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The surface modification of coal-based carbon membranes by different acids

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ABSTRACT

Coal-based carbon membranes were modified with H_2O_2, HNO_3 and H_3PO_4 to improve hydrophilicity properties so as to enhance its permeability. XPS, TGA, TPD, and FT-IR analyses were employed to characterize the changes on their surface chemistry. Meanwhile, the performance of the membranes modified was investigated by the filtration of 200 mg/L oily wastewater. The results showed that there were no obvious changes on the pore structure, the oil and COD rejection after modification. However, the purewater fluxes of the membranes modified with H_2O_2 and HNO_3 increased to 299.7 and 224.8 L/(m^2 h bar) from the original purewater flux of 131.1 L/(m^2 h bar), whereas that modified with H_3PO_4 decreased to 60.6 L/(m^2 h bar). The changes of the flux were related to the changes on the chemistry properties of membrane surface. The hydrophilicity of the membranes modified by H_2O_2 and HNO_3 was improved as a result of the increase in the content of hydroxylic, carboxyl groups, etc., leading to an improved purewater flux. However, an increase in the content of esters and lactones on the membrane surface modified by H_3PO_4 leaded to the formation of hydrophobic surface on the membranes and the decline in the purewater flux of the membrane.

Keywords: Coal-based carbon membranes; Surface modification; Surface oxygen groups; Hydrophilicity; Oily water treatment

1. Introduction

Inorganic membranes have been a hot topic of new membrane technology development in the past two decades [1–3]. Among them, coal-based carbon membranes have attracted enormous research activities and commercial interests due to their superior chemical, mechanical and thermal stability, as well as a wide range of pore sizes for different applications. Especially, they are very cost-effective owing to their preparation materials coal precursors [4–7]. For example, Sachdeva et al. [8] reported that the rejection of carbon membrane on rhodamine B dye was in the range of 90–100%, which depended on the pressure and concentration of the dye. Song et al. [6] investigated the effects of pore size of coal-based carbon membranes, trans-membrane pressure and crossflow

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velocity on the filtration flux in the treatment of 120–400 mg/L oily wastewater. The results showed that the oil rejection coefficients of oily wastewater by the carbon membrane with pore size of 1.0 μm could be up to 97% at the operation conditions of 0.10 MPa trans-membrane pressure and 0.1 m/s crossflow velocity. Obviously, coal-based carbon membranes show a bright prospect of application in the difficult-to-handle organic wastewater treatment such as oily wastewater, dye wastewater, etc.

However, the hydrophobic properties of coal-based carbon membranes result in serious membrane fouling and low permeate flux which hinders their wide application in organic wastewater treatment and special separation. Therefore, it is crucial to improve their hydrophilicity. Yang et al. [4] reported that TiO_2 as hydrophilic agent was coated onto a tubular carbon membrane by a sol–gel approach to prepare a TiO_2/carbon membrane to improve the membrane permeability. The results showed that the permeability of TiO_2/carbon membrane enhanced 30% by comparison with the original carbon membrane for the treatment of 200 $mg\,L^{-1}$ oily water. At the same time, the removal rates of oil and chemical oxygen demand (COD) was 68.0 and 58.6% for the original carbon membrane and 78.6% and 83.7% for the TiO_2/carbon membrane, respectively. Although the permeability and rejection of the TiO_2/carbon membrane were higher than that of the original carbon membrane, it still suffered from serious membrane fouling.

It is well known that the surface oxygen groups have a great influence on chemistry properties of membrane materials [9,10]. Therefore, the permeabilities can also be enhanced by changing the chemistry properties of membrane surface through introducing hydrophilic surface oxygen groups [4,11]. The basic materials of coal-based carbon membrane are inert carbons. Different surface oxygen groups (e.g. carboxylic acids, hydroxyl groups, lactones and phenols) can be easily introduced onto the surface of carbon materials [12]. Generally, functionalization of inert carbons could be achieved by gas oxidation (e.g. oxygen, ozone, air, steam, carbon dioxides,and nitrogen oxides) and liquid oxidation (e.g. nitric acid, hydrogen peroxide, and ammonium persulfate) [13–15]. For instance, Zhou et al. [15] studied carbon nanofiber (CNF) functionalized by liquid and gas oxidation. The results showed that the CNF surfaces possessed more CO-producing oxygen complexes than CO_2-producing ones. The liquid oxidation increased those of both carboxyl and anhydride groups and the gas oxidation mainly increased the concentration of carbonyl groups. However, gas oxidation has a great impact on physical and mechanical properties of carbons [13–15]

The aim of this present study is to modify coal-based carbon membranes with different acids (nitric acid, hydrogen peroxide, and phosphoric acid) so as to improve their hydrophilicity and enhance their permeate fluxes in case of no damage to their pore structures. X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD), and Fourier transform infrared spectroscopy (FT-IR) analyses were used to analyze the changes on their surface chemistry of coal-based carbon membranes. The pore structure and performance of the membranes after modification were also examined.

2. Experimental

2.1. Materials

Coal-based carbon membranes were made by our laboratory. The synthesis process are as follows: The coal was ground into fine particles first with the average size of 4 μm, and then mixed with binder into a dough, which was extruded into a tube of 10 mm external diameter by a hydraulic extruder at 2.5–3.0 MPa. After drying at ambient atmosphere, the tubular membrane was carbonized up to 900˚C at the rate of 3˚C/min and held for 1 h under the protection of Ar. The final sample was cooled to room temperature naturally [6]. HNO_3 (14.4 mol/L), H_2O_2 (9.82 mol/L), H_3PO_4 (14.75 mol/L), HCl (9.45 mol/L) and Tween-80 were purchased from Tianjin Chemical Reagent Co. Ltd., China. All other chemicals were of analytic grade. $0^{\#}$ petrol was obtained from a local petrol station in Tianjin, China. All solutions were prepared with vdistilled water.

2.2. Modification processes

Coal-based carbon membranes were firstly pretreated with HCl solution (0.47 mol/L) for 24 h at 25˚C to remove the ash from the membranes and then dried in an oven at 120˚C for 12 h. The ash content of coal-based carbon membranes was measured according to China Standard GB/T 212-2001. Then, the pretreated coal-based carbon membranes were submerged into HNO_3 solution (7.22 mol/L), H_2O_2 (9.82 mol/L) and H_3PO_4 (14.75 mol/L) at 25˚C for 12 h, respectively. After that, they were washed with distilled water till pH kept neutral and dried at 120˚C in oven for 24 h. The coal-based carbon membranes with HCl pretreatment were referred as CM-0 in the text. Those modified by H_2O_2, HNO3 and H_3PO_4 were referred as CM-1, CM-2 and CM-3, respectively.

2.3. Surface chemistry characterization

XPS experiments were carried out on a K-alpha (ThermoFisher) spectrometer with Al–Ka radiation. The X-ray anode was run at 250 W and the high voltage was kept at 12.0 kV. The spectra of carbon with a very high resolution were recorded. The pressure of the analysis chamber was maintained below 10^{-9} Torr. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). Peak areas were estimated by calculating the integral of each peak after subtraction of the background and fitting the experimental peak. The thermogravimetric analysis (TGA) experiments were carried out on TGA/STA409PC (Germany) in the flowing nitrogen at a rate of 50 mL/min. The heating rate was 10℃/min and the heating temperature range was from 25 to 1000℃. The FT-IR spectra of the samples were recorded on a TENSOR37FT-IR spectrometer by the KBr pellet at a ratio of 1:500. Temperature-programmed desorption (TPD) spectra were obtained with a fully automated AutoChem II 2920 Catalyst Characterization Instrument, equipped with a quadrupole mass spectrometer. The sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated at 10℃/min from 25 to 1000℃ using a constant flow rate of helium equal to 30 cm^3/min.

2.4. Pore structure characterization

The pore structure characteristics of coal-based carbon membranes were measured on Pore Size Distribution Tester (Dalian University of Technology, China) by bubble-pressure method with wetting liquid of isopropanol and porometry gas of nitrogen at room temperature. The average pore size of coal-based carbon membrane was calculated with the recommended method in Ref. [16]. The porosity of coal-based carbon membrane was measured by the criterion method of China Standards [6].

2.5. Oily wastewater treatment experiments

Oily wastewater was obtained by mixing distilled water and $0^{\#}$ petrol with emulsifier Tween-80 (mass ratio:oil/Tween-80 = 10/1) through the ultrasonic emulsification into oil-in-water emulsion. After 0.5 h, the 200 mg/L oily wastewater became stable and uniform. Filtration experiments were conducted by coal-based carbon membranes with different wall thicknesses (1.5, 2.0 and 3.0 mm) under trans-membrane pressure (1.5 bar) for 3 h. After that, to recover membrane permeation, the fouled membrane was conducted by back flushing with distilled water under trans-membrane pressure (1.5 bar) for 0.5 h. The flux of permeation (J_p) was calculated as follows:

$$J_p = Q/(A \times \Delta P \times \Delta t) \tag{1}$$

where J_p is the permeation flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), Q is the permeated volume (L). A is the membrane area (m^2). ΔP is the pressure (bar) and Δt is the time (h).

The oil rejection ratio (R_{oil}) was calculated by the following equation:

$$R_{oil} = \left(1 - \frac{C_{oil}^{permeate}}{C_{oil}^{feed}}\right) \times 100\% \tag{2}$$

where $C_{oil}^{permeate}$ is the oil concentration in the permeate (mg/L); C_{oil}^{feed} is the oil concentration in the feed (mg/L).

UV–vis spectrometer (TO-1901) was used for measuring oil concentration. The COD values of feed and permeation were measured by HACH 2800.

3. Results and discussion

3.1. Surface chemistry analyses of the carbon membrane

3.1.1. XPS analysis

XPS was employed to characterize the surface oxygen groups of CM-0, CM-1, CM-2 and CM-3 so as to analyze the surface chemistry change. The distribution of different kinds of oxygen groups on membrane surface had been calculated by deconvolution of the XPS spectra, fixing the binding energy in the values. The fit lines of C1s of carbon membranes are shown in Fig. 1. The binding energy values calibrated were 284.6 eV for carbon–carbon monobond (C–C), 286.1 eV for C1s of C–O, 287.3 eV for C1s of C=O and 288.5 eV for C1s of O–C=O [14,18].

It can be seen from Fig. 1(a) that the C1s spectra exhibits a dominant peak at 284.6 eV generated from carbon atoms (C–C) of the graphite sheets. It indicates that there were few oxygen groups on the surface of unmodified coal-based carbon membrane. The C1s of C–O (Fig. 1(b)) was attributed to carbon atoms singly coordinated to an oxygen atom as in hydroxyl groups. It implies that lots of hydroxyl groups were generated on carbon membrane surface after modification with H_2O_2. The C1s spectra of carbon membrane modified with HNO_3 represent the peaks of C–O, C=O and COO as shown in Fig. 1(c). It suggests that different kinds of surface groups were introduced on the surface of carbon membrane. However, the Cls of C=O at 287.3 eV illustrates that abundant carbonyl groups or/and ketone groups were introduced on the membrane

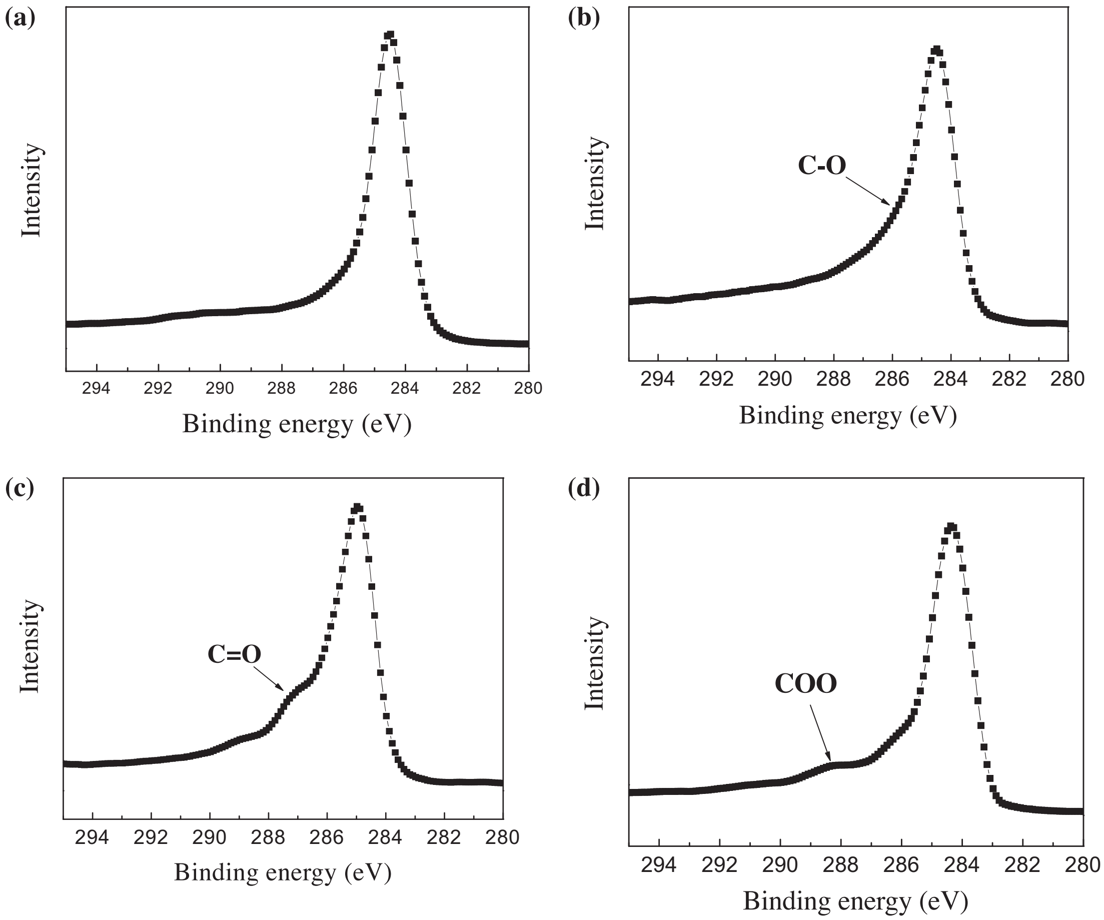

Fig. 1. XPS C1s core level spectra: (a) CM-0, (b) CM-1, (c) CM-2, and (d) CM-3.

surface (Fig. 1(c)). The C1s of COO at 288.5 eV may be generated from carboxylic groups, lactones or esters, which were produced on membrane surface after modification with H_3PO_4 (Fig. 1(d)), [14,17,18]. Actually, the content of each kind of groups could be obtained from the corresponding XPS peak areas as summarized in Table 1.

As can be seen in Table 1, the content of all surface oxygen groups on carbon membranes after modification with H_2O_2, HNO_3 and H_3PO_4 increased from 19.51% of the original carbon membrane (CM-0) to 24.08% of CM-1, 30.14% of CM-2 and 25.44% of CM-3, respectively. It also can be found from Table 1 that the C–O groups (such as hydroxyl groups), C=O groups (carbonyl or ketone groups) and COO groups (carboxylic, lactone and ester groups) were mainly generated on the surface of carbon membrane by H_2O_2, HNO_3 and H_3PO_4, respectively. The kind and content of surface oxygen groups on the membranes after modification were further investigated by TGA, TPD and FT-IR analyses.

Table 1
Comparison of C1s peak areas of carbon membrane samples in XPS spectra

	C (%)	C–O (%)	C=O (%)	COO (%)	Total number of surface oxygen groups (%)
CM-0	80.48	7.08	8.82	3.61	19.52
CM-1	75.92	10.81	8.91	4.36	24.08
CM-2	69.86	11.41	14.02	4.71	30.14
CM-3	74.56	7.22	9.71	8.51	25.44

3.1.2. TGA and TPD analyses

Different oxygen groups on carbon membrane surface could be decomposed at different temperatures released as CO, CO_2 and H_2O above 200℃ as shown in Table 2 [18,19]. Herein, derivative thermogravimetric analysis (DTG) curves of coal-based carbon membranes

Table 2
The decomposition temperatures of various materials and surface oxygen groups

Surface oxygen groups or materials on the surface of carbon	Desorption temperature (℃)
Absorb H_2O, CO, CO_2	<200
Carboxylic groups and their anhydrides	200–430
Hydroxyl groups, phenols, ketones	500–750
Lactones, esters	450–800
Carbonyl groups	600–900

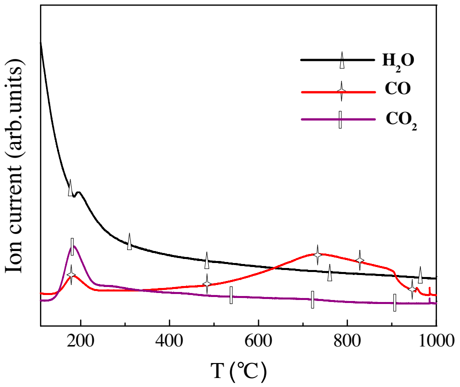

Fig. 3. TPD profiles for carbon membrane oxidated by HNO_3.

are shown in Fig. 2. The first peak around appeared around 95℃ on the DTG curves as a result of the desorption of the physically adsorbed water [19]. The sharp peak from CM-2 around 160℃ was generated from the adsorbed CO_2, CO and H_2O, which might be produced in the fierce oxidation process. This can be concluded from TPD profiles of coal-based carbon membrane modified with HNO_3 as shown in Fig. 3.

Generally, carboxylic groups are decomposed mainly to generate H_2O and CO_2 in the range of 200–430℃. Hydroxyl groups and carbonyl groups are decomposed mainly to generate H_2O and CO in the range of 450–900℃ [14,18]. It can be clearly found from Fig. 3 that the desorption gases around 160℃ were the adsorbed H_2O, CO and CO_2. And the desorption gases in the range of 500 to 900℃ were mainly composed of CO and H_2O, which were probably from the decomposition of hydroxyl groups, carbonyl groups, etc. [14,18]. Moreover, although the content of released gas CO_2 in the range of 200–430℃ were low (Fig. 3), it still indicates that some carboxyl groups had been generated on membrane surface after modification with HNO_3.

Further, it can be also seen from Fig. 2 that the mass lost rate of carbon membranes modified with different acids at the range of thermal decomposition from 600 to 900℃ was obviously more than that of the original carbon membrane. It implies that there were more oxygen groups generated on the carbon membrane surface. Actually, the mass lost rate of carbon membranes could be easily observed by TG analysis as shown in Fig. 4. It can be seen from Fig. 4 that the order of mass lost rate was CM-2 > CM-3 > CM-1 > CM-0. It is interesting to find that the content of total surface oxygen groups in Table 1 showed the same order as the mass lost rate.

Moreover, it can be concluded from the data in Table 3 that the main mass loss of carbon membrane modified with H_2O_2 took place in the range of 430–1000℃. Note: the data obtained in Table 3 were the average value of the results of three parallel experiments with below 5% of average error. It is attributed to the decomposition of hydroxyl groups (Table 2). The total mass lost rate of carbon membrane modified by HNO_3 was the highest rate with 13.0%. It is consistent with XPS results obtained in Section 3.1.1. It indicates that the most amount of oxygen groups were introduced on membrane surface after modification by HNO_3. The main mass loss of the membrane modified by H_3PO_4 took place in the range of 430–1000℃ rather than in the range of 200–430℃. It implies that the surface oxygen groups appeared on the carbon

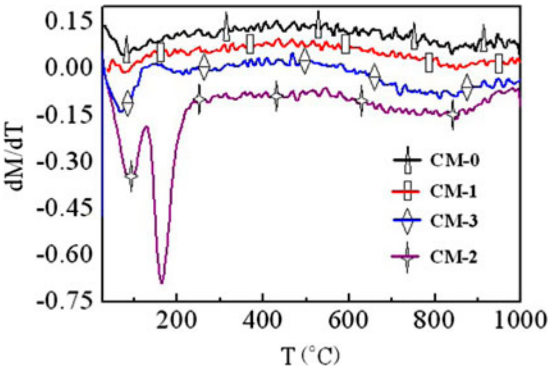

Fig. 2. DTG curves of coal-based carbon membranes.

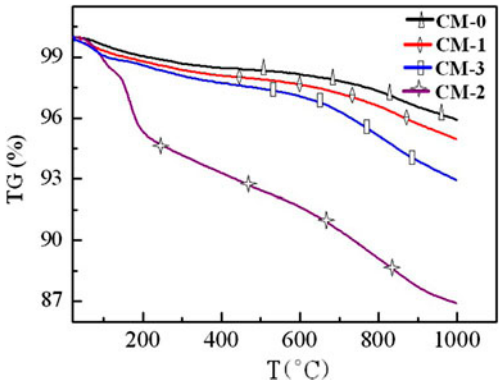

Fig. 4. TG curves of coal-based carbon membranes.

Table 3
Mass lost rate of coal-based carbon membrane samples during thermal decomposition

	25–200℃ (wt.%)	200–430℃ (wt.%)	430–1000℃ (wt.%)	Total (wt.%)
CM-0	0.95	0.61	2.53	4.09
CM-1	1.20	0.76	3.06	5.02
CM-2	4.67	2.28	6.12	13.07
CM-3	1.39	0.96	4.70	7.05

membrane modified with H_3PO_4 were mainly lactones and esters rather than carboxylic groups.

3.1.3. FT-IR analysis

The surface chemical characterization of original and modified coal-based carbon membranes were further investigated by FT-IR spectra as shown in Fig. 5. In general, the bands at peaks 1750 and 1465 cm^{-1} were attribute to C=O bands [18]. The bands at the peaks 3431, 1630 and 1100 cm^{-1} were properly generated from H_2O adsorbed in membrane itself, which made it difficult to discriminate the absorption bands of hydroxyl and other groups that contained C–O bands (usually at the range of 1000–1300 cm^{-1}) [20]. Therefore, it could clarify the changes on surface chemistry properties of coal-based carbon membranes after modification with H_2O_2, HNO_3 and H_3PO_4 from the peaks at 1710–1750 cm^{-1}

It can be found from Fig. 6 that the presence of a small band at 1710–1750 cm^{-1} from CM-2 and CM-3 could be assigned to C=O bands. It indicates that the surface oxygen groups (containing C=O bands) such as ketones, carbonyl, lactones, etc. were introduced on membrane surface after modification with HNO_3 and H_3PO_4, whereas no peaks at 1710–1750 cm^{-1} was observed from CM-1. That is to say, few groups of ketones, carbonyl, lactones, etc. appeared on the surface of membrane modified with H_2O_2. These are consistent with XPS results (Fig. 1).

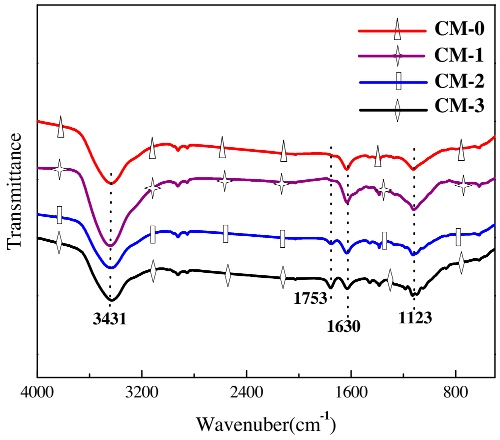

Fig. 5. The FT-IR spectra of carbon membrane samples.

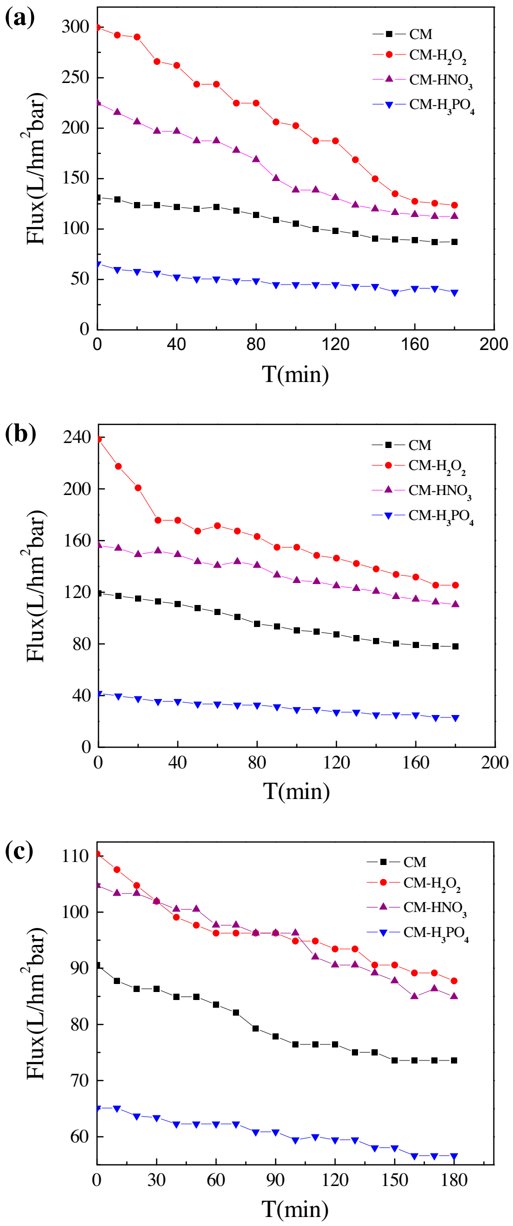

Fig. 6. The permeate flux decline of coal-based carbon membranes with different wall thicknesses: (a) 1.5 mm, (b) 2.0 mm, and (c) 3.0 mm.

3.2. Pore structure and ash content characterization of coal-based carbon membranes

Pore structure changes of coal-based carbon membranes with different wall thicknesses after modification with different acids were summarized in

Table 4. Note: The data in Table 4 were the average value of the results of three parallel experiments and the fluctuation range is within 5%. It is found from Table 4 that there are no obvious changes both in the average pore size and porosity of carbon membranes modified by different acids. Further, the ash content of original carbon membrane obtained was 10.6 wt.% and decreased to 4.2 wt.% after pretreatment by HCl (CM-0). The ash content reduced to 3.9, 3.6 and 3.7 wt.% after modification with H_2O_2, HNO_3 and H_3PO_4, respectively. It implies that there was little change on the ash content of the carbon membranes after modification with different acids.

3.3. Performance characterization of coal-based carbon membranes

The permeate flux of coal-based carbon membranes with different wall thicknesses during the treatment of 200 mg/L oily wastewater are illustrated in Fig. 6. It can be seen from Fig. 6(a) that the purewater flux of carbon membrane with 1.5 mm of wall thickness increased from 131.1 to 299.7 L/(m^2 h bar) and 224.8 L/(m^2 h bar) after the modification by H_2O_2 and HNO_3, whereas that of the membrane modified with H_3PO_4 decreases to 65.6 L/(m^2 h bar).

It also can be found from Fig. 6(a) that the permeate flux for the membranes declined with the operation time. The permeate flux of the original carbon membrane obtained after 180 min of fouling operation was lower than that of the membrane modified by H_2O_2 and HNO_3, and higher than that of the membrane modified by H_3PO_4. The changes on the purewater flux of the membranes were related to the changes on the surface chemistry properties of the carbon membranes after modification by different acids. The increase in permeate fluxes of coal-based carbon membranes modified with H_2O_2 and HNO_3 results from the improvement of the membrane hydrophility due to the introduction of hydroxyl groups or/and carboxylic groups on the surface of membranes. However, the hydrophobicity of coal-based carbon membranes modified with H_3PO_4 was improved because of the introduction of lactones and esters on membrane surface, leading to the decrease in the permeate fluxes.

Table 4
Pore structure and separation characteristics of coal-based carbon membranes

	Wall thickness (mm)	Average pore size (μm)	Porosity (%)	Oil rejection (%)	COD rejection (%)
CM-0	1.5	0.450	40.2	93.0	79.2
CM-1		0.433	41.1	90.8	79.4
CM-2		0.386	38.2	89.1	75.4
CM-3		0.406	42.5	94.9	81.5
CM-0	2.0	0.465	41.6	97.0	88.3
CM-1		0.417	41.9	96.2	87.4
CM-2		0.390	40.0	95.9	82.3
CM-3		0.462	42.3	96.6	88.0
CM-0	3.0	0.434	41.2	97.0	89.0
CM-1		0.426	43.5	96.2	88.5
CM-2		0.366	39.3	95.9	90.3
CM-3		0.398	42.5	96.8	88.9

Similar phenomena for the membranes with the wall thickness of 2 mm and 3 mm could be observed in Fig. 6(b) and (c). An interesting phenomenon is that the purewater flux of the membrane with 1.5 mm, 2.0 mm, and 3.0 mm of wall thickness after H_2O_2 modification was 299.7, 238.5 and 110.4 L/(m^2 h bar). This is because the permeate resistance of the membrane increased with an increase in the thickness of membrane wall.

The oil rejection and COD remove rate (Table 4) increased with an increase in the wall thickness. The oil rejection and COD remove of carbon membranes with wall thickness 2.0 and 3.0 mm were higher than that with 1.0 mm wall thickness. However, the rejection of carbon membranes after modification with different acids showed little difference. It also suggests that the pore structure of carbon membrane would not be damaged by the acid modification.

After two cycles of back flashing with distill water, the purewater fluxes of membranes with 2.0 mm of the wall thickness modified with H_2O_2 and HNO_3 were restored to 96.8% and 94.1% of the initial value. However, the purewater fluxes of original membrane and the one modified with H_3PO_4 were only restored to 80.5% and 71.8%, respectively. This phenomenon is related to the changes on the chemical properties of membrane surface and antifouling performance.

4. Conclusions

Coal-based carbon membranes have been successfully modified by H_2O_2, HNO_3 and H_3PO_4. The purewater fluxes of coal-based carbon membranes modified with H_2O_2 and HNO_3 increased by 128.6% and 71.5% by comparison with the original carbon membrane, whereas that modified with H_3PO_4 decreased approximately by half of the original purewater flux. There is little influence on the pore structure of coal-based carbon membranes after modification with the acids. Meanwhile, there were little changes on the oil and COD rejection of the carbon membrane modified with different acids during 200 mg/L oily wastewater treatment. The changes on the permeate fluxes are related to the changes on the surface chemistry of the carbon membranes. The hydrophilicity of coal-based carbon membranes modified with H_2O_2 and HNO_3 have been improved by increasing the content of surface oxygen groups such as hydroxyl groups and carboxylic groups, etc., leading to an increase on the permeate fluxes of membranes. However, the hydrophobicity of coal-based carbon membranes modified with H_3PO_4 has been improved by increasing the number of surface oxygen groups such as lactones and esters, leading to a decline on the permeate flux of the membrane.

Acknowledgments

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