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The performance improvement of hollow fiber composite reverse osmosis membranes by post-treatments

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ABSTRACT

While the technology of spiral-wound reverse osmosis membrane tends to be more and more mature, the reports of hollow fiber reverse osmosis membranes are still relatively sparse. In this report, the hollow fiber composite reverse osmosis membranes were prepared by the interfacial polymerization of m-phenylenediamine (mPDA) and trimesoyl chloride (TMC) using polysulfone ultrafiltration membrane as the support. Post-treatments including with NaOCl solution and polyvinly alcohol (PVA) solution were employed to improve the performance of the membranes. The chemical composition and surface structure of the membranes obtained at the different post-treatment conditions were characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and atom force microscopy (AFM). The results showed that the salt rejection of the membranes increases dramatically but the permeate flux decreases slightly after NaOCl and PVA solution treatment. The membrane treated with 500 ppm of NaOCl solution and 20 ppm of PVA solution by turn exhibited the salt rejection of 96.3% and pure water flux of 10.9 $l \cdot m^{-2} \cdot h^{-1}$) at 500 ppm NaCl solution, 100 psi and 25°C.

Keywords: Hollow fiber; Reverse osmosis; Thin-film composite membrane; Post-treatment; Hypochlorite treatment; Polyvinyl alcohol

1. Introduction

Due to the increasing demand for water coupled with a shortage of reliable water sources, the water treatment industry has a booming development in recent years. Reverse osmosis (RO) has become one of the most efficient approaches for sea water desalination, grey water reuse and pure water production. However, the current commercial RO membranes are mostly in the form of spiral-wound. Hollow fiber membranes have the advantages of high surface to volume ratio and low cost manufacturing process [1]. But there are very few research on hollow fiber RO membranes [2,3]. Modern RO membranes for water purification are predominantly thin film composite (TFC) polyamide (PA) membranes. For these reasons, it is important to develop TFC membranes based on hollow fiber ultrafiltration membranes combining the advantages of TFC membranes and hollow fiber membranes.

Post-treatment is an effective method to improve membrane performance. Treatment of TFC PA membranes has been demonstrated to lead to improved membrane performance [4]. Among them are chlorine treatment [5–7] and PVA coating [8–11]. Chlorine treatment has been disclosed in patents to be capable of enhancing either the membrane permeability or salt rejections. Its mechanism has been studied in detail [5–7].

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The PVA coating on commercial RO membranes were demonstrated to impart the membrane enhanced hydrophilicity and anti-fouling properties in addition to improved solute rejection.

In this work, a novel hollow fiber reverse osmosis TFC membrane was developed by interfacial polymerization of TMC and MPDA on polysulfone(PSF) membranes as support membranes. Post-treatment was conducted to improve membrane performances. The chemical and morphological structure of the treated membranes was characterized in detail by using ATR-FTIR, scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), to better understand the relationship between the membrane performance improvements with the membrane structure changes.

2. Experimental

2.1. Materials

Outside-in polysulfone (PSF) hollow fiber membrane with an outer diameter of 0.38 mm (MWCO-20000, Tianjin MoTiMo Membrane Engineering and Technology Co.Ltd., Tianjin, China) was used as the support membrane for preparation of TFC RO membrane. Trimesoyl chloride (TMC) and m-phenylenediamine (mPDA) were purchased from Tianjin Guangfu Chemical Plant Co. (China). (+)-10-champhor sulfonic acid (CSA) was purchased from Shanghai Jingchun Reagent, Ltd. Hexane, triethyl amine (TEA), dodecyl sulfonic acid sodium salt (DDS) and sodium chloride were all analytical grade and used as received without any purification.

2.2. TFC membrane preparation

PSF hollow fiber membrane stored in 10% isopropanol aqueous solution was taken out and directly immersed in MPDA (2%) aqueous solution (2% of TEA, 0.1% of DDS and 4.6% of CSA 4.6%) for a 15 min. Excess aqueous solution was removed from the PSF hollow fiber membrane surface by dipping with filter paper. Then the PSF support membrane saturated by MPDA solution was immersed into TMC (0.1%) solution for 30 s. After preparation, the fibers were left to dry over night and then the module was built. Twenty fibers were glued inside a module having an effective membrane area of 59.7 cm^2.

2.3. Post-treatments

Membrane chlorine treatment experiments were performed using laboratory equipments constituted by a feed tank of 1 l, a centrifugal pump, a manometer for measuring the inlet pressure and a hollow membrane cell made in our laboratory. The membrane was contaced with the aqueous solutions of 10 ppm, 100 ppm, 500 ppm and 1000 ppm NaOCl (pH was adjusted 10 with hydrochloric acid and sodium hydroxide) at pressure of 0 psi, the feed flow rate of 3.5 l·min^{-1} and temperature of 25°C, in a continuous process, respectively. The polyvinyl alcohol (PVA) coating was conducted in the same way with PVA concentrations at 10 ppm, 20 ppm and 50 ppm.

2.4. Membrane characterization

All tests for thin film composite RO membranes performance were conducted at 100 psi using a 500 ppm NaCl solution at room temperature by using a cross-flow type apparatus. Both permeate and retentate were recycled back to the feed tank during the tests. All membrane samples were prepared and tested at least twice with a total of 3 membranes tests for RO performance, results of which have been averaged. The salt rejection (R) was calculated from the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% ,$$

where C_p and C_f are the salt concentrations (mg·l^{-1}) of permeate and feed which were measured by a conductance meter (DDS-11A, Shengbang Co., Tianjin, China), respectively.

The flux (F) was calculated from the following equation:

$$P = \frac{\delta\sigma}{\delta t} \cdot \frac{(V_0 - \Delta V)}{S \cdot \sigma_m \cdot C}$$

where V is permeate volume (L); S are the effective surface area of membrane (m^2); t is the penetration time (h).

ATR-FTIR spectra were obtained using a Nexus 470 FTIR spectrometer (Nicolet) equipped with an ATR element and Omnic 6.2 software (Thermo Electron Corporation). The membrane active layers were pressed tightly against the crystal plate, and carbon dioxide and water vapor were removed during the measurements.

Surface chemical structure was analyzed by using a ThermoFisher K-alpha X-ray photoelectron spectroscopy (XPS) employing a monochromated Al-Ka X-ray source (hv = 1486.6 eV). Survey spectra were recorded with a pass energy of 200 eV, and high resolution spectra with a pass energy of 50 eV. Two regimes with a diameter of 400 μm on each TFC membrane were radiated by X-ray to collect atomic information. Relative atomic concentrations of the membrane surface were calculated by normalizing peak areas with the elemental sensitivity factor data provided in the ThermoFisher database.

Membrane surface roughness was determined by atomic force microscopy (AFM, Agilent AFM5500, USA) imaging and analysis, equipped with standard silicon nitride cantilever (MikroMasch, USA).

3. Results and discussion

3.1. Chlorination

3.1.1. ATR-FTIR analysis

The surface chemical composition of the unmodified and the modified membranes were characterized by the ATR-FTIR spectroscopy and the spectra are presented in Fig. 1. As shown in Fig. 1(a), the peak at 1667 cm^{-1} is due to C=O stretching (amide I peak) and the peak at 1542 cm^{-1} is due to in-plane N–H bending (amide II peak) [12]. A small but well resolved peak at 1609 cm^{-1} is associated with the hydrogen-bonded carbonyl of the amide. Which clearly indicate that the interfacial polymerization occurred and polyamide was formed. It is shown in Fig. 1 (a) to (e) that the peaks corresponding to amide I and II modes changed remarkable after chlorination, indicating that chlorine reacts with the amide hydrogen generating CON–Cl groups [13]. The shift to higher frequency of amide I and the weaken peak at 1609 cm^{-1} both indicated that hydrogen bonds between C=O and N–H were weakened. This finding allows us to surmise that CON–Cl groups may affect the adjacent aromatic ring or the chlorine atom of CON–Cl rearranges itself to the adjacent aromatic ring.

3.1.2. XPS analysis

XPS analysis of TFC membrane treated with chlorine for 1 h is shown in Fig. 2. There are peaks at 530 eV, 400 eV, 285 eV, which can be assigned to oxygen, nitrogen and carbon respectively. The new peaks at 200 and 270 are due to chlorine atom attached to the polyamide membrane [13]. The new peaks increase with the concentration of hypochlorous acid. The XPS study on TFC membranes exposed to chlorine reveals the presence of new peaks at 200 eV and 270 eV due to chlorine atom in addition to oxygen, nitrogen and carbon as shown in Fig. 2. This indicated chlorine atom is attached to the polyamide membranes.

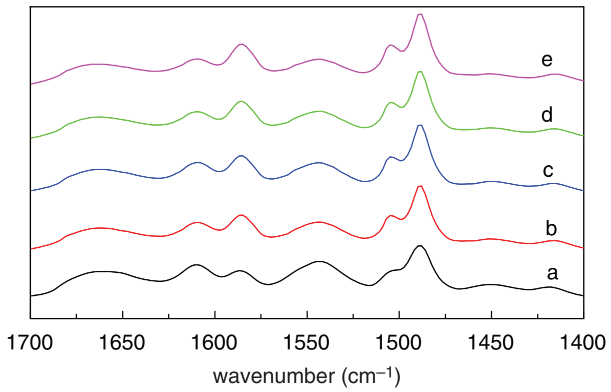

Fig. 1. ATR-FTIR spectra for (a) unmodified TFC membrane, (b) post-treatment TFC membrane (100 ppm NaOCl), (c) post-treatment TFC membrane (200 ppm NaOCl), (d) post-treatment TFC membrane (500 ppm NaOCl), (e) post-treatment TFC membrane (1000 ppm NaOCl) over 1400–1700 cm^{-1}.

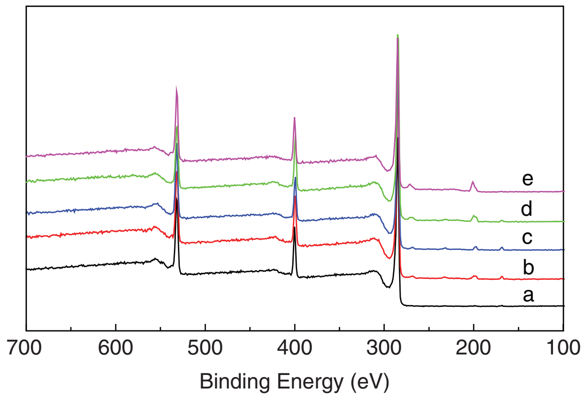

Fig. 2. XPS of the polyamide TFC membrane treat with different NaOCl concentration for 1 h: (a) 0 ppm, (b) 100 ppm, (c) 200 ppm, (d) 500 ppm, (e) 1000 ppm.

3.1.3. Membrane performance

Fig. 3 shows the effects of NaOCl solution treatment time on the composite membrane performance. It can be seen that the rejection increases along with the time, however the flux remained unchanged. For the treatment over 50 min, the flux declined significantly. Since the composite membrane surface is negatively charged, the rejection of the inorganic salt is influenced by both the electrostatic and the screening effect, while the electrostatic effect

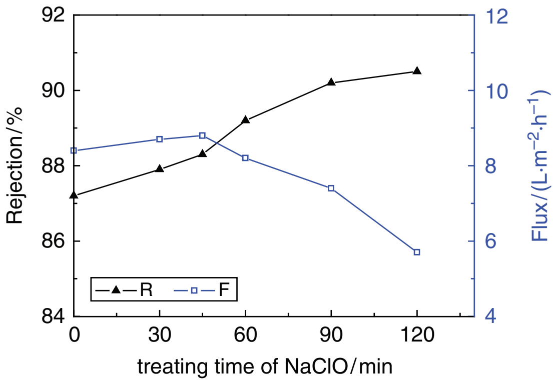

Fig. 3. Effect of treating time of NaOCl solution on the composite membrane performance.

plays a dominate role. The more negatively charged is the membrane surface; the better is the membrane performance. After the treatment of NaOCl, oxidation reaction will occur on the membrane surface, which reduces the amount of terminal amino groups of the membrane surface and increases the negative charge along with the rejection of composite membrane.

Fig. 4 shows effects of NaOCl concentration on the composite membrane performance. It can be seen that the membrane rejection increased for a certain treatment, with the increasing concentration of NaOCl solution, the flux decreases slightly. When the concentration reached 500 ppm, along with the treating solution concentration, the rejection began a slight decline, while the flux remaining at a stable value unchanged.

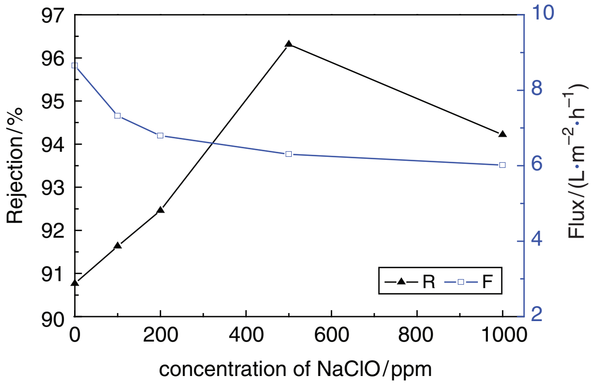

Fig. 4. Effect of NaOCl concentration on the composite membrane performance.

3.2. PVA coating layer

3.2.1. Surface morphology

The morphological variation of the membranes treated with PVA of different concentration was monitored by AFM. The pictures are shown in Fig. 5. It can be seen that the composite membrane roughness significantly decreased with PVA treatment, that is, the membrane surface becomes smoother. The untreated composite membrane (Fig. 5-a) has the typical ridge-and-valley structures commonly observed for this type of PA membranes [14–16]. And the "valley" structure on the surface of PVA treated composite membrane (Fig .5-b) disappeared. The reason is that the "valley" was filled by PVA molecules, leading to a smoother membrane surface. At the same time, the defects of the membrane surface were repaired leading to increased salt rejection.

3.2.2. Membrane performance

Fig. 6. shows effect of the time of PVA treatment on the composite membrane performance. It can be seen that the salt rejection of the membranes rapidly increased firstly and then kept stable with an increase in treating time of PVA. When the PVA concentration was 50 ppm, the change of rejection was the most significant. With increase of treating time, the flux began to decrease rapidly and then came to a plateau at the treatment time over 40 min. When the PVA concentration was 50 ppm, the flux decreased obviously. So it can be concluded that although modification with PVA improves the rejection, it leads to decreased flux, the effects increasing with increasing PVA concentration.

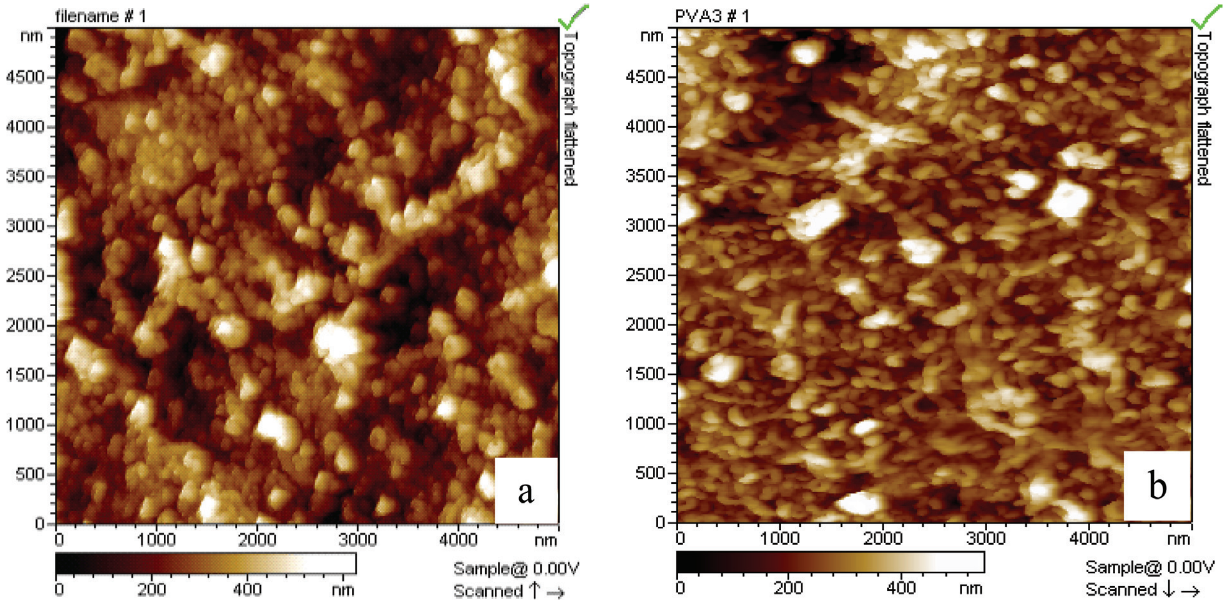

Fig. 5. AFM images of the polyamide TFC membranes with different PVA concentration for 1 h: (a) 0 ppm, (b) 50 ppm.

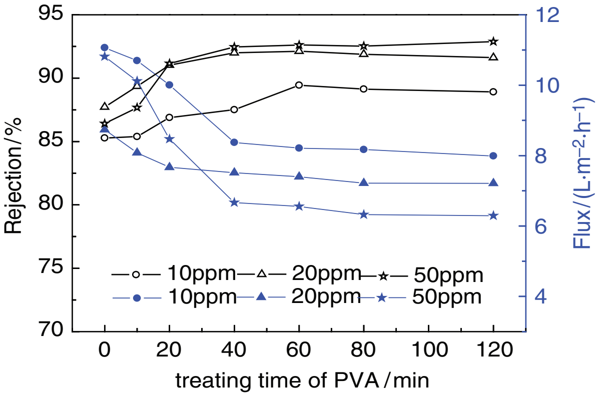

Fig. 6. Effect of treating time of PVA solution on the composite membrane performance: flux (F) and rejection (R) after membrane coated with 10 ppm, 20 ppm and 50 ppm PVA, respectively.

4. Conclusions

A novel polyamide hollow fiber reverse osmosis membrane was synthesized by interfacial polymerizaiton on a polysulfone ultrafiltration support membrane, followed by post-treatments to improve membrane performance. Both the treatment with alkaline hypochlorite and PVA can improve membrane rejection dramatically with medium trade off of membrane flux. When the membrane rejection is considered as a premium for membrane performance, these treatments can be potential methods to improve membrane performance.

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References

[1] A.E. Allegrezza Jr., R.D. Burchesky, G. Gotz, R.B. Davis and M.J. Coplan, Hollow fiber composite reverse osmosis membrane, Desalination 20 (1977) 87–94.

[2] R.W. Baker and R.P. Barss, Reverse osmosis composite hollow fiber membrane, GB Patent 2075416 (1981).

[3] S. Veríssimo, K.V. Peinemann and J. Bordado, Thin-film composite hollow fiber membranes: An optimized manufacturing method, J. Membr. Sci., 264 (2005) 48–55.

[4] U. Tadahiro, F. Hideo and I. Toshihiro, Process of producing composite semipermeable membrane, US Patent 5051178 (1991).

[5] S. Wu, J. Xing, G. Zheng, H. Lian and L. Shen, Chlorination and oxidation of aromatic polyamides. II. Chlorination of some aromatic polyamides, J. Appl. Polym. Sci., 61 (1996) 1305–1314.

[6] N.P. Soice, A.C. Maladono, D.Y. Takigawa, A.D. Norman, W.B. Krantz and A.R. Greenberg, Oxidative degradation of polyamide reverse osmosis membranes: Studies of molecular model compounds and selected membranes, J. Appl. Polym. Sci., 90 (2003) 1173–1184.

[7] S.D. Jons, K.J. Stutts, M.S. Ferritto and W.E. Mickols, Treatment of composite polyamide membreanse to improve performance, US Patent 5,876 602 (1999).

[8] J.S. Louie, I. Pinnau, I. Ciobanu, K.P. Ishida, A. Ng and M. Reinhard, Effects of polyether–polyamide block copolymer coating on performance and fouling of reverse osmosis membranes, J. Membr. Sci., 280 (2006) 762–770.

[9] S.W. Myung, I.H. Choi, S.H. Lee, I.C. Kim and K.H. Lee, Use of fouling resistant nanofiltration and reverse osmosis membranes for dyeing wastewater effluent treatment, Water Sci. Technol., 51 (2005) 159–164.

[10] A.C. Sagle, E.M. VanWagner, H. Ju, B.D. McCloskey, B.D. Freeman and M.M. Sharma, PEG-coated reverse osmosis membranes: desalination properties and fouling resistance, J. Membr. Sci., 340 (2009) 92–108.

[11] C.Y. Tang, Y.N. Kwon and J.O. Leckie, Probing the nano-and micro-scales of reverse osmosis membranes-a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements, J. Membr. Sci., 287 (2007) 146–156.

[12] G.D. Kang, C.J. Gao, W.D. Chend, X.M. Jie, Y.M. Cao and Q. Yuan, Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane, J. Membr. Sci., 300 (2007) 165–171.

[13] J.Y. Koo, J.H. Lee, Y.D. Jung, S.P. Hong and S.R. Yoon, Chlorine resistant membrane and the mechanism of membrane degradation by chlorine, WEFTEC, (2008) 2958–2969.

[14] E.M. Vrijenhoek, S. Hong and M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, J. Membr. Sci., 188 (2001) 115–128.

[15] C.Y. Tang, Y.N. Kwon and J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes II, Membrane physiochemical properties and their dependence on polyamide and coating layers, Desalination, 242 (2009) 168–182.

[16] M.H. Liu, D.H. Wu, S.C. Yu and C.J. Gao, Influence of the polyacyl chloride structure on the reverse osmosis performance, surface properties and chlorine stability of the thin-film composite polyamide membranes, J. Membr. Sci., 326 (2009) 205–214.