Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22050

119 (2018) 83–89
July

Homogeneous-reinforced polyvinyl chloride hollow fiber membranes fabrication via homogeneous surface modification techniques

Hailiang Liu[a,*], Nana Liu[b], Changfa Xiao[a], Qinglin Huang[a], Wei Shu[c]

[a]*State Key Laboratory of Separation Membranes and Membrane Processes, School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China, Tel. +86 22 8395 5397; emails: liuhailiang723@163.com (H. Liu), cfxiao@tjpu.edu.cn (C. Xiao), 45246663@qq.com (Q. Huang)*
[b]*School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China, email: 532868474@qq.com*
[c]*School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China, email: 312717221@qq.com*

Received 7 August 2017; Accepted 14 December 2017

ABSTRACT

Homogeneous-reinforced (HR) polyvinyl chloride (PVC) hollow fiber membranes consisting of separation layer and porous supported matrix layer were fabricated via homogeneous surface modification techniques. The mixture polymer solution was uniformly coated on the porous supported matrix membrane which was prepared through the melt-spinning method. The structure and performance of HR PVC hollow fiber membranes were mainly decided by the PVC porous supported matrix membrane's properties. The results showed that the HR PVC membranes had a dense and smooth outer surface compared with the matrix membrane. The infiltration degree of PVC casting solution to the outer surface of dioctyl phthalate (DOP) existed matrix membrane was more serious than that of DOP extracted matrix membrane. A dense interface layer formed in the HR PVC membrane which prepared by DOP existed matrix membrane. The tensile strength of HR PVC membranes was higher than 15 MPa which was slight lower than their matrix membranes. The porosity of prepared HR PVC hollow fiber membranes was almost the same as their matrix membranes. The pure water flux of HR PVC membrane prepared by DOP existed matrix membrane was lower than that prepared by DOP extracted matrix membrane. The BSA rejection rate of HR PVC membrane prepared by the DOP extracted matrix membrane reached to 93% after 60 min filtration and the recovery rate of permeate flux was 80%.

Keywords: Polyvinyl chloride; Homogeneous-reinforced; Hollow fiber membrane; Tensile strength; Surface modification

1. Introduction

It was well known that the reinforced hollow fiber membranes were composed of two layers, including the surface separation layer provided good separation accuracy and incomparable pollution resistance, and the supported matrix layer provided high tensile strength and low membrane resistance. These reinforced hollow fiber membranes which possessed excellent separation performance and high tensile strength were considered to be more suitable for membrane bioreactor system [1–3]. Generally speaking, the traditional reinforced membranes contained the fiber reinforced hollow fiber membrane and the tubular braid reinforced hollow fiber membrane [4,5]. The fiber reinforced hollow fiber membrane was based on the dry–wet spinning process and nonsolvent induced phase separation (NIPS) method. In the spinning process, the long fibers were introduced into the membrane along with the membrane wall through the spinneret design

---

* Corresponding author.

Presented at 2017 Qingdao International Water Congress, June 27–30, 2017, Qingdao, China.

[4]. In comparison, the tubular braid reinforced hollow fiber membrane was based on the coating process and the NIPS method. In this preparation process, the polymer solution was evenly coated on the out of the tubular braid under the constant traction force [6,7]. Based on the reinforcement introducing, the tensile strength of membrane was improved obviously, which became one of the important methods to solve the mechanics problem of NIPS hollow fiber membranes.

Similarly, the homogeneous-reinforced (HR) hollow fiber membrane that fabricated via homogeneous surface modification techniques was also another method to improve the membrane mechanical properties. In general, the porous matrix membrane as the reinforcement and the same material in polymer solution as the separation layer were utilized to fabricate the HR hollow fiber membrane. Moreover, the materials in the reinforcement and the separation layer were usually different for the commercial reinforced hollow fiber membranes, such as the polyester (PET) threads reinforced polyvinylidene fluoride (PVDF) hollow fiber membrane [8] and the PET tubular braid reinforced PVDF hollow fiber membrane [9]. However, this kind of hollow fiber membrane exhibited a problem that the separation layer was easily peeled from the threads or tubular braid due to the thermodynamically incompatible between the separation layer and reinforcement [10]. Thus, the HR hollow fiber membrane could avoid the peeling of the separation layer and obtain the favorable interfacial bonding.

In this article, the HR polyvinyl chloride (PVC) hollow fiber membranes consisting of separation layer and porous supported matrix layer were fabricated via homogeneous surface modification techniques. Dioctyl phthalate (DOP) as the plasticizer and composite powder as the pore-creating agent were used to prepare the PVC hollow fiber matrix membrane. The post-stretched and DOP extraction were used to adjust the performance of matrix membrane. Then the mixture polymer solutions were uniformly coated on the different porous supported matrix membrane. Finally, the influences of PVC porous supported matrix membrane's properties on structure and performance of HR PVC hollow fiber membranes were investigated by morphology, pure water flux, porosity and mechanical property measurements.

2. Experimental

2.1. Materials

PVC (fiber grade, DG-1000k, the average degree of polymerization is 1,030 ± 50) resin was purchased from Tianjin Dagu Chemical Plant (Tianjin, China). DOP (>99.5%) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Calcium/zinc compound thermal stabilizer was supplied by Shenzhen AIMSEA Industrial Co., Ltd. (Shenzhen, China). The composite powder (a mixture of nanosized KCl and SiO_2) was provided by Tianjin Motian Membrane Engineering and Technology Co., Ltd. (Tianjin, China). N,N-dimethylacetamide (DMAc, analytical reagent), ethanol (EtOH, analytical reagent) and polyvinylpyrrolidone (PVP, analytical reagent, K30, Mw = 10,000) were bought from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Bovine serum albumin (BSA, analytical reagent, Mw = 68,000) was supplied from Beijing Aoboxing Universeen Bio-tech Co., Ltd. (Beijing, China).

2.2. Preparation of hollow fiber matrix membrane

The PVC (28.9 wt%), calcium/zinc compound thermal stabilizer (4.5 wt%), DOP (16.6 wt%) and composite powder (50 wt%) were mixed in high speed mixer. Then, the mixtures were spun into hollow fibers via melt-spinning method by a twin-screw spinning machine at 155.0°C [11]. N_2 was introduced into the spinneret for hollow formation. The spun fibers were coagulated in a water bath at 20.0°C and then take-up. At this moment, the precursor PVC hollow fiber membranes (described as M0) were prepared. After that, the precursor PVC hollow fiber membranes were post-stretched under a constant speed with 3.0 draw ratio at 80°C in the water bath and fastened in water bath at 50°C for 1.0 h to retain the membrane structure. The prepared membranes were washed and stored in water for at least 48 h to completely leach out the residual additives. The prepared PVC hollow fiber membranes with 3.0 draw ratio (described as M1) were washed in ethanol for at least 48 h to completely leach out the DOP. After the DOP extraction, the membrane was washed by deionized water to leach out the residual ethanol. Thus, the PVC hollow fiber matrix membranes with 3.0 draw ratio and DOP extraction (described as M2) were prepared.

2.3. Fabrication of HR PVC hollow fiber membranes

The HR PVC hollow fiber membranes were fabricated via homogeneous surface modification techniques. Fig. 1 shows the schematic diagram of the preparation system. The polymer solutions consisted of PVC (10 wt%), PVP (10 wt%) and DMAc (80 wt%) were blended under constant mechanical stirring in a three-necked round-bottom flask for 4 h at 70°C. Then, the prepared polymer solutions were coated on the matrix outer surface (M1 and M2) at 20°C. In this process, the PVC matrix membrane went through the coating device and came into coagulation bath (20°C ± 2.0°C) under the traction force. The air gap distance and the take-up speed were set as 8.0 cm and 2.2 m min^{-1}, respectively. After the formation of the HR PVC hollow fiber membranes, the prepared membranes were stored in water for at least 48 h to remove the residual solvents and water soluble additive. In the end, the HR PVC hollow fiber membranes were prepared.

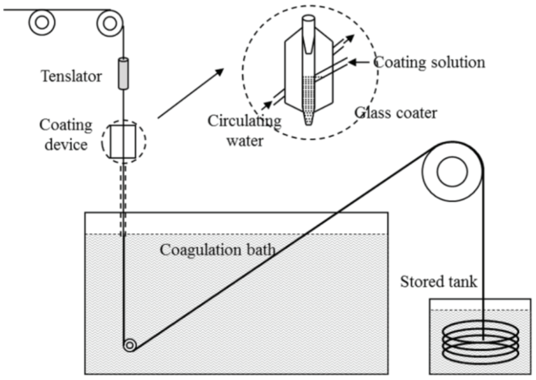

Fig. 1. Schematic diagram of the preparation system.

2.4. Membrane characterizations

2.4.1. Morphology observation

Scanning electron microscope (Quanta 200, Netherlands FEI) was utilized to investigate the morphology of surface and cross-section of prepared membranes. The membranes were immersed in liquid nitrogen for 10–15 s and were frozen. Then the frozen membranes were broken for cross-section observation. Samples were all gold sputtered before testing.

2.4.2. Permeation performance experiments

The schematic diagram of filtration experimental setup is shown in Fig. 2. All experiments were performed in hollow fiber modules. The pure water flux was measured with hollow fiber membranes at 0.1 MPa pressure under the condition of outside pressure and was calculated by Eq. (1):

$$J = \frac{V}{At} \tag{1}$$

where J is the permeate flux of membrane (L m^{-2} h^{-1}), V is the quantity of permeation (L), A is the effective area of membrane (m^2) and t is the testing time (h).

The filtration experiments were carried out by 1 g L^{-1} BSA solution. The concentration of feed solution and permeate solution was determined by UV spectroscopy at a wavelength of 280 nm, using a PERSEE TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The separation efficiency of the membrane was defined by Eq. (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_f and C_p are the concentration of protein in the feed and the permeate solution, respectively.

2.4.3. Porosity determination

The membrane porosity was defined as the pore volume divided by the total volume of the porous membrane. It can be determined by gravimetric method which can be calculated according to Eq. (3) [12]:

$$\varepsilon(\%) = \frac{W_1 - W_2}{(\pi/4)(D^2 - d^2)\,l\,\rho} \times 100\% \tag{3}$$

where W_1 is the weight of wet membrane (g), W_2 is the weight of dry membrane (g), ρ is the water density (ρ = 1.0 g cm^{-3}), D is the outer diameter (cm), d is the inner diameter (cm) and l is the length of sample membrane (cm).

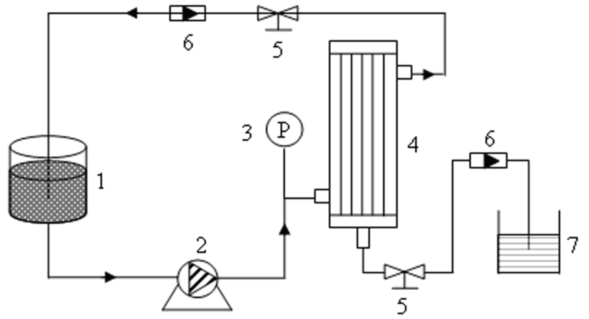

Fig. 2. Schematic diagram of filtration system: (1) feed tank, (2) feed pump, (3) manometer, (4) membrane cell, (5) control valve, (6) rotameter, (7) permeate tank.

2.4.4. Determination of pore size and its distribution

The pore size and its distribution of each sample were determined using the capillary flow porometer (Porous Materials Inc. USA), and values were calculated from the pressure of gas flow.

2.4.5. Measurement of mechanical property

At room temperature, mechanical properties of membrane samples were measured by Electromechanical Universal Testing Machine (CMT4204, MTS Systems, China). The gripping range and the tensile rate were 100 mm and 20 mm×min^{-1}, respectively. Each sample was tested five times to evaluate the average value.

3. Results and discussion

3.1. Morphology

The different PVC hollow fiber matrix membranes were used to prepare HR PVC hollow fiber membranes. The cross-section morphologies of PVC hollow fiber matrix membranes with different post-treatment process and HR PVC hollow fiber membranes with different matrix membranes were shown in Fig. 3. M0, M1 and M2 were described as the precursor PVC matrix membrane without any post-treatment, the PVC matrix membrane with 3.0 draw ratio post-stretched, the PVC matrix membrane with 3.0 draw ratio post-stretched and DOP extraction, respectively. Meanwhile, M1-1 and M2-1 were described as the HR PVC hollow fiber membranes prepared with M1 and M2 matrix membranes, respectively. As can be seen from Figs. 3(a1) and (a2), the prepared PVC hollow fiber matrix membrane was a kind of homogeneous membrane having obvious sponge-like structure. Also, comparing the cross section of M1 and M2 membranes, the numbers of membrane cross-section micro pores increased obviously after DOP extraction which could improve the cross-section porosity from Figs. 3(a1) and (a2). The increase of the porosity was due to the extraction of DOP from M1 membrane and the original location of DOP formed the microporous structure. Because the DOP molecular weight was small and evenly penetrated into the PVC matrix, the small extraction pores were more or less of half-open pores which had limited improvement to the membrane permeability.

From Figs. 3(b1) and (b2), the prepared HR PVC hollow fiber membranes were consisted of the surface separation layer and the matrix layer. The separation layer of M1-1

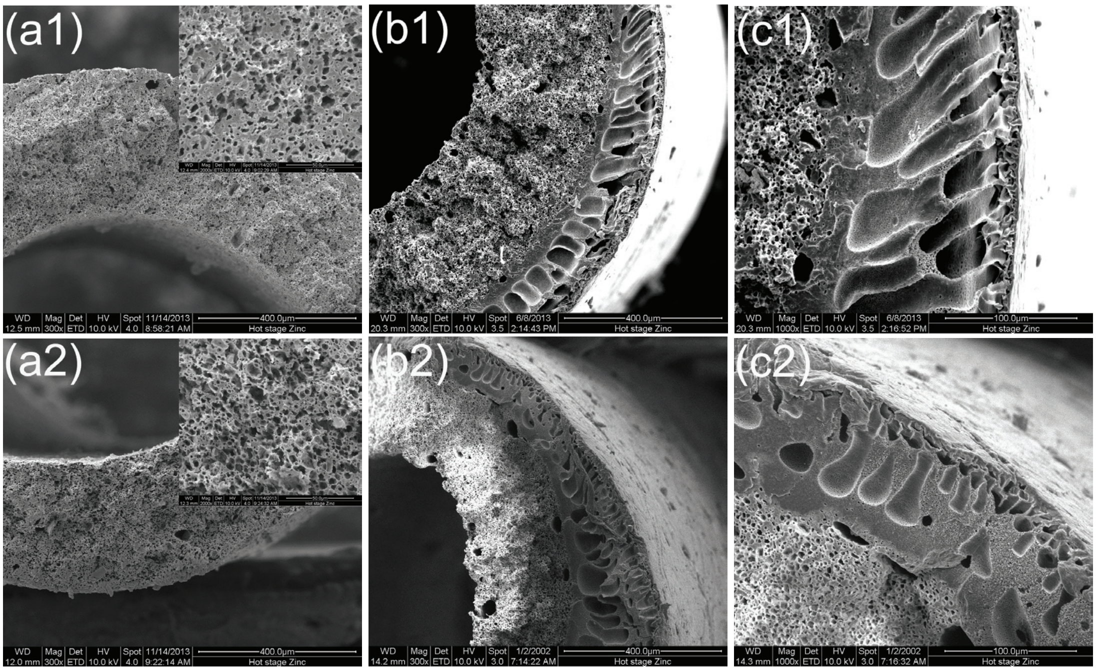

Fig. 3. Cross-section morphologies of PVC hollow fiber matrix membrane and HR PVC hollow fiber membranes. ((a1) M1, (b1) and (c1) M1-1, (a2) M2, (b2) and (c2) M2-1).

and M2-1 membranes showed typical finger-like structure. Contrasting the outer edge morphologies of M1-1 and M2-1 membranes from Figs. 3(c1) and (c2), the infiltration degree of PVC casting solution to the outer surface of M1 membrane was more serious than that of M2 membrane. Part of the pores in M1 outer surface was blocked and easily formed dense interface which would reduce the HR membrane permeability. However, the infiltration phenomenon of PVC casting solution to outer surface pores of M2 membrane was not observed obviously. These changes were attributed to the following two reasons. First, the pore sizes on M2 membrane outer surface were shrunk after DOP extraction (Fig. 4). Thus, the outer surface pore size of M2 membrane was smaller than that of M1 which would retard the intrusion process and protect the M2 outer edge pores [13]. Second, the high DMAc concentration (80 wt%) would lead to the swelling or even dissolving of PVC matrix when the matrix membrane came into the casting solution in the preparation process. The swelling or even dissolving of PVC matrix outer edge occurred secondary gelation and curing as HR membrane came into the coagulation bath. The existence of DOP would reduce the gelation rate. The long-time exposure of PVC matrix to casting solution would lead to collapse of the outer edge pores which resulted in the formation of the polymer-rich regions and formed the dense interface during the HR membrane preparation process.

The outer surface morphologies of PVC hollow fiber matrix membranes with different post-treatment process and HR PVC hollow fiber membranes with different matrix membranes are shown in Fig. 4. From Figs. 4(a) and (b), the outer surface pores of M1 membranes can be observed big and long after the post-stretched with 3.0 draw ratio. Fig. 4(c) shows that the pore sizes on M2 membrane outer surface were shrunk after DOP extraction compared with M1 membrane.

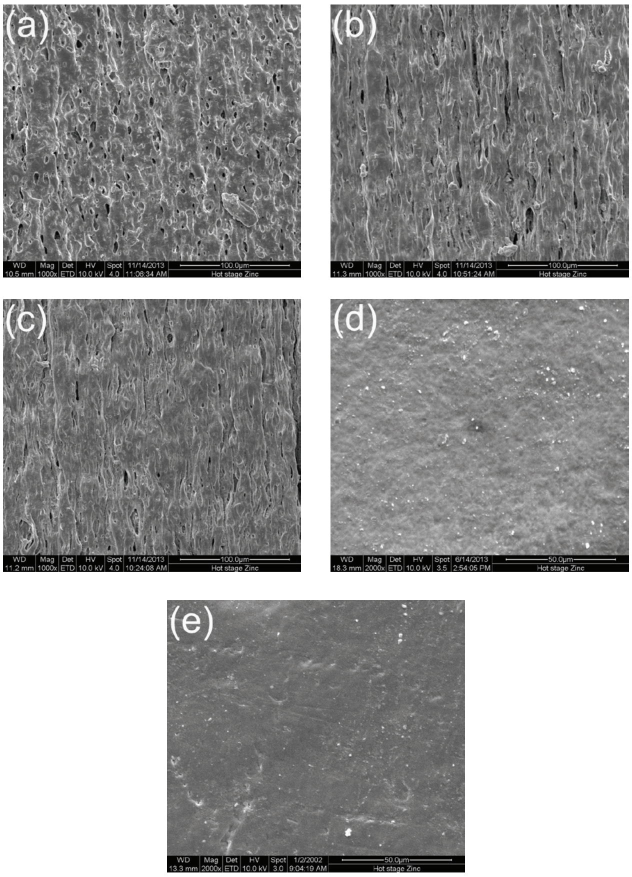

Fig. 4. Outer surface morphologies of PVC hollow fiber matrix membrane and HR PVC hollow fiber membranes. (a) M0, (b) M1, (c) M2, (d) M1-1, (e) M2-1.

In the fabrication process, the plasticizer DOP penetrated into PVC resin and formed a two phase system of liquid–solid called gelation in the plasticizing process. Then the gelation was melted when it was fed into the twin-screw and these two phases transformed into a single solid phase [14]. The phase separation of the plasticizer DOP and PVC resin did not occur in the formation process of M0 and post-stretched process of M1 for the excellent compatibility. However, the DOP could be extracted from PVC amorphous structure in the extraction process. Thus the PVC macromolecular state of aggregation structure changed which revealed that the membrane shrunk on the macro level. Figs. 4(d) and (e) show that the prepared HR PVC hollow fiber membrane possessed a dense and smooth outer surface with no obvious big pores. The formation of dense outer surface could improve the separation accuracy in the separation process and declined the embedded pollution in the membrane inner pores which was hardly removed by backwashing in the organic separation process [15].

3.2. Mechanical performance

The tensile strength and elongation at break of PVC hollow fiber matrix membranes (M0, M1, M2) and HR PVC hollow fiber membranes (M1-1, M2-1) are shown in Fig. 5. As can be seen, the tensile strength of M1 membrane was higher than that of M0 membrane, while the elongation at break was opposite. The increase of tensile strength was due to the increase of the orientation degree. The PVC macromolecular chains were forced to orientate when it was stretched in 80°C hot water. The macromolecular chains possessed orderliness and the intermolecular force was large. Compared with the M1 membrane, the tensile strength of M2 membrane increased after DOP extraction. It was attributed that the plasticizer DOP was penetrated into PVC amorphous structure which decreased the intermolecular force and increased the macromolecular flexible. Moreover, the extraction of DOP decreased the PVC macromolecular free volume and increased the macromolecular intermolecular force which resulted in the increase of the tensile strength and decrease of the elongation at break. It also can be seen that both of the tensile strength of M1-1 and M2-1 membranes were higher than 15 MPa which was slight lower than the M1 and M2 membranes, respectively. But the elongation at break of HR PVC hollow fiber membranes was similar to their matrix membrane. This was because the tensile strength of HR PVC hollow fiber membranes mainly depended on the matrix membrane. In the preparation process, the swelling or even dissolving of the matrix membrane in the casting solution might reduce the tensile strength of HR PVC hollow fiber membranes [16].

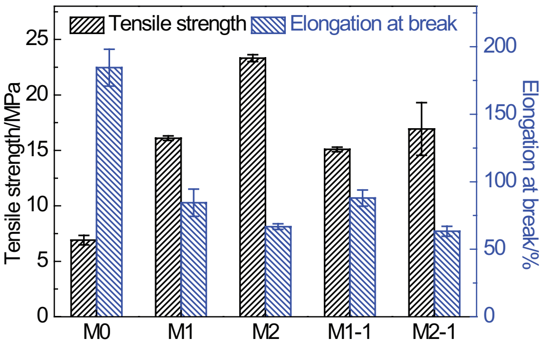

Fig. 5. Mechanical properties of prepared PVC matrix and HR PVC hollow fiber membranes.

3.3. Membrane porosity and pore size distribution

The porosity of PVC hollow fiber matrix membranes (M0, M1, M2) and HR PVC hollow fiber membranes (M1-1, M2-1) are shown in Fig. 6. As can be seen that both of post-stretched and DOP extraction could increase the membrane porosity. As mentioned above, the pores became big and long after post-stretched as shown in Fig. 4. Pore number per unit volume decreased and pore size increased which increased the membrane porosity. The extraction of the plasticizer DOP increased the pore number in per unit volume and the original location of plasticizer DOP formed microporous structure. These changes of porosity were agreed with the observed morphology of M1 and M2 membranes from Fig. 3. It also can be seen that the porosity of prepared HR PVC hollow fiber membranes (M1-1, M2-1) was similar to their matrix membranes (M1, M2), respectively.

Fig. 7 shows the pore size distribution of PVC hollow fiber matrix membranes (M0, M1, M2). As can be seen from Fig. 7, the pore size distribution range of M0 membrane was narrow

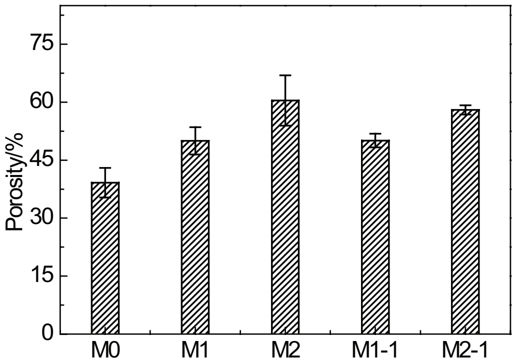

Fig. 6. Porosity of prepared PVC matrix and HR PVC hollow fiber membranes.

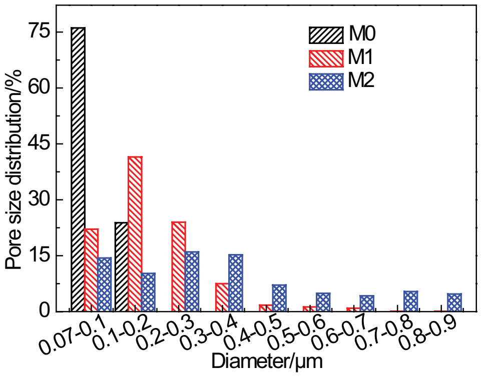

Fig. 7. Pore size distribution of PVC hollow fiber matrix membrane.

and 99% pores distributed in the range of 0.07–0.2 μm. But the pore size distribution range became wider after post-stretched and DOP extraction. The M1 membrane pores that were distributed in the range of 0.07–0.3 μm were 87%, while M2 membrane pores that were distributed in the range of 0.07–0.4 μm were only about 55%. The mean pore size of the PVC hollow fiber matrix membrane increased from 0.087 μm for M0 to 0.183 μm for M1 after post-stretched, while increased to 0.352 μm after DOP extraction. This could be explained that the pores became big and long after post-stretched (Fig. 4(b)), while the porosity of membrane cross section increased and the pore connectivity improved after DOP extraction (Fig. 3(a2)). Thus, the mean pore size increased.

3.4. Membrane permeation property

The pure water flux of PVC hollow fiber matrix membranes (M0, M1, M2) and HR PVC hollow fiber membranes (M1-1, M2-1) is shown in Fig. 8. As can be seen, the pure water flux of M1 membrane increased dramatically after post-stretched. This was due to the increase of the membrane mean pore size and porosity after post-stretched. Compared with M1 membrane, the pure water flux of M2 membrane was decreased after DOP extraction. This could be explained that the membrane outer surface pores shrunk after DOP extraction which increased the membrane filtration resistance in the outside pressure cross-flow filtration. Also, the polar groups in plasticizer DOP had facilitated the water transportation in the un-extract fiber matrix. Thus, the pure water flux of M2 membrane decreased after DOP extraction. The pure water flux of prepared HR PVC hollow fiber membranes (M1-1, M2-1) was lower than that of their matrix membranes (M1, M2), respectively. Especially, the pure water flux of M1-1 membrane was close to 0. These reducing of the flux were due to the infiltration of the polymer solutions into the matrix membrane porous outer surface during the HR membrane preparation process. The infiltration degree of PVC casting solution to the M1 membrane outer surface was more serious than that of M2 membrane from Fig. 3. The formation of the interface for M1-1 membrane was denser than that for M2-1 membrane. Thus, the pure water flux of M2-1 membrane was higher than that of M1-1 membrane.

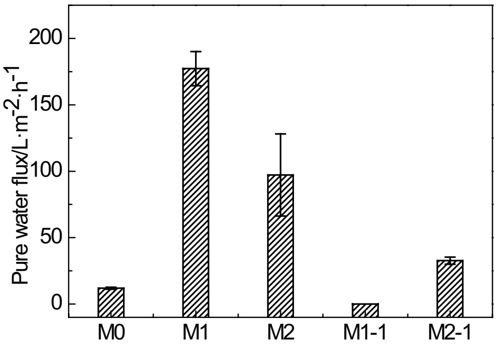

Fig. 8. Pure water flux of prepared PVC matrix and HR PVC hollow fiber membranes.

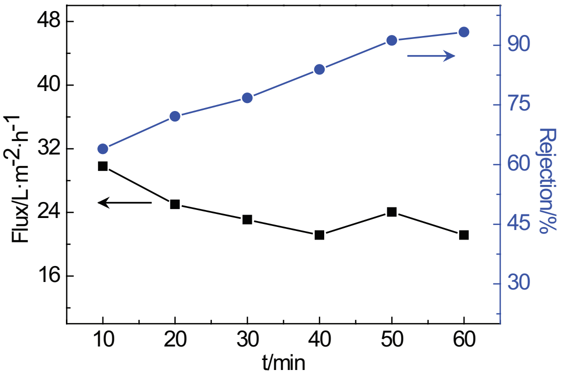

Fig. 9. Variation of permeate flux and rejection rate with time. (M2-1, operating pressure: 0.1 MPa, testing temperature: 20°C).

The filtration experiments were performed in hollow fiber modules. The effective membrane area of each membrane module was 30.0 cm^2 in this test. The BSA aqueous solution as model feed solution was used to test the filtration performance of the prepared HR PVC hollow fiber membrane, including the permeation, rejection and flux recovery rate. The variation of permeate flux and rejection rate with time is shown in Fig. 9. As observed from Fig. 9, the permeate flux decreased first and then arrived at a balance, while the rejection increased with the prolonging of operating time. In the initial filtration process, the adsorption of the BSA molecules on the membrane surface and inner pores would pollute the membrane and decrease the permeate flux. With the prolonging of operating time, a deposited layer near the membrane surface was formed for the concentration polarization effect which decreased the membrane pore size and the permeate flux. All these caused the increase of the BSA rejection rate. In this study, the BSA rejection rate reached 93% after 60 min filtration. Then the membrane was thoroughly washed for 10 min. The recovery rate of permeate flux was 80%.

4. Conclusions

The HR PVC hollow fiber membranes including separation layer and porous supported matrix were fabricated via homogeneous surface modification techniques. The HR PVC membranes exhibited a dense and smooth outer surface compared with matrix membrane. The infiltration degree of PVC casting solution to the M1 membrane outer surface was more serious than that of M2 membrane. A dense interface layer formed in the HR PVC membrane which was prepared by M1 membrane. Moreover, the tensile strength of M1-1 and M2-1 membranes was higher than 15 MPa which was slight lower than the M1 and M2 membranes, respectively. The porosity of the prepared HR PVC hollow fiber membranes was similar to their matrix membranes. The pure water flux of HR membrane prepared by M1 membrane was lower than that prepared by M2 membrane. The BSA rejection rate of M2-1 membrane reached 93% after 60 min filtration and the recovery rate of permeate flux was 80%.

Acknowledgments

The authors gratefully acknowledge the research funding provided by the National Natural Science Foundation of China (51603146, 51673149), the Science and Technology Plans of Tianjin (No. 15PTSYJC00240).

References

[1] X.L. Zhang, C.F. Xiao, X.Y. Hu, Q.Q. Bai, Preparation and properties of homogeneous-reinforced polyvinylidene fluoride hollow fiber membrane, Appl. Surf. Sci., 264 (2013) 801–810.

[2] H.L. Liu, C.F. Xiao, Q.L. Huang, X.Y. Hu, Structure design and performance study on homogeneous-reinforced polyvinyl chloride hollow fiber membranes, Desalination, 331 (2013) 35–45.

[3] Q. Quan, C.F. Xiao, H.L. Liu, Q.L. Huang, W. Zhao, X.Y. Hu, G.L. Huan, Preparation and characterization of braided tube reinforced polyacrylonitrile hollow fiber membranes, J. Appl. Polym. Sci., 132 (2015), DOI: 10.1002/app.41795.

[4] J. Liu, P.L. Li, L.X. Xie, S.C. Wang, Z. Wang, Preparation of PET threads reinforced PVDF hollow fiber membrane, Desalination, 249 (2009) 453–457.

[5] Z.W. Fan, C.F. Xiao, H.L. Liu, Q.L. Huang, J. Zhao, Structure design and performance study on braid-reinforced cellulose acetate hollow fiber membranes, J. Membr. Sci., 486 (2015) 248–256.

[6] Z.W. Fan, C.F. Xiao, H.L. Liu, Q.L. Huang, Preparation and performance of homogeneous braid reinforced cellulose acetate hollow fiber membranes, Cellulose, 22 (2015) 695–707.

[7] M. Mailvaganam, L. Fabbricino, C.F.F. Rodrigues, A.R. Donnelly, Hollow Fiber Semipermeable Membrane of Tubular Braid, US 5472607, 1995–12–5.

[8] K. Murase, H. Habara, H. Fujiki, T. Hirane, M. Mizuta, Porous Membrane, US 2002/0046970 A1, 2002–04–25.

[9] M.S. Lee, S.H. Choi, Y.C. Shin, Braid-reinforced Hollow Fiber Membrane, US 7267872 B2, 2007–09–11.

[10] X.L. Zhang, C.F. Xiao, X.Y. Hu, X. Jin, Q.Q. Bai, Study on the interfacial bonding state and fouling phenomena of polyvinylidene fluoride matrix-reinforced hollow fiber membranes, Desalination, 330 (2013) 49–60.

[11] H.L. Liu, C.F. Xiao, X.Y. Hu, Fabrication and properties of polyvinyl chloride hollow fiber membranes plastified by dioctyl phthalate, Desal. Wat. Treat., 51 (2013) 3786–3793.

[12] H.L. Liu, C.F. Xiao, X.Y. Hu, M.T. Liu, Post-treatment effect on morphology and performance of polyurethane-based hollow fiber membranes through melt-spinning method, J. Membr. Sci., 427 (2013) 326–335.

[13] B. Bikson, J.E. Miller, J.K. Nelson, Permeable Membranes for Enhanced Gas Separation, US Patent 4881954, 1989.

[14] M.A. Semsarzadeh, M. Mehrabzadeh, S.S. Arabshahi, Dynamic mechanical behavior of the dioctyl phthalate plasticized polyvinyl chloride-epoxidized soya bean oil, Eur. Polym. J., 38 (2002) 351–358.

[15] M.T. Liu, C.F. Xiao, X.Y. Hu, Fouling characteristics of polyurethane-based hollow fiber membrane in microfiltration process, Desalination, 298 (2012) 59–66.

[16] H.L. Liu, C.F. Xiao, Q.L. Huang, X.Y. Hu, W. Shu, Preparation and interface structure study on dual-layer polyvinyl chloride matrix reinforced hollow fiber membranes, J. Membr. Sci., 472 (2014) 210–221.