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Enhancing the anti-fouling property of the SWRO membrane through the surface coating with the styrene-PEGA copolymer

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ABSTRACT

Polyamide-based reverse osmosis membranes have been used as a wastewater treatment process in recent years. However, natural organic materials present in the filtration medium cause severe membrane fouling problem, which makes the system less competitive. It is well known that membrane fouling can be influenced by the surface property of the membrane — surface morphology, chemical composition, surface charge, etc. To introduce hydrophilic materials on the membrane is one of the promising modification methods to mitigate membrane fouling. In this study, we investigated the effect of amphiphilic comb polymer coating layer on anti-fouling property of seawater reverse osmosis (SWRO) membranes. Styrene–PEGA amphiphilic copolymer was synthesized by a free radical solution polymerization method. The chemical structure and properties of the synthesized styrene–PEGA copolymer were determined by Fourier transform-infrared spectroscopy (FT-IR), atomic force microscopy (AFM), and ξ-potential. Obtained copolymer was coated on the membrane surface via a simple dipping method. The performance of the coated membrane was evaluated in a cross flow mode. The anti-fouling property of the surface coated membrane was investigated using model foulant solution filtration. Bovine serum albumin was used as a model foulant. The modified membranes were less fouled than pristine RO membranes, and recovered 95% of its initial flux after hydraulic cleaning.

Keywords: Styrene–PEGA copolymer; Desalination; Bio-fouling; Surface modification; Anti-fouling.

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1. Introduction

Pressure driven reverse osmosis (RO) has been widely used in the field of water desalination, ultra-pure water production, and wastewater treatment. The thin film composite membranes for RO are the membranes typically consistijng of an ultra-thin polyamide (PA) active layer and porous, non-selective support layer [1–3]. In the TFC membranes, the active layer is the key component, which controls the separation property of the membrane, while the porous support layer gives the mechanical strength needed [4,5].

However, fouling is one of the significant problems in RO application. Several approaches have been developed to mitigate membrane fouling including pretreatment, developing new types of membranes [6–8], and surface

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modification [9–12]. Surface modification is generally classified into surface coating, grafting hydrophilic monomers, blending with hydrophilic polymers. It is very difficult to control the reaction between the solid surface of the membrane and liquid monomer. So grafting method often results in irregular coverage of the reactant on the membrane surface [13,14]. Blending technique is often attempted to fabricate the bulk properties of the membrane. But blending technique typically degrades the desirable filtration performance of membranes [4,6,8,22].

The amphiphilic comb-like polymers with polyethylene oxide (PEO) side chains have been widely used in surface modification. The amphiphilic comb-like polymer is designed so that the relatively hydrophobic backbone provides an adhesion force with the membrane surface and stability in the aqueous system, while hydrophilic side chains form a dense PEO brushing layer. PEO brushes can prevent adsorption of foulant, following the steric repulsion mechanism. In this study, we synthesized styrene-PEGA comb-like copolymer to modify the surface of a commercial seawater reverse osmosis (SWRO) membrane. The incorporation of styrene moieties in the copolymer was expected to provide a site for hydrophobic interaction by its aromatic ring [15]. Also the solubility of the copolymer can be controlled with manipulating the composition of the styrene site. Thus we could obtain a copolymer which was not soluble in water but soluble in volatile solvent.

The chemical composition of the copolymer and surface morphology of the coated membrane were investigated using Fourier transform infrared spectroscopy (FT-IR) and atomic force microscopy (AFM). The fouling experiment was performed with model foulant solution.

2. Experiments

2.1. Materials

Seawater reverse osmosis membranes (SHN) were obtained from Woongjin Chemical Co., Ltd. Styrene, poly(ethylene glycol) acrylate (Mn 375 g/mol), bovine serum albumin (BSA), benzoyl peroxide (BPO) were purchased from Aldrich Chemical (Korea) and used as received. Toluene, ethanol, petroleum ether, methanol were purchased from Samchun Chemicals (Korea) and used without further purification.

2.2. Synthesis and characterization of styrene–PEGA copolymer

Styrene–PEGA copolymer was synthesized by free radical polymerization. Styrene (23.5 g), PEGA (56.5 g) and BPO (0.8 g) were dissolved in toluene (20 g). Toluene (300 g) in the 1000 mL 4-neck round bottom flask was placed in the water bath and preheated to 95±1°C under nitrogen atmosphere and gently stirred for 30 min. Monomer solution was added drop-wise to the reaction mixture using a dropping funnel for 3 h. Polymerization was allowed to proceed for 20 h in refluxing conditions.

The resulting styrene–PEGA copolymer was precipitated in 1:3 mixture of methanol/petroleum ether solution and dissolved in ethanol again. This procedure was repeated at least 3 times to obtain pure styrene–PEGA copolymer. After purification, the polymer was dried under vacuum at room temperature for 24 h. The obtained copolymer was characterized by 1H NMR in dimethylsulfoxide using a 600-MHz high-resolution NMR spectrometer (AVANCE 600 FT-NMR, Bruker, Germany). Styrene–PEGA copolymer was also characterized using a Midac Nicolet Magna 550 series II FT-IR.

2.3. Preparation of surface modified SWRO membranes

The SWRO membranes were rinsed in a fresh deionized water bath for at least 24 h to remove glycerin they were treated with to protect the pore of the support layer. In this study, a surface coating layer was introduced via a simple dip-coating method. To avoid any harmful effects on the membrane surface, volatile and non-toxic solvent was needed. Finally, ethanol was used as the solvent of the coating solution. 1 g of dried copolymer was dissolved by stirring in 1000 g of ethanol. The surface of the membranes taken out of DI water was gently wiped off before coating process to remove excess amount of water. After the polymer had been dissolved completely in ethanol, the SWRO membranes were dipped in the solution for 1 min. The immersed membranes were taken out of the solution and pressed out to confirm a uniform coating layer. The coated membranes were kept in fresh DI water before the filtration experiment.

2.4. Surface characterization of modified membranes

Atomic force microscopy (XE-150, PSIA, Co.) was used to quantify the roughness of the SWRO membranes. Images were obtained in air at room temperature on dry, unused membrane samples. Since the membrane surface is very sensitive, tapping mode was preferable [13]. AFM was operated in tapping mode using silicon nitride cantilever. AFM images were recorded over an area of 5 μm ×5 μm.

2.5. Flux decline (fouling) study using model fouling solution

SWRO membranes were evaluated using a cross-flow membrane filtration unit. The effective area of the RO membrane was 30 cm^2. Before the filtration test, the SWRO membranes were compacted using DI water for at least 1 h under 900 psi, and the temperature was adjusted to 25±1°C. The initial performance of the membrane was obtained at 800 psi using 35,000 ppm of bay salt solution. The flow rate was maintained at 4 L/min, and the reservoir volume was 20 L. Conductivity of the feed and permeate was measured to obtain rejection of the membrane. A conductance meter (Orion model 115) was used to measure conductivities of both feed and permeate. Water flux and rejection were obtained using the following equations:

$$J_w = \frac{V}{A \cdot t} \tag{1}$$

$$R(\%) = (1 - \frac{C_{\text{per}}}{C_{\text{feed}}}) \times 100 \tag{2}$$

where J_w is the pure water flux (L/m^{2}h), V is the permeate volume (L), A is the membrane area (m^2), t is the time (h), C_{per} and C_{feed} mean conductance of the permeate and feed, respectively.

BSA was used as a model protein to evaluate the antifouling property of the SWRO membrane. After measuring the initial water flux and rejection, 1 g of BSA was added to the reservoir. The flux was measured for 20 h, and the membrane was cleaned by washing with DI water for 15 min at low pressure (70 psi). The foulant solution flux was measured again under the same conditions as mentioned above. Flux recovery (FR) was calculated according to the following equation:

$$\text{FR } (\%) = \frac{J_w}{J_i} \times 100 \tag{3}$$

where J_i is the initial water flux, J_w is water flux after membrane cleaning.

3. Results and discussion

3.1. Styrene–PEGA copolymer identification

FT-IR measurement was performed to confirm the successful polymerization reaction. Fig. 1 shows the FT-IR spectrum of styrene–PEGA copolymer. The polymer shows an absorbance band at 1724.2 cm^{-1}, which is the characteristic band for carboxyl group. This peak is expected for C=O vibration in an ester group. Intense peaks at 1098.6 cm^{-1} and 2866.5 cm^{-1} are ascribed to C–O and the CH$_2$ symmetric stretches of PEG, respectively [14]. The sharp peak at 702.4 cm^{-1} is for aromatic hydrocarbon.

Fig. 2 shows an example of the ^{1}H NMR spectra of the styrene–PEGA copolymer. The characteristic peak at 7.1 ppm corresponds to the hydrogens of the aromatic group (C6H5) in the styrene structure [15]. The signals of methylene protons (denoted in Fig. 2 as c and d) were observed at about 4.4 and 3.7, 3.4 ppm, respectively. They are the characteristics of the PEG chains [16]. Strong signals at 2.5 and 3.3 ppm are from the DMSO. The actual styrene/PEGA molar ratio calculated as styrene : PEGA = C_6H_5 peak area/5 : OCH_2 peak area/2 was 65.8 : 34.5 (mol : mol). The actual PEGA content obtained in this work was lower than the feed composition (60 : 40). It is mainly due to the difference of reactivity of monomers [15]. The styrene–PEGA copolymer had the number average molecular weight (Mn) of 80,000, a weight average molecular weight (Mw) of 190,000, and a polydispersity index (PDI) of 2.4 by gel permeation chromatography.

These observations suggested that the styrene–PEGA copolymer was successfully synthesized.

3.2. Surface zeta potential of SWRO membranes

SWRO membranes were coated by the aforementioned dip-coating method with 0.1–0.4 wt% of the coating solution. Fig. 3 shows the zeta potentials of the SWRO membranes measured at various pHs. All membranes are negatively charged over the whole range of pH. It was found that the charge density on the surface of the unmodified membranes was higher than that of the modified membranes. It is expected that neutral PEG chains lower the charge density on the surface of SWRO membranes [17].

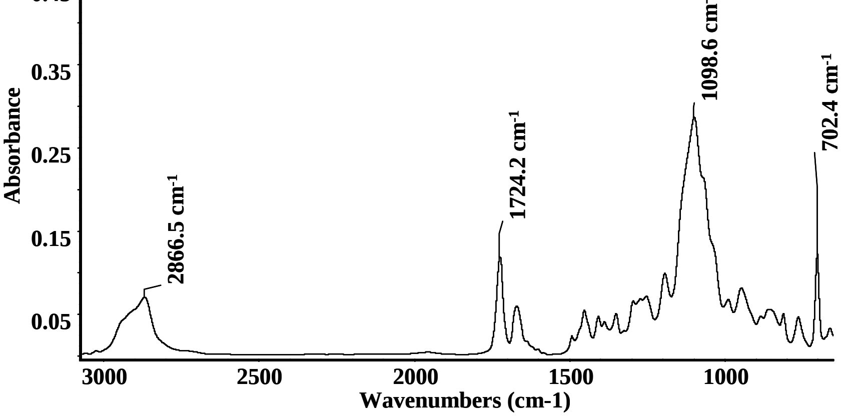

Fig. 1. FT-IR spectrum of styrene-PEGA.

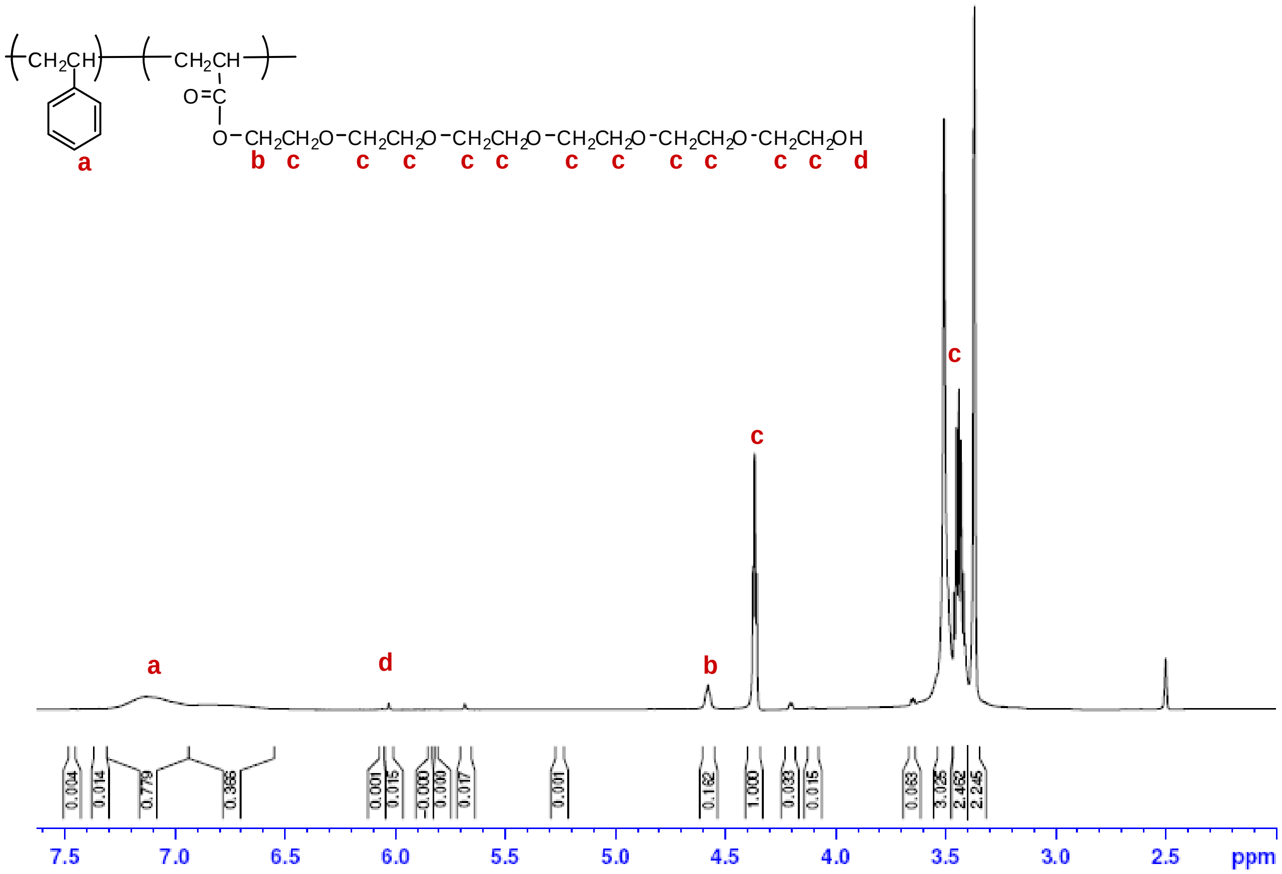

Fig. 2. The 600 MHz 1H NMR spectra of styrene-PEGA copolymer.

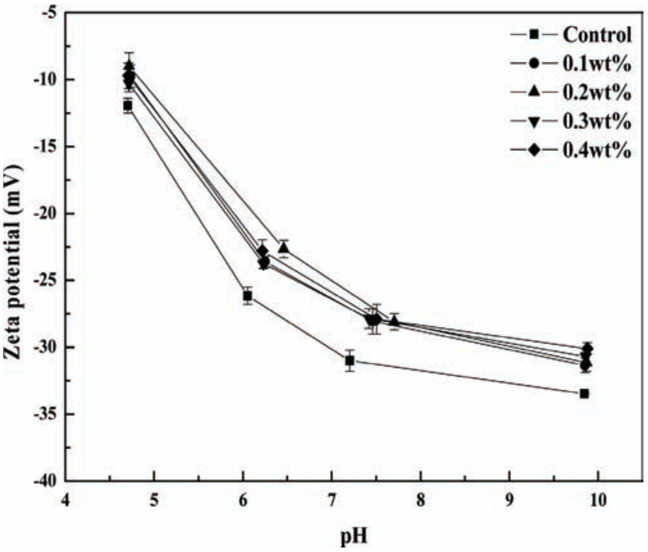

Fig. 3. Zeta potential of styrene-PEGA coated membranes at various pH values.

3.3. *Surface roughness*

AFM technique was also used to characterize the surface of the SWRO membranes. AFM is one of the most commonly used instruments to investigate surface topology [18,19]. The three-dimensional AFM images of the modified and unmodified membranes are shown in Fig. 4. All AFM images were obtained in the air using dried membranes. A typical nodular (ridges and valleys) structure is observed in the figure. Although no obvious difference was observed, the roughness slightly decreased in the order of SWRO, $0.1 < 0.2 \approx 0.3 < 0.4$. When the coverage on the surface was insufficient, increasing roughness was observed [14]. In our experiment, the surface topology was almost unchanged during the coating process. A further experiment was conducted to elucidate the effect of the coating layer on the membrane performance. It is considered that the difference in the performance between the modified and unmodified membrane can produce a convincing evidence of the surface coating layer indirectly.

3.4. *Effect of coating layer on filtration performance*

Water permeation measurement was carried out to characterize the permeation properties of the modified membranes. Filtration performance of the membrane was obtained at 800 psi using 35,000 ppm of bay salt solution, and the solution temperature and flow rate

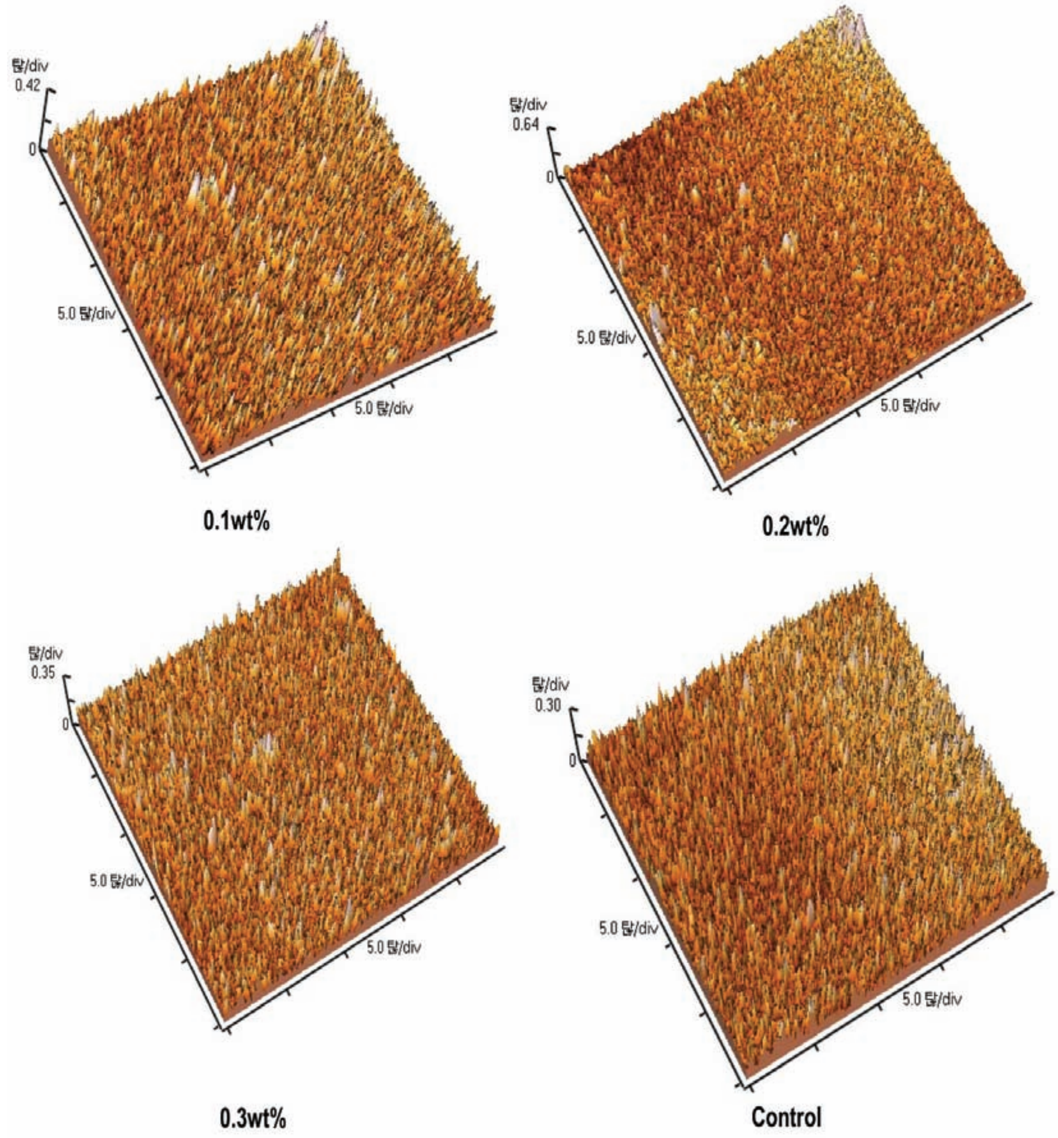

Fig. 4. AFM images of the SWRO membranes (a) 0.1 wt% coated membrane (b) 0.2 wt% coated membrane (c) 0.3 wt% coated membrane (d) untreated membrane.

were adjusted to 25±1°C and 4 L/min respectively. Fig. 5 shows the results of the performance test for the non-treated and coated SWRO membranes. It can be seen that with increasing the concentration of the coating solution, the water flux decreases. Almost 20% of fluxes decrease when treated with 0.3, 0.4 wt% of the coating solution. Good operating practice calls for chemical cleaning of the membranes if either normalized permeate flow decreases by 10%, feed channel pressure loss increases by 15% or normalized salt rejection decreases by 10% from the initial conditions during the first 48 h of plant operation [1]. So it was thought that the modified membrane can be applicable in desalination industry.

3.5. Fouling experiments

To investigate the fouling resistance of the prepared membranes, protein solution permeation process was conducted. It is well known that the nonspecific adsorption of protein on the membrane surface is the main cause for membrane fouling [20]. 50 ppm of BSA in bay salt solution (35,000 ppm) was used as a model foulant solution. The absolute fluxes of the coated membranes are compared in Fig. 6a, and normalized according to the flux normalization method suggested by Belfort and coworkers (Fig. 6b) [21]. The initial fluxes of neat and 0.1, 0.2, 0.3, 0.4 wt% solution treated SWRO membranes decreased

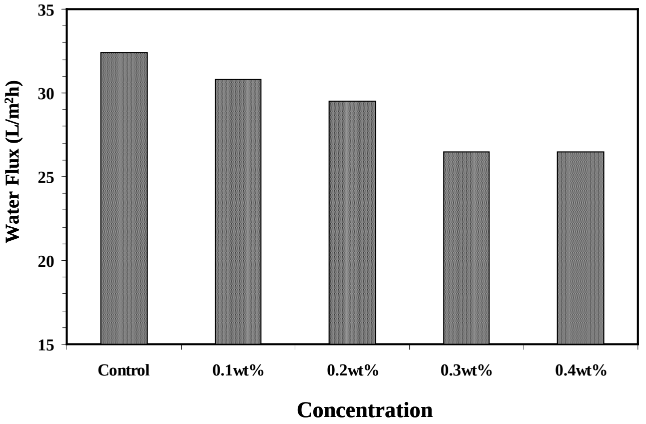

Fig. 5. Water permeability of the SWRO membranes (35,000 ppm aq. bay salt solution, 800 psi, 25±1°C, 4 L/min).

from 32.4 to 30.8, 29.5, 26.5, 26.5 L/m^{2}h, respectively. The flux decline shows a slow decline over the course of filtration (~15% after 24 h). About 24 h later, the styrene–PEGA 0.1 wt% coated RO membrane allowed a higher flux than the unmodified one. The flux decline values of the styrene–PEGA 0.3 and 0.4 wt% coated membranes after 24 h were 90.1 and 89.8%, respectively. But their absolute fluxes are still lower than those of the unmodified membrane. It is mainly due to the hydraulic resistance increased by the additional surface coating layer [10].

Fig. 7 shows flux recovery values obtained after hydraulic cleaning. All of the modified membranes show ~95% recovery after rinsing with DI water. The high flux recovery results from the styrene–PEGA coated membranes were due to the increased hydrophilicity and immobilization of flexible PEG side chains on the membrane surface.

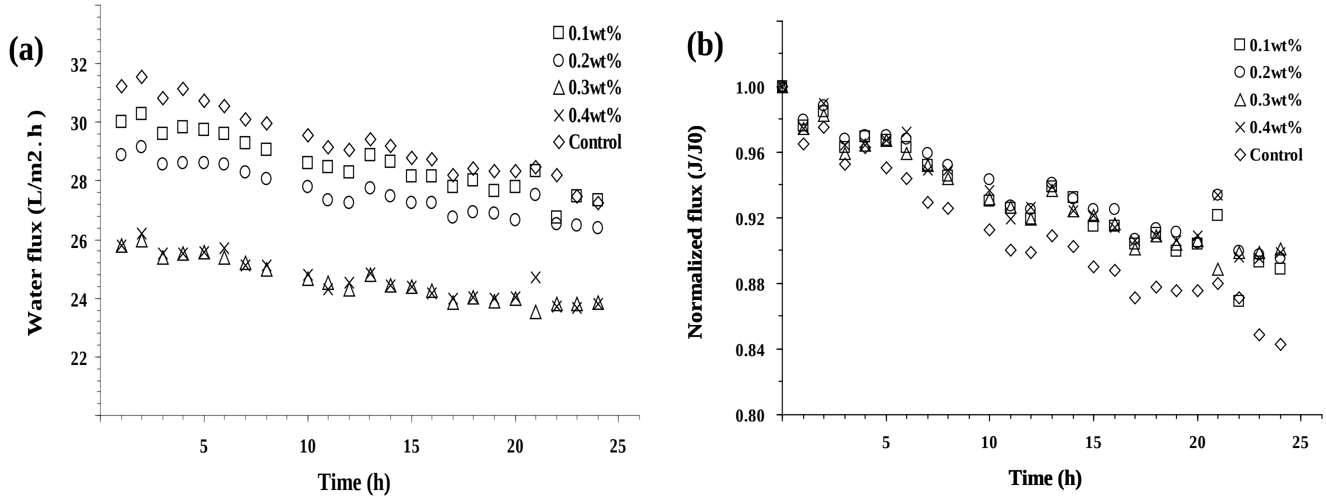

Fig. 6. Decline in the permeation flux of the SWRO and styrene-PEGA coated membranes during cross-flow filtration (BSA 50 ppm, 35,000 ppm aq. bay salt solution, 800 psi, 25±1°C, 4 L/min); (a) absolute flux; (b) normalized flux (J/J_0).

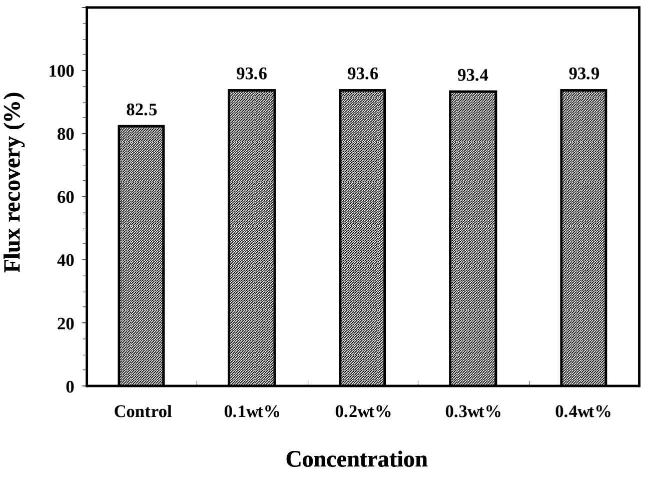

Fig. 7. Flux recovery of membranes after hydraulic cleaning (deionized water, 70 psi (5 kgf/cm^2), 25±1°C, 4 L/min, 15 min).

4. Conclusions

In this study, we synthesized styrene–PEGA comb like copolymer by free radical polymerization. The chemical structure of the obtained polymer was characterized with FT-IR and ^{1}H NMR spectra. The surface properties of the modified membranes indicated that the coating layer was formed via dip-coating method. After the surface modification, the initial fluxes of the modified SWRO membranes decreased slightly. During the fouling experiment with BSA solution, the modified membranes were less fouled than the unmodified membranes and showed higher flux recovery after hydraulic washing. Further studies on durability of coating layers should be taken to confirm their ability of enhancing anti-fouling properties.

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