Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1081834

57 (2016) 16384–16394
July

Taylor & Francis
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Densely grafting quaternary ammonium cation and salicylaldehyde on the APA-TFC membrane surface for enhancing chlorine resistance and anti-biofouling properties

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Received 10 February 2015; Accepted 3 August 2015

ABSTRACT

For the sake of enhancing chlorine resistance and anti-biofouling simultaneously, the surface of an aromatic polyamide (APA) thin film composite (TFC) membrane was densely modified by quaternary ammonium cation (QAC) and salicylaldehyde (SA) in this work. The aza-Michael reaction was implemented on the APA-TFC membrane surface with the aid of dimethylaminoethyl methacrylate as a Michael receptor and the N–H groups belonged to amide, residual aromatic amines, and polyamides as Michael donors. Then, the dimethylamino groups of the APA-TFC membrane surface were furthermore converted into the QAC through the quaternarization of 5-chloromethylsalicylaldehyde. The experimental results showed that QAC and SA synergistically endowed the membrane with the durable anti-biofouling properties by acting as the anti-microbial agents and bacteria contact-killers, alternatively SA endowed the membrane with the high chlorine resistance as the chlorine-consumer, and QAC could also endow the membrane with the high hydrophilicity as the hydrophilic material. Under the optimized modifying conditions, the chlorine and biofouling had almost no influence on the water flux and salt rejection of the modified membrane during the filtration process fortunately.

Keywords: Polyamide membrane; Quaternary ammonium cation; Salicylaldehyde; Chlorine resistance; Anti-biofouling

1. Introduction

Since more than a half century, seawater desalination technique is considered as one of the most efficient ways to produce fresh water so far [1]. Nanofiltration membrane or reverse osmosis (RO) membrane is a core element used in the seawater desalination technique. Now the popular membrane is a thin film composite (TFC) composed of a support membrane and an aromatic polyamide (APA) functional layer, and aromatic amines and acyl chlorides are used as monomers to fabricate the membrane by the interfacial polymerization [2]. However, the widespread applications of the APA-TFC membranes

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have presented a challenge of the membrane fouling [3], which results in decreased water productivity and deteriorated permeation quality. Among all types of fouling, biofouling has been regarded as the most pervasive and serious problem in the process of the RO [4]. Many strategies have been used to control the biofouling of membranes, such as the chlorine pretreatment of feedwater, dosing biocide in feedwater and periodic chemical cleaning of the existing membranes. As a standard practice to control biofouling, the chlorine pretreatment has been widely used in desalination systems, while the APA-TFC membranes are susceptible to the residual chlorine that can cause the chlorination degradation of the APA-TFC membranes and generate the reduced salt rejection in the feedwater. Therefore, the current operational attempts are numerously devoted to create the new functional monomers, the novel modification and the fabrication processes in order to improve the chlorine resistance and anti-biofouling. Many researchers suggested an effective way to use piperazine or secondary amines instead of aromatic primary amines as monomers in membrane fabrications for eliminating chlorine-sensitive sites of the APA-TFC membrane [5,6]. Additionally, other polyamine monomer with the electron-withdrawing groups (such as –F or $–NO_2$) was used in the APA-TFC membrane fabrication, which minimize any N-chlorination of the polyamides [7]. However, these approaches to improve membrane chlorine resistance were at the expense of reduced salt rejection and increased cost. Moreover, to eliminate chlorine-sensitive sites of the APA-TFC membrane, diglycidyl ether and polyisocyanates were used to react with N–H groups of the top layer polyamide, which presented the high chlorine resistance and brought the water flux decline [8,9].

Membrane surface modification was considered as a potential route to prepare an anti-biofouling membrane by linking hydrophilic polyol, tethering antimicrobial moieties, and grafting ionic monomers to achieve biocide leaching, bacterial adhesion resistance, and contact-killing [10]. Yet, there was still a risk of the chlorine degradation for the above modified membranes, because they always had high anti-biofouling properties without any chlorine resistance [11]. Summarily, it can be seen that improvements of chlorine resistance and anti-biofouling property are the main challenges for the APA-TFC membranes. There would be a strong desire to simultaneously improve both chlorine resistance and anti-biofouling properties of the APA-TFC membranes by a facile multifunctional modification, however rare information about improving the both properties has been reported so far [12].

As is well known that the quaternary ammonium salt has been widely used as a surfactant or a bactericide [13], meanwhile salicylaldehyde (SA) has been used as an antibacterial or a preservative. Besides, SA can play as a chlorine-consumer on account of the features that it easily undergoes an electrophilic substitution and redox reaction with free chlorine and hypochlorite. In our previous work [14], the quaternary ammonium cation (QAC) and SA were simultaneously used to modify the APA-TFC membrane surface [15], which showed that QAC and SA could endow the APA-TFC membrane with high hydrophilicity and high chlorine resistance, as well as powerful anti-biofouling properties. But the defect was the low density of QAC and SA on the modified membrane surface.

To enhance the density of QAC and SA on membrane surface, here we gave a novel surface modification of the APA-TFC membrane, of which the perfect results were that QAC and SA were densely grafted on the APA-TFC membrane surface at the same time. The N–H groups of the APAs are inherent functional groups on the APA-TFC membrane surface, which is attributed to the amidation of m-phenylenediamine (MPD) with the residual acyl chloride groups derived from incomplete reactions of aromatic acyl chlorides with aromatic amines monomers during the APA-TFC membrane fabrication by the interfacial polymerization [6,16]. We all know aromatic amines are not good Michael donors to α,β-unsaturated compounds in the aza-Michael additions, and neutral amides or imides have also very restricted nucleophilicity. Under effective catalytic conditions, they can all become more convenient nucleophiles in aza-Michael additions [17]. So we chose dimethylaminoethyl methacrylate (DMAEA) classified in tertiary amino acrylates as a Michael receptor, and the superiority was that the tertiary amino groups are easily connected on APA-TFC membrane surface through the aza-Michael addition, furthermore converted into the QAC through quaternarization with 5-chloromethylsalicylaldehyde (CSA) [18].

2. Experimental section

2.1. Materials

The microporous polyethersulfone support membrane was supplied by Vortron Technology Co. Ltd (Beijing, China). Trimesoyl chloride (TMC), MPD and triethyl amine (TEA) were purchased from Jingchun Chemical Reagent Co. Ltd (Shanghai, China). DMAEA used as a Michael acceptor was purchased from Fuchen Chemical Reagent Co. Ltd (Tianjin, China).

4-Diethylaminopyridine (DEAP) and 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) used as the catalyst was purchased from Alpha Chemicals Co. Ltd (Zhengzhou, China). CSA was prepared according to literature [18]. Sodium hypochlorite solution (NaClO, 4.6wt.%) used in membrane chlorination experiments was purchased from Times Supermarket (Lianyungang, China). Other reagents such as n-hexane and sodium chloride were of analytical grade and used without further purification.

2.2. Fabrication of APA-TFC membrane

In order to unravel the relations between N–H bonds and the density of QAC and SA on the membrane surface, firstly the APA-TFC membrane was fabricated by reacting TMC with MPD on the supported membrane surface. And then the residual acyl chloride groups on the APA-TFC membrane surface could further react with MPD [6]. The result was that lots of N–H groups belonged to the APAs and aromatic amines were possessed on the APA-TFC membrane surface. The APA-TFC membrane containing the residual acyl chloride groups was made via the interfacial polymerization of TMC (1.2 wt.%) in n-hexane, MPD (0.5 wt.%), and TEA (1.1 wt.%) in aqueous phase [16]. The process was that MPD/TEA solution was coated over the support membrane for 60 s, and then dried. The MPD/TEA saturated support membrane was then immersed into TMC solution for 60 s, heat curing at 35˚C for 5 min, and at 80˚C for 15 min. Finally, the nascent membrane was formed, which contained the residual acyl chloride groups. The nascent membrane was followed by rinsing with MPD/TEA solution at 50˚C for 60 min, and converted into the new membrane containing the amide and the aromatic amines on its surface (referred to as AA-membrane).

2.3. Preparation of modified APA-TFC membranes

The AA-membrane was immersed into water, and DMAEMA and DBU were also added into water. The aza-Michael addition was conducted at 25˚C for 6, 12, 18, 24 h or at 50˚C for 6, 12, 18, 24 h, respectively. After that, the tertiary aminated membranes (referred to as TA-membrane) were formed. Then TA-membrane was covered with CSA solution at room temperature for 2 h followed by rinsing with acetone. QAC and SA were grafted on the surface of the APA-TFC membrane (referred to as M-membrane).

2.4. Characterization of M-membrane

2.4.1. Membrane chemical composition and morphology analysis

The membrane samples including the nascent membrane, AA-membrane, TA-membrane, and the M-membrane were dried at 40˚C before the following analyses. Attenuated total reflectance Fourier transform infrared spectroscopy ATR-FTIR (MAGNA-560, Thermo Nicolet Corp., USA) was used as the surface characterization technique to investigate the surface chemical structure and morphology before and after the modification, and each ATR-FTIR spectrum was averaged from 100 scans collected at 4 cm^{-1} resolution. The morphology of the membrane samples were observed by scanning electron microscope (JEOL J5M-6700F, JEOL, Japan).

2.4.2. Contact angle measurements

The water contact angle of the membrane surface was measured with Dropmeter A-200 equipment (Jiangdong testing instruments Co. Ltd, Ningbo, China) in order to characterize the hydrophilicity using a sessile drop method, with pure water as the probe liquid. Before the measurements, all membrane samples were conditioned overnight at 40˚C with a relative humidity of 50%. Each data point given was an average value based on three contact angle measurements at three random locations on the membrane specimens.

2.4.3. Zeta-potential determinations

The zeta-potential value of the membrane was determined from electrophoretic mobility measurement using a commercially available electrophoresis measurement apparatus (ELS-8000, Otsuka Electronics, Japan) in a background electrolyte solution containing 10 mmol L^{-1} KCl over a pH range of 3–10 at room temperature. The initial pH of the background electrolyte solution was adjusted to pH of 3 using HCl solution (1 mol L^{-1}). Then, solution pH was increased in small steps by adding KOH solution (0.2 mol L^{-1}). The streaming potential (ΔE) at each pH was obtained after stabilization. ΔE at five different pressures (ΔP) ranging from 0.1 to 0.5 bar were measured and the zeta potential (ζ) determined using the streaming potential slope vs. pressure plots based on the Helmholtz–Smoluchowski Eq. (1) [19]:

$$\xi = \frac{\Delta E \cdot \mu \cdot \eta}{\Delta P \cdot \varepsilon} \quad (1)$$

where ε is the dielectric constant, and μ and η are the viscosity and conductivity of the solution, respectively.

2.4.4. Chlorination experiments of membranes

Short-time exposures of membranes to high free chlorine concentrations were professionally accepted [20] to evaluate the membranes chlorine resistance in this paper. The chlorination solutions with concentrations of 1,000, 3,000, 5,000, and 7,000 ppm were prepared by diluting a commercial sodium hypochlorite solution with pure water. The pH value of the free chlorine solutions was adjusted by HCl solution (1 mol L^{-1}). Membrane chlorination experiments were carried out by soaking tests under various chlorine concentrations at pH of 4.0 for 20 h at room temperature. The performances of the AA-membrane, TA-membrane, and M-membrane were tested after being thoroughly rinsed with pure water and immersed in pure water for 48 h. The water fluxes and salt rejections were tested under 1.6 MPa using 2000 ppm NaCl solution at 25˚C and at pH of 7.0. The water fluxes were determined by direct measurement of the permeate flow in terms of liter per square meter per hour (L m^{-2} h^{-1}). The salt rejection rate was calculated using the following equation: rejection (%) = $100 \times (1 - (C_p/C_f))$, in which C_p and C_f were solute concentrations in permeate and feed, respectively. C_p and C_f were determined by measuring the electrical conductance using a conductance meter (DDSJ-308A, Cany Precision Instruments Co. Ltd, China).

2.4.5. Evaluation of membrane anti-biofouling abilities

Generally, the anti-biofouling improvement of the membranes was implemented with two strategies: adhesion resistance and contact killing. *Escherichia coli* (*E. coli*) was professionally used as a model microorganism to test the antimicrobial functions of the membranes [21,22]. The antimicrobial abilities were described below: A diluted *E. coli* suspension at about 1.0×10^6 colony forming units per milliliter (cfu mL^{-1}) concentration was firstly prepared. The *E. coli* suspension were covered onto the membrane (2.5 cm diameter), and the inoculum containing 1 wt.% bactotryptone, 0.5 wt.% yeast extract, and 0.1 wt.% NaCl was added to the *E. coli* suspension, and then the cells were incubated at 37˚C for 24 h. After a desired period of cultivating, the membrane was taken out and rinsed with water, and then observed for adhesion and contact killing by SEM. The water fluxes of the membranes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25˚C.

3. Results and discussion

3.1. Characterization of modified APA-TFC membrane surface

3.1.1. Modifications of nascent membrane

Fig. 1 presented the surface modification processes of the APA-TFC membrane with QAC and SA. We can clearly know that the more tertiary amino groups grafted on the APA-TFC membrane surface, the greater number of QAC and SA could be obtained, as well as the higher hydrophilicity, higher chlorine resistance, and more powerful anti-biofouling properties. Additionally, the introduction of the tertiary amino groups onto the APA-TFC membrane surface was based on the aza-Michael additions of the N–H groups reacting with DMAEA.

Although the N–H groups of the barrier layer polyamide can react with DMAEMA under the condition of catalysis [17], they are one kind of the main factors to keep the structures of the membrane surface stable. To retain the original polyamide H-bond structures as much as possible, MPD was used to have a new amidation with the residual acyl groups on the nascent membrane surface. Hence, lots of the new N–H groups belonged to amides and aromatic amines were formed and expected to react with DMAEMA in the aza-Michael additions on the AA-membrane surface under the condition of catalysis.

It was reported that DBU was a most effective catalyst in the aza-Michael additions of the aromatic amines and the neutral amides [17,23]. As a part of our research in the membrane, we found that DEAP had a same effective catalysis like DBU. So the reaction time and temperature became the main factors to influence the tertiary amination degree in the aza-Michael additions, which were investigated and the results were shown in Fig. 2.

The experiments showed that the tertiary amination degrees were improved as the increase of time and temperature, and it reflected in the weight increment of TA-membrane. Fig. 2 showed that the tertiary amination degrees of TA-membrane were higher at 50 ± 2˚C than at 25 ± 2˚C. It could be attributed to the fact that high temperature can increase the degree of the aza-Michael additions. It is a fact that CSA has a high active chloromethyl group and reacts simply with tertiary amino groups of TA-membrane [18]. According to hydroxylamine hydrochloride potentiometric titration analysis, the analytic results presented that the higher the degree of tertiary amination groups was, the more aromatic aldehyde groups could be introduced onto the surface of the modified membrane.

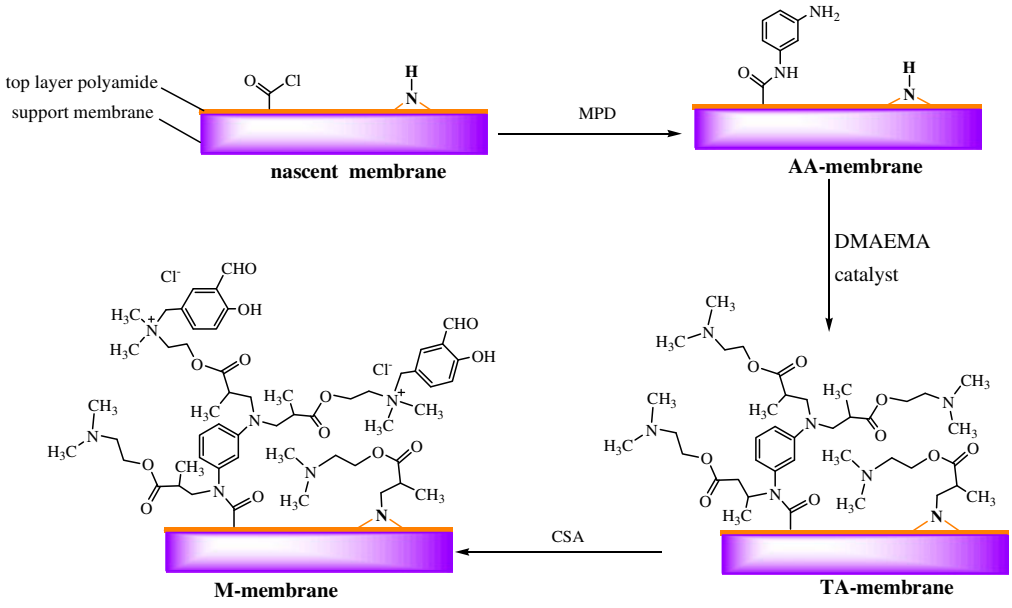

Fig. 1. Modification processes of nascent membrane.

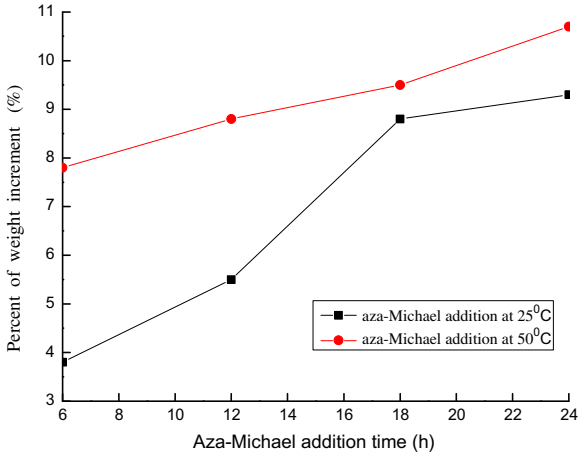

Fig. 2. Weight increase of nascent membrane after aza-Michael addition.

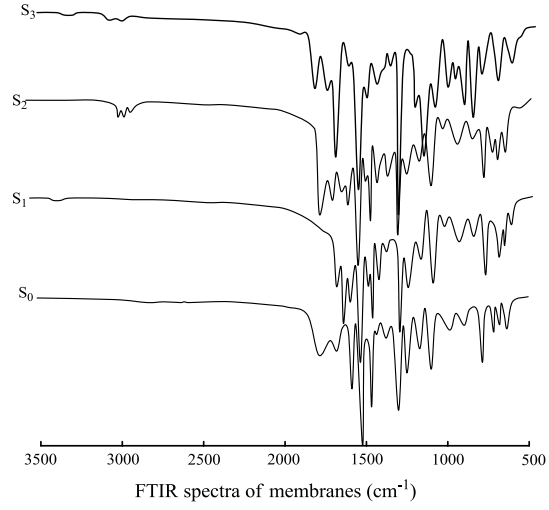

Fig. 3. ATR-FTIR spectra of all membrane specimens.

3.1.2. ATR-FTIR analysis

S_0 showed the FTIR spectrum of the nascent membrane in Fig. 3, the intense bands at 1,767, 1,680, and 1,521 cm^{-1} corresponding to residual acyl chloride C=O, polyamide C=O stretching, and benzene-ring C=C stretching, respectively, are characteristics for APA in the barrier layer. The bands at 1,264 and 1,153 cm^{-1} corresponding to Ar–O–Ar stretching (Ar denotes an aromatic ring) were characteristic for polyethersulfone in the support layer. S_1 was the FTIR spectrum of AA-membrane, compared with the nascent membrane, which the new weak adsorption appeared at 3,437 cm^{-1} belonged to aromatic amine N–H while the residual acyl chloride C=O stretching adsorption disappeared at 1,767 cm^{-1}. After the aza-Michael additions, the new strong adsorption appeared at 1,732 cm^{-1}, which was attributed to the ester C=O stretching vibrations, and the weak adsorptions 2,968 and 2,876 cm^{-1} were attributed to the C–H stretching vibrations of CH_3 or CH_2 in the FTIR spectrum of TA-membrane. Then S_3 was the FTIR spectrum of M-membrane containing QAC and SA. The results indicate that the new stretching vibration

appeared at 1,687 cm^{-1} of the aromatic aldehyde carbonyl [24]. So it could be confirmed that the expected amidation, aza-Michael addition and quaternarization had been completed on the surface of the nascent membrane.

3.2. Contact angles

The results of water contact angles of the AA-membrane, TA-membrane, and the M-membrane were 78˚, in the range of 73–46˚ and 43–28˚, respectively. It can be seen that the water contact angles of TA-membranes were decreased with the growth of aza-Michael addition time and temperature in Fig. 4.

The water contact angles of the M-membrane were observably smaller than that of TA-membranes. It was clear that higher weight increment percent of the membranes could lead to smaller water contact angles. The first reason was that DMAEMA was a hydrophilic Michael receptor [25]. The second one would be that not only did N–H groups of both the amide and aromatic amines take part in the aza-Michael additions on the membrane surface, but also the N–H groups of polyamide involved in the reaction with the increase of time and temperature. So the increase degree of tertiary amination resulted in decrease of the water contact angles [25]. After TA-membrane was transformed into M-membrane by the quaternarization, M-membrane had higher hydrophility than TA-membrane, which would be attributable to that the QACs had stronger hydrophility than the tertiary amino groups [26].

3.3. Zeta potential analysis

The zeta potentials of the nascent membrane after hydrolysis, AA-membrane, TA-membrane, and M-membrane were all measured at different pH values in the range from 3.0 to 10.0, and the results were shown in Fig. 5.

We all know that the residual acyl chloride groups of the nascent membrane undergo hydrolysis in aqueous solution to form carboxylated membrane. Because the aromatic carboxylic acid pKa of the carboxylated membrane is 4.5–5, the zeta-potential value of the nascent membrane after hydrolysis was below 0 mV at pH 4.8. This showed that the carboxylated membrane begins to possess a negative charged property above pH 4.8. Most of the carboxylic acids were deprotonated when the pH was up to 6.5. The zeta-potential values of AA-membrane and TA-membrane were nearly 0 mV at pH 7.0 and 7.9, respectively. [27] This was attributed to that the tertiary amino group has a bigger value of pKb than the aromatic amine. The zeta potential of M-membrane equals 0 mV at pH 9.5. The reason was that QAC lost Cl^- and SA lost H^+ at the same time, and the number of the residual positive charges was equal to that of the negative ions on the modified membrane.

3.4. Chlorination resistance abilities

The water fluxes of the nascent membrane after hydrolysis, AA-membrane, TA-membrane, and M-membrane were all tested before and after the treatment with 1,000, 3,000, 5,000, and 7,000 ppm chlorine

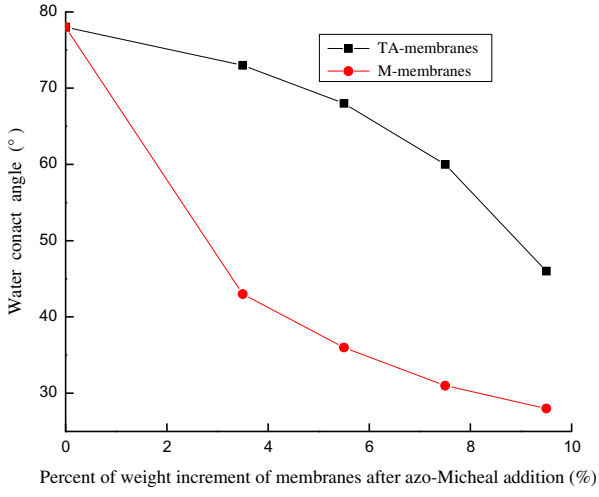

Fig. 4. Water contact angles of TA-membranes and M-membranes.

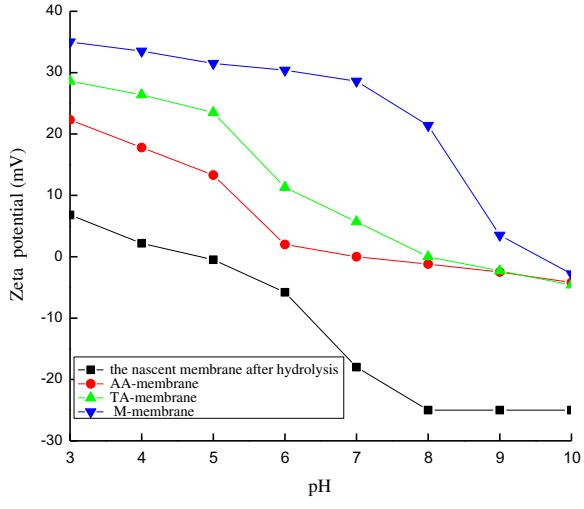

Fig. 5. Zeta potentials of membrane specimens at different pH.

solution at pH of 4 for 20 h during the filtration for 2–32 h, and the results were shown in Figs. 6–11. It could be clearly seen that there were apparent changes in both the water flux and salt rejection of all membrane specimens.

Fig. 6 showed that the water fluxes of all membrane specimens had almost no changes during the filtration, but it is apparent from the Figs. 7–11 that their water fluxes were all increased with the increase of the chlorine concentration and the chlorination time. For example, in 7,000 ppm chlorine solution, the water flux increment percents of the membrane specimens before and after the chlorination were 44.6, 27.7, 28.9, and 4.3%, respectively. This would be attributed to that the barrier layer structures of the hydrolyzed nascent membrane were seriously destroyed after the chlorination in 7,000 ppm chlorine solution, so there not be any chlorine-consumer to protect the membrane from the chlorine attack. In addition, the water flux increment percents of AA-membrane and TA-membrane were lower than that of the hydrolyzed nascent membrane. This may reveal that the aromatic amines with high reactivity with chlorine were used as the sacrificial materials and could give some protection to the membranes. Among the membrane specimens, M-membrane had the lowest percent in the water flux increment after the chlorination. The explanation was that there were both aromatic amines and SA on M-membrane surface, which give enough protection to the membrane.

From Figs. 12 and 13, it can be seen that the salt rejections of the nascent membrane after hydrolysis,

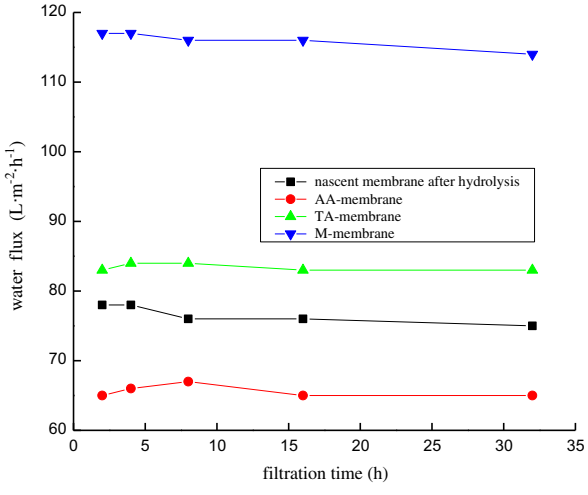

Fig. 6. Membrane stability before chlorination during filtration.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 before chlorination.

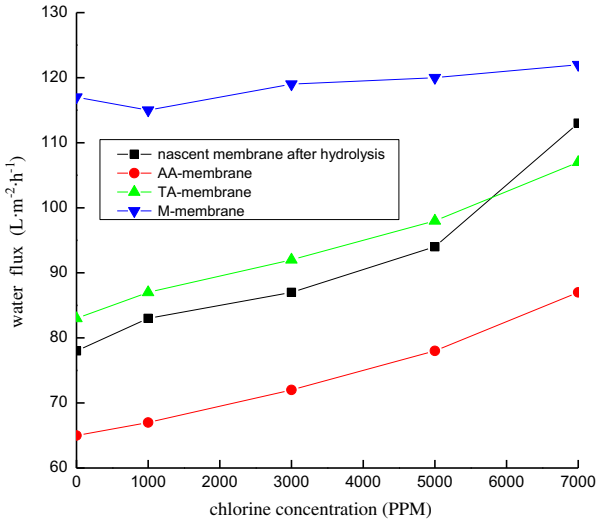

Fig. 7. Water fluxes of membranes after chlorination.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 for 2 h filtration.

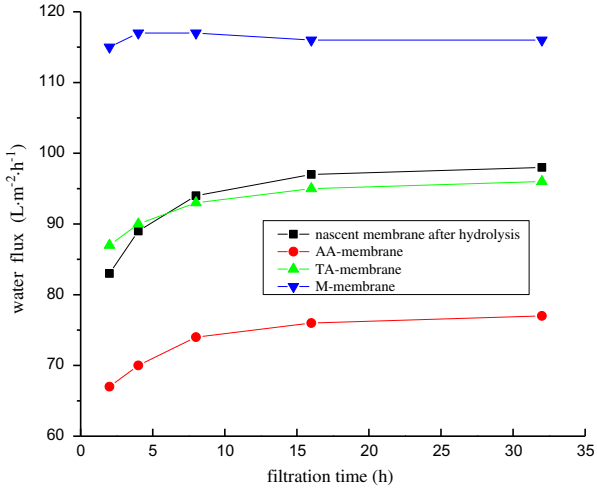

Fig. 8. Membrane stability after 20 h chlorination during filtration.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 after 20 h chlorination with 1,000 ppm chloride solution.

AA-membrane and TA-membrane after chlorination decreased during the performance tests, respectively. Inversely, the salt rejection of the chlorinated M-membrane was only slightly decreased in comparison with that of the above three membranes, which was demonstrated that the chlorine resistance of the modified polyamide membrane is much better than that of the other membranes. The observed notable performance decline for the nascent membrane after

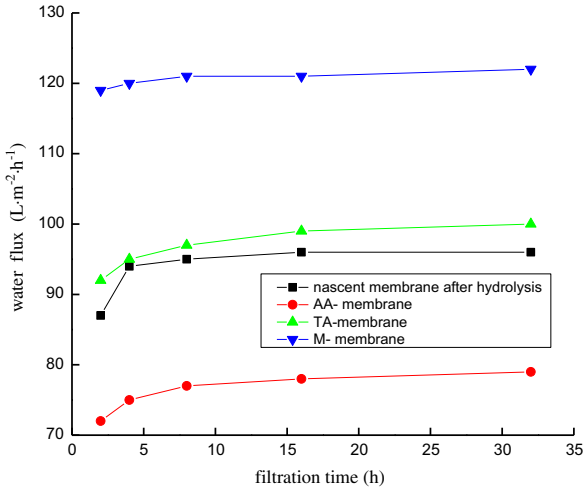

Fig. 9. Membrane stability after 20 h chlorination during filtration.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 after 20 h chlorination with 3,000 ppm chloride solution.

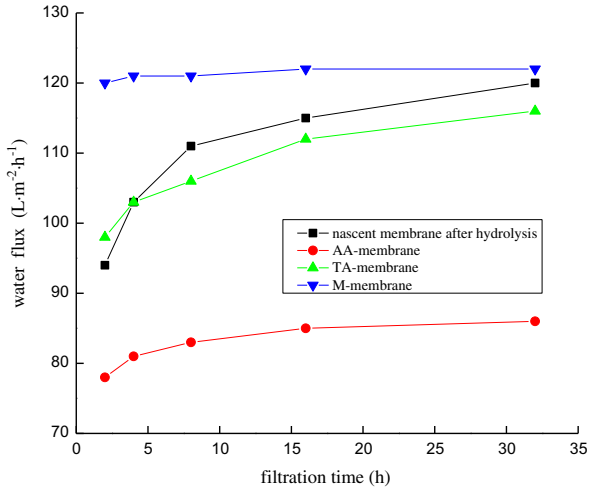

Fig. 10. Membrane stability after 20 h chlorination during filtration.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 after 20 h chlorination with 5,000 ppm chloride solution.

hydrolysis, AA-membrane and TA-membrane with increasing chlorine exposure is attributed to the great conformational deformations of polyamide chains of the membranes' top layer. In a word, the significant increases in the water fluxes of the M-membranes should be mainly due to the obvious increases in the membrane surface hydrophilicity after modifications with QAS and SA, and they also acted by the sacrificial materials to protect the M-membrane from the chlorine attacks.

3.5. Anti-biofouling properties

The microscope images (A)–(C) in Fig. 14 showed the results of the adhered bacteria on the surfaces of the hydrolyzed nascent membrane, TA-membrane, and the M-membrane after cultivated in *E. coli* cells suspension, respectively. The microscope images (D)–(E) showed the adhered bacteria on the microscope images (A)–(C) after being stained by SYTO9 and propidium iodide, respectively. The living bacteria will be stained by SYTO9 and shown in green. Only the dead bacteria will be stained by propidium iodide and shown in red [28].

It can be seen that the number of adsorbed bacteria on M-membrane surface was significantly decreased in comparison with either the hydrolyzed nascent membrane or TA-membrane in Fig. 10. This result showed that M-membrane had remarkable adhesion resistance to microorganisms, and the fluorescent images showed that almost two-thirds of the adhered bacteria on the surface of M-membrane

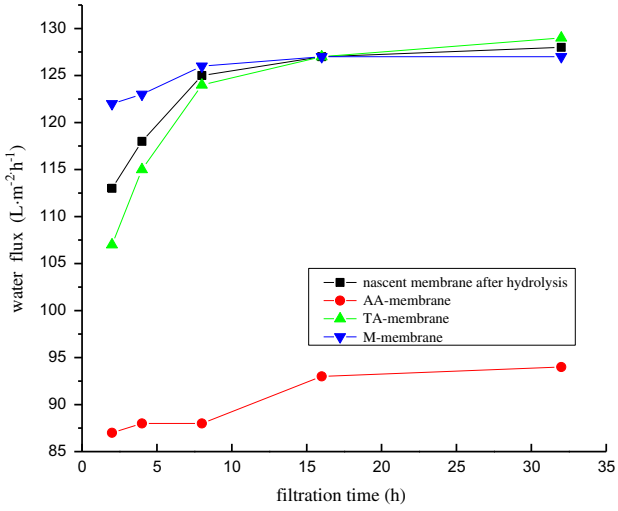

Fig. 11. Membrane stability after 20 h chlorination during filtration.
Note: The water fluxes were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 after 20 h chlorination with 7,000 ppm chloride solution.

were killed. And it also indicated that M-membrane had the powerful sterilization functions, which could be attributed to the synergetic disinfection and sterilization actions of quaternary ammonium salt and SA [29].

Fig. 15 showed the water flux changes of the membranes before and after exposure to microbial cell suspension. It was obviously seen that the water

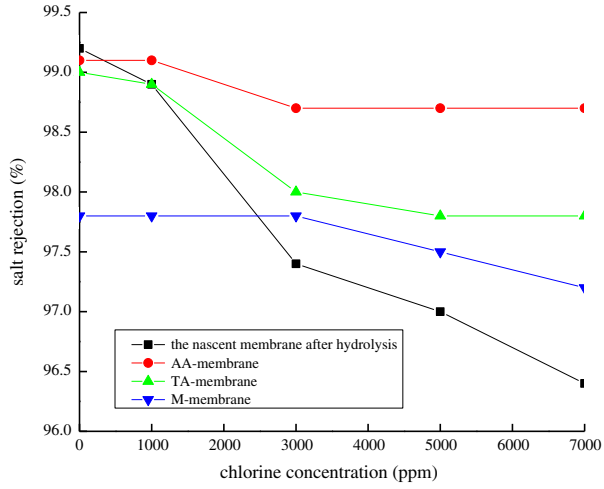

Fig. 12. Effects of chlorine concentration on salt rejection. Note: The salt rejections were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 during the filtration process for 2 h.

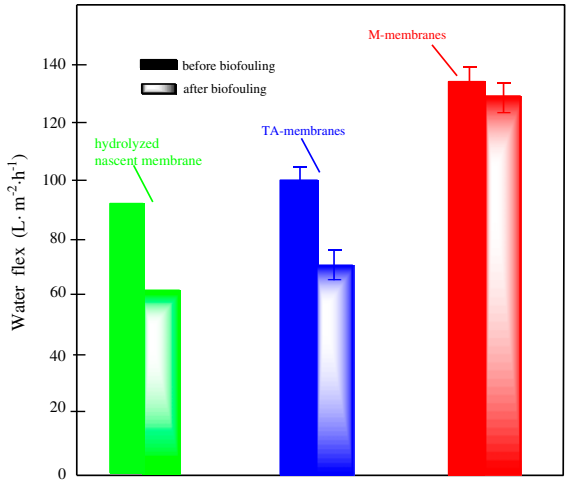

Fig. 15. Water flexes of membranes before and after biofouling.

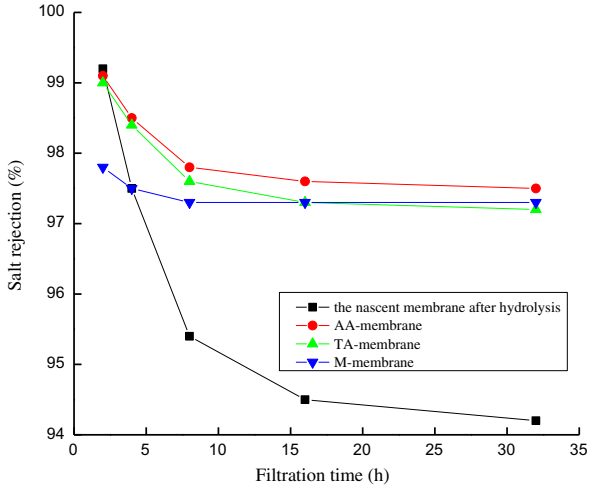

Fig. 13. Stability of membranes during filtration processes. Note: The salt rejections were tested under 1.6 MPa using 2,000 ppm NaCl solution at 25℃ and at pH 7.0 during the filtration process for 32 h.

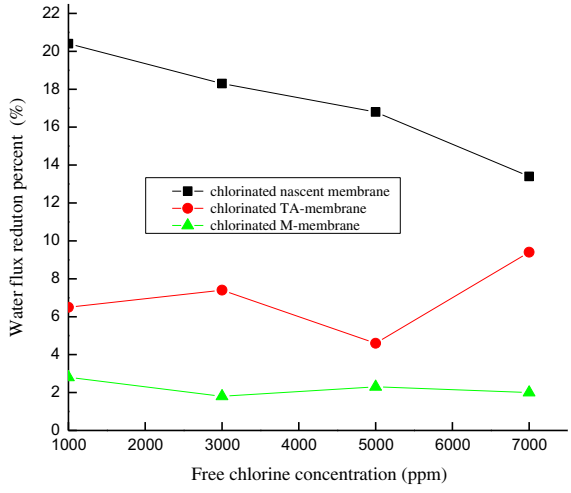

Fig. 16. Water fluxes reduction of chlorinated membranes after biofouling.

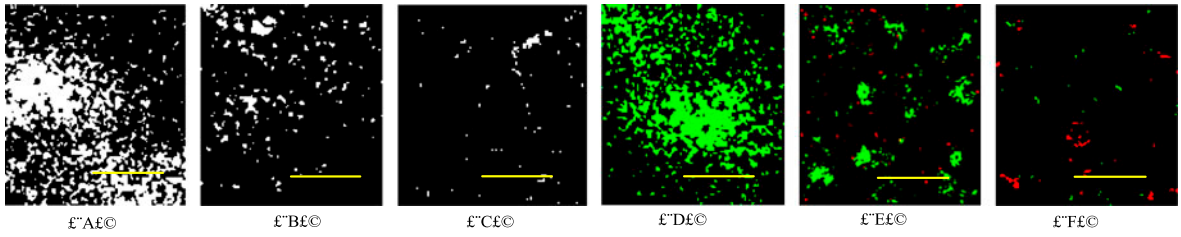

Fig. 14. Microscope images of bacteria adhered membranes. Note: Scale bar represent 20 μm.

fluxes decreased for all the biofouling membranes. During 24 h under the same fouling conditions, the water flux declines of the modified membranes after exposure to microbial cell suspension were very little compared with that of the hydrolyzed nascent membrane and TA-membrane. After 24-hour exposure to cells suspension, the hydrolyzed nascent membrane lost 37% of its original water fluxes, TA-membrane lost 43–57% of its original water fluxes, and there were 2.0–2.8% of water flux losses for M-membranes, respectively. The reason was that the first two membranes had been clogged with the adhered microbial cells.

In addition, we can also know from Fig. 16, there were some changes of the water fluxes for the chlorinated membranes compared with their original membranes under the same fouling conditions. The higher free chlorine concentrations during the chlorination period was, the smaller the water fluxes reduction percent of the chlorinated nascent membrane would be after cultivated in *E. coli* cells suspension. However, there was almost no difference of M-membranes about the water fluxes before and after chlorination under the same fouling conditions. The experimental results further indicated that QAs and SA on M-membrane surface had the synergetic disinfection and sterilization, as well as high resistance to the microbial cells and chlorine.

4. Conclusion

In conclusion, the QAC and SA units were successfully anchored to the APA-TFC membrane surface through aza-Michael addition and quaternarization. Firstly, the chemical composition of the M-membrane surface was determined by the instrumental and chemical analysis, respectively. The anti-biofouling efficiencies of the M-membrane were expressed by the reduction rate of *E. coli* cells. Then, the water contact angles of M-membrane decreased obviously in comparison with the hydrolyzed nascent membrane. The zeta-potential of the M-membrane was nearly 0 mV at pH 9.5. Finally, the M-membrane had almost changeless water fluxes after the chlorination, and the positive charges on the top surface of the M-membrane had some negative effects on salt rejections. Even if exposed in 20 × 7,000 ppm h chlorination solution or incubated in the microbial cells suspension at 37℃ for 24 h, the M-membrane had stable performance in water fluxes and salt rejections, and had high resistance to biofouling and chlorine.

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