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Development of fouling-resistant RO membranes using PEGA macromer

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ABSTRACT

Reverse osmosis membranes are widely used in many industrial fields including seawater desalination, ultrapure water production, medical and food processing. But the decrease in performance of RO membranes in water reuse and purification systems due to fouling is one of the concerns. In this study we investigated the anti-fouling property of PEGA homopolymer-coated RO membranes. PEGA homopolymer was synthesized by a free radical solution polymerization method. PEGA-coated membrane was prepared via a simple dip-coating method. Glutaraldehyde was used as a cross linker in our experiment. After chemical modification, membrane surface properties were characterized using X-ray photoelectron spectroscopy (XPS), water contact angle measurement, atomic force microscopy (AFM). Surface modified membranes showed lower roughness, more hydrophilicity compared to unmodified RO membranes. Fouling tests were conducted in the cross-flow mode using various foulants, including bovine serum albumin (BSA), humic acid, and *E. coli* broth. As a result, surface modified membranes exhibited better anti-fouling properties compared to unmodified RO membranes. After physical cleaning, the modified membrane recovered almost 100% of its initial filtration performance.

Keywords: Polyethylene glycol acrylate (PEGA); Reverse osmosis; Biofouling; Surface modification; Anti-fouling

1. Introduction

Membrane filtration processes have been applied to many fields, especially wastewater treatment and removal of natural organic matter from water, food and chemical processing. It is a simple physical process that can effectively eliminate suspended solids, bacteria and viruses without the generation of toxic byproducts. Membrane filtration is generally classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Especially RO has attracted a significant attention of researchers as an economic process in the field of desalination [1].

Operational problems in membrane installations for RO can be caused by fouling. All raw waters contain biotic debris such as bacterial cell wall fragments and microorganisms such as bacteria, fungi, algae, viruses and higher organisms such as protozoa. Due to the concentration

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polarization, dissolved organic nutrients are concentrated at the membrane surface [2]. Microorganisms entering an RO system therefore find ideal growth conditions resulting in possible formation of a biofilm [3]. Fouling will lead to higher operational costs — higher energy demanded, increase of cleanings and reduced lifetime of membrane elements [4]. It is generally known that physicochemical membrane surface properties — roughness, electrostatic charge, and hydrophilicity — are the main factors influencing membrane fouling [5]. A hydrophobic adsorption of microbial products such as extracellular polymeric substances (EPS) on membrane surfaces plays a key role in membrane fouling, hydrophilic modification of the polymeric membrane surface may be one of the methods for mitigating fouling [6].

In this study, we synthesized PEGA homopolymer by a free radical solution polymerization method. The obtained polymer was used as surface coating material to enhance anti-fouling property of reverse osmosis membranes. Glutaraldehyde (GA) was used to prepare a stable coating layer. The surfaces of the modified membranes were characterized by X-ray photoelectron spectroscopy (XPS), water contact angle measurement and atomic force microscopy (AFM). The objective of this study is to investigate the fouling-resistant property of the RO membranes. Fouling experiments using various model organic foulants — BSA, humic acid, E.coli — were conducted with a cross-flow cell unit, and fouling resistance was evaluated.

2. Experiments

2.1. Materials

Reverse osmosis membranes (RE8040 BE) were purchased from Woongjin chemical Co., Ltd. Poly(ethylene glycol) acrylate (Mn~375 g/mol), bovine serum albumin (BSA), azobisisobutyronitrile (AIBN), sodium citrate, KH_2PO_4, $CaCl_2{\cdot}2H_2O$, $NaHCO_3$, $MgSO_4{\cdot}7H_2O$, ammonium chloride were purchased from Aldrich Chemical, Korea Ltd. (Korea) and used as received. Tetrahydrofuran (THF), petroleum ether, methanol, HCl, NaOH were purchased from Samchun Chemicals (Korea) and used without further purification.

2.2. Synthesis and characterization of PEGA homopolymer

PEGA homo polymer was synthesized by free radical polymerization. PEGA (80 g) and AIBN (1.6 g) were dissolved in THF (20 g) in a dropping funnel. THF (300 g) in the 1000 mL 4-neck round bottom flask was placed in the water bath and preheated to 66±1°C under nitrogen atmosphere and stirred gently for 30 min. Monomer solution was added drop-wise to the reaction mixture for 3 h. Polymerization was allowed to proceed for 12 h in refluxing condition.

The resulting homopolymer was precipitated in methanol/petroleum ether mixture solution and dissolved again in ethanol three times. After purification, the polymer was dried under vacuum at room temperature for 24 h.

2.3. Preparation of surface modified RO membranes

RO membranes were rinsed in a fresh deionized (DI) water bath for at least 24 h to remove glycerin treated to protect the pore of the support layer. To investigate the effect of coating solution concentration on the membrane permeability, 0.005–3% (w/w) of PEGA homopolymer solution in DI water was prepared, subsequently the RO membranes were dipped in the homogeneous coating solution for 1 min. Then the excess amount of the solution was removed. PEGA homopolymer coated RO membranes were cross-linked by the glutaraldehyde solution to enhance the durability of the coating layer [7,8]. The reaction scheme is shown in Fig. 1. The immersed membranes were taken out of the GA solution and dried in the air for a given time. Coated membranes were kept in fresh DI water before performance evaluation.

2.4. Surface characterization of modified membranes

To compare the hydrophilicity of RO membranes, the water contact angle was measured using a sessile-drop technique (Erma Inc., Japan). 1 μl of DI water was dropped onto the membrane surface and observed on the video contact angle system. The surface chemical composition of RO membranes was characterized using X-ray photo-

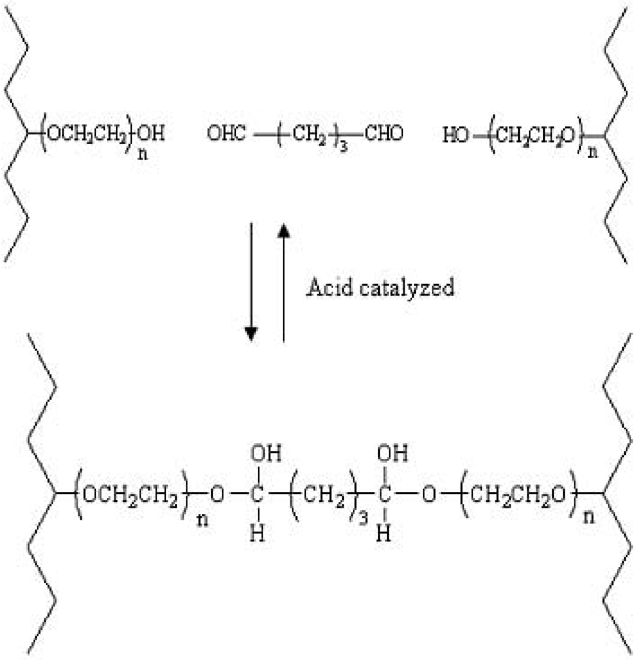

Fig. 1. Schematic diagram of acetal linkage formation.

electron spectroscopy (XPS) (Sigma Probe, Thermo VG, UK). Atomic force microscopy (XE-150, PSIA Co.) was used to measure the roughness of the RO membranes.

2.5. Membrane filtration experiment

The filtration performance was evaluated using a cross-flow membrane filtration unit. The test membrane was placed between the top and bottom plates and was held tightly by an o-ring. The effective area of the RO membrane was 15.4 cm^2.

Before the filtration test, the RO membrane was compacted using DI water at least for 1 h under 225 psi, at 25±1°C. The initial performance of the membrane was obtained at the same condition. The water flux value was obtained using the following equation:

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

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), and t is the time (h).

Conductivity of the feed and permeate was measured to obtain the salt rejection value. Electrical conductance of the permeate and the feed was measured using a conductance meter (Orion model 115). Rejection was calculated by the following equation:

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

Anti-fouling behavior of the RO membranes was investigated using BSA, humic acid, and *E. coli* broth. The *E. coli* was grown in Luria-Bertani (LB) medium (10 g of tryptone per liter, 5 g of yeast extract per liter, and 5 g of NaCl per liter) that was used for flask cultures. The *E. coli* was cultured in a 1-L flask containing 250 mL of LB medium in a shaking incubator at 37°C and 200 rpm for 24 h.

The fouling performance was measured with 100 ppm of BSA, Humic acid 30 ppm + $CaCl_2$ 30 ppm solution of humic acid, and *E. coli* broth having a 0.34 optical density at 225 psi, pH 7.2, 25°C, cross-flow rate was 3.0 l/min. After the fouling experiment, the cake layer formed on the surface of the RO membrane was removed using ultrasound sonicator (Power Sonic, Hwashin Instrument Co., Ltd.) to calculate the flux recovery value:

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

where J_i is the initial water flux, J_w is water flux after the fouling layer was washed with ultrasonication treatment.

3. Results and discussion

3.1. Surface characterization of PEGA homopolymer-coated RO

The XPS results are listed in Table 1. It shows that the N/O value was decreased when the surface of the RO membrane was coated with PEG homopolymer. Since PEGA homopolymer was only comprised of C, O, H, the higher N/O ratio means incorporating of PEG on the RO membrane surface.

Further investigation was conducted with C1s core level (Fig. 2, Table 2). It is noteworthy that the intensity of C–O stretching peak was slightly increased with the surface coating, meanwhile the intensity of CONH peak

Table 1
Elemental surface compositions for RO and PEGA homopolymer coated membranes

Membranes	Atomic percentage (%)			Atomic ratio		
	C1s	O1s	N1s	N/O	O/C	N/C
RO	73.39	16.85	9.77	0.58	0.23	0.13
Only PEGA homopolymer coated membrane	71.72	20.26	8.02	0.40	0.28	0.11
PEGA homopolymer + GA coated membrane	72.58	19.52	7.90	0.40	0.27	0.11

Table 2
Fraction of C1s in various chemical structures

Group assignment	Peak position (eV)	Relative fraction(%)		
		RO	Only PEGA 0.1 wt%	PEGA 0.1 wt% + GA 0.01 wt%
CH,–C–C–,–C=C–	285.0	58.97	52.69	55.34
–C–C–	283.9	4.10	6.25	5.76
C–O,C–N	286.16	15.32	21.26	19.35
CONH	286.95	10.47	8.25	6.62
COO,COOH	288.27	11.13	11.54	12.94

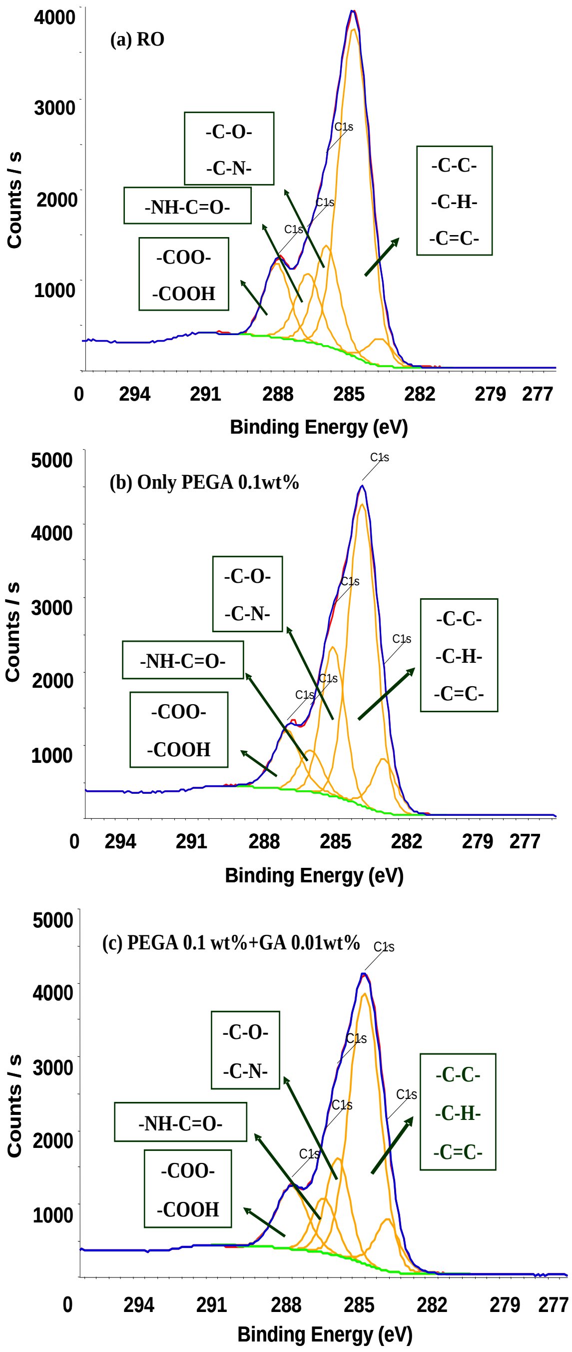

Fig. 2. XPS C 1s core-level spectra of the membranes. (a) RO membrane (b) only PEGA 0.1 wt% coated, (c) PEGA 0.1wt% + GA 0.01 wt% coated membrane.

originated from the polyamide skin layer of the RO membrane was decreased. From these results we confirmed that PEGA coating layer had been effectively introduced on the RO membrane surface.

3.2. Contact angle measurements

The relative hydrophilicity of the membrane can be obtained by water contact angle measurement. As can be seen in Fig. 3, after treatment with GA solution only, the contact angle increased slightly. It is mainly due to the hydrophobic nature of GA [7,8]. But only PEGA 0.1wt% treated membrane shows the lowest value compared to others, the water contact angle decreases in the order of only PEGA0.1 (Fig. 3d) > PEGA 0.1 + GA (Fig. 3a) > RO (Fig. 3b) > GA(Fig. 3c).

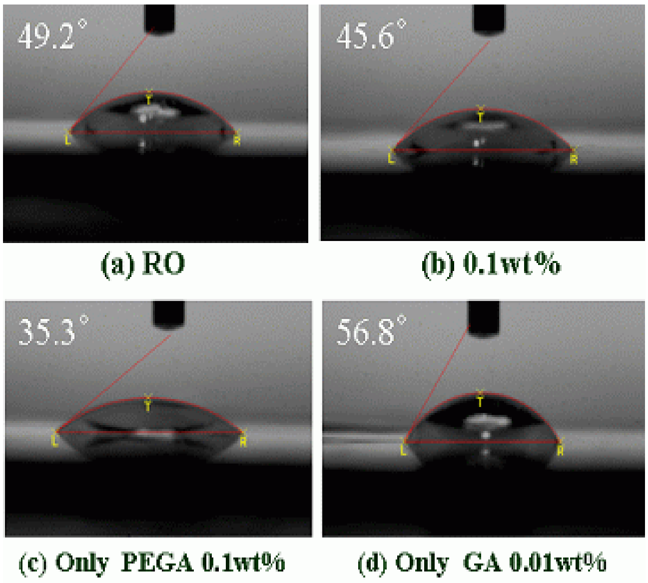

Fig. 3. Water contact angle and digital images of RO and modified RO membranes.

It is considered that the added cross-linking agent formed a denser coating layer and consumed hydrophilic –OH group of the coating layer [8]. The effect of GA on the coating layer will be described in greater detail in section 3.4.

3.3. Surface roughness

Due to the tendency to “valley clogging” [9], it is generally known that a rough membrane surface would lead to water flux decline during the filtration process. AFM image can provide information about the surface topology [10] (Fig. 4). Ridges and valleys structure is observed in the figure. As can be seen that the surface roughness decreased when the PEGA coating layer was introduced. The average roughness of the RO (Fig. 4a) is 255.42 nm and coated membrane (Fig. 4b) is 125.06 nm. Also in Fig. 4c and 4d (5 μm × 5 μm AFM image of RO and PEGA 0.1 wt% coated membrane, respectively), the average roughness is 170.54 nm for the neat RO membrane and 111.07 nm for the coated membrane. It can be concluded that the PEGA coating layer can make a smoother surface compared to the uncoated RO membrane.

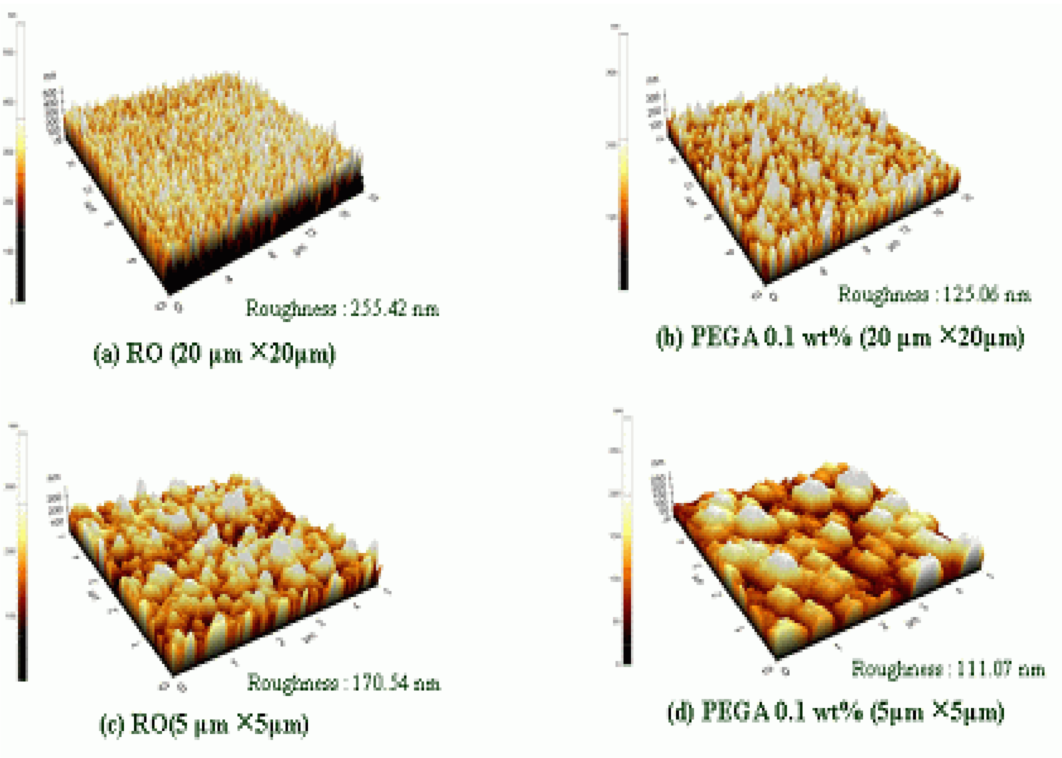

Fig. 4. AFM image of the RO and PEGA 0.1 wt% coated membranes (a) RO (20 μm × 20 μm), (b) PEGA 0.1 wt% (20 μm × 20 μm), (c) RO (5 μm × 5 μm), (d) PEGA 0.1 wt% (5 μm × 5 μm).

3.4. Influence of PEGA and GA concentration on the membrane performance

The effect of GA and PEGA solution concentration on the membrane performance is investigated in this section. The filtration performance of the membrane was obtained at 225 psi using DI water as feed, the solution temperature and flow rate were adjusted at 25±1°C and 3 L/min, respectively. The water flux with increasing coating concentration is illustrated in Fig. 5. In the preliminary experiments, we concluded that at least 40 s were required to exchange the water presoaked in the membrane bulk for the coating solution. So every membrane was dipped in the coating solution for 1 min. The water flux decreased with increasing the solution concentration. From 0 to 0.1, a significant flux decline can be seen. Almost 20% of flux decreased when treated with 0.1 wt% of the coating solution. The flux declined gradually > 0.1 wt% concentration. It is considered that sufficient surface coverage of PEG occurred below 0.1 wt% [10].

Fig. 6 illustrates the effect of GA concentration on the performance of the RO membranes. The concentrations of the aqueous PEGA solution were fixed as 0.1wt %, at pH 3. The RO membranes were first dipped in the aqueous PEGA solution for 1 min, the excess solution was removed subsequently and the membranes were dipped in the GA solution for 30 s. After 10 min of drying, the RO membranes were stored in a fresh water bath. As illustrated in Fig. 6, increasing GA concentration leads to decreasing of pure water flux of the PEGA coated membrane. GA is used as a cross-linker in this study. As shown in Fig. 1, hydroxyl chain end of PEGA reacts with the aldehyde group of GA. So hydrophilic –OH groups are consumed during the cross linking reaction and a denser coating layer formation is expected.

3.5. Fouling of PEGA-coated RO membrane

Fouling behavior of PEGA coated RO membranes were investigated using various model fouling solutions. Figs. 7a and 7b show the flux decline of the PEGA coated membrane during BSA filtration. The neat RO membrane undergoes a rapid flux decline at the beginning of the experiment. About 20% of flux decreases during the first hour. But PEGA 0.1 wt% coated membrane shows only 5% of flux decline. And a lower flux decline rate is shown as PEGA concentration increases. After 20 h, the water flux is reversed, and the flux decline ratio is 28%, 10% respectively. Flux recovery (Fig. 7c) of the RO membrane is 85%. However, PEGA 0.1 wt% coated membrane shows 95.1% of flux recovery.

Fig. 8 illustrates the membrane performance during humic acid filtration. Water flux increases slightly at

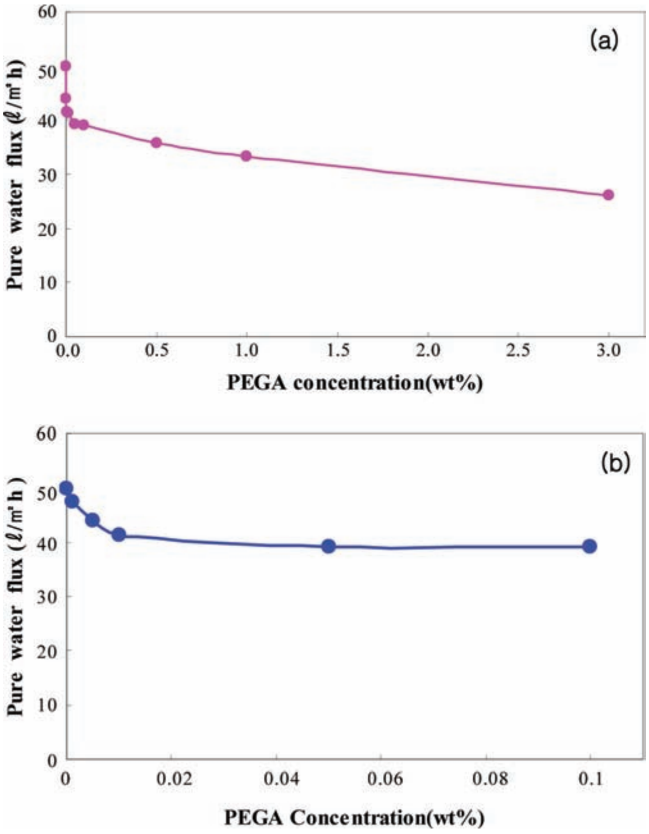

Fig. 5. Flux decline behavior of the RO membrane during cross-flow filtration with DI water as a function of PEGA homopolymer concentration.

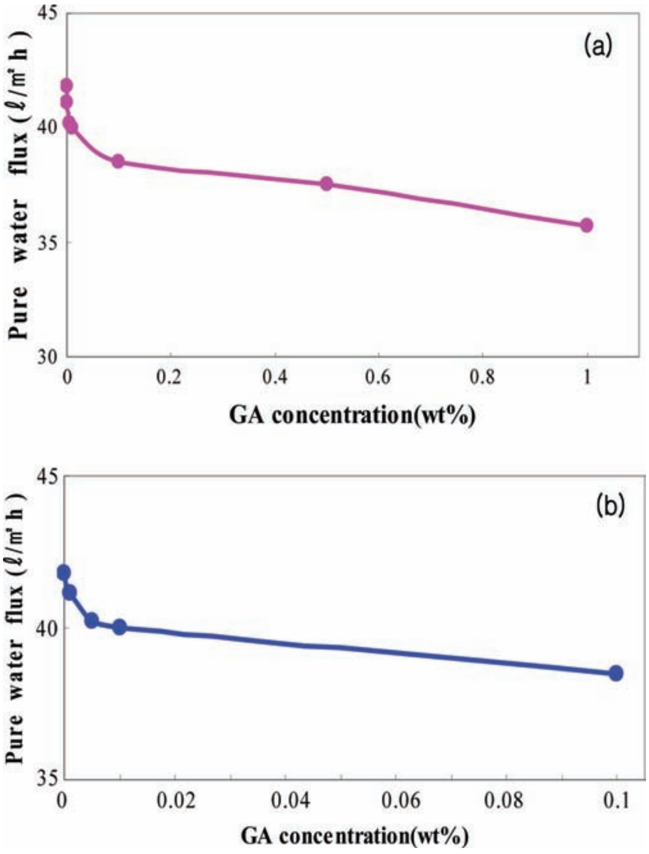

Fig. 6. Flux decline behavior of the RO membrane during cross-flow filtration with DI water as a function of GA concentration.

the beginning of the filtration experiment. The same phenomenon was observed by other researchers [11]. It is explained that hydroxyl groups of humic acid increase the hydrophilicity of the membrane instantly. The PEGA coated membrane shows a better anti-fouling property in this case as well. At the end of the filtration and flux decline ratio of RO and PEGA 0.1wt% coated membrane is 25.9% and 10%, respectively. Flux recovery shows almost the same behavior as in the BSA experiment (Fig. 8c).

To investigate more the anti-fouling property of the PEGA coating layer, an actual microbial cell is used as a foulant. *E. coli* broth was used as a model microorganism in this experiment. As shown in Fig. 9, the initial water flux of the neat RO membrane was higher than that of the PEGA 0.1 wt% coated membrane. About 6 h later, the PEGA 0.1 wt% coated RO membrane was allowed higher flux compared to the unmodified one. The flux decline rate of the coated membrane is much slower than that of the unmodified membrane. 2 days later, both membranes were cleaned using the sonication method. After physically washed, the initial flux of the coated membrane showed almost the same performance as that of the neat RO membrane, and maintained a higher flux value during the second period. The flux recovery of the unmodified membrane is 89.1% for the first step, and 82.8% for the second step respectively. Almost 100% of flux recovery was achieved for the coated RO membrane, which showed an excellent anti-fouling property in our experiment.

4. Conclusions

In this study, the RO membranes were coated with poly(ethylene glycol)acrylate homopolymer and cross-linked using the glutaraldehyde solution to enhance the durability of the coating layer. The surface properties of the modified membranes were studied with XPS, water contact angle and AFM. After the surface modification, the RO membranes showed a lower surface roughness, more hydrophilicity compared to the unmodified ones. The modified membranes showed better performance compared to the unmodified RO membranes during the test with various model fouling solutions. The modified RO membranes recovered almost 100% of their initial water flux after physical cleaning.

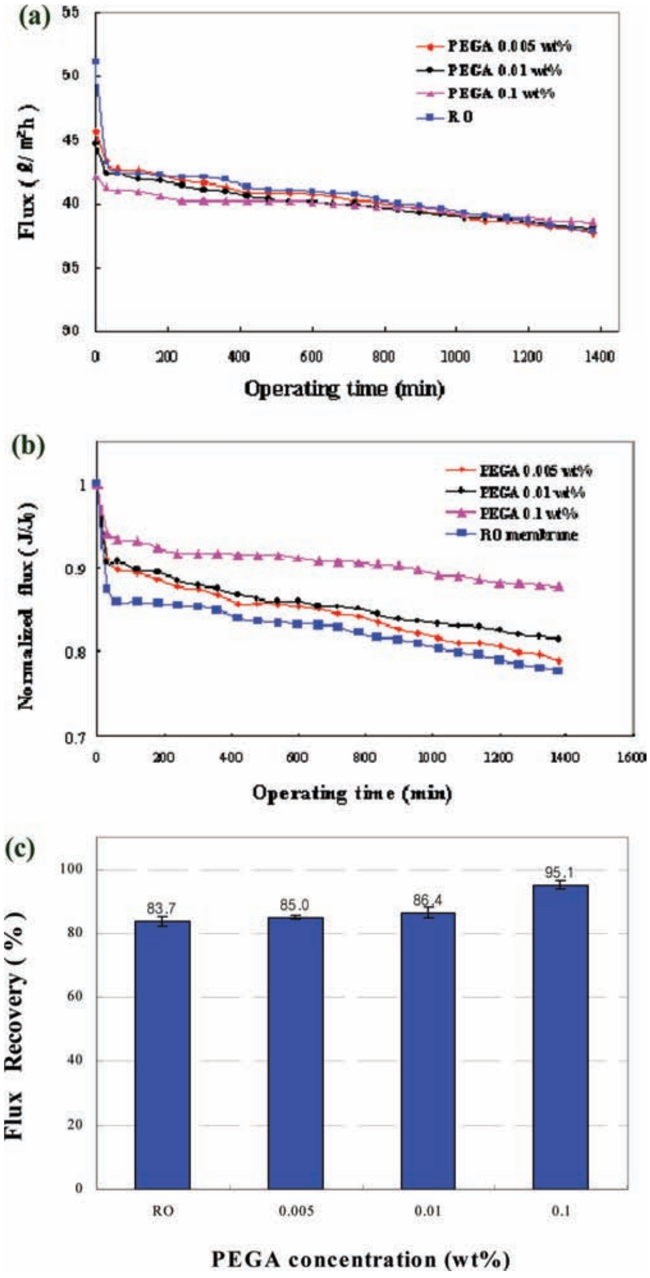

Fig. 7. Permeation flux behavior and flux recovery of the RO and PEGA coated membranes — 100 ppm BSA solution, 225 psi, 25°C, 3.0 l/min (cleaning condition: 60 MHz, 220 W, 1 min).

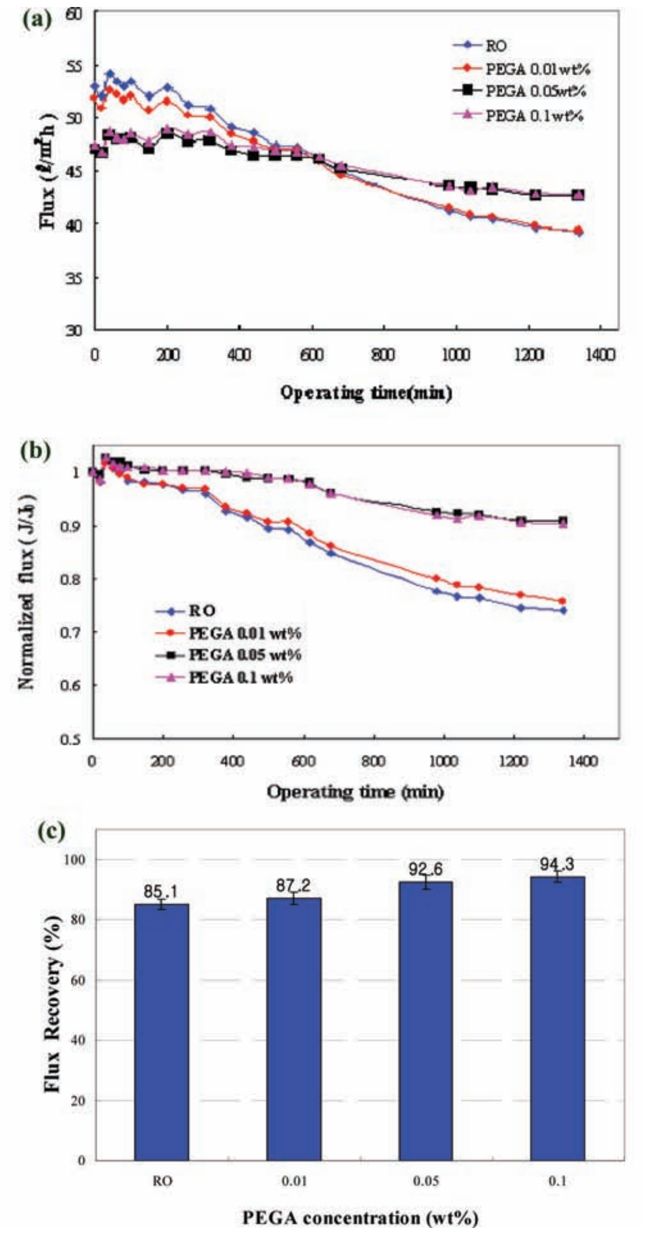

Fig. 8. The permeation flux behavior and flux recovery of the RO and PEGA coated membranes — humic acid 30 ppm + $CaCl_2$ 30 ppm solution, 225 psi, 25°C, 3.0 l/min (cleaning condition: 60 MHz, 220 W, 1 min).

Acknowledgements

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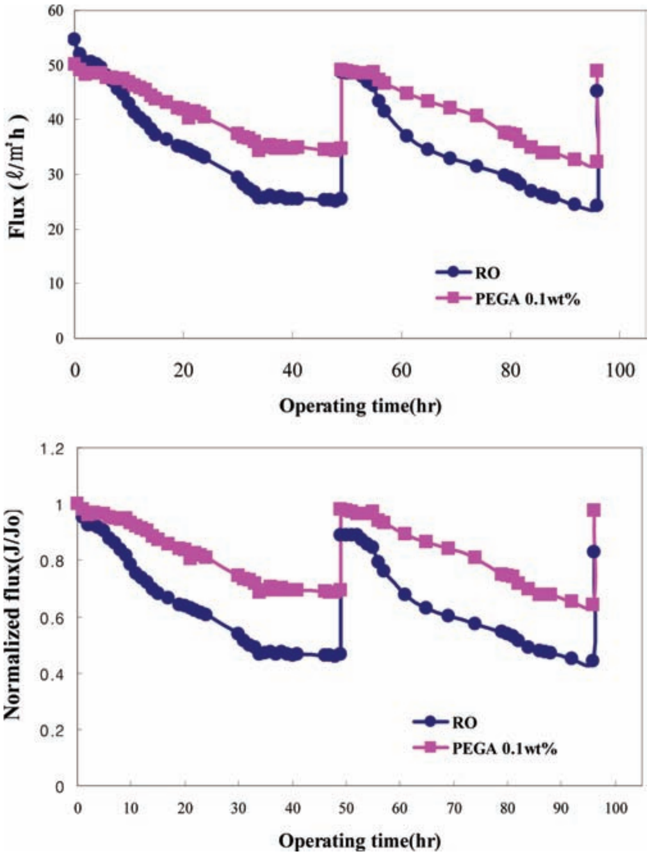

Fig. 9. Decline in the permeation flux of the RO and PEGA 0.1 wt% coated membranes during cross-flow filtration with E. coli solution as a function of operating time.

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