

Preparation of high performance polycarbonate/acrylonitrile-butadiene-styrene blend ultrafiltration membrane for water treatment

Habib Etemadi^{a,*}, Hamidreza Qazvini^a, Naser Hosseinnezhad Alishah^b

^aDepartment of Polymer Science and Engineering, University of Bonab, Bonab, Iran, emails: h_etemadi@ubonab.ac.ir (H. Etemadi), hamidreza77214@gmail.com (H. Qazvini)

^bDepartment of Chemical Engineering, Islamic Azad University, Omidiyeh Branch, Omidiyeh, Iran, email: naser.hosseinnezhad@yahoo.com

Received 24 April 2020; Accepted 16 December 2020

ABSTRACT

Ultrafiltration membranes were prepared from blends with polycarbonate (PC) and acrylonitrilebutadiene-styrene (ABS) by non-solvent induced phase separation technique. The blend membranes were prepared with ABS composition from 0 to 10 wt.%. Different techniques such as field-emission scanning electron microscopy (FESEM), atomic force microscopy, differential scanning calorimetry, contact angle, pure water flux (PWF) mechanical tensile strength and filtration experiment of humic acid (HA) in a submerged membrane system were applied to evaluate the morphology and performance of membranes. The optimum PC/ABS blend ratio (PC/ABS-5) was selected by discussing the hydrophilicity, PWF, and tensile strength. FESEM images showed that when ABS was added to the PC membrane, macrovoids developed in number and size, promoting the formation of many finger-like pores, WHICH quantized lengthened to the bottom of the membranes. The obtained results from antifouling performance revealed that the blend membrane had higher antifouling properties as compared to neat PC membrane due to the presence of a hydrophilic nitrile group on the blend membrane surface. Also, the PC/ABS-5 blend membrane significantly decreased the irreversible fouling ratio from 14.8% to 1.8%. As a final result, the neat PC membrane showed 84.6% removal of HA, while this value increased to 98.6% for the blend membrane.

Keywords: Ultrafiltration; Polycarbonate membrane; Acrylonitrile-butadiene-styrene; Membrane morphology; Antifouling

1. Introduction

Due to growth in industries and population, there is an increasing need for clean water and in this case, water scarcity has turned into an issue for many areas in the world. Water reuse is a pragmatic and sustainable approach to solve this problem and supply freshwater [1]. Although, surface waters are one of the most important water sources, there is concern about of pollution of such waters. The presence of natural organic matter, such as humic acid (HA), should be removed from surface waters in order to reuse [2].

There are several techniques available for the effective removal of HA from water. Among them, membrane separation processes have met a large expansion in water treatment [3]. Ultrafiltration (UF) membranes could obtain high flux at low energy consumption, but an effective removal may not be achieved [4]. Meanwhile, the concentration polarization and membrane fouling are the challenges of UF in the pressure-driven membrane process which leads to poor performance [5]. Therefore, it seems that membrane modification is essential to overcome these disadvantages.

Various methods such as membrane surface modification [6,7], nanocomposite membrane [8–10], and blending of different polymers [11,12] widely used to modification

^{*} Corresponding author.

^{1944-3994/1944-3986 © 2021} Desalination Publications. All rights reserved.

of membranes. Among them, blending is one of the most practical ways for polymeric membrane modification which can be applied to an industrial scale production due to the least expensive from an economical point of view [11,13]. The asymmetric membranes used in blend UF are generally made from polymers such as cellulose acetate, polyvinyl chloride (PVC), polysulfone, polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF) and polyethersulfone [13–17].

Polycarbonate (PC) is known as engineering and glassy plastic containing carbonate groups [18]. PC has been extensively used in a wide range of applications due to its unique physical and chemical properties such as its excellent physical properties, good mechanical strength, high heat and chemical resistance and low cost [19,20]. Thus, PC can be considered as a good candidate for membrane fabrication. However, the hydrophilicity, porosity of PC, as well as effective removal of pollution (such as HA), still need to be improved.

Behboudi et al. [13] prepared PVC/PC blend UF membrane for Bovine serum albumin removal from contaminated water. They showed that PVC/PC blend membranes were high performance and fouling resistant membranes in comparison with neat PVC membrane. In other work, thermoplastic polyurethane (TPU) was added to PC for preparation of PC/TPU blend membrane in a submerged membrane bioreactor (MBR) [21]. The obtained results showed that the membrane with a polymer composition of 85/15 (PC/TPU) presented a better performance than other prepared membranes in MBR. However, membrane hydrophilicity decreased when TPU was blended.

We expected that nitrile groups onto the surface of the ultrafiltration membrane would effectively improve the antifouling and high removal ability of the PC membrane. In this case, acrylonitrile-butadiene-styrene (ABS) can be a candidate for this purpose. The main superiority of ABS compared with PC is the presence of nitrile functional groups on its structure. These groups may have further influence on membrane performance. ABS is a commercially available copolymer with an appropriate price, good mechanical, thermal properties, chemical resistance, reasonable processability and solubility in common solvents [22,23]. ABS is composed of a dispersed butadiene phase in a styrene-acrylonitrile (SAN) copolymer matrix. In fact, SAN is an amorphous continuous phase while butadiene is a rubbery dispersed phase. In the case of ABS, styrene and butadiene are hydrophobic components while acrylonitrile is hydrophilic [24]. However, to our knowledge, there is no report on PC/ABS blend membrane. In the present work, PC/ABS flat sheet membranes with various ABS contents are produced through the phase inversion method.

According to the literature, a large number of research groups have focused on the preparation of PC membrane via the track-etching method [25], and there are few reports about the preparation of PC membrane via phase inversion process. Porous polycarbonate membrane via phase inversion process was prepared by Bodzek and Bohdziewicz [25]. They found that the porosity of the membranes can be controlled by the time and temperature of gelation. Also, the obtained membranes are reasonably symmetrical, having a spongy structure with identical pore sizes and a skinned external structure. In this study, membranes with various ABS content were prepared via the non-solvent induced phase separation (NIPS) method and were characterized by field-emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC), atomic force microscopy (AFM), contact angle, mechanical tensile, and pure water flux (PWF). Moreover, the performance and antifouling properties of neat PC and PC/ABS blend UF membranes were evaluated by filtration of HA solution in a submerged membrane system.

2. Experimental

2.1. Materials

Polycarbonate (PC, grade: 0710) was supplied by Khouzestan Petrochemical Company (Iran), and used as the base polymer for membrane preparation. ABS (Grade SD0150) was supplied from Tabriz Petrochemical Company (Iran). The molecular structure of PC and ABS are given in Fig. 1 schematically. 1-Methyl-2-pyrrolidone (NMP) as solvent and polyethylene glycol (PEG) with a molecular weight of 400 Da as pore former were purchased from Merck (Darmstadt, Germany). HA powder obtained from Sigma-Aldrich (USA) was used as the organic foulant during the experiment without further purification. Deionized (DI) water was used as a non-solvent in the NIPS method.

2.2. PC/ABS membrane preparation

In this study, PC/ABS flat sheet membranes were prepared via the NIPS method. A given amount of polymer (PC or PC/ABS with a specific weight ratio of 100/0, 97.5/2.5, 95/5, 92.5/7.5, and 90/10 which corresponded neat PC, PC/ABS-2.5, PC/ABS-5, PC/ABS-7.5, and PC/ABS-10, respectively) was dissolved in an appropriate amount of NMP solvent to obtain a 17 wt.% polymer solution. The mixture was then allowed at constant stirring for 15 h to obtain a homogeneous solution. At the completion of the blending, the dope was kept as such overnight, until the air bubbles disappear. The casting solution was cast onto a smooth glass plate to form a film of 150 µm thickness and subsequently, was immersed into a water coagulation bath at room temperature. Finally, in order to complete the phase inversion process, the cast film is instantaneously immersed in a DI water bath for 24 h.



Fig. 1. Schematic molecular structure of (a) PC and (b) ABS.

148

2.3. Membrane characterization

The surface of PC/ABS blend membranes was analyzed by Fourier-transform infrared spectroscopy (FTIR). For FTIR analysis, Shimadzu (Kyoto, Japan-IRAffinity-1S) spectrometer was employed in the range of 400–4,000 cm⁻¹. The surface and cross-sectional morphologies of the neat PC and PC/ABS blend membranes were characterized using a field-emission scanning electron microscope (FESEM; MIRA-3 FEG SEM, TESCAN-Brno, Czech Republic) operating at 15 kV. Membrane samples were cut into an appropriate size and coated with a thin film of the gold layer, then mounted on the sample holder. In order to observe the cross-section of prepared membranes, samples were cryogenically fractured in liquid nitrogen. Atomic force microscopy (AFM, Nanosurf Mobile S microscope - Liestal, Switzerland) was used to analyze the surface roughness of the prepared membranes. Small squares of the prepared membranes were cut and glued on a glass substrate. The membrane surfaces were imaged in a scan size of 5 μ m × 5 μ m. The surface roughness parameters of the membranes are expressed as the mean roughness $(R_{a})_{t}$ the root mean square roughness (R_a) and the mean roughness depth (R_z) .

To examine variations in the surface wetting characteristics of the PC/ABS membrane as a function of ABS concentration, the water contact angle was measured for membrane surface using a contact angle measuring instrument (PGX, Thwing-Albert Instrument Company, USA). The obtained results were at least an average of five tests at different locations on the membrane surface. The mechanical properties of membranes were evaluated by a tensile testing machine (Santam STM-5, Iran). The membrane samples were cut into a rectangular shape, and the loading velocity was set as 10 mm/min.

The compatibility between PC and ABS as well as thermal behavior of blend membranes were studied via differential scanning calorimetry (DSC Q600 TA, USA) in an argon atmosphere. The samples were heated from 25°C to 200°C at the rate of 10°C/min.

The porosity of neat PC and PC/ABS blend membranes was determined by a gravimetric method according to Eq. (1) [26]:

$$\varepsilon(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{A \times L \times D_W} \times 100 \tag{1}$$

where W_{wet} and W_{dry} are weights of wet and dry membranes (g), *A* is the area of membrane (m²), *L* is the average thickness of the membrane (m), and D_W is the density of water (0.998 g cm⁻³).

2.4. Filtration experiment

In this study, a lab-scale submerged membrane system was used to the filtration of HA solution. Flat sheet membrane modules with an effective membrane surface area of 14.7 cm², were immersed in a 3 L influent tank containing the HA solution with a concentration of 1 g L⁻¹ to be treated. The solution pH was adjusted at 6 by adding a small amount of either 0.1 M HCl or 0.1 M NaOH.

The membrane tank was continuously fed with HA solution at a constant rate to fix the volume. The filtration transmembrane pressure was maintained at 0.2 bar by a vacuum pump. Airflow was provided at a rate of 4 L min⁻¹ to produce scouring on the membrane surface as well as to keep the HA particles in suspension in the tank.

Prior to the UF experiment, both neat PC and PC/ABS blend membranes compacted for 60 min using DI water at a vacuum pressure of 0.8 bar in a submerged membrane tank. Then, vacuum pressure was decreased to 0.2 bar for 30 min. PWF of membranes was measured using the following Eq. (2) [27]:

$$J_0 = \frac{M}{At} \tag{2}$$

where J_0 is PWF, *M* is the collected a mass of water, *A* is the area of membranes and *t* is the time.

The experiments were followed by HA solution and the flux of HA (J_{HA}) was measured at a vacuum pressure of 0.2 bar for 5 h. After HA filtration, the membrane was cleaned with distilled water and then was submerged in the pure water tank to measure PWF after fouling (J_1).

Fouling parameters of the membranes were evaluated using the following Eqs. (3)–(6) [8,13]:

$$RFR(\%) = \frac{J_1 - J_{HA}}{J_0} \times 100$$
(3)

$$IFR(\%) = \frac{J_0 - J_1}{J_0} \times 100$$
 (4)

TFR(%) = FRF(%) + IFR(%) =
$$\frac{J_0 - J_{HA}}{J_0} \times 100$$
 (5)

$$FRR(\%) = \frac{J_1}{J_0} \times 100 \tag{6}$$

where RFR, IFR, TFR and FRR are reversible fouling ratio, irreversible fouling ratio, total fouling ratio and flux recovery ratio, respectively.

The HA rejection (*R*) of membranes was calculated by Eq. (7):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\tag{7}$$

where C_p and C_f are the HA concentrations in the permeate and feed solutions, respectively. The HA concentrations of feed and permeate solutions were determined by using a UV spectrophotometer (Bio Quest CE2501).

3. Results and discussion

3.1. FTIR analysis

Fig. 2 shows the FTIR spectra of neat PC, neat ABS and PC/ABS blend membrane surfaces. For neat PC membrane,



Fig. 2. FTIR spectra of membrane surface of neat PC, ABS, and PC/ABS-5 blend membranes.

the existence of the peak at about 1,770 cm⁻¹ is contributed C=O band [28]. The characteristic IR bands of C–H from the aromatic rings are observed in the 2,960–3,000 cm⁻¹ region. The stretching of the C–C bond from the phenyl group (benzene ring) occurs at ≈1,600 cm⁻¹. The stretching of the ester group (O–C–O) occurs from 1,080 to 1,244 cm⁻¹ [29].

For neat ABS membrane, an absorption peak occurred in the 2,235 cm⁻¹ that is related to nitrile groups (C=N) in the ABS. Also, absorptions in the 1,494 and 1,600 cm⁻¹ are attributed to the double bonds of styrene blocks in the ABS terpolymer. The peak around 1,454 cm⁻¹, is related to double bonds of butadiene blocks. The deformation of C–H for hydrogen atoms attached to alkenic carbons is seen at 967 cm⁻¹ for 1,4-butadiene units and 911 cm⁻¹ for 1,2-butadiene units [30]. Meanwhile, C–H bending in monosubstituted benzene rings was observed at 685 and 759 cm⁻¹ [31]. Moreover, the absorptions in 2,918 and 3,026 cm⁻¹ correspond to vibrations of aliphatic and aromatic CH bonds, respectively [32].

Compared to the FTIR spectra of the neat PC membrane, the two new peaks appeared around 2,235 and 685 cm⁻¹ in the spectra of PC/ABS blend UF membrane confirmed that the ABS was successfully incorporated into the PC macromolecular.

3.2. Hydrophilicity, porosity, and mechanical properties of membranes

Increasing the membrane hydrophilicity is a good method for the improvement of the antifouling properties of membranes. As the surface hydrophilicity increases, water molecules win the race [23]. The effect of ABS concentration on the hydrophilicity of the PC membrane is shown in Table 1. According to Table 1, the contact angle of a neat PC membrane is 66.5°. By adding ABS to the PC membrane, especially a concentration of 5 wt.%, a relatively considerable increase in the membrane surface hydrophilicity was observed. Hydrophilicity change in PC/ABS blend membrane is explained by the presence of hydrophilic functional groups such as nitrile group (C=N) as shown in Fig. 2. According to literature, nitrile groups are highly polar and hydrophilic groups [33]. However, at the loading of more than 5 wt.% ABS, the water contact angle increased. This may be due to the presence of hydrophobic components such as styrene and butadiene, which at high loading of ABS affected surface hydrophilicity of PC membrane.

Porosity is considered an important characterization of the membrane. The porosity of all the prepared blend membranes is shown in Table 1. For neat PC membrane porosity is found to be 74.2%; with the addition of 2.5 wt.% ABS, the porosity of the membrane is increased to 76.5%, in principle, would lead to an increase in the permeability; further porosity enhances to 81% when there is an increase in the ABS composition to 10 wt.% in the blend solution. During the phase inversion process, the solvent and the non-solvent exchange rate increase due to the increase in hydrophilicity of the PC/ABS blend membrane. This leads to the formation of a membrane with high porosity. On the other hand, as Kamelian et al. [34] reported, acrylonitrile can migrate from the cast film into the water coagulation bath during the preparation of the ABS membrane. Thus, this reason can illustrate increasing in porosity by increasing ABS concentration.

Tensile strength and elongation tests at the point of breakage for hybrid membranes were conducted to determine their mechanical strength. These values are reported in Table 1. As shown in Table 1, Tensile strength and elongation at break of blend membranes decreased with increasing ABS. These decreases can be partly attributed to the increasing in the porosity of the membrane. It is generally accepted that the increase in the porosity of UF membranes will cause the decline of the mechanical strength of membranes [35,36]. As shown in Table 1, by adding ABS, membrane porosity increases and therefore, the tensile strength of the PC/ABS blend membrane decreases. However, it seems that the mechanical properties of PC/ABS-10 are very low with respect to other samples. Mechanical stress studies are of utmost importance for UF membranes, as they are operated under pressure conditions. According to the literature, the addition of ABS to PC polymer resulted in decreasing in tensile strength [37]. We found that at high loading of ABS to PC membrane (higher than 10 wt.%),

Table 1 Water contact angle, porosity, and mechanical properties of prepared blend membranes

Membranes	Water contact angle (°)	Porosity (%)	Tensile strength (MPa)	Elongation at break (%)
Neat PC	66.5	74.2	12.2	11
PC/ABS-2.5	59.3	76.5	11.4	10.4
PC/ABS-5	48.2	79.8	9.6	9.1
PC/ABS-7.5	51	80.2	5.5	2.6
PC/ABS-10	53.2	81	3.2	1.9

tensile strength significantly decreased and these membranes cannot use in the UF process (data not shown).

3.3. Pure water flux

The PWF of neat PC and PC/ABS blend membranes under vacuum pressure of 0.8 bar is represented in Fig. 3. According to Fig. 3, all blend membranes showed higher PWF as compared to neat PC membrane. It can be seen that the PWF increased from 122 L m⁻² h⁻¹ for neat PC membrane to about 260 L m⁻² h⁻¹ for PC/ABS-5 blend membrane. An increment in PWF is indeed due to the higher surface hydrophilicity of the membranes. However, as the amount of the ABS content reaches above 5 wt.%, the PWF reduces due to decreasing in hydrophilicity as shown in Table 1.

As the PC/ABS-5 sample shows higher hydrophilicity, PWF and suitable mechanical properties with respect to other UF blend membranes, so this membrane was selected as the optimal sample.

3.4. DSC analysis

The glass transition temperatures (T_g) for the neat PC and PC/ABS-5 blend membranes were measured by DSC analysis and the results are shown in Fig. 4. According to the DSC curves of membranes, a change of the T_g can be seen. The T_g value for neat PC membrane was 154.8°C. While for the blend membrane, it was perceived that by the addition of 5 wt.% ABS, the T_g of the blend membrane decreased from 154.8°C to 148.5°C. According to the literature, the T_g value for ABS was about 110°C [37]. Therefore, it is acceptable that by the addition of ABS to PC polymer, T_g value decreases. Moreover, a single T_g in the curves indicates that there was no secondary phase transition in the blend membrane [13]. This means that PC and ABS form compatible and miscible membranes without any segregation at a low concentration of ABS.

3.5. Morphological studies of the membranes

Fig. 5 shows the surface FESEM micrographs of the top surfaces of neat PC and PC/ABS-5 blend UF membranes at different magnifications. As shown in Fig. 5, the neat PC and PC/ABS-5 membranes have similar structures with small pore sizes. However, the surface morphology was



Fig. 3. PWF of blend membranes under vacuum pressure of 0.8 bar.

not significantly affected by the addition of ABS in terms of pore sizes and pore size density.

On the contrary, the cross-sectional morphology was greatly influenced by the addition of ABS. Fig. 6 shows the cross-sectional morphology of both membranes with two resolutions. These images show that the neat PC and PC/ABS blend membranes have asymmetric structure. It can be seen that neat PC membrane consists of three layers: top layer with finger-like structure (20 µm), middle layer with small macrovoids and sponge-like structures (70 µm), and bottom layer with sponge-like structure (10 um). As the ABS was added to PC, the finger-like pores become larger and the middle porous structure changes, as shown in Fig. 6b. PC/ABS membrane show two-layer: top layer with small finger-like structure (10 µm), and sublayer or porous layer with larger finger-like or macro finger-like and sponge-like structures (90 µm). By comparing Figs. 6a and b, it is clear that the bottom layer in the neat PC membrane was removed after the addition of ABS.

From Fig. 6, it is obvious that when ABS was added to the PC membrane, macrovoids developed in number and size, promoting the formation of many finger-like pores. The finger-like pores quantized lengthened to the bottom of the membranes and resulted in a more porous membrane. Also, in a sponge-like structure, the spherulites were more prominent in PC/ABS blend membrane than neat PC membrane. This made the structure of the blend membrane more porous than a neat membrane. A similar observation was occurred in the PAN/PVDF blend membranes [17]. The influence of ABS on the PC membrane morphology is described below.

Due to the presence of highly polar and hydrophilic nitrile functional groups on the PC/ABS membrane surface (as shown in Fig. 2), instantaneous demixing takes place which results in the formation of finger-like cavities in the sub-layer [38]. From another point of view, during precipitation in a water coagulation bath, the hydrophilic acrylonitrile chains are segregated spontaneously to the membrane/ water interfaces, creating a hydrophilic surface and developing a macropore finger-like structure in the presence of sponge-like structure with larger spherulites pores [34]. In other words, as reported by Kamelian et al. [34], in the phase inversion process and in the water coagulation bath,



Fig. 4. DSC curves for neat PC and PC/ABS-5 blend membranes.



Fig. 5. Surface FESEM images of the (a) neat PC and (b) PC/ABS-5 membranes.

nitrile groups can migrate from the cast film into the water coagulation resulted in increase in porosity.

Fig. 7 demonstrates the three-dimensional surface AFM images of neat PC and PC/ABS-5 membranes at a scan size of 5 μ m × 5 μ m. This is clear that the surface morphology of the neat PC membrane was influenced by the addition of 5 wt.% ABS in the casting solution. In this case, the surface roughness parameters of the membranes were calculated and presented in Table 2. The roughness parameters of neat PC membrane decreased with an addition of 5 wt.% concentration of ABS in the casting solution. These data indicated that the PC/ABS-5 blend UF membrane had a smoother surface than the neat PC membrane. Therefore, it is expected that the blend membrane displays better antifouling property. According to the literature, the membrane fouling phenomena tended to be more significantly related to roughness owing to contaminants accumulating in the valleys of the rough membrane surfaces [38,39]. This phenomenon could be further explained by Wenzel's model, in which the degree of roughness correlated proportionally to the surface hydrophilicity or hydrophobicity [40]. Hence, the addition of ABS to the PC membrane would definitely enhance the membrane properties by providing a smoother membrane structure.

3.6. Antifouling properties and rejection

The flux-time curves for the neat PC and PC/ABS-5 membranes during filtration of HA solution under vacuum

pressure of 0.2 bar are shown in Fig. 8. It can be seen that the flux of PC/ABS-5 blend membrane was higher than that of neat PC membrane and its value increased from 8.7 L m⁻² h⁻¹ to about 27.5 L m⁻² h⁻¹ at the steady-state of filtration. Fig. 8 indicates that the neat PC membrane undergoes a flux reduction of around 55% (relative to first data of HA filtration), which means the unmodified PES membrane loses 55% of its water permeability only by being used after 135 min of HA filtration. This value significantly decreased when PC/ABS-5 blend UF membrane was used (about 25%). This phenomenon was possibly due to the deposition of HA onto the membrane surface which led to the decrement of flux. However, for blend membrane, this decrement was less than neat PC membrane. It is well known that antifouling properties of the membranes increase with increasing hydrophilicity [13,41], and as shown in Table 1, the contact angle of the neat PC membrane decreased with the addition of ABS in the dope solution due to the presence of nitrile group in the ABS chains.

To provide more information about antifouling properties, the fouling parameters for both membranes are presented in Fig. 9. In this case, reversible fouling ratio (RFR) due to the attached foulant on the membrane surface, irreversible fouling ratio (IFR) due to the adsorption of foulant on the membrane surface/pore, total fouling ratio (TFR), and flux recovery ratio (FRR) were calculated using Eqs. (3)–(6). As shown in Fig. 9, the values of fouling parameters (RFR, IFR, and TFR) for PC/ABS-5 blend membrane was less than



Fig. 6. Cross sectional FESEM images of the (a) neat PC and (b) PC/ABS-5 membranes.



Fig. 7. Tree-dimensional AFM images of surface of (a) neat PC and (b) PC/ABS-5 membranes.

those of neat PC membrane. In the other words, the fouling tendency for blend membrane was lower than that of the neat PC membrane. Since both membranes were tested at the same hydrodynamic conditions, the different fouling behavior can be attributed to the impact of surface properties of the membrane on fouling mitigation. As mentioned previously, the fouling of the blend membrane was enhanced mainly by increasing hydrophilicity and decreasing in roughness. According to Fig. 9, the result clearly showed that IFR was considerably reduced when PC/ABS-5 blend

Table 2 Roughness parameters of neat PC and PC/ABS-5 blend membranes

Membrane	R_a (nm)	R_q (nm)	R_{z} (nm)
Neat PC	25.8	31.6	130.1
PC/ABS-5	6.6	8	33.5



Fig. 8. Flux-time curve for HA filtration under vacuum pressure of 0.2 bar for neat and blend membranes.

membrane was used. The IFR value for neat PC membrane was 14.8%, while this value was 1.8% for blend membrane. Because of the more hydrophilic surface of the blend membrane, a relatively low amount of HA molecule adsorbed irreversibly on the surface and cake layer formed during HA solution permeation.

The FRR of the PC/ABS-5 membrane was increased to 98.4%, which represented an improvement compared to the 85.2% recovery ratio obtained using the neat PC membrane. As the higher FRR shows the better antifouling property for the membrane, the results showed the best antifouling property was achieved for the blend membrane. The improvement in hydrophilicity and antifouling property of blend membrane is due to the presence of nitrile group in the blend membrane surface that prevents HA molecule adsorption on the surface of the membrane.

The effluent quality of both membranes in terms of HA rejection is shown in Fig. 9. As can be seen, HA rejection for both membranes is more than 80%. The rejection enhances to almost 98.6% for PC/ABS-5 blend membrane. The addition of ABS with nitrile group caused to decrease in the interaction between HA molecule and membrane surface and improve HA rejection. According to the literature, improvement in hydrophilicity of the membranes resulted in lower affinity and interaction between hydrophobic foulants such as HA and membrane surface and higher rejection was achieved [8,9,42,43].

It should be noted that the PC/ABS-5 blend membrane, provides a high potential for HA removal from surface water, and it means that this blend membrane has a similar performance with nanofiltration processes for HA removal.



Fig. 9. Fouling parameters and rejection for neat and blend membranes.

4. Conclusions

In this study, PC/ABS blend UF membranes were prepared via the NIPS method in order to water treatment for the first time. The FTIR results of the PC/ABS blend membrane confirmed the existence of a hydrophilic nitrile group on the membrane surface. It was observed that the addition of ABS up to 5 wt.% to PC resulted in a reduction in the membrane's contact angle. Also, membrane performance analysis proved that the PWF attained their ultimate values at the optimum concentration of 5 wt.% of ABS. However, by addition of ABS, the tensile strength of the PC/ABS blend membrane was decreased. Therefore, the optimum PC/ABS blend ratio (PC/ABS-5) was selected by discussing the hydrophilicity, PWF, and tensile strength.

FESEM images showed that the cross-sectional morphology was greatly influenced by the addition of ABS. As the ABS was added to PC, the finger-like pores become larger and the middle porous structure changes. AFM analysis revealed that the blend membrane shows a smoother surface as compared to the neat PC membrane. The obtained results from the antifouling performance of membranes in HA filtration showed that the addition of ABS to PC membrane significantly improved antifouling properties of blend membrane, and in this case, IFR considerably decreased. Meanwhile, PC/ABS-5 blend membrane revealed a higher value in FRR and HA removal (more than 98.5%) with respect to neat PC membrane, which had a similar performance with nanofiltration processes.

References

- H. Etemadi, R. Yegani, M. Seyfollahi, V. Babaeipour, Preparation and performance evaluation of cellulose acetate/ nanodiamond nanocomposite membrane in the treatment of pharmaceutical wastewater by membrane bioreactor, Desal. Water Treat., 76 (2017) 98–111.
- [2] H. Huang, N. Lee, T. Young, A. Gary, J.C. Lozier, J.G. Jacangelo, Natural organic matter fouling of low-pressure, hollowfiber membranes: effects of NOM source and hydrodynamic conditions, Water Res., 41 (2007) 3823–3832.
- [3] R. Kumar, A.M. Isloor, A.F. Ismail, S.A. Rashid, T. Matsuura, Polysulfone–chitosan blend ultrafiltration membranes: preparation, characterization, permeation and antifouling properties, RSC Adv., 3 (2013) 7855–7861.
- [4] W.R. Bowen, T.A. Doneva, H.-B. Yin, Separation of humic acid from a model surface water with PSU/SPEEK blend UF/NF membranes, J. Membr. Sci., 206 (2002) 417–429.

- [5] A.R. Costa, M.N. de Pinho, Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions, J. Membr. Sci., 255 (2005) 49–56.
- [6] C. Qiu, F. Xu, Q.T. Nguyen, Z. Ping, Nanofiltration membrane prepared from cardo polyetherketone ultrafiltration membrane by UV-induced grafting method, J. Membr. Sci., 255 (2005) 107–115.
- [7] H.-Y. Yu, M.-X. Hu, Z.-K. Xu, J.-L. Wang, S.-Y. Wang, Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH₃ plasma treatment, Sep. Purif. Technol., 45 (2005) 8–15.
- [8] H. Etemadi, R. Yegani, V. Babaeipour, Performance evaluation and antifouling analyses of cellulose acetate/nanodiamond nanocomposite membranes in water treatment, J. Appl. Polym. Sci., 134 (2017) 44873, https://doi.org/10.1002/app.44873.
- [9] K. Ekambaram, M. Doraisamy, Surface modification of PVDF nanofiltration membrane using carboxymethylchitosan-zinc oxide bionanocomposite for the removal of inorganic salts and humic acid, Colloids Surf., A, 525 (2017) 49–63.
- [10] M. Kumar, Z. Gholamvand, A. Morrissey, K. Nolan, M. Ulbricht, J. Lawler, Preparation and characterization of low fouling novel hybrid ultrafiltration membranes based on the blends of GO–TiO₂ nanocomposite and polysulfone for humic acid removal, J. Membr. Sci., 506 (2016) 38–49.
- [11] M.H. Razzaghi, A. Safekordi, M. Tavakolmoghadam, F. Rekabdar, M. Hemmati, Morphological and separation performance study of PVDF/CA blend membranes, J. Membr. Sci, 470 (2014) 547–557.
- [12] L.-L. Hwang, H.-H. Tseng, J.-C. Chen, Fabrication of polyphenylsulfone/polyetherimide blend membranes for ultrafiltration applications: the effects of blending ratio on membrane properties and humic acid removal performance, J. Membr. Sci, 384 (2011) 72–81.
- [13] A. Behboudi, Y. Jafarzadeh, R. Yegani, Polyvinyl chloride/ polycarbonate blend ultrafiltration membranes for water treatment, J. Membr. Sci., 534 (2017) 18–24.
- [14] G. Arthanareeswaran, D. Mohan, M. Raajenthiren, Preparation and performance of polysulfone-sulfonated poly (ether ether ketone) blend ultrafiltration membranes. Part I, Appl. Surf. Sci., 253 (2007) 8705–8712.
- [15] L. Krishnamoorthy, P.M. Arif, R. Ahmedkhan, Separation of proteins from aqueous solution using cellulose acetate/ poly(vinyl chloride) blend ultrafiltration membrane, J. Mater. Sci., 46 (2011) 2914–2921.
- [16] R. Mahendran, R. Malaisamy, G. Arthanareeswaran, D. Mohan, Cellulose acetate–poly(ether sulfone) blend ultrafiltration membranes. II. Application studies, J. Appl. Polym. Sci., 92 (2004) 3659–3665.
- [17] M.-C. Yang, T.-Y. Liu, The permeation performance of polyacrylonitrile/polyvinylidine fluoride blend membranes, J. Membr. Sci., 226 (2003) 119–130.
- [18] J.-A. Park, S.-B. Kim, Anti-biofouling enhancement of a polycarbonate membrane with functionalized poly (vinyl alcohol) electrospun nanofibers: permeation flux, biofilm formation, contact, and regeneration tests, J. Membr. Sci., 540 (2017) 192–199.
- [19] M. Delavar, G. Bakeri, M. Hosseini, Fabrication of polycarbonate mixed matrix membranes containing hydrous manganese oxide and alumina nanoparticles for heavy metal decontamination: characterization and comparative study, Chem. Eng. Res. Des., 120 (2017) 240–253.
- [20] A. Idris, Z. Man, A.S. Maulud, Polycarbonate/silica nanocomposite membranes: fabrication, characterization, and performance evaluation, J. Appl. Polym. Sci., 134 (2017) 45310.
 [21] S. Nazemidashtarjandi, S.A. Mousavi, D. Bastani, Preparation
- [21] S. Nazemidashtarjandi, S.A. Mousavi, D. Bastani, Preparation and characterization of polycarbonate/thermoplastic polyurethane blend membranes for wastewater filtration, J. Water Process Eng., 16 (2017) 170–182.
- [22] M. Mandegari, H. Fashandi, Untapped potentials of acrylonitrile-butadiene-styrene/polyurethane (ABS/PU) blend membrane to purify dye wastewater, J. Environ. Manage., 197 (2017) 464–475.
- [23] F.S. Kamelian, S.M. Mousavi, A. Ahmadpour, Al₂O₃ and TiO₂ entrapped ABS membranes: preparation, characterization and study of irradiation effect, Appl. Surf. Sci., 357 (2015) 1481–1489.

- [24] J.K. Fink, Handbook of Engineering and Speciality Thermoplastics. 3. Polyethers and Polyesters, Scrivener Publ., Austin, Texas, 2011.
- [25] M. Bodzek, J. Bohdziewicz, Porous polycarbonate phaseinversion membranes, J. Membr. Sci., 60 (1991) 25–40.
- [26] S. Zhao, P. Wang, C. Wang, X. Sun, L. Zhang, Thermostable PPESK/TiO₂ nanocomposite ultrafiltration membrane for high temperature condensed water treatment, Desalination, 299 (2012) 35–43.
- [27] A. Behboudi, Y. Jafarzadeh, R. Yegani, Incorporation of silica grafted silver nanoparticles into polyvinyl chloride/ polycarbonate hollow fiber membranes for pharmaceutical wastewater treatment, Chem. Eng. Res. Des., 135 (2018) 153–165.
- [28] G.-P. Lin, L. Lin, X.-L. Wang, L. Chen, Y.-Z. Wang, PBT/PC blends compatibilized and toughened via copolymers in situ formed by MgO-catalyzed transesterification, Ind. Eng. Chem. Res., 54 (2015) 1282–1291.
- [29] C. Larosa, N. Patra, M. Salerno, L. Mikac, R.M. Meri, M. Ivanda, Preparation and characterization of polycarbonate/multiwalled carbon nanotube nanocomposites, Beilstein J. Nanotechnol., 8 (2017) 2026–2031.
- [30] J. Li, F. Chen, L. Yang, L. Jiang, Y. Dan, FTIR analysis on aging characteristics of ABS/PC blend under UV-irradiation in air, Spectrochim. Acta, Part A, 184 (2017) 361–367.
- [31] N.T.T. Truc, B.-K. Lee, Selective separation of ABS/PC containing BFRs from ABSs mixture of WEEE by developing hydrophilicity with ZnO coating under microwave treatment, J. Hazard. Mater., 329 (2017) 84–91.
- [32] A.E. Amooghin, H. Sanaeepur, A. Moghadassi, A. Kargari, D. Ghanbari, Z.S. Mehrabadi, Modification of ABS membrane by PEG for capturing carbon dioxide from CO₂/N₂ streams, Sep. Purif. Technol., 45 (2010) 1385–1394.
- [33] M. Guo, B. Liu, S. Guan, L. Li, C. Liu, Y. Zhang, Z. Jiang, Novel sulfonated poly(ether ether ketone)s containing nitrile groups and their composite membranes for fuel cells, J. Power Sources, 195 (2010) 4613–4621.
- [34] F.S. Kamelian, S.M. Mousavi, A. Ahmadpour, V. Ghaffarian, Preparation of acrylonitrile-butadiene-styrene membrane: investigation of solvent/nonsolvent type and additive concentration, Korean J. Chem. Eng., 31 (2014) 1399–1404.
- [35] F. Zhang, W. Zhang, Y. Yu, B. Deng, J. Li, J. Jin, Sol-gel preparation of PAA-g-PVDF/TiO, nanocomposite hollow fiber membranes with extremely high water flux and improved antifouling property, J. Membr. Sci., 432 (2013) 25–32.
- [36] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, J. Niu, B. Zhou, X. Qian, Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes, J. Membr. Sci., 458 (2014) 1–13.
- [37] R. Greco, L. Dong, PC/ABS blends: compatibilization and mechanical behaviour, Macromol. Sym., 78 (1994) 141–153.
- [38] J. Hong, Y. He, Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning, Desalination, 332 (2014) 67–75.
- [39] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nano-sized Al₂O₃-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci., 276 (2006) 162–167.
- [40] A. Ahmad, A. Abdulkarim, S. Ismail, B. Ooi, Preparation and characterisation of PES-ZnO mixed matrix membranes for humic acid removal, Desal. Water Treat., 54 (2015) 3257–3268.
- [41] Y.T. Chung, E. Mahmoudi, A.W. Mohammad, A. Benamor, D. Johnson, N. Hilal, Development of polysulfone-nanohybrid membranes using ZnO-GO composite for enhanced antifouling and antibacterial control, Desalination, 402 (2017) 123–132.
- [42] H. Rabiee, M.H.D.A. Farahani, V. Vatanpour, Preparation and characterization of emulsion poly(vinyl chloride) (EPVC)/ TiO, nanocomposite ultrafiltration membrane, J. Membr. Sci., 472 (2014) 185–193.
- [43] H. Etemadi, R. Yegani, M. Seyfollahi, M. Rabiee, Synthesis, characterization, and anti-fouling properties of cellulose acetate/ polyethylene glycol-grafted nanodiamond nanocomposite membranes for humic acid removal from contaminated water, Iran. Polym. J., 27 (2018) 381–393.