ORIGINAL RESEARCH PAPER

Application of wet chemical surface functionalization method in preparation of anti-fouling polysulfone microporous membrane for water treatment

Milad Fonouni[1,2], Habib Etemadi[3]*, Reza Yegani[1,2]*, Masoumeh Safary Dehnavi[1,2], Naeime Jodeiry[1]

[1] *Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran*
[2] *Membrane Technology Research Center, Sahand University of Technology, Tabriz, Iran*
[3] *Department of Polymer Science and Engineering, University of Bonab, Bonab, Iran*

ABSTRACT

In this work, $KClO_3$, $K_2Cr_2O_7$, and $KMnO_4$, dissolved in sulfuric acid, were used to functionalize microporous Polysulfone (PSf) membranes; fabricated by phase inversion method. The optimum concentrations of oxidizing agent and sulfuric acid and membrane immersion times were determined. FTIR results revealed that the absorbance intensities of -OH and C=O peaks as well as the variety of functional groups in the samples treated by $KClO_3$ are remarkably higher than in the samples treated by $K_2Cr_2O_7$ and $KMnO_4$, respectively. Bovine serum albumin (BSA) filtration experiments revealed that the total fouling ratio (TFR) and irreversible fouling ratio (IFR) decreased from 73.4% for pristine PSf membrane to 52.9%, 49.4% and 60.4% for treated membranes by Set A ($K_2Cr_2O_7$), Set B ($KClO_3$) and Set C ($KMnO_4$), respectively. Moreover, IFR of membranes decreased from 45.4% for pristine PSf membrane to 29.9%, 22.4% and 36.1% for treated membranes by Set A, Set B, and Set C, respectively.

Keywords: *Microporous Polysulfone Membrane; Wet Chemical Oxidation; Functionalization; Anti-Fouling, Water Treatment*

INTRODUCTION

Microfiltration (MF) and Ultrafiltration (UF) are low-pressure membrane filtration processes that are used for protein, pathogen and suspended solids removal, wastewater treatment and water purification [1-4]. Poly (arylsulfone) such as polysulfone (PSf) and polyethersulfone (PES) polymers are considered as the most famous initial materials to prepare suitable membranes for MF and UF filtration processes [5]. They are well known for their resistance in extreme pH conditions and high thermal stability and have been widely used for separation and purification purposes [1, 6, 7]. The chain rigidity in poly(arylsulfone) is derived from the relatively inflexible and immobile phenyl and SO_2 groups, whereas their toughness is derived

from the connecting ether oxygen [8].

Although these materials have excellent overall properties, their intrinsic hydrophobic nature precludes their use in membrane applications, which require a hydrophilic character (i.e., protein purification recovery and membrane bioreactors). Therefore, such polymers should be modified to improve their performance for specific applications in wastewater treatment and grant anti-fouling and organic material repellency [8]. However, in protein purification recovery and membrane bioreactors, protein adsorption takes place on the membrane surface and in the membrane pores due to the inherent hydrophobic characteristics of poly(arylsulfone).

Several surface modification techniques on fouling mitigation of poly (arylsulfone)

* Corresponding Author Email: *h_etemadi@ubonab.ac.ir,*
ryegani@sut.ac.ir

membranes have been developed and divided into six main groups. These main groups consist of coating [9], blending [10], grafting[11], composite[9, 12], chemical [13, 14] and plasma [15, 16] methods. Surface modification of membranes is thought to be equally important to the membrane industry as membrane material and process development; surface functionalization has already become a key technology, the major aims being performance improvement (flux and selectivity) by reduction of protein fouling which is often considered as the first step for biofouling in membrane bioreactors [17].

Previous studies regarding the application of PSf revealed that modification of PSf based UF membrane via controlling the casting solution or coagulation bath will bring positive results to morphology and membrane properties [18-22]. Moreover, each technique gives different membrane characteristics, e.g. average pore size, uniformity of the pore size; porosity, mechanical properties, and even selectivity towards permeate species. It is generally accepted that an increase in membrane hydrophilicity offers better fouling resistance because protein and many other foulants are hydrophobic in nature [23].

Among the various surface modification techniques, the wet method involves either deposition of a suitable on the membrane surface through physical adsorption of charged amphiphilic molecules, copolymer layer, layer-by-layer (LBL) self-assembly or through chemical modification using self-assembled monolayers (SAM), UV grafting or direct treatment with reactive chemicals like piranha solution [24]. In wet chemical oxidation methods, conventional acids such as nitric acid, sulfuric acid, and phosphoric acid, alone or in combination with oxidizing agents such as hydrogen peroxide, sodium hypochlorite, permanganate, chromate or dichromate of potassium and transition metal nitrates are used [25].

Akon Higuchi et al. [26] tried to chemically modify the PSf hollow fibers using vinyl pyrrolidone to achieve blood compatible membrane. They found that in comparison with plasma treatment and surface-modification methods, PVP-PSf membranes exhibit lower protein adsorption. Dirk Möckel et al.[27] studied the effectiveness of the chemical modification method on the static protein adsorption of PSf membranes during protein filtration. They concluded that static adsorption and protein binding strength were lower at pH=3 than the pH =9 and reached to a maximum value at the isoelectric point of protein at pH=4.8. The hydrophilic PSf membranes

showed less static adsorption and lower UF flux reduction than neat membranes. Xinyu Wei et al. [28] utilized citric acid (CI) and sodium bisulfite (SB) as simple pre-adsorption agents methods to modify PSf membrane. They found that hydrogen bonding and van der Waals attraction could be responsible for the adsorptions of CI and SB onto membranes, respectively. After modification with CI or SB, the membrane surfaces became more hydrophilic. Membrane permeability improved when modified by SB while decreased a little when modified by CI. The modified membranes exhibited an increase in PEG and BSA rejections and better antifouling properties with higher flux recovery ratios during filtration of a complex pharmaceutical wastewater.

In the most wet chemical treatment methods, researchers mainly focused on the polymer surface without paying attention to the microporous structure and the least required mechanical strength of the membrane. For the membrane related researches, it is very important to functionalize the surface without inflicting any serious damage to the membrane mechanical stability. Due to the microporous structure of PSf membrane fabricated via phase inversion method, it is expected that the oxidizing solution could penetrate into microporous structure during wet chemical functionalization method. Therefore, in addition to the surface of the membrane, the inner parts and bulk of the membrane will also be affected.

In our previous works, we present the most suitable oxidizing solution to functionalize the polyolefin-based polymer membrane including high-density polyethylene (HDPE) and polypropylene (PP), however, the effectiveness and degree of functionalization of each oxidizing agent were different for different membrane prepared from different materials [29, 30]. Functionalization for fouling reduction is practiced in several publications. In those publications, the authors only focused on the one oxidizing agent or one immersion time for functionalization. In this study, in order to improve the membrane performance and protein repellency of PSf membrane, various oxidizing agents including potassium chlorate ($KClO_3$), potassium dichromate ($K_2Cr_2O_7$), and potassium permanganate ($KMnO_4$) in sulfuric acid solution were used to chemically modify the PSf membrane. In order to clarify the fouling mitigation of oxidized membranes, BSA protein filtration experiments were carried out and obtained results were analyzed via dynamic filtration of BSA protein solution in a dead-end filtration setup.

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

309

EXPERIMENTAL

Materials

Commercial grade PSf Udel P3500 (Mw=77 kDa, T_g=195°C), was purchased from Solvay, used as membrane materials. Reagent grade n-methyl-2-pyrrolidone (NMP) purchased from Dae-Jung were used as solvents. Analytical grades of potassium chlorate ($KClO_3$), potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Merck, used as oxidizing agents. Reagent grade of sulfuric acid was purchased from Merck, used as a solvent for oxidizing agents. Polyethylene glycol (PEG 200) purchased from Merck, was used as the nonsolvent pore-forming additive in the casting solution. Bovine serum albumin $(BSA, M_n = 67 \, kDa)$, purchased from Sigma-Aldrich, was used as organic model foulant to evaluate the membrane performance. The buffer solution was prepared using analytical grade HPLC grade water (less than 18 MΩ) and pH was adjusted at 4.8 to keep BSA protein in isoelectric conditions. All chemicals were used as received without any further purification unless otherwise described.

Fabrication of flat sheet microporous PSf membrane

Flat sheet PSf membranes were fabricated by phase inversion method according to the optimum amounts of polymer, additive, and solvent described in our previous work [31]. Measured amounts of PSf and PEG 200 were dissolved in NMP solvent. The prepared dope solution was kept in 60°C without further stirring for 24h to release bubbles. After that, dope solution was cast using a doctor blade with 250mm thickness onto electrostatic glass plate and subsequently immersed into a coagulation bath containing deionized (DI) water to induce phase separation. Fabricated membranes were dried in vacuum oven at room temperature for 24h. Differential scanning calorimetry (DSC-Shimadzu 60) analysis confirmed that no NMP remained in the fabricated membrane (data not shown).

Membrane surface modification and characterization

Oxidizing solutions were prepared by dissolving of measured amounts of oxidizing agents in measured values of sulfuric acid at ambient conditions. Membrane surface modification was carried out by immersing the PSf membranes in the oxidizing solutions. In this regard, PSf membranes were soaked in oxidizing solutions for specific time intervals and subsequently were immersed in DI water to stop the oxidation reaction. Treated

membranes were dried in vacuum oven at room temperature for 24 h.

Membrane characterization
Static contact angle measurement

The surface hydrophilicity of the treated membrane was examined by measuring the static contact angler between membrane surface and water droplet using a contact angle goniometer (PGX, Thwing-Albert Instrument Co.). In order to minimize the inaccuracy of measurement, at least 5 contact angles on different locations of samples were averaged to get a reliable result.

Tensile strength

The tensile strength of the fabricated membranes was determined by using a tensile testing machine (STM-5, Santam, Iran) at an extension rate of 50 mm/min. The samples were cut into 5.0 cm × 0.5 cm in length and width, respectively. The thickness of each sample was measured by a micrometer. Four trials were conducted for each sample and mean values were reported.

Attenuated total reflectance Spectra-Fourier-transform infrared spectroscopy (ATIR/FTIR) analysis

In order to investigate the chemical structure and the type of functional groups created on the membrane surface, ATR-FTIR analyses were carried out by infrared spectroscopy apparatus (BRUKER-TENSOR 27).

Scanning electron microscopy (SEM)

The microscopic morphology of the fabricated membranes was characterized by Scanning Electron Microscope (SEM) (MV2300CAM SCAN) with an accelerating voltage of 15kV. Cross-section samples were prepared by fracturing the membranes in the liquid nitrogen. The fractured samples were then gold-sputtered prior to the scanning. To determine the mean size and pore size distribution membranes, the SEM images of membrane surface were analyzed using Digimizer image analysis software.

Pure water flux (PWF) analysis

Pure water flux of membranes was determined using an in-house fabricated dead-end filtration system having 7 cm^2 of membrane area. To minimize compaction effects, the pre-wetted membranes were compacted for 30 min at 2.0 bar. Then the pressure was reduced to 1.4-1.5 bar and after reaching steady state, water flux was calculated

310

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

through the following equation [30]:

$$J = \frac{M}{(A\,t)} \qquad (1)$$

where J is pure water flux, M is collected a mass of water (kg), A is membrane area (m²) and t is the time (h).

Filtration experiments and fouling analyses

In order to evaluate the fouling behavior of the treated membrane, BSA protein solution was filtered using a dead-end filtration set up with an effective membrane area of 7 cm². Filtration analyses were conducted using neat and modified PSf membrane and obtained results were used to compare the efficiency of neat and treated membranes using a similar approach reported by Jafarzadeh et al. [32, 33] and Yang et al.[34]. The amount of total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) was calculated using the following equations:

$$TFR = (\frac{J_0 - J_1}{J_0}) \times 100 \qquad (2)$$

$$RFR = (\frac{J_2 - J_1}{J_0}) \times 100 \qquad (3)$$

$$IFR = (\frac{J_0 - J_2}{J_0}) \times 100 \qquad (4)$$

$$FR = (\frac{J_2}{J_0}) \times 100 \qquad (5)$$

where J_0, J_1, J_2 are pure water flux through a clean membrane, pure water flux of the fouled membrane and pure water flux of the membrane after cleaning and removing the cake layer with sponge over the membrane surface. In all experiments, the filtration analyses were conducted under the constant trans-membrane pressure (1.4 bar), constant room temperature (20°C) and constant stirring speed (400 rpm) of the reservoir.

RESULTS AND DISCUSSION
Selecting the appropriate conditions for surface treatment of the PSf membranes

The optimized concentration of sulfuric acid, the type as well as the concentration of proper oxidizing agent and immersion time are key parameters for better control of the rate of oxidation reaction and the effectiveness of surface modification. The

higher acid concentration, the stronger oxidizing agent and the longer immersion time correspond with the higher potential for membrane to be destroyed. Lower acid concentration and weak oxidizing agents will result in insufficient degree of functionalization. In order to obtain satisfactory level of functionalization, longer treatment would be required. In this regard, a set of experiments was carried out to determine the appropriate concentrations of sulfuric acid and oxidizing agents and immersion time. Among several oxidizing agents, $KClO_3$, $KMnO_4$, and $K_2Cr_2O_7$ were selected as the most conventional oxidizing agents [35]. Experiments were carried out in three different sets; Set A, B, and C correspond with $K_2Cr_2O_7$, $KClO_3$, and $KMnO_4$ oxidizing solutions, respectively. Three different concentrations of sulfuric acid consisting 60 wt.%, 50 wt.% and 40 wt.% nominated as "strong", "moderate" and "weak" acidic solutions, respectively, were prepared, while the concentrations of oxidizing agents were kept constant. PSf membrane samples were immersed in prepared solutions for different time intervals, e.g. 30, 60 and 90 min, and subsequently were soaked into the DI water for 30 min to stop the oxidation reaction. The comparison between effectiveness of various oxidizing agents was performed at constant weight percent of each oxidizing agent in various acidic solutions. The comparison between effectiveness of various oxidizing agents was performed at constant weight percent of each oxidizing agent in various acidic solutions. The oxidizing solutions circumstances were labeled as (a:b:c) where a, b and c represent the weight percent of the oxidizing agent, the weight percent of acid solution and immersion time (min), respectively. In all sets of experiments, measured amount of oxidizing agent was dissolved in "strong", "moderate" and "weak" concentrations of sulfuric acid. According to the literature, the weight percent of oxidizing agents in all solutions was kept constant at 1 wt.% [36]. The results of contact angle and mechanical strength measurements for Set A are shown in Fig. 1a and 1b, respectively. As can be seen in Fig. 1a as acid concentrations increased, contact angle decreased for all samples. It can be observed that the rate of decrease in contact angle is more pronounced when the "strong" sulfuric acid is used. However, Fig. 1b shows that the mechanical strength of treated membranes with "strong" sulfuric acid is severely decreased to the lower than the threshold value of mechanical tensile, which is
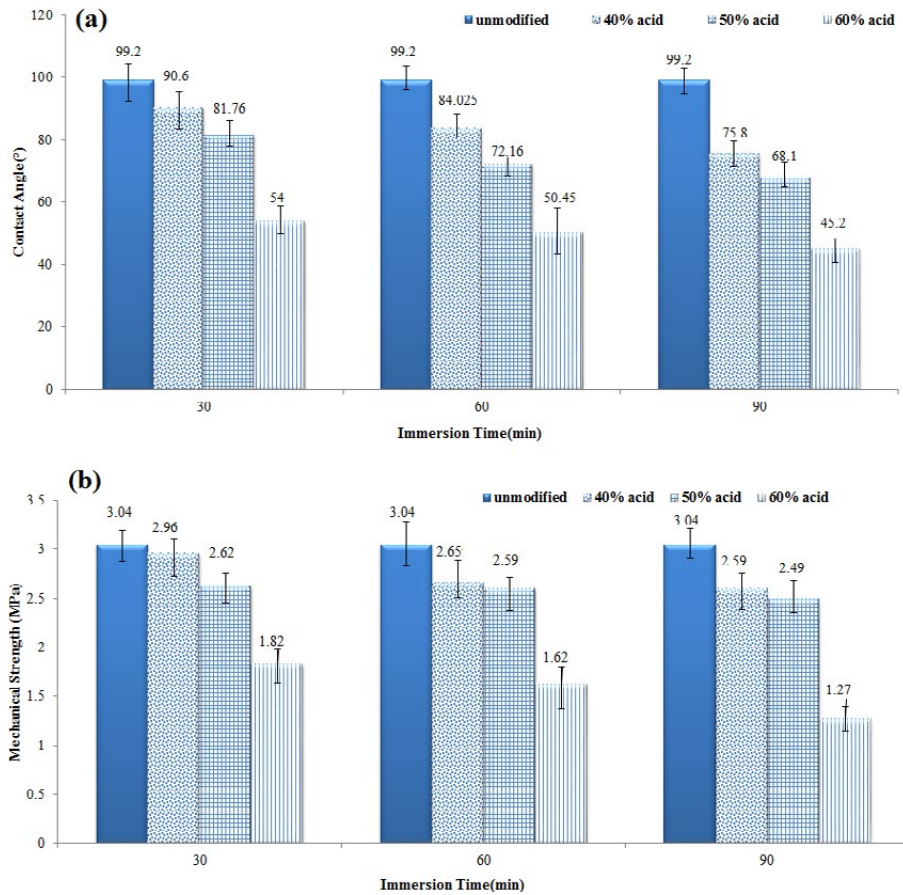
Fig. 1. The effect of the sulfuric acid concentrations containing 1 wt.% of $K_2Cr_2O_7$ in various immersion time on the (a) static contact angle and (b) mechanical strength of PSf microporous membrane (Set A of treatment oxidizing solution).
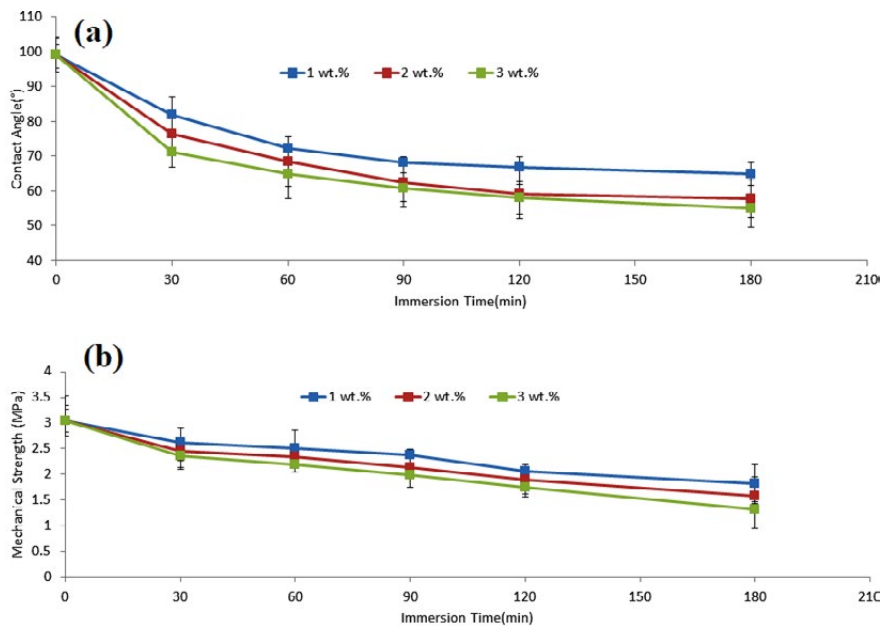

Fig. 2. The effect of $K_2Cr_2O_7$ oxidizing agent concentrations in 50 wt.% sulfuric acid in various immersion time on the (a) static contact angle and (b) mechanical strength of PSf microporous membrane (Set A of treatment oxidizing solution).

312

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

essentially required for MF and UF operations [31]. On the other hand, for the membranes treated with "weak" sulfuric acid, the decrease in contact angle is obviously slower. Therefore, the sulfuric acid with "moderate" concentration (50wt.%) was selected as an appropriate acid concentration for the rest of the experiments. In order to select the appropriate concentration of oxidizing agents, three different concentrations of $K_2Cr_2O_7$ e.g. 1, 2 and 3 wt.% in "moderate" sulfuric acid were prepared.

Obtained results for contact angle and mechanical strength for the acid concentration of 50% are shown in Fig. 2a and Fig. 2b, respectively. Fig. 2a shows that the rate of decrease in contact angle is remarkably high in the initial immersion time intervals (< 60 min). Fig. 2b depicts that with increasing the concentration of oxidizing agent (> 1wt.%), mechanical strength again decreases to the lower values than the threshold mechanical tensile. It is mainly due to the breakage of interconnected microporous structure of membrane network. In other words, due to the increase in pore size of membranes with increasing in immersion time, mechanical strength decreased. Similar experiments were carried out for Set B and Set C.

Obtained results are summarized in Tables 1 and 2. The selection strategy to determine the optimized compositions of oxidizing solutions was based on the fact that treated membranes should

expose a reasonable degree of hydrophilicity, contact angle (as lower as possible) and mechanical strength. Therefore, the optimum values for Set A, B, and C were selected as (2:50:60), (2:50:60) and (1:50:120), respectively, hereafter will be mentioned as the optimized oxidation circumstances.

According to the results shown in Table 1, it is necessary to explain that the variation of membrane roughness (data not are shown) versus immersion time in moderate acidic condition (Set B(1:50:t)), was negligible, therefore, contact angel was mainly affected by the only density of functional groups, created on the membrane surface. In weak acidic conditions, however, variation of surface roughness was significant, in which when immersion time was increased from 30 min to 60 min, surface roughness was decreased and resulted in slightly higher CA value [28, 29]. Longer immersion time in all acidic circumstances resulted in lower mechanical strength, therefore was laid aside from our discussion. This phenomenon is mainly due to the strong corrosive property of $KClO_3$, in which longer immersion time caused that treated membranes to be easily torn.

Cross-section and surface morphology

SEM analysis is an important technique to study the membrane morphology and qualitative information regarding cross-sectional and upper

Table 1. Obtained results for the effect of the sulfuric acid concentrations containing 1 wt.% of $KClO_3$ (Set B) and $KMnO_4$ (Set C) in various immersion time on the static contact angle (CA) and mechanical strength (M.S) of treated PSf microporous membrane.

Experiment Set	Immersion time			
Characterization	Set B	30 min	60 min	90 min
CA	(1:60:t)	*	*	*
M.S		*	*	*
CA	(1:50:t)	67.64	66.66	68.28
M.S		2.4456	2.4224	1.38
CA	(1:40:t)	74.54	79.95	76.45
M.S		2.5843	2.5642	1.89
Characterization	Set C	30 min	60 min	90 min
CA	(1:60:t)	92	81.8	80.9
M.S		2	1.9	1.83
CA	(1:50:t)	93.3	83.7	81
M.S		3.1	2.8	1.95
CA	(1:40:t)	105	100	97.1
M.S		3.34	3.14	2.98

*The brown precipitate was formed on the membrane surface

Table 2. Obtained results for the effect of KClO$_3$ (Set B) and KMnO$_4$ (Set C) oxidizing agent concentrations in 50wt.% of sulfuric acid in various immersion time on the static contact angle (CA) and mechanical strength (M.S) of treated PSf microporous membrane.

| Experiment Set			Immersion time			
Characterization	Set B	30 min	60 min	90 min	120 min	180 min
CA	(1:50:t)	74.9	73.44	72.37	69.68	68.22
M.S		2.92	2.65	1.92	1.76	1.48
CA	(2:50:t)	72.66	69.2	68.9	64.78	61.68
M.S		2.25	2.46	1.97	1.35	0.81
CA	(3:50:t)	69.64	68.27	65.975	60.97	55.66
M.S		2.16	1.96	1.151	0.91	0.76
characterization	Set C	30 min	60 min	90 min	120 min	180 min
CA	(1:50:t)	88.5	85.9	80.6	78.8	78.2
M.S		3.01	2.78	2.395	2.11	1.59
CA	(2:50:t)	89.17	91.2	79.8	71.9	71.5
M.S		2.53	2.13	1.739	1.45	1.23
CA	(3:50:t)	83.9	71.2	67.9	61.3	57.82
M.S		2.45	1.69	1.117	1.06	0.99
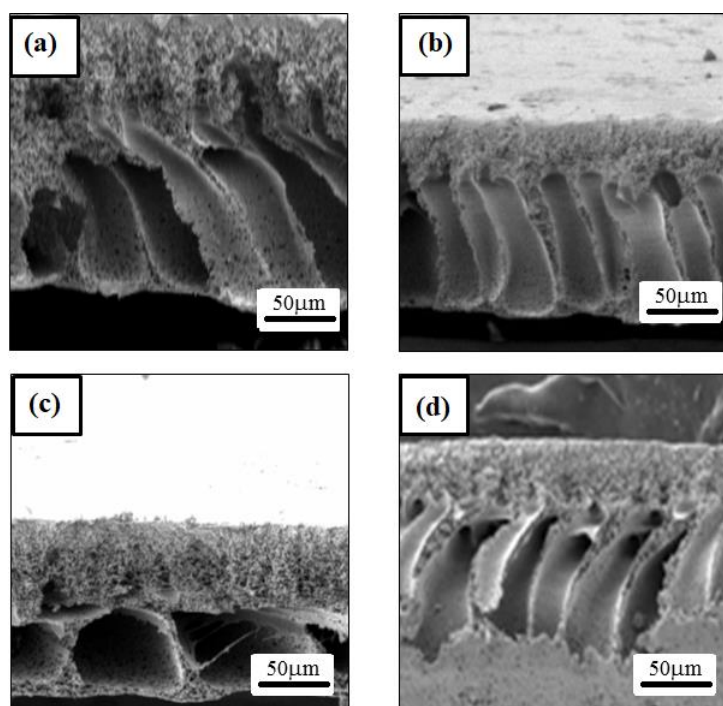
Fig. 3. The cross-sectional SEM micrographs of PSf membranes (a) Pristine PSf membrane, (b) treated by optimized Set A (K$_2$Cr$_2$O$_7$wt.%: H$_2$SO$_4$wt.%: Immersion time (min)) (2:50:60), (c) treated by optimized Set B (KClO$_3$ wt.%: H$_2$SO$_4$wt.%: Immersion time (min)) (2:50:60), (d) treated by optimized Set C (KMnO$_4$ wt.%: H$_2$SO$_4$wt.%: Immersion time (min)) (1:50:120).

surface morphology of the membranes can be obtained. The SEM images of the cross-section of the pristine PSf membranes and modified membrane with different optimized oxidation circumstances were compared in Fig. 3. The membranes had an asymmetric structure consisting of a dense top surface layer (skin layer, airside) and a porous sublayer (support layer, glass side (The skin layer acted as a separation layer and the support layer provided the mechanical strength. The sublayer

314

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

seemed to have sponge-like pores beneath the top surface layer and finger-like cavities near the bottom surface layer. The membrane modified with Set A decreased the thickness of sponge-like pores and increased the length and the number of finger-like pores in the membrane prepared (Fig. 3b). The results were a little different from the membranes prepared with PEG 200 as a pore-forming agent [37].

Fig. 4 showed the upper surface SEM images of pristine PSf membranes and modified membrane with different optimized oxidation circumstances. The surface SEM images reflected the surface pore size of the membranes in a dry state, which could stand for the real pore size, indirectly. It was obvious from Fig. 4 that the number of large pores decreased for membrane treated by Set C (Fig. 4d). The surface morphology might be due to the instantaneous demixing of membrane casting solution and rapid precipitation of polymer matrix. The rapid exchange of solvent and nonsolvent brought about increase of the volume fraction of polymer in the

surface layer and spinodal decomposition occurred consequently. The formation of the top surface was possibly due to spinodal demixing of the casting solution by means of nucleation and growth of the polymer-rich phase i.e. the solid phase and the demixing led to larger pore size [38, 39].

Fig. 5 shows the pore size distribution of unmodified and modified membranes. As shown in Fig. 5, modified membrane in all set, showed larger pore size with respect to pristine PSf membrane. According to this figure, the mean pore size of pristine PSf, functionalization with Set A, B, and C were calculated about 2.3, 3.7, 4.1, and 2.6 µm, respectively. As mentioned above and according to Fig. 5, the number of large pores decreased for membrane treated by Set C.

ATR /FTIR Analysis

The FTIR spectra of the pristine and treated PSf membranes are depicted in Fig. 6. The aromatic vibration ether band of PSf is detected at around $1241 cm^{-1}$. The peak observed at around 1241cm⁻
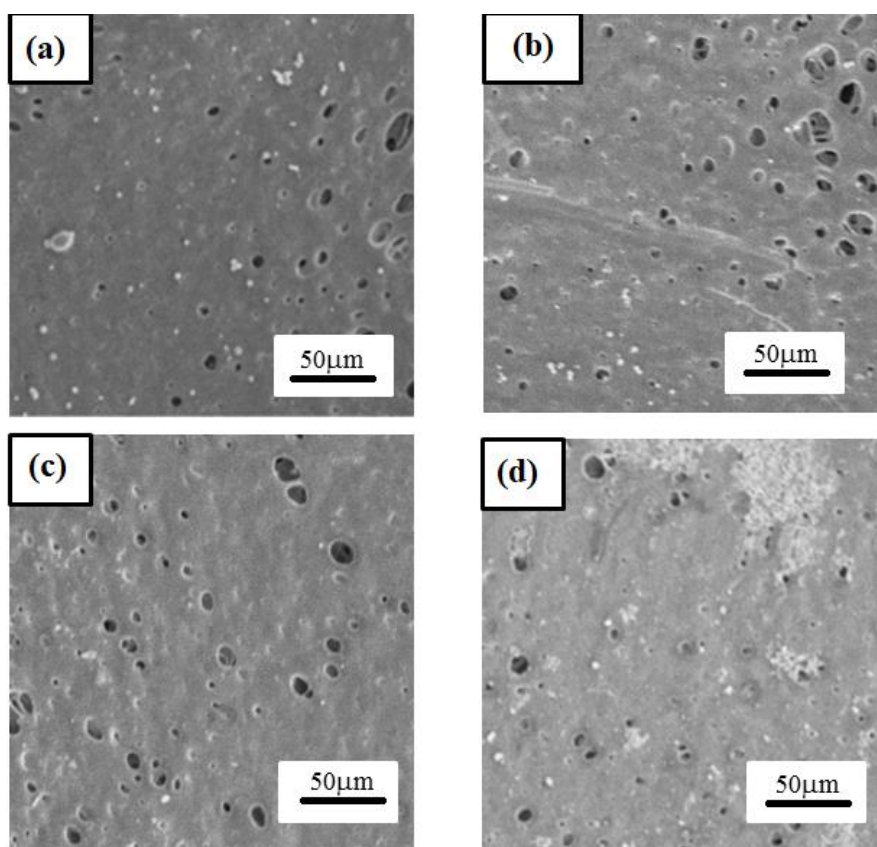

Fig. 4. The surface SEM micrographs of PSf membranes (a) Pristine PSf membrane, (b) treated by optimized Set A ($K_2Cr_2O_7$wt.%: H_2SO_4wt.%: Immersion time (min)) (2:50:60), (c) treated by optimized Set B ($KClO_3$ wt.%: H_2SO_4wt.%: Immersion time (min)) (2:50:60), (d) treated by optimized Set C ($KMnO_4$ wt.%: H_2SO_4wt.%: Immersion time (min)) (1:50:120).

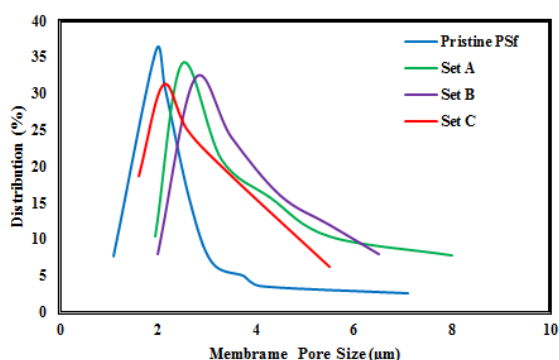*J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019*

315

Fig. 5. Pore size distribution of unmodified and modified membranes.

[1] was ascribed to the stretching vibration of the SO$_2$ group. The absorptions at 1900, 1775, 1605, 1488 and 1169 cm^{-1} are attributed to the aromatic ring of PSf. The vibration at 2968 cm^{-1} is attributed to the two methyl groups of PSf. The presence of OH vibration peak in the range of 3050-3700 cm^{-1} for membrane modified with the Set B (Fig.6c) also indicates that they are able to interact with water and perform as a hydrophilic membrane. The findings are in accordance with those reported elsewhere [40] and it is believed that this characteristic has contributed to an increase of pure water flux of the modified membrane, which will be further discussed in the following section. The peaks in the range of 1610-1820 cm^{-1} correspond to the C=O bond stretching vibration. The obtained results show that the absorbance intensities of -OH and C=O peaks in the samples treated by the Set B are remarkably higher than the samples treated by Set A and Set C, respectively. The peaks in the range of 1166 and 1045 cm^{-1} correspond with C-O bond stretching vibration of carboxylic acid and alcohol functional groups, respectively. Similar to the –OH and C=O functional groups, the absorbance intensities of C-O peaks in the samples treated by the Set B are extremely higher than the samples treated by other oxidizing agents. Finally the peaks in the range of 850-910 cm^{-1} correspond to the S-O bond stretching vibration [41]. These results confirmed the successful attachment of various functional groups to the PSf membrane. They also revealed the strength as well as effectiveness of various oxidizing agents in creation of variety of functional groups, which are essential to expose anti-fouling behavior of PSf membrane in purification of proteins. The following sections, however, investigate the performance of treated membrane.
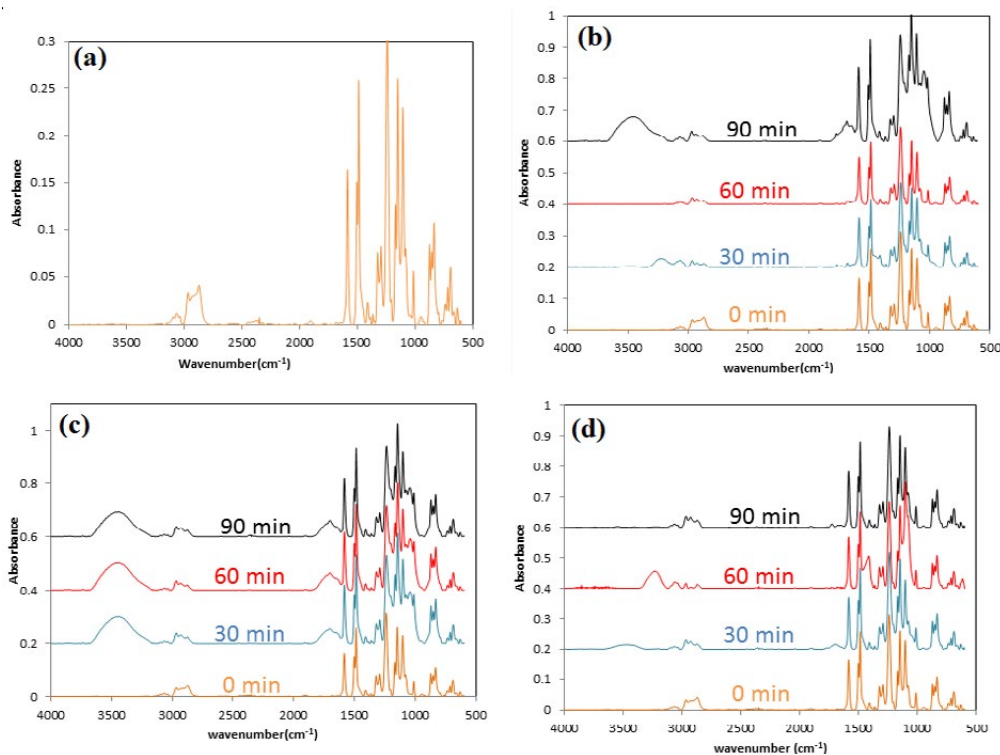

Fig. 6. ATR-FTIR spectra of (a) PSf microporous membrane (b) PSf microporous membrane treated by Set A, (c) PSf microporous membrane treated by Set B, and (d) PSf microporous membrane treated by Set C.

Effect of surface modification on pure water flux

Pure water flux tests were carried out for treated membranes with optimized oxidizing agents of Sets A, B and C vs. immersion time and the obtained results are shown in Fig. 7. The pure water flux (PWF) of the pristine PSf membrane is about 280 L/m^2.h; corresponds with the data shown by zero (0) immersion time. The obtained results show that PSf membranes treated by all oxidizing agents always keep higher PWF. The maximum PWFs for the PSf membranes treated by Set A, Set B, and Set C are obtained when the membranes were immersed for 60, 60 and 120 min, respectively. To our surprise, the PWF results for all sets are consistent with the optimized oxidation circumstances. In fact, for permeation process, the pore size and surface hydrophilicity are key parameters influenced water flux [42]. The membrane modified with Set A decreased the thickness of sponge-like

pores and increased the length and the number of finger-like pores in the membrane prepared (Fig. 3b). Therefore, only pore size dominates the improvement in PWF. Beside, increment of functional group on membrane surface remarkably increased PWF for treated membrane. Similar to our previous findings [32, 33] degree of roughness amplifies the wettability of the surface toward its intrinsic properties. For a hydrophilic surface in which contact angle is lower than 90°, roughening will decrease the contact angle resulting in higher PWF.

Protein filtration and fouling analyses

Dynamic BSA protein filtration tests were carried out to compare the surface properties and anti-fouling performances of the neat and chemically treated PSf membranes. In order to omit the effect of electrostatic repulsion on the
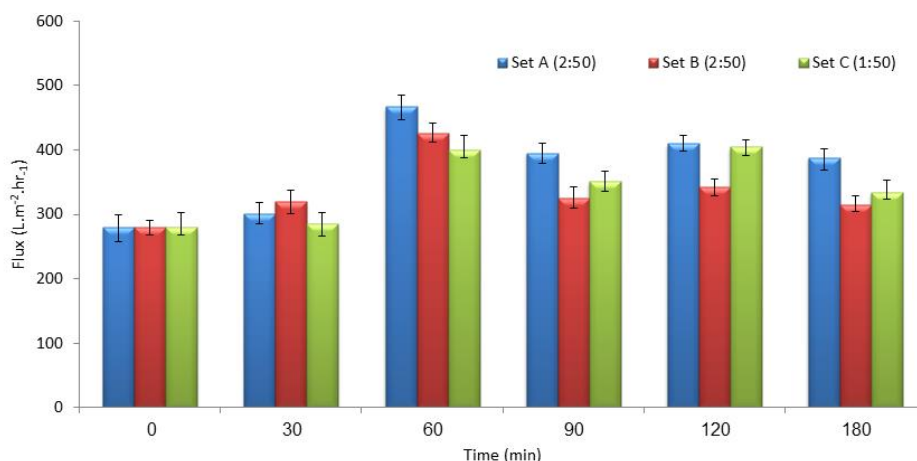

Fig. 7. Effect of immersion time on pure water flux of PSf microporous membrane treated by Set A, Set B and Set C, at fixed concentrations of oxidizing agent and sulfuric acid.
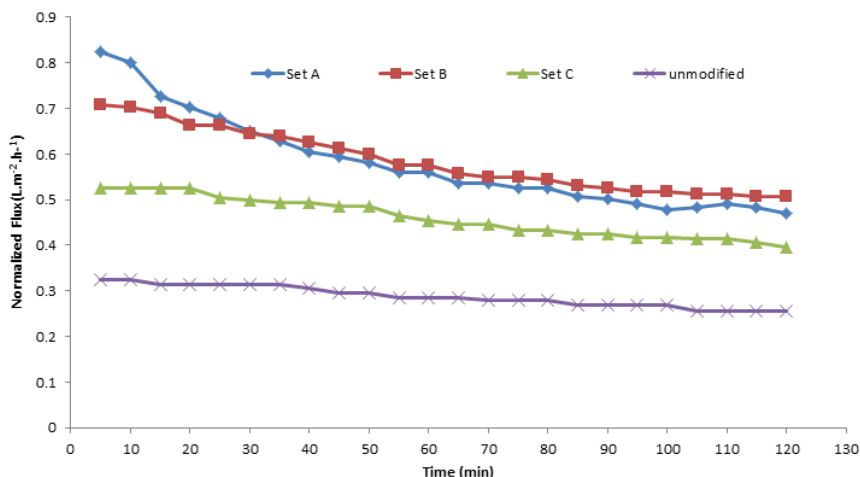

Fig. 8. Performance of PSf microporous membrane at optimized oxidation circumstances.

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

317

Table 3. Analyses of fouling properties of pristine and treated PSf microporous membrane by optimized oxidizing solution circumstances of Set A, Set B and Set C.

Samples	J_0 (L.m^{-2}.h^{-1})	J_1 (L.m^{-2}.h^{-1})	J_2 (L.m^{-2}.h^{-1})	RFR(%)[a]	IFR(%)[b]	TFR(%)[c]	FR(%)[d]
Untreated PSF	280	72	153	28.9	45.4	74.3	54.6
Treated by Set A (2:50:60)	467.32	220	327.7	23.0	29.9	52.9	70.1
Treated by Set B (2:50:60)	425	215	330	27.1	22.4	49.4	77.6
Treated by Set C (1:50:120)	404	160	258	24.3	36.1	60.4	63.9

Table 4. Comparing the performance of various treated polymer membranes with different oxidizing agents (Digits inside of parentheses show the percentages of the achieved improvement/enhancement).

Membrane type	Max. intensity in OH functional group	Max. improvement in PWF	Max. reduction in TFR	Max. reduction in IFR	Max. improvement in FR	Min. impact on re-construction	Ref. no
HDPE membrane	$KClO_3$	$K_2Cr_2O_7$ (>130%)	$KClO_3$ (>26%)	$KClO_3$ (>37%)	$KClO_3$ (>27%)	$KClO_3$ (4.7%)	[27]
PP membrane	$KClO_3$	$K_2Cr_2O_7$ (>235%)	$KClO_3$ (33%)	All oxidizing agents (>56%)	All oxidizing agents (>99%)	$KClO_3$ (3.1%)	[28]
PSf membrane	$KClO_3$	$KClO_3$ (>67%) & $K_2Cr_2O_7$ (>51%)	$K_2Cr_2O_7$ (>33%)	$K_2Cr_2O_7$ (>50%)	$K_2Cr_2O_7$ (>42%)	----	Current work

antifouling properties which might occur during chemical treatment processes, the pH of protein solution was kept at 4.8; using acidic buffer, since the isoelectric point (IEP) of BSA is 4.8. Fig. 8 presents the normalized flux for the pristine and treated PSf membranes with different oxidizing agents. The obtained results show that the existence of polar functional groups on the surfaces of treated membrane imposes the hydrophilic property and resists against protein fouling in the absence of electrostatic interactions.

Additional information about membranes fouling including total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) are summarized in Table 3. It can be seen that the pristine PSf membrane showed the highest TFR, confirming that this membrane is easily fouled by BSA molecules. Hydrophilic properties of treated membranes decreased TFR from 74.3% for pristine PSf membrane to 52.9%, 49.4% and 60.4% for treated membranes by Set A, Set B, and Set C, respectively. Moreover, IFR of membranes decreased from 45.4% for pristine PSf membrane to 29.9%, 22.4% and 36.1% for treated membranes by Set A, Set B, and Set C, respectively. This indicates that incorporation of hydrophilic functional groups on the surface of PSf membranes not only increased the fouling resistance but also decreased the irreversible fouling ratio. A similar trend was obtained for the FR values, in which treated membranes showed enhanced flux recovery

in comparison with pristine membrane.

Table 4 summarizes the effectiveness of various oxidizing agents on the different polymer membranes. In comparison with our previous findings it is obvious that different polymer membrane requires different oxidizing agents and circumstances. This finding implies that depends on the required level of functionality, type of application and operation circumstances, specific polymer material and oxidizing agent are required.

This Table provides very useful information for the readers. According to the desired goal of the selected polymer membrane, one may select specific oxidizing agents with optimum composition and treatment time to achieve desired characteristics.

CONCLUSION

Polymer membranes prepared by hydrophobic polymer materials such as PSf and polyolefin including polyethylene and polypropylene suffer from poor functionality which restricts their application in protein purification recovery and membrane bioreactors. Their intrinsic hydrophobic nature also causes them to be easily fouled in protein filtration and purification processes. Surface functionalization is an efficient, easy, scalable and cost-effective method to introduce a polar group on the surface of polymeric membrane. Three strong and well-identified oxidizing agents including $KClO_3$, $K_2Cr_2O_7$, and $KMnO_4$ were dissolved in sulfuric acid to prepare oxidizing

318

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

solutions. The optimum concentration of oxidizing agents, sulfuric acid and membrane immersion time were determined. According to the obtained results, it was concluded that the PSf membrane treated by $KClO_3$ shows better performance and stability for extended periods with comparatively lower contact angel saturation values than the $K_2Cr_2O_7$ and $KMnO_4$, respectively. SEM analysis showed that modified membranes, the sublayer seemed to have sponge-like pores beneath the top surface layer and finger-like cavities near the bottom surface layer. ATR-FTIR results showed that the absorbance intensities of –OH, C=O and C-O peaks in the samples treated by $KClO_3$ are remarkably higher than the samples treated by $K_2Cr_2O_7$ and $KMnO_4$, respectively. Also, pore size distribution showed that the functionalization of membranes led to larger pore size on the membrane surface. BSA filtration experiments showed that the total fouling ratio (TFR) is remarkably decreased for the membranes treated by oxidizing solutions. Moreover, the portions of irreversible fouling ratios were decreased for treated membrane while the portions of reversible fouling ratios and flux recoveries increased. This indicates that incorporation of hydrophilic functional groups on the surface of PSf membranes not only increased fouling resistance but also decreased irreversible fouling ratio. In order to summarize our previous and recent results, we may clearly state that certain polymer membrane requires specific oxidizing agents. It is not easily possible to specify a certain oxidizing agent for a broad range of applications.

CONFLICTS OF INTEREST

There are no conflicts to declare.

REFERENCES

1. M. Pilutti, J.E. Nemeth, P. Nemeth, Technical and cost review of commercially available MF/UF membrane products, Desalination, (2003) 1-15.
2. Etemadi H, Yegani R, Babaeipour V. Performance evaluation and antifouling analyses of cellulose acetate/nanodiamond nanocomposite membranes in water treatment. Journal of Applied Polymer Science. 2017;134(21).
3. S.S. Madaeni, T. Akbarzadeh Arbatan, Preparation and Characterization of Microfiltration Membrane Embedded with Silver Nano-Particles, Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 29 (2010) 105-111.
4. A. Vedadghavami, F. Minoei, S.S. Hosseini, Practical techniques for improving the performance of polymeric membranes and processes for protein separation and purification, Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 37 (2018) 1-23.
5. Sharma N, Purkait MK. Preparation of hydrophilic polysulfone membrane using polyacrylic acid with polyvinyl pyrrolidone. Journal of Applied Polymer Science. 2015;132(22):n/a-n/a.
6. S.P. Nunes, K.-V. Peinemann, Membrane technology: in the chemical industry, John Wiley & Sons, 2006.
7. Yunos MZ, Harun Z, Basri H, Ismail AF. Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG). Desalination. 2014;333(1):36-44.
8. Ioan S, Filimo A. Biocompatibility and Antimicrobial Activity of Some Quaternized Polysulfones. A Search for Antibacterial Agents: InTech; 2012.
9. Bae T-H, Tak T-M. Effect of TiO2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. Journal of Membrane Science. 2005;249(1-2):1-8.
10. Fan Z, Wang Z, Sun N, Wang J, Wang S. Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers. Journal of Membrane Science. 2008;320(1-2):363-71.
11. Park J, Acar M, Akthakul A, Kuhlman W, Mayes A. Polysulfone--poly(ethylene glycol) graft copolymers for surface modification of polysulfone membranes. Biomaterials. 2006;27(6):856-65.
12. Fan Z, Wang Z, Duan M, Wang J, Wang S. Preparation and characterization of polyaniline/polysulfone nanocomposite ultrafiltration membrane. Journal of Membrane Science. 2008;310(1-2):402-8.
13. Van der Bruggen B. Chemical modification of polyethersulfone nanofiltration membranes: A review. Journal of Applied Polymer Science. 2009;114(1):630-42.
14. Wang S, Li J, Suo J, Luo T. Surface modification of porous poly(tetrafluoraethylene) film by a simple chemical oxidation treatment. Applied Surface Science. 2010;256(7):2293-8.
15. Gancarz I, Poźniak G, Bryjak M. Modification of polysulfone membranes. European Polymer Journal. 2000;36(8):1563-9.
16. Bryjak M, Gancarz I, Poźniak G, Tylus W. Modification of polysulfone membranes 4. Ammonia plasma treatment. European Polymer Journal. 2002;38(4):717-26.
17. Nady N, Franssen MCR, Zuilhof H, Eldin MSM, Boom R, Schroën K. Modification methods for poly(arylsulfone) membranes: A mini-review focusing on surface modification. Desalination. 2011;275(1-3):1-9.
18. Yang S, Liu Z. Preparation and characterization of polyacrylonitrile ultrafiltration membranes. Journal of Membrane Science. 2003;222(1-2):87-98.
19. Shohur MF, Harun Z, Lau WJ, Yunos MZ, Jamalludin MR. Performance of PSf Ultrafiltration Membrane: Effect of Different Nonsolvent on Coagulation Medium. Jurnal Teknologi. 2013;65(4).
20. Pakizeh M, Mansoori SAA, Pourafshari Chenar M, Namvar-Mahboub M. Modification of PSf membrane nanostructure using different fabrication parameters and investigation of the CO2 separation properties of PDMS-coated PSf composite membranes. Brazilian Journal of Chemical Engineering. 2013;30(2):345-54.
21. M.S. Abdel Aal, A.M.M. Ahmed, A. Rahman, H. Hammam, S.H. Kandil, Enhancing the performance of polysulfone ultrafiltration membranes by mixing with polyacrylic acid for canal water treatment. Advanced Journal of Chemistry-Section A, 1(2018), 86-95.
22. Ji M, Luo J, Wei J, Woodley J, Daugaard AE, Pinelo M. Commercial polysulfone membranes pretreated with

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019

319

ethanol and NaOH: Effects on permeability, selectivity and antifouling properties. Separation and Purification Technology. 2019;219:82-9.

23. Rana D, Matsuura T. Surface Modifications for Antifouling Membranes. Chemical Reviews. 2010;110(4):2448-71.

24. Maji D, Lahiri SK, Das S. Study of hydrophilicity and stability of chemically modified PDMS surface using piranha and KOH solution. Surface and Interface Analysis. 2011;44(1):62-9.

25. Xu Z, Wan L, Huang X. Surface Engineering of Polymer Membranes. Advanced Topics in Science and Technology in China: Springer Berlin Heidelberg; 2009.

26. Higuchi A, Shirano K, Harashima M, Yoon BO, Hara M, Hattori M, et al. Chemically modified polysulfone hollow fibers with vinylpyrrolidone having improved blood compatibility. Biomaterials. 2002;23(13):2659-66.

27. Möckel D, Staude E, Guiver MD. Static protein adsorption, ultrafiltration behavior and cleanability of hydrophilized polysulfone membranes. Journal of Membrane Science. 1999;158(1-2):63-75.

28. Wei X, Wang Z, Wang J, Wang S. A novel method of surface modification to polysulfone ultrafiltration membrane by preadsorption of citric acid or sodium bisulfite. Membrane Water Treatment. 2012;3(1):35-49.

29. M. Fonouni, R. Yegani, S. Anarjani, A. Tavakoli, Antifouling behaviors of surface functionalized high density polyethylene membrane in microfiltration of BSA protein, Polyolefins Journal, (2016).

30. M.F. Reza Yegani, Akram Tavakkoli,Sanaz Mollazadeh, Investigation the Impact of Various Oxidizing Agents on the Surface Functionalization and performance of Polypropylene Membranes, Journal of Textiles and Polymers, (2016).

31. P. Amirabedi, R. Yegani, M.R. Aghjeh, Experimental design applied to fabrication of PSf membranes via NIPS method, Part1: Influential parameters on membrane porosity and mechanical strength, J Text Polym, 1 (2013) 24-30.

32. Jafarzadeh Y, Yegani R. Analysis of fouling mechanisms in TiO2 embedded high density polyethylene membranes for collagen separation. Chemical Engineering Research and Design. 2015;93:684-95.

33. Jafarzadeh Y, Yegani R, Sedaghat M. Preparation, characterization and fouling analysis of ZnO/polyethylene hybrid membranes for collagen separation. Chemical Engineering Research and Design. 2015;94:417-27.

34. Yang Y-F, Wan L-S, Xu Z-K. Surface hydrophilization for polypropylene microporous membranes: A facile interfacial crosslinking approach. Journal of Membrane Science. 2009;326(2):372-81.

35. Eriksson JC, Go¨lander CG, Baszkin A, Ter-minassian-saraga L. Characterization of kmno4/h2so4-oxidized polyethylene surfaces by means of ESCA and45ca2+ adsorption. Journal of Colloid and Interface Science. 1984;100(2):381-92.

36. A. Shoushtari, R. Malek, M. Abdous, Effect of chemical oxidation treatment on dyeability of polypropylene, Dyes and pigments, 63 (2004) 95-100.

37. Ma Y, Shi F, Wang Z, Wu M, Ma J, Gao C. Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive. Desalination. 2012;286:131-7.

38. Wahab MFA, Ismail AF, Shilton SJ. Studies on gas permeation performance of asymmetric polysulfone hollow fiber mixed matrix membranes using nanosized fumed silica as fillers. Separation and Purification Technology. 2012;86:41-8.

39. Malaisamy R, Mohan D, Rajendran M. Polyurethane and Sulfonated Polysulfone Blend Ultrafiltration MembranesI. Preparation and Characterization Studies. Journal of Colloid and Interface Science. 2002;254(1):129-40.

40. Yuliwati E, Ismail AF. Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment. Desalination. 2011;273(1):226-34.

41. D. Pavia, G. Lampman, G. Kriz, J. Vyvyan, Introduction to spectroscopy, Cengage Learning, 2008.

42. Yang Q, Xu Z-K, Dai Z-W, Wang J-L, Ulbricht M. Surface Modification of Polypropylene Microporous Membranes with a Novel Glycopolymer. Chemistry of Materials. 2005;17(11):3050-8.

320

J. Water Environ. Nanotechnol., 4(4): 308-320 Autumn 2019