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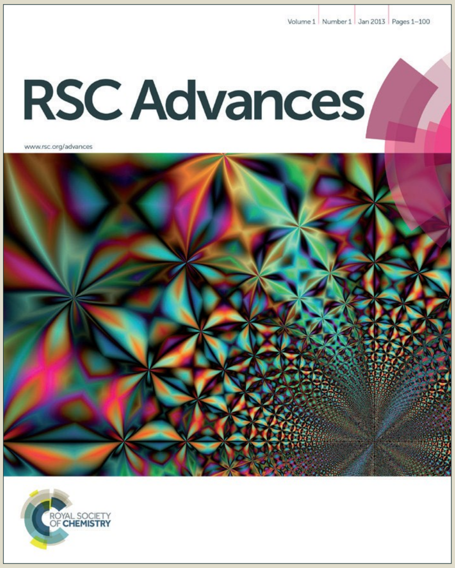

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Enhancement in membrane performances of a commercial polyamide reverse osmosis membrane via surface coating of polydopamine followed by the grafting of polyethylenimine

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Abstract

Membrane fouling and chlorine degradation are two of the major challenges the reverse osmosis (RO) membrane industry is facing in recent years. In the present study, a commercial aromatic polyamide RO membrane (XLE-400, DOW Co., Ltd.) was modified via surface coating of polydopamine (PDA) followed by the grafting of polyethylenimine (PEI). The successful modification was confirmed by X-ray photoelectron spectroscopy (XPS). Membrane surface properties were characterized through scanning electron microscopy (SEM), atomic force microscopy (AFM), zeta potential and contact angle. The results showed that modification enhanced the surface hydrophilicity, moved the surface charge towards the positive side and made the surface slightly rougher without damaging the surface peak-and-valley substrate. The influence of modification on the permselectivity of the membrane was also examined. The modified membrane had a higher salt rejection and a slightly lesser water flux than the unmodified membrane. Furthermore, the chlorination, fouling and simulated biofouling experiments were done. The results showed that, due to the abundant presence of grafted amino groups coming from PEI, the modified membrane exhibited higher chlorine resistance, anti-fouling and antibacterial properties.

Key words: reverse osmosis membrane; surface modification; anti-fouling; anti-biofouling; chlorine resistance.

1. Introduction

Shortage of clean drinking water and water pollution are two of the biggest challenges facing human and social development. Reverse osmosis technology provides an energy efficient and economical way of treatment for drinking water, water reclamation from wastewater, and desalination of seawater/brackish water [1-3]. However, this promising water treatment technology is often hampered by the fouling of membrane, especially the biofouling of the membrane [4-6]. Although many strategies have been proposed to control this phenomenon, yet the most efficient way in current systems is the addition of free chlorine to feed water, followed by the dechlorination process before the feed solution enters the RO system [7, 8]. However, the process of dechlorination of the RO feed water cannot be 100% effective. A small amount of free chlorine can still be left in the feed water. Polyamide (PA) membranes are the most commonly used commercial RO membranes. These membranes are easily influenced by the chlorine. The residual free chlorine in the feed solution causes the irreversible deterioration of PA, which results in shortening the membrane's life [9-11].

A number of studies have been carried out to solve membrane-related problems, such as enhancing the anti-fouling properties of the membranes [12, 13], and developing antibacterial [14, 15] or chlorine resistant membranes [16, 17]. Nevertheless, most of these studies have only partially addressed these problems due to which the stable operation of RO systems is still limited.

Surface modification is the most widely used strategy to improve the performance of membranes [12-16]. The modification processes largely influence the surface properties of the membranes. Such modifications usually introduce a protecting or antibacterial group which enhances the anti-fouling properties (by increasing hydrophilicity, decreasing surface roughness and reducing surface charge [18, 19]), chlorine resistance and the antibacterial properties of the membranes. Hence, finding a suitable modifier which can simultaneously improve all these properties has become the key issue in this field of research.

The N–H group is highly hydrophilic and shows high chemical reactivity with free chlorine [9-11]. Therefore introducing N-H group into membrane surface can retard the membrane fouling and protect the N-H bonds from being chlorinated in PA membranes. In addition N-Cl, which is the product of N-H chlorination, has strong antibacterial properties and can be converted back to N–H group by sterilizing microorganisms [16, 20, 21]. Hence, N-H group can give the membranes continuous anti-biofouling and chlorine-resistant properties. Therefore, finding a suitable polymer containing abundant N-H groups and then introducing it into membranes was the main focus and outcome of our recent research.

In the present study, surface coating of polydopamine (PDA) followed by the grafting of polyethylenimine (PEI) were used to modify a commercial thin-film composite (TFC) aromatic polyamide reverse osmosis membrane (XLE-4040). PDA could form a thin film on the surface of a wide range of inorganic and organic materials through self-polymerization of DA [22, 23], which does not harm the membrane structure and can provide a large number of active groups for the subsequent grafting [24, 25]. PEI bonds with primary and secondary amines. Some of the amine groups can covalently be grafted on the surface via Michael addition reaction and/or Schiff base reaction with the quinone functional groups of the PDA layer[25,26], while rest of them can act as functional groups to enhance the performance of the membrane (shown in Fig.2). In the present work, the permselectivity of modified and unmodified membranes are studied. Surface properties of membranes such as membrane surface morphology (characterized by SEM), membrane surface roughness (characterized by AFM), membrane surface hydrophilicity (characterized by contract angle), membrane surface charge (characterized by zeta potential) and the surface elemental composition (characterized by XPS) of both modified and unmodified membranes have been analyzed. The chlorination, fouling and imitated biofouling of unmodified and modified membranes were also studied to evaluate the influence of modification on the membrane properties.

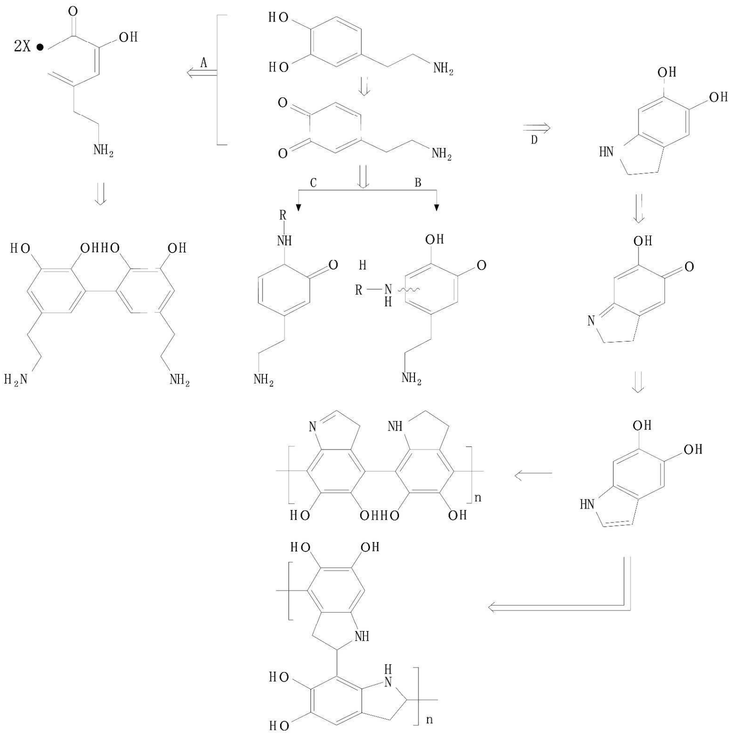

Fig.1. Possible structural evaluation and polymerization mechanism of dopamine: (A) Schiff based substitution; (B) Michael-type addition; (C) intra-molecular cyclization; (D) aryl-aryl coupling.

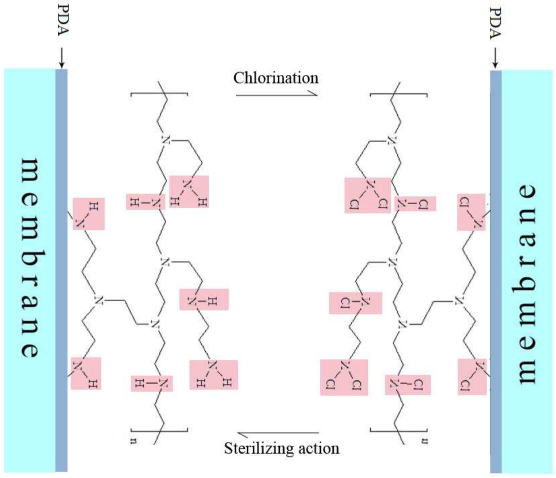

Fig.2. Schematic representation of the anti-biofouling and chlorine resistant

properties of PDA-PEI modified membrane

2. Materials and methods

2.1. Chemicals and reagents

XLE-4040 (DOW) was purchased from Jiangsu Hersbit Environmental Protection Technology Co. Ltd., China and was used as the original membrane. Dopamine hydrochloride (≥ 98.5%) was purchased from Shanghai Ryon Biological Technology Co. Ltd., China. Polyethylenimine (≥ 99.0%), which was liquid with a molecular weight of 10000, was purchased from Shanghai Aladdin Reagent Co. Ltd., China. Both DA and PEI were used as modifiers. Sodium hypochlorite (6-14% effective components) was purchased from Shanghai Aladdin Reagent Co. Ltd., China and was used to chlorinate the membranes. It was stored in a fridge at 4°C and was recalibrated before use. Bovine serum albumin (≥ 96%) and dodecyltrimethylammonium bromide (≥ 99%) were purchased from Shanghai Aladdin Reagent Co. Ltd., China. These two compounds were used as fouling agents in fouling experiments. All other reagents such as isopropyl alcohol, tris (hydroxymethyl) aminomethane, hydrochloric acid, sodium hydroxide and sodium chloride were purchased from Sinopharm Chemical Reagent Co. Ltd., China and were used without further purification.

2.2. Modification of PA membranes

Modification of the XLE-4040 membrane was carried out through self-polymerization of DA followed by the grafting of PEI. The modification was conducted using the apparatus shown in Figure 3. The apparatus was designed such that the reactant solution only reacted with the active PA layer.

Prior to the modification, flat sheet membranes were cut down from membrane module and, were immersed in 25% (v/v) aqueous isopropanol solutions for 30 min to remove the preservative materials from the membrane surface. After immersion, these were washed thoroughly with deionized (DI) water and stored in ultrapure water overnight at 4 °C. After that, the membrane was fixed in the apparatus. Dopamine solution (50mL) was poured into it and the apparatus was put into a shaker (75rev/min). The DA solutions were prepared by dissolving 0.1g DA into 50ml of 50mM tris-HCl (pH of 8.8). After 2h reaction at 25 °C, the membrane was washed thoroughly with DI water and then was exposed to 50ml PEI solutions for 30min at 37°C. The PEI solution was prepared by dissolving 0.1g PEI into 50ml ultrapure water. Finally, the PDA-PEI modified membrane was washed thoroughly with DI water and stored in ultrapure water prior to using.

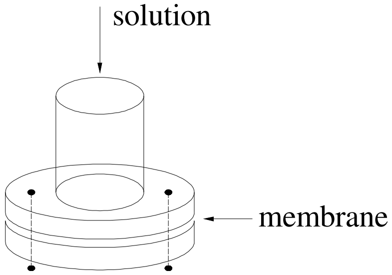

Fig.3. Schematic of the self-made apparatus used for membrane modification and chlorination

2.3. Surface characterization

Surface properties of membranes have significant influence on the performance of membranes. Several analytical instruments were employed to analyze the unmodified and modified membranes. All the membranes used were dried under vacuum at 50 °C for 2 hr before being analyzed for characterization.

XPS analysis

XPS was used to measure the elemental percentage on the surface of each membrane. The measurement was conducted using an ESCALAB 250Xi analyzer obtained from Thermo Fisher with a monochromatic AlKα radiation.

Contact angle analysis

The hydrophilicity of the membranes was measured by using a contact angle analyzer (JC2000D2, zhongchen digital technic, shanghai, China). Deionized water was used as the probe liquid. Each measurement lasted for 50s and the results were recorded every 5s. At least 5membranes of each sample were analyzed for hydrophilicity.

SEM analysis

The surface morphology of membranes was photographed by SEM (FEI Quanta 200, Holland) at 15 kV. To avoid charging effects, membranes were coated with a uniform gold layer before making observations.

AFM analysis

Three-dimensional images and surface roughness results of the membranes were obtained from AFM (SHIMADZU, Kyoto, Japan) through non-contact mode. The scanning area was set to 5 μm× 5 μm and the scan rate was 0.5 Hz.

Zeta potential analysis

The surface charge of membranes was measured using streaming potential over a pH range of 4 - 10 by a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Austria). 1.0 mM KCl was used as the background electrolyte solution.

2.4. RO membrane permselectivity

The permselectivity of membranes was evaluated through a laboratory scale cross-flow test unit. The details of this cross-flow unit have already been published in one of our previous works [27]. The water flux and salt rejection were determined at a NaCl concentration of 1000 mg/L, a pressure of 1 MPa and a temperature of 25°C. The water flux and salt rejection were calculated by using the following equations:

Water flux (L/m2h) = permeate volume / (membrane area×time) (1)

Salt rejection (%) = (1- concentration of permeation/ concentration of feed solution) ×100 (2)

The reported values are averages obtained from at least three samples for each membrane type.

2.5 Evaluation of anti-fouling

BSA (200ppm and having a pH of 6.3) and DTAB (20ppm and having a pH of 6.2) were used as fouling agents to evaluate the antifouling property of PDA-PEI modified membranes. The BSA brought negative charge and the DTAB brought positive charge under the experimental conditions.

At the beginning of the fouling experiment, the un-fouled membrane flux was measured with NaCl solution. Then the pump was turned off and the fouling agents were added in the feed tank to achieve the desired concentration of fouling agents. Once the fouling agents were dissolved, the pump was turned on again. The time varying permeate flux was recorded for three hours. At the end of fouling experiments, the fouled membrane was washed with DI water for 2 h. After washing the membrane, tests with NaCl solution to measure the recovered water flux were conducted. Values of the water flux were normalized to make the comparison simpler. The normalized water flux was defined as the ratio of water flux of the fouled membrane to the water flux of the membrane before fouling.

2.6 Evaluation of chlorine resistance

The chlorination of PA membrane was achieved in two steps. First the reversible N-chlorination and then the subsequent irreversible ring-chlorination via Orton Rearrangement were done [9-11]. In our previous study, we found that alkali treatment could initiate the reversible regeneration of chlorinated membranes [28]. So in order to investigate the irreversible chlorination extent of membranes, we designed a two-step experiment as a cycle. These steps included: (1) chlorinating the membranes and then measuring the chlorinated membrane flux. (2) Chlorinated membrane was given alkali treatment and then the membrane flux was measured. Membrane chlorination experiments were carried out using 100ml NaClO solution having a concentration of 100mg/L, pH of 7 and at a temperature of 25 °C for 1 hr. Alkali treatment experiments were carried out using 100ml NaOH solution having a pH of 4 at a temperature of 25 °C for 3 hr. Each membrane was washed thoroughly with DI water before measurement of the membrane flux.

2.7 Imitation of biofouling

Biofouling occurs due to the bacteria which get adsorbed onto the RO membranes. They can grow on the membrane surface, produce extracellular polymeric substances and ultimately form biofilms. These biofilms have a severe impact on the operation of RO systems [29-31]. Biofouling can be evaluated through the analysis of these biofilms. Experiments on the imitation of membrane biofouling were conducted by immersing the membranes in deionized water which contained approximately 0.3~0.5 ppm NaClO. The deionized water was not disinfected and contained a small quantity of bacterium. The added NaClO imitated the rudimental free chlorine after pretreatment of feed water. The concentration of NaClO was monitored and kept constant. After the immersion for 90 days, the membranes were dried and characterized through SEM to observe the biofilms formed on the surface of membranes.

3. Results and discussion

3.1 Surface analysis

3.1.1 Surface elemental composition

XPS is a surface sensitive technique that probes only about 2-5nm into the surface of membranes [32]. It is employed to quantify the elemental composition of the top-most layer of the membrane sample. Table 1 presents the results from XPS analyses for an unmodified membrane, PDA modified membrane and PDA-PEI modified membrane. The contents of N, C and O in DA and PEI were also calculated and presented in Table 1. The results showed that compared to the unmodified membrane, the O mol% of PDA modified membrane increased from

17.42% to 17.94% while the N mol% of PDA modified membrane decreased from 13.02% to 11.55%. Higher O and lower N concentrations (mol%) in PDA membrane confirmed the successful coating of PDA. Similarly, after PEI modification, a decrease in C and O concentrations while an increase in N concentration indicated that the PEI had successfully been grafted onto the surface of membrane.

Table 1

Results of the surface elemental analysis for unmodified and modified membranes (mol %).

Sample	XPS surface elemental analysis			Relative ratio		
	C (%)	O (%)	N (%)	O/C	N/C	O/N
Unmodified membrane	69.56	17.42	13.02	0.25	0.187	1.338
DA	72.8	18.2	9	0.25	0.125	2
PDA modified membrane	70.5	17.94	11.55	0.254	0.164	1.553
PEI	66.6	-	33.3	0	0.5	0
PDA-PEI modified membrane	67.71	14.93	17.37	0.22	0.257	0.86

3.1.2 Surface hydrophilicity

Membrane surface hydrophilicity has significant influence on the performance of a membrane [18,33]. A hydrophilic surface can enhance the water flux and reduce the membrane fouling. The surface-water contact angles for unmodified and modified membranes were measured to characterize surface hydrophilicity. As shown in Figure 4, both modification steps reduced the surface-water contact angle. After the modification of PDA the contact angle decreased from 65.7°±5.8° of unmodified membrane to 56.1°±4.2° of PDA modified membrane. After the PEI modification, the contact angle further decreased to 49.2°±3.4°. The decrease in the values of contact angles was expected and suggested that the modification gave the membrane a more hydrophilic surface.

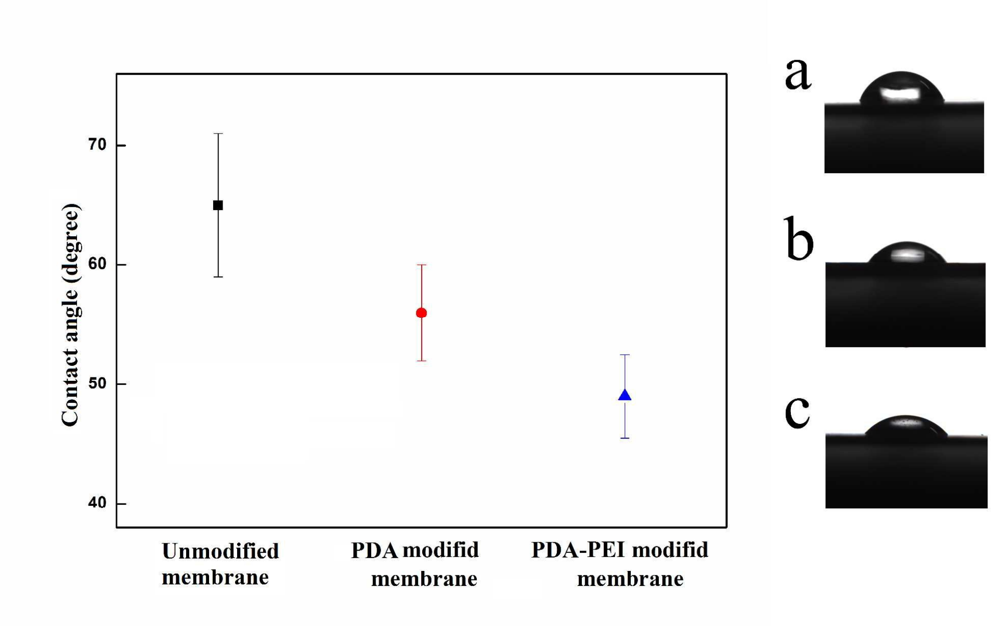

Fig. 4. Measured water contact angle results: (a) Unmodified membranes; (b) PDA modified membrane; (c) PDA-PEI modified membranes

3.1.3 Surface morphology

AFM and SEM were employed to analyze the surface morphology of unmodified and modified membranes. The SEM images and three-dimensional AFM images have been shown in Figure 5. The surface roughness was calculated and has also been showed in Figure 5. It can be seen that both the unmodified and the modified membranes showed characteristic peak-and-valley structure of aromatic polyamide [34]. No remarkable change prior to and after the modification can be observed. This indicated that the modification did not damage the surface peak-and-valley substrate.

The surface roughness of membranes was quantified in terms of root mean square roughness (RMS) [35]. As shown in Figure 5, after the modification, the RMS value increased slightly. This may have been caused by the addition of PEI chains on the surface of membrane. It is worth mentioning that the increase in surface roughness may also damage the antifouling properties of membranes.

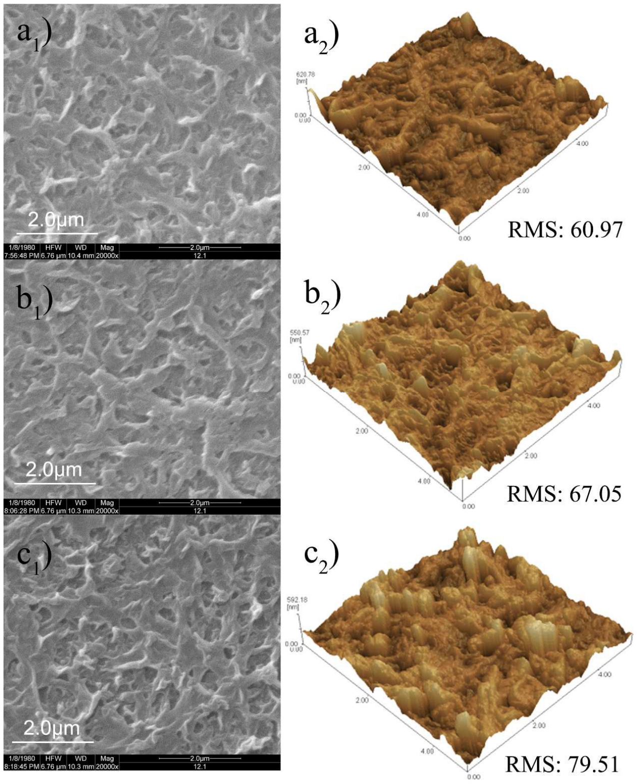

Fig.5. Scanning electron microscopy (×20000) and atomic force microscopy images (5μm×5μm,

including RMS results) of (a) Unmodified membrane, (b) PDA modified membrane, (c) PDA-PEI modified membrane

3.1.4 Surface charge

Membrane surface charge has a significant influence on the antifouling properties of a membrane [36]. Zeta potential was used to measure the influence of modification on the surface charge of membranes. As shown in Fig.6, due to the presence of carboxylic acid and amine groups on the surface, the unmodified membranes turned out to be amphoteric. The zeta potential was 14.75 at a pH of 3.99 due to the protonation of amine groups. The value of zeta potential changed to -43.56 at a pH of 10.98 due to the dissociation of carboxylic acid group. The PDA modified membrane showed similar zeta potential as was observed for the unmodified membrane. After the PEI modification, the membrane surface charge moved towards the positive side. The isoelectric point changed from 4.71 for unmodified membrane to 5.82 for PDA-PEI modified membrane. Thus it could be safely said that the modification of PDA did not introduce any electrified groups. However, the subsequent PEI modification introduced a large number of amine groups, and hence brought a huge quantity of positive charge after protonation.

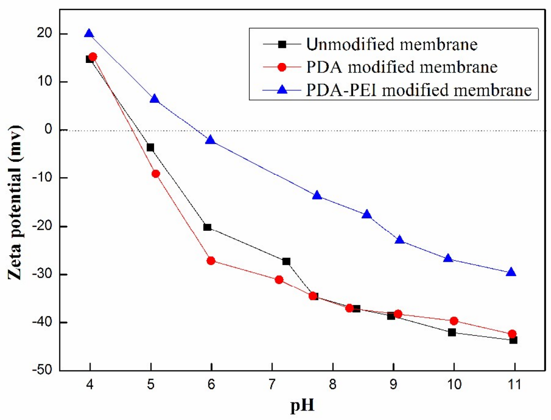

Fig.6. Surface zeta potential as a function of pH for the unmodified and modified membranes

3.2 Membrane permselectivity

Figure 7 shows the influence of modification on the permselectivity of the membrane. The normalized water flux was defined as the ratio of water flux of the modified membrane to the water flux of the membrane before modification. As shown in Figure 7, the water flux reduced significantly during the first step of PDA modification. It showed a slight decrease during the subsequent step of PEI modification. According to the Solution Diffusion theory, the influence of modification on water flux had two aspects. These aspects were: (1) the modification formed a coating on membrane surfaces, which increased the resistance to water diffusion through membrane, hence leading to a decline of water flux. (2) The modification grafted hydrophilic groups on membrane surface. These groups benefited the dissolution of water on membrane surface, leading to an increase in water flux. Thus, the difference in the values of water flux during the two modification steps indicated that the increase in resistance for water diffusion was the major outcome of PDA modification. The influence of modification on water flux for both aspects was almost equal for PEI modification.

The salt rejection rates were also presented in Figure 7. The salt rejection did not show significant changes after PDA modification. However, it increased slightly after the PEI modification. This could be explained through zeta potential analysis. The PDA modification did not influence the electrostatic repulsion between the membranes and the ions in feed solutions. However, the PEI modification increased the electrostatic repulsion between membranes and the Na+ ions, hence increasing the salt rejection rate.

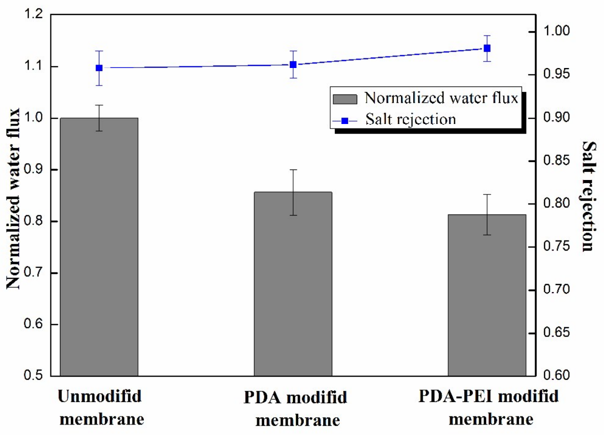

Fig.7. The permselectivity of unmodified and modified membranes

3.3 Anti-fouling

To study the anti-fouling properties, the membranes were fouled by two commonly used contaminants, namely BSA (200ppm, pH 6.3, negative charge) and DTAB (20ppm, pH 6.2, positive charge). The results have been shown in Figure 8. Values of the water flux were normalized to make the comparison simpler. The normalized flux reduced significantly at the beginning. This was due to the addition of contaminants. Addition of contaminants could enhance the osmotic pressure and hence reduce the driving force, leading to the decline of water flux [37]. The subsequent decline of the normalized flux was due to the adsorption of contaminants on the surface of membrane [38]. For BSA fouling experiments, the modified membranes showed slightly better performance than the unmodified membrane. The normalized flux for PDA-PEI modified membranes reduced to 64.5% at the end of fouling, and after washing recovered to a value of 84.2%. The normalized flux for unmodified membrane reduced to 61.5% at the end of fouling, and after washing recovered to a value of 80.7%. For DTAB fouling experiments, the modified membranes showed significantly better performance than the unmodified membrane. The normalized flux for PDA-PEI modified membranes reduced to 56.9% at the end of fouling, and after washing recovered to a value of 69.5%. The normalized flux for unmodified membrane reduced to 45.1% at the end of fouling, and after washing recovered to 57.3%. According to the previous reports [12, 13, 39], the modification influences the anti-fouling properties of a membrane in the following aspects: (1) the modification might have enhanced the hydrophilicity of membrane surface. This could effectively slow down the fouling of membrane. (2) The modification might have moved the membrane surface charge towards the positive side. This would benefit the adsorption of negatively charged BSA on membrane and disadvantage the adsorption of positively charged DTAB on membrane. (3) The modification slightly increased the roughness of membrane surface which was harmful to the fouling resistance of the membrane. Generally speaking, the differing anti-fouling performances of the membranes were due to a combined effect of the three pathways as stated above. The modification enhanced the anti-fouling properties of membranes for both contaminants, especially for the positively charged DTAB.

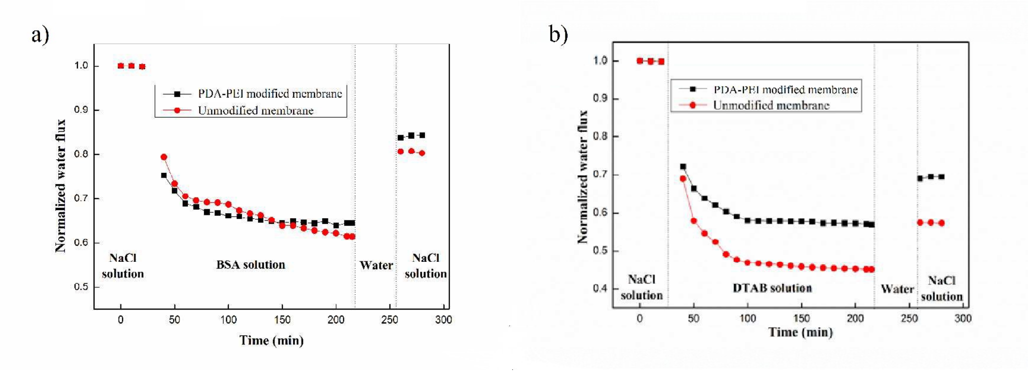

Fig. 8. Results of the fouling/cleaning experiments for the unmodified and PDA-PEI modified membrane: (a) BSA solution; (b) DTAB solution.

3.4 Chlorine resistance

The chlorination of commercial PA RO membranes consists of reversible N-chlorination and irreversible ring-chlorination. Therefore, to investigate the chlorine resistance of membranes, a two-step experiment was designed as a cycle (as mentioned in section 2.6). Figure 9 shows the water flux of unmodified and PDA-PEI modified membranes after seven cycles of treatment. For unmodified membrane, the water flux reduced after chlorination while it recovered after NaOH treatment. The reduction in water flux was due to the chlorination, while the recovery of flux took place due to the reversible regeneration of N-chlorination [28, 40]. As shown in Figure 9, although the water flux recovered modestly after NaOH treatment, it still was less than the original water flux. This indicated that the irreversible ring-chlorination has taken place. With an increase in number of cycles, the water flux of NaOH treated membranes declined continuously. This indicated that the degree of irreversible ring-chlorination degree continued to deepen. In addition, the recovered flux in each cycle dropped consistently, indicating that the degree of reversible N-chlorination was reducing. For the modified membranes, the water flux increased after chlorination at the beginning. Similar to the results of J. Xu et al. [41], this was due to the fact that the chlorination weakened the hydrogen between PEI and membranes, and consumed the part which did not combine strongly with membrane surface, hence reducing the resistance of water diffusion. With increasing number of cycles, the values for water flux of NaOH treated membranes and the recovered flux in each cycle were almost stable, indicating that the degree of chlorination remained unchanged These different water flux values clearly demonstrated that the modified membranes had better chlorine resistance than the unmodified membrane.

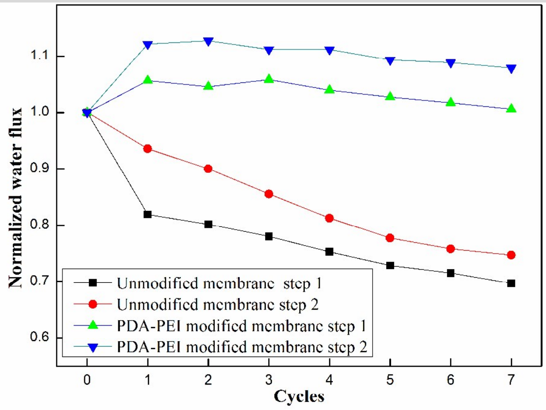

Fig.9. Normalized water flux values for unmodified and modified membranes during seven cycles of treatment.

3.5 Anti-biofouling

Membranes were immersed in unsterilized deionized water to imitate the biofouling of membranes. Figure 10 shows the SEM images of the unmodified and PDA-PEI modified membranes after being immersed in unsterilized deionized water for 90 days. The morphology of original membrane was also shown in the Figure 10. It can clearly be seen that the original membrane has a characteristic peak-and-valley structure. After being immersed for 90 days, the peak-and-valley seemed to have reduced for the surface of PDA-PEI modified membrane. This may due to the bio-fouling caused by the biofilm which was produced by the bacterium on the surface of membranes. On the other hand, after being immersed for90 days, the surface of unmodified membrane changed a lot. The peak-and-valley structure almost disappeared. This indicated that the unmodified membrane suffered more serious biofouling than the PDA-PEI modified membrane, whose surface was covered by the biofilm formed by the bacterium. These differences confirmed that the modification enhanced the anti-biofouling properties of the membrane.

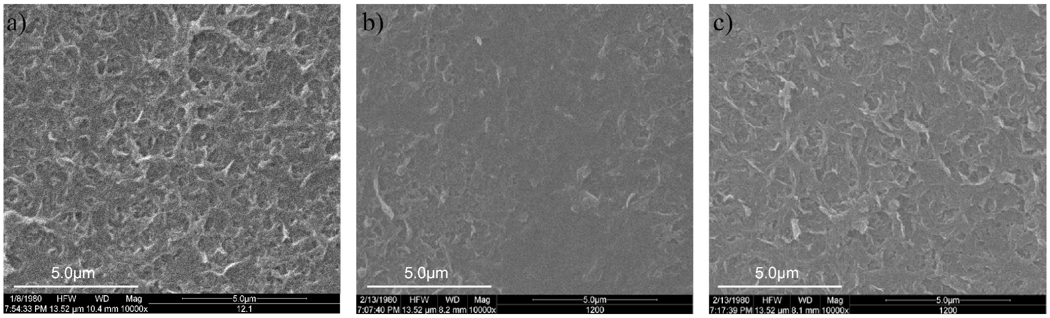

Fig.10. Surface morphologies (×10000) of (a) original membrane; (b) biofouled unmodified membrane; (c) biofouled PDA-PEI modified membrane

4. Conclusions

In this study, an XLE-400 RO membrane was modified with DA followed by PEI. DA self-polymerization formed a thin, hydrophilic film on membrane surface followed by the PEI grafting. PEI grafting introduced a large number of amino groups on membrane surface, which acted as functional groups to enhance the performance of membranes. The successful modification was confirmed by XPS analysis. Surface modification resulted in the increase of membrane surface hydrophilicity. The contact angle reduced from $65.7^{o}\pm5.8^{o}$ for unmodified membrane to $49.2^{o}\pm3.4^{o}$. The modification also influenced the membrane surface charge. The SEM and AFM images of membranes showed that the modification did not damage the surface peak-and-valley substrate and that it increased the surface roughness of membranes slightly. The influence of modification on the performance of membranes was also examined. The PDA-PEI modified membrane showed a lower water flux and a higher salt rejection than unmodified membrane. The PDA-PEI modified membrane had increased chlorine-resistance and better anti-fouling as well as anti-biofouling properties than the unmodified membrane.

Acknowledgments

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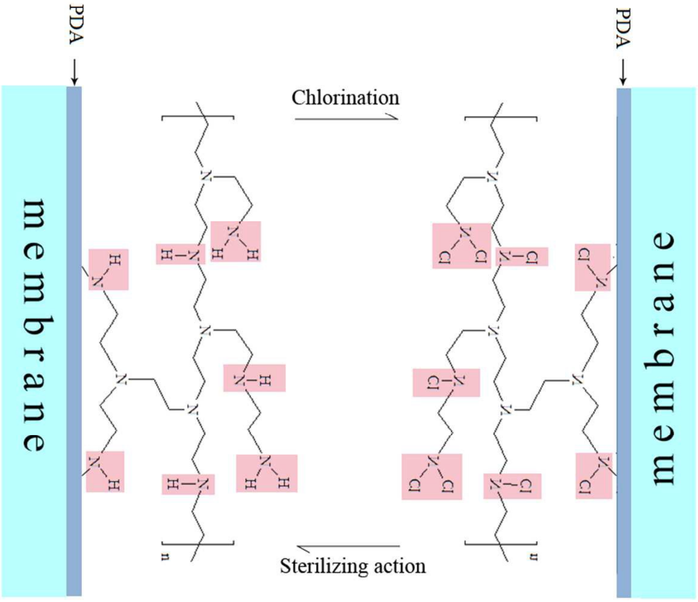
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