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RESEARCH ARTICLE

On the fouling mechanism of polysulfone ultrafiltration membrane in the treatment of coal gasification wastewater

Xue Zou[1,2], **Jin Li** (✉)[1]

1 School of Civil Engineering, Beijing Jiaotong University, Beijing 100044, China
2 College of Architectural Engineering, North China University of Technology, Beijing 100144, China

Abstract Membrane fouling has been investigated by using a polysulfone ultrafiltration membrane with the molecular weight cutoff of 20 kDa to treat crushed coal pressurized gasification wastewater. Under the conditions of different feed pressures, the permeate flux declines and rejection coefficients of pollutants referring to three parameters (total organic carbon (TOC), chroma and turbidity) were studied. The membrane fouling mechanism was simulated with three classical membrane fouling models. The membrane image and pollutants were analyzed by scanning electron microscopy and gas chromatography-mass spectrography (GC-MS). The results indicate that the permeate flux decreases with volume reduction factor before reaching a constant value. The rejection coefficients were also measured: f_{TOC} = 70.5%, f_C = 84.9% and f_T = 91%. Further analysis shows that the higher the feed pressure is, the sooner the permeate flux reaches constant value and the more sharply the permeate flux declines. Constant flux indicates a nonlinear growth with feed pressure (P_F): when P_F equals 1.2 bar, the mark for the critical flux, slight membrane fouling occurs; when P_F exceeds 1.2 bar, cake layer pollution aggravates. Also the rejection coefficients of global pollutant increases slightly with P_F, suggesting the possibility of cake compression when P_F exceeds 1.2 bar. Through regression analysis, the fouling of polysulfone ultrafiltration membrane could be fitted very well by cake filtration model. The membrane pollutants were identified as phthalate esters and long-chain alkenes by GC-MS, and a certain amount of inorganic pollutants by X-ray photoelectron spectroscopy.

Keywords membrane fouling, ultrafiltration membrane, coal gasification wastewater, rejection coefficient

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E-mail: jinli@bjtu.edu.cn

1 Introduction

With the development of coal chemical industry in China, pollution caused by coke wastewater from coal coking, coal gasification and by-product of recovery coking processes becomes a serious environmental problem [1,2]. The wastewater contains complex inorganic and organic pollutants, such as ammonium, sulfate, cyanide, thiocyanate, phenolic compounds, polynuclear aromatic hydrocarbons and polycyclic nitrogen-containing acyclic compounds [3–8]. Focusing on these pollutants, scientists often use biological treatment such as anoxic-oxic (A-O), anaerobic-anoxic-oxic (A1-A2-O), sequencing batch reactor (SBR) and biofilm system (BF) in secondary treatment processes [9–11]. Li et al. studied a BF system for the treatment of coke wastewater, and revealed that an acidogenic stage beneficial to the removal of organic-N and the A1-A2-O system was more useful for total nitrogen removal than the A-O system (the chemical oxygen demand (COD) in the effluent was 131 mg/L) [12]. Maranon et al. studied the treatment of coke wastewater in a pilot plant equipped with a 400 L stripping tank, a 350 L neutralization/homogenization tank and a 6 m high, 1500 L SBR and final effluent concentrations of 1.8 mg phenols/L, 5.4 mg SCN^-/L, 206 mg COD/L and 78 mg $N\text{-}NH_4^+$/L were obtained [13]. In these cases, COD in secondary effluent varies from 100 to 500 mg/L. Thus, more and more advanced treatments must be used to realize "zero emissions" and meet the requirements of the National Discharge Standard in China and to further realize the healthy development of coal chemistry.

Among the advanced treatments, membrane technology has been used in the recycling of both municipal and industrial wastewater [14–16]. Particularly pressure-driven membrane separation processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) play an important role in the purification of wastewater because of low cost and small environmental impact [17,18]. MF membranes with pores ranging from 0.1 to 2 μm at pressure below 5 bar, are useful for the removal of suspended matter [19,20], whereas UF membranes remove macromolecules with molecular weight between 1000 and 100 KDa at pressure ranging from 2 to 8 bars. However, UF membranes does not remove those compounds that have low molecular weight or are soluble. Therefore, NF membranes and RO membranes operated at pressure between 10 and 100 bar have been studied to remove small organic compounds as well as ions [21]. Moreover, some membrane technologies have been employed to recycle coke wastewater. Wen et al. have demonstrated a combination of UF and NF membranes could finally afford an effluent with 60 mg COD/L, 10 mg N-NH_4^+/L, 1 NTU hardness, and 20 mg total hardness/L [22]. Ma et al. found that a combined immerse UF and RO membranes with the optimized operative flux worked well based on data gained over long-term study [23].

Despite the strong potential in water recycling, membrane filtration processes are mainly limited by membrane fouling, which causes flux decline and can be externally reversible and internally irreversible. Specifically, externally reversible fouling is determined by both concentration polarization and deposition of solids (cake layer formation). The concentration polarization is due to the accumulation of solutes onto the membrane surface and the formation of a layer with relatively high concentration. On the contrary, internally irreversible fouling is caused by the deposition of macromolecules within membrane pores and the adsorption of solutes on membrane walls [24].

To ensure a sound water production, it is necessary to investigate membrane fouling by analyzing the water quality to evaluate possible fouling substance, identifying the pollutants in membrane dissection test, and analyzing the running state in filtering procedure [25]. But till now there has been few research on the membrane fouling of coke wastewater. In this paper, the UF membrane was selected to treat real coal gasification wastewater [26,27]. The operating condition of batch concentration with partial recycling of retentate stream was used, and the effect of the main operating parameters (feed pressure, feed flow rate) on the permeate flux was established. Besides, because of the existence of refractory organics in coal gasification wastewater, the rejection coefficients of total organic compound (TOC), chroma and turbidity were used as the pollution indices to evaluate the effect of UF membrane. The membrane fouling mechanism which predominates the filtration process was also established by fitting three membrane fouling models with the experimental data. Finally, membrane pollutants were analyzed by gas chromatography-mass spectrography (GC-MS) and X-ray photoelectron spectroscopy (XPS).

2 Materials

2.1 Feed quality

The raw wastewater in this experiment came from a coal gasification plant, and SBR was used as the secondary process. The effluent from SBR was pretreated by activated coke adsorption and sand filtration, and then used as the feed of UF membrane device. The water quality parameters of the effluent from SBR and the feed into UF are shown in Table 1.

2.2 UF device and membrane module

The UF device consists of feed tank, diversion system, water pump, backwashing pump, membrane modules, valves, and meters, as shown in Fig. 1. When operation is running, valves V-1, V-2 and V-3 are turned on.

The UF membrane module is made of polysulfone (PS) with the molecular weight cut-off of 20 kDa, hollow fiber type, provided by Beijing Tsing Mem Higher Technology Co., Ltd. The membrane module parameters are: length L = 215 mm, diameter D = 35 mm, wire number = 20, and nominal effective membrane area = 0.01 m^2. The UF device was operated on internal pressure filtration mode. And the operating parameters are shown in Table 2.

3 Methods

3.1 Experiment of permeate flux

While the feed flow rate (Q_F) was constant, the feed pressure (P_F) was varied in five operating conditions as shown in Table 3. For cross flow filtration, retentate returned to the feed tank and permeate was collected separately. In this operating mode, the volume reduction factor (VRF = V_0/V_R, where V_0 is the initial feed volume, and V_R is the retention volume) of the feed tank was used to evaluate the change of permeate flux and pollution indices such as TOC, chroma, and turbidity under each of five operating conditions. To guarantee the same initial condition, a new membrane module would replace the old one when the operating condition is changed. In the membrane filtration process, the separate system was taken

Table 1 Water quality of the effluent from SBR and the feed into UF membrane

Index	COD /($mg \cdot L^{-1}$)	Turbidity /NTU	Conductivity /($\mu s \cdot cm^{-1}$)	pH	NH_3-N /($mg \cdot L^{-1}$)	Chroma
SBR effluent	717.37	110	1560	8.04	12.38	80
UF feed	94	15	1628	8.47	11.38	35

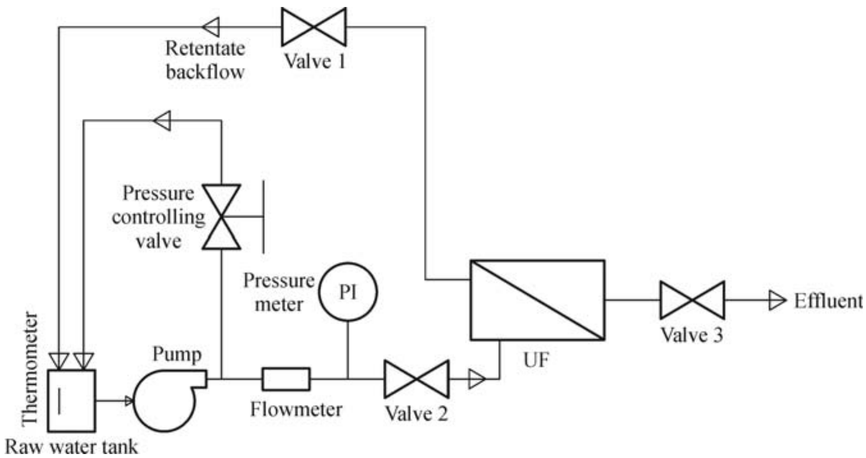


Fig. 1 Schematic diagram of UF system

to ensure that Q_F and P_F remained constant in each operating condition. Pure water was filtered before wastewater was filtered.

Table 2 Parameters of UF device operating

Index	Value
Pure water permeate flux /($L \cdot m^{-2} \cdot h^{-1}$)	400–600
Temperature of feed /°C	5–50
pH	1–13
Maximum feed turbidity /NTU	200
Maximum pressure /bar	2.0
Maximum trans-membrane pressure /bar	1.0
Backwashing pressure /bar	1–1.5

Table 3 The operating conditions of UF process

No.	Q_F /($L \cdot h^{-1}$)	P_F /bar
1	2	0.6
2	2	0.8
3	2	1.0
4	2	1.2
5	2	1.4

3.2 Analysis of membrane pollutants

The polluted membrane wires were dissected and soaked in hexane for 24 h, and the chemical composition of pollutants were analyzed using GC-MS and XPS.

3.3 Testing methods

COD, turbidity, pH, conductivity, NH_3-N and chroma were measured according to the literature method [28]. TOC was determined by using a total nitrogen and total organic carbon analyzer from Elementar Company of Germany (the detection limit is 10 mg/L). Pure water flux and permeate flux were measured using measuring cylinder as the time interval, and the temperature correction formula was used to converse the test flux into standard flux.

$$J_v = J_T \times K, \tag{1}$$

where J_v is the permeate flux after temperature correction, $L/(m^2 \cdot h)$, $K = e^{0.019(T-20)}$ (provided by Beijing Tsing Memhigher Technology Co., Ltd) is the temperature correction factor, T is the feed temperature (°C), and J_T is the permeate flux when feed temperature is at T, $L/(m^2 \cdot h)$.

The pollutant rejection coefficient can be defined as:

$$f = (f_{\text{feed}} - f_{\text{permeate}})/f_{\text{feed}}, \tag{2}$$

where f_{feed} is the pollutant concentration of feed stream, and f_{permeate} is the pollutant concentration of permeate stream.

Chemical composition of pollutants were measured using a GC-MS analyzer (Agilent 6890N GC-5975C MSD) and XPS (Thermo Fisher Scientific ESCALAB 250). The ultrapure water was from Beijing Jiaotong University Environmental Engineering Lab and the conductivity was 0.055 µS/cm (25 °C).

3.4 Fitting of membrane fouling models

Three membrane fouling models, which relate permeate fluxes with filtration time as shown in Table 4 [29,30], were used to assess the membrane fouling mechanism of the present work: J_0 is the initial permeate flux (at the beginning of the filtration experiment), J_v is the permeate flux at any time t, and k is the fouling coefficient which describes the rate at which the permeate flux declines and is proportional to deposition or cake formation rate. The k coefficients of the three models could be obtained by calculating the slopes of curves $1/J_v$, $1/J_v^2$ and ln J_v *vs.* t, respectively.

Table 4 Fouling models reported in the literature

Membrane fouling model	Formula	Control factors
Transient blocking model	$J_v = \frac{J_0}{1 + J_0 kt}$ or $\frac{1}{J_v} = \frac{1}{J_0} + kt$	Membrane
Cake filtration model	$J_v^2 = \frac{J_0^2}{1 + J_0^2 kt}$ or $\frac{1}{J_v^2} = \frac{1}{J_0^2} + kt$	Pollution layer
Complete pore blocking model	$J_v = J_0 \exp(-kt)$ or $\ln J_v = \ln J_0 - kt$	Membrane pore

4 Results and discussion

4.1 The variation of permeate flux and the removal of pollutants

Membrane fouling is usually presented by the decrease of permeate flux. Figure 2 shows the variation of J_v with VRF under each of five operating conditions. As can be seen, J_v rapidly decreases with VRF and then slowly reaches constant values under each operating condition. Furthermore, the higher P_F is, the sooner J_v reaches a stable value, and the more sharply the flux declines. Finally, the flux decreases as much as 35.7%.

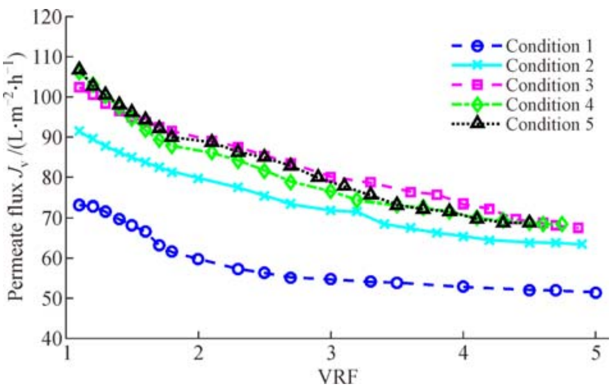


Fig. 2 Variation of permeate flux with VRF

To investigate the efficiency of UF membrane, the pollutant removal was measured as rejection coefficients in several pollution indices including TOC, chroma and turbidity. Figure 3 shows the values of f_{TOC}, f_C and f_T when VRF is 1.5, 2.5, 3.5, 4.5, respectively, at $T = 20$ °C, $Q_F = 2$ L/h, and P_F = 0.6 bar. As can be seen, f_{TOC}, f_C and f_T slightly wave with increasing VRF, and their average values are 70.5%, 84.9%, 91%, respectively. Hence, UF membrane has a positive effect on treating coal gasification wastewater, and the quality of permeate has reached the integrated wastewater discharge standard: Grade 1.

4.2 Analysis of the membrane fouling mechanism

4.2.1 Critical flux test

In this study, to decrease membrane fouling, an adsorption process was used to pretreat coal gasification wastewater. If the membrane could filter the wastewater below the critical flux, irreversible membrane fouling would be reduced as much as possible [31]. Therefore, UF membrane filtration process was carried out under the condition of constant P_F [32], by which critical flux was tested.

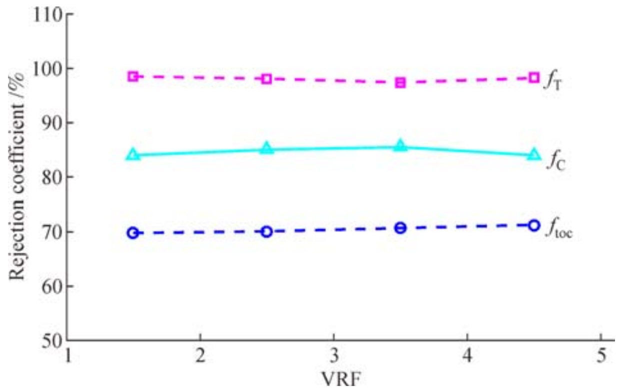


Fig. 3 Effect of VRF on rejection coefficient f

Darcy equation is usually used to evaluate the relationship between transmembrane pressure and membrane flux [31,33]:

$$J_v = \frac{P}{\eta \cdot (R_m + R_{fo} + R_{fn})}, \tag{3}$$

where R_m is membrane resistance, R_{fo} is the resistance connected with reversible fouling, R_{fn} is the resistance connected with irreversible fouling, ΔP is transmembrane pressure, η is viscosity of the liquid, and J_v is the permeate flux after temperature correction. The total resistance (R_t) is calculated by:

$$R_t = R_t + R_{fo} + R_{fn}. \tag{4}$$

Some research have attested that when J_v exhibits a linear growth with the increase of ΔP, membrane fouling is slight, whereas when J_v exhibits a non-linear growth with ΔP, membrane fouling is serious [34,35]. In our experiments, when J_v reached constant values (Table 5), the relation between J_v and ΔP was compared with that between pure water flux and ΔP (in an open circuit system, ΔP is equal to P_F supplied by feed pump), and the results are shown in Fig. 4. Also as shown in this figure, when pure water is filtrated, the pure water flux increases linearly

Table 5 UF membrane filtration experiments by pure water and coal gasification wastewater under five operating conditions[a)]

Water	Operating conditions	Q_F /(L·h^{-1})	P_F /bar	$J_v^{(note)}$ /(L·m^{-2}·h^{-1})	f_{TOC} /%	f_C /%	f_T /%
Coal gasification wastewater	1	2	0.6	51.5	70.1	85.1	91.3
	2	2	0.8	64.4	73.5	86.4	91.9
	3	2	1.0	67.5	74.4	88	92.4
	4	2	1.2	68.4	75.1	90	93.5
	5	2	1.4	68.7	75.5	91.3	93.5
Pure water	1	2	0.6	69.3	–	–	–
	2	2	0.8	92.6	–	–	–
	3	2	1.0	114.6	–	–	–
	4	2	1.2	137.8	–	–	–
	5	2	1.4	162.1	–	–	–

a) J_v has reached a constant value in each operating condition

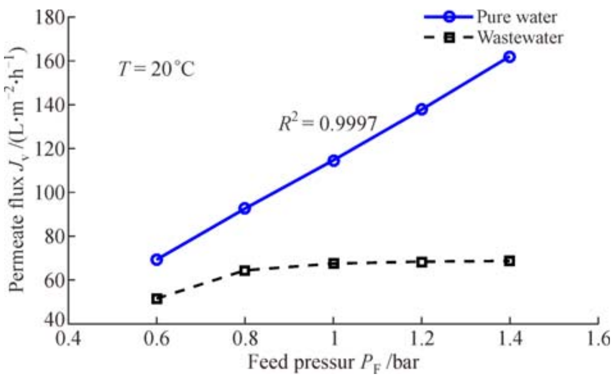


Fig. 4 Effect of P_F on J_v for UF membrane filtration

with the increase of P_F, and the slope of the regression line L_p is known as the pure water permeability, which is related to the composition, morphology, hydrophilicity of membrane. L_p of polysulfone membrane module used in this experiment is 115.4 L/(m^2·h·bar). In filtrating coal gasification wastewater, J_v initially increases with the increase of P_F, but when P_F approaches 1.2 bar, J_v almost reaches a constant. According to some research, cake layer is formed and compacted gradually with the variation of P_F. P_F can be considered the optimum when J_v reaches a constant value (critical flux). In this experiment, the optimum P_F is 1.2 bar, because at this point the cake layer is formed, and the membrane is still reversible, making the subsequent fouling effect low [36,37]. However, when P_F exceeds 1.2 bars, J_v stops increasing further and cake layer pollution aggravates.

Table 5 shows the values of pollutant rejection coefficients, f_{TOC}, f_C, and f_T, when J_v reaches constant values in each operating condition. As can be seen, f_{TOC}, f_C, f_T increase with increasing P_F, indicating that cake layer compaction leads to more pollutants intercepted.

4.2.2 Model fitting of J_v *vs.* t

To determine the mechanism of fouling in MF/UF, Hermii's model is applied [29]. It is based on the change in the efficiency of the process by the equation:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n, \tag{5}$$

$$or\ \frac{dJ}{dt} = -kJ(JA_0)^{2-n} \quad J = \frac{1\cdot dV}{A_0\ dt}, \tag{6}$$

where V is volume of permeate, t is time of the filtration process, A_0 is filtration area, n, k are constants describing various mechanisms for flux decreasing during filtration process at constant pressure, and J is permeate flux (in this paper, J has been replaced by J_v, which is corrected by temperature). They can be used as criterion for the identification of different blocking mechanisms of pores in the membrane at constant pressure. Assuming that the parameter n can take on four discrete values: n = 2 (complete blocking of pores), n = 3/2 (standard blocking in the inside of the pores), n = 1 (transient blocking pores), n = 0 ("cake" mechanism of pore blocking), so the physical interpretation of the phenomena presented in the model has been preserved. In this experiment, we used the integral form of equation 6 as the three frequent fouling models to evaluate the UF membrane fouling mechanism, and they are listed in Table 4 at n = 1, 0, 2. From the models we can see that a plot of $1/J_v$, $1/J_v^2$ or ln J_v *vs.* t should be linear and the slopes obtained would provide the k constants. The experiment data of J_v *vs.* t under each of five operating conditions are shown in Fig. 5.

After regression analysis, the regression coefficients (R^2), root mean square error (RMSE) and the initial permeate flux J_0 are summarized in Table 6 and Fig. 6. The results indicate that the R^2 increases obviously when fitting

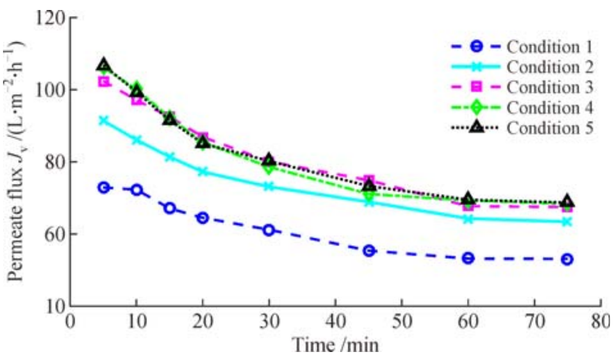


Fig. 5 Variation of permeate fluxes with processing time

for the cake filtration model, and the deduced $J_{0,2}$ = 72.54, 100.00, 105.41, 105.41, 105.41 L/(m^2·h), which is close to the measured initial flux (73.9, 90.2, 102.4, 106.2 and 106.8 L/(m^2·h)). Therefore, cake filtration model could closely simulate the membrane fouling mechanism when coal gasification wastewater is treated using a PS ultrafiltration membrane. This indicates active coke adsorption does not totally avoid particulate sedimentation on the membrane surface.

4.3 Composition analysis of membrane pollutants

Figure 7 shows the images of clean and fouled PS hollow fiber membrane recorded by SEM. It can be seen from Fig. 7(a) that the surface of cleaned membrane fiber is gully like, and from Fig. 7(b) that the gully-like surface of fouled membrane is covered by foultant. After the membrane anatomy test, the mixture of hexane and pollutants were analyzed by GC-MS.

The results are shown in Table 7. The structures of mass spectrometric fragmentation indicate that the pollutants are composed of two series: phthalate esters and long-chain hydrocarbon. These two series are hydrophobic nonpolar substances, and some researches indicate that they come from raw water or soluble microbial product (SMP) [38,39]. Because these two substances are viscous, pollutants become flocculated and gradually compacted on the membrane surface to finally form the cake layer, indicating that activated coke adsorption could not remove these two substances completely.

Table 8 shows the atomic percentage in the membrane foulants by XPS analysis. The Si/Al ratio is near1, suggesting that membrane foulants could contain inorganic pollutants. On the basis of bound energy data, carbon element is most likely to exist in C−C and C−H bonds, which represents hydrocarbons; oxygen element is most likely to exist in C = O bond, which represents phthalates. The result of XPS is consistent with that of GC-MS.

5 Conclusions

UF membrane has been applied to treat coal gasification wastewater under the operating condition of batch concentration with partial recycling of the retentate stream. The permeate flux J_v significantly decreases with increasing VRF before gradually reaching constant values with varying P_F. Rejection coefficients referring to three pollution indices were evaluated in different VRF: f_{TOC} = 70.5%, f_C = 84.9%, and f_T = 91%. The higher P_F is, the sooner J_v reaches stable values, and the more greatly the flux declines (by as much as 35.7%).

Comparison of the relations between J_v and P_F shows that J_v increases linearly with the increase of P_F when pure water is treated and that the slope of the regression line reflects the pure water permeability of the membrane. When coal gasification wastewater is treated, J_v initially increases with the P_F and then gradually becomes constant, indicating a nonlinear growth with P_F. When J_v reaches the constant value (critical flux), the corresponding P_F equals 1.2 bar, indicating that the membrane fouling is slight. When J_v exceeds 1.2 bar, serious fouling of membrane occurs. Furthermore, rejection coefficients such as f_{TOC}, f_C and f_T increase with P_F, also indicating cake layer compression. Among the three membrane fouling models, the cake filtration model seems to be the best one to explain the permeate flux decline.

The section membrane image by SEM and the results of GC/MS and XPS analysis show that the pollutants mainly consist of phthalates, long-chain hydrocarbons, and inorganic substance, suggesting that activated coke adsorption could not remove these pollutants completely.

Table 6 The RMSE and R^2 of fouling models fitting

Operating modes	Model 1		Model 2		Model 3	
	R^2	RMSE	R^2	RMSE	R^2	RMSE
1	0.95	2.01	0.96	1.69	0.93	2.37
2	0.95	2.54	0.97	2.01	0.92	3.05
3	0.97	2.49	0.98	1.76	0.95	3.28
4	0.92	4.41	0.95	3.43	0.88	5.38
5	0.93	4.16	0.96	3.22	0.89	5.05

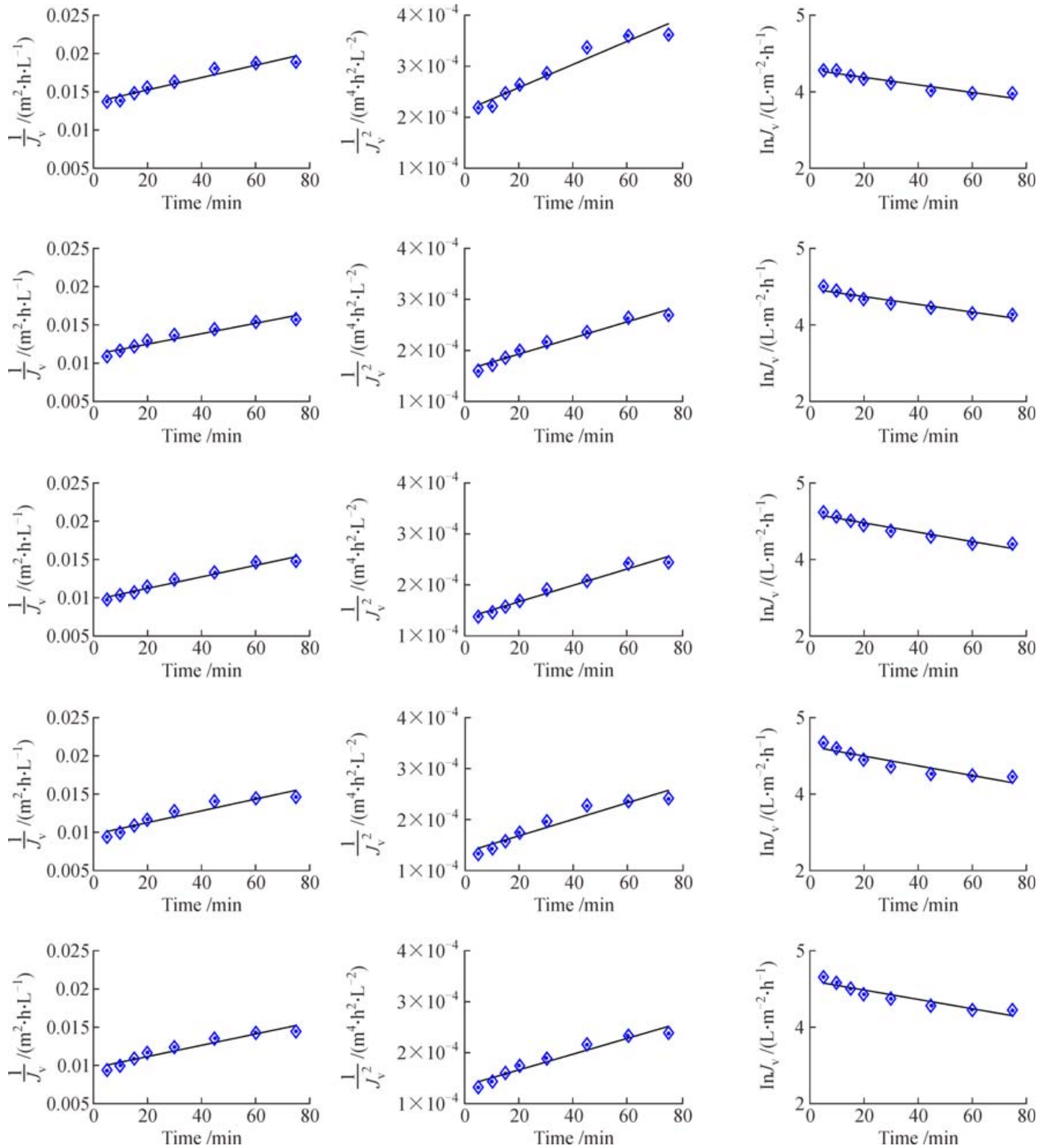


Fig. 6 Linear relationship of 3 models under 5 operating conditions

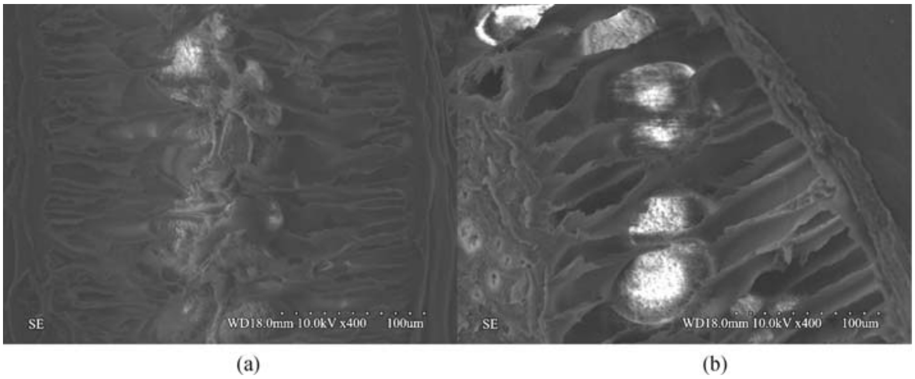


Fig. 7 The images of PS hollow fiber membranes recorded by SEM: (a) clean membrane, and (b) fouled membrane: dynamic voltage, 10.0 kV; amplified factor, ×400; and focus distance, 100 μm

Table 7 The results of GC-MS analysis

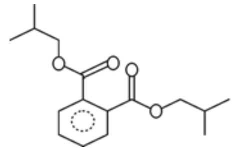
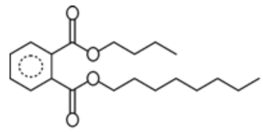
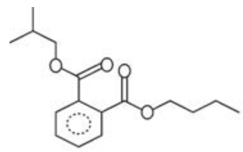
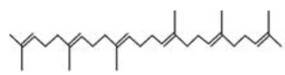
No.	Remaining time/s	Name	Molecular formula	Area	Structure	Fitting level
1	29.647	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	29926496		91
2	30.450	1,2-Benzenedicarboxylic acid, butyl octyl ester	$C_{20}H_{30}O_4$	49074335		90
3	31.248	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester	$C_{16}H_{22}O_4$	42158678		95
4	43.053	2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-, (all-E)-	$C_{30}H_{50}$	9783950		60

Table 8 Atomic percentage in the membrane foulants

Element	Peak bound energy /eV	At /%
C1s	283.74	44.59
O1s	530.14	37.34
Al2p	74.3	9.51
N1s	405.71	1.88
S2p	168.3	2.19
Si2p	101.61	6.49

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