Desalination and Water Treatment
www.deswater.com

doi: 10.1080/13540602.2013.830805

52 (2014) 5052–5060
July

Taylor & Francis
Taylor & Francis Group

The effect of PVDF concentration on PVDF/woven tube composite membranes and the application of composite membranes in SMBR

ZhiYong Rong[a,*], Lei Wang[a], LiCheng Chen[b], XuDong Wang[a], DanXi Huang[a]

[a]*School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology,*
Yan Ta Road, No. 13, Xi'an 710055, China
Tel. +86 15116258615; email: rzy1989126com@126.com
[b]*College of Environment and Chemical Engineering, Xi'an Polytechnic University, South Jin Hua Road, No. 19,*
Xi'an 710048, China

Received 7 May 2013; Accepted 17 July 2013

ABSTRACT

Using fiber woven tube for support layer, the poly vinylidene fluoride (PVDF)/woven tube composite hollow fiber membrane with high strength and high water flux was prepared through the coating technology and immersion-precipitation technique. The effect of PVDF contents on membrane flux and porosity was investigated; using the homemade composite membrane in the sequencing batch membrane reactor (SMBR) reactor. The rejection effect on particles and the changes of the composite membrane performance were also studied. With the increase of PVDF concentration, pure water flux and the average pore diameter of the composite membrane decreased, but the burst pressure increased; the porosity increased at first and then decreased. In this research, porosity of composite membrane is always above 45%, the burst pressure is higher than 0.30 MPa, and the tensile strength of the composite membrane is very high. Although the membrane is operated at a high flux ($20 \pm 0.5\,\mathrm{L\,m^{-2}\,h^{-1}}$) in the SMBR system, the transmembrane pressure remains 5.5–6.5 kPa and the membrane permeability is up to $3.7\,\mathrm{L\,m^{-2}\,h^{-1}\,kPa^{-1}}$. The study shows that the homemade composite hollow fiber membrane can be operated at a high flux and low pressure the membrane bioreactor. Furthermore, the composite membrane has a good ability to resist pollution and a high effect of particle rejection.

Keywords: Woven tube; Poly(vinylidene fluoride); Composite membrane; Membrane fouling

1. Introduction

Currently, polymers are still the main materials in membrane technology with the advantages of good membrane forming ability, flexibility, and low cost [1,2]. As an excellent crystalline polymer, poly vinylidene fluoride (PVDF) is often used in the preparation of the microporous membrane due to its good chemical and thermal stability [3,4]. However, limited chemical, mechanical, and thermal resistance restrict the application of polymer membranes [5].

Obviously, composite membranes could combine the basic properties of organic and inorganic materials and offer specific advantages for the preparation of

---

*Corresponding author.

Presented at the Conference on Water Resources and Urbanization Development, 26–27 September 2012, Tianjin, China

membranes with excellent separation performances, good thermal and chemical stability and adaptability as well as membrane forming ability [6,7]. Therefore, organic–inorganic composite materials as new membrane materials have attracted more and more attention [8–10].

But all these polymeric membranes were prepared by phase-inversion method. In this method, a casting solution consisting of polymer, solvent, and additives is immersed into a nonsolvent coagulation bath [11–13]. When the membrane is used in wastewater treatment process, this polymer membrane prepared by the immersion-precipitation phase-inversion method has the following disadvantages: low mechanical strength and the membrane breaking phenomenon often appear in the membrane bioreactor. The water volume and water quality of the effluent cannot meet the requirement. Thus, how to continue to improve membrane strength has attracted more and more attention.

Today, there are two main methods of improving the strength of the membrane. Firstly, strengthen the membrane by improving the membrane preparation process or through membrane modification. Secondly, increase the strength of the membrane by adding fiber or a braided fabric support layer. This method one can ensure the performance of the membrane separation and improve the membrane strength at the greatest degree, but its preparation process is complicated and difficult to operate.

In this research, the PVDF casting solution is coated on the fiber woven tube, which is used as the support layer, by using the self-developed coating technology and the homemade composite membrane spinning device. The PVDF/woven tube composite hollow fiber membranes with high strength and water flux are prepared through the coating technology and the immersion-precipitation technique. Besides, the effect of PVDF content in the casting solution on the properties of composite membranes is discussed in this research. At the same time, the homemade composite membrane is applied to the sequencing batch reactor (SBR) to build the sequencing batch membrane reactor (SMBR) system. Additionally, the rejection effect on particles and the performance changes of the composite membrane are studied as well.

2. Experimental

2.1. Materials

(PVDF, Solef® 6020) was purchased from solvay Advanced Polymers, L.L.C.N,N-dimethylactamide. (DMAC; >99%) was obtained from the Tianjin FuCheng Reagent Company. Polyvinyl pyrrolidone (PVP) was purchased from BASF Chemical Company, Germany. Lithium choride (LiCl, analytical grade) was purchased from the Tianjin Kermel Chemical Reagent Co. Ltd. Sodium hydroxide (NaOH, analytical grade) was purchased from the Tianjin Kermel Chemical Reagent Co. Ltd. Fiber woven tube was purchased from the XuZhou Henghui Knitting Machinery Factory.

2.2. Composite hollow fiber membrane preparation

2.2.1. Fiber woven tube pretreatment

The inner diameter of a 2.0 mm polyester fiber woven tube was immersed in a solution of NaOH in order to remove greasy dirt on the woven tube. Then deionized water was used to wash the woven tube in order to remove the surface residues of NaOH. Finally, the woven tube was placed in the oven to dry.

2.2.2. Preparation of the casting solution

The materials of PVDF, DMAC, LiCl and PVP were added in a mixer tank in a certain ratio, and then transferred to a deaeration tank after stirring the dissolved contents for a particular time at certain temperature. On standing deaeration, a homogeneous membrane casting solution is obtained.

2.2.3. Preparation of the composite hollow fiber membrane

The coating technology and immersion-precipitation technique were used to prepare the PVDF/woven composite hollow fiber membrane. The process of preparation was as follows: the deaeration homogeneous casting solution was squeezed into the spinneret under the pressure from the deaeration tank, then the pretreated woven tube through the spinneret center under the action of the supply wheel and the traction wheel, casting solution, and the woven tube co-squeezed from the spinneret under the common action of the woven tube carrying and nitrogen pressure, casting solution uniform coating on the outside surface of the fiber woven tube, and then enter into the coagulation bath and phase convert into membrane. The membrane was soaked in water for certain time after collecting through the wire winding wheel. Finally, PVDF/woven tube composite hollow fiber membrane was prepared the spinning process is shown in Fig. 1.

2.3. Membrane morphology observation

The morphologies of the cross-section, the external outside surface of hollow fiber membrane were observed with a scanning electron microscope (SEM; JSM5800, JEOL, Japan). The fibers were immersed into liquid nitrogen for a few minutes and cut off by knife, then coated with gold under vacuum before testing.

2.4. Mechanical properties, porosity, and average pore size

Mechanical properties included tensile strength and burst pressure, and the tensile strength of the hollow fiber membranes were measured by a test machine at a loading velocity of 500 mm/min. The report values were measured thrice for each sample and then averaged. The burst pressure of hollow fiber membranes were measured by a self-made explosive device.

The membrane porosity ε (vol.%) was defined as the volume of the pores divided by the total volume of the porous membrane. It could be determined by the gravimetric method, determining the weight of liquid (here pure alcohol) contained in the membrane pores. The inner and outer diameters of the samples (10 pieces of hollow fibers) are measured under a microscope to obtain the bulk volume (V_b). The porosity (ε) of the sample is calculated according to Eq. (1):

$$\varepsilon = \frac{m_1 - m_2 - (m_3 - m_4)}{\rho \cdot \Delta V} \tag{1}$$

where m_1 is the weight of the wet composite membrane (g), m_2 is the weight of the dry composite membrane (g), m_3 is the weight of the wet woven tube (g), m_4 is the weight of the dry woven tube (g), ρ is the alcohol density (0.78 g cm^{-3}), and ΔV is the membrane layer volume of the composite membrane.

The membrane average pore size is determined through the filter velocity method and the pore size (r) was obtained by Eq. (2):

$$r = \sqrt{\frac{8 \times (2.9 - 1.75\varepsilon) \cdot \mu \cdot I \cdot J}{\varepsilon \cdot A \cdot \Delta P}} \tag{2}$$

where ε is the porosity of the composite membrane (%); I is the thickness of the composite membrane (m); μ is the viscosity of the filtered fluid (here water viscosity) (Pa s); J is the membrane pure water flux (m^3 s^{-1}); A is the filtration area of the membrane (m^2); and ΔP is transmembrane pressure (Pa).

2.5. Membrane performance measurement

The permeation flux and rejection of the hollow fiber membranes were measured by the self-prepared UF experimental equipment. Deionized water was used to measure the pure water flux. Three modules were tested in parallel, and the average of their performance was reported.

The newly developed membranes were prepressured at 0.15 MPa for 30 min. The pure water of the hollow fiber membranes was measured at 0.1 MPa and at room temperature, respectively. Deionized water was fed at a constant pressure of 0.1 MPa from outer surface to the inner lumen of composite membranes and was collected and measured. Pure water flux (J_w) is obtained by Eq. (3):

$$J_w = \frac{V}{A \cdot \Delta T} \tag{3}$$

where V is the total volume of the permeation water during experiment (L). A is the effective membrane area of the module (m^2), and ΔT denotes the measuring time (h).

3. Results and discussion

3.1. The effect of PVDF concentration on morphologies of composite hollow fiber membrane

In this experiment, the casting solution was consisted of the PVDF, PVP, LiCl, and DMAC. The PVP content was 6% and the LiCl content was 3%, adjusting the PVDF and DMAC concentration. The temperature of the casting solution was 40℃, and the coagulation bath was tap water at 35℃ .

3.1.1. The cross-section structure of the composite membrane

The cross-section structure of the composite hollow fiber membrane is shown in Fig. 2. The

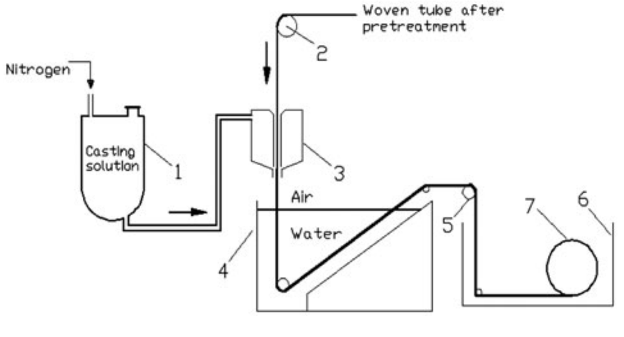
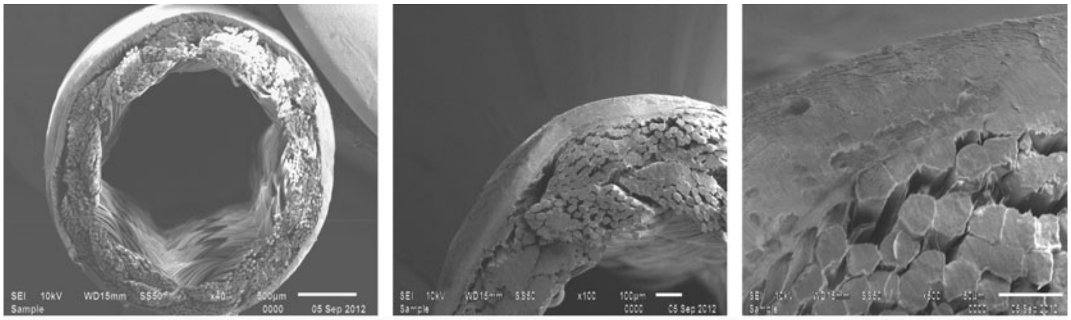


Fig. 1. The spinning process diagram of PVDF/woven tube hollow fiber composite membrane. (1) deaeration tank (2) supply wheel (3) spinneret (4) coagulation bath (5) the traction wheel (6) wire winding bath (7) wire winding wheel.



(×40) (×100) (×500)

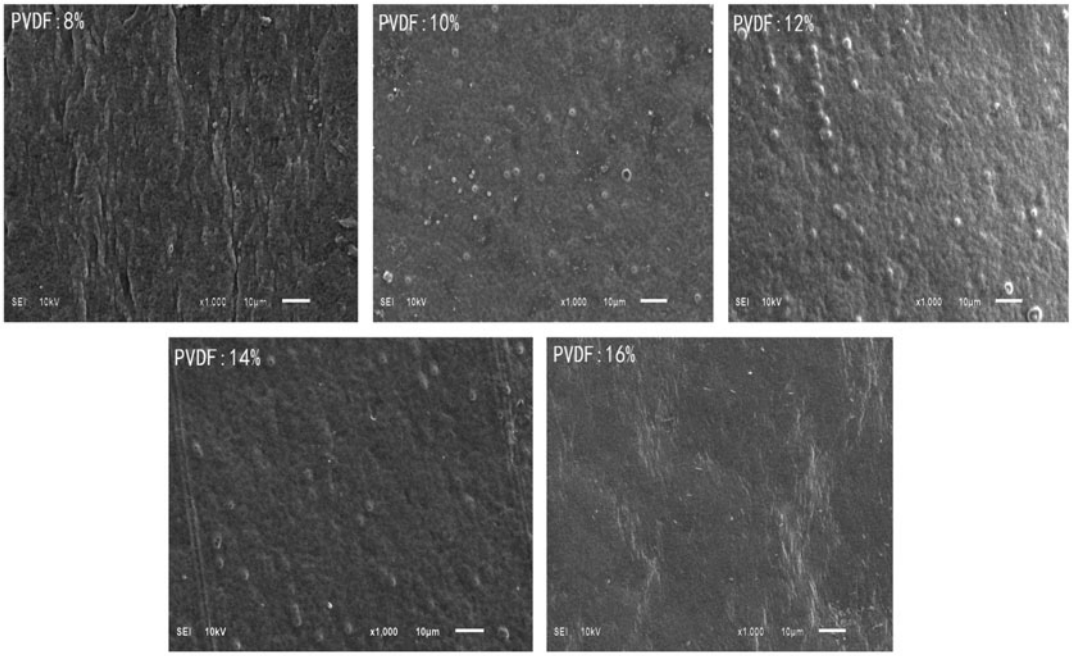
Fig. 2. The cross-section structure of the composite hollow fiber membrane (PVDF concentration was 12%, DMAC content was 79%).

cross-section structure showed that the polymer layer of casting solution was uniformly wrapped on the outer surface of the woven tube, and some casting solution has been embedded into the crevice of the woven tube filament. The coating layer and the woven tube layer were merged closely. The thickness of the coating layer was only about one-fifth of the total thickness of composite membrane, and the coating layer has a thin and compact structure. Because the woven tube is used as the support layer, the coating layer has little effect on membrane tensile strength, and the tensile strength of the composite membrane is still high.

3.1.2. The effect of PVDF concentration on the composite membrane surface morphology

The surface morphology of composite membrane in different PVDF concentrations is shown in Fig. 3. As Fig. 3 shows, the polymer (PVDF) concentration in casting solution was increased from 8 to 16%. The surface of the composite membrane from chapped macroporous structure changed gradually into a dense structure. When the PVDF concentration reached to 16%, the membrane surface showed rough rugged.

In the specific spinning conditions, when the PVDF concentration in casting solution is less than 8%, the



(×1000)

Fig. 3. The surface morphology of composite membrane in different PVDF concentration (PVDF concentration was from 8 to 16%, DMAC contents was from 83 to 75%).

DMAC concentration exceeds 85%, and the polymer viscosity is too small to coat the casting solution on the outer surface of the woven tube [14]. When the PVDF concentration exceeds 16%, the casting solution viscosity is too high, the discharging quantity of polymer casting solution has large fluctuation, and the coating layer thickness changes with the discharging quantity, some uneven node protuberance appeared on the membrane surface, membrane performance was poor. While the PVDF concentration in casting solution ranged from 10 to 14%, the membrane surface was smooth and accompanied by a uniform distribution of the pore structure. Especially, when the PVDF concentration was 12%, there are most pores on the membrane surface. Therefore, the concentration of the PVDF selected is from 8 to 16% in this experiment to adjust the DMAC concentration.

3.2. *The changes of PVDF concentration on the performance of composite membrane*

3.2.1. *The effect of PVDF concentration on water flux and average pore size*

The effect of PVDF concentration on water flux and average pore size of the composite membrane are shown in Fig. 4.

Fig. 4 indicates that the effect of PVDF concentration on water flux and average pore size of the composite membrane is very significant. With the increase of PVDF concentration in the casting solution, composite membrane pure water flux and the average pore size decrease. And when the PVDF concentration increased from 8 to 16%, flux decreases from 4300 to 671.9 $\mathrm{L\,m^{-2}\,h^{-1}}$, the average pore size from 0.231 μm drops to 0.099 μm. The reason is that the viscosity of the low-concentration casting solution is low, which leads to the limited discharging quantity of it. When the primary membrane enters into the nonsolvent coagulation bath (water), an extremely fast and transient liquid–liquid phase separation process will happen in the system. The lack of coherence of the membrane layer contributes to the apertures and large pores appear on the membrane surface. Thus the water flux and the average pore size of the membrane is high.

With the increase of PVDF concentration, the solvent contents in the casting solution decreases, and the viscosity of the casting solution increases. The viscosity will affect the exchange rate between the solvent and nonsolvent. The cortex was easy to form on the membrane surface through phase separation. And when the polymer concentration is increased, the discharge quantity, as well as the thickness of the film increased, but the speed of the precipitation phase separation was slow. Therefore, the surface pore size and water flux of the composite membrane declined [15,16].

3.2.2. *The effect of PVDF concentration on porosity and burst pressure*

The effect of the PVDF concentration on the porosity and the burst pressure of the composite membrane are shown in Fig. 5. As the PVDF concentration increases, the composite membrane porosity increased at first and then decreased, which are associated with different polymer solvent ratios on membrane structure characteristics. When the PVDF concentration was 12%, the composite membrane porosity reached the maximum value of 59.3%. In low PVDF concentrations, a large number of holes on the membrane surface appeared and the membrane porosity declined. In high PVDF concentrations, the coating layer thickness was larger and the coating layer structure was compact, so the porosity was low. When PVDF

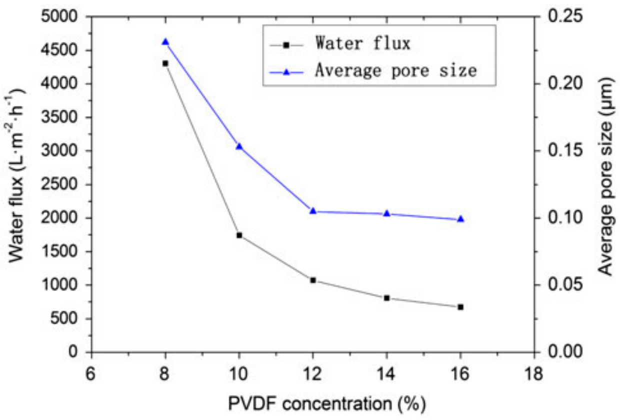


Fig. 4. The effect of the PVDF concentration on water flux and average pore size of the composite membrane.

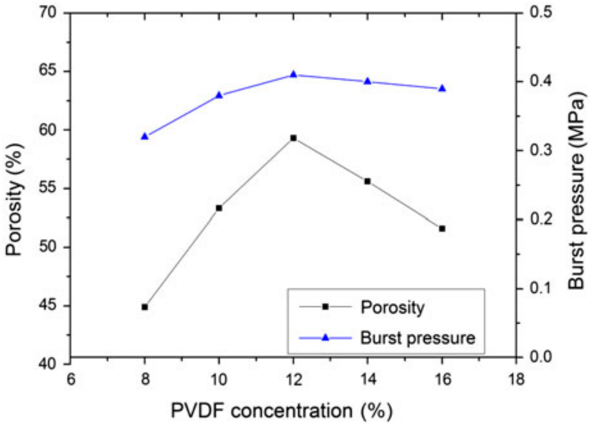


Fig. 5. The effect of the PVDF concentration on porosity and burst pressure of the composite membrane.

concentration ranged from 10 to 14%, the membrane morphology structure was more reasonable, and the surface of the composite membrane polymer layer was evenly distributed with a microporous structure (as shown in Fig. 3). When the PVDF concentration is 12%, the distribution of membrane surface pore is the most intensive. Thus the porosity is high.

As Fig. 5 shows, with the concentration of PVDF increasing from 8 to 12%, the burst pressure of composite membrane increased from 0.32 to 0.41 MPa. When the PVDF concentration increases from 12 to 16%, the composite membrane burst pressure changes gently and decreases slightly. The changes of burst pressure are directly related to the composite membrane structure; with the increase of PVDF concentration the membrane structure becomes compact gradually, but when the PVDF concentration reaches 12%, the viscosity of the casting membrane solution system increases, the binding force between woven tube layer and the coating layer declined, so the burst pressure also decreased.

Because the woven tube support layer exists, the coating layer has little influence on membrane tensile strength. Tensile strength is mainly decided by woven tube is not related to the coating process, thus tensile strength of composite membranes is higher than the measurable range of our apparatus.

Combining the results of 3.2.1 and 3.2.2 in the optimization of the other spinning condition, the composite fiber membrane has the best overall performance when the PVDF content is 12%. The parameter of composite membranes is shown in Table 1.

3.3. The application of a composite membrane in an SBR reactor

In the optimization of the spinning condition, the composite hollow fiber membranes was prepared. A curtain type of hollow membrane module was made by using composite membranes, whose parameters are shown in Table 1. The membrane modules are placed in an SBR reactor and an SMBR system was constructed. The rejection effect on particles and performance changes of composite membranes in the SMBR system were studied. The main parameters of the SMBR system are shown in Table 2.

Table 1
The parameter of composite membranes

Parameter	Value
External diameter, mm	2.3 ± 0.05
Thickness of polymer membrane layer, mm	0.08 ± 0.02
Average pore size, μm	0.1 ± 0.02
Porosity, %	55 ± 5
Tensile strength, MPa	>100
Pure water flux (0.1 MPa), $\mathrm{L\,m^{-2}\,h^{-1}}$	1,000 ± 50

Table 2
The main parameter of the SMBR system

Parameter	Value
Sludge concentration, $\mathrm{mg\,L^{-1}}$	3–8
Reactor volume, L	7
Membrane area, $\mathrm{m^2}$	0.15
Membrane module flux, $\mathrm{L\,m^{-2}\,h^{-1}}$	20 ± 0.5
Operation, h	
Mixing	2
Aeration	4
Raw wastewater quality (average value), $\mathrm{mg\,L^{-1}}$	
COD	420.4
$\mathrm{NH_4^+}$-N	42.6
TN	45.1
TP	3.55

The SMBR system was applied to treat the synthetic wastewater, and the reactor was operated by sequencing batch, 6 h a cycle and four cycles a day. The influent time was less than 10 min, while effluent time achieves 60 min in single cycling. The effluent was suctioned by a suction pump.

The effluent of the process adopt constant flow filtration, the membrane fouling and membrane stability were indicated through the transmembrane pressure (TMP) and permeability change [17,18]. In order to reduce the membrane fouling and extend membrane cleaning cycle, the effluent adopts the intermittent suction water outlet, suction 10 min and stop suction 5 min, the SADp value controlled among 30–60 ($\mathrm{m^3}$ air·$\mathrm{m^{-3}}$ water) to guarantee the effect of aeration scouring on the membrane. Stopped pumping makes the membrane obtain short relaxation, which can promote pollutants reverse diffusion migration away from the membrane surface under the action on the concentration gradient, furthermore, the shear effect produced by air scour can further enhance this effect [19,20].

3.3.1. Removal of particles by composite membranes

The contents of suspended particulate matter in the effluent are presented by turbidity, under the action of membrane high efficient retention, the turbidity of the membrane effluent was very low and kept under 0.05 NTU, the average value was

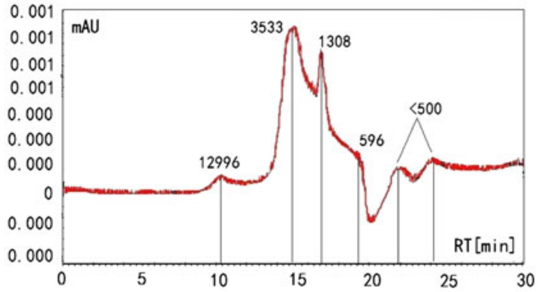


Fig. 6. Molecular weight distribution of the membrane effluent is shown.

0.01 NTU. At the same time, a Hitachi high performance liquid chromatography (HPLC) (LC-2000, Japan) equipped with a gel column (Waters Ultrahydrogel 250) was used to analyze the molecular weight distribution of the membrane effluent. The molecular weight distribution of the membrane effluent is shown in Fig. 6. It could be seen that most of the molecular weight of the effluent was lower than 15 KDa, indicating that the composite membrane had a good rejection effect on particles in wastewater treatment.

The experimental results also showed that the average removal rates of COD, NH_4^+–N, TN, and TP were greater than 90, 95, 70, and 86% under the action of biological treatment and high efficient rejection by composite membranes.

3.3.2. *The changes of membrane fouling in the SMBR system*

(1) The contrast of the composite membrane surface morphology before and after fouling

The contrast of the membrane surface morphology before and after fouling is shown in Fig. 7. As Fig. 7 shows, the changes of the color of the membrane surface show that the membrane surface has been fouled by the pollutants. It can be seen from the comparison of b1, b2 membrane surface SEM scans that pollutants formed a cake layer on the membrane surface. The cake layer appeared some uplift and cracked after drying. It is indicated that the cake layer was thicker but relatively loose, and the effect of this cake layer on the membrane filtration flux was low.

(2) The changes of composite membrane TMP and permeability

The changes of TMP and permeability under the experimental condition are shown in Fig. 8.

Without following any cleaning procedure of the membrane in the whole experiment, the membrane operating flux was $20 \pm 0.5\,L\,m^{-2}\,h^{-1}$. In the first month, the TMP in the first 2 d increased significantly, from 4.4 kPa to 4.8 kPa, the membrane fouling rate was high. This phenomenon was caused by the initial membrane fouling which sludge mixed liquid particles adsorb on the membrane surface and cause the membrane pore blocking [21,22], and membrane self-resistance formed in filtering initial stage; therefore,

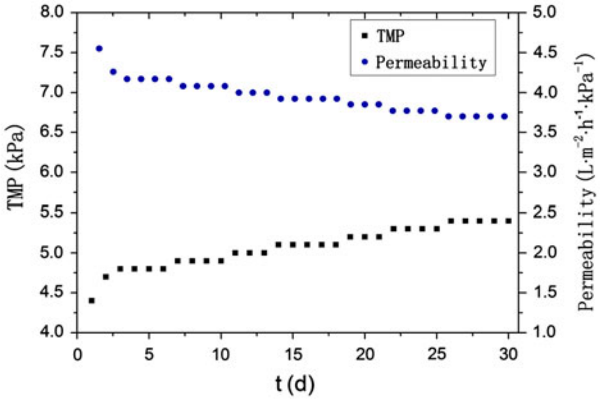


Fig. 8. The variation of permeability and TMP under the research condition.

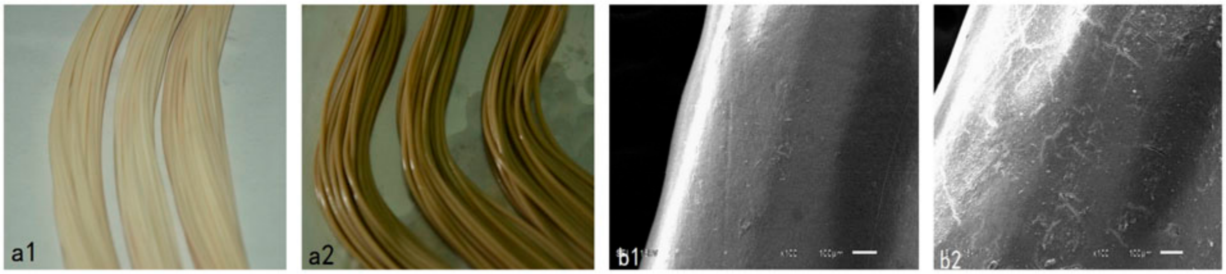


Fig. 7. The contrast of the membrane surface morphology before and after using (a1 is the original membrane module, a2 is the membrane module after fouling, b1 is the initial membrane surface SEM scan, b2 is the membrane surface SEM scan after fouling).

the TMP increased fast. When the membrane self-resistance and membrane pore blocking has been fully formed, the TMP increased from 4.8 to 5.4 kPa in the subsequent 28 d. Moreover, the membrane fouling process was slow and the membrane fouling rate was low, this stage was the membrane slow fouling [22]. In a slow fouling stage, pollutants were not only adsorbed in the membrane pores, but also occurred on the membrane surface. The biological floc in sludge mixed liquid began to form a cake layer on the membrane surface, but this cake layer had little effect on TMP growth, TMP increased slowly [23,24]. The serious membrane fouling phenomenon did not occur in the experiment, the anti-pollution performance of composite membranes was good.

In the whole research, although the membrane operated at high flux ($20 \pm 0.5\,\mathrm{L\,m^{-2}\,h^{-1}}$), the TMP was kept under 5.5 kPa, the permeability of membrane was up to $3.7\mathrm{L\,m^{-2}\,h^{-1}\,kPa^{-1}}$. The experimental results showed that homemade composite hollow fiber membranes have good ability to resist pollution and can operate at high flux and low pressure in a membrane bioreactor.

4. Conclusions

Using a self-made device for preparation of composite hollow fiber membranes, the PVDF/woven tube composite hollow fiber membrane was prepared by the coating technology and immersion-precipitation technique. And we drew the following conclusions from the research:

(1) The polymer layer of the casting solution was uniformly wrapped in the outer surface of the woven tube, and the coating layer and the woven tube layer merged closely. The thickness of the coating layer was only about one-fifth of the total thickness of the composite membrane, the coating layer had a thin and compact structure. The pure water flux reached $4{,}300\,\mathrm{L\,m^{-2}\,h^{-1}}$, and burst pressure reached 0.32 MPa. In the research, the porosity of the composite fiber membrane is always above 45%, burst pressure is higher than 0.30 MPa, and due to the existence of the woven tube support layer, the tensile strength of the composite membrane is very high.

(2) The effect of PVDF concentration on the composite membrane performance is very significant. With the increase of PVDF concentration in the casting solution, the composite membrane pure water flux and the average pore size decrease, while with increasing the burst pressure, the porosity increases at first and then decreases. When PVDF content is 12%, the overall performance of the composite hollow fiber membrane is the best.

(3) Although the membrane operates at a high flux of $20 \pm 0.5\,\mathrm{L\,m^{-2}\,h^{-1}}$ and the pollutants removal efficiency is high, the TMP was kept under 5.5 kPa, the permeability of the membrane is up to $3.7\,\mathrm{L\,m^{-2}\,h^{-1}\,kPa^{-1}}$. The study shows that homemade composite hollow fiber membranes have a good ability to resist pollution; the membrane fouling process becomes slow along with the membrane fouling rate. The composite membrane can operate at a high flux and low pressure in a membrane bioreactor, and the rejection effect on particles is very good.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of P.R. China (Grant Nos. 51008243, 51178378, 51278408); Shanxi Province technology and science innovation project (Grant No. 2012KTCL03-06).

References

[1] J. Xu, Z.L. Xu, Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent, J. Membr. Sci. 208 (2002) 203–212.

[2] Z.L. Xu, F.A. Qusay, Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution, J. Membr. Sci. 233 (2004) 101–111.

[3] R.D. Noble, S.A. Stern, Membrane Separation Technology: Principles and Applications, Membrane science and technology series, vol. 2, Elsevier Science, London, 1995, pp. 1–20.

[4] L.P. Cheng, T.H. Young, W.M. You, Formation of crystalline EVAL membranes by controlled mass transfer process in WATER-DMSO-EVAL copolymer systems, J. Membr. Sci. 145 (1998) 77–90.

[5] A.V.R. Reddy, D.J. Mohan, A. Bhattacharya, V.J. Shah, P.K. Ghosh, Surface modification of ultra-filtration membranes by pre-adsorption of a negatively charged polymer. I. Permeation of water soluble polymers and inorganic salt solutions and fouling resistance properties, J. Membr. Sci. 214 (2003) 211–221.

[6] Z.H. Lu, G.J. Liu, S. Duncan, Poly(2-hydroxyethyl acrylate-co-methylacrylate)/SiO_2/TiO_2 hybrid membranes, J. Membr. Sci. 21 (2003) 113–122.

[7] A. Taniguchi, M. Cakmak, The suppression of strain induced crystallization in PET through sub micron TiO_2 particle incorporation, Polymer 45 (2004) 6647–6654.

[8] Y.N. Yang, P. Wang, Preparation and characterizations of a new PS/TiO_2 hybrid membranes by sol–gel process, Polymer 47 (2006) 2683–2688.

[9] S. Yu, X.T. Zuo, R.L. Bao, X. Xu, J. Wang, J. Xu, Effect of SiO_2 nanoparticle addition on the characteristics of a new organic–inorganic hybrid membrane, Polymer 50 (2009) 553–559.

[10] C.J. Liao, J.Q. Zhao, P. Yu, H. Tong, Y.B. Luo, Synthesis and characterization of low content of different SiO_2 materials composite poly (vinylidene fluoride) ultrafiltration membranes, Desalination 285 (2012) 117–122.

[11] P.V. Witte, P.J. Dijkstra, Phase separation process in polymer solution in relation to membrane formation, J. Membr. Sci. 117 (1996) 1–31.
[12] D.J. Lin, C.L. Chang, Preparation and characterization of microporous PVDF/PMMA composite membranes by phase inversion in water/DMSO solution, Eur. Polym. J. 42 (2006) 2407–2418.
[13] S.P. Deshmukh, K. Li, Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fiber membranes, J. Membr. Sci. 150 (1998) 75–78.
[14] M.L. Yeow, K. Li, Isothermal phase diagrams and phase inversion behavior of polymer/solvents/additives/water systems, J. Membr. Sci. 90 (2003) 2150–2155.
[15] L.P. Cheng, T.H. Young, The formation mechanism of membranes prepared from the nonsolvent-solvent-crystalline polymer systems, Polymer 42 (2001) 443–451.
[16] D.J. Lin, L.C. Cheng, Effect of salt additive on the formation of microporous poly(vinylidene fluoride) membranes by phase inversion from $LiClO_4$/Water/DMF/PVDF system, Polymer 44 (2003) 413–422.
[17] I. Ivanovic, T. Leiknes, Membrane reactor design as a tool for better membrane performance in a biofilm MBR (BF-MBR), Desal. Water Treat. 25 (2011) 259–267.
[18] A. Salahi, T. Mohammadi, A.R. Pour, F. Rekabdar, Oily wastewater treatment using ultra-filtration, Desal. Water Treat. 6 (2009) 289–298.
[19] S.P. Hong, T.H. Bae, T.M. Tak, S. Hong, A. Randall, Fouling control in activated sludge submerged hollow fiber membrane bioreactors, Desalination 143 (2002) 219–228.
[20] H.C. Chua, T.C. Arnot, J.A. Howell, Controlling fouling in membrane bioreactors operated with a variable throughput, Desalination 149 (2002) 225–229.
[21] T. Jiang, M.D. Kennedy, Optimising the operation of a MBR pilot plant by quantitative analysis of the membrane fouling mechanism, Water Sci. Technol. 51 (2005) 19–25.
[22] J. Zhang, H.C. Chua, J. Zhou, A.G. Fane, Factors affecting the membrane performance in submerged membrane bioreactors, J. Membr. Sci. 284 (2006) 54–66.
[23] Y. Choi, H. Oh, S.H. Lee, Y.J. Choi, T.M. Hwang, G.S. Baek, Y.K. Choung, Large-pore membrane filtration with coagulation as an MF/UF pretreatment process, Desal. Water Treat. 15 (2010) 149–159.
[24] I. Ivanovic, T.O. Leikness, The biofilm membrane bioreactor (BF-MBR)—A review, Desal. Water Treat. 37 (2012) 288–295.