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Performance and characteristics of modified PES-based membranes upon exposure to harsh cleaning conditions by sodium hypochlorite

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Abstract

Overcoming the increased protein fouling of polymeric polyethersulfone-based membranes (e.g. PES-PVP, PES-pluronic, and PES-Tetronic) is an essential target for wider ultrafiltration-based applications of such fabricated membranes. Hence, this study has been actively devoted to trace both performance and characteristics changes of modified PES-based membranes upon exposure to harsh cleaning conditions by sodium hypochlorite (400 ppm for 10 days). Simultaneously, different characterization tools have been adopted to study such purposes as SEM, FTIR, tensile strength, performance patterns. SEM analysis has proved the increment in pore size after contacting the fabricated membranes with NaOCl agent. However, tensile strength, contact angle, and overall porosity criteria showed a slight change. For instance, overall porosity ranged between 70-80 %, contact angle difference was about 3-4 deg, and tensile strength decrement was negligible. Further, AFM data proved that the relative roughness of all membranes did not dramatically. what is more, performance patterns in terms of pure water permeability is boosted two-three fold compared to untreated membranes with preserving BSA rejection ability (e.g. maximum BSA rejection loss is recorded for PES-T904 membrane; decrease from 70 % to about 55 %; about 21 % loss). Such preserved ultrafiltration behaviour may be ascribed to the more formed negative charge, and preservation hydrophilic nature even after NaOCl exposure. to end with, the fabricated modified PES membranes showed a preserved ultrafiltration performance after such harsh cleaning conditions.

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Introduction

Polyethersulfone (PES) is the most widely used material for micro- and ultrafiltration (MF/UF) membranes [1] due to its stability against a variety of chemical and physical attacks [2]. However, PES possesses a hydrophobic nature which often results in fouling of the membrane during its application [3]. With the purpose of decreasing the hydrophobic nature of PES, it was blended with many hydrophilic modifiers such as polyvinylpyrrolidone (PVP) [4], polyethylene glycol (PEG), and other copolymers [2,

[5]. Previously, we found that the modified PES-PVP (3 wt.%), PES-pluronic (P31R1; 5 wt.%), and PES-tetronic (T904; 5 wt.%), membranes are promising for submerged membrane bioreactors (SMBRs) due to their improved characteristics and performance in terms of having high pure water permeability (PWP) with a reasonable high bovine serum albumin (BSA) rejection, in addition to good mechanical stability [2]. The SMBR is one configuration from available MBR configurations at the global market, in which the membrane is contacted directly with suspended

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mother liquor [6]. The presence of suspended mother liquor increases the opportunity of membrane fouling. Therefore, the cleaning of these modules is carried out on a regular basis with different cleaning agents. Consequently, studying the effects of membrane cleaning issues is urgently needed.

Sodium hypochlorite (NaOCl) and hydrogen peroxide (H₂O₂) are the commonly-used oxidants that aim to remove irreversible fouling of the membranes caused by organic and biological foulants through oxidation and/or disinfection [7]. Much concern is directed to the use of NaOCl solution for cleaning purposes of MF/UF membranes because it offers many advantages such as availability, reasonable price, and ability to prevent fouling via efficient cleaning [8]. The typical chemical cleaning process in wastewater treatment facilities is performed by back flushing of 1 min with 2–8 mg L^{-1} of NaOCl, or by soaking in 20–400 mg L^{-1} free chlorine for approximately 1 h [9]. Many studies are interested in the influence of the exposure of UF membranes to NaOCl [3, 10-14]. The observed distortion of UF/MF membranes after NaOCl treatment was attributed to the chain breaking in polysulfone (PSF) molecules after extended exposure to NaOCl [15, 16]. It is well established that commercial PVP-modified PES membranes lose PVP, used in the initial casting of PES membranes as a pore former and hydrophilizer, upon treatment with NaOCl; nevertheless, such an effect was viewed as an advantage due to the increase in membrane flux and the narrowed pore-size distribution after the hypochlorite treatment [10, 17]. Also, a decrease in elastic elongation of PES membranes exposed to hypochlorite solution was reported by Thominette et al. [16].

Thus, in this paper, the stability of modified PES flat sheet membranes which had been prepared and tested in previous research [2] is investigated under severe cleaning conditions using NaOCl solution. Membrane topography was examined with the aid of scanning electron microscopy (SEM) and atomic force microscopy (AFM). Porosity, surface chemistry by Fourier transform infrared (FTIR) spectroscopy, membrane hydrophilicity, surface zeta

potential (ZP), the tensile strength, the transport property by water permeability, and the protein rejection were used as indicators to evaluate the stability of the membranes.

Experimental methods

Membrane fabrication

Flat sheet PES-based membranes were fabricated by nonsolvent-induced phase separation (NIPS) method using commercial PES (Ultrason E 6020 P, BASF, Ludwigshafen, Germany) polymer as the major component. PVP with a molecular weight ~ 40,000 g mol^{-1} (Sigma Aldrich, Germany), T904, and P31R1 (BASF, Germany) were used as additives. The detailed fabrication procedure is reported in our previous work [2]. The chemical structures of the PES polymer and the additives are illustrated in Figure 1. The ratios of the additives to PES in the N,N-dimethylformamide (DMF) (TEDIA, USA) solvent (i.e., compositions of casting solutions) are listed in Table 1.
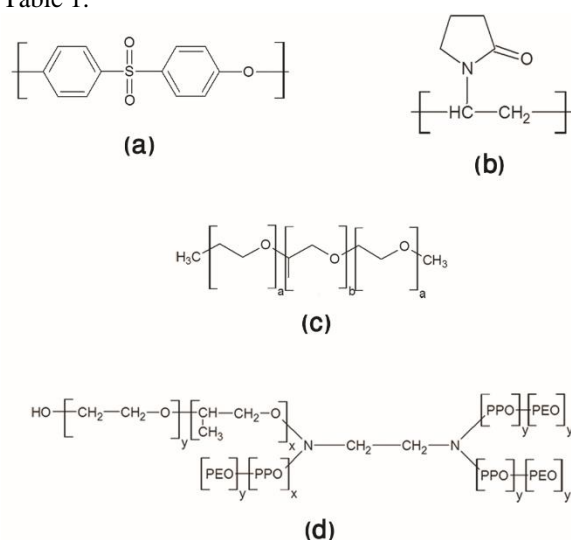

Figure 1. Chemical structures of (a) PES, (b) PVP, (c) pluronic 31R1, and (d) tetronic 904.

Table 1. Compositions of the casting solutions.

Group	Composition (wt.%)			
	PES	DMF	Additive	Additive/PES ratio
PES	20	80	0	0
PES-PVP	20	77	3 (PVP)	0.15
PES-P31R1	20	75	5 (pluronic)	0.25
PES-T904	20	75	5 (tetronic)	0.25

Stability test

The stability of macromolecular additives in PES polymeric matrix against NaOCl was tested by soaking the prepared flat sheet membranes in NaOCl solution (active chlorine concentration = 400 mg L^{-1}) for up to 10 days at 20±1 °C according to the

procedure described in [5]. The used concentrations of active chlorine and the soaking time are representative of the most drastic conditions for membrane chemical cleaning [5].

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Membrane characterization

Surface chemistry of the untreated and treated membranes with hypochlorite was analyzed by FTIR spectrometer (Bruker Vertex 70, Germany) equipped with a horizontal attenuated reflection (ATR) device. A total of 16 scans were performed at a resolution of 4 cm^{-1}.

Membranes surface morphology was imaged utilizing SEM (QUANTA FEG250, USA). The dried samples were sputtered with platinum (5–6 nm Pt layer) using an MTM 10 Thickness Monitor (Cressington; CA, USA) to provide electrical conductivity to the samples. Subsequently, micrographs of the membranes were imaged under an accelerating voltage of 20 kV.

AFM 3D micrographs of the untreated and treated membranes were obtained in noncontact mode with Shimadzu instrument, model number 9600. The scan area was 5.0×5.0 μm^2.

The membrane porosity ε (%) was determined through a gravimetric method reported by Abdel-Karim et al. [2]. Briefly, the dried membranes were immersed in DI water for 24 h at room temperature. Thereafter, the membranes were carefully taken out, wiped by means of tissue paper to remove excess water on their surface, and their weights were recorded. ε was calculated as follows:

$$\varepsilon = \frac{W_w - W_d/\rho_w}{(W_w - W_d/\rho_w) + (W_d/\rho_P)} \times 100 \qquad (1)$$

where, W_w is the weight of the wet membrane, W_d is the weight of the dry membrane. The density values of the water (ρ_w) and polymer (ρ_P) are 0.998 g cm^{-3} and 1.37 g cm^{-3}, respectively. The reported values were calculated as the average of three measurements.

Contact angle (CA) measurements were conducted at room temperature utilizing a contact angle goniometer (Rame-Hart 500, USA) equipped with a video camera and image analysis system (DROP image Advanced Software).

ZPs of the flat sheet membranes, before and after treatment with NaOCl, were measured by SurPASS electro-kinetic analyzer (Anton-Paar GmbH, Austria) at a pH range of 4–10 for each membrane sample. The measurement conditions were described in detail previously [2]. The measured streaming current was converted to the ZP (ζ) using the following Helmholtz-Smoluchowski equation [18]:

$$\zeta = (\frac{dU}{dp}) \times (\frac{\eta_o}{\varepsilon \times \varepsilon_o}) \times (\frac{L}{A \times R}) \qquad (2)$$

where, $\frac{dU}{dp}$ is the slope of streaming potential versus pressure (mV/mbar), η_o is the electrolyte viscosity (mPa-s), ε_o is the vacuum permittivity (F m^{-1}), ε is the dielectric constant of the electrolyte (V m^{-1}), L is the length of the streaming channel (mm), A is the cross-section of the streaming channel (mm^2), and R is the Ohm resistance inside the measuring cell (ohm).

The tensile strength test is used as an indicator for the mechanical stability of the fabricated membranes before and after treatment with NaOCl solution. The experimental conditions were described in detail previously [2].

Hydraulic permeability and BSA rejection measurements

The influence of NaOCl treatment on the hydraulic pure water permeability (PWP) of the flat sheet PES-based membranes was tested by using a custom-made dead-end filtration cell with a capacity of 100 mL and an inner diameter of 17 mm (full specifications are available in [2]). The *PWP* was calculated using the following equation [19]:

$$PWP = \frac{V}{A \times t \times P} \qquad (3)$$

where, V (L) is the volume of the permeate, A (9.0746 × 10^{-4} m^2) is the effective area of the tested membrane, P (1 bar) is the applied pressure, and t (h) is the elapsed time.

BSA (MW = 67 kDa; Sigma Aldrich, MO, USA) of 1000 mg L^{-1} concentration was used for protein rejection experiments. All rejection experiments were conducted at a constant transmembrane pressure of 1 bar and pH = 5.9 ± 0.2. No change in pH was observed during these experiments. The percentage of BSA rejection (R_{BSA}(%)) was calculated according to the formula [4]:

$$R_{BSA}(\%) = \left(1 - \frac{C_{out}}{C_{feed}}\right) \times 100 \qquad (4)$$

where, C_{out} and C_{feed} are the concentrations of BSA (mg L^{-1}) in permeate and feed solutions, respectively. The concentration of BSA was monitored by measuring its UV absorbance at 279 nm using UV-VIS spectrophotometer (JASCO-630, Japan) according to the standard procedure [20].

Results and discussion

Effect of NaOCl treatment on membranes chemical characteristics

The change in membrane chemistry was investigated by FTIR technique after the treatment of fabricated PES-based membranes with NaOCl. Figure 2 demonstrates the FTIR spectra overlay of the untreated and treated membranes. The four distinctive bands of PES were observed in all membranes. These bands appeared at 1,578 cm^{-1}, 1,485 cm^{-1}, 1,240 cm^{-1}, and 1,150 cm^{-1} which can be assigned to the aromatic bands of the benzene ring, C=C bond stretch, aromatic ether, and sulfone group, respectively. In order to facilitate the explanation of the experimental observation, the characteristic peaks were compared relatively to a reference peak at 1250 cm^{-1} as depicted in Table 2. It is noted that the characteristic peaks in the case of PES decreased

after the treatment with NaOCl with specific notice to the peak at 1,150 cm^{-1} which may confirm partial degradation of PSF upon the treatment [16, 21]. Besides, the peak at 1,440 cm^{-1} slightly changed after treatment in the case of PVP. This may illustrate the probability of leaching small fractions of PVP also. Additionally, in the case of P31R1 and T904 the intensity of the ether peak in treated membranes is increased by 7% and 14% for P31R1 and T904, respectively. This may reflect a stable behavior of these additives in the PES matrix. To sum up, the untreated and treated membranes have been affected during the exposure to NaOCl to different degrees.

In addition, the band around 1,440 cm^{-1} (which is credited to the vibration of the C−H bond from the $CH_2C = O$ group of PVP [21]) did not disappear and this confirms the stability of PES-PVP against NaOCl (Figure 2(b)). Similarly, the characteristic peak for P31R1 and T904, which is around 1,105 cm^{-1}[2], did not disappear after NaOCl treatment for PES membrane (Figure 2(c) and 2(d)). Conclusively, the treated membranes are chemically stable against NaOCl treatment.
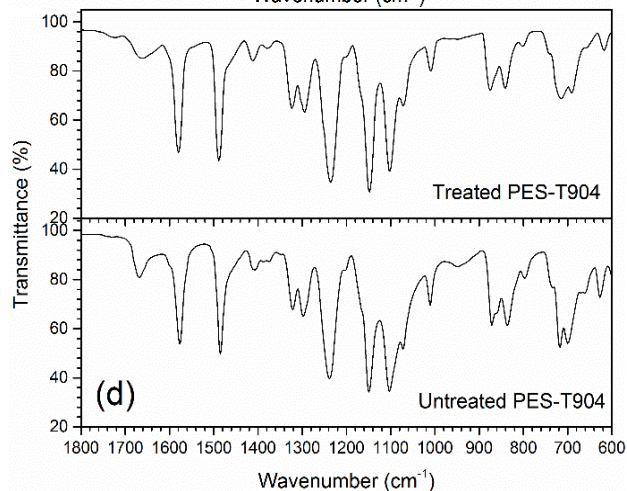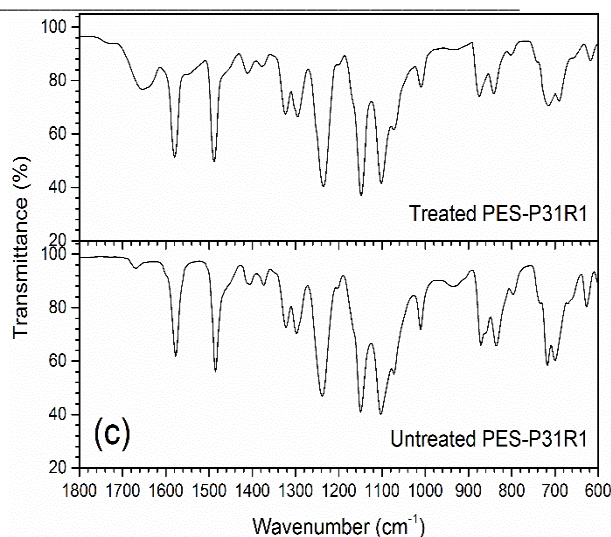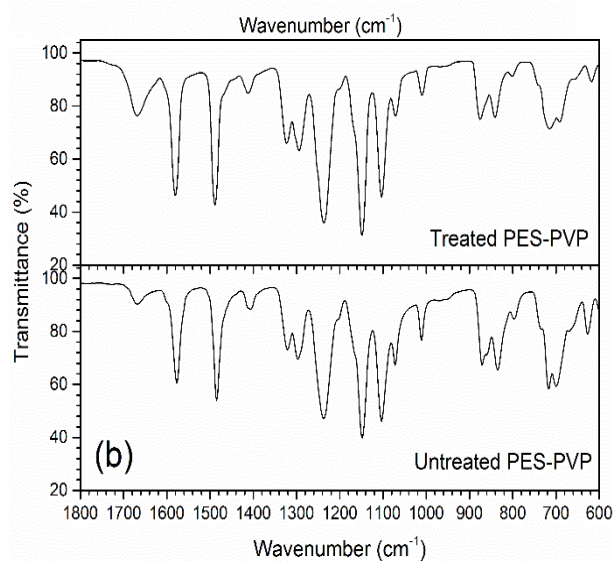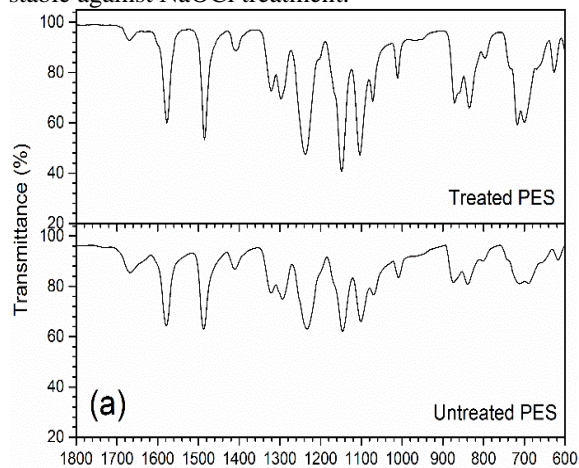

Figure 2. FTIR spectra of untreated and treated membranes: (a) PES, (b) PES-PVP, (c) PES-P31R1, and (d) PES-T904.

NaOCl effect on morphology

Untreated and treated membrane samples were microscopically analyzed for any surface deformation by SEM (Figure 3). The mechanism of pore formation and the comparison between the untreated modified membranes using different additives were discussed in detail in our previous work in [2]. After the treatment with NaOCl, no surface cracks were observed and the size of pores was increased not only in the modified PES membranes but also in the neat PES membrane. The increment in pore size was more pronounced in modified membranes relative to the bare PES membrane. Consequently, this would explain the dramatic increment of PWP after the treatment with NaOCl as will be shown later. Different increment trends in pore size of treated membranes may be attributed to the different solubilities of additives in NaOCl solution. In other words, the solubility of tetronic in NaOCl is higher than that of pluronic as

hydrophilic-lipophilic balance (HLB) value of T904 is 12–18 while for P31R1 it equals 1–7 [2], leading to wider pores as shown in SEM images (Figure 3).

The surface topography of untreated and treated membranes was characterized by 3D AFM images at a scan area of 5 μm × 5 μm as shown in Figure 4. The lowest and highest sites on the membrane surface are represented by dark and bright regions in the images, respectively. For better evaluation of surface roughness, the average surface roughness is listed in Table 3. Neat PES membrane showed higher susceptibility to be affected with NaOCl. However, the modified membranes showed withstanding against treatment with NaOCl solution. As a result, this makes treated modified membranes having a more tendency to resist fouling as discussed in detail by Cai et al. [22]. This observation is not pronounced in PES-T904 as roughness did not change significantly after treatment which may result in more fouling susceptibility than other modified membranes. This behavior encourages the application of modified membranes in water/wastewater treatment.

Table 2. Transmittance ratio (relative to the reference peak at wavenumber 1,250 cm^{-1}) of selected peaks for the hypochlorite aged modified PES membranes: (a) PES, (b) PVP, (c) P31R1, and (d) T904.

Wavenumber (cm^{-1})	Functional group	Transmittance ratio	
		Untreated PES	Treated PES
1,250	Core aromatic	1.00	1.26
1,105	C-O ether	0.81	1.16
1,485	C=C	0.91	1.09
1,578	C=C	1.03	1.11
1,150	SO$_2$	0.70	1.09
		Untreated PES-PVP	Treated PES-PVP
1,250	Core aromatic	1.00	0.92
1,105	C-O ether	0.80	0.87
1,485	C=C	0.92	0.80
1,578	C=C	1.03	0.82
1,150	SO$_2$	0.69	0.53
1,440	vibration of C−H bond in the CH$_2$=O group of PVP	1.61	1.55
		Untreated PES-P31R1	Treated PES-P31R1
1,250	Core aromatic	1.00	1.01
1,105	C-O ether	0.70	0.75
1,485	C=C	0.96	0.89
1,578	C=C	1.06	0.89
1,150	SO$_2$	0.70	0.64
		Untreated PES-T904	Treated PES-T904
1,250	Core aromatic	1.00	1.05
1,105	C-O ether	0.69	0.79
1,485	C=C	0.96	0.89
1,578	C=C	1.04	0.93
1,150	SO$_2$	0.66	0.61

NaOCl effect on the membrane porosity

Porosity is considered a vital parameter that controls permeation and separation behaviors of the membranes [2]. As well, some properties are related strongly to membrane porosity (e.g., equilibrium water content and surface hydrophilicity) [23]; thus measuring membrane porosity is urgently required. The membrane porosity was determined via the gravimetric method as illustrated in many publications including but not limited to these references [2, 23-26]. Hence, the gravimetric method is considered an efficient procedure for the evaluation of membrane porosity. In this work, the porosity measurements were carried out for both untreated and treated membranes and the obtained results are shown in Figure 5. After treating the membranes with NaOCl solution, minor changes were observed in the overall porosities for all membranes indicating the stability of these membranes. However, significant changes in the surface porosity were observed during SEM investigations (see Figure 3; quantitative data in Table 4). A plausible explanation of this mismatch may be that the top portions of pores of modified membranes are affected strongly with NaOCl but the bottom layer was not fully affected by NaOCl.
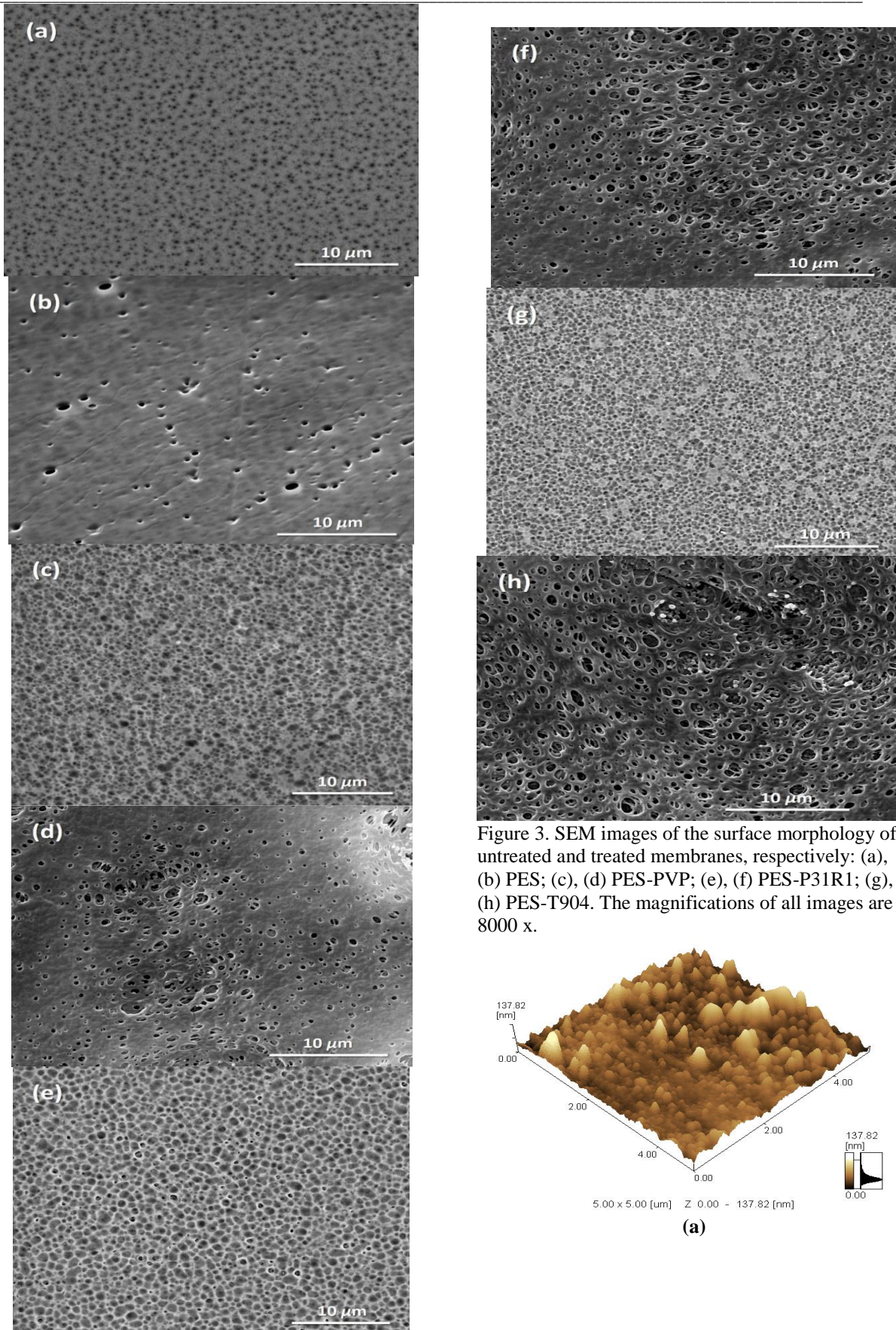
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Figure 3. SEM images of the surface morphology of untreated and treated membranes, respectively: (a), (b) PES; (c), (d) PES-PVP; (e), (f) PES-P31R1; (g), (h) PES-T904. The magnifications of all images are 8000 x.

(b)

(f)

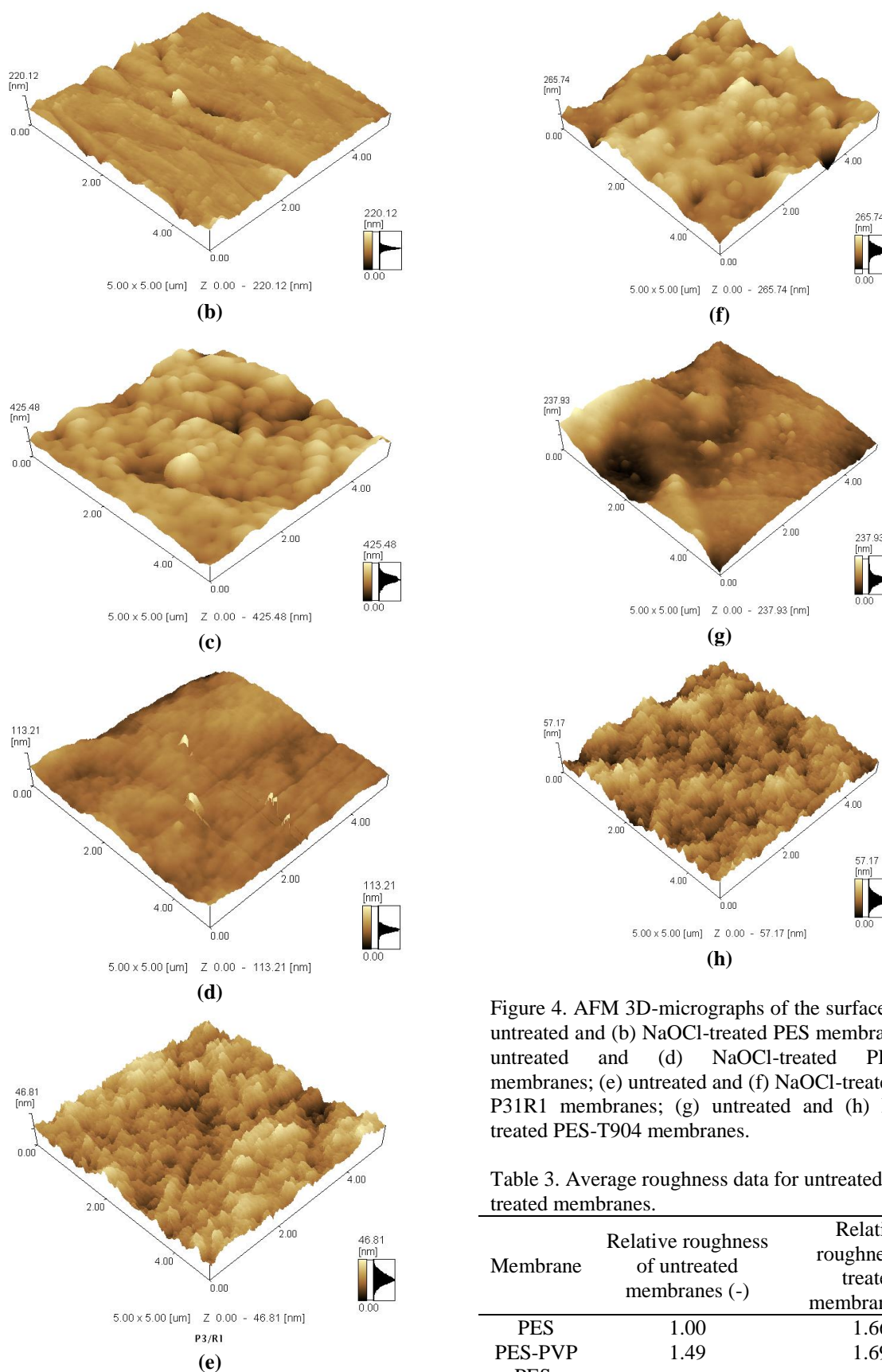
(c)

(g)

(d)

(h)

Figure 4. AFM 3D-micrographs of the surfaces of (a) untreated and (b) NaOCl-treated PES membranes; (c) untreated and (d) NaOCl-treated PES-PVP membranes; (e) untreated and (f) NaOCl-treated PES-P31R1 membranes; (g) untreated and (h) NaOCl-treated PES-T904 membranes.

(e)

Table 3. Average roughness data for untreated and treated membranes.

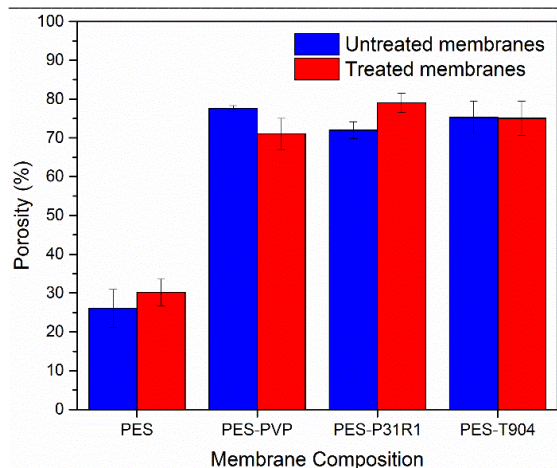| Membrane	Relative roughness of untreated membranes (-)	Relative roughness of treated membranes (-)
PES	1.00	1.66
PES-PVP	1.49	1.69
PES-P31R1	1.42	1.54
PES-T904	1.32	1.29

Figure 5. Volume porosities of untreated and treated membranes measured by gravimetric method.
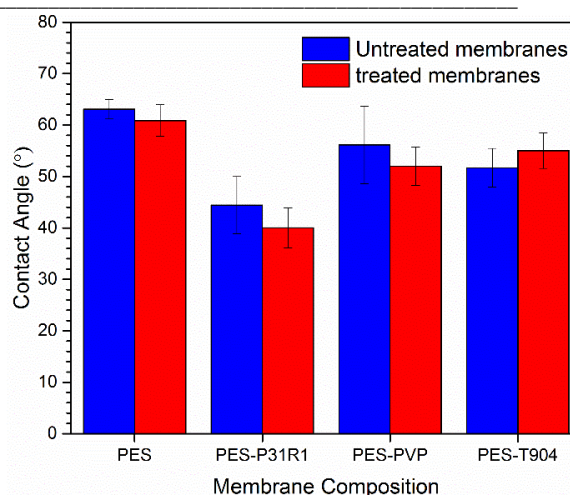

Figure 6. Static water contact angles of untreated and treated membranes.

Table 4 Surface porosity (%) from SEM data calculated using imageJ software [27].

	Surface porosity± (SD) (%)	
	Untreated membranes	Treated membranes
PES	1.9± (0.6)	3.3± (0.5)
PES-PVP	4.8± (0.9)	5.0± (0.7)
PES-P31R1	3.9± (0.8)	5.9± (0.8)
PES-T904	5.1± (1.0)	9.4± (1.2)

NaOCl effect on the hydrophilicity

The wetting topic has received marvelous interest from both fundamental and applied points of view. It plays an important role in many industrial processes, such as membrane application [25]. Wettability studies usually involve the measurement of contact angle (CA), which indicates the degree of wetting when a solid and liquid interact. Small CA (<90°) corresponds to high wettability/hydrophilic, while large CA (>90°) corresponds to low wettability/hydrophobic [28]. The hydrophilicity of the treated and untreated membranes was assessed from the CA measurements between the membrane surface and the air/water interface (Figure 6). It is depicted that CA of modified membranes (either untreated or treated membranes) is lower than that of unmodified PES membranes (either treated or untreated membranes), that is, it dropped from 63.1° for untreated PES to reach 40° for treated PES-P31R1 membrane. Besides, the change in CA after NaOCl treatment is within the experimental error; this confirms that only minor changes in surface hydrophilicity of membranes occurred under the tested conditions.

NaOCl effect on the surface charge

The surface charge of the membrane plays an important role in the membrane-based separation process [4]. Therefore, it is necessary to determine the effect of NaOCl treatment on the zeta-potential (ZP) of the membranes, especially that the prepared membranes need to have a more negative surface charge to promote electrostatic repulsion with the negatively charged foulants [29] or to be neutral to be fouling resistant at a wide range of conditions. Measurements were carried out at pH values ranging from 4 to 10 as shown in Figure 7. All membranes have negative values of ZPs at 6–8 pH range, which is the most favored range in membrane-based separation applications. Neat PES and PES-T904 became less negatively charged after treatment with NaOCl which would decrease the repulsion with pollutants during the filtration process. The decrease of negative charge after NaOCl treatment is presumably explained by the chemical interaction of NaOCl with N-derived functional groups of T904 (e.g., leading to NH_2) producing a more positive charge on the membrane surface. In the case of PES-PVP and PES-P31R1, the treatment with NaOCl increased the negative charge of treated membranes so it is assumed that these membranes have more resistance for fouling (when compared with the same membrane composition but with lower negative ZPs) [22]. In the case of PES-PVP and PES-P31R1, the treatment with NaOCl caused more resistance for fouling by increasing the negativity of ZP in the studied pH range (i.e., more resistant to negatively ionizable foulants as BSA). To sum up, treatment of the fabricated membranes with NaOCl did not deteriorate their surfaces. However, it amended their fouling resistance by increasing the surface ZP values.
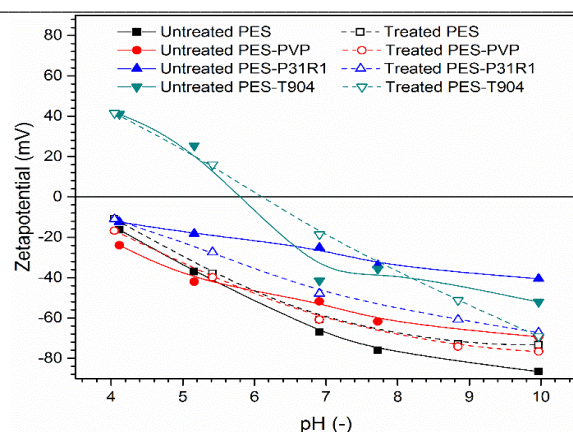
Figure 7. ZPs of untreated and treated membranes.

Figure 8. Tensile strengths of untreated and treated membranes.

The effect of NaOCl on the tensile strength

The wide application of UF membranes in SMBR is due to the feasibility of UF technology of reliable physical disinfection with an adequate price [30], where the presence of pores facilitates the hydraulic cleaning step. The hydraulic cleaning is performed at a frequency of 30 min to 1 h with the same applied pressure as the pressure used in the wastewater treatment itself [9]. Accordingly, during routine filtration work, the membrane module is exposed to continuous stress from alternating applied pressures (TMPs) of 3–4 bars, which results in gradual aging and eventual loss of integrity of UF membranes [31]. Subsequently, damage to membrane integrity decreases filtrate quality and limits the lifetime of polymeric membranes used in SMBR. Therefore, the effect of NaOCl as a cleaning agent is studied in this work. The presented values are the average tensile strengths values of four tested samples from each prepared membrane. The average tensile strength values of untreated and treated membrane samples are depicted in Figure 8. Generally; modified membranes have lower tensile strength than neat PES membranes. This may be attributed to the macrovoids structure formed as a result of the presence of pore formers (i.e., PVP, P31R1, and T904) in dope solution. Furthermore, the tensile strength is decreased after treatment with NaOCl solution for all tested membranes which might be accredited to the intrinsic property of the polymer and/or the difference in pore structure after NaOCl treatment.
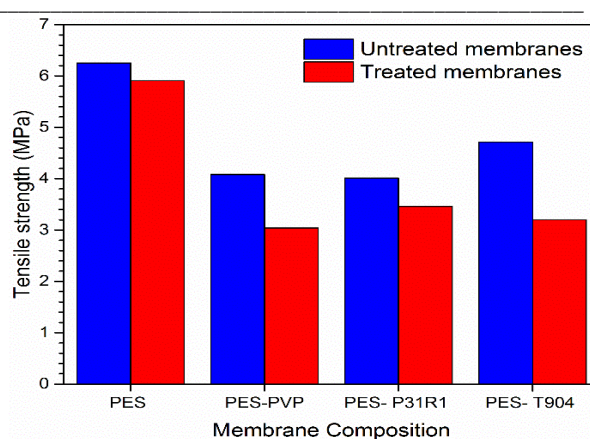
The effect of NaOCl on the performance of membranes

In this section, the influence of NaOCl on membrane permeability was evaluated by deionized water filtration. Moreover, BSA, as a typical foulant in domestic wastewater, was used to test the sieving properties of membranes after soaking in NaOCl solution.

Effect on the hydraulic permeability

Figure 9 depicts a comparison for PWP between treated and untreated membranes at the maximum the time of experiment (2 h). Water permeance ranged from ~2 to 117 L m^{-2} h^{-1} bar^{-1} in case of untreated membranes and increased dramatically to be in the range of ~12 to 255 L m^{-2} h^{-1} bar^{-1} for treated membranes because of increasing pore size and surface porosity (Figure 3 and Table 4). It is also worth noting that the effect of NaOCl treatment was more pronounced in the modified membranes than neat PES ones because wider pores, as well as more surface porosity were observed in modified membranes relative to neat PES after the treatment (Figure 3 and Table 4). Consequently, the increment of PWP for treated PES-PVP, PES-P31R1, and PES-T904 membranes is higher than that of PES alone.
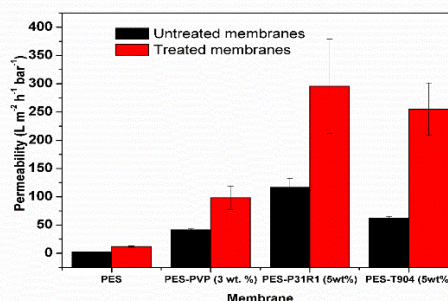

Figure 9. Hydraulic water permeabilities of untreated and treated blended membranes. Permeability was

measured after 2 h of operation at 1 bar applied pressure.

Effect on the BSA rejection

Figure 10 depicts the performance of the membranes towards the BSA rejection before and after soaking in NaOCl solution. All untreated membranes have relatively high BSA rejection values compared to the treated membranes except the PES-P31R1 membrane. This can be explained by the increase in the pore size effect. In the case of treated PES-P31R1 membrane, the high BSA rejection compared to untreated one can be attributed to the significant increase in the surface negativity upon NaOCl treatment, as well as the increment of hydrophilicity (i.e., presence of hydration layer which prevents part of the BSA molecule to approach membrane surface). The effect of NaOCl on the BSA rejection of membranes is lower than its effect on PWP. Consequently, this will reduce the operating pressure after cleaning and hence reducing the operating cost as stated previously in the literature [7].
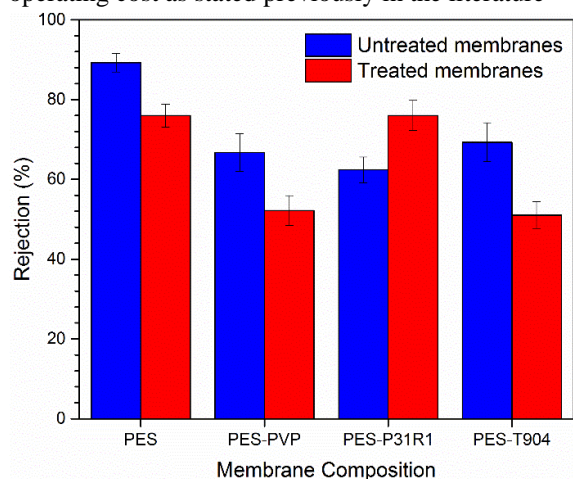

Figure 10. BSA rejections via untreated and treated blended-PES membranes.

Conclusions

It was expected that long exposure to sodium hypochlorite (400 mg L^{-1} Cl_2-dose/10 days) may cause a drastic change for the ultrafiltration membranes prepared from PES using different hydrophilic polymeric additives. However, the prepared blended membranes in this study showed a withstanding behavior against NaOCl treatment as proved from FTIR spectroscopy results. The surface charges of treated membranes were more negative than those of untreated membranes (except for PES-T904), which provides more resistance against negatively charged foulants. In addition, the tensile strength after treatment showed a slightly decreasing trend when compared to untreated membranes. Water

permeance ranged from ≈2 to 116 L m^{-2} h^{-1} bar^{-1} and from 12 to 254 L m^{-2} h^{-1} bar^{-1} for untreated and treated membranes, respectively, as a result of increasing barrier porosity pore size, which had also been proven by SEM analyses. Rejection of BSA as test protein ranged from 66% to 89% and from 51% to 76% for untreated and treated membranes, respectively. Conclusively, the treated membranes posed stability of their ultrafilter properties against harsh cleaning conditions. Thus, the obtained data also confirms the stability of the hydrophilic polymeric modifiers and their integration into the PES membranes against NaOCl treatment.

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