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Preparation and characterization of modified activated carbon/polysulfone blended ultrafiltration membrane

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ABSTRACT

Modified activated carbon with good adsorption performance and specific functional groups was prepared by oxidation of nitric acid and reduction of ammonium hydroxide. When the concentration of nitric acid and ammonia solution was 20%, the adsorption capacity of modified activated carbon was 226 mg/g and 266 mg/g, respectively. At the concentration of 10%, the modified active carbon have the highest content of acid group and basic group on the surface, which is 0.970 mmol/L and 0.315 mmol/L, respectively. Meanwhile, the composite ultra filtration membrane was prepared by filling the modified activated carbon into the polysulfone. It was found that the flux and rejection of the composite membrane were changed. The composite membrane filled activated carbon modified by the concentration of 20% nitric acid (PSF/HAC-20) could reach the highest water permeability of 116.5 L·M^{-2}·h^{-1}. Meanwhile, the retention rate was increased by 35% .

Keywords: Modified activated carbon; Polysulfone blended ultrafiltration membrane; Membrane flux; Rejection rate

1 Introduction

Activated carbon (AC) is an amorphous carbon made from bio-organic materials such as coal, husks and so on through carbonization, activation and other processes [1]. Activated carbon material has the characteristics of large specific surface area, unique pore structure, narrow pore size distribution and controllable surface functional groups [2–6]. It is widely used in environmental protection, petrochemical, chemical industry, electric power, dye stuff and food processing area because of its high mechanical strength, insolubility in water and organic solvent, and regeneration [7–9]. The excellent adsorption properties of activated carbon not only are related to its well-developed pore structure, but also have bearing on the chemical properties of activated carbon surface, which is closely associated with the oxygen-containing groups and nitrogen-containing groups on the activated carbon surface [10,11]. To a certain extent, the combination of activated carbon and ultra filtration system can make full use of their advantages to complement each other, overcoming the shortcomings of the single treatment. Activated carbon adsorption and membrane separation technology used in water treatment have similarities, but also have significant differences, the combination of the two is widely studied and applied to the field of water treatment [12]. The modification of activated carbon can significantly change the surface functional groups, specific surface area and microstructure characteristics. After functional modifying according to the application requirements, modified activated carbon with specific structural and chemical groups can be obtained [13]. Yet, recently Liao et al. [14,15] prepared the hybrid oxidized single-walled carbon nanotube (SWCNT)-polyaniline (PANi) nanofibers by a novel flash welding technique. After flash welding, both conductivity and pure water permeability of the membranes improves by nearly a factor of 10, while maintaining silica nanoparticle rejection levels above 90%.

Polysulfone (PSf)-based membranes are the most widely used because of their chemical stability, excellent heat resistance and good film-forming properties. However, there are some disadvantages including electrical resistance over a wide pH range and the essentially hydrophobic. There-

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fore, researchers are looking for a membrane with finely-balanced characteristics. For example, Hoek et al. [16] prepared blend polysulfone membrane by the addition of polyaniline, when containing up to 75%, 10–20% more permeable were obtained than pure polysulfone membranes. Liao et al. [17,18] used highly dispersible polypyrrole (PPy) nano spheres to produce polysulfone (PSf) nano composite ultra filtration membranes, which demonstrate much improved hydrophilicity with respect to pure polysulfone membranes.

In this paper, activated carbon was modified by simple, practical and effective oxidation-reduction. The adsorption properties and specific functional groups of modified activated carbon were investigated in order to prepare active carbon with good adsorption properties and specific chemical groups. Meanwhile, the composite membrane was prepared by filling polysulfone with modified activated carbon, and the water flux and retention rate of the prepared composite membrane were also investigated.

2 Experimental

2.1. Chemicals and materials

Polysulfone polymer (molecular weight: 77–83 kg/mol) was provided by Shanghai Shuao Chemical Co., Ltd., China. Polyethylene glycol (PEG 400) and bovine serum albumin (BSA) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. N,N- dimethylacetamide (DMAc), ammonium hydroxide ($NH_3{\cdot}H_2O$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Nanjing Chemical Reagent Co., Ltd., Nitric acid (HNO_3) was supplied by Shanghai Pilot Chemical Corporation, China. Activated carbon (200 mesh) and methylene blue were obtained from Jiangsu Zhuxi Activated Carbon Co., Ltd. and Tianjin Chemical Reagent Research Institute, respectively. All reagents used in the experiments were of analytical grade. Deionized water was used throughout all the studies.

2.2. The process of redox modification of activated carbon

Oxidation modification of nitric acid: 6 parts of 5 g activated charcoal, which was washed with water to remove its surface impurities prior to experiment, were weighed and mixed in 25 ml of 5%, 10%, 20%, 30%, 40% and 50% nitric acid solution. After being stirred for 6 h at 30°C and 200 rpm, the reaction mixture was thoroughly washed with deionized water and dried at 105°C for 12 h to obtain the corresponding modified activated carbon tagged HAC–5, HAC–10, HAC–20, HAC–30, HAC–40, HAC–50.

Reduction modification of ammonium hydroxide: 6 parts of 5 g were added to 25 ml concentration of 5%, 10%, 20%, 30%, 40%, 50% ammonia solution, respectively. The next operation is the same as oxidation modification shown above-mentioned. The modified activated carbon was denoted as NAC–5, NAC–10, NAC–20, NAC–30, NAC–40, NAC–50.

2.3. Preparation of modified activated carbon/polysulfone (MAC/PSF) blend membrane

MAC/PSF blend membranes were fabricated by phase inversion method using a casting solution containing DMAc as the solvent, 15 wt% PSf, 8% PEG 400 and 1 wt% modified active carbon based on the previous work [19]. After heated at 50°C for 1 h to make the polymer fully swelled, the casting solution was vigorously stirred at 50°C for 6 h to obtain transparent homogeneous solution. The fully dissolved casting solution was rested overnight at room temperature for degassing. After spreading the casting solution onto clean glass using a doctor blade, the films were immersed, with 60 s of evaporation, into distilled water for 24 h with deionized water altered every 5 h to remove the residual solvents and additives, and dried at 60°C for use. During the preparation process of membrane, temperature and humidity were 25°C ± 2°C and 62% ± 2%, respectively.

2.4. Properties and characterization of modified activated carbon

2.4.1. Determination of adsorption of modified activated carbon to methylene blue

Methylene blue solution (1.5 g/L): The methylene blue were added to the buffer solution, which of temperature is 60°C. After fully dissolved, the solution was cooled to room temperature and poured into a 1000 ml volumetric flask, then dilute to the mark with buffer solution.

The dry activated carbon (0.010 g) were placed in the test tube, and 5 ml of methylene blue solution was added to obtain suspension solution. After shaking for 10 min on an electric shaker, the suspension solution was filtered. The resulting solution was measured by UV visible spectrophotometer (JH752 Shanghai Jinghua Technology Instrument Co., Ltd.,China) at 665 nm. The methylene blue adsorption value is expressed in mg/g and is calculated as follows Eq. (1):

$$A = \left(c_0 - c_1\right)\frac{V}{m} \tag{1}$$

where A is the adsorption value of methylene blue, C_0, C_1 were the initial concentration of methylene blue and the concentration after adsorption, V is the methylene blue test solution added amount, M is the amount of activated carbon.

2.4.2. Determination of acid and base groups on the surface of activated carbon

Boehm titration method, which based on quantitative reaction of different strength alkali ($NaHCO_3$, Na_2CO_3 and NaOH) and acidic groups, was used to determine the content of acidic groups on the activated carbon surface. Three parts of 1 g modified activated carbon samples were added to 25 mL of $NaHCO_3$, Na_2CO_3, and NaOH solutions with a calibration concentration of 0.05 mol/L, respectively. After a rotational speed of 150 rpm at constant temperature 30°C for 24 h, the mixture was separated by suction filtration and washed several times using deionized water. The concentration of $NaHCO_3$, Na_2CO_3 and NaOH in the filtrate, which can be calculated on the surface of activated carbon acid group content were determinate by titrating with 0.05 mol/L HCl solution [20].

The content of acidic functional groups on the surface of activated carbon, n (mmol/g) according to the following formula:

$$n = \frac{\left(c_{NaOH}V_{NaOH} - c_{HCl}V_{HCl}\right)}{W} \quad (2)$$

The total basic functional groups were titrated with 0.1 mol/L HCl solution to ensure the hydrochloric acid is excessive, and then the supernatant was titrated with 0.05 mol/L NaOH solution, and the total basic functional group of activated carbon was determined according to formula (3) as follows:

$$n = \frac{\left(c_{HCl}V_{HCl} - c_{NaOH}V_{NaOH}\right)}{W} \quad (3)$$

2.4.3. FT-IR analysis of activated carbon

After dried at 120°C for 6h, 0.5–2 mg of dried sample and 100–200 mg of dry KBr powder (spectral purity) were mixed and crushed in an agate mortar. The surface functional groups of the sample were characterized by Fourier infrared spectrophotometer (FTIR-8400S, Shimadzu). The scanning range was 4000–400 cm^{-1} and the resolution was 4 cm^{-1}. Each sample was scanned 16 times.

2.5. The characterization of composite membrane performance

2.5.1. The morphological studies of composite membrane

The surface morphology and cross-sectional structure of the composite membranes were imaged using scanning electron microscopy (SEM) (3400N scanning electron microscope, Hitachi, Tokyo, Japan) prior to which the were first dried in a freeze drier, fractured in the liquid nitrogen to ensure the structural integrity of the sections and then coated with gold to provide electrical conductivity.

2.5.2. Determination of membrane water flux

Membrane testing equipment in the previous work was used. The membrane was pre-pressurized with water at 0.2 MPa for 0.5 h at room temperature. The pure water flux of the membrane was then determined at 0.1 MPa and calculated according to Eq. (4):

$$J = \frac{V}{At} \quad (4)$$

where *J* is the permeate flux, $L \cdot m^{-2} \cdot h^{-1}$; *V* is the volume of the permeate, L; *A* is the effective area of the membrane, m^2; *t* is the time required to pass through the filtrate volume *V*, h.

2.5.3. Determination of membrane retention

The retention rate of the membrane was characterized with 1 g/L BSA solution at a pressure of 0.1 MPa using membrane test device. The concentrations of BSA in permeate and feed solution were determined by UV visible spectrophotometer (Shanghai Jinghua Technology Instrument Co.,Ltd.,China; JH752) at 280 nm. Rejection could be expressed by Eq. (5)

$$R = \frac{\left(C_0 - C_1\right)}{C_0} \quad (5)$$

where *R* is the retention rate; C_0 and C_1 are the concentration of BSA in the original and permeate solution, g/L, respectively.

3. Results and discussion

3.1. Adsorption effect of modified activated carbon to methylene blue

As can be seen from Fig. 1, the regression equation of methylene blue absorbance curve is $y = 0.467x - 0.0195$, $r = 0.9929$, which showing a good linear relationship in the selected wavelength and concentration range and indicating that the measured value of absorbance can better reflect the concentration of methylene blue.

During the nitric acid modification of AC, nitric acid reacts with ash on the surface of activated carbon, and more developed microporous structures appear because of the influence of the gas generated by oxidative decomposition, and the specific surface area of activated carbon increases gradually with the increase of nitric acid concentration, so the adsorption effect of methylene blue is enhanced. As shown in Fig. 2, when the concentration is more than 20%, the specific surface area of the active carbon becomes smaller and the content of the oxygen-containing acid groups on the surface of activated carbon increases with the concentration continues to increase due to the strong oxidizing reaction make micropores change into mesopores and even large pores. Meanwhile, the surface polarity of activated carbon is changed and its hydrophilicity is enhanced. The adsorption amount of water increases and the adsorbed water forms cluster structure on the surface of activated carbon, which hinders the entry of methylene blue into the pore of activated carbon, thereby reducing the adsorption capacity of them.

From Fig. 2 it can be seen that during the process of ammonia reduction of activated carbon, the degree of reaction between ammonia and alkali-soluble impurity on the surface of AC gradually increased, and more basic groups appeared on AC surface. The effect of adsorbing methylene blue was better with the pore volume and specific surface area increased before the ammonia concentration reaches

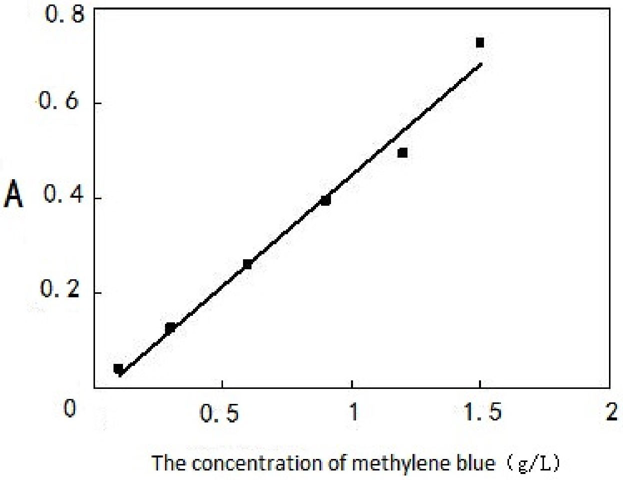

Fig. 1. The standard curve of methylene blue.

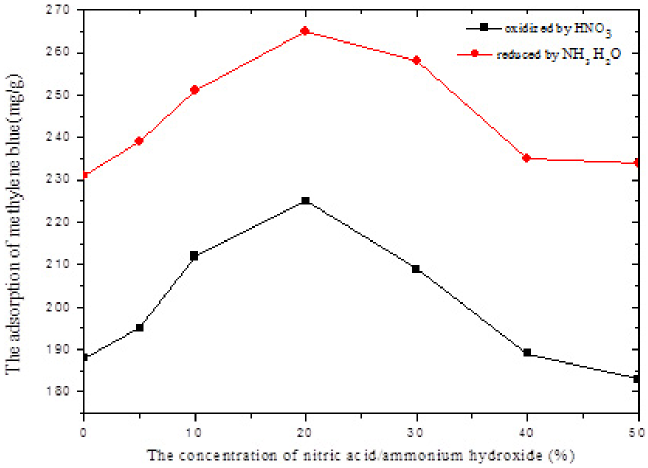

Fig. 2. Effect of modified activated carbon oxidized with HNO_3 and reduced with $NH_3 \cdot H_2O$ on adsorption of methylene blue

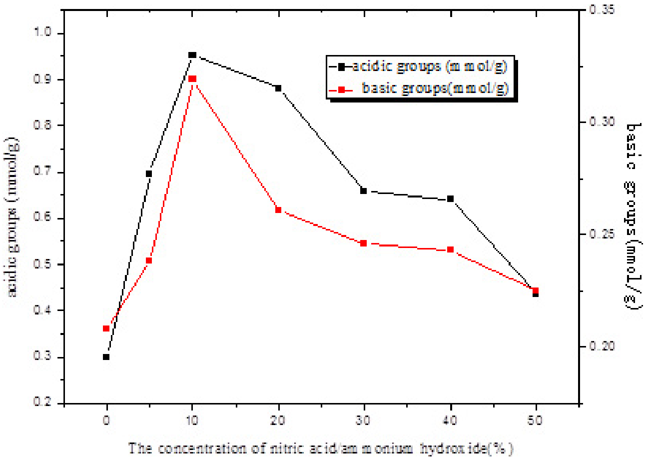

Fig. 3. Determination of the acidic/basic groups content of HAC and NAC

20%. Optimal adsorption value is obtained at 20%. As the ammonia concentration continues to increase, the newly generated alkaline groups are limited. Pore volume and specific surface area became smaller because AC was further alkaline washing. As a result, the adsorption capacity of methylene blue is reduced.

3.2. Effect of redox modification on surface groups of activated carbon

The results show that with the increase of the concentration of nitric acid, the acid groups formed on the surface of activated carbon increased, but then decreased, which may be due to the oxidation of nitric acid destroyed

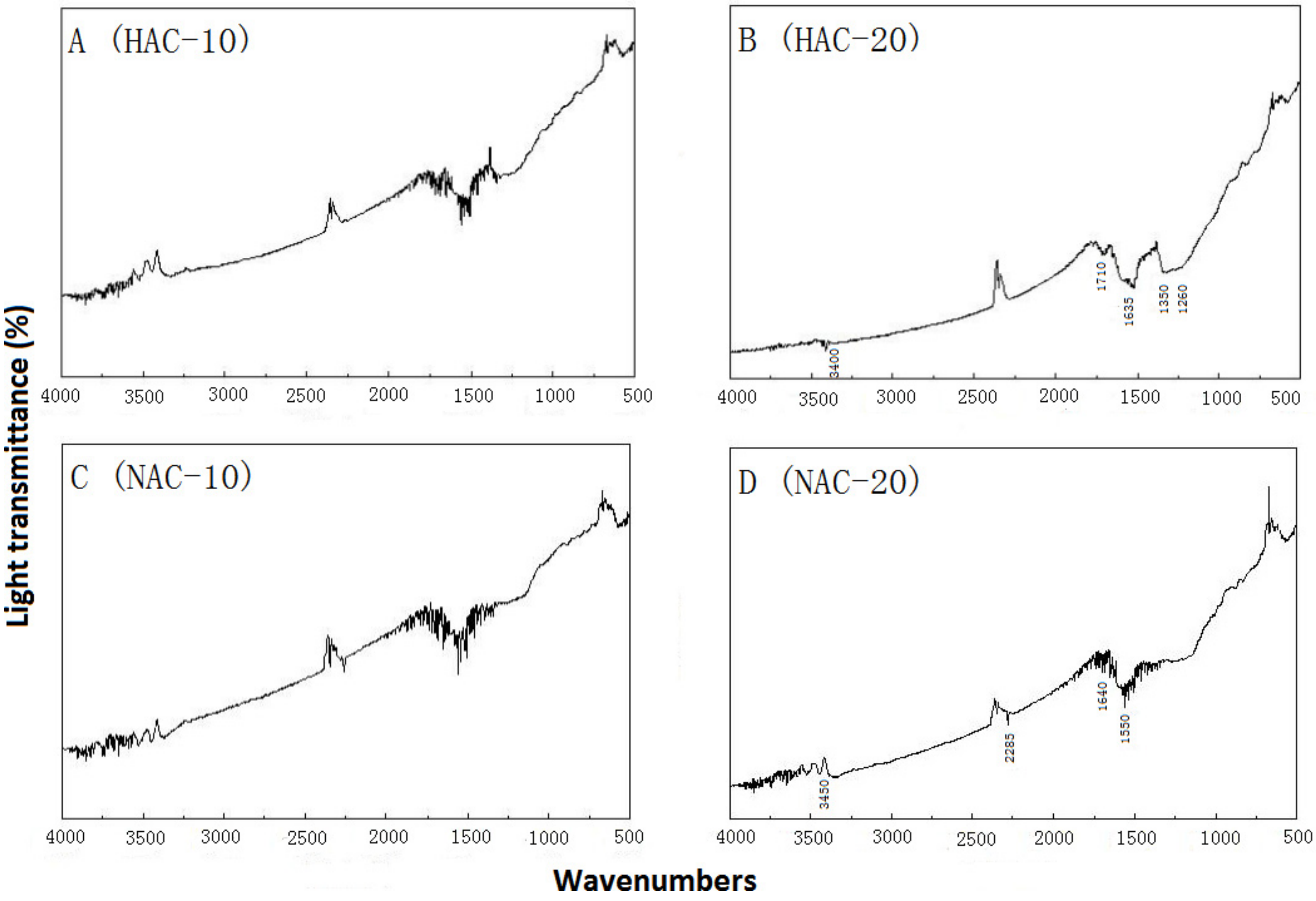

Fig. 4. The FT-IR spectra of redox modified activated carbon

the internal structure of activated carbon and the oxidation reaction of the contact surface becomes smaller, so that the production of the group is inhibited. The similar trend is obtained in the process of ammonia reduction, as shown in Fig. 3. Compared with the unmodified activated carbon, the corresponding acid-base groups produced by oxidation and reduction of activated carbon were increased.

3.3. The FT-IR spectra of redox active carbon

The FT-IR spectra of redox modified activated carbon is shown in Fig. 4. The major peak for oxidative modified activated carbon in Fig. 4 A and B can be assigned as follows: the peak located at 3400 cm^{-1} corresponds to the stretching vibration of –OH is the characteristic peak of carboxyl or lactone groups [21]. The peak at 1710 cm^{-1} belongs to the characteristic stretching vibration absorption peak of C=O group [22]. The peak at 1635 cm^{-1} because of the C=C group on surface of activated carbon. The vibration absorption peak of COO– group is associated with the peak at 1350 cm^{-1} [23]. The peak at 1260 cm^{-1} is the result of stretching vibration peak of CO group [24]. Compared with the unmodified AC, the intensities of absorption peak of HAC-10 and HAC-20 were obviously enhanced, which indicated that the oxidative modification of nitric acid promoted the increase of carboxyl groups and other oxygen-containing groups on the activated carbon surface. The FT-IR spectrum of reduced modified activated carbon by ammonia-water (Fig. 4C and D) shows the peak at 3450 cm^{-1} is due to the characteristic peak of –OH or –NH groups. A strong absorption peak at 2285 cm^{-1} is the attribution of C≡C bond. The peak at 1640 m^{-1} corresponds to the characteristic peak of C=C or C=N band. The intensity of the absorption peak near 1550 cm^{-1} is higher than that of unmodified activated carbon due to the more common results of the existence of more –NH, –CN and –NO$_2$ groups [25], indicating that the modification of ammonia to make the unsaturated functional groups and nitrogen-containing basic groups on the surface activated carbon increase.

3.4. Effect of redox-modified activated carbon on properties of composite membrane

3.4.1. Effect of redox-modified modified activated carbon on the morphology of the composite membranes

Fig. 5 shows the micro structure of the composite membranes, consisting of top surface and cross sections. It is observed from that in the present of activated carbon, the pores are very large with the cross section full of uniform finger-shaped hole due to the activated carbon is distributed in the membrane surface and pore walls, which are consistent with the separation performance of composite membranes.

3.4.2. Effect of redox-modified activated carbon on water flux and rejection of composite membrane

It can be seen from Fig. 6 that the optimal overall performance was obtained when the composite membrane filled with HAC-20 due to the large content of hydrophilic groups in the HAC-20. According to the principle of similar compatibility, the smaller of resistance of water through the membrane, the better the water permeability, so the water

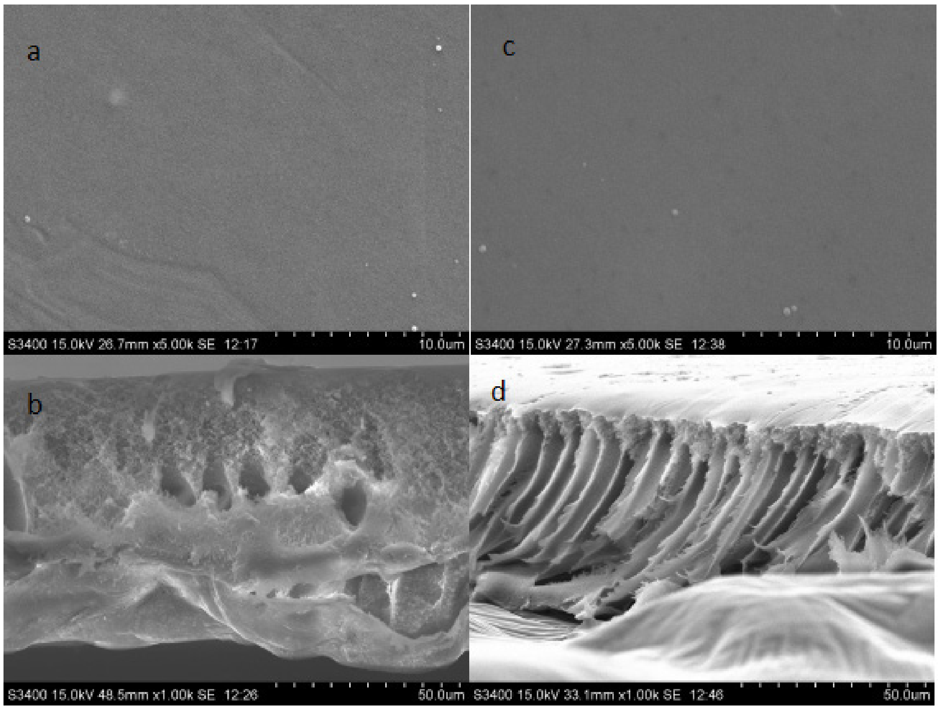

Fig. 5. SEM graphs of surface and cross-section of PSF and PSF/HAC membranes.(a) Surface of PSF membrane (b) Cross-section of PSF membrane (c) Surface of PSF/HAC membrane (d) Cross-section of PSF/HAC membrane.

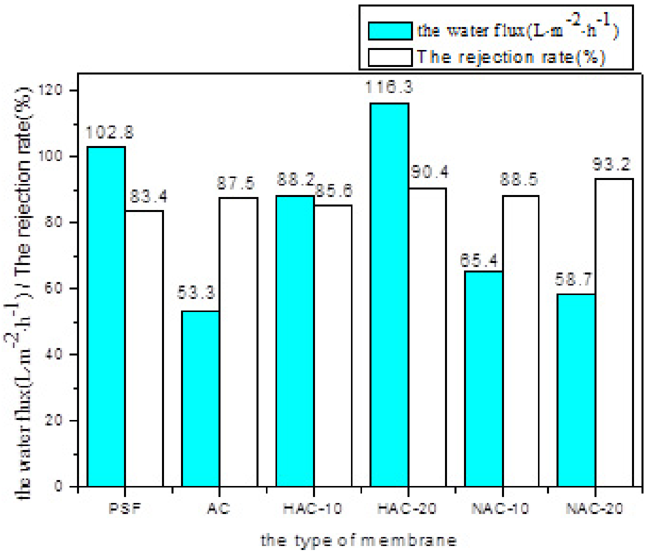

Fig. 6. The performance of composite membranes filled with modified activated carbon

flux is larger [26], while the activated carbon adsorption synergy to ensure a higher rejection rate of membrane.

The rejection rate of the composite membrane prepared with NAC-20 was 93.2%, but the water flux was low. It can be explained that although the modified activated carbon has higher adsorption capacity, which is favorable for the adsorption and retention of BSA, it is not conducive to the passage of water because of the strong hydrophobicity of the basic groups on the surface [27]. However, compared with the unmodified filled membrane, the performance of the modified activated carbon filled composite membrane has been improved.

3.4.3. Effect of redox-modified modified activated carbon on the stability of composite membrane

From Fig. 7 and Fig. 8, the water flux of PSF/HAC-20 composite membrane increases obviously with the increase of operating pressure, and decreases by only 12.5% with time in 1 h. It shows good anti-pollution performance. The increase of operating pressure facilitated the rapid permeation of water in the membrane pores, and the anti-fouling property of the membranes was mainly due to the increase of hydrophilicity and the decrease of membrane fouling after the membrane was filled with modified activated carbon. The porous structure and hydrophilic groups of the activated carbon facilitated the transfer of water in the membrane pores [28].

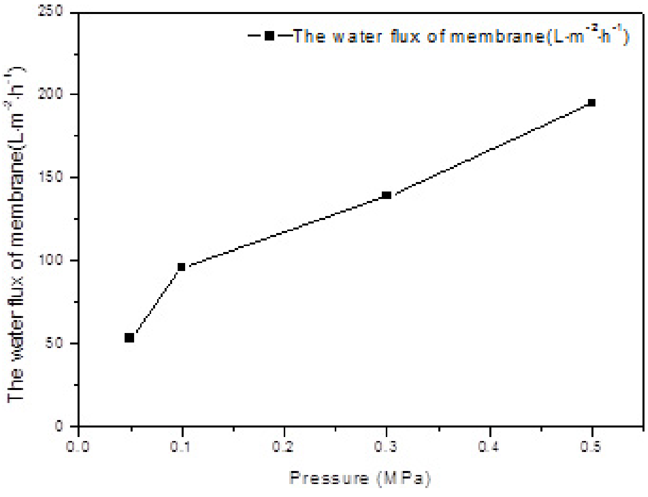

Fig. 7. Effect of pressure on water flux of composite membrane

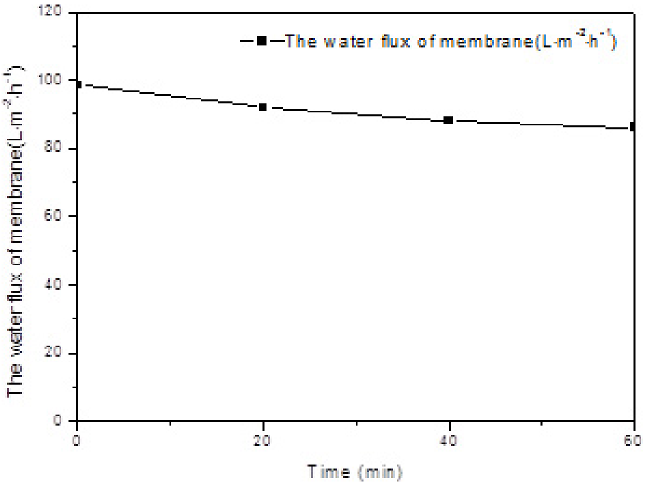

Fig. 8. Effect of time on water flux of composite membrane

4. Conclusion

The modified activated carbon with good adsorption performance and specific functional groups have been prepared by oxidation with nitric acid and reduction with ammonium hydroxide. When the concentration of nitric acid and ammonia hydroxide is 20%, the adsorption capacity of the modified activated carbon is 226 mg/g and 266 mg/g, respectively. At the concentration of 10%, the content of acidic group and basic group was the highest, the content of acid group and basic group of modified active carbon is 0.970 mmol /L, 0.315 mmol/L, respectively. Meanwhile, the composite membrane was prepared by filling the modified activated carbon into polysulfone. The results show that the water flux and retention rate of the composite membrane are changed. The concentration of 20% nitric acid modified activated carbon filled membrane can reach the highest water flux of 116.5 L·M^{-2}·h^{-1}, which was increased by 14 L·m^{-2}· h^{-1} compared to the pure polysulfone membrane at 102.5 L·m^{-2}·h^{-1}, and the rejection increased by 35%.

References

[1] P. Veerakumar, V. Veeramani, S.M. Chen, R. Madhu, S.B. Liu, Palladium nanoparticle incorporated porous activated carbon: electrochemical detection of toxic metal ions, ACS. Appl. Mater. Inter., 8 (2016) 1319–1326.
[2] Y. Abbas, W. Olthuis, A.V.D. Berg, Activated carbon as a pseudo-reference electrode for electrochemical measurement inside concrete, Conster. Build. Mater., 100 (2015) 194–200.

[3] X.F. Li, Q. Xu, Y. Fu, Q.X. Guo, Preparation and characterization of activated carbon from Kraft lignin via KOH activation, Environ. Prog. Sustain., 33 (2014) 519–526.

[4] M. Ahmaruzzaman, R.A. Reza, J.K. Ahmed, A.K. Sil, Scavenging behavior of schumannianthus dichotomus–derived activated carbon for the removal of methylene blue from aqueous phase, Environ. Prog. Sustain., 33 (2013) 1148–1157.

[5] M. Hefti, L. Joss, D. Marx, M. Mazzotti, An experimental and modeling study of the adsorption equilibrium and dynamics of water vapor on activated carbon, Ind. Eng. Chem. Res., 54 (2015) 12165–12176.

[6] M. Wang, H. Liu, Z.H. Huang, F. Kang, Activated carbon fibers loaded with MnO_2, for removing NO at room temperature, Chem. Eng. J., 256 (2014) 101–106.

[7] R. Wang, P. Wang, X. Yan, J. Lang, C. Peng, Q. Xue, Promising porous carbon derived from celtuce leaves with outstanding super capacitance and CO_2 capture performance, ACS Appl. Mater. Int., 4 (2012) 5800–5806.

[8] C. Peng, X.B. Yan, R.T. Wang, J.W. Lang, Y.J. Ou, Q.J. Xue, Promising activated carbons derived from waste tea-leaves and their application in high performance super capacitors electrodes, Electrochim. Acta, 87 (2013) 401–408.

[9] C.Y. Wang, J.L. Gray, Q. Gong, Y. Zhao, J. Li, E. Klontzas, G. Psofogiannakis, G. Froudakis, A.D. Lueking, Hydrogen storage with spectroscopic identification of chemisorption sites in Cu-TDPAT via spillover from a Pt/activated carbon catalyst, J. Phys. Chem. C., 118 (2014) 26750–26763.

[10] M.M.A. Daiem, J. Rivera-Utrilla, M. Sánchez-Polo, R. Ocampo-Pérez, Single, competitive, and dynamic adsorption on activated carbon of compounds used as plasticizers and herbicides, Sci. Total Environ., 537 (2015) 335–342.

[11] L. Wang, H. Zhang, G. Cao, W. Zhang, H. Zhao, Y. Yang, Effect of activated carbon surface functional groups on nano-lead electro deposition and hydrogen evolution and its applications in lead-carbon batteries, Electrochim. Acta, 186 (2015) 654–663.

[12] J.S. Kim, S.J. Lee, S.H. Yoon, C.H. Lee, Competitive adsorption of trace organics on membranes and powdered activated carbon in powdered activated carbon-ultrafiltration system, Water Sci. Technol., 34 (1996) 223–229.

[13] H. Oda, A. Yamashita, S. Minoura, M. Okamoto, T. Morimoto, Modification of the oxygen-containing functional group on activated carbon fiber in electrodes of an electric double-layer capacitor, J. Power Sources, 158 (2006) 1510–1516.

[14] Y. Liao, D.G. Yu, X. Wang, W. Chain, X.G. Li, E.M. Hoek, R.B. Kaner, Carbon nanotube-templated polyaniline nanofibers: synthesis, flash welding and ultrafiltration membranes, Nanoscale, 5 (2013) 3856–3862

[15] Y. Liao, X.G. Li, E.M.V. Hoek, R.B. Kaner, Carbon nanotube/polyaniline nanofiber ultrafiltration membranes, J. Mater. Chem. A., 1 (2013) 15390–15396.

[16] G.R. Guillen, T.P. Farrell, R.B. Kaner, E.M.V. Hoek, Pore-structure, hydrophilicity, and particle filtration characteristics of polyaniline-polysulfone ultrafiltration membranes, J. Mater. Chem., 20 (2010) 4621–4628.

[17] Y. Liao, T. Farrell, G. Guillen, M. Li, J.T. Temple, X.G. Li, E.M.V. Hoek, R.B. Kaner, Highly dispersible polypyrrole nanospheres for advanced nanocomposite ultrafiltration membranes, Mater. Horiz., 1 (2013) 58–64.

[18] Y. Liao, X. Wang, W. Qian, Y. Li, X. Li, D.G. Yu, Bulk synthesis, optimization, and characterization of highly dispersible polypyrrole nanoparticles toward protein separation using nanocomposite membranes, J. Colloid Interf. Sci., 386 (2012) 148–157.

[19] D.D. Hao, J.Q. Chen, X.Q. Liao, Y. Zheng, Y.B. Ji, Concentration of astragalus polysaccharide by polysulfone-activated carbon modified with nitric acid blend ultrafiltration membranes, J. Mem. Sep. Technol., 2 (2013) 27–35.

[20] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon, 32 (1994) 759–769.

[21] P.M. Alvarez, J.F. García-Araya, F.J. Beltrán, F.J. Masa, F. Medina, Ozonation of activated carbons: effect on the adsorption of selected phenolic compounds from aqueous solutions, J. Colloid. Interf. Sci., 283 (2005) 503–512.

[22] M.S. Shafeeyan, M.A.W.D. Wan, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, J. Anal. Appl. Pyrol., 89 (2010) 143–151.

[23] A. Zhou, X. Ma, C. Song, Effects of oxidative modification of carbon surface on the adsorption of sulfur compounds in diesel fuel, Appl. Catal. B-Environ., 87 (2009) 190–199.

[24] A. Macías-García, M.A. Díaz-Díez, E.M. Cuerda-Correa, M. Olivares-Marín, J. Gañan-Gómez, Study of the pore size distribution and fractal dimension of HNO_3-treated activated carbons, Appl. Surf. Sci., 252 (2006) 5972–5975.

[25] J. Przepiórski, Enhanced adsorption of phenol from water by ammonia-treated activated carbon, J. Hazard. Mater., 135 (2006) 453–456.

[26] J.W. Lim, J.M. Lee, S.M. Yun, B.J. Park, Y.S. Lee, Hydrophilic modification of polyacrylonitrile membranes by oxyfluorination, J. Ind. Eng. Chem., 15 (2009) 876–882.

[27] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of pvdf membranes, J. Membr. Sci., 375 (2011) 1–27.

[28] J. Przepiórski, Enhanced adsorption of phenol from water by ammonia-treated activated carbon, J. Hazard. Mater., 135 (2006) 453–456.