Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.918903

55 (2015) 304–314
June

Taylor & Francis
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Improved oil/water emulsion separation performance of PVC/CPVC blend ultrafiltration membranes by fluorination treatment

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Received 29 October 2013; Accepted 23 April 2014

ABSTRACT

The introduction of perfluoroalkyl groups played an important role in enhanced antifouling ability in oil/water emulsion membrane separation. Polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (CPVC) blend membranes were used to prepare the novel fluorinated membranes. Amination treatment of PVC/CPVC blend membranes was first carried out through chemical grafting with ethylenediamine (EDA). Fluorination treatment was then achieved through chemical reaction between the redundant amino group of EDA and the carboxyl group of pentadecafluorooctanoica acid. The component of the fluorinated membrane surfaces was measured by X-ray photoelectron spectroscopy. The structure change was observed by scanning electron microscope. The fluorinated membranes were fully wetted by water in short time according to water contact angle measurement. The fluorinated membranes had higher permeate fluxes and higher flux recovery than PVC/CPVC blend membranes in oil/water emulsion membrane separation.

Keywords: Oil/water emulsion separation; PVC/CPVC blend membranes; Fluorination treatment; Antifouling ability

1. Introduction

A large amount of oily wastewater is generated in the petrochemical industries and petroleum refineries, as well as in the food processing, metallurgical industries [1–3]. There are three forms of oil in wastewater: free oil in large droplets, emulsified oil, and dissolved oil. Gravity separation, dissolved air flotation, de-emulsification, coagulation as well as flocculation, have been used to separate free oil droplets from wastewater. But for the emulsified oil (the micron- or submicron-sized oil droplets in wastewater), these traditional technologies are found to be ineffective, because the emulsified oil droplets are so stable that it requires either a long residence time to rise up or some special additives in order to destroy the surfactant film which covered the emulsified oil droplets.

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Ultrafiltration is a separation process using membranes with pore sizes in the range 2–50 nm [4–6]. As green- and low-energy consumption technology, ultrafiltration membrane separation has become a potential technology to remove the micron- or submicron-sized oil droplets from the wastewater without any de-emulsification processes [7–17]. However, nonspecific adsorption and deposition of the emulsified oil droplets on the membrane surfaces cause serious membrane fouling. Membrane fouling in oil/water separation results in substantial decline in water flux with operation time and very low flux recovery even by chemical cleaning, which limits its wide application [18].

In order to solve this problem, antifouling membranes are thought to be the key influence factor in the oil/water emulsion separation. The most efficient antifouling material for resisting protein adsorption and deposition is well known as hydrophilic polymers, such as poly (ethylene glycol) (PEG), PEG-based polymers, and zwitterionic polymers [9–12,19]. Membranes made from blends of poly (vinylidene fluoride) (PVDF) and polycarbonate (PC) were prepared to increase the hydrophilicity of membrane surface, resulting in recovery of water from the emulsified oily wastewater [20]. Sadeghi et al. managed to significantly improve surface hydrophilicity of membrane corona air plasma technique [7]. In the membrane-based filtration of oily wastewater with hydrophilic modification of membranes, flux recovery property is indeed improved to some extent, but water permeate flux is still often reduced by 1–2 orders of magnitude compared with the initial permeate flux.

Low surface energy polymers, such as fluoropolymers, are reported potentially as excellent material to fabricate antifouling ultrafiltration membranes for oil/water emulsion [21–25]. Low surface energy fluoro-containing groups enhanced the diffusion of emulsified oil droplets away from membrane surfaces. Membrane fouling was nearly eliminated and water permeate flux decline was decreased to an ultralow level for oil/water emulsion separation [23,24]. In the present work, novel fluorinated membranes were prepared with polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (CPVC) blend membranes. With the aid of the chlorine atoms on the backbone of PVC, the membrane surface was simply modified by EDA via facile and mild nucleophilic substitution reaction. In order to introduce more chlorine atoms onto membrane surface for amination treatment, a certain amount of CPVC was blended with PVC. The introduction of CPVC was also reported to increase the permeability of support membrane in our previous study [26]. Oil/water emulsion was used to evaluate the antifouling ability of the fluorinated membranes. The experimental results demonstrated that the grafting of perfluoroalkyl groups onto the membrane surfaces did improve antifouling property in the oil/water emulsion membrane separation.

2. Experimental

2.1. Materials

PVC resin with average polymerization degree 800 was purchased from Dagu Chemical factory (Tianjin, China). CPVC was obtained from Cangzhou Yuanzhen New Material Co. (Hebei Province, China). PEO-PPO-PEO block copolymer Pluronic F127 with a molecular weight of 12,600 and a PEO content of 70 wt% was purchased from Sigma. EDA, N, N-dimethylacetamide (DMAC) were supplied by Kewei Chemical Reagent Co. (Tianjin, China). Pentadecafluorooctanoic acid (PFOA) was purchased from Boman Chemical Co. (Zhangjiagang, China). Bovine serum albumin (BSA) was purchased from Institute of Hematology, Chinese Academy of Medical Science (Tianjin, China). High-speed vacuum pump oil (GS-1) with density of 807 kg/m^3 and average viscosity of 100 Pa s at room temperature was purchased from Beijing Sifang Special Oil Co. (Beijing, China). Sodium dodecyl sulfate (SDS) was purchased from Dingguo Bio-Technology Co. (Beijing, China).

2.2. Membrane preparation

PVC/CPVC blend membrane was prepared by non-solvent-induced phase separation method [26]. The membrane materials (PVC/CPVC weight ratio was 1:1) and the additive (additive Pluronic F127/membrane material was 1:2) were dissolved in DMAC (membrane material concentration in DMAC was 16 wt%) and stirred at 60℃ for about 4 h to ensure homogeneous mixing. Then the homogeneous solution was kept still for 5 h to allow complete release of bubbles. After cooling to room temperature, the solution was cast on glass plates with a steel knife, and then immediately immersed into the coagulation bath of water. The blend membrane with a wet thickness of about 240 μm was peeled off and subsequently rinsed with water to remove the residual solvent and additive. The resultant PVC/CPVC blend membrane was kept in water before use.

The schematic illustration of grafting perfluoroalkyl group onto PVC/CPVC blend membrane surface is presented in Fig. 1. PVC/CPVC blend membrane was first immersed into 30% EDA aqueous solution for 2 h at temperature of 60℃. Herein, the amination temperature was selected to guarantee high reaction rate while inhibiting the side reactions, such as elimination reaction and crosslinking reaction. Then the treated membranes were taken out and rinsed with water until neutral pH value was arrived. Subsequently, the treated membranes were immersed in saturated PFOA solution (about 0.4 wt% PFOA aqueous solution) for 12 h at a rather low temperature of 30˚C, because the additive of membrane, Pluronic F127, tends to release into aqueous solution at higher temperatures. At last, the obtained fluorinated membrane was taken out, rinsed with water, and stored in water before use.

2.3. Characterization of the fluorinated membranes

The surface and cross-section morphologies of the fluorinated membranes were observed by Nanosem 430 field emission scanning electron microscope (FESEM). Surface element distribution was characterized by energy dispersive X-ray spectrometry (EDS) during scanning electron microscope (SEM) observation. The surface composition of the modified membranes was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) using the radiation source Al Kα (1361.0 eV). The survey spectra were collected over a range of 0–1,100 eV and the take-off angle of photoelectron was set to 90˚. The static water contact angle analysis of membrane surfaces was conducted by a contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China) at room temperature. The relationship between water contact angle and measurement time was recorded.

2.4. Membrane filtration experiment

A dead-end stirred cell filtration system (Model 8200 with volume capacity of 200 mL, Millipore Co., USA) connected with a N_2 gas cylinder and solution reservoir was designed to evaluate the filtration performance of the fluorinated membranes. The effective area of the membrane was 28.7 cm^2. The operation pressure in the system was maintained by nitrogen gas. All the ultrafiltration experiments were carried out at a stirred speed of 400 rpm and a room temperature of about 20˚C. Each membrane was initially compacted for 0.5 h at operation pressure of 0.15 MPa; then the pressure was lowered to a certain operating pressure (0.02, 0.04, 0.06, 0.08, and 0.1 MPa). The water flux J_w (L/(m^2 h)) was calculated by Eq. (1):

$$J_w = \frac{V}{A\Delta t} \tag{1}$$

where V is the volume of permeated water (L), A is the membrane area (m^2), and Δt is the permeation time (h). The membrane hydraulic resistance (R_m) was determined using the relationship from Eq. (2):

$$J_w = \frac{\Delta P}{\eta R_m} \tag{2}$$

where ΔP is trans-membrane pressure and η is the dynamic viscosity of water. R_m was determined from a linear regression of the measured pure water fluxes and trans-membrane pressure data.

In order to investigate the separation performance of PVC/CPVC blend membrane and the fluorinated membrane, the rejection ratio (R) of protein BSA was calculated by Eq. (3):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{3}$$

where C_p and C_f (mg/mL) are solute (here refers to BSA) concentration of permeate and feed solutions, respectively, which were measured by UV-spectrophotometer (Hitachi, UV-9200 spectrophotometer) at a wavelength of 278 nm.

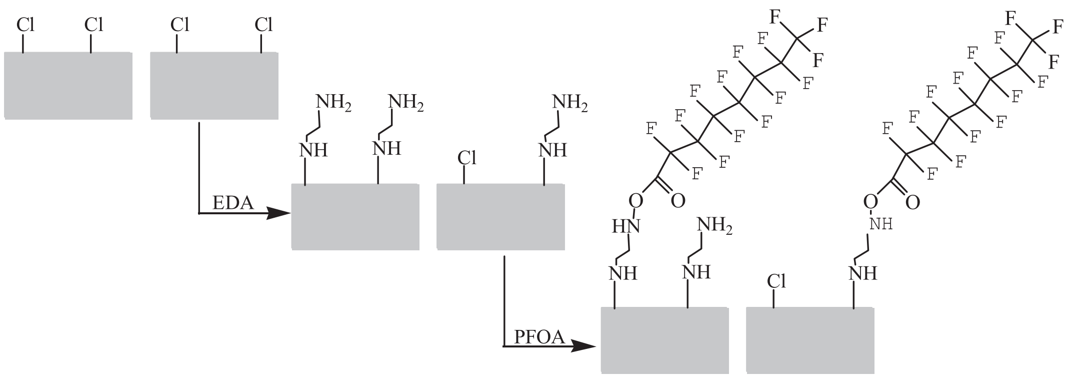


Fig. 1. Schematic illustration of grafting perfluoroalkyl groups onto PVC/CPVC blend membrane surface for preparing the fluorinated membrane.

2.5. Evaluation of antifouling ability

The oil/water emulsion was prepared with high-speed vacuum pump oil and surfactant SDS (oil/SDS weight ratio of 9:1) dispersed in water with total organic concentration 1,000 ppm. The solution was mixed by high-shear emulsifying dispersion for 30 min. The size of the emulsified oil droplets measured by Malvern Mastersizer Particle size analyzer was in the range of 0.12–29.98 μm with a volume average particle diameter of 2.1 um. The rejection ratio of emulsified oil was calculated with Eq. (3), in which C_p and C_f were measured by UV-spectrophotometer at a wavelength of 531 nm.

In order to evaluate the oil fouling-resistant ability of the fluorinated membranes, the oil/water emulsion flux decay ratio (DR) was calculated using Eq. (4):

$$\mathrm{DR} = \left(\frac{J_{w1} - J_{wt}}{J_{w1}}\right) \times 100\% \tag{4}$$

where J_{w1} is the initial water permeate flux, and J_{wt} is the water permeate flux at a certain time of oil/water emulsion filtration operation. The lower DR value means a better antifouling property of the ultrafiltration membrane, corresponding to slight deposition or adsorption of foulant on membrane surface. For observing the flux recovery property, the used membranes were cleaned directly with water in the filter cell for 20 min under magnetic stirring. The cleaning water was then poured out and the permeate fluxes of pure water were measured again (J_{w2}). Flux recovery ratio (FRR) was calculated using Eq. (5):

$$\mathrm{FRR} = \left(\frac{Jw2}{Jw1}\right) \times 100\% \tag{5}$$

The higher FRR value means a better antifouling property of the membrane.

3. Results and discussion

3.1. Characterization of the fluorinated membranes

PVC/CPVC blend membranes were prepared by non-solvent-induced phase separation process with water as coagulation bath. PVC/CPVC blend membranes with additive of Pluronic F127 have excellent antifouling property in protein separation and purification [26]. However, PVC/CPVC blend membranes have serious flux decline and very low flux recovery in the oil/water emulsion separation. The emulsified oil droplets adsorb and deposit on membrane surfaces resulting in membrane fouling and consequently serious flux decline.

Because of the small atomic radius, high electro-negativity, and the helical structure of the fluorocarbon chain, fluoropolymers gradually emerged as the most promising material for the low adhesion application, such as water-repellent fabrics, marine anti-fouling coating, and self-cleaning anti-fog coatings [21–25]. In order to improve antifouling ability of PVC/CPVC blend ultrafiltration membrane in oil/water emulsion separation, it was proposed to graft perfluoroalkyl group onto the membrane surfaces. The aminated membranes were synthesized by immersing PVC/CPVC blend membrane in aqueous EDA solution. Some chloride atoms on the surface of PVC/CPVC blend membrane were substituted by amine groups of EDA molecules [27]. After immersion into PFOA saturated solution, amide bond would be formed between the amino groups of EDA and the carboxylic acid groups of PFOA molecules, and the fluorinated segments would be retained on the membrane surfaces. The obtained fluorinated membranes were used in the subsequent experiment.

The SEM images of the surface and cross-section of PVC/CPVC blend membrane and the fluorinated membrane are presented in Fig. 2. Both the membranes showed the typical asymmetric membrane morphology consisting of a dense skin layer and a porous support layer. The pore size and density of PVC/CPVC blend membrane was smaller than that of the fluorinated membrane's, and the probable reason was that some Pluronic F127 molecules as pore-forming agents were further released from PVC/CPVC blend membrane. In order to confirm the deduction, the stability of the additive in the preparation of PVC/CPVC membrane was studied. The PVC/CPVC membrane was immersed into water bath (60℃) for 2 h, which was the same condition in the amination process. After the heat treatment, the static contact angle of the membrane became higher than that of the control membrane's indicating that the hydrophilic additive was released after the heat treatment [28,29].

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. In the present work, EDS was used to investigate the chemical composition of PVC/CPVC blend membrane and the fluorinated membrane. Fig. 3 shows the element distribution on the surfaces of PVC/CPVC blend membrane and the fluorinated membrane, respectively. PVC/CPVC blend membrane surface was mainly covered by chlorine element (93.57% in the membrane surface) which may be due to surface segregation of chlorine element in the high vacuum environment during measurement. For the fluorinated membrane, there was a peak at about 0.70 keV which

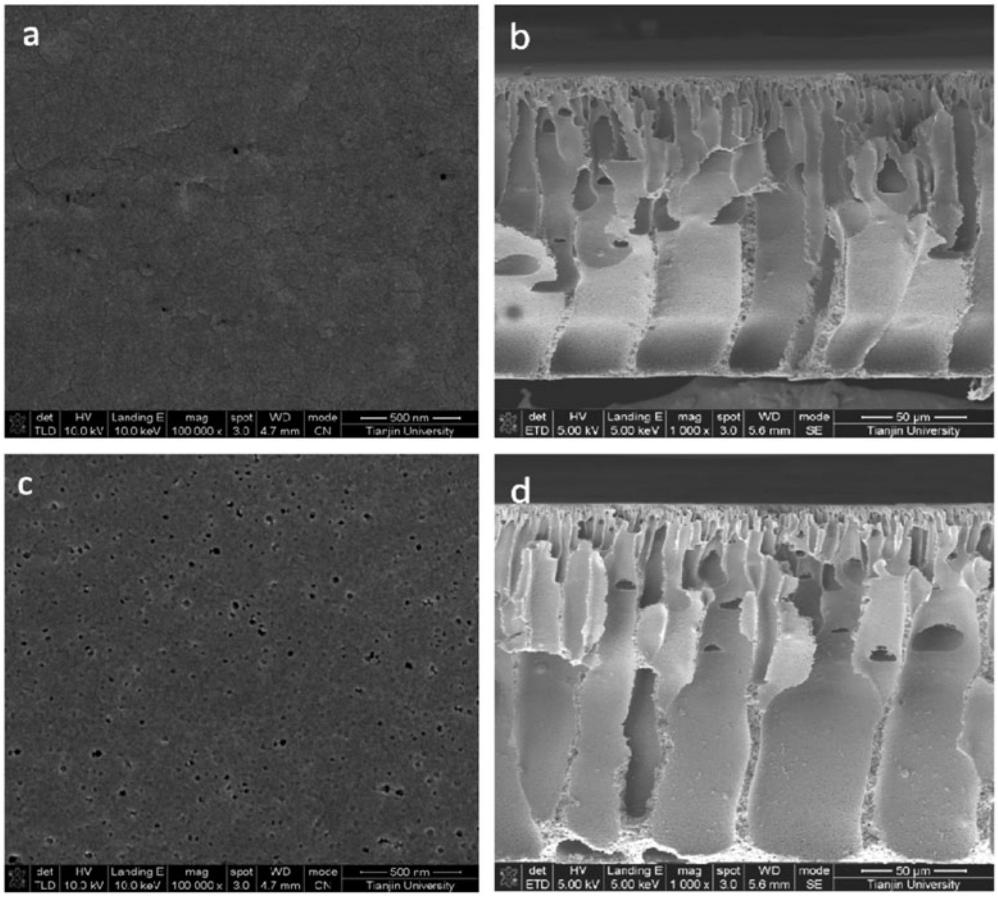
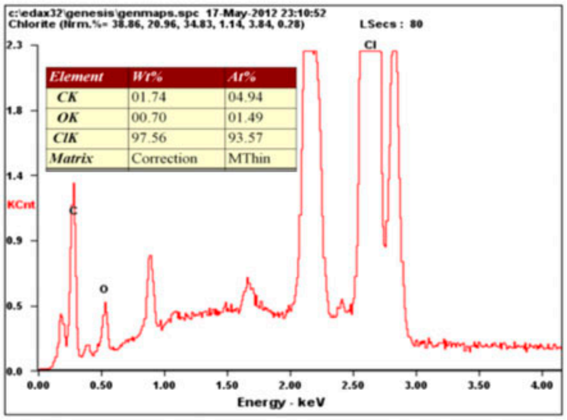


Fig. 2. The surface and cross-section SEM morphologies of (a, b) PVC/CPVC blend membrane and (c, d) the fluorinated membrane.

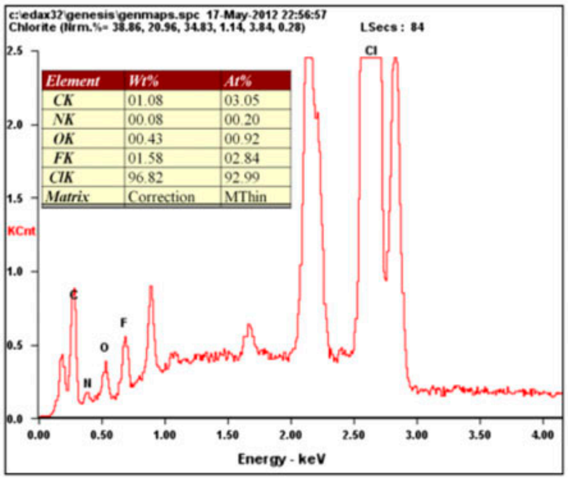
was attributed to fluorine element, and fluorine element content at the membrane surface was 2.84 at%, which clearly illustrated the introduction of low surface energy fluorocarbon segments on the membrane surface.

The chemical feature in the near-surface region of the fluorinated membrane was further determined by XPS. In Fig. 4(a), five characteristic XPS signals for Cl, C, N, O, and F are clearly observed. The F 1s peak at 687.0 eV also demonstrated that PFOA was successfully grafted onto the membrane surface. Fig. 4(a) shows that the fluorine element content at the membrane surface was 6.44 at%, which was higher than that obtained from EDS data. Since the probing depth of EDS is quite larger than XPS, the result from XPS could better represent the surface fluorine element content. The C 1s core-level XPS spectra of the fluorinated membrane is shown in Fig. 4(b), which could be further fitted with five peaks using a sum of Lorentzian–Gaussian functions. The C 1s component peaks at the binding energy of 284.6, 285.7, 287.3, 291, and 293.2 eV were attributed to C–C, C–N and C–Cl, C=O, $-CF_2$ and $-CF_3$, respectively. The single peak for C–N and C–Cl at 287.3 eV cannot be further distinguished because of their quite similar binding energy values (285.6 eV for C–N and 285.9 eV for C–Cl).

The amount of perfluoroalkyl group introduced on the membrane surface could be further calculated based on the atomic percentage of Cl, N, and F. Considering the fact that one EDA molecule (containing two N atoms) substitutes one Cl atom of PVC or CPVC during the amination process, the percentage of N-substituted Cl atom at the surface was calculated to be 5.53%. Similarly, for the fluorination process, two amino groups of EDA correspond to a PFOA molecule, which contains 15 F atoms or 7 perfluoroalkyl groups. Thus, the percentage of grafted PFOA based on EDA was calculated to be 42.1%, and the molar ratio of perfluoroalkyl group to EDA was 2.95. In this way, the molar ratio of perfluoroalkyl group to the C–Cl bond at membrane surface was further calculated to be 0.17. That is, at the surface of the fluorinated membrane, every 5.8 C–Cl bonds corresponded to one perfluoroalkyl group. Considering the high content of C–Cl bond in CPVC, the above



PVC/CPVC blend membrane



Fluorinated membrane

Fig. 3. EDS spectra of PVC/CPVC blend membrane and the fluorinated membrane.

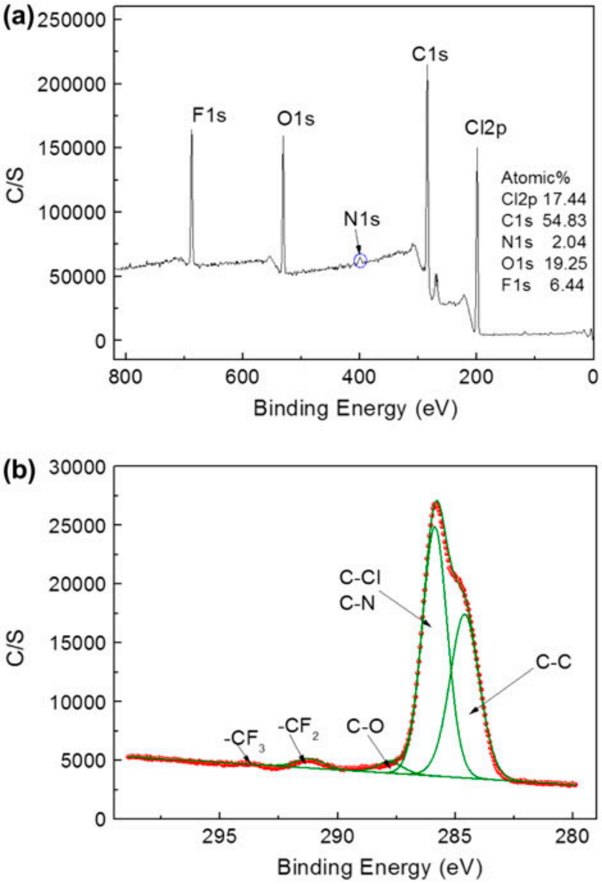


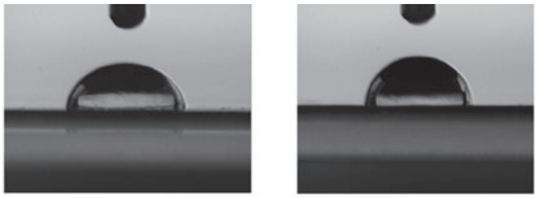
Fig. 4. (a) XPS spectra of the fluorinated membrane; (b) C1s core level spectra resolving results of the fluorinated membrane.

results indicate rather large amount of perfluoroalkyl group at the membrane surface.

The surface wetting property of the fluorinated membranes was further evaluated by static water contact angle. The time-dependent water contact angles are shown in Fig. 5. The contact angle of fluorinated membrane was higher than PVC/CPVC blend membrane in the initial measurement time, because the perfluoroalkyl groups led to increased hydrophobicity of the fluorinated membrane surface [23,24]. The water contact angles of PVC/CPVC blend membrane and the fluorinated membrane were gradually decreased with an increase of measurement time. Since additive Pluronic F127 was retained and segregated to surface [26], PVC/CPVC blend membrane having a certain wetting ability, water could penetrate into the membrane pores gradually decreasing the water contact angle. The fluorinated membrane showed a sharp decrease of contact angle, with a water contact angle that was nearly 0° at 4 min. When water was dropped onto the membrane surface, the fluorinated groups may be able to reorganize to allow for penetration of water into the hydrophilic subsurface [22,25]. The increased pore density may also play an important role in the sharp decrease of water contact angle for the fluorinated membrane.

3.2. Permeability of the fluorinated membranes

For a given membrane module design, the main factors affecting permeate flux are the trans-membrane pressure, the solute concentration, and the cross-flow velocity. The pure water fluxes of PVC/CPVC blend membrane and the fluorinated membranes as a function of operation pressure are given in Fig. 6. There was nearly a linear relationship between pure water fluxes and operation pressure. The membrane resistance of the fluorinated membrane was about 60.9% of



PVC/CPVC blend membrane Fluorinated membrane

Contact angles measured at 0 min

PVC/CPVC blend membrane Fluorinated membrane

Contact angles measured at 10 min

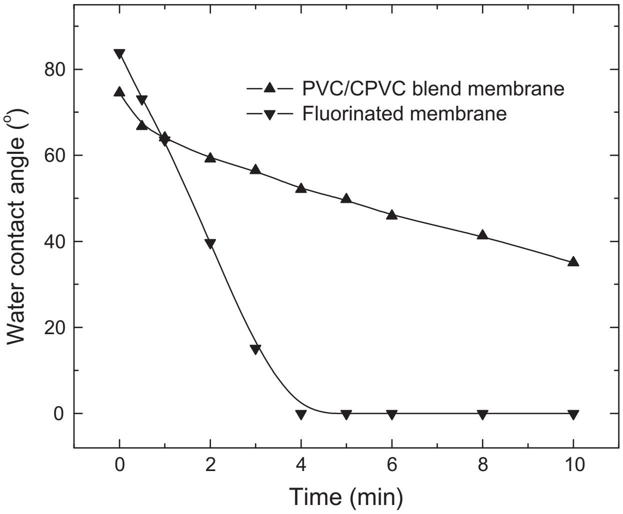


Fig. 5. (Top) Photographs of water contact angles measured at 0 and 10 min. (Bottom) The relationship between water contact angles of PVC/CPVC blend membrane and the fluorinated membrane as a function of measurement time.

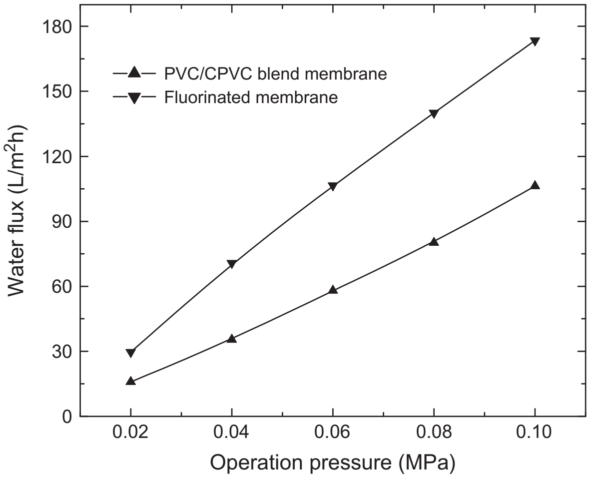


Fig. 6. Pure water fluxes of PVC/CPVC blend membrane and the fluorinated membrane as a function of operation pressure.

PVC/CPVC blend membrane. The fluorinated membrane has high water flux and low membrane resistance due to the increased pore density and its specific surface property.

Protein BSA with molecular weight of 66.5 kDa was used to investigate the pore size change between PVC/CPVC blend membrane and the fluorinated membrane. It is seen in Fig. 7 and Table 1 that BSA rejection ratio was 84.05% for PVC/CPVC blend membrane and 66.54% for the fluorinated membrane at operation pressure of 0.1 MPa. According to the separation mechanism of ultrafiltration membrane (sieving effect), when molecule size is smaller than the membrane pores, the molecule will pass through the membrane into the permeate solution; when the molecule size is similar or larger than the membrane pores, the molecule will be retained in the retentate side. In this study, the BSA rejection of fluorinated membranes was lower than that of PVC/CPVC blend membrane's, therefore it could be induced that the pore size of the fluorinated membranes was larger than that of PVC/CPVC blend membrane's. The result was also in accord with the SEM image.

The rejection data of emulsified oil droplets was also studied. As shown in Fig. 7 and Table 2, the rejection ratios of PVC/CPVC blend membrane and the fluorinated membrane were both over 99.3%, suggesting that the emulsified oil droplets were completely rejected by ultrafiltration membranes.

3.3. *Antifouling ability of the fluorinated membranes*

Ultrafiltration membrane separation is a powerful technology to remove the micron- or submicron-sized oil droplets from the wastewater [7]. Fig. 8 presents permeate fluxes of oil/water emulsion with PVC/CPVC blend membrane and the fluorinated membrane as a function of operation time at pressure of 0.04 MPa. PVC/CPVC blend membrane has poor antifouling ability for oil/water emulsion membrane separation. The fluxes were gradually decreased from initial 39.7 to 16.7 L/(m^2 h) at operation time of 400 min, the DR value was as high as 60.4%. At operation time of 180 and 360 min, PVC/CPVC membrane was cleaned with

Table 1
BSA rejection ratios of PVC/CPVC blend membrane and the fluorinated membrane at different operation pressure

Operation pressure (MPa)	0.02	0.04	0.06	0.08	0.1
BSA rejection ratio (%) of PVC´CPVC blend membrane	95.21	92.34	89.45	87.59	84.05
BSA rejection ratio (%) of the fluorinated membrane	84.48	80.22	76.01	71.75	66.54

Table 2
Emulsified oil droplets rejection ratios of PVC/CPVC blend membrane and the fluorinated membrane at different operation pressure

Operation pressure (MPa)	0.02	0.04	0.06	0.08	0.1
Emulsified oil rejection ratio (%) of PVC/CPVC blend membrane	99.5	99.4	99.6	99.3	99.4
Emulsified oil rejection ratio (%) of the fluorinated membrane	99.6	99.8	99.3	99.7	99.5

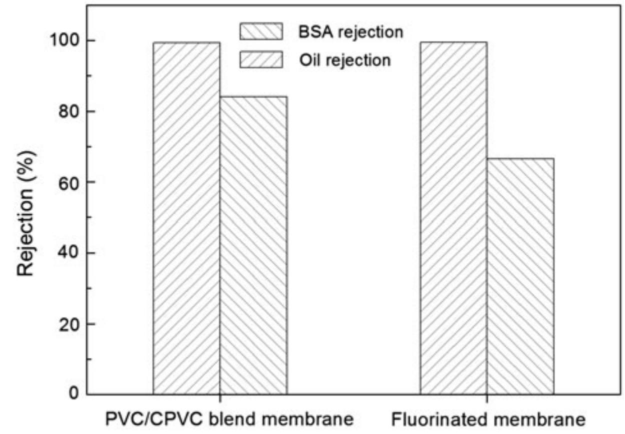


Fig. 7. The BSA and emulsified oil droplets rejection ratios of PVC/CPVC blend membrane and the fluorinated membrane.

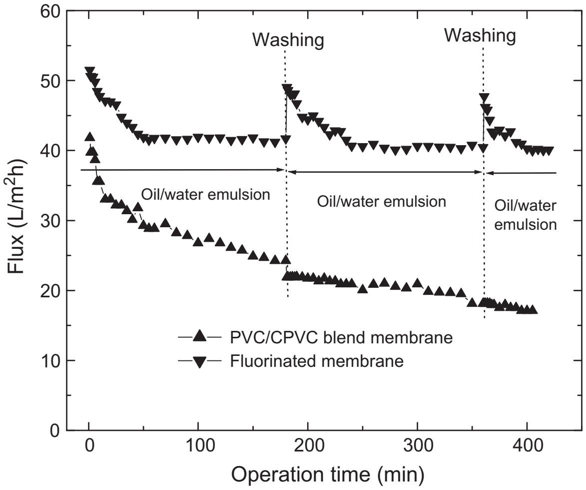


Fig. 8. Water permeate fluxes of PVC/CPVC blend membrane and the fluorinated membrane as a function of operation time in oil/water emulsion separation at pressure of 0.04 MPa. The membranes were cleaned by water at time of 180 and 360 min, and reused in the oil/water emulsion separation.

water, there was no flux recovery. PVC/CPVC blend membrane has poor antifouling ability in the oil/water emulsion membrane separation. The emulsified oil droplets adsorbed or deposited on PVC/CPVC blend membrane surfaces may prefer to deform, coalesce with each other, and rapidly spread to form continuous oil film covering on the surface, resulting consequently in serious flux decline and poor flux recovery after water cleaning [8,9,24,30].

Low surface energy fluoropolymers were reported as the most promising material for the low adhesion and containments "release" application [21–25]. Fluoropolymers incorporated in polymer membrane possess great potential to form excellent oleophobic micro-domains on surface, which would endow the membranes with excellent antifouling property in oil/water emulsion membrane separation [23,24]. As shown in Fig. 8, for the fluorinated membrane, the permeate fluxes of oil/water emulsion were only decreased from initial 51.5 to 39.7 L/(m^2 h) at long-term filter operation of 400 min, the DR value was only 22.9%. The small DR value was mainly due to the dramatically reduced adsorption or deposition of oil droplets on membrane surface. The fluorinated membrane was directly cleaned with water in the filter cell, the permeate fluxes were increased to 49.1 and

47.6 L/(m^2 h) at operation time of 180 and 360 min, respectively. The high flux recovery indicated that most of deposited emulsified oil droplets on the membrane surface could be eliminated by simple hydraulic washing [23,24,30,31].

The influence of operation pressure on water fluxes of the fluorinated membrane as a function of operation time is shown in Fig. 9. The fluorinate membrane retained high permeate flux of 75.7 and 91.1 L/(m^2 h) at operation pressures of 0.06 and 0.08 MPa in oil/water emulsion membrane separation. The DR values were 22.9, 31.3, and 35.5% at operation pressures of 0.04, 0.06, and 0.08 MPa, respectively. At higher operation pressure, the higher permeate flux would push more-retained emulsified oil droplets into the boundary layer adjacent to the membrane surface, which would cause larger flow decline than that at lower operation pressure. Low surface energy fluoro-containing groups repel oil droplets. The perfluoroalkyl modification of membrane surface can provide a way to decrease emulsified oil droplet adsorption and increase permeate flux at high operation pressure. The fluorinated membranes were cleaned with water after oil/water emulsion membrane separation. FRR values of the cleaned fluorinated membranes were 96.8, 95.3, and 97.8% at operation pressures of 0.04, 0.06, and 0.08 MPa, respectively. The increased FRR value means improved antifouling property of membrane. In order to better understand the morphology of the membrane surface after oil/water emulsion filtration, the surface SEM images of PVC/CPVC blend membrane and fluorinated membrane after oil/water emulsion filtration are given in Fig. 10. For the fluorinated membrane, most of the contaminations were removed after water cleaning. However, the PVC/CPVC membrane was covered by a thick layer of oil contaminants. It was implied that membrane fouling caused by oil could be remarkably suppressed by perfluoroalkyl modification, and the fluorination treatment endowed PVC/CPVC blend membranes with excellent antifouling property in oily wastewater treatment.

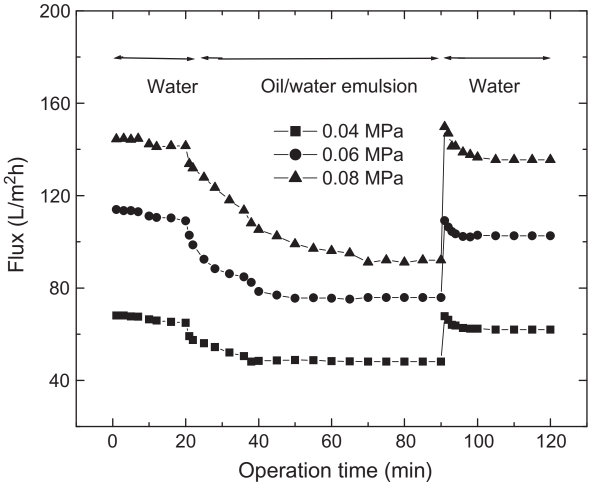


Fig. 9. The influence of operation pressure on water permeate fluxes of the fluorinated membrane as a function of operation time.

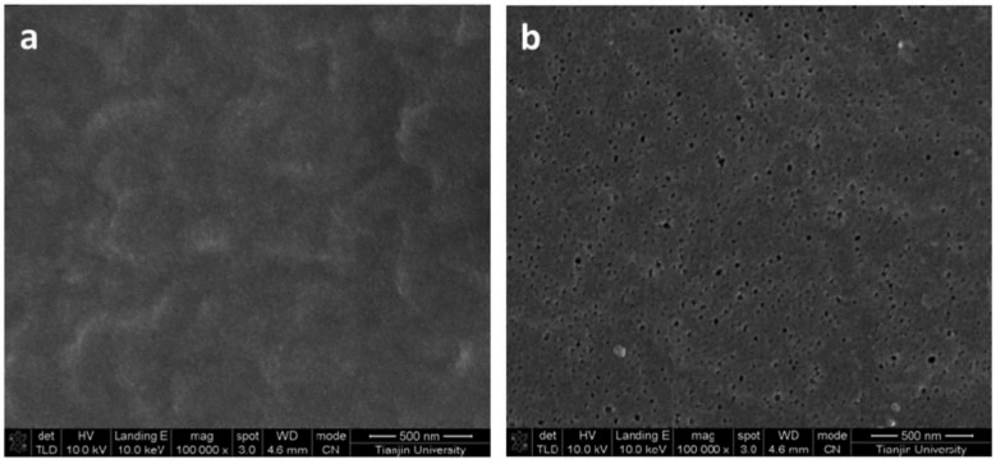


Fig. 10. Morphology of membrane surface after fouling experiment: (a) PVC/CPVC blend membrane; (b) the fluorinated membrane.

4. Conclusions

The novel fluorinated ultrafiltration membranes were prepared through amination and fluorination treatment of PVC/CPVC blend membranes. The pore density and pore size of the fluorinated membranes were slightly increased compared to that of PVC/CPVC blend membranes'. The fluorinated membranes exhibited high permeate fluxes, low flux decline, and high flux recovery in oil/water emulsion membrane separation, which demonstrated the feasibility of grafting perfluoroalkyl groups onto PVC/CPVC blend membranes to improve antifouling property.

Acknowledgements

This research is supported by Tianjin Natural Science Foundation (No. 13JCYBJC20500), National Science Fund for Distinguished Young Scholars (21125627), and the Program of Introducing Talents of Discipline to Universities (B06006).

Nomenclature list of symbols

A	—	membrane area (m^2)
C_f	—	solute concentration of feed solutions (mg/mL)
C_p	—	solute concentration of permeate (mg/mL)
DR	—	flux decay ratio
J_w	—	water flux ($L/(m^2\,h)$)
J_{w1}	—	initial water permeate flux
J_{wt}	—	water permeate flux at a certain time
R	—	rejection ratio
R_m	—	membrane hydraulic resistance
V	—	volume of permeated water (L)

Greek letters

η	—	dynamic viscosity of water
ΔP	—	trans-membrane press
Δt	—	the permeation time (h)

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