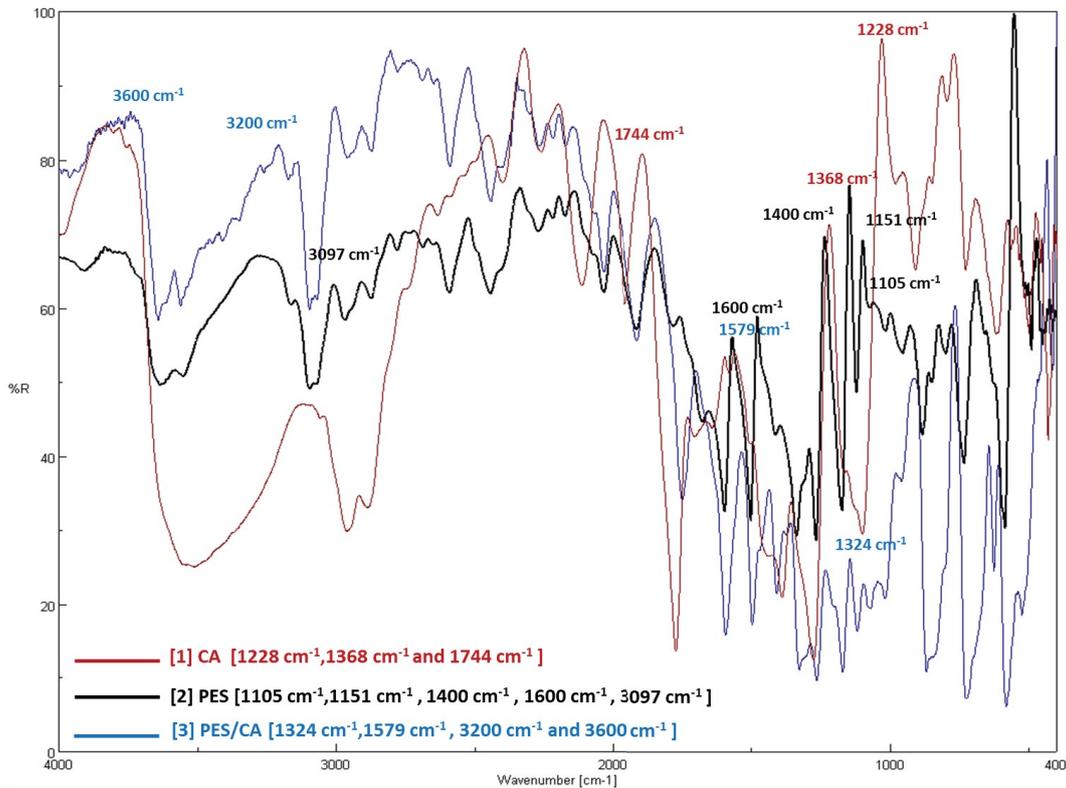


Fig. 6. FTIR for different prepared membranes [1] CA, [2] PES, and [3] PES/CA blend membrane.

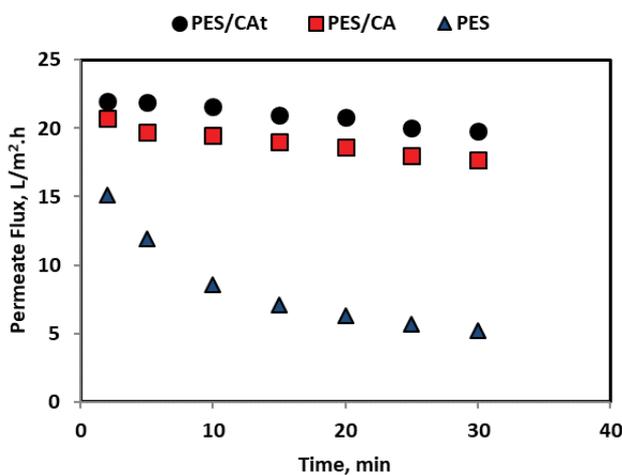


Fig. 7. Comparison between blank PES and prepared blend membranes PES/CA and PES/CAt according to permeate flux.

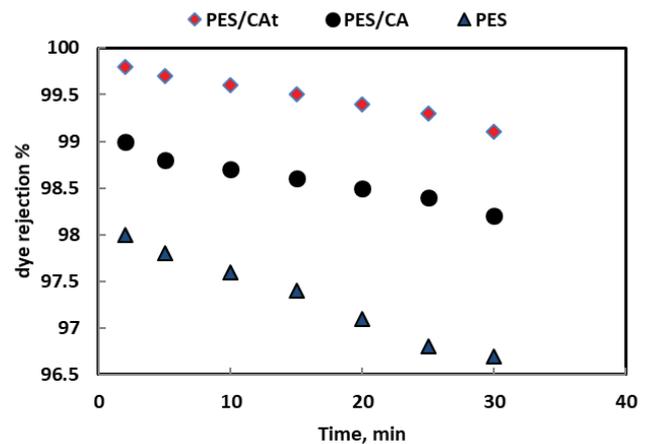


Fig. 8. Comparison between blank PES and prepared blend membranes PES/CA and PES/CAt according to dye separation.

The analysis of treated water indicates that the blend membranes provide excellent removal of dyes at using PES/CA and excellent removal for both dye and salt at using PES/CAt. However, the surface wash of membranes was carried out every 1 h, which means the hydrophilicity of the membranes surface enhanced the permeability, removal percentage and antifouling properties. PES/CAt can be considered the best membrane that can be used for dye and salt removal at the same time.

4. Conclusion

Three membranes were prepared in this work by immersion precipitation process; PES, blend polyethersulfone with cellulose acetate (PES/CA), and annealed blend PES with cellulose acetate PES/CAt. The following conclusions can be drawn from this work:

- The addition of CA on PES polymeric solution enhanced the membrane hydrophilicity and form dense selective top layer.

Table 5
Analysis of treated water after using PES/CA and PES/CAt blend membranes

Elements	Analysis of wastewater	After using PES/CA	After using PES/CAt	Reference range according to 93/1963 (modified by executive law (44/2000))
Temperature, °C	32	25	25	43
Color	Faint blue	No color	No color	
TSS, mg/L	188	1.8	0.36	<800
pH	6.7	6.4	6.2	6–9.5
TDS, mg/L	1,090	383.6	2.19	<2,000
BOD, mg/L	240	0	0	<600
COD, mg/L	380	1.1	0.24	<1,100
Nitrates [NO ₃], mg/L	2.7	0.04	0	100
Phosphate [PO ₄] ⁻³ , mg/L	0.4	0.02	0	25
Sulfides [S ⁻²], mg/L	0.3	0.005	0	10

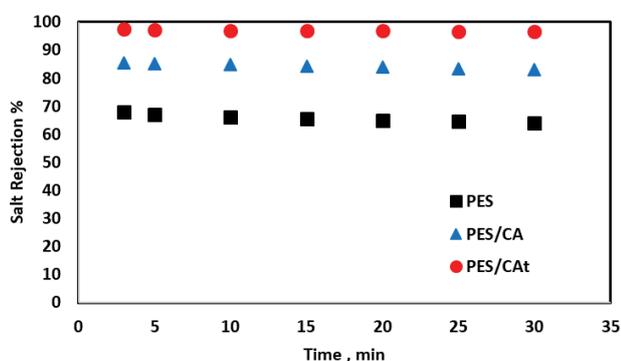


Fig. 9. Comparison between PES, blend membranes PES/CA, and PES/CAt according to salt rejection.

- The heat treatment at 60°C for 2 min for blend PES/CA membrane enhanced the hydrophilicity of the surface and produced a membrane with high dense top layer and spongy structure.
- PES/CA membrane has the highest value of the roughness compared with the blank PES and annealed PES/CAt blend membrane, while PES/CAt exhibited small pores size and the formation of nodules on the membrane surface was low.
- The further rising in annealing temperature can lead to shrinkage of pores size and form a thicker membrane, which led to a reduction in the membrane porosity, then a decline in the permeate flux due to fast clogging of the membrane pores during dye separation test.
- Dye separation and salt rejection % of prepared blend membranes were improved, after annealing for blend membrane which was 99.8% dye separation and 99% for salt rejection; this means that the annealed blend membrane is a good modifier for the formation of NF PES membranes without further treatment of membrane surface.
- Long term experiment on real wastewater from the textile factory was applied on prepared membranes, which indicated excellent membranes performance for dye and salt removal.

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