Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.961172

56 (2015) 2276–2283
November

Taylor & Francis
Taylor & Francis Group

Surface modification of PVDF membrane by simultaneously using low temperature plasma and ammonium carbonate solution

Ru-Jin Zhao*, Wei-Sheng Wang, Fei-Fei Zhu, Teng Liu, Yi-Hui Li, Ying-Lei Bian

College of Environment and Safety Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, Jiangsu, P.R. China, Tel. +86 511 88790931; Fax: +86 511 88790955; emails: zhaorujin@ujs.edu.cn (R.-J. Zhao), 786218244@qq.com (W.-S. Wang), 919516518@qq.com (F.-F. Zhu), 526084903@qq.com (T. Liu), 825468217@qq.com (Y.-H. Li), 1050199193@qq.com (Y.-L. Bian)

Received 15 October 2013; Accepted 26 August 2014

ABSTRACT

Polyvinylidene fluoride (PVDF) hollow fiber membrane was surface modified by low temperature O_2 and H_2O plasma and ammonium carbonate solution treatment, and used in membrane bioreactor (MBR). Effect of the modification on surface characteristics of PVDF membrane was investigated. The FE-SEM and AFM images of membrane showed that low temperature O_2 and H_2O plasma and ammonium carbonate solution treatment could markedly increase surface roughness of PVDF membrane. Water contact angle decreased obviously with the increase of low temperature plasma treatment time. Hydrophilicity of modified membrane enhanced distinctly. The mass fraction of oxygen of PVDF membrane surface increased markedly after plasma and ammonium carbonate solution treatment. The modification of membrane surface had no significant effect on the removal rates of pollutants when used in a MBR. It could improve antifouling property of membrane and decrease filtration resistance of membrane. The modification using low temperature plasma and ammonium carbonate solution did not reduce membrane flux. And moreover, ammonium carbonate solution treatment could markedly enhance the stability of plasma modification membrane.

Keywords: Surface modification; Polyvinylidene fluoride hollow fiber membrane; Low temperature plasma; Ammonium carbonate solution; Antifouling characteristic; Stability

1. Introduction

The surface modification has been an important and simple way to improve surface properties of membrane [1]. The treatment by plasma is regarded as one of the advantageous modification techniques and studied extensively. In the existing literatures, plasma modification ranges from simple plasma treatment, plasma polymerization to plasma deposition. Several research groups had carried out studies of surface modification by simple plasma treatment using gases like air, N_2, H_2O, NH_3, CF_4, He, O_2, CO_2, acrylic acid vapor, etc. [2–13]. Gulec, Liu, Huang, Zou, Wang et al. [14–18] modified membrane surface via plasma polymerization to improve hydrophilicity and antifouling characteristic. Lue et al. [19] achieved the surface modification of a perfluorosulfonic acid (PFSA) membrane using perfluoroheptane and argon plasma treatment. The plasma mixture led to the deposition of a thin

---

*Corresponding author.

fluorocarbon polymerized top layer onto the PFSA membrane. Hosseini et al. [20] prepared PVC/ SBR heterogeneous cation exchange membrane and carried out surface modification with silver nanoparticles in a vacuum reactor by argon plasma treatment to increase the performance. Plasma modification can evidently improve surface properties of membrane without affecting the bulk of membrane. But, the changes of surface properties induced by simple plasma treatment are time dependent. After some time, the surface properties of modified membrane may deteriorate. Plasma polymerization and plasma deposition are likely to reduce membrane flux.

Unstability of surface properties of membrane modified by simple plasma treatment may be preferable to the reaction of polar groups and substance around modified membrane, interreactions and migrating of polar groups. So our group had been searching for stabilizing agents of modified membrane. The stabilizing agent can prevent mentioned interreactions and migrating of polar groups. It may react with polar groups, and more polar groups are introduced onto the surface of membrane. As a common reagent, ammonium carbonate solution was selected as one of the stabilizing agents.

Based on previous studies, polyvinylidene fluoride (PVDF) hollow fiber membrane was modified by simultaneously using low temperature O_2 and H_2O plasma and ammonium carbonate solution, and then used in MBR in this research. The purpose of the research is to investigate the effect of surface modification by low temperature O_2 and H_2O plasma and ammonium carbonate solution on surface characteristics of PVDF membrane.

2. Materials and methods

2.1. Materials

The PVDF hollow fiber microporous membrane used in this study is from an enterprise manufacturing hollow fiber membrane in China with the average pore diameter of 0.2 μm. The inner and outer diameters of PVDF hollow fiber microporous membrane are 0.6 and 1.1 mm. The total area of the membrane module is about 0.01 m^2. The ammonium carbonate is analytical reagent.

2.2. Surface modification of PVDF membrane

Before plasma treatment, PVDF membrane was washed with acetone to remove any chemicals and wetting agents absorbed on the membrane surface, then dried in a vacuum oven at room temperature for 20 h, and stored in a desiccator.

A self-made dielectric barrier discharge plasma generator (Fig. 1) was used to produce low temperature plasma. The diameter of stainless steel central electrode is 15 mm, which is high voltage electrode. The dielectric is quartz glass tube with the wall thickness of 1.5 mm. The case metal electrode is earth electrode. The length of discharge zone is 220 mm. Discharge gap is 3 mm.

H_2O was atomized by ultrasonic nebulizer. The ultrasonic frequency of nebulizer was 1.7 MHz ± 10%. Atomized H_2O and O_2 were injected into generator after being mixed. The ratio of flow rate of atomized H_2O to O_2 was 1:1. Under the action of high voltage source, low temperature plasma could be generated in the reactor by dielectric barrier discharge.

The plasma in generator was blown out to the surface of PVDF membrane, when PVDF hollow fiber microporous membrane was modified. Discharge voltage and discharge frequency were 14 kV and 30 kHz, respectively. Flow rate of atomized H_2O and O_2 was 0.1 m^3/h. Unless otherwise specified, plasma treatment time of all modified membrane was 4 min in this paper. Then the modified membrane via plasma is quickly put into 1 mol/L ammonium carbonate solution for 1 h. After taken out from ammonium carbonate solution, the membrane was washed with deionized water for 3 min. Finally, the membrane was dried in vacuo over molecular sieves for at least 1.5 h before being analyzed.

Concentration of ammonium carbonate and standing time of modified membrane in ammonium carbonate solution were determined by single-factor test. Stability of plasma modified membrane was enhanced with the increase of ammonium carbonate concentration, when ammonium carbonate concentration was less than 1 mol/L. When ammonium carbonate concentration was more than 1 mol/L, the stability increased little. Stability of plasma modified

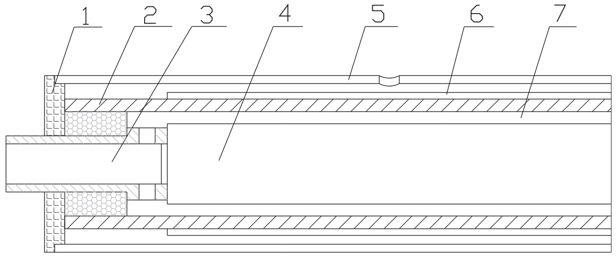

Fig. 1. Structure sketch-map of dielectric barrier discharge plasma generator: (1) seal insulating material, (2) insulating dielectric layer, (3) inlet, (4) central electrode, (5) glass cover, (6) case metal electrode, and (7) discharge space.

membrane was enhanced with the increase of standing time, when standing time was less than 1 h. But, when standing time was more than 1 h, the stability decreased slightly.

2.3. Antifouling characteristic measurement

A submerged membrane bioreactor experimental apparatus (Fig. 2) was designed to characterize the filtration performance of original and modified PVDF membrane. The original and modified curtain-shaped hollow fiber membrane modules were, respectively, used in bioreactor, which were operated under the same conditions.

Transmembrane pressure was monitored using pressure gage. During filtration of microfiltration membrane, the relationship of membrane flux and operation pressure can be described by the following equation:

$$J = \Delta p/\mu R \tag{1}$$

where J is membrane flux, Δp is transmembrane pressure, μ is viscosity of filtrate, and R is filtration resistance.

R in Eq. (1) can also be described by the following equation.

$$R = R_{\mathrm{m}} + R_{\mathrm{c}} + R_{\mathrm{p}} \tag{2}$$

where R_{m} is intrinsic resistance of membrane, R_{c} is sludge cake resistance, and R_{p} is membrane pore fouling resistance.

Measuring methods of total filtration resistance, intrinsic resistance, sludge cake resistance, and membrane pore fouling resistance are as follows:

(1) A clean membrane is used for filtrating clear water under certain pressure. The membrane flux is determined, and then the intrinsic resistance of membrane is calculated by Eq. (1).
(2) Total filtration resistance is calculated using Eq. (1) with transmembrane pressure, and membrane flux is noted at the end of experiment.
(3) The sludge cake on the surface of the membrane used in the experiment is removed with clear water. Then the clear water is filtrated by the membrane under certain pressure, and the membrane flux is determined. The membrane resistance R_1 is calculated. The difference value of R_1 and R_{m} is the membrane pore fouling resistance.
(4) The sludge cake resistance can be calculated by Eq. (2).

In the above calculation process, let us consider the filtrate viscosity as 1 × 10^{-3} Pa s, which is the same as the viscosity of clear water.

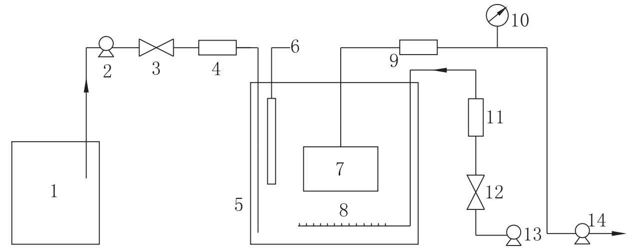

Fig. 2. Sketch-map of experimental apparatus: (1) water tank, (2) influent pump, (3) valve, (4) liquid flowmeter, (5) bioreactor, (6) temperature controller, (7) membrane module, (8) perforated aeration pipe, (9) liquid flowmeter, (10) pressure gage, (11) gas flowmeter, (12) valve, (13) air pump, and (14) effluent pump.

2.4. Analytical methods

Surface morphology of the original and modified PVDF membrane was observed using the field emission scanning electron microscope (S-4800, Japan) and atomic force microscope (Veeco MultiMode, America). The water contact angle of original and modified PVDF membrane was measured by the sessile drop method using a contact angle system (OCA20, Germany). The contact angle was measured at room temperature. Surface elemental composition analysis of PVDF membrane was performed using XPS (PH15400ESCA, America).

COD was measured according to potassium dichromate method. NH_4^+-N concentration was measured through spectrophotometry using multiparameter bench photometer for laboratories (HI 83200, Hanna Instruments Inc., America). Dissolved oxygen (DO) was real-time online monitored using DO probe (JPB-607, Shanghai Jingsheng Scientific instrument Co. Ltd., China). Influent pH was monitored using a pH probe (pHS-3B, Shanghai Leici instrument Co. Ltd., China). Mixed liquid suspended solid (MLSS) was measured according to the gravimetric method.

3. Results and discussion

3.1. FE-SEM and AFM analysis

Figs. 3 and 4 show the surface morphology of the original and modified PVDF membrane by FE-SEM. Figs. 5 and 6 are AFM images of the original and

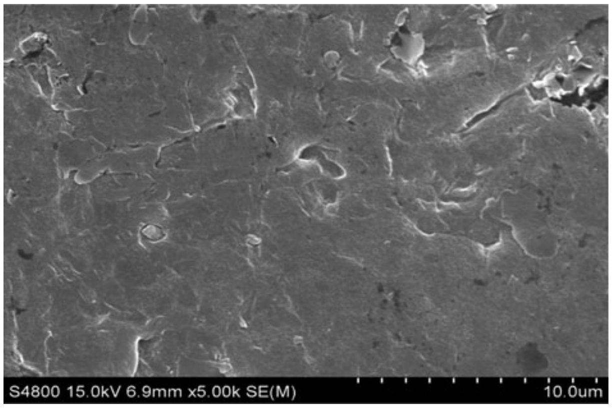

Fig. 3. FE-SEM image of original PVDF membrane.

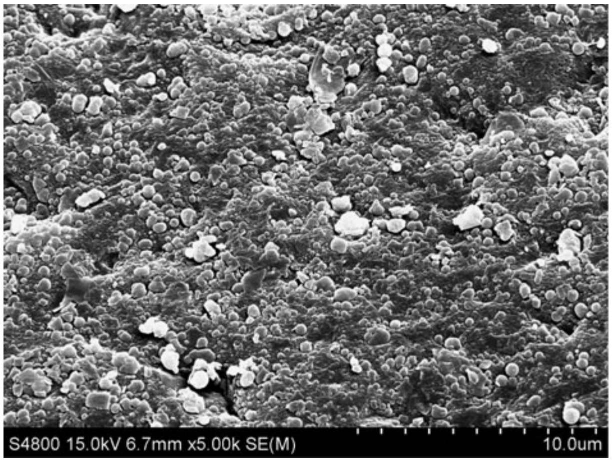

Fig. 4. FE-SEM image of modified PVDF membrane.

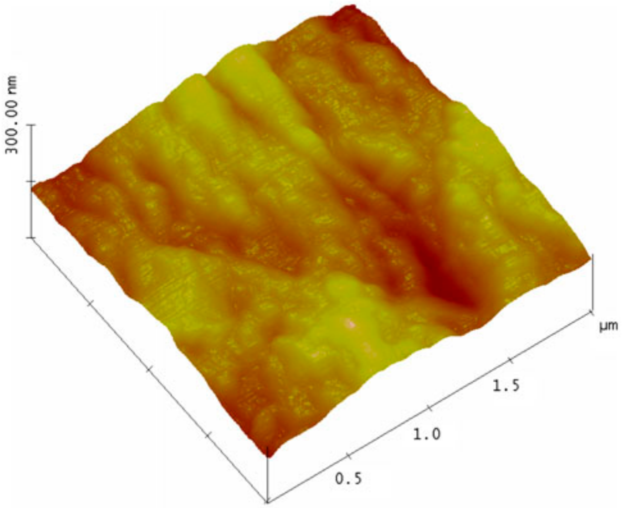

Fig. 5. AFM image of original PVDF membrane.

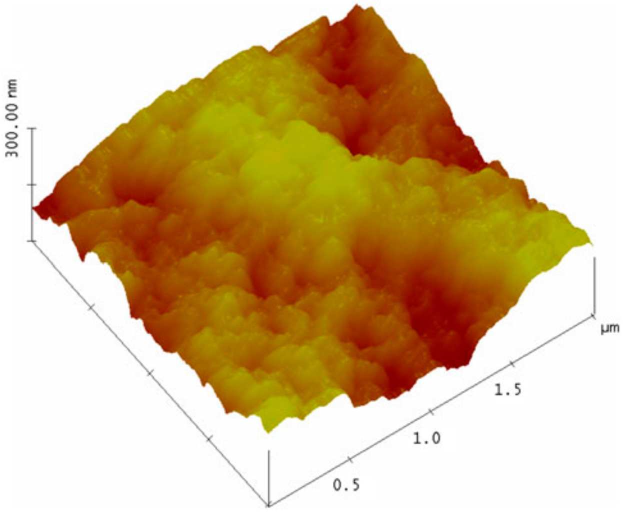

Fig. 6. AFM image of modified PVDF membrane.

modified PVDF membrane. The change of surface morphology can be seen in FE-SEM and AFM pictures. The mean roughness (Ra) of the original PVDF membrane is 11.613 nm. The mean roughness (Ra) of modified PVDF membrane is 26.023 nm. The low temperature plasma treatment markedly increases the surface roughness of PVDF membrane maybe because the ion bombardment causes surface sputtering and surface activation.

3.2. Hydrophilicity

The hydrophilicity of the original and modified PVDF membrane can be obtained using water contact angle measurement. Water contact angles on the original and modified membrane surfaces are shown in Fig. 7. Fig. 7 indicates that the water contact angle decreases obviously with the increase of low temperature plasma treatment time. The reduction in water contact angle means the increase of hydrophilicity.

The hydrophilicity of the original and modified membrane can also be expressed using water absorption rate of membrane. The original and modified membranes were soaked in water for 30 min, and then taken out. The adherent water was removed by natural slipping and evaporating. The dry membrane and soaked membrane were weighed, respectively. The ratio of increased mass after soak to dry membrane mass was water absorption rate of membrane. The water absorption rates were determined every 10 min after soaked membrane being taken out. The results are shown in Fig. 8. It indicates that the water absorption rates of modified membrane are more evident than that of the original membrane after soaking. So

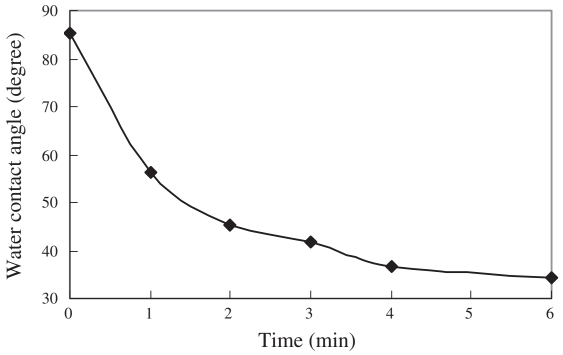

Fig. 7. Water contact angle changes with low temperature plasma treatment time.

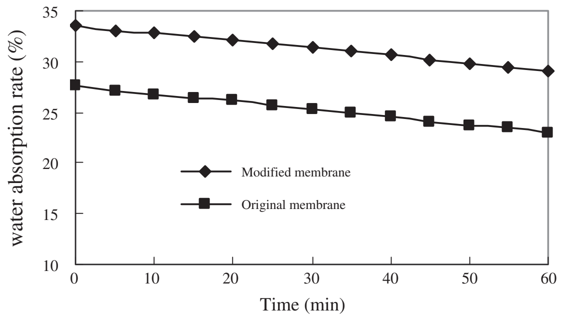

Fig. 8. Water absorption rate of original and modified membrane.

the modification by low temperature plasma and ammonium carbonate solution can increase the hydrophilicity of PVDF membrane.

The low temperature plasma with large volume and high energy density can be obtained using dielectric barrier discharge. When plasma is blown on the surface of PVDF membrane by gas current from discharge space, high-energy electrons, ions and other active groups in plasma can react with membrane surface. The reaction types probably include rupture of chain, degradation, crosslink, etc. When chemical bonds are ruptured, reactive activity is produced on membrane surface. Meanwhile a lot of hydrophilic polar groups such as hydroxyl, carbonyl, etc. can be introduced onto the surface of membrane. It is likely that the treatment of ammonium carbonate solution further increases the type and amount of hydrophilic groups on membrane surface. So hydrophilicity and antifouling property of membrane surface are improved.

3.3. XPS

XPS analyses were performed on the original and modified PVDF membrane. Table 1 shows surface elemental compositions of the original membrane and modified membrane.

Table 1
Surface elemental compositions of original membrane and modified membrane

	Mass fraction (%)			
Membrane type	C	F	O	N
Original membrane	63.5	20.9	12.4	3.2
Modified membrane	64.3	12.6	19.8	3.3

The modified membrane in Table 1 was obtained by plasma treatment for 4 min and ammonium carbonate solution treatment for 60 min. The mass fraction of oxygen on membrane surface increases markedly after O_2 and H_2O plasma and ammonium carbonate solution treatment. The mass fraction of nitrogen rises a little, but the mass fraction of fluorine decreases. There is a positive correlation between mass fraction of oxygen and hydrophilicity of PVDF membrane.

3.4. Separation property

The original and modified PVDF membrane modules were installed in bioreactor, respectively. Two membrane bioreactors (MBRs) were assembled and used to treat domestic wastewater. The experimental apparatus is shown in Fig. 2. The MBRs were kept running for 50 d with the conditions of aeration rate of 0.1 m^3/h, influent pH of about 7.7, influent temperature of about 25℃, hydraulic retention time of 6 h, MLSS of 5,100 mg/L. The suction time and pause time of effluent pump were 10 and 2 min, respectively. The filtration properties of the original and modified PVDF membranes were studied.

The experimental results are shown in Table 2. The COD and NH_4^+-N of influent and effluent in Table 2 are average value on the 50th day. It can be seen that the COD and NH_4^+-N removal efficiencies in MBR with the modified PVDF membrane (MBR2) are somewhat lower than in MBR with the original PVDF membrane (MBR1). So the modification of PVDF membrane with low temperature O_2 and H_2O plasma and ammonium carbonate solution has no significant effect on the removal rates of pollutants.

3.5. Transmembrane pressure

Experimental apparatus were same with 3.4. Experiments were performed with the operating parameters of aeration rate of 0.1 m^3/h, influent pH of about 7.7, influent temperature of about 25℃,

Table 2
Removal efficiencies of pollutants in two MBRs

	MBR1			MBR2		
Item	Influent (mg/L)	Effluent (mg/L)	Removal efficiency (%)	Influent (mg/L)	Effluent (mg/L)	Removal efficiency (%)
COD	358.4	13.1	96.3	358.8	14.9	95.8
NH_4^+-N	24.7	1.9	92.1	24.7	2.4	90.3

membrane flux of 12.5 L/(m^2 h), MLSS of 5,100 mg/L. The suction time and pause time of pump were 10 and 2 min, respectively.

The transmembrane pressure changes of MBR1 and MBR2 in the operation are shown in Fig. 9. Fig. 9 indicates that the changes of transmembrane pressure include two stages: slowly rising stage and quickly rising stage. Although transmembrane pressure of MBR2 increases gradually, increasing rate of it is obviously less than MBR1. Transmembrane pressure of MBR2 begins to rise rapidly on the 46th day of stable operation with membrane pore being constantly plugged. The rate of membrane fouling increases. The stable running time with low transmembrane pressure of MBR2 is 10 d longer than MBR1. So the surface modification via low temperature plasma and ammonium carbonate solution treatment can improve antifouling property of membrane. The result is concordant with the increase of hydrophilicity.

3.6. Distribution of filtration resistance

After experiments about transmembrane pressure, the resistance distributions of the original membrane and modified membrane were analyzed. The results are shown in Table 3, Figs. 10 and 11.

Table 3, Figs. 10 and 11 show that the sludge cake resistance and membrane pore fouling resistance are the main parts of filtration resistance to the original membrane and modified membrane after running for 50 d in MBR. So decreasing sludge cake resistance and membrane pore fouling resistance is the prime measure of membrane pollution control. The total resistance, intrinsic resistance, sludge cake resistance and membrane pore fouling resistance of the modified membrane are less than that of the original membrane. The decreasing amplitude of total resistance and sludge cake resistance is very large after modification. This shows that modification using low temperature O_2 and H_2O plasma and ammonium carbonate solution is effective to decrease filtration resistance of membrane and delay the development of sludge cake.

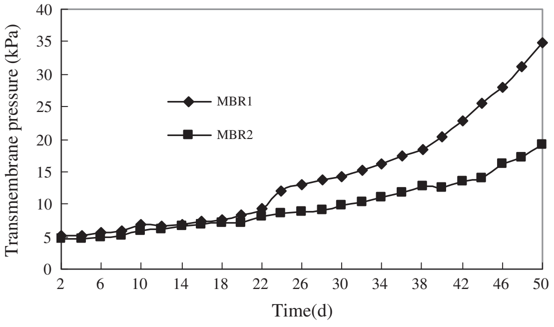

Fig. 9. Transmembrane pressure changes of MBR1 and MBR2.

Above all, intrinsic resistance of membrane decreases slightly after modification. It means that the modification using low temperature plasma and ammonium carbonate solution does not reduce membrane flux.

3.7. Stability of modified membrane

To investigate the stability of modified membrane, two modified membranes were prepared. One was modified by simple low temperature O_2 and H_2O plasma treatment for 4 min. Another was modified via low temperature O_2 and H_2O plasma treatment for 4 min and ammonium carbonate solution treatment for 1 h. Then the two membranes were placed in the air for 30 d. The water contact angles of the two modified membranes were measured every 5 d. The results are shown in Fig. 12.

Fig. 12 shows that the water contact angle of modified membrane using simple plasma treatment increases with time and reaches 66.9° on the 30th day after modification. Hydrophilicity reduces, but nothing much has changed with time for the water contact angle of modified membrane by plasma and ammonium carbonate solution treatment. The water contact angle increases only from 36.5° to 41.7°. This indicates that ammonium carbonate solution treatment can markedly enhance the stability of plasma modified membrane. The interreactions and migrating of polar groups on PVDF modified membrane may be restricted.

Table 3
Resistances of original membrane and modified membrane

Membrane	R (10^{12} m^{-1})	R_m (10^{12} m^{-1})	R_c (10^{12} m^{-1})	R_p (10^{12} m^{-1})
Original membrane	10.05	1.03	6.07	2.95
Modified membrane	5.53	0.79	2.50	2.24

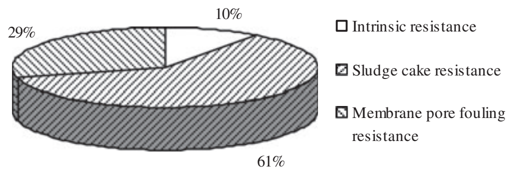

Fig. 10. Resistance distribution of original membrane.

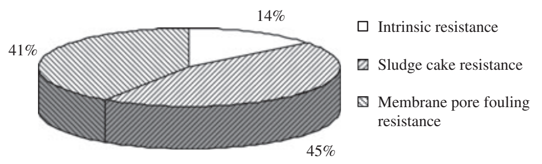

Fig. 11. Resistance distribution of modified membrane.

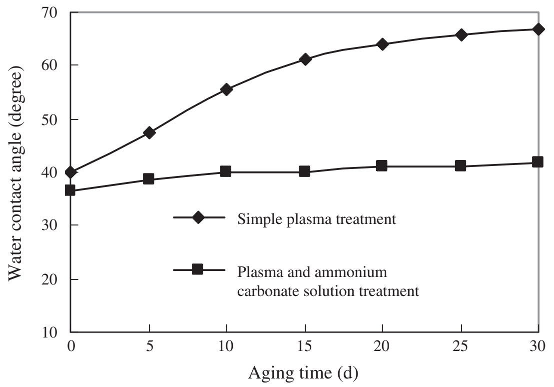

Fig. 12. Changes of water contact angle on modified membranes with time.

Plasma modification can evidently improve surface properties of membrane without affecting the bulk of membrane. But, the biggest problem of this technique is that the surface properties induced by plasma treatment are time dependent at present. In this study, ammonium carbonate solution treatment can markedly enhance the stability of plasma modified membrane. The plasma modification has the advantages of low cost, high efficiency, less pollution, etc. And, the price of ammonium carbonate is low as a common reagent. So the cost of this modification is also low. The modification technique has potential for industrial application.

4. Conclusions

PVDF hollow fiber membrane was surface modified by low temperature O_2 and H_2O plasma and ammonium carbonate solution treatment. The FE-SEM and AFM images of membrane showed that the plasma and ammonium carbonate solution treatment could markedly increase the surface roughness of PVDF membrane. The hydrophilicity of modified membrane increased distinctly. The mass fraction of oxygen on membrane surface increased markedly after O_2 and H_2O plasma and ammonium carbonate solution treatment. The modification of membrane surface had no significant effect on the removal rates of pollutants when used in MBR. At the same time, it could improve antifouling property of membrane and decrease filtration resistance of membrane. The modification using low temperature plasma and ammonium carbonate solution did not reduce membrane flux. And moreover, ammonium carbonate solution treatment can markedly enhance the stability of plasma modification membrane.

Acknowledgment

Financial support from the Special Fund of Jiangsu University for High-level Talent (No. 09JDG074) is gratefully acknowledged.

References

[1] W. Chinpa, D. Quémener, E. Bèche, R. Jiraratananon, A. Deratani, Preparation of poly(etherimide) based ultrafiltration membrane with low fouling property by surface modification with poly(ethylene glycol), J. Membr. Sci. 365 (2010) 89–97.

[2] H.-Y. Yu, M.-X. Hu, Z.-K. Xu, J.-L. Wang, S.-Y. Wang, Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH plasma treatment, Sep. Purif. Technol. 45 (2005) 8–15.

[3] H.-Y. Yu, L.-Q. Liu, Z.-Q. Tang, M.-G. Yan, J.-S. Gu, X.-W. Wei, Surface modification of polypropylene microporous membrane to improve its antifouling characteristics in an SMBR: Air plasma treatment, J. Membr. Sci. 311 (2008) 216–224.

[4] E. Alkan, E. Kır, L. Oksuz, Plasma modification of the anion-exchange membrane and its influence on fluoride removal from water, Sep. Purif. Technol. 61 (2008) 455–460.

[5] B.D. Tompkins, J.M. Dennison, E.R. Fisher, H_2O plasma modification of track-etched polymer membranes for increased wettability and improved performance, J. Membr. Sci. 428 (2013) 576–588.

[6] M.-G. Yan, L.-Q. Liu, Z.-Q. Tang, L. Huang, W. Li, J. Zhou, J.-S. Gu, X.-W. Wei, H.-Y. Yu, Plasma surface modification of polypropylene microfiltration membranes and fouling by BSA dispersion, Chem. Eng. J. 145 (2008) 218–224.

[7] X. Wei, B.-L. Zhao, X.-M. Li, Z.-W. Wang, B.-Q. He, T. He, B. Jiang, CF4 plasma surface modification of asymmetric hydrophilic polyethersulfone membranes for direct contact membrane distillation, J. Membr. Sci. 407–408 (2012) 164–175.

[8] T.D. Tran, S. Mori, M. Suzuki, Plasma modification of polyacrylonitrile ultrafiltration membrane, Thin Solid Films 515 (2007) 4148–4152.

[9] X.-C. He, H.-Y. Yu, Z.-Q. Tang, L.-Q. Liu, M.-G. Yan, J.-S. Gu, X.-W. Wei, Reducing protein fouling of a polypropylene microporous membrane by CO_2 plasma surface modification, Desalination 244 (2009) 80–89.

[10] D. Tyszler, R.G. Zytner, A. Batsch, A. Brügger, S. Geissler, H. Zhou, D. Klee, T. Melin, Reduced fouling tendencies of ultrafiltration membranes in wastewater treatment by plasma modification, Desalination 189 (2006) 119–129.

[11] D.E. Weibel, C. Vilani, A.C. Habert, C.A. Achete, Surface modification of polyurethane membranes using acrylic acid vapour plasma and its effects on the pervaporation processes, J. Membr. Sci. 293 (2007) 124–132.

[12] J. Pang, W.-J. Jian, L.-Y. Wang, C.-H. Wu, Y.-N. Liu, J. He, X.-F. Tang, X-ray photoelectron spectroscopy analysis on surface modification of Konjac glucomannan membrane by nitrogen plasma treatment, Carbohydr. Polym. 88 (2012) 369–372.

[13] M.-S. Li, Z.-P. Zhao, N. Li, Y. Zhang, Controllable modification of polymer membranes by long-distance and dynamic low-temperature plasma flow: Treatment of PE hollow fiber membranes in a module scale, J. Membr. Sci. 427 (2013) 431–442.

[14] H.-A. Gulec, A. Topacli, C. Topacli, N. Albayrak, M. Mutlu, Modification of cellulose acetate membrane via low-pressure plasma polymerization for sugar separation applications: Part I. Membrane development and characterization, J. Membr. Sci. 350 (2010) 310–321.

[15] Z.-M. Liu, S. Tingry, C. Innocent, J. Durand, Z.-K. Xu, P. Seta, Modification of microfiltration polypropylene membranes by allylamine plasma treatment: Influence of the attachment route on peroxidase immobilization and enzyme efficiency, Enzyme Microb. Technol. 39 (2006) 868–876.

[16] C. Huang, W.-C. Ma, C.-Y. Tsai, W.-T. Hou, R.-S. Juang, Surface modification of polytetrafluoroethylene membranes by radio frequency methane/nitrogen mixture plasma polymerization, Surf. Coat. Technol. 231 (2013) 42–46.

[17] L. Zou, I. Vidalis, D. Steele, A. Michelmore, S.P. Low, J.Q.J.C. Verberk, Surface hydrophilic modification of RO membranes by plasma polymerization for low organic fouling, J. Membr. Sci. 369 (2011) 420–428.

[18] C.-C. Wang, F.-L. Yang, J.-L. Duan, H.-M. Zhang, Nonwoven membrane modification by 4-vinyl pyridine grafted polyvinyl alcohol for resistance the adhesion of bacteria, Desalin Water Treat. 18 (2010) 206–211.

[19] S.J. Lue, S.-Y. Hsiaw, T.-C. Wei, Surface modification of perfluorosulfonic acid membranes with perfluoroheptane (C_7F_{16})/argon plasma, J. Membr. Sci. 305 (2007) 226–237.

[20] S.M. Hosseini, S.S. Madaeni, A.R. Khodabakhshi, A. Zendehnam, Preparation and surface modification of PVC/SBR heterogeneous cation exchange membrane with silver nanoparticles by plasma treatment, J. Membr. Sci. 365 (2010) 438–446.