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Reverse osmosis membrane design for reclamation and removal of perfluorooctanoic acid

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ABSTRACT

Perfluorooctanoic acid (PFOA) as an important basic processing aid exhibits superior physicochemical properties and is extensively used in the manufacture of fluoropolymer materials. As a persistent organic pollutant (POP), PFOA is increasingly found in the water environment with increased industrial applications, destroying the water ecosystem and affecting the health of animals and plants through the food chain. However, PFOA as an important dispersant of synthetic fluoride is expensive, recycling PFOA can lead to high economic benefits. In this study, the reclamation and removal of PFOA were researched by using reverse osmosis (RO) membrane technology. The PFOA removal rate property was evaluated using the high flux RO membrane and a multi-stage RO was designed. In accordance with the mechanism for electrostatic repulsion and pore exclusion, the PFOA rejection and membrane regeneration performance were analyzed. The results indicated that the RO membrane permeation flux was 55 L/m^2·h at 1.5 MPa and the PFOA rejection rate was over 99%. The concentrated solution of PFOA was further disposed using the multi-stage RO unit, the rejection rate of which remained stable. The regenerative capacity of the RO membrane by physical flushing for 5 min was 85%.

Keywords: Perfluorooctanoic acid removal; Regeneration; High flux RO membrane; Multi-stage RO

1. Introduction

Perfluorooctanoic acid (PFOA) is derived from hydrocarbon, with fluorine atoms replacing all hydrogen atoms. PFOA entails high costs because of its strong carbon fluorine bonds and excellent physicochemical properties such as chemical resistance, thermal oxidation, and high surface activity. PFOA is extensively used in industrial manufacturing and daily consumer products such as flame retardants, surfactants, dispersant, fabrics and food packaging. PFOA is very expensive, which price is about 25,000–30,000 RMB/kg. The industrial wastewater contains a large amount of PFOA, which is about 6–10 mg/L. If the wastewater treatment capacity is 3,300 t/a, the amount of PFOA in all the recycled wastewater is about 20–30 kg/a. According to the market price of PFOA, the value is about 400–600 million RMB. Therefore, the recovery of PFOA can produce huge economic benefits. In addition, PFOA is not only expensive, but also its emissions as persistent organic pollutant (POP) can be produced directly and indirectly to influence the water environment with industrial development and agriculture [1,2]. PFOA in wastewater is discharged into rivers and lakes without treatment, which will cause serious damage to the water environment. The toxicity and mobility of PFOA results in the potential for adverse effects on human health if exposures are sufficiently great. The World Health Organization (WHO) has classified PFOA as a 2B carcinogen and its use is highly regulated. Increasing

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attention has recently been directed toward the control of POPs, PFOA resistance to conventional treatment and biodegradation. Therefore, the environmental pollution of PFOA recycling and removal was presented a serious challenge [3].

Several methods for PFOA degradation and segregation have been reported, including advanced oxidation, photocatalytic, chemical, adsorption, and so on [4–8]. However, the application of these techniques for large-scale PFOA removal is limited by several concerns, such as their by-products, costly post-treatment, large doses of chemical reagents, and slow reaction transformation. Specifically, industrial wastewater has low PFOA content, resulting in increasing recovery costs. Filtration processes such as nanofiltration (NF) and reverse osmosis (RO) membrane are effective in removing organic and inorganic compounds and facilitates separation of concentrated PFOA from water/wastewater [9,10]. The RO membrane had higher effectiveness in separating PFOA than NF according to literature, because of the thicker functional separation layer and smaller pores (Tang et al., 2007). Thus, RO membrane is increasingly used by industry removal chemicals. RO membrane is one possible option to remove the PFOA, but rejection rate, water flux rate, and membrane performance degradation restricts the practical application.

In this paper, combined with the advantage of RO membrane, the multi-stage RO unit was proposed and designed to explore the PFOA recycling technology from raw PVDF manufacturing wastewater. On the one hand, PFOA as an important dispersant of synthetic fluoride is expensive, recycling PFOA can lead to high economic benefits; on the other hand, it can reduce emissions and to protect the environment. The multi-stage unit designed was primarily concerned with election performance parameter of the membrane and predicated the unit scale. Thus, this study can provide insights into PFOA removal and recycling, further to lay the foundations of industrial application.

2. Materials and methods

2.1. Materials

The raw water was provided by some plants of PVDF manufacture. Nanofiltration (NF) and RO membrane were purchased from TianGong New Material Technology Co., Ltd., Tianjin, China. The standard substance of PFOA is obtained by Tianjin Kemiou Chemical Reagent Company, China. The Deionized water (DI 18.2 MΩ/cm) was prepared by a Millipore Milli-Q advantage A 10 water purification system (Billerica, MA, USA). All the chemical reagents were analytical grade and without further purification.

2.2. Membrane and facility

The filtration performance and permeation flux were measured by the laboratory-made cross-flow equipment. The nanofiltration (NF) membrane as a contrast experiment) and RO membrane composite membrane were selected to use for filtration test.

The membrane was cut into an effective area of 7.07 cm^2 and put into the cross-flow equipment to test at room temperature. The circulation reservoir was equipped with 50 L mother liquid. Before the testing, the membrane was pressured for 20 min to acquire stable flux. Driving pressure of NF and RO membrane was 0.6 and 1.5MPa, respectively. The multistage RO reaction system was designed to treat concentration water of PFOA for further to improve the membrane rejected and recycled PFOA.

The raw water permeate flux of membrane was calculated as Eq. (1):

$$F = \frac{V}{At} \tag{1}$$

where F is the permeation flux of water (L/m^2·h), V is the volume of permeation (L), A is the membrane effective surface area (m^2), t is the permeation accumulate time (h).

The PFOA rejection of membrane was measured with different fluorinion concentration and the rejection rate was calculated as follows

$$J = \frac{C_f - C_p}{C_f} \tag{2}$$

where C_f is the feed concentration, C_p is the permeate concentration.

All the measuring of flux and rejection repeated three times to obtain the mean value in order to make the results more accurate.

The multi-stage unit RO device is formed by layer stacking on the basis of the single RO device. The concentrated water of first level RO device passed the second level RO device to filter separation, by parity of reasoning, the PFOA continuous enrichment. This design of multi-stage unit intends to build four level RO devices and which will effectively recycle PFOA.

2.3. Membrane characterization and performance

The membrane surface elemental was assessed by X-ray photoelectron spectroscopy (XPS, FEI Co., Ltd. USA) with a monochromatic Al Ka X-ray source (1486.6 eV photons) at a pass energy of 93.9 eV. The measurements were conducted at a take-off angle of 45°. The raw water of PVDF manufacture wastewater quality analysis was monitored by ion chromatography including ammonia nitrogen, sulfate radical, Na^+, Ca^{2+}, Cl^-, and so on. The COD was detected via digestion spectrophotometer and the fluorinion was discovered by liquid chromatography-mass spectrometry and the raw water quality results are shown in Table 1.

3. Result and discussions

3.1. Membrane rejection property

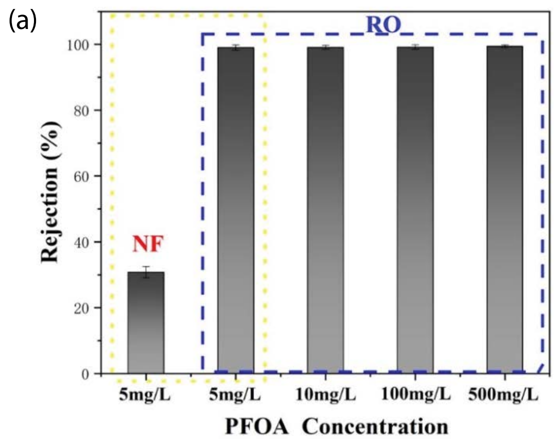
The porosity and pore size of membranes, which influence permeation flux and rejection properties, is primarily determined using the compact polyamide layer according to the Carman and Kozeny equation [11,12]. The NF and RO membrane rejection rates of PFOA were compared at low concentrations of 5 mg/L with PFOA as the standard substance. The results are shown in Fig. 1a. It was revealed that the NF membrane rejection rate is only 30.8%, and the RO membrane rejection rate is 99.05% after the circulation in the filtration equipment is stabilized. The molecular weight of PFOA is reasonably large at 414 Da, and the rejection range of the NF is 150–500 Da. However, the NF membrane could not reject PFOA. It was due to which is attributable to the multiple action mechanism of the dissolve-diffuse mechanism, electrostatic repulsion, and pore exclusion. Compared with the molecules of aromatic and aliphatic organic compounds, PFOA has highly linear molecules with minimal molecular dimensions [13,14]. Thus, the molecular shape determines passage through the membrane, the RO membrane with a denser structure can more efficiently remove PFOA. Further increase in the feed solution concentration of PFOA from 10 to 500 mg/L, the rejection rate of PFOA remained stable higher than 99%. The result is presented in Fig. 1a. The multi-stage RO device is designed to further to increase the PFOA rejection efficiency. The design process of the multi-stage RO is shown in Fig. 1b. The RO membrane had stable rejection efficiency in extreme concentration PFOA solution according to the single RO experiment results. It is beneficial to simulate multi-stage treatment with the higher the concentration of concentrated water and it is expected to improve the effluent quality.

3.2. Membrane fouling and regeneration

The permeation flux was the important RO membrane parameter for determining membrane properties. The results are shown in Fig. 2a. The RO membrane initially

Table 1
PFOA raw water quality index

Water quality parameter	Detection result (mg/L)
Fluorine ion	6.86
Ammonia nitrogen	0.21
SO_4^{2-}	9.93
TDS	79
pH	7.4
COD	102.83
Fe	0.13
Ca^{2+}	13.13
Cl^-	10.94
NO_3^-	4.78
NO_2^-	2.17
Na^+	14.18



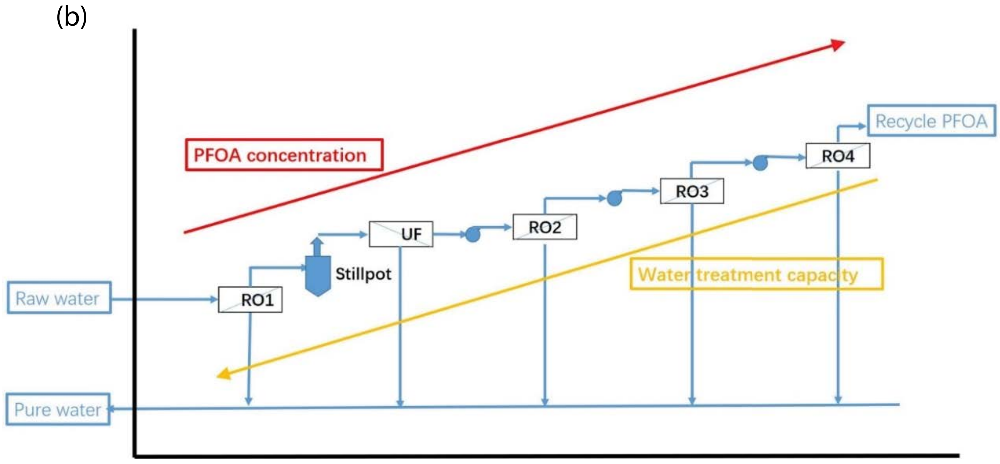


Fig. 1. The membrane rejection with different PFOA initial concentration (a), and the multi-stage RO unit technological process (b).

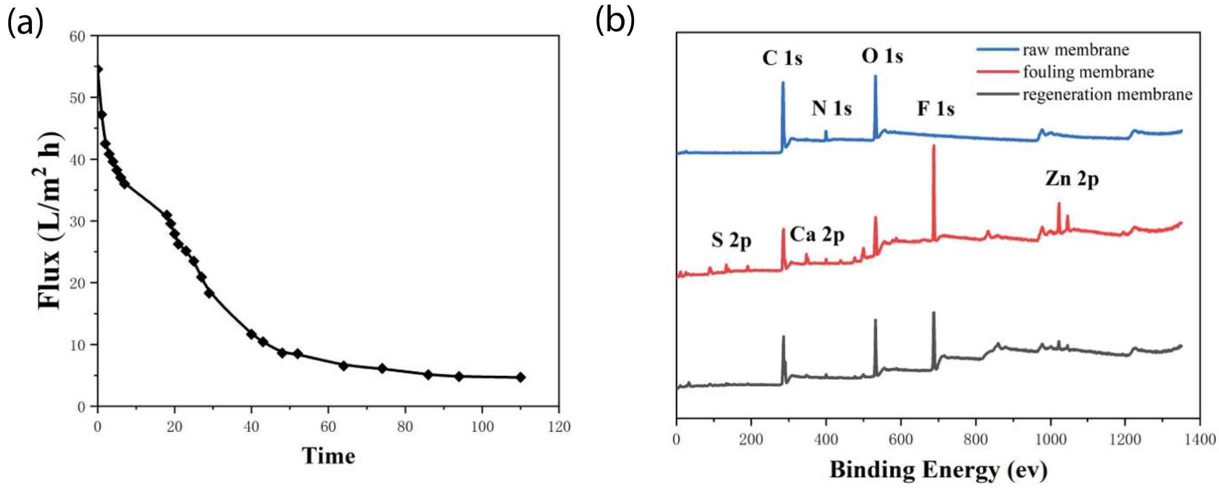


Fig. 2. The raw water flux of membrane (a), XPS wide spectra of origin membrane, fouling membrane and regeneration membrane (b).

had a raw water flux of 55 L/m²·h at 1.5 MPa. The permeation flux gradually declined to 4.69 L/m²·h with an increase in time to 110 h. This decline was attributed to the entrapped PFOA that accumulated on the polyamide layer surface of the membrane. On the one hand, the PFOA molecular weight is 414 Da but the RO membrane rejection molecular weight is above 100 Da. On the other hand, raw water of PFOA simultaneously includes a mass of other pollution sources. The reasons for two aspects are further to affect the pure water flux and lead to improving the transmembrane pressure and accelerate the production of membrane surface pollution [12,15,16]. Cleaning was performed by simple physical flushing without any agents to prevent impurities. The result indicated that 85% of the permeation flux recovery capability was retained by the physical flushing for 5 min. The composition of the membrane surface was further analyzed by XPS with the raw membrane, fouling membrane, and regeneration membrane for the treatment of raw water. The results are shown in Fig. 2b, and the membrane surface composition is shown in Fig. 3. The membrane surface of the pollutant content decreases but still contains residual pollutants even after flushing. It was illustrated that large numbers of interfering ions were present in the raw water, which led to colloidal fouling deposition and continuous accumulation on the membrane surface [17]. RO membrane permeation flux is significantly decreased by concentration polarization.

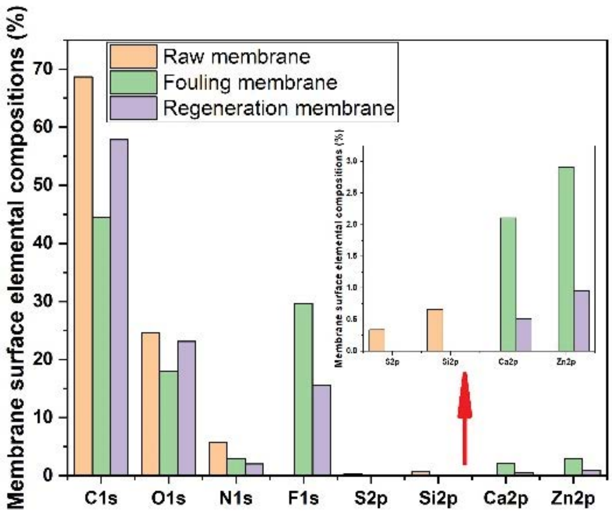


Fig. 3. Elemental surface compositions of raw membrane, fouling membrane, and regeneration membrane.

4. Conclusion

The RO membrane could efficiently reject PFOA from industrial wastewater. According to the result of the experiment, the PFOA rejection rate higher than 99% was maintained with an increase in the PFOA feed solution concentration from 5 mg/L to 500 mg/L. The PFOA accumulation on the membrane surface will lead to the transmembrane pressures increasing and accelerated the production of membrane surface pollution. On this basis, the multi-stage RO membrane equipment was designed to contribute to the increase in filtration efficiency and further to increase the rejection and recycle of PFOA. In addition, this multi-stage device will be beneficial for reducing the releasing of rejected contaminates to the environment. Thus, the RO membrane is an effective and prospective technology for PFOA removal from the PVDF manufacture wastewater.

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