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Surface modification of polyamide membrane with silane compounds and its effect on the performance of reverse osmosis

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ABSTRACT

Thin-film-composite (TFC) membranes based on aromatic polyamides (PAs) are widely used in commercial high-performance reverse osmosis (RO) for the desalination of seawater and brackish water. In this study, surface modification of PA-based RO membranes was performed using silane compounds with various functional groups to improve the performance of membranes (permeate flux and salt rejection). Lab-scale tests demonstrated that the salt rejection of PA-based RO membranes coated with TMOHES (trimethoxy[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]silane) was barely improved despite the hydrophobicity of its epoxy groups, but the permeate flux was significantly improved by using AEAP ([3-(2-aminoethylamin)propyl]trimethoxysilane) due to its hydrophilic amino groups. Based on the results, RO membranes treated with 2.0% AEAP concentration showed the best performance due to their highly improved permeate flux and competitive salt rejection.

Keywords: Permeate flux; Salt rejection; Polyamide membrane; Reverse osmosis; Silane compounds

1. Introduction

Recently, reverse osmosis (RO) has become a popular technology for the desalination of seawater and brackish water. The semi-permeable membrane used in RO eliminates ionic substances dissolved in water and allows pure water to pass through the membrane. Compared to the conventional evaporation method, RO has many advantages such as higher energy efficiency, faster production of fresh water, low operating cost, and ease of application to a large-scale process [1].

For the past few decades, materials have been developed for RO membranes to make them more effective and efficient. Since Petersen conducted a comprehensive examination of materials for thin film composite (TFC) membranes in 1993 [2], various related studies have been reported such as surface modification of RO membranes, novel polymeric membranes, application of nanotechnology, and so forth [3,4]. For example, Chen et al. modified TFC membranes by using a new class of hydrophilic polymeric amines, namely sulfonated cardo poly (arylene ether sulfone) ($SPES-NH_2$), to improve the membranes' permeate flux [5]. In 2003, Kim et al. developed RO membranes exhibiting significantly high permeate flux with proper salt rejection. Poly(m-aminostyrene-co-vinyl alcohol) (P(mAS-VA)) containing various amounts of VA was explored as a new polymeric material for the barrier layer of TFC membranes [6]. However, Li et al. pointed

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out that the loosely formed VA structure has a tendency to degrade salt rejection [7,8]. Among many studies on widely used TFC membranes based on aromatic polyamides (PAs) thanks to their wide operating pH range and stability [9–13], Matsuura et al. reported that PA surface modification with the formation of hydrophilic macromolecules through the reaction of 4,4′-diphenylmethane diisocyanate and polyethylene glycol (PEG) changes the charge of membrane surfaces to be more suitable for desalination [14,15]. Liu et al. also reported a similar surface modification with a hydrophilic copolymer coating using poly(N-isopropylacylamide-co-acrylamide)(P(NIPAM-co-Am)) [16].

Meanwhile, silane compounds are well known as coupling agents with two reactive groups, one of which is reactive with inorganic materials and the other with organic materials [17–20]. More specificly, reactive groups such as methoxy, ethoxy and silanolic hydroxyl groups form a chemical bond with the surface of various inorganic materials of glass, metals, silica, and so on, while reactive groups such as vinyl, epoxy, methacryl, amino and mercapto groups react with various organic materials and synthetic resins. As an example, a probable reaction pathway for the surface modification of PA-based TFC membranes with methoxy-based silane compounds is presented in Fig. 1. The reaction initates with the hydrolysis of silane compounds to produce silanetriols, $RSi(OH)_3$, and the first step is regarded as the rate-determining step. Then, several sialnetriols condense to form ogligomers. For the surface with many hydroxyl groups as in PA-based TFC membranes, dehydration as a result of the reaction between the surface and oligomers would lead to modified surfaces with various functional groups. This process can also be called sol-gel coating [21]. The hydrolysis and condensation to form ogligomers is nothing but the process of monomer conversion into a colloidal solution (sol), which acts as the precursor for an intergrated network (or gel) on the surface. Dehydration by drying, accompanied by significant shrinkage and densification, finalizes the formation of molecular-level monolayers on the surface. Along with the simplicity of the process, one of the distinct advantages is that densification is achieved at low temperatures (for example, at 70°C and room temperature in our study).

In this study, we employed silane-based coupling compounds for the surface modification of PA-based RO membranes. Then, we investigated the effect of surface modification by various silane compounds on the performance (salt rejection and permeate flux) of RO membranes on lab-scale experiments, focusing on a fundamental understanding for future practical research. A simple dip coating was employed as a way to avoid using complex equipment.

2. Materials and methods

2.1. Materials

The commercial RO membrane (RE-12040 model) was purchased from Ungjin chemical (Korea). For the surface modification of the RO membrane, the following five silane compounds were used.

a. Trimethoxy[2-0(7-oxabicyclo-[4.1.0]hept-3-yl)ethyl] silane (TMOHES, 98%, Aldrich)
b. (3-Glycidyloxy-propyl)trimethoxysilane (GPTMS, 98%, Aldrich)

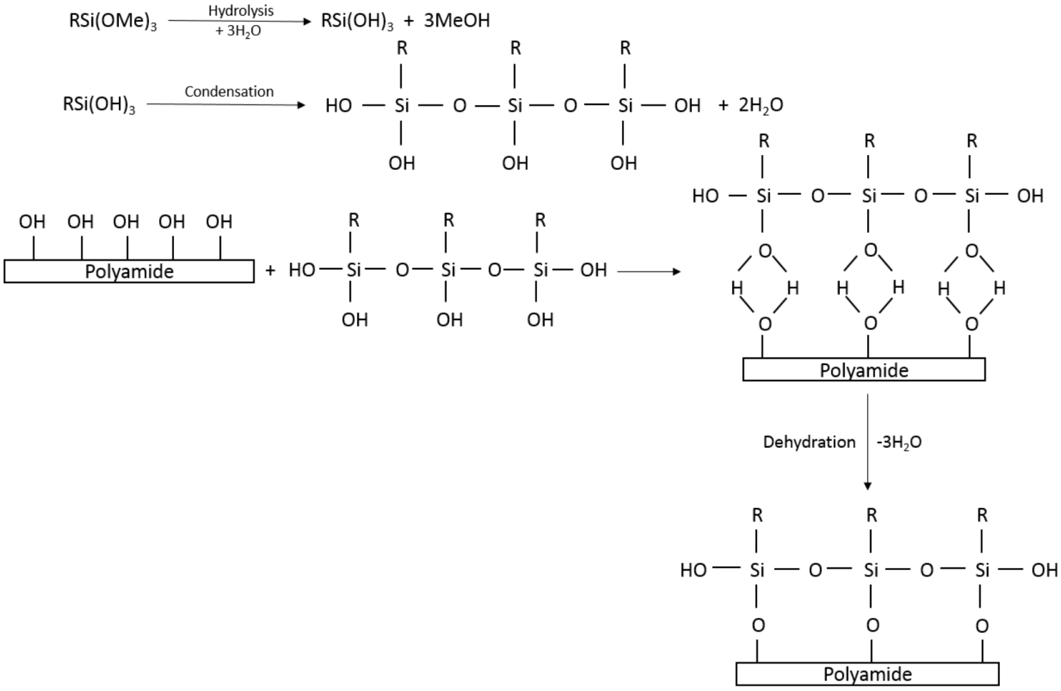

Fig. 1. A probable reaction pathway for the surface modifcation of PA-based TFC membranes with methoxy-based silane compounds.

c. [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAP, 80%, Aldrich)
d. 3-Aminopropyltrimethoxysilane (APTMS, 97%, Aldrich)
e. 3-(Trimethoxysilyl)propylmethacrylate (TMSPM, 98%, Aldrich)

TMOHES and GPTMS are compounds containing epoxy groups while TMSPM contains acryl groups. These were all used to modify the membrane surface to be hydrophobic. On the contrary, AEAP and APTMS, having amino groups, were used to form a hydrophilic surface. Ethyl alcohol (99,99%, B&J) and propylene glycol (99%, Samchun) diluted in deionized water were used as solvents for the sol-gel reaction and to increase the wettability of the RO membrane, respectively. The molecular structures of the selected silane compounds mentioned above are presented in Fig. 1S (see supplementary information). An aqueous solution of potassium metabisulfite (95%, Junsei) and potassium persulfate (99%, Samchun) was used as the initiator for the interfacial reaction by forming hydroxyl (·OH) radicals on RO membrane surface [22,23]. Artificial brackish water was made from Coralife Marine salt (Coralife, USA).

2.2. Apparatus

The schematic of the apparatus used for lab-scale performance testing of the RO membranes is presented in Fig. 2. The feed tank volume was 100 L and the pump was fitted for high pressure operation (more than 70 bar). PVC and SUS316 were used for the piping to prevent corrosion. A cooler was employed for the control of water temperature, which was not influenced by the heat generated from the pump. A flow meter on the outflow line maintained a constant flow rate. The membrane sheet cell was 60 × 100 mm^2, and spacers were inserted to prevent damage to the membranes. The feed was taken in from the bottom of the membrane sheet cell and the permeate was flown out from the top. The permeate was harvested every hour in a scale for 1 min and weighed to obtain the permeate flux as given in Eq. (1), and the total dissolved solids (TDS) was measured by using a conductivity meter (Pro30, YSI Enviromental) to determine the salt rejection as given in Eq. (2). Experiments were performed at 25°C and 20 bar, and the salt concentration of the artificial brackish water was 7 g/L. The duration of each experiment was 10 h.

$$\text{Flux} = \frac{\text{Permeate}}{\text{Membrane area} \times \text{time}} \quad (1)$$

$$\text{Rejection}(\%) = \left(1 - \frac{\text{Permeate conductance}}{\text{Feed conductance}}\right) \times 100 \quad (2)$$

2.3. Coating and Characterization

The commercial RO membrane samples were cut to be fitted in a rectangular tray of 349 × 249 × 60 mm^3 (coring PYREX). The samples were washed repeatedly with distilled water and sodium bisulfate (SBS) to remove impurities and then immersed in an aqueous solution of 5% propylene glycol for 30 min to improve the wettability of the membranes. After being dried at 70°C for 10 min, the samples were dipped in an aqueous solution of 0.01 M potassium metabisulfite and potassium persulfate for 30 min at room temperature to initiate the formation of active surface hydroxyl (·OH) radicals. After the unreacted initiator solution was removed, the samples were completely immersed in an aqueous solution of silane compounds prepared at various concentrations for 5 min. Unreacted silane compounds were then washed with distilled water and the samples were dried at 70°C for 10 min and kept at room temperature for over 24 h to continue drying.

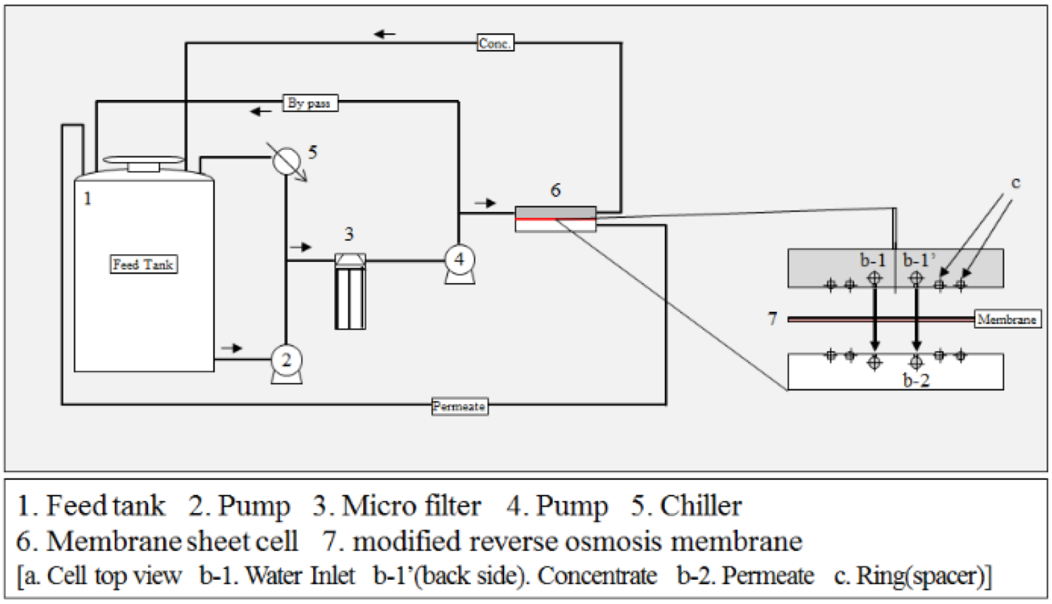

Fig. 2. Schematic of the apparatus used for lab-scale performance tests of RO membranes.

Comparison of the silane compounds was performed in terms of salt rejection and permeate flux at the same concentration of 2.0% in the coating solution. Then, TMOHES and AEAP were selected for subsequent experiments to check the concentration dependence because TMOHES and AEAP showed the best performance in terms of salt rejection and permeate flux, respectively. The same coating methodology was applied for TMOHES and AEAP, while the concentration of silane compounds was changed by 0.5, 1.0 and 2.0%. The solvent for silane compounds was used as a mixture of water and ethanol due to the low solubility of silane compounds in water and the pH was kept constant during the reaction by adding acetic acid [24].

To measure the morphology of the membrane surface, scanning electron microscopy (SEM, HITACHI S-2400, Japan) was used and energy dispersive spectroscopy (EDS, KEVEX Ltd. SIGMA, USA) identified the elements on the membrane surface quantitatively. The chemical bonding states of surface elements were analyzed by using X-ray photoelectron spectroscopy (XPS, THERMO VG SCIENTIFIC MultiLab2000, UK).

3. Results and discussions

3.1. Surface analysis of RO membranes

To evaluate whether the surface modification with silane compounds was successful, SEM micrographs were obtained and EDS was employed to identify Si elements on the membrane surface before and after surface modification. Unfortunately, there was insufficient data to confirm the surface morphological change by SEM in different conditions as shown in Figs. 2S–4S (see supplementary information). Table 1 shows the elemental analysis results by EDS for PA-based RO membranes without surface modification. After the performance test, Na and Cl elements were clearly identified. The elemental analysis results for surface-modified PA-based RO membranes with TMOHES and AEAP are given in Tables 2 and 3, respectively. The detection of Si elements was confirmed and the relative content appeared to be proportional to the concentration of silane compounds. The increase of oxygen content (16 to 19%) compared to that (15%) of unmodified membranes also confirms successful surface modification with silane compounds. However, the amount of Si and oxygen elements decreased drastically after the performance test, especially for membranes modified with AEAP. This is probably due to the presence of unreacted silane compounds on the membrane surface despite cleaning with diluted water coupled with the destruction of the membrane surface by the high pressure performance test. However, the degree of surface modification was higher with TMOHES than with AEAP at the same concentration of silane compounds and was also proportional to the concentration of silane compounds.

Table 1
Elemental analysis results by EDS for bare PA-based RO membranes; before and after the performance test

	Before		After	
Element	wt.%	at.%	wt.%	at.%
C	76.85	84.14	75.25	83.29
O	15.46	12.71	15.34	12.74
S	7.69	3.15	7.50	3.11
Na			0.71	0.41
Cl			1.20	0.45
Total	100.00		100.00	

Table 2
Elemental analysis results by EDS for surface-modified PA-based RO membranes with various TMOHES concentrations (0.5, 1.0, and 2.0%); (a) before and (b) after the performance test

		2.0 %		1.0 %		0.5 %	
	Element	wt.%	at.%	wt.%	at.%	wt.%	at.%
(a)	C	73.07	80.72	74.40	82.07	74.86	82.40
	O	19.30	16.00	17.49	14.48	17.34	14.33
	Si	2.22	1.05	1.63	0.77	0.84	0.40
	S	5.41	2.23	6.48	2.68	6.96	2.87
	Total	100.00		100.00		100.00	
(b)	C	74.61	82.83	74.00	82.52	74.89	83.15
	O	15.62	13.01	15.55	13.02	15.11	12.60
	Na	0.54	0.32	0.80	0.46	0.72	0.42
	Si	0.72	0.34	0.54	0.26	0.44	0.21
	S	7.51	3.12	7.53	3.14	7.56	3.14
	Cl	1.00	0.37	1.59	0.60	1.28	0.48
	Total	100.00		100.00		100.00	

Table 3
Elemental analysis results by EDS for surface-modified PA-based RO membranes with various AEAP concentrations (0.5, 1.0, and 2.0%); a) before and (b) after the performance test

		2.0 %		1.0 %		0.5 %	
	Element	wt.%	at.%	wt.%	at.%	wt.%	at.%
(a)	C	69.87	78.57	71.51	79.96	76.55	83.73
	O	19.87	16.77	18.90	15.86	16.11	13.22
	Si	5.64	2.71	2.81	1.34	0.70	0.33
	S	4.62	1.95	6.78	2.84	6.64	2.72
	Total	100.00		100.00		100.00	
(b)	C	71.63	81.35	73.11	82.18	75.47	83.69
	O	14.97	12.76	15.01	12.66	14.51	12.08
	Na	1.84	1.09	1.47	0.86	0.83	0.48
	Si	0.33	0.16	0.11	0.05		
	S	7.99	3.39	8.00	3.37	7.53	3.13
	Cl	3.24	1.25	2.30	0.88	1.66	0.62
	Total	100.00		100.00		100.00	

As for Na and Cl elements, the amount of both elements after the performance test for the bare membrane and the membrane modified with TMOHES was in a similar range, while the amount for the modified membrane with AEAP was significantly increased. This is probably related to the hydrophilicity of the modified surface with AEAP as intended.

3.2. Identification of Si-O bonding state by XPS

To further verify the surface modification with silane compounds, X-ray photoelectron spectroscopy (XPS) was employed to identify the bonding states of C, O, N, and Si elements. The C 1s peak showed almost the same shape for all unmodified membrane surfaces as well as for surfaces modified with TMOHES and AEAP, as shown in Fig. 5S (see supplementary information). The Si $2p_{3/2}$ peak appeared at about 102 eV only for modified surfaces as shown in Fig. 6S (see supplementary information). However, the Si $2p_{3/2}$ peak position does not provide definite evidence of the Si-O bonding state because Si is known to have a lot of bonding states around 102 eV such as SiOH, SiO_2, Si-O (Si-C), and so on [24–27]. Thus the change in the O 1s bonding state was found only in Fig. 3. Unlike the unmodified surface, the O 1s peaks were deconvoluted into three peaks on the modified surfaces. While two small peaks at about 531 eV and 533 eV correspond to those of the unmodified surface, a new high peak at about 532 eV indicates the Si-O bonding state, suggesting that silane compounds are chemically adsorbed (or coated) on the membrane surfaces. As for the N 1s peak, it is deconvoluted into two peaks only for the modified surface with AEAP as shown in Fig. 4. Similarly, a newly grown high peak at about 399 eV indicates amino groups in AEAP. The comparison of XPS peaks for unmodified and modified surfaces clearly demonstrates that the surface modification with silane compounds was successfully completed.

3.3. Performance evaluation of surface-modified RO membranes

As mentioned above, we used TMOHES and GPTMS containing epoxy groups and TMSPM containing acryl groups to modify the membrane surface to be hydrophobic. On the other hand, AEAP and APTMS with amino groups were chosen to form a hydrophilic surface. Previous research [28–30] demonstrated that surface modification with silane compounds could improve the membrane's performance (salt rejection and permeate flux) and this was related to the functional groups of silane compounds as well as the modified surface properties.

Fig. 5 shows a plot of the measured salt rejection and permeate flux for the commercial RO membrane (denoted by "blank") and the surface-modified membranes with various silane compounds. Only the 2% TMOHES-treated membrane showed a minimal increase (0.96%) in salt rejection compared to the commercial membrane. Interestingly, TMSPM and GPTMS, which were expected to form hydrophobic surfaces similar to TMOHES, degraded the salt rejection. Although these compounds were all used to increase the hydrophobicity of the surface of the commercial membrane, which is already highly hydrophobic, to improve salt rejection, surface modification (in other words, surface coating) could also degrade the inherent performance of the bare membrane by blocking the innate hydrophobic surface. Only TMOHES, which has both epoxy and hexyl groups, compensated the degradation at a high concentration (2%).

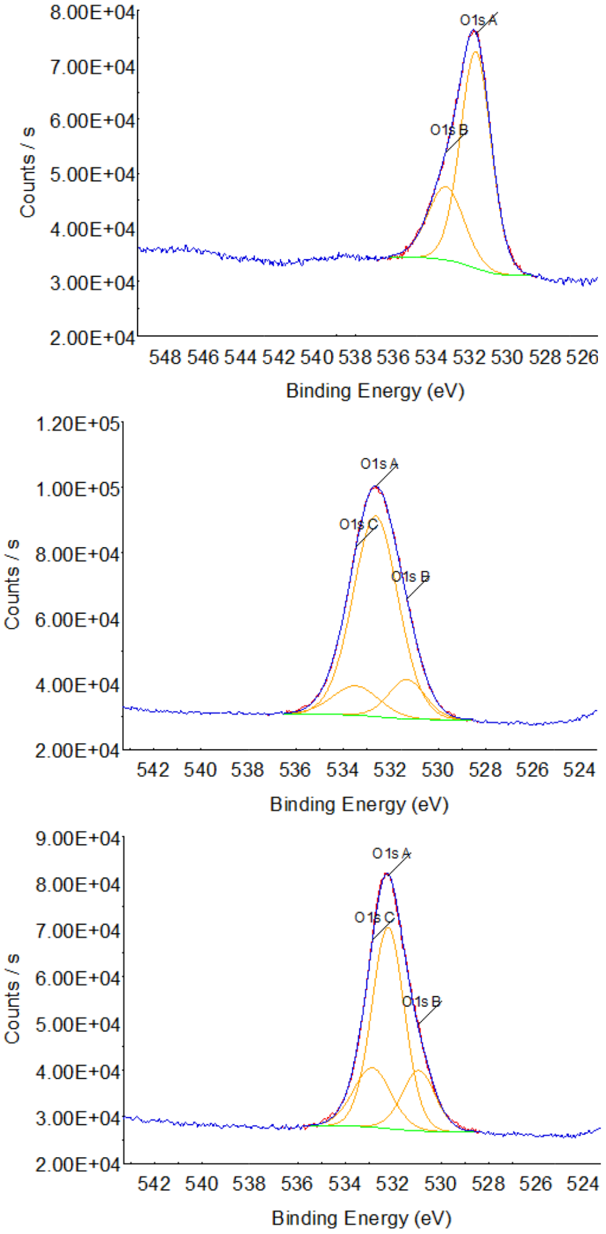

Fig. 3. XPS analysis for the bonding states of O 1s peaks; (a) unmodified membrane surface, (b) surface modified with TMOHES (conc. = 2.0%), and (c) surface modified with AEAP (conc. = 2.0%).

In terms of permeate flux, AEAP and APTMS-treated membranes yielded much better performance compared to the commercial membrane as expected. This is attributed to the enhancement of the hydrophilic surface property by the amino groups in AEAP and APTMS.

The concentration dependence of the membrane performance was measured and plotted in Fig. 7S and 8S (see supplementary information) for TMOHES and AEAP, which showed relative ascendancy in terms of salt rejection and permeate flux, respectively. Table 4 compares the average salt rejection and permeate flux with respect to the silane compounds used for surface modification and their concentrations. The TMOHES-treated membrane exhibited 94.6% (conc. = 2.0%) salt rejection, only minimally better than the

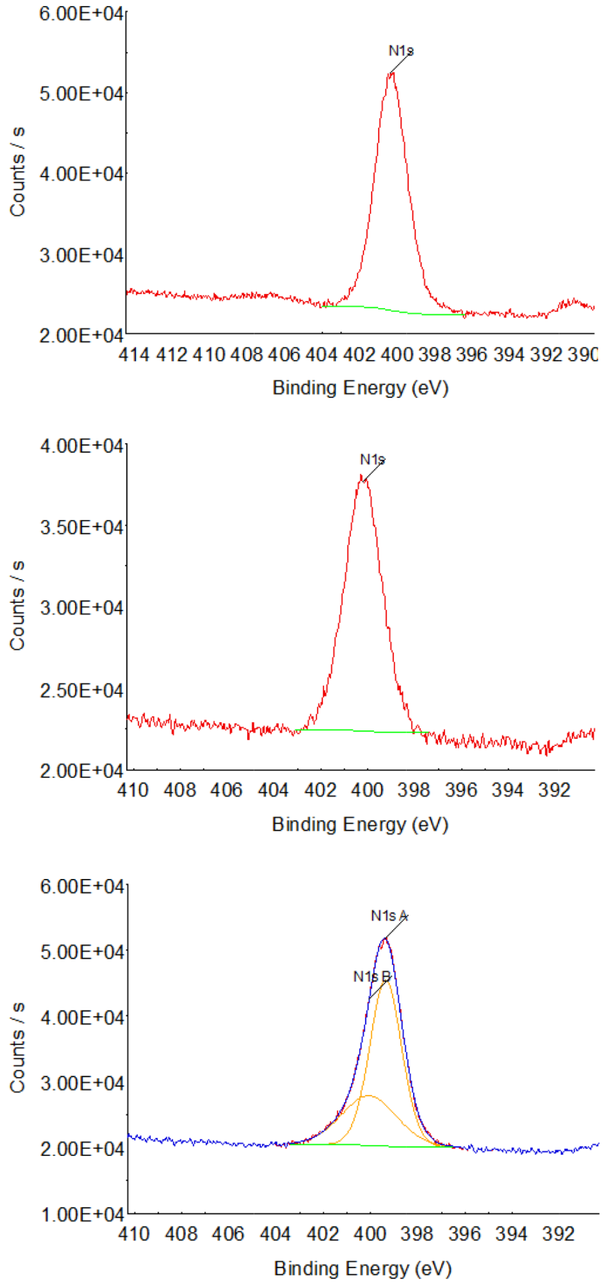

Fig. 4. XPS analysis for the bonding states of N 1s peaks; (a) unmodified membrane surface, (b) surface modified with TMOHES (conc. = 2.0%), and (c) surface modified with AEAP (conc. = 2.0%).

93.7% of the commercial membrane. With the decrease of the concentration of TMOHES (from 2.0 to 0.5%), the salt rejection was also decreased. Meanwhile, the permeate flux of the TMOHES-treated membrane showed a slight increase compared with that of the commercial membrane, proportional to the decrease of TMOHES concentration. The reciprocity between the permeate flux and TMOHES concentration is reasonable, but the general increase of permeate flux is unusual especially compared to the large decreases with GPTMS and TMSPM. This might be related to the surface chemistry among those compounds, which requires further rigorous investigation.

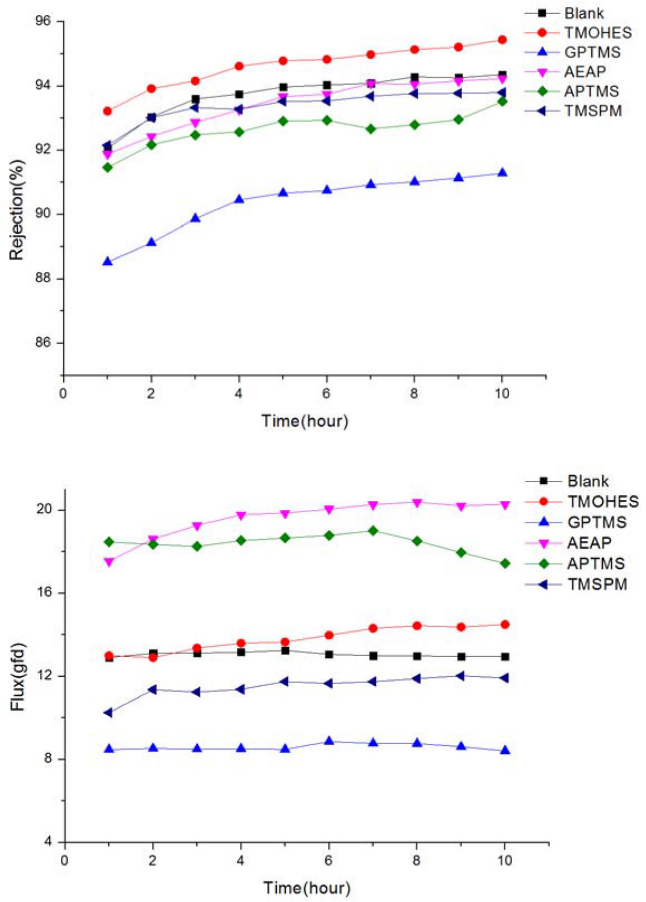

Fig. 5. Salt rejection (a) and permeate flux (b) of surface-modified RO membranes with various silane compounds. The unmodified commercial membrane is denoted by "blank" as a reference.

Table 4
Comparison of membrane performance with respect to the silane compounds used for surface modification and their concentrations. The unmodified commercial membrane is denoted by "blank" as a reference

Reagents		Average salt rejection (%)	Average permeate flux (gfd, gallon/ft^2/day)
Blank		93.7	13.0
TMOHES	2.0 %	94.6	13.8
	1.0 %	93.0	14.1
	0.5 %	92.6	14.5
GPTMS	2.0 %	90.4	8.6
AEAP	2.0 %	93.4	19.6
	1.0 %	91.5	19.5
	0.5 %	91.5	18.6
APTMS	2.0 %	92.6	18.4
TMSPM	2.0 %	93.4	11.5

However, the AEAP-treated membrane had a significantly improved permeate flux of 19.6 gfd (1 gfd (gallons/ft^2/day) = 1.70 L/m^2/h), a nearly 1.5 fold increase from the 13.0 gfd of the commercial membrane, at a high AEAP concentration (2%). Compared to APTMS, the additional amino groups in AEAP probably contributed to this improvement. Based on the results, the RO membranes treated with 2.0% AEAP concentration were preferred due to their highly improved permeate flux and competitive salt rejection.

4. Conclusions

The effect of surface modification of RO membranes on their performance has been examined with various silane compounds. First, the XPS results demonstrated that Si-O bonding occurs on the membrane surface with our simple dip-coating method. The Si 2p$_{3/2}$ peak appeared as well as an additional O 1s bonding state. Efforts to improve salt rejection by imparting more hydrophobicity to the surface of commercial membranes with TMOHES barely succeeded with a 0.96% increase even at a high TMOHES concentration of 2% because the bare commercial membrane is already highly hydrophobic. On the contrary, surface modification with AEAP, which has two hydrophilic amino groups, significantly improved the permeate flux of membranes by 1.5 times (13.0 gfd to 19.6 gfd).

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Supplementary Information

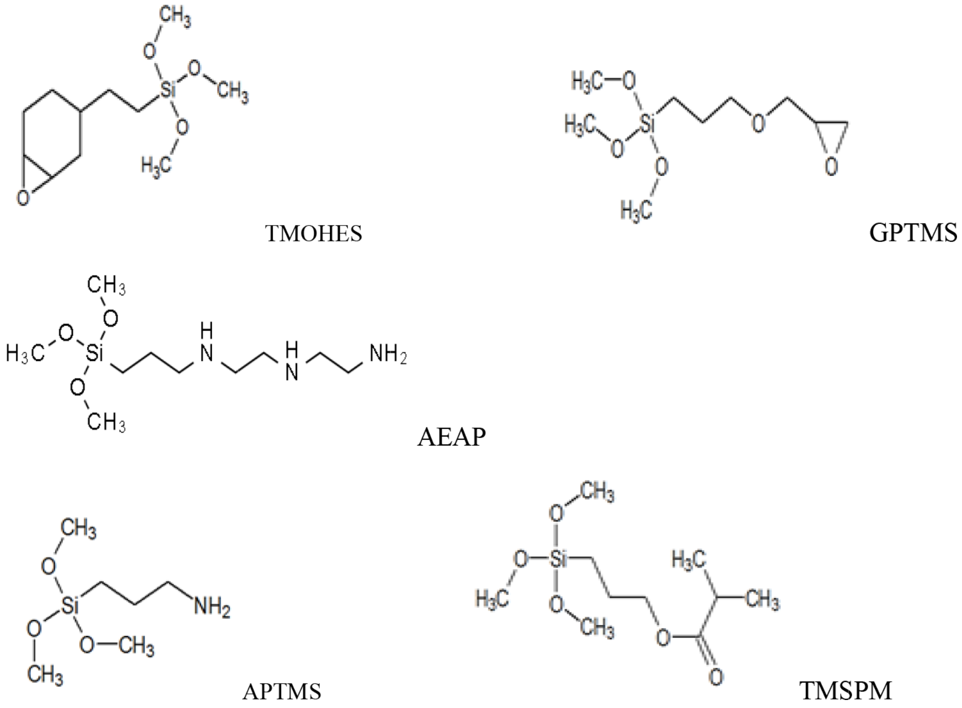

Fig. 1S. Molecular structures of selected silane compounds in this study.

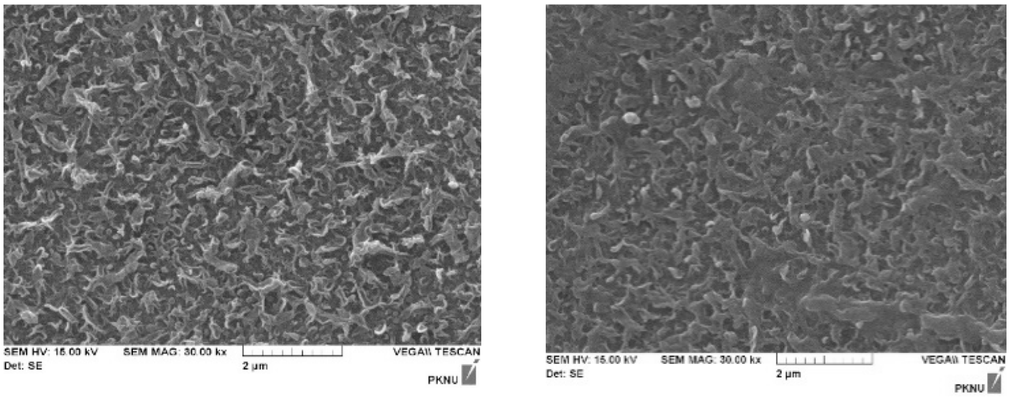

Fig. 2S. SEM micrographs of PA-based RO membranes; (a) before and (b) after the performance test.

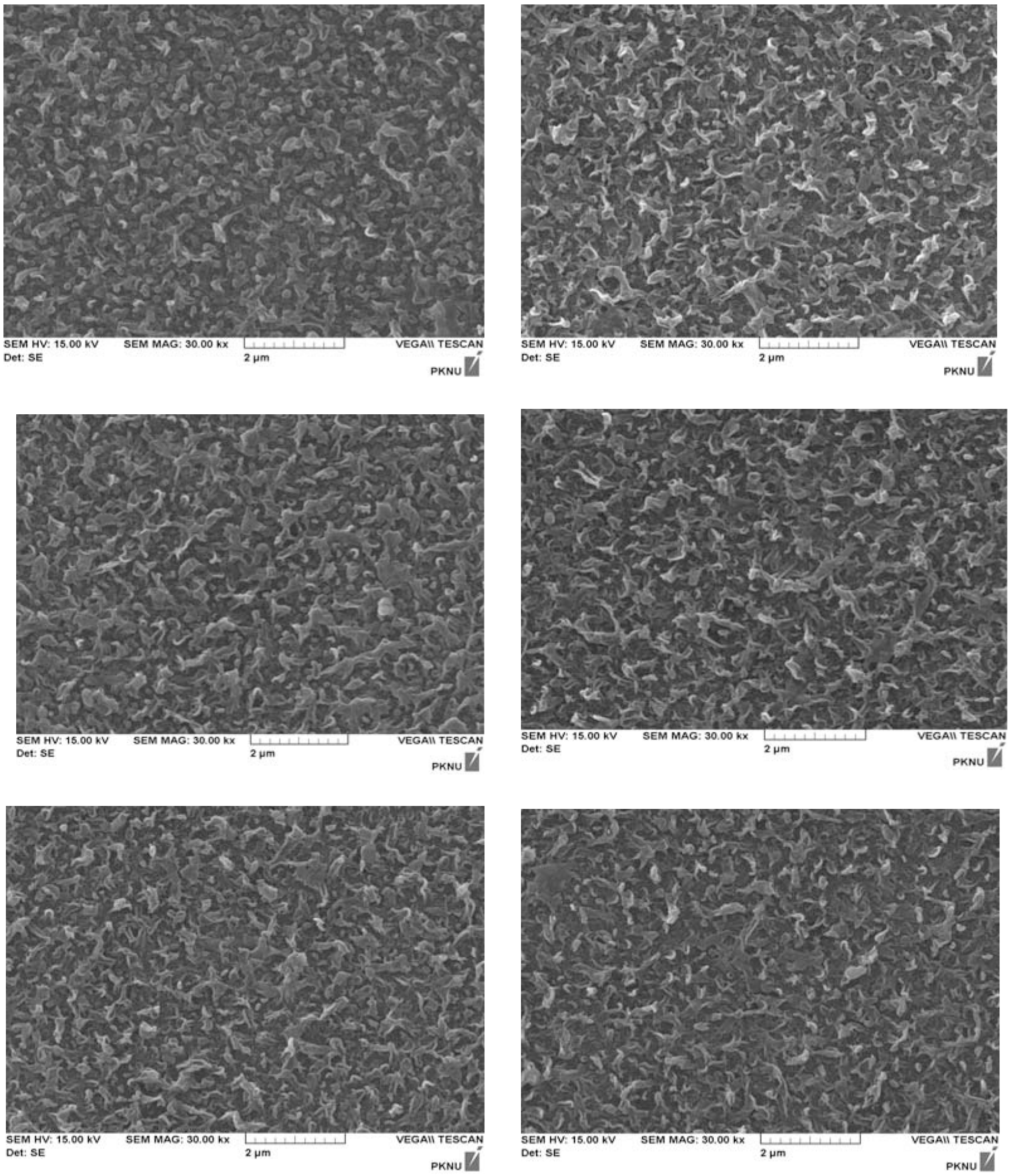

Fig. 3S. SEM micrographs of surface-modified membranes with various TMOHES concentrations; (a) 2.0%, (b) 1.0%, and (c) 0.5% (left column: before the performance test, right column: after the performance test).

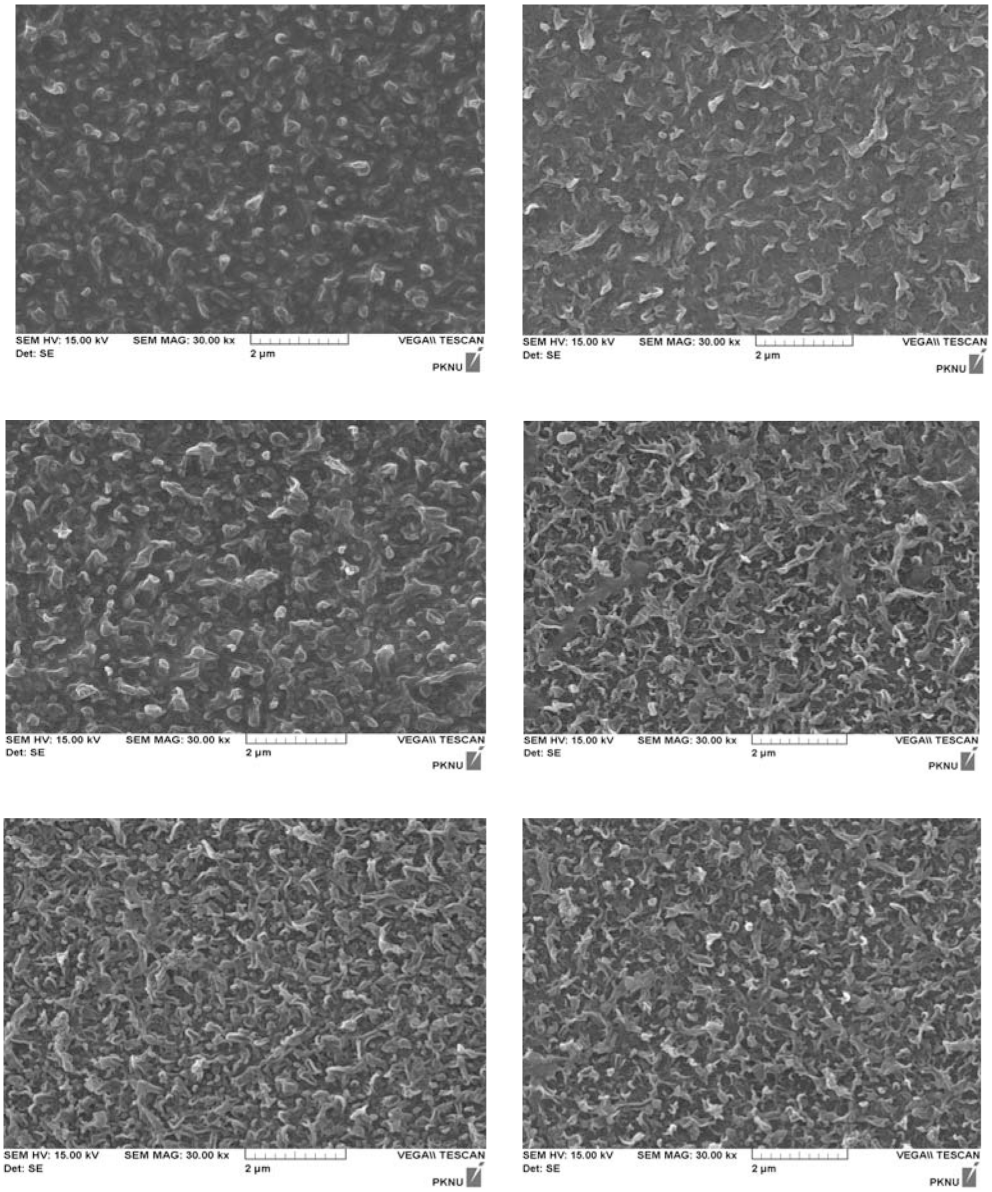

Fig. 4S. SEM micrographs of surface-modified membranes with various AEAP concentrations; (a) 2.0%, (b) 1.0%, and (c) 0.5% (left column: before the performance test, right column: after the performance test).

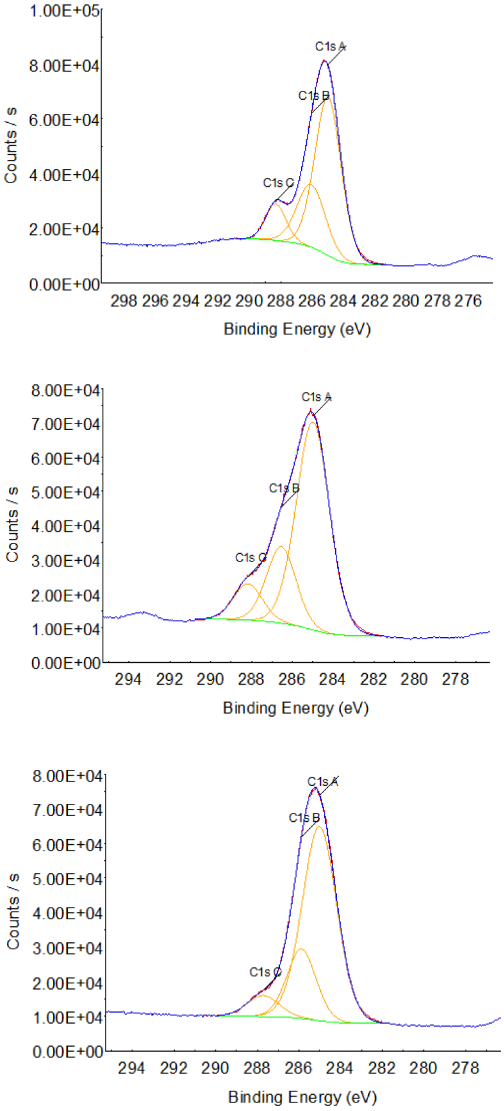

Fig. 5S. XPS analysis for the bonding states of C 1s peaks; (a) unmodified membrane surface, (b) modified surface with TMOHES (conc. = 2.0%), and (c) modified surface with AEAP (conc. = 2.0%).

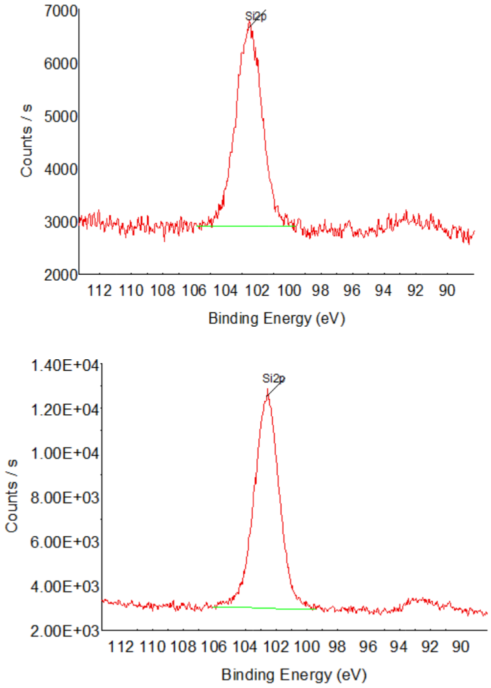

Fig. 6S. XPS analysis for the bonding states of Si 2p3/2 peaks; (a) modified membrane surface with TMOHES (conc. = 2.0%) and (b) modified surface with AEAP (conc. = 2.0%).

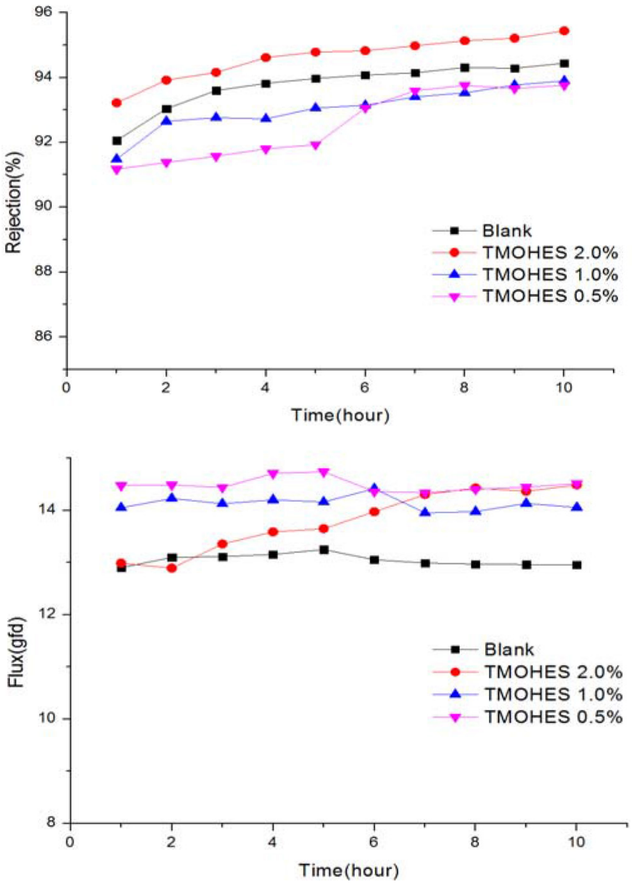

Fig. 7S. Salt rejection (a) and permeate flux (b) of TMOHES-treated membranes with respect to the TMOHES concentration.

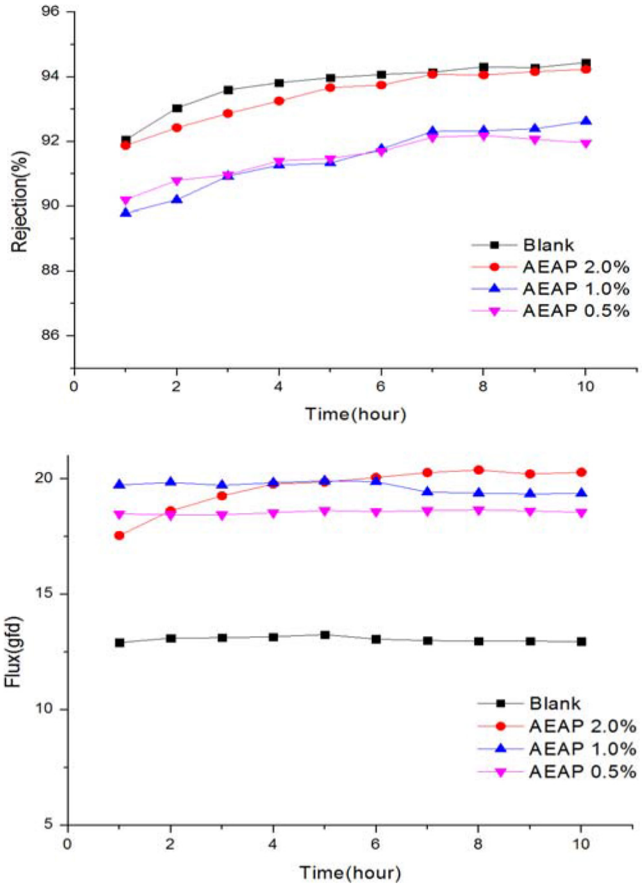

Fig. 8S. Salt rejection (a) and permeate flux (b) of AEAP-treated membranes with respect to the AEAP concentration.